

WOODHEAD PUBLISHING INDIA IN ENERGY



Coal Science and Engineering

B. Mazumder

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Preface

Coal has been the mainstay for power generation in both commercial and domestic sector till 1960. With adequate supply of petroleum and absence of cold war, in the post 1960 era, oil and gas started replacing coal mostly because of latter's environment incompatibility. However after Gulf

War, petrol became a strategic commodity and following Iraq war, the price of oil started shooting up. This scenario once again generated fresh interest in coal as a primary source of energy.

Attempts were made in the recent past to find an alternate fuel source particularly by harnessing non-conventional energies (like solar, biomass, wind, etc.) but with enough research done in last four decades, it is now concluded that non-conventional energy can substitute only a small fraction of our present energy demand. The other alternative, nuclear energy, having reached its optimum developmental stage by now, economic calculation indicates that it will be profitable to coal for power generation only at a scale of 800 MW and above. Moreover in recent past earthquake and tsunami in Japan has shifted the choice towards coal as a primary energy source.

Further progress in research in the last two decades have provided us means to generate power from coal in a more environmentally compatible manner. With the advent of fluidized bed technology, it has now been possible to effectively utilize our ever growing ash in coal in a profitable manner while the technology helped bring down overall size of the power plant to a minimal. The technology has also provided a means for utilizing non-caking and non-coking high ash coal which is abundant in our country.

Coal-derived tar and pitch have already proven a unique store house for a large number of important chemicals, which make them competent to petrol. In fact, fresh calculations indicate that days are not far ahead when hydrogenated tar can be used as an alternative to liquid fuel like petrol.

In view of the fact that India has a large reserve of coal, emphasis should be laid more on study and exploitation of coal for both our energy and essential chemical feed stock. Unfortunately with easy availability of petroleum fuel in last few decades, research and studies on coal has been

neglected to a point when essential knowledge and information with respect to coal has become very difficult to find.

The book is written with the above objective in mind and incorporates ample references for further studies for serious readers. I hope the book will be a helpful unified source of information on coal for both students specializing in coal while provide a reference source for entrepreneurs working on coal. Finally I would like to express my gratitude to the large number of authors, partial list of whom have been given at the end of the book, without whose generous contribution it would not have been possible for me to write this book.

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Oil embargo of 70s, together with uncertainty in future regarding supply of oil, has resulted in the resurgence of interest in coal, an abundant raw material reserve of our country. Geological Survey of India estimates that at least 200 years of sustainable deposit of coal exists in our country at current rate of consumption. Further technological advances towards burning of coal in most environmentally competitive manner have given our planners necessary confidence to go for long planning strategy with coal, particularly in large scale power generation for our country. Consideration of coal for mobile applications, till now, has been difficult and oil remained the preferred fuel, but with rapid increase in cost of imported oil, scenario might change in near future towards conversion of coal to liquid fuel. As we know the technology of hydrogenating coal to oil in commercial scale has already been successfully demonstrated in the SASOL plant in South Africa. Upgradation of older technology in last two decades has also provided us means to burn coal and utilizes its residue (ash) in an environment friendly manner. Voluminous ash generated by large coal-based thermal power plants is already finding its way to brick kilns as well as in cement and aggregate manufacturing plants. In steel sector, in particular, coal has posed problem in recent times with constant increase in ash and loss of caking index. Both these problems have now been effectively resolved through development of sponge iron and solvent extraction plants, the later is being used basically to enhance caking property of coal fines. With better understanding of coal structure and consequent control over its properties, a new era in carbon molecular engineering has ushered upon us which has opened new avenues for making new products hitherto unknown to us. One such example is the carbon fibre derived from coal liquids, which is 100 times lighter but 10 times stronger than steel. Similarly, gaseous fuel generated from coal has opened up possibility for generating power without generating pollution or noise. These devices called “fuel cells” are currently at developmental stage for commercial power generation. These cells are now projected as the most viable future options for power generation. Coal being a metamorphosed product, its molecular configuration continuously changed with geological time. Elucidation of such variation in structure and properties of coal with

time, modern coal science has been successful in producing a number of industrially important products from matured coal and its precursors. In view of above facts, it is helpful if we discuss first nature of coal and its structural changes with geological time and then look at various means of utilizing various grade of coal. Understanding these basic structures will also help us to understand basic techniques of producing various industrial products from coal. Being a relatively more diluted form of energy than liquid petroleum, transportation and processing of coal contributes heavily towards economic utilization of coal.

1.1 What is coal?

Geological evidences indicate that coal is a product of plant remains. Thus geological conditions, earth's pressure and temperature, slowly brought about changes in the structure of the basic plant molecules, essentially reducing hydrogen and oxygen content of the molecule, and converting it to pit, lignite, sub-bituminous coal, bituminous coal, anthracite and ultimately to graphite, a bare carbon skeleton devoid of all hetero-atoms. These morphological changes evidently bring about physical and chemical changes in the basic starting molecules. Now, as to how these molecular transformations took place under earth's condition, is a matter of debate, as various scientists hold different views regarding this morphological changes, but even then there is a general consensus at least to following basic facts:

(a) Looking at the similarity in structural composition of plant and plant debris, it indicates that these materials have converted to peat, precursor of coal.

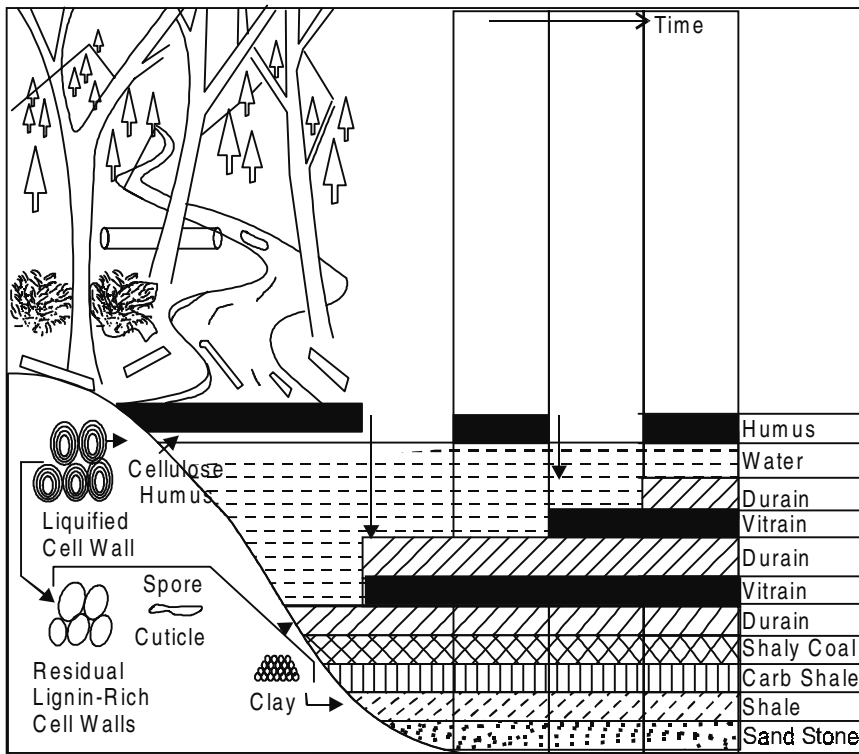
(b) These materials must have been carried away by some natural forces like water streams or river or sea and deposited at one place for subsequent conversion to coal by geological pressure, as the later hypothesis is corroborated by the fact that coal has layered structure and deposits are found in different areas at one place. Most scientists hold the view that layered sequences in coal (alternate deposit of bright and dull lithotypes) is due to distinct biochemical stages occurring during coalification process. These bright bands are called "vitrain" and "clarain," and the dull bands "durain" and "fusain". Inorganic materials, like silica, alumina, etc., are found in the coal macerals known as "inertinite". Vitrain and durain are the most commonly occurring lithotypes. Besides above, shale coals (an impure variety of coal), carbonaceous shale and other types, like sand shale, frequently occur within a coal seam. Banded structure is most conspicuous in bituminous

coal while in lower rank coal, the same is indistinct. Vitrain (its micro-lithotype known as “vitrinite”), a major constituent of coal, invariably occurs as pure but as thin band with distinct lamination covering wide lateral extension. This lithotype is remarkably free from adventitious mineral impurities. Microscopic examination, especially with the help of etching, reveals that megascopically pure vitrain constitute of both “collinite” and “telenite”. It may be noted here that Fox (in 1931) identified a 6 m long vitrinitised bark in the coal in Jharia coalfield, India. Stach (in 1970) under methylene-iodide lens recognized cell cavities of telenite which are completely filled-up with collinite. Stach also reported that vitrinite cell walls of telenite show virtual floating in a collinite mass. In no case vitrain shows gradation to other lithotype or carbonaceous cell, though it frequently occurs as lamination within thicker durain bands. Filling with carbonate minerals within cracks are generally restricted to vitrain band and are not continued either to underlying or overlying lithotypes. Fusain in contrast to vitrain rarely occurs as distinct and uncontaminated band covering wide lateral extent. Fusinite and semi-fusinite in intimate association with exinite and other macerals of inertinite group and with large proportions of adventitious minerals found to form the thick band of “durain.” Fusinite and semi-fusinite are identified by their typical and well-developed cell structure. In some cases, fusinite cell structure is crushed, giving rise to bogen structure. Cell lumen of telenite is commonly found to be filled up with collonite but in no case with mineral matter, while the reverse is true in case of lumen of fusinite. Fusinite has been found to contain lower amount of hydrogen and higher amount of carbon. Degree of aromaticity is higher in fusain as compared to other lithotypes. In general occurrence of semi-fusinite is more common in all coals than that of fusinite. Semi-fusinite shows intermediate properties between vitrinite and fusinite. Cell wall of semi-fusinite found to be always thicker than fusinite. In contrast to vitrain, durain commonly found in shale-coal as well as in other carbonaceous shales. Gondwana coal mines also show existence of shale at the bottom of the mine. Durain is found to grade into canneloid coal, both horizontally and vertically. The lateral gradation of durain in canneloid coal is more common especially toward deeper part of the basin. Above findings point to the fact that coal is essentially a derivative of floral assemblage arrested in various stages of decay in response to chemical and biological action, followed by subsequent digenesis and metamorphosis to various degrees. The factors which determine the primary characteristics of coal seam, have been identified as the type of deposition, plant communities, depositional milieu, supply of nutrients,

pH value, and redox potential. These factors determine the type of carbonaceous material to be differentiated in the biochemical stages and thus can be referred to as “heritage” and “environment.” Heritage of a coal accordingly consists of plant organic matter, like cellulose, hemicellulose, pectocellulose, lignin, and hydrogen-rich ingredients. Chemically lignin is quiet stable and, in contrast to cellulose, consists of aromatic ring structure. Carbon percent in lignin is 63% while that in cellulose is 44%. The hydrogen rich plant matter, such as spores, cuticles, wax, and resins, being chemically very stable do not deteriorate much. Besides vegetable debris, inorganic minerals, chiefly argillaceous (clay matter), may also be considered as important heritage of carbonaceous deposit, the precursor of coal. Once the plants fall on the forest floor, it is acted upon by three distinct forces – physical attrition, chemical action, and fungal or microbial attack essential in the presence of air. Besides these, in some cases trees may be ravage by forest fire, producing a variety of fusinite (or pyrofusinite). In the extreme cases, plants fragments may be entirely destroyed by insects, fungi, and anaerobic bacteria, without producing substantial humic substance. In still some other adversaries, following flood or due to sudden influx of large amount of sand and silts, the dead plants may be completely covered by sands for a prolonged period during which plant tissues may be entirely replaced by silica gel producing purified wood. In case of undecomposed wood being buried by impervious clay, the resultant type would perhaps be a variety of vitrinite showing well-defined cell structure (telenite). Under identical conditions, cuticles, spores, and resins form mainly “exinite,” sometimes differentiated as cutinite, sporinite, or resinite. The most favorable condition for development of coal seam depends on copious supply of vegetable debris and their preservation under after-logged condition prior to final burial by sediments. There are divergent views on the origin of humous decomposition of plant ingredients. It is now generally believed that both chemical and microbial action can convert wood into humic substances (Sandor and Smith, 1950). White (1933) considered the toxicity of a pit swamp chiefly controls the biochemical decomposition. In highly toxic conditions, decomposition will be negligible and thus will favour development of vitrain. With decrease in toxicity and increasing aeration, decomposition will be accelerated when hemicellulose, cellulose, and lignin will be progressively destroyed leading to the formation of clarain, durain, and pseudo-cannel, respectively. Marshall (1954) considered a variety of fusinite apart from that formed due to forest fire, may also be developed by chemical and bacterial activities. It is generally believed that exposure of vegetable matter to prolonged aerobic microbial attack would lead to fusain

formation, while anaerobic conditions are conducive to the development of vitrain. In a tropical country, wood fragments, on exposure to atmosphere and microbial attack, develop black patches on selective tissues resembling charcoal. In lignified tissues of wood, the middle lamella lying between adjacent cell walls constitute lignin. If the cellulosic layer of tertiary and secondary walls are progressively removed or destroyed by microbial attack and/or decomposed and extracted by alkaline solution, the residual part of the wood tissue is lignin-rich cell walls of the middle lamellae which appear to be the precursor of fusinite. Aromatic ring structure, high carbon content, physical strength, and rigidity of both lignin-rich cell walls and fusinite as well as typical cellular structure of both the constituents, strongly support this view. It is also conceivable that in nature, complete removal of cellulose from lignified tissues would be seldom achieved owing to change in environmental conditions or increase in toxicity. Under such circumstance, partial impoverishment of cellulose would be a common feature leading to formation of intermediate product like semi-fusinite. From geological stand point, however, it may be argued that isolated cellulose or its altered products, extracted from lignified and non-lignified tissues, would not be totally destroyed or dissipated. Instead under favorable conditions, the extracted material deposited separately as humic substance, an important coal forming constituent. A part of cellulose extract is likely to be utilized by the microorganisms for metabolism but a substantial part is carried away in aqueous solution, preferably rich in lime, as a chemical sediment and deposited as the precursor of vitrain. In a coalfield the associated sandstone show current bedding indicating that the deposits were laid down in shallow basin. The great thickness of sediments throughout, showing evidence of shallow water deposition, indicates that the basin floor was gradually shrinking owing to the load of the sediment itself. A sedimentary deposit can be divided into two broad classes, namely exogenic and endogenic deposits (Pettijohn, 1948). The bulk of the sedimentary rock is of exogenic type, consisting detrital or clastic rocks, while the endogenic type represented by amorphous or crystalline chemical precipitates from solution. Most sedimentary deposits are, however, a mixture of detrital or clastic sediments as well as chemical precipitates. In case of coral deposits also a mixed or hybrid type of sedimentation is expected; especially when the deposits are of allochthonous variety. The resultant type of coal would, however, be largely dependent on heritage and environment. We may now visualize in the light of field and microscopic evidences, as well as on the basis of some of the gathered information on heritage, that the series of event that were responsible for converting vegetal debris to the layered

sequence of coal structure. The environmental conditions of the surroundings have experienced seasonal fluctuations that have profoundly affected the vegetal debris undergoing deposition. There must have been seasonal and occasional rains to account for the growth of luxuriant forests. Evidently, flowing water played an important role in transporting the forest litters consisting of decayed vegetal matter, humic substances already formed in the forest floor, lignin-rich residual cell walls, spores, cuticles, resins, freshly fallen forest wood including bark as well as argillaceous mineral matter. The course of events likely to follow in a shallow basin where vegetal matters and their altered products would be brought in from the forest floor and accumulated (Fig. 1.1). Running water would wash the forest floor and carry considerable amounts of load consisting of clastic material and solution, representing exogenetic and endogenetic sediments, respectively. Besides drift, wood, and logs of variable sizes ranging from as big as a tree trunk to small pieces of branch, bark, and leaf more or less in undecomposed state, would also reach the water logged basin in flowing condition. Exogenetic sediments



1.1 Layered structure of coal seam.

comprise lignin-enriched residual tissues mingled with variable proportions of argellicious matter and hydrogen-rich sticky ingredients. Muddy water and clay will also enter the emptied cell lumens of lignin-enrich residual cell walls, thereby considerably increasing their specific gravity, while spores, resins, and waxes owing to their sticky nature would be thoroughly intermixed with clay and heavier residual cell walls. The running water, including rivers and streams, carry the heavier clastic sediments partly in suspension and partly in dragging (depending upon their weight and dimension).

After reaching the destination, which is most likely a shallow water logged depression of considerable dimension, the light or wood fragments and humic substances together with a small fraction of hydrogen rich ingredients, continue to float while the heavier detrital admixture of mud, lignin enriched woody tissues, waxes, and spores tend to settle at the bottom of the basin. In still waters, exogenetic sediments sorted out according to their shape, size, and specific gravity. Coarser sandy particles which are likely to be deposited during the time of flood, would settle quickly, particularly toward the periphery of the basin. Silts, clay, and finely divided fragments of lignin-rich cell walls would settle gradually, while the finest particles of clay, wax, resin, and spores remain in suspension for longer period. Under ideal condition of still water, a sequence of shale – carbonaceous shale – shaly coal – durain in ascending order is established. Lime and water soluble silicates, which are expected to be present in the aqueous medium, may destabilize colloidal particles thereby greatly accelerating the process of sedimentation and stratification. The detrital mass collected from the forest floor thus merge as units of stratified sedimentary rocks having wide lateral extension. Toward the center, far away from the marginal part of the basin, finest particles of clay and lighter hydrogen-rich ingredients may accumulate giving rise to local deposits of canneloid coal. A layer of durain may therefore locally grade into a layer of canneloid coal toward the deeper part of the basin. Apart from exogenetic sediments, humic substances formed from the cellulose extracts from both lignified and non-lignified tissues, either in solution or as colloidal solution, are brought into the shallow basin as endogenetic sediments. It is well known that humus is readily soluble in alkali but so sparingly in water. The alkali extracted humus may be precipitated as complex humic acids (Sandor and Smith, 1950). The colloidal hydrosol of humic acid tend to float over the aqueous medium together with lighter plant fragments, specially bark, forming a single unit of hybrid sedimentary rock. In such a system the tissues of plant fragments floating over the surface is thoroughly mixed and impregnated with humic substances and simultaneously, because of the

intervening water layer, they get completely free from contamination of adventitious mineral impurities. The aqueous medium, however, experiences fluctuation in acidity and alkalinity owing to seasonal variation, influx water with variable pH, and production of phenolic substances from certain plant ingredients. Under favorable pH conditions, some of the undecomposed plant fragments, especially those exposed to the atmosphere, are acted upon by anaerobic micro-organisms and form layer of localized patches of fusain. The tissues of plant fragments, coated with resinous or waxy materials or phenolic substances, however, escape such microbial attack and eventually form the "telenite" with cell lumens filled with resinous substances or telenite impregnated with collinite. The height of water level of the shallow basin also experience occasional fluctuations due to seasonal variations and in dry season the opposite layer composed of humic hydrosol would be entirely different. With the advent of summer, desiccation of water in the basin cause the top hydrosol layer to descent slowly and with complete desiccation, the humic hydrosol layer come in contact with the earlier formed stratified layer of clastic sediments. Thus a uniform thin layer of organic colloidal jelly, dropllerite, the precursor of "vitrain," is formed which on drying become shinny, brittle, and insoluble in water but soluble in alkali. This layer may also develop shrinkage cracks due to syneresis which are likely to be filled up with calcareous incrustation. With the superimposition of dropllerite layer over the earlier formed durain, an ideal sequence of stratification comprising shale – carbonaceous shale – shaly coal – durain – vitrain in ascending order emerge. In subsequent wet seasons, the basin is recharged with muddy water when fresh in flux or exogenetic and endogenetic sediments are deposited. The dropllerite layer, which is insoluble in water when dried, is firmly preserved as a thin uniform lamination covering wide lateral extension at the bottom of the new aqueous medium. In still water a new series of clastic sediments are sorted out and deposited over the dropllerite layer. Development of type of exogenetic layers largely depend on the relative abundance of decayed vegetal debris and argellectious matter as well, as the factors that determine the rate of settling. If the influx of exogenetic sediment is deficient in argellectious matter, instead of several units of clastic sedimentary layers, only a solitary unit of durain may develop over the earlier formed vitrain (dropllerite). It is therefore conceivable that the sequence as well as thickness and character of lithotype is dependent upon the quantum of various ingredients of clastic material and their rate of settling; whereas the development of maceral depends upon largely on heritage and environment. The cycle of sedimentation is repeated for a long time, imprinting the basic structure of stratification in the very

early stage of peat formation. In peat and low rank lignite banding or layering is megascopically hardly perceptible. This is evidently owing to the occurrence of incompressible plant fragments in different layers, masking layers by brownish tinge of humic substances as well as extremely high moisture content of the coaly layers and dull appearance of all constituent layers. In very low rank coal, even the plant fragments constituting vitrain and durain are apparently similar, though the plant remains associated with vitrain are constituted of both lignified and non-lignified tissues together, whereas the vegetal fragments constituting durain and fusain represent residual lignified cell walls essentially impoverished in cellulose content. In course of time when the overburden pressure increases, the complex process of digenesis and lithification set in, causing the carbonaceous layers to be sufficiently compacted, indurated, and demoiurised. At the late lignite stage, the plant fragments in different layers are greatly flattened parallel to the bedding when the coal tends to appear black instead of brown. In the subsequent bituminous stage, developed sole by geochemical action, vitrain layers develop glossy luster whereas the other layers remain dull. It is near the threshold region of bituminous stage that the banding of coal becomes distinct owing to the development of contrast in brightness of vitrain in relation to other lithotype as well as the effect of demoiurising, removal of brownish tinge and flattening of plant fragments associated with different layers. Thus finally the coalification process can be summarized as follows – on falling to the forest floor, the plant material are acted upon by physical attrition, microbial attack, and chemical degradation to various degrees, and depending upon the environmental condition, especially when the pH is high, the cellulose content of the plant cells are removed. The residual lignin-rich cell wall thus produced is the precursor of fusain formed on agglomeration with sticky hydrogen-rich plant ingredients such as pores, cuticles, resin, and wax, as well as argellicious mineral matters. The residual detrital or clastic debris, representing exogenetic sediments, were carried away by running water and deposited in shallow depressions and sorted out forming layered sequence of shale – carbonaceous shale – shaly coal – durain, in ascending order. Thickness and characteristic of lithotype that would emerge in such a sequence would largely depend upon the relative abundance of vegetal debris and argellicious matter and also various other factors such as specific gravity, shape, and fineness of the particles. It may be argued from geological standpoint that the cellulose derivatives obtained from both lignified and non-lignified part of cell wall would not be totally destroyed or dissipated. Instead these would form the principal source of endogenic or chemical sediments which under acidic conditions would form a layer of humic

acid occupying the uppermost layer of the aqueous medium together with some undecomposed drift wood including bark. During summer owing to dessication of water, the humic hydrosol layer would descent and superimpose over the earlier formed clastic sediments. With further drying, the layer would develop syneresis cracks and turn into a thin uniform band of depplerite, the precursor of vitrain. The process of sedimentation and stratification repeats with fresh influx of turbid water carrying endogenous and exogenous sediments. The basic structure of layering imprinted in coal in its initial stage of formation would, however, emerge as conspicuous bands near the threshold of bituminous stage owing to sufficient compaction, induration, demoisturising, removal of brown tinge, and thus giving rise to vitrain with its typical luster.

1.2 Coal the primary energy source for mankind

Among all the fuel reserves confirmed till today, oil and gas is projected to last for 30–40 years, whereas coal is going to last for 200–500 years. In India, with present rate of consumption, coal is going to last for at least 200 years. This vast difference in deposit itself indicates why we should plan our long term future based on coal. The present state of our knowledge with respect to power generation by various fuels indicates that the only competitor to coal in large scale power generation is nuclear energy. But economic calculations indicate that nuclear power plant needs to have capacity 800 MW or above to compete with coal. Moreover, waste generated by nuclear power plants is still a major problem with respect to its safe disposal. Further, coal not only serves as a source of power but also a store house of a number of important chemicals. From operational standpoint, it is a lot easier to run coal-based thermal power plant than a nuclear power plant. The quantum of coal deposits mentioned above is based on testing results up to a depth of 2500 m only. If secondary deposits which lie beyond 2500 m are considered, then the total coal reserve will extend as much as 300% of above figure. Accordingly there is no long-term substitute for power fuel except coal. In recent time, extensive researches are being carried out on another non-polluting energy source, which is fusion technology. However, this technology is still in its infant stage and harnessing the benefit in commercial scale by this means seems to be far away. Until then coal will be the mainstay for all our energy needs. Steel is the primary need of our modern day society which also heavily dependent on coal for its production. Even indirect method of steel production (e.g. secondary steel making via sponge iron route) needs coal for production of its reducing gas – hydrogen. Advancement of technology in last two decades now guarantees coal combustion without harming the environment. Additional costs accrued through adoption of

pollution abating machinery are easily offset by present day high cost of importing petroleum fuel from abroad.

1.3 Commercial coal grades and prices

Coal available in open market is graded according to its quality and sizes. Prices are also tagged as per above two parameters. For uniform pricing policy, commercial coals are graded by a set of rule and prices are fixed accordingly. Such guidelines are issued by Govt. of India, Ministry of Energy (ref: Gazette of India, Extraordinary Part-II, Section-3II, vide notification dated 26 May, 1982), Department of Coal. Summary of the above guidelines is presented below:

- (a) Run of mine coal – This is also called ROM coal in short and comprises all sizes as it come out of the mine without any further crushing or screening.
- (b) Steam coal – The fraction of ROM coal as is retained on a screen when subjected to screening or is picked out by a fork shovel during loading, is called steam coal.
- (c) Slack coal – The fraction that remains after steam coal has been removed from the ROM coal is called “slack coal.” Alternatively, if ROM coal is subjected to successive screening by two different screens of different apertures resulting in segregation into three different sizes, then the fraction that is retained on the screen with the larger aperture shall be termed as “steam coal”; in the fraction that passes through this screen but retained by the smallest screen is termed as “rubble coal”; and the fraction passing through both the screens shall be termed as “slack coal.”
- (d) Hand-picked coal – These comprise lump coals picked up from ROM coal by hand selection process in the collieries.

1.3.1 Pricing system

Although actual price of coal is determined and varies with production or mining cost, general guidelines for pricing related to coal quality followed are given below:

For ascertaining moisture and ash, the equilibration is done at 60% relative humidity and 40°C temperature and then above two values are determined by ISO: 1350 (1959) process. Under this procedure, “useful heat value” is defined by following formula:

$$\text{Useful heat value (kcal/kg)} = 8900 - 138 (\text{ash}\% + \text{moisture}\%).$$

In case of coal having moisture less than 2% and volatile content less than 19%, the useful heat value shall be the value arrived as above, reduced by 150 kcal/kg for each 1% reduction in volatile content below 19% fractions on pro-rata basis. When moisture content with “as received” basis, as defined in IS: 1350(1959) of middlings at the washery and exceeds 10% the price of middlings fixed in general, shall be reduced by Rs 1/- for each 1% increase in moisture content in excess of 10% fraction on pro-rata basis. When “useful heat value” of non-coking coal exceeds 6400 kcal/kg, the general price of middlings for grade A coal shall be increased at the rate of Re 1 for every 100 kcal by which the actual “useful heat value” exceeds 6400 kcal/kg fraction, on pro-rata basis. ROM coal which has been screened or crushed to limit the top size to any maximum limit within the range 200–250 mm shall be priced at the same rate as slack coal. Pit-head price fixed by Government of India are F.O.R colliery siding prices but where separate agreement for carrying coal or coke over long distance by road from the pit-head to the loading point exist or are entered into the cost of such carriage from pithead shall be governed by such agreement. Prices also vary on the nature of coke (hard or soft) they produce. Prices fixed for by product for hard coke, premium, beehive coke is increased at the rate of Rs 30/- per ton for every 1% decrease in ash content below 23% fraction at the pro-rata basis. When the ash plus moisture content of semi-coking grade coal is less than 17%, the general price of semi-coking coal shall be increased at the rate of Rs 5/- for every 1% decrease in cash plus moisture content below 17% fraction on pro-rata basis. Prices fixed as above will not apply to coke or coal sold for export outside India. Readers also make them updated in this respect with amendments issued by Govt. of India circulars from time to time.

1.4 Coal transportation

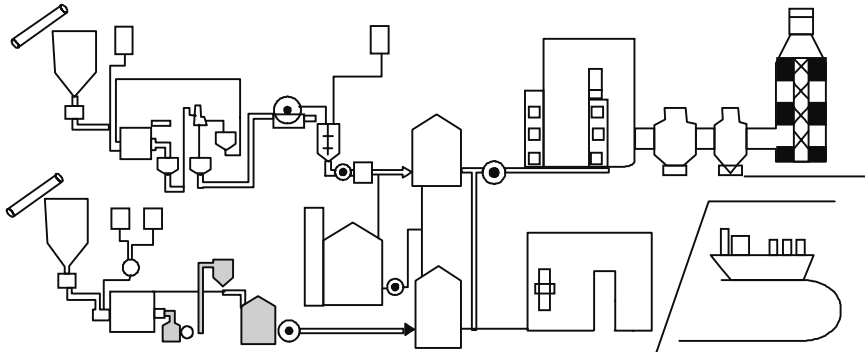
Generally lump coals are carried from pithead to consumers either by truck or by rail. On comparative basis, transportation by rail becomes much cheaper than transportation by road. Further, if waterways are available, transportation cost per ton of coal still reduces by carrying in ships. Interestingly, since good amount of coal fines are generated at pithead (particularly in friable coal mines), they can also be transported as coal slurry by pipelines or burnt by pulverized fuel burner for supplying necessary energy at the mine head itself. Transportation of coal fines by slurry transportation is especially attractive when cost in terms of kilocalorie of fuel transported is considered. For slurry transportation, development of necessary surface active chemicals which prevent fine coal particles from settling down at the bottom of suspension medium during

transportation or storage becomes important. This part of chemical development we discuss in more detail in later section. In India, Regional Research Laboratory, Bhubaneswar, made a thorough study for pipeline coal slurry transportation. Demonstration unit is being set up with capacity of 50 ton/h, covering a distance of 25–50 km is completed. The estimated cost of this project was about Rs 50 crore and time required for its completion is about 2.5 year. Installation locations for such project recommended by M/s Engineers India Ltd were Kothagundum (A.P.), Patratu (Bihar), and Talcher (Orissa). Major routes are from East India Coalfields to Northern Coalfields and Central Coalfields to Western Coalfields. At present in India need for such fuel is 34 million metric ton per year, through a distance of 3200 km. The total capital investment, including know-how development and engineering cost, is expected to be Rs 4000 crore. BHEL (Tiruchirappalli, India) is developing process for burning such coal slurry in fluidized bed, while CFRI (Dhanbad, India) has generated technical know-how for producing stabilizing chemicals for coal slurry (both in oil and in water). CMERI (Durgapur, India) has worked on development of special burners suitable for such coal slurries. Among various types of coal slurries coal-water mixture (CWM) is nearing commercialization for use as a low cost substitute for heavy fuel oil. Price differential between CWM and COM (coal-oil mixture) is over Rs 100/GJ. Tokyo Electric Power Co., Japan, has already commercialized COM technology by installing two 265 MW electric generators and completing CWM demonstration test in its 75 MW unit in 1988. Properties of CWM and COM are shown in Table 1.1.

Flow diagram of CWM demonstration unit of Tokyo Electric Power Co. (Japan) jointly developed with Joban Power Co. at its 75 MW Nakoso Power Station is shown in Fig. 1.2. For CWM combustion, 3.2 ton/h (60 million Btu/h) steam atomized type burner with special flame holders and wear resistance tips were installed. Later at Nakoso plant 11 ton/h burner for 600 MW boiler was also installed. Test results show CWM combustion is quiet smooth and stable.

Table 1.1 General characteristics of COM and CWM

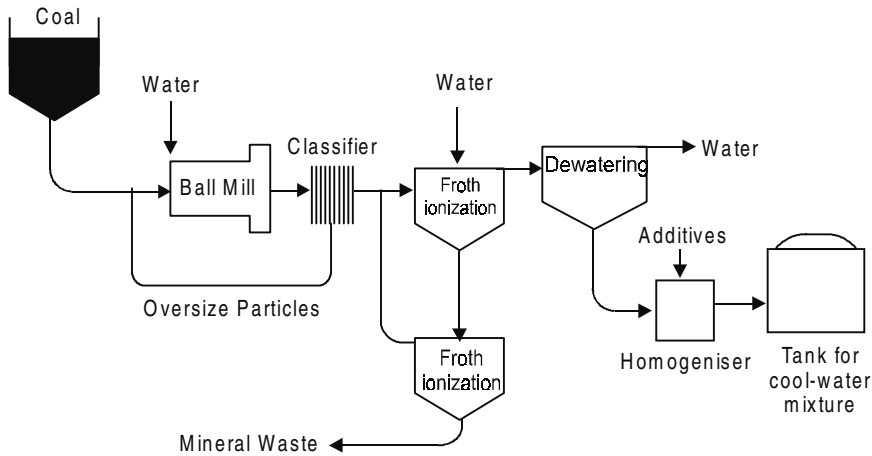
	Coal	Heavy Oil	COM	CWM
Physical state	solid	liquid	liquid like	liquid like
Components	—	—	coal 50 % heavy oil 50%	coal 60-75%, water 40-25%
Gross CV(kcal/kg)	6700	13,300	8,500	4,500
Specific gravity	1.35	0.95	1.10	1.25
Viscosity (CP)	—	75(70°C)	1000-2000(70°C)	1000(25°C)



1.2 Flow diagram of test facility for CWM demonstration plant.

There is no difference of load change ratio and minimum load between CWM fired operation within limit and guaranteed operation of 2000 h. Exhaust gas also meets all environmental regulations. Efficiency of CWM combustion was only 1% less than that of pulverized coal fired plant. CWM pressure and flow was regulated within the range 6–8 kg/cm² and 33–43 m³/h, respectively. Unburnt carbon in flyash was 0.7–8.0% and carbon conversion efficiency was 98.72–99.87%. CWM fuel pump life was about 2000 h. Solid loading of CWM was 62–67% (+100 mesh 76–86% and –200 mesh 76–86%) corresponding to viscosity of 1000 cp. Storage of such fuel for a period of 2 months posed no problem and beyond 2 months, 1 or 2 h recirculation for a day was sufficient to stabilize the fluid. Comparative costs of COM and CWM in Japan with respect to other fuels are as follows: oil = 100, coal = 128, CWM = 137, and COM = 160. These costs also include environmental measure costs. In small plants, if flue gas treatment is required then CWM comes nearly same as oil. IIT Kharagpur (India) is experimenting with triple simultaneous combustion of coal, water, and oil, which reportedly has superior combustion characteristics over CWM or COM alone. It may be noted here that addition of water to coal (as in COM) reduces its calorific value by 2–3% only. Figure 1.3 shows the entire process of COM making by line diagram.

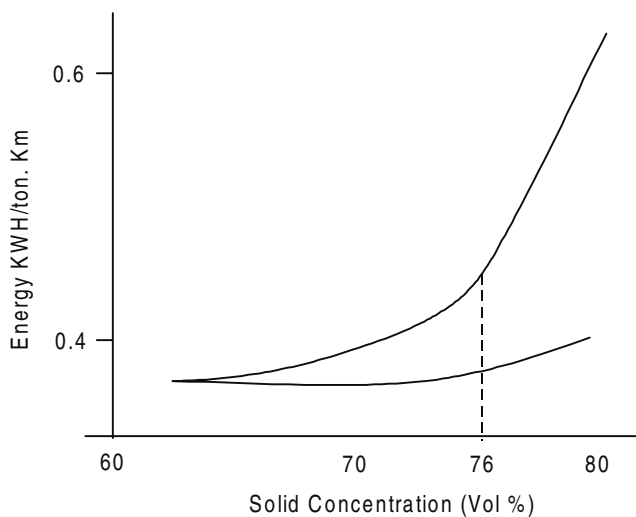
Nowadays generally two types of coal water slurry are being prepared commercially: one with high solid loading and the other with low coal loading. Pipelines are already commercially carrying slurries, containing up to 30% coal, in USA and USSR. Russia is also building a pipeline 260 km long to carry COM having coal content 65–75%. Grinding of coal to fine sizes also separate majority of its inherent inorganic matter (ash), which creates problem in boilers. Further separation of ash takes place when the pulverized coal is put into water (where mineral matter separates and settles at the bottom of the tank while coal particles float



1.3 Preparation of coal-water slurry (steel bars in the tumbling mill pulverize the coal). The classifier sorts out the particles and passes them to froth tanks which wash out mineral wastes. Additives help to reduce the viscosity of the coal-water mixture, which is 70-80% coal.

up). Considerations have also been given for assessing overall technical and economic implications of adopting high concentration coal slurry in place of pulverized coal in a 450 MW thermal power unit using 2.64 million tons of coal per year containing 40% ash. The overall performance of this power plant was found to be low. PLF (plant load factor) being 30% for old plants run by SEB (State Electricity Boards of India) which is attributed to high down time and increased maintenance cost, caused by high ash in our coal. If coal is to be used as substitute for fuel oil (which is devoid of ash), every unit of ash reduction becomes beneficial as 1% of water is less detrimental compared to 1% ash. Therefore, a portion of the ash can be traded with water, provided the useful heat, combustion intensity, flame temperature, and gas volume are maintained at the same level as for burning dry coal. Studies on rheological behavior of high concentration coal slurry indicate that beyond 75% of solids by volume the specific energy for transportation increases exponentially and solids weight percentage in high concentration coal slurry is always maintained between 60% and 70%. Therefore 30% by weight is the low limit for water in coal slurry. Calculations therefore have been carried out to arrive at the combustion characteristics of burning coal water slurry with coal having 6.5% moisture on air dried basis, and C = 74.5%, H = 4.8%, N = 2.8%, S = 0.9%, and O = 17% (by difference) on dry, mineral-matter-free (dmmf) basis. With above characteristic of coal used in above plant, characteristic parameters evaluated are as follows: adiabatic flame temperature, enthalpy of product gas, useful heat available considering the exhaust gas temperature to economizer as 350°C for different

conditions of ash and water in the slurry. About 10% excess air and 100°C air preheat temperature is assured. Trade-off between ash and water in slurry is considered for the same level of useful heat available when dry coal with 6.5% moisture is burnt. The first curve in Fig. 1.4 indicates the variation of UHF with ash (%) for various water concentrations in slurry against dry coal. The estimated cost of burning 1 ton of coal-water slurry is 1.5 times that of burning 1 ton of raw coal. It is believed that this increase in cost would be more than offset by the benefits gained through increase in PLF and low cost of maintenance. The reason for this belief is that the effective ash in slurry is only 15% compared to 40% in dry coal and benefits estimated even for marginal reduction in ash earlier are very significant. Further characteristics of Indian coals are such that grinding to a very fine size would be essential for effective liberation of ash and therefore wet method of separation becomes binding and resultant product being slurry in form; it becomes more convenient for pipeline transportation and economical for use without dewatering. Under such compelling situation, CWS seems attractive for two reasons – a dewatering step which is difficult to operate and expensive can be avoided, and CWS substituted in the existing pulverized fired installations with least modifications. Even those changes considered for ash removal while replacing oil by CWS would not be necessary as problems of ash removal gets reduced with deashed coal compared to use of raw coal as such. Theoretically, coals containing mineral matter below 18% can be burnt as coal-water fuel provided other technical and economic



1.4 Specific energy requirement for two viscosities coal-water slurry.

considerations are taken care of. In coal-water slurry, relation between wt% and vol% of solids in the mixture is

$$S_w = (P_s \times 10) / [P_f (100/S_v - 1) + P_s]$$

$$S_v = (P_f \times 100) / [P_s (100/S_w - 1) + P_f]$$

where, S_w = solid content by wt%, S_v = solid content by vol%,
 P_f = sp. gravity of fluid, P_s = sp gravity of solid, $S_v = P_b \times 100/P_s$.

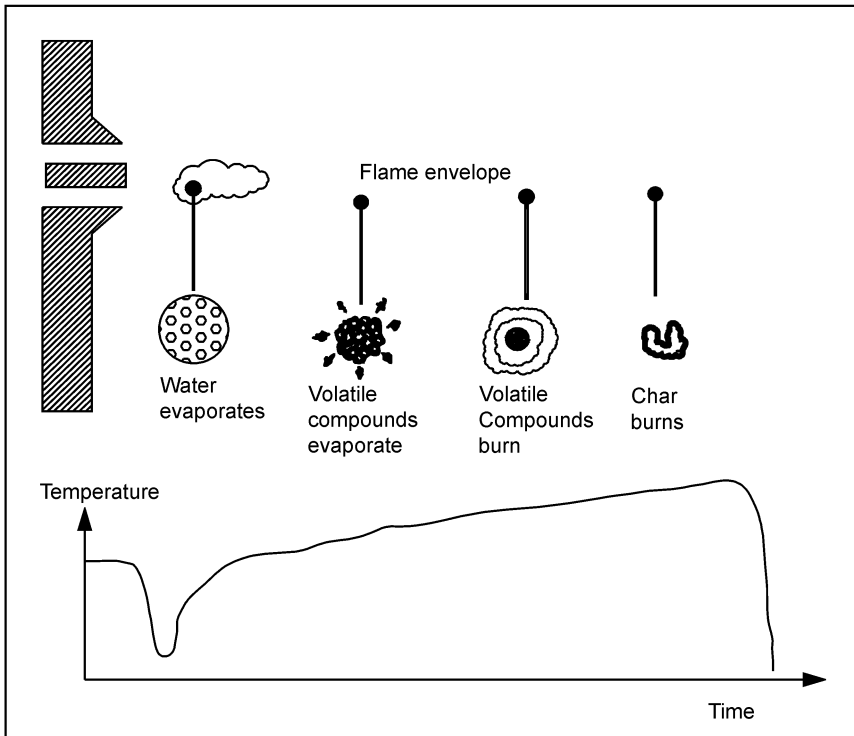
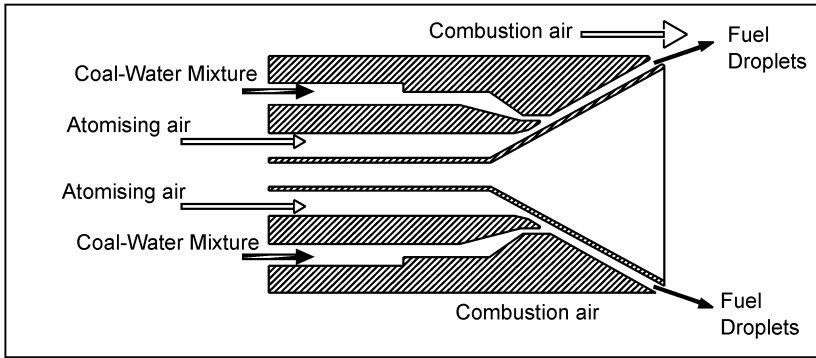
For highly loaded CWS, it is essential that S_v should be as high as possible. For low ash coal used in industries as pulverized fuel, S_v is between 60% and 62% which is far below of around 70% required for the preparation of CWS. For high ash coal used in India, S_v is much lower. To increase S_v , either P_s is to be reduced by reducing ash or void space is to be decreased by artificially adjusting the particle size distribution. Note here that coal surface is hydrophobic in nature. One of the most important requirements for coal-slurry fuel is that it should be pumpable and readily atomizable in the furnace burner. This essentially determines slurry rheology for any atomization nozzle design such that a fine enough dispersal is obtained. Shear thinning behavior (Bingham plastic or pseudoplastic) is desired so as not to have rapid settling characteristics, yet low enough viscosity for good atomization under high shear rates. For good combustion, particles need to be small. Coal slurry fuels typically require a particle size distribution with 75–80% of -74 micrometer (-200 BS mesh), the standard boiler feed size or finer. Recently the use of micronized coal with a median particle diameter (d_{50}) less than 15 micrometer and 98% passing 44 micrometer (325 BS mesh) has been promoted. To maximize the concentration of coal in the slurry, a broad size distribution is desirable and requires additional control points on the size distribution curve. Multimodal distribution is used to enhance particle packing efficiency. Thus the grinding technology is important. Primary and secondary coal crushing (top size distribution between 20 cm and 7.6 cm, and between 5 cm and 3.2 cm) as well as coarse pulverization (-3.2 mm) are standard coal preparation processes. The process of coarse (-1 mm), fine (-250 micrometer), and ultra-fine (-44 micrometer) grinding of coal which can be performed either dry and wet are as follows: according to US coal grinding task force, grinding mills are divided into two main categories: mechanical and fluid energy mills. Mechanical mills employ direct mechanical action on individual coal particles or assemblies of particles and operate on impact, crushing, or attrition principle. Fluid energy mills employ the kinetic energy of particles accelerated by compressed air or superheated steam jets to grind the material by impact against other particles or target plates on the

chamber walls. Fluid energy milling consumes large amount of energy and may not be economical for coal slurry preparation. The coal grinding task group concluded that it would seem reasonable that if coal-water slurry is the end product, the most practical approach to grinding would be a wet process using a mechanical grinding mill. The report further concluded that –

- (a) To minimize coal grinding energy requirement, the maximum particle size that can be operated when coal is burnt in boilers, gas turbines, and diesel engines must be determined.
- (b) To make a high density, finely grounded coal-water slurry, the required particle size distribution must be ascertained and a fuel specification should be prepared.
- (c) Knowing the coal-water slurry characteristics, the type of grinding mill best utilized for production can be investigated.
- (d) There are sufficient commercial grinding mills to produce 10 micron product in quantity; however, they have not been proven for coal operation.
- (e) The energy cost of producing a 10 micron product is estimated between 5 and 15 dollar per ton (at \$0.05 per kWh, 1987 price).

This will depend primarily on the hardness of coal and on the type of mill used, wet or dry operation, and particle size distribution. The first four types of mills listed above can be used for dry grinding. The mills are air swept and the coal is subjected to air classification. The required size fraction is collected in cyclones and bag-house filters, while the oversize fraction rejected by the classifier is returned to the mill for further grinding. The classifier cut size can be adjusted to yield the required fineness. This is an efficient process but requires drying of coal; the grinding system and certainly the powdered coal storage should be blanketed by inert gas for safety reason. Wet grinding is simpler and appears to be the preferred method for slurry fuel preparation. Typically two mills are used to achieve a bimodal particle size distribution. If coal is to be beneficiated before slurrying by a wet method, then the preferred mode of grinding is definitely wet as well. Boiler derating when firing coal slurry depends on boiler type. A 10.4 MW boiler in Sweden, fired with coal-water slurry, is reported to reach a maximum of 73% of its designed rating for oil firing and 140% of its rating for coal. In a package oil/gas fired boiler derating of 25% should be feasible, especially by improved fuel atomization and swirl intensity, while today derating in excess of 50% is common. Canadian utility boilers reported values varying from 39% to 65%, depending upon boiler type and size. The limiting parameters are tube-bank gas velocity, tube-bank spacing, or

furnace exit temperature. Beneficiation of coal causes increase in heat value of CWM and thus reduce boiler derating, as well as its low ash content reduces the rate of convection tube erosion and hence allows higher gas velocity. Thus a desirable fuel is really a beneficiated and micronized coal slurry. Ash build up in the furnace may be a problem depending on boiler design but most of it exists as fly-ash. Ash accumulation in general, can be dealt with “soot blower,” if tube pacing allows. Ash falling to the bottom of the furnace has to be removed as in coal fired system. The combustion of coal-water fuel starts with evaporation of the water. While this occurs rapidly at 100–150°C, a slight delay in coal ignition occurs; but increased coal reactivity after water evaporation more than offset the delay. As with coal-oil, coal agglomeration inside coal-water droplets is a serious issue and is accentuated by the high furnace temperature. Agglomerates of coal particles in a droplet are formed during evaporation and heating. Devolatilization and flame combustion then commence and other cenospheres are formed, followed by char combustion, fragmentation, and burn out. Volumetric heat release rates are a measure of fuel combustibility and indicate how practical it is to fire such slurry fuel in oil and gas fired boilers. Ignition and flame stability are important considerations. Ignition must occur close to the burner or flame and will be erratic and unstable. Higher fuel volatility and air preheating help; strong recirculation of the flame as a must for stable combustion. Atomization strongly influence the combustibility of the slurry and determines the combustion efficiency. For coal, char combustion is controlled by mass transfer process for particles longer than 100 micrometer, while in smaller ones rate is limited by chemical kinetics. Coal–oil–water mixtures burn essentially in a similar manner to COM. In addition, micro-explosions caused by rapid evaporation of trapped water may prevent coal agglomeration and hence improve carbon burn out. During combustion of COM, the water provides hydroxyl radicals that react with the CO gas produced when the char burns, and the result is less CO to react with oxygen which leaves more oxygen to burn the carbon. COM behaves more like a heavy oil rather than pulverized coal during combustion. The rate at which a coal-water mixture burns depends upon the size of its atomized droplets, rather than the size of coal particles in the droplet. Figure 1.5 shows how mixtures containing a high proportion of small particles tend to be more viscous and more difficult to atomize. Atomized liquid fuel burns at a rate that is directly proportional to the surface area of the droplet. In other words, combustion rates vary with the inverse square of the droplet size. Figure 1.5 shows the atomizer used with CWM. As can be seen, in principle, CWM



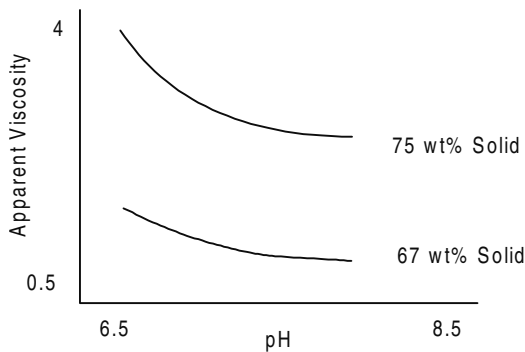
1.5 Pictures showing how coal-water mixture burns through atomizer in a CWM furnace.

atomizers are similar to those used for heavy fuel oil, but in practice they are different. For example, coal particles are varying abrasive, so the atomizing air must not carry them along too quickly.

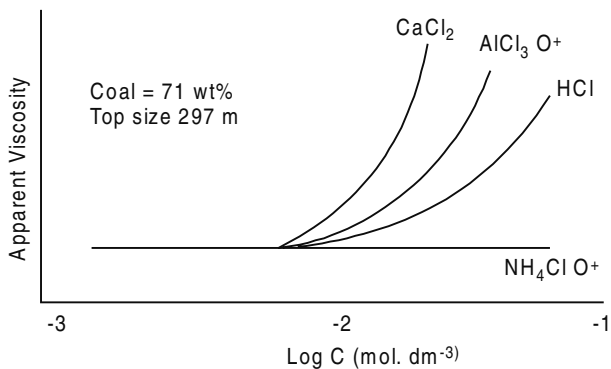
But the air must not travel so slowly through the atomizer narrow orifice that the larger coal particles get stuck. That is why atomizers in boilers sometime have circular ports rather than the individual orifices used to atomize oil. Good atomization helps to prevent the flame from going out, but modified burners and other measures are some time needed to keep the mixture alight. Sometime the air supply is limited, for example, so that there is just sufficient air to burn the fuel but too little to cool the flame. If the temperature of the flame falls, it cannot ignite all the particles that enter the furnace. The flame then separates from (blows off) the burner or the particles “sparkle” and prevent a homogeneous flame developing. Adding 6% oil to the mixture helps to prevent both blow-off and sparkle. The water penalty of coal-water fuel has been an important factor in determining the technological approaches to fuel preparation. As water must be evaporated, more coal is needed and the energy density of the fuel is adversely affected. This impacts not only in fuel transportation but also in storage requirements, and contributes to boiler derating. These problems have led to the development of techniques for preparing highly loaded coal-water slurry fuels, which contain 65–75% coal. By adopting a bimodal or polymodal size distribution, voids left by large particles, are occupied by progressively smaller ones, leading to optimized particle packing. Water then acts as a lubricant between the particles. Additives (concentration up to 1%) reduce the viscosity of the slurry, enhance wetting of particles surfaces, and free the entrapped air. They should not be foaming nor interfering with the stabilizing additives. Anionic additives when adsorbed on the coal surface impart a negative charge to the particle. Cations are then attracted to the coal surface and an electrical double layer is established. Repulsive force within the double layer prevents interparticle interaction. Due to the resulting larger separation of the particles, shearing can occur without signs of dilatant behavior. Various sulfonates are effective dispersants. Additionally, stabilizing additives must also be used with coal-water fuel. While minimal settling might be expected with highly loaded slurries, the viscosity reducing additives not only enhance the settling rate but also encourage the formation of a hard solid sediment. This must be counteracted. The additives used cause flocculation of fine particles and provide a particle network structure necessary for mixture stability and soft sediments. Non-ionic amphoteric polymers of polyoxyethylene as well as predispersed clays and water soluble resins have been found to be effective coal-water slurry stabilizer.

In contrast to coal-oil mixtures which are flocculated suspensions, coal-water slurries are typically “aggressively” stable. This is a result of the need to achieve high coal concentration. Flocculated suspensions contain void which led to lower maximum concentrations. In coal-water slurry, repulsive forces (steric hindrance) imparted to coal particles through the use of dispersants, promote rolling of particles on top of each other and help to achieve high solids loading in the slurry. Coal-oil-water or coal-water-oil contains 50–63% coal (80% pass through 74 micrometer sieve), 30–40% oil, and 10–15% water. These blended mixtures are subjected to ultrasonic agitation which leads to emulsification of water in oil. The idea of coal-water-oil came from the cheap coal which is recovered from waste coal washing streams by oil agglomeration, a precursor to coal-oil-water or coal-water-oil. The cost of oil remaining in the fuel is trivial compared to the advantages gained by using a cheap source of coal and having superior fuel properties. The major component of the coal-water fuel preparation is the cost of the additive, reported to be around \$15–20 per ton of coal for 1% addition. Suggested alternatives include use of lower concentrations (50–60 wt%) and oil or gas firing for flame stability. Stack losses for water evaporation, increases from 13% to 18% approximately with coal concentration reduced from 70% to 60%, but no additives are needed. Hitachi Research Laboratory, Japan reported (January 1987) trial runs with anionic and non-ionic dispersants. The anionic dispersants used are sodium salts of sulfonated naphthalene-formaldehyde condensate. The non-ionic dispersant had an average molecular weight of 55,000. Salts of these varieties were of reagent grade. Coal was first ground to under 3 mm size and then pulverized in the presence of water and dispersing agent to form a homogenous fluid CWM. The amounts of anionic and non-ionic dispersants were 0.7 and 1 wt% on dry coal basis, respectively. During the preparation of CWM using anionic dispersant, an appropriate amount of NaOH was added to adjust pH. The pH of resulting CWM was 8.1. No attempt was made to adjust the pH of the CWM with non-ionic dispersant, which had a pH value of 2.2. As with all well-dispersant colloids, CWM has a shear-thickening property at shear rates greater than about 10 per second (top size solid concentration was 297 micrometer with concentration 72%, 74 micrometer 72 wt%, and 37 micrometer 70 wt%, in three samples). Coal particles in CWM with anionic dispersant are expected to be negatively charged due to the adsorption of dissociated dispersant molecules. The effect of pH and cations on the apparent viscosity of a CWM can be interpreted as resulting from the partial neutralization of the electrical charge of the particles by the compression of the electrical double layer around them, thus decreasing the repulsive interaction forces caused by

the overlap of the double layers. Cation concentration at which the sharp increase in apparent viscosity of a CWM occurs depends on the valency of the cation (i.e., higher the valency, lower is the critical concentration). This behavior is in accordance with the empirical rule for the critical flocculation concentration for coagulation of hydrophobic colloids, known as the Schulze-Hardy rule, and supports the previous interpretation that the coal particles in a CWM with anionic dispersant are dispersed mainly by electrical repulsive forces arising from negative surface charges. In such system electrolytes in the solution strongly influence the degree of particle dispersion and thus govern the CWM rheology. As shown in Fig. 1.7, variation in concentration of hydrogen ion affects the CWM viscosity much more strongly than other monovalent ions. Similar effects have been noted in other colloid systems (Fig. 1.6).



1.6 Change in viscosity with pH.



1.7 Change in viscosity with different ions.

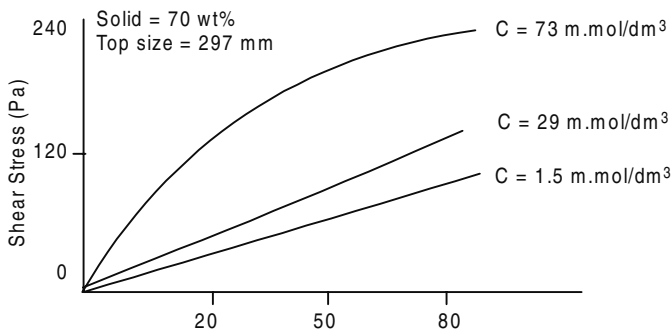
This may be indicative of an enhanced adsorption of H^+ onto the surface of the coal particle due to its small ionic radii. Critical flocculation

concentration is those at which the CWM has an apparent viscosity of 1 Pa.s. Concentration of ionic species in such supernatant solution is as follows:

1.5 Concentration of ionic species in supernatant solution

Species	Na ⁺	K ⁺	NH ⁴⁺	Ca ⁺²	Mg ⁺²	Al ⁺³	Cl ⁻	F ⁻	S ⁻²
Concentration (m.mol/dm ³)	316	5.1	2.6	3.9	0.5	0.007	25.6	1	28.3

In above table high concentration of sodium ion is due to its presence in the dispersant and the addition of NaOH for pH adjustment during CWM preparation. Na⁺ concentration is assumed to be balanced by the unabsorbed dispersant anions in the supernatant. Electrolytes also affect flow characteristics of CWM to a great extent. As shown in Fig. 1.8, when the electrolyte concentration is low and the particles are well dispersed, the CWM displays a shear-thickening behavior over the range of shear rates examined. As the electrolyte concentration increases, the shear stress at low shear rates increases sharply, the CWM begins to have a quasi-yield stress and the flow characteristics shift to shear thinning. The property of heopexy becomes significant at high electrolyte concentration. The emergence of quasi-yield stress can be explained qualitatively by considering the formation of a network structure, principally incorporating small particles, due to increased attractive forces. Particles are expected to flocculate upon collision when the attractive forces between them are greater than viscous and/or inertial force. The shear thinning behavior may result from the breakdown of the network structure by the greater viscous force at high shear rates. The property of rheopexy may result from the difference in the rates of formation and rupture of the structural linkages at given shear rate. The rate of flocculation may be a function of the relative magnitude of forces acting on the particles and the collision



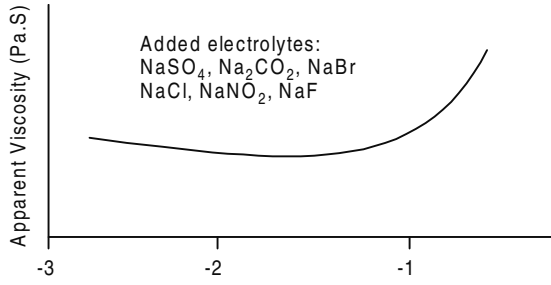
1.8 Change in flow curve of CWM on addition of CaCl₂.

frequency between them, both of which are influenced by the rate of shear, particle size, and the solid concentration. In a CWM with larger top sizes, the formation of structural linkages by small particles may be retarded by the presence of the large particles. Moreover, these structural linkages may be ruptured easily by the motion of the large particles induced by the external shear. Viscous forces may be of sufficient magnitude to break up the structure even at very low shear rates, resulting in diminished quasi-yield stress. As top size decreases, there is average particle separation at constant solid concentration. Here the structural linkages between particles are expected to be denser and firmer and to form faster due to high collision frequency of smaller particles, than in case of CWM with larger top sizes. In regard to particle size, smaller the size more is the effect of CaCl_2 addition due to formation of stronger particle linkages in the low shear rate region. With larger size particle, flow curve does not change appreciably with the addition of CaCl_2 . Studies involving effect of adding sodium salts of various anions on apparent viscosity of CWM shows that presence of anions do not alter the CWM flow properties. Concentration of co-ions (positive zeta potential) is negligibly small compared to the counter-ions (negative zeta potential). Coal particles, thus as per Boltzman principle in the present CWM, were determined to have negatively charged. Hence, anions are expected to have little effect on the rheological characteristics of the present CWMs. A slight increase in apparent viscosity at concentrations higher than about 0.1 mol/dm^3 is attributed to the presence of positively charged sodium ions mentioned earlier.

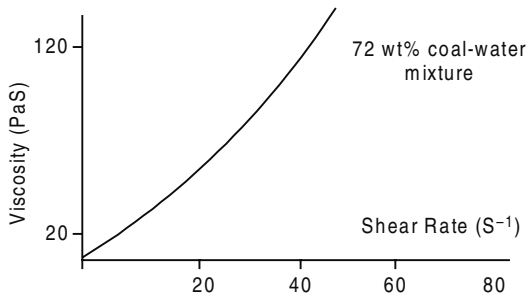
1.6 CWM with non-ionic dispersant

As shown in the Fig. 1.8, CWM exhibits shear thickening behavior identical to that of CWM employing an anionic dispersant with no additional electrolyte, in which particles are well dispersed.

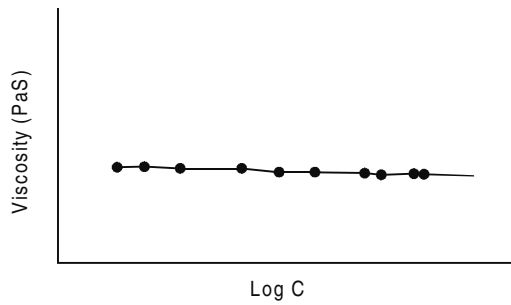
However, addition of electrolytes results in marked different behavior. Coal particles suspended in water are known to be negatively charged even in the absence of anionic dispersant. This is probably due to the dissociation of the surface functional groups. However as shown in Fig. 1.11 (with CaCl_2 addition), electrolyte addition do not change the apparent viscosity of the CWM with non-ionic dispersant. The flow curve is also affected. It appears that the electrostatic repulsive force may not influence significantly dispersion of particles in the CWM. These results indicate that particle coagulation is prevented and dispersion is effected solely by a steric stabilization effect. Chemicals mostly used as additive are dodecyl sulfonate, lignin sulfonate, C16/C18 sulfonate, dibutyl naphthalene sulfonate, naphthalene sulfonate, calcium ligno-sulfonate,



1.9 Effects of anions on viscosity of CWM.



1.10 Flow curve of CWM with nonionic dispersant.



1.11 Effect of CaCl_2 addition on viscosity of CWM with non-ionic dispersant.

formaldehyde condensed naphthalene sulfonate, sodium bis-(2 ethyl hexyl) sulfosuccinate, soluble anionic organo-sulfonate, sodium ultra polyphosphate, non-ionic starch, sodium tetra-polyphosphate, alkyl aryl sulfonate (anionic), etc.

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2.1 Coal deposits

Coal is estimated to have been formed about 200–300 million years ago. Their classification according to geological system and corresponding rank are shown in Table 2.1. Coal occurs in Gondwana system of permo-carboniferous age and in the tertiary age, both in the Eocene and Miocene era. There are unimportant and little known areas in the Jurassic and Cretaceous period.

The older coals occur only in the Damuda series of the lower Gondwana system. The Damuda series overlies the Talchir series, which is of glacial origin. The geological condition in India strongly resemble to those of South-Africa and Australia, where the coals of Permo- carboniferous group are indirectly associated with glacial deposits and they depict same type of plants in the Callosopteris flora group. Earlier Australia-India- South-America-Africa-Madagascar and Antarctica, represented a unified region termed as Gondwana land, and coals of these regions were called Gondwana coal. From geological point of view, coalfields of India are clubbed into three categories – Gondwana, Jurassic, and Tertiary. In the evolution stage of coal from plant material, it is believed that highly toxic, stagnant water decomposed by bacteria all but cellulose material. Unaltered

Table 2.1 Normal age of coal deposits

Geological system		Approx. mean age in terms of $\times 10^6$ year	Normal rank of coal formed
Era	Period		
Paleozoic	Carboniferous	300	Anthracite and semi-anthracite
	Permian	245	Bituminous
Mesozoic	Triassic	200	Bituminous
	Jurassic	160	Bituminous
	Cretaceous	120	Bituminous and sub-bituminous
Tertiary	Eocene	60	Sub-bituminous and lignite
	Oligocene	40	Lignite
	Miocene	20	Lignite
Quaternary	Pleistocene	less than one	peat

cellulose (or partly altered to hemicellulose and gave lignin) gave rise to vitrain and clarain, which in-turn gave birth to caking coal. Whereas less toxic (better aerated) decomposed microbiologically all but lignin and hydrogenous matter (only resins and spores remained). This material gave birth to Durain and Cannel coal, which turned ultimately into non-caking coals. All these morphological changes have been dealt in detail in Chapter 1. Thus on the basis of above geological age, world coal deposits can be categorized into three groups:

- a) *Carboniferous coal* – Formed during carboniferous age, i.e., about 360 million years ago. These deposits are found in Europe, Belgium, France, Germany, U.K, Holland, Poland, Russia, Spain, Canada, and USA. It is distributed in Northern Hemisphere covering all above countries. In Carboniferous era all these countries were distributed round the equator and belonged to the continent known as Laurentia. These coals range from bituminous to anthracite and are of superior quality as they contain low ash.
- b) *Gondwana coal* – These coals are found in Antarctica, India, Australia, Madagaskar, South-Africa, and South America. They all belonged to one continent known as Gondwana land. These countries were in the neighborhood of sub-arctic and arctic region having similar climatic and geographical environment. These coals are of Permian age (formed about 270 million years ago); although coals in South-America (Brazil) are regarded as upper Carboniferous in age. Gondwana coals are mainly of bituminous in rank, although occasionally some semi-anthracite is also found. The occurrence of true anthracite in Gondwana coal deposit is extremely rare. Gondwana coals are characterized by high ash content and thus inferior in quality to that of Carboniferous coals. Indian coals are of drift origin (thus high in ash), but carboniferous coals are in-situ deposit and thus low in ash.
- c) *Mesozoic and Tertiary coals* – These coals are less matured than carboniferous or gondwana coal. Mostly these are high moisture content brown and sub-bituminous or lignitic coals. Following Table 2.2 published by (National Coal Association, Washington DC, USA, in 1972) country wise proven reserve of as against percent of total world reserve:

India ranks ninth in terms of coal reserve in the world and sixth in terms of annual coal production. The most important coalfields are in Ranigunj (West Bengal), Jharia and Bokaro (Bihar). The best coking coal comes from Giridhi, Jharia and Ranigunj. Other states where coal occur include M.P, Orissa, A.P, Maharashtra, Assam, to some extent in Nagaland, Arunachal Pradesh, U.P, Jammu- Kashmir, and Meghalaya. The total (all types including

Table 2.2 World coal reserve (country wise)

	Country	% of world total	Total
Asia	USSR	19.9	
	China	16.7	
	India	1	37.9
	Japan	0.2	
	Others	0.1	
North America	USA	48.2	
	Canada	1.4	49.7
	Mexico	0.1	
Europe	Germany	4.8	
	UK	2.8	
	Poland	1.3	
	Czechoslovakia	0.3	10
	France	0.2	
	Belgium	0.1	
	Netherland	0.1	
	Others	0.4	
Africa	South Africa	1.1	
	Others	Nil	1.1
South and Central America	Venezuela	0.1	
	Others	Nil	0.3
			100%

lignite) proven, indicated and inferred reserve in India stands at 86,428 million tones with seam of 1.2 m and above and generally upto a depth of 600 m from surface. Out of this total, coking coal reserve is placed at 23391 million tones. The output of lignite in 1980 was 4.5 million tons in India. Significant reserves of lignite occur in the state of Gujrat, Jammu-Kashmir, Rajasthan and Tamil Nadu. The total estimated reserve in this respect stands at 2100 million tons of which Neyveli field in Tamil Nadu alone contains 1919 million tons. In 1983, total mineral production in India was Rs 6417 crores of which 88.8% were due to fuel. 1994–1995 fuel production figure in India were – coal 254 million ton, lignite 18.8 million ton, natural gas 14644 million cu. m, and crude petroleum 32 million tone.

Because of drift origin, Indian coals occur in thick seams and less defined. Whereas carboniferous coals are well defined. Distribution of gondwana coalfields in India are as follows:

- (a) *Himalayan area* – inaccessible, thus of less economic importance.
- (b) *Rajmahal area* – 160 km north of Suri (south bank of Ganga river). These coals are non-coking inferior quality, suitable for thermal power plant in North Bengal, Bihar, and Bangladesh (Ganges region).
- (c) *Deochar area* – east of Giridhi, covering only a few square kilometer.
- (d) *Damodar Valley coalfields* – Raniganj, Jharia, Bokaro, Ramgarh, North Karanpur and South Karanpura.

- (e) *Palamau coalfields* – coalfields in Aurangabad, Hutar, and Daltangunj. Among them Daltangunj and Hutar coalfields are of economic importance.
- (f) *Valley coalfields* – Singrauli, Sohapur (this coal is being used in Bhilai Steel Plant).
- (g) *Chattisgarh region* – they constitute 18 coalfields encompassing this region.
- (h) *Mahandi valley coalfields* – Amongst these, Talcher coalfield of Orissa is important.
- (i) *Satpura region* – Pench and Kanham valley coalfields are most important. Some of the coals in Kanham coalfields are medium coking coal. Outside Damodar valley coalfields, it is rare to find medium coking coal.
- (j) *Nagpur region* – Umrer and Kamptee are two coalfields of this region. Kamptee coals are used in Koradih (Maharashtra) super thermal power (1100 MW) plant.
- (k) *Wardha valley coalfields* – Situated on the bank of river Wardha, these seams are thick and mostly above 4 m. In Ghughres-Telwasa seam 21 m thick deposit has been found.
- (l) *Godavari valley coalfields* – These coalfields are continuation of Wardha valley coalfields and occur in godavari basin area. Amongst these, Singareni coalfields are most important.
- (m) *Tertiary coal deposits of Assam and Meghalaya state* – Geological and geographical distribution of tertiary coalfields are as follows:

Early Pleistocene to upper Pliocene:	Lignites in Karewa formations of Kashmir valley.
Miocene:	Lignites of Neyveli in Tamil-Nadu. Lignites of Verkala and Quilon in Kerala.
Oligocene to Upper Eocene:	Lignituous coal of Barail (Jaipur), Nazira, Namchik and Makum (Assam).
Middle Eocene:	Lignites of Polana (Rajasthan); Vimarsar, Panandaro, and Akrimota (Gujrat).
Lower Eocene:	Jaintia series in Mikir Hill (Assam), Jaintia-Khasi Hills (Meghalaya) and also Kalakot, Metka, Mahogala, Chakur, Dhanscoal Swalkot of Jammu.

Neyveli (south Arcot district of Tamil-Nadu) lignites have ash content 4–6%. Kutch (Gujrat) lignites are estimated to 160 million tons and the Palamau (Rajasthan) lignites reserves estimated at 20 million tons. Reserves of major coalfields are shown in Table 2.3 below.

Major consumers of above commercial coals in India and change in coal consumption in different sectors between 1975 and 1987 in India is shown in following Table 2.3a.

Table 2.3 Major coalfields with their coal reserves (in thousand million ton)

Coalfields	Coking	Non-coking	Total
Raniganj	2	25	27
Jharia	8	11	19
Karanpura	3	12	15
Bokaro	8	–	8
Singrauli	–	10	10
Talcher/Ib-valley	–	–	6
Wardha valley	–	–	2
Korba	–	–	1
Godavari valley	–	8	8

Table 2.3a

Consuming sector	1986–1987	1974–1975
Steel	10.11 million tons	13.94 million ton
Power (utility)	71.26	19.15
Locomotive	6.83	12.82
Cement	6.46	3.48
Fertilizer	3.66	0.95
Brick and other industries	38.04	24.01
Export	0.16	0.53
Colliery consumption	3.53	2.33
Total	141.65	78.11

2.2 Petrographic constituent of coal

Megascopic appearance of coal shows two distinct layers – bright layer known as Vitrain and Clarain, and a dull layer containing Durain and Fusain. Under ordinary microscope coal appears as banded structure. These bands are distinguished by varying order of brightness. These banded constituents (micro-constituents) are called petrographic structure and these lithotypes are known as macerals (micro-constituent) bodies. These lithotypes along with their micro-constituents (macerals) are shown in Table 2.4. India's major workable coal deposits occur in two distinct stratigraphic horizons – the lower gondwana of Permian age and the tertiary coal deposits as mentioned in previous section. Gondwana coals constitute bulk of the coal resources (about 99%) and are located in the south-eastern quadrant bounded by 78°E longitude and 24°N latitude leaving three-fourth of the country virtually devoid of major coal deposits. The gondwana coals are characteristically high in ash and are inferior in quality to carboniferous coal. Petrographic composition of Talcher (Orissa) coals are as follows:

Coal mines	Vitrinite	Exinite	Inertinite	Reflectance
Talcher (bottom seam I)	40–45 vol%	5–10 vol%	45–50 vol%	0.50–0.55 (av)
Talcher (Jagnnath II seam)	60–65 vol%	5–10 vol%	25–30 vol%	0.50–0.55 (av)

Table 2.4 Stopes-Herlen system of classification

Macro-constituents	Micro-constituents
Lithotype	Macerals
Vitrain	Vitrinite having further divisions – collinite and tellenite
Clarain	Variable composition: Vitrinite – distinctive band Exinite – sporinite, cutinite, algaenite, resinite Inertinite – less distinctive micrinite, fine grained seleroinite, semi-fusinite, and fusinite
Durain	Inertinite and exinite
Fusain (Jagnnath II seam)	Fusinite

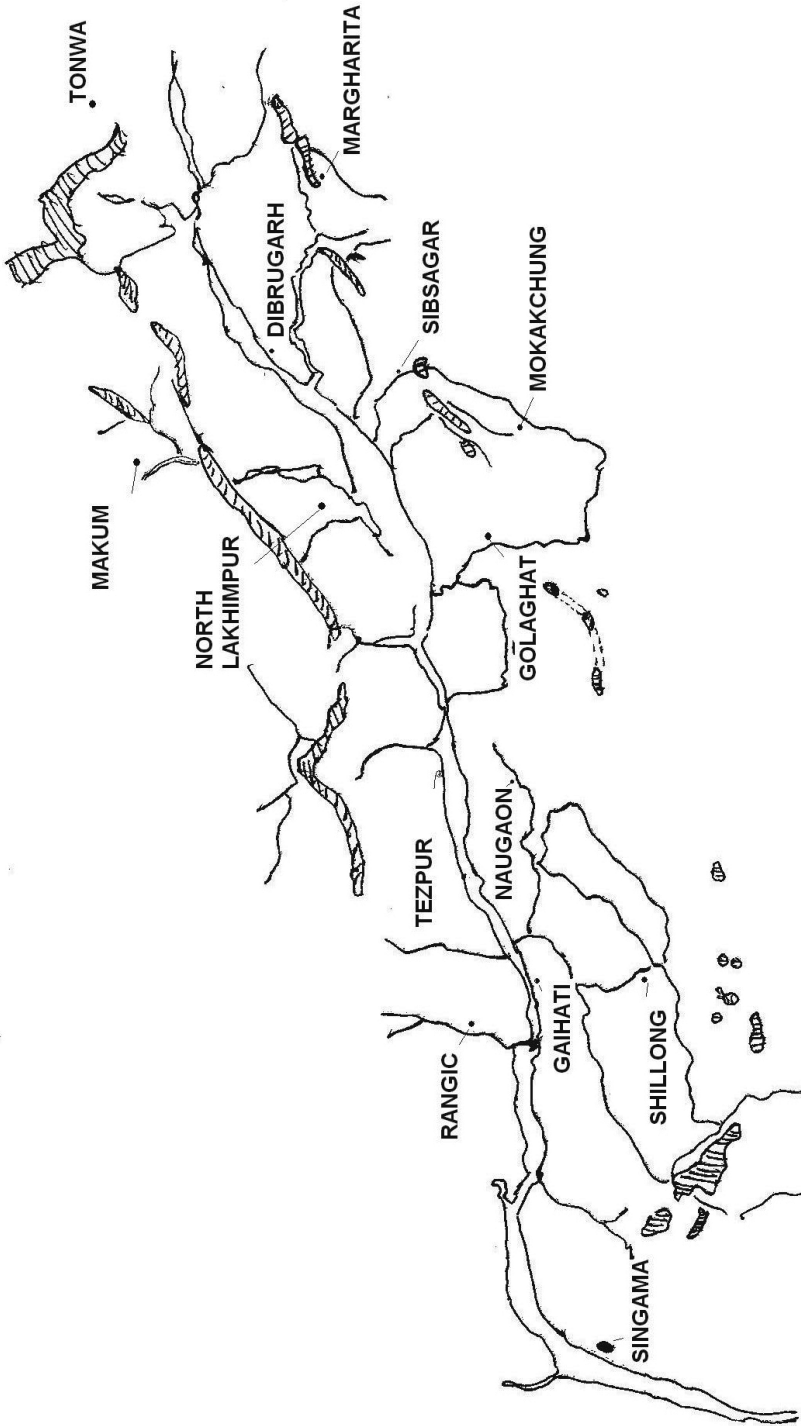
It is normal practice in reserve studies followed by GSI to estimate coal through preliminary data and report it as “inferred reserve.” Thereafter the reserves are confirmed by indirect method and reported as “indicated reserve.” Finally bore hole samples are drawn actually in the field and based on analysis of these bore hole samples “proven reserves” are declared. Thus studies with North-eastern coals in 1950’s inferred reserve was declared as 200 million tons and later in 1960’s indicated reserve was declared as 900 million tons and finally till this date 200 million tons has been concluded as proven reserve. However in Himalayan region all coals are not accessible due to high terrains and actual reserve could be much higher while recoverable amount is much low. Further North-eastern coals contain large amount of organic sulfur. Tertiary coals are entirely confined to the foothills of the Himalaya and the North-Eastern region. Gondwana coals occur in isolated basins situated along prominent rivers as mentioned above. Nearly 50 such coal basins are known varying in size from few square kilometers to as much as 1500 sq kilometer; in addition there are over 20 small tertiary coalfields in North-Eastern region.

Coalfields in the Schuppen zone (North-Eastern India) are – Makum coalfields in Assam, Dilli-Jaypur coalfields in Assam, Namchik-Namphuk coalfields in Arunachal Pradesh, Nazira-Borazan coalfields in Nagaland, Jhanji-Disai small coalfields of Nagaland. These tertiary coals of North-Eastern region belong to Eocene and Oligocene ages (Table 2.5).

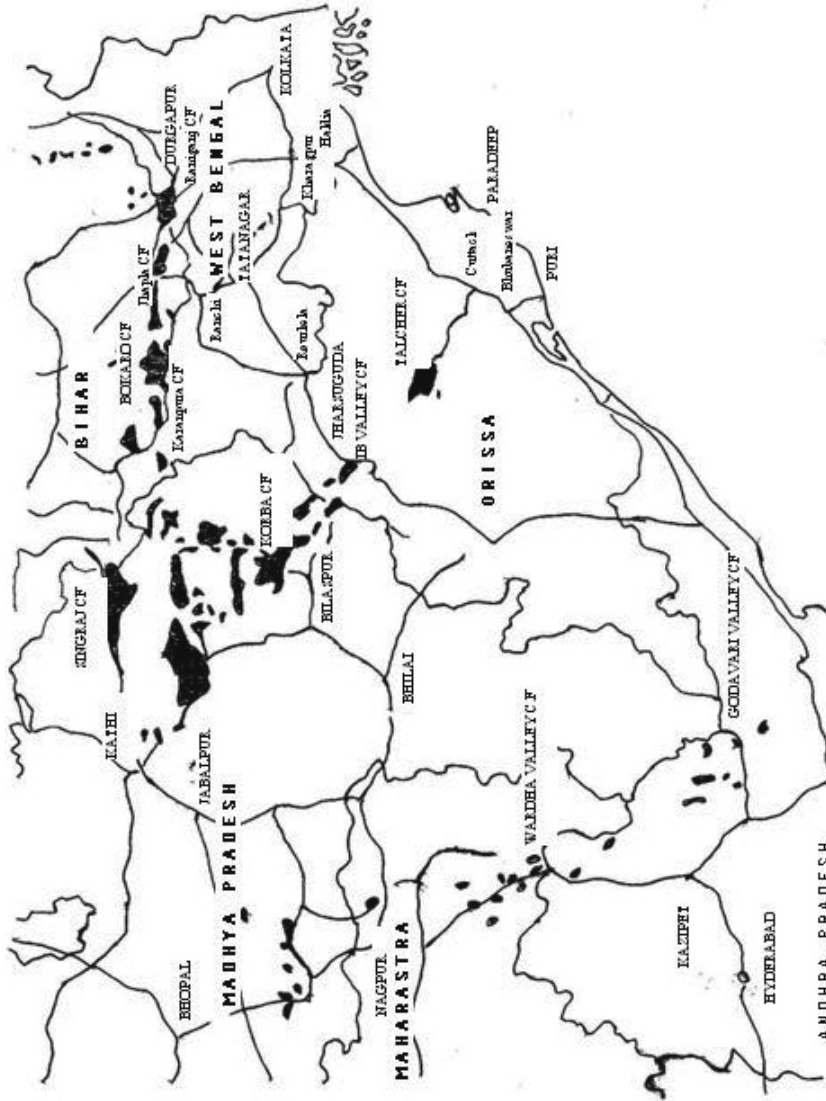
Assam coal is particularly characterized by high caking index, low ash but high organic sulfur (2–7%). These coals are unique in the sense they are very homogeneous (90% and above is vitrinite) in all layers. Comparative studies on vitrinite reflectance and sporinite fluorescence in relation to coal properties show that the vitrinite reflectance is more closely associated with volatile matter content and calorific value as well as maximum fluidity. Northeastern coals on carbonization yields double the amount of tar than Gondwana coals. These coals are also very much

Table 2.5 Proximate analysis of North-Eastern coals
 (Properties serial numbered in the Table: 1 = moisture, 2 = ash, 3= volatile matter, 4 = fixed carbon, 5 = fuel ratio, 6 = carbon, 7 = hydrogen, 8 = oxygen, 9 = nitrogen, 10 = sulfur, 11 = caking index, 12 = calorific value (btu/lb), and 13 = mineral matter).

Property S. No.	Name of mines												
	Boragolai	Tikok	Namdung	Tipong	Ledo	Laitrynge	Mikir	Garó	Dilli	Joypur			
1	2.1	2.7	2.2	3.5	3.4	3.8	10.9	7.4	4.4	6.2			
2	1.9	3.4	3.2	19.4	16.3	14.8	41.4	8.7	6	6.6			
3	45.2	43.5	42.1	36.8	36.3	43.8	30	37.9	44	39			
4	50.8	50.4	52.5	40.3	44	38.2	17.7	46	47	48			
5	1.12	1.16	1.25	1.10	1.21	1.15	0.60	1.42	1.06	1.22			
6	73.3	75.2	77.2	61	64.3	62.9	31.9	63.5	72.5	65			
7	5.5	6.4	5.6	4.8	4.4	5	2.3	4.5	5.8	4.7			
8	8.8	9.1	8.3	7.1	9.4	9.7	14.6	14.8	11.1	13.5			
9	1.25	1.31	1.1	1.0	0.9	0.8	0.4	0.8	1.7	1.2			
10	4.6	3.5	2.8	2.5	1.8	3.9	2.1	1.9	2.5	6.5			
11	24	16	22	13	14	17	-	-	7	2			
12	13990	13680	13930	0940	11550	11400	5590	11100	13230	11710			
13	2.1	3.8	3.9	23.1	18.6	17	-	9.7	7	-			



2.1 Location map of coal fields of north-eastern India.



2.2 Part map of India showing major coal fields.

amenable to liquefaction like low rank coals. Coke quality is the first parameter dictating suitability of coal for steel industry. Table 2.6 shows the coke quality obtained from North-Eastern coals.

Both ash and sulfur content in coal is critical for metallurgical application. For example, since ash in coke requires more heat for melting and as a thumb rule, each kg of ash requires about 1.5 kg of limestone which results in increase in slag volume by about 2–2.5 kg per ton of hot metal. Similarly sulfur being removed as calcium-sulfide in blast furnace, more limestone is required for each percentage increase in sulfur giving rise to still higher amount of slag.

Normally, sulfur content of Namdung and Boragolai coalfields are in the range of 2.5–4.0 while that for Ledo and Tipong are still on higher side. The highest sulfur in above coals is 70–80% of above sulfur content. Delli-Joypur coals also contain high sulfur (3–4.5%) but pyretic sulfur in these coals is more (upto 60% of above sulfur content). Kailajan coals have sulfur content 3.65–6.35%. Average sulfur content in other mines are – Laitengrew = 3.9%, Jaintial hills (Bapung coalfield) = 6.6%, Borzan coalfields (Nazira coals) = 2.5–9.4%. Variation in sulfur content with depth has also been recorded and in Namdung coal mines sulfur content at 20 ft depth found to be 5%, while at 60 ft depth found to be 3.3%.

Because of above unique nature of Assam coal, its use mainly has been restricted to railways and tea gardens. The main reason for such restricted use is being high volatile matter, which generates profuse smoke during burning and subsequent extinction of fire, their high caking nature which causes agglomeration in the bed during combustion and hence blocks passage of air through it, their friability during storage, yielding friable coke on carbonization, and due to high sulfur content. Present author has experimented with the coke generated from these coals and found that

Table 2.6 Coke quality of various N-E coals

(million ton)			
States	Coalfields	Nature of Coke	Reserve
Arunachal	Namchik	Non-caking	91
	Namphuk	Non-caking	
Assam	Makum	Caking	235.66
	Dilli-Joypur	Non-caking	20
	Kailajan	Non-caking	0.60
Meghalaya	Garohill	Non-caking	388.72
	Lungrew	Non-caking	133
	Cherapunji	Non-caking	9.50
	Laitengew	Caking	11.0
	Laitengew	Caking	11.0
Nagaland	Nazira	Non-caking	10
	Jhanzi-desai	Non-caking	2.5

60% of the total sulfur in coal is retained in the coke matrix. Later these cokes were successfully used in cement making by vertical shaft kiln technology where use of retarder calcium sulfate in the generated cement was drastically reduced because of the sulfur on the coke. However direct use of these coals in cement making by VSK technology was not successful as it generates too much smoke. Carbonization characteristics of these coals are shown in Table 2.7.

The caking power of coal (i.e., its ability to form a hard coherent mass on heating) varies from zero for lignite type coal to a maximum with coals of about 88% carbon content, and then again decrease sharply to zero again at about 92% carbon. It follows therefore that coal required for manufacture of hard coke, must be chosen from the range in which caking power is well developed (i.e., in the range 83–90%). If the main objective is to derive gas (coke the secondary product) as in gas production industry, the choice will be high volatile caking coal. As the caking power increases, the coal passes through the stage of plastic and the starting structure slowly replaced by cellular structure which hardens to the coke form. During coking devolatilization is always complete below 1000°C and the left over volatile matter remains in coke. For any given coal reactivity of the generated coke decreases with decrease in carbonization rate (i.e., more time required for the carbonization). The most strongly coking coal produces the most unreactive coke. Bituminous coal have specific gravity in the range 1.12 – 1.35, while that for middlings is 1.40–1.80 and carbonaceous shales 1.60 – 2.20. Assam coal having high caking index suitable for blending with non-coking coals. This blending technique while generates better (hard) coke from non-coking coals, simultaneously brings down total sulfur content of the blending Assam coal. Such a trial was first carried out at TISCO, Jamshedpur (India) in 1952. Further studies at Central Fuel Research Institute, Dhanbad (India) in 1975 at Bhilai Coke Oven by SAIL and CIL, established possible blending upto 6% ash coal obtained from 60 ft seam of Boragolai coal to the extent of 10%. Afterward in 1982, SAIL (steel Authority of India) experimented blending these coals upto 15% limit, but the results were not encouraging. Subsequent trial

Table 2.7 Gray King Assay at 600°C of NE-coals (in terms per ton coal)

Source	Coke	Tar	Liquor	Ammonia	Gas	Coke type
Namdung quarry	672 kg	128 liters	70 liters	0.8 kg	118.7 m ³	E
Deep mine	682	151	63	0.8	107.3	G
Boragolai	684	161	56	1	109.4	G1
	Caking index	Swelling index	Micum index			
Namdung CF	24	3.5	M ₄₀ = 70, M ₁₀ = 12			
Tipong CF	20	2.5	M ₄₀ = 65, M ₁₀ = 12			

runs at Durgapur Steel Plant, West-Bengal (India) with 4% and 8% Assam coal failed to pass Micum test.

As mentioned earlier, due to presence of organic sulfur in Assam coal, they are very much amenable to liquefaction and the tests were carried out by Central Fuel Research Institute, Dhanbad in 1960 although found technically feasible, was not pursued further due to low price petroleum oil at that time. However the scenario has changed considerably in last 45 years and crude petrol price has jumped from \$15 a barrel to \$72 a barrel and the process now warrants a fresh look into it. In such an effort, Govt of West Bengal (India) in 1998 made a fresh study based on technical data available at that time, and now it seems coal to oil is economically feasible. SASOL plant in South Africa during World War II has proven commercial scale technical feasibility of converting coal to oil. We further discuss this point in detail in Chapter related to coal liquefaction.

2.3 Coal beneficiation

When we mention washability characteristics of a coal, in broad sense it implies its amenability towards quality enhancement through beneficiation technique. Washability characteristics of a coal, in turn, varies with the amount of impurity present in it, as well as nature of these impurities. A particular mined coal is first tested for its cleaning potentiality in the laboratory and then send to washery for cleaning. These lab scale tests are known as “float sink test.” Size of the coal is another factor for beneficiation of coal by these methods and coals are crushed to the desired size depending on the proximity of the dirt or its adherence with coal particles, and also depends on the particular use of the coal after beneficiation. For ascertaining this size distribution, coals are crushed to different size ranges in small scale first and washability tests are carried out in order to find percent recovery of clean coal with respect to size variation. Similarly studies on the cleaning characteristics of individual size fractions within narrow limit, give greater flexibility in the subsequent combination of results in required size limits that conform to the duty specification of commercial washing units. In cases like coking coals, a large amount of middlings or sinks are obtained, and thus it becomes necessary to repeat the experiments on middlings alone in various size ranges in order to assess further clean coal recovery potentiality.

Various organic liquids are also used for these float-sink tests and their specific gravity varies from benzene (0.86) to carbon-tetrachloride (2.80). Specific gravity in between ranges is being varied by blending two liquids of two different specific gravity to obtained desired specific gravity. Chlorinated salt solutions, especially zinc-chloride, are recommended for testing coal samples above 3 mm size. Zinc-chloride can be used to prepare

solutions with specific gravity varying between 1.25 and 1.80. For coals above 13 mm size, sulfuric acid solutions (sp gr = 1.25–1.80) can be used provided the coal contains low carbonate ash in it. Separations involving use of higher specific gravity liquid such as carbon-tetrachloride, bromoform, calcium chloride solutions, or pulp in water is also sometime used and such separation is termed as “dense media separation.” Calcium-chloride is corrosive and densities above 1.4 are too viscose to use. Jigging is a process for ore concentration, carried out in any fluid and depends upon its effectiveness on difference in specific gravity of the granular mineral particles. It basically consists of stratification of the particles into layers of different specific gravities, followed by removal of stratified layers. The stratification is achieved by repeatedly allowing a very thick suspension of the mixed particles an opportunity to fall until settled. Fine particles are further accelerated to settle by consolidation trickling in a pulsating jig (suction is applied along with pulsation). Small coal particles (less than ¼th inch in size) are difficult to settle by these wet float-sink method and require very long time to settle. This cause decreases in efficiency of output from the washery. In such case, dense media dry cyclone can be used to effect its rapid separation. In cyclone dust particles enter tangentially downward into the cylindrical chamber and after whirling down the cyclone and separation of the particles, the gas passes through the central axis directly upward outside the separation chamber. Thus dynamic situation within the cyclone develop the unusual property of decreasing viscosity of the medium in contrary to a conventional liquid settling tank where agitation will ruin the separation process. The limit of the lowest size of coal particles that can be treated in a cyclone washer is determined not by the cyclone itself but by the problem of recovering the medium from such small particles. This limit is generally set at ½ mm for all practical purpose and at this size, the separation is both reasonably rapid and efficient. The upper size limit of the particle is determined by the aperture in the cyclone and can be upto 2 inch, although this is unusual. In Australia, the top size is generally maintained at 1/4th over an inch. The cyclone is at its maximum efficiency hen the specific gravity of separation is as close as possible to the specific gravity of the medium (Table 2.8).

To achieve this, the diameter of the vortex finder should be slightly greater than that of the spigot.

Capacity of a 14 inch diameter cyclone is about 25 ton/h throughput while that of 20 inch diameter is 50 ton/h throughput. CFRI (Dhanbad), India has developed an apparatus for float-sink test of fine coal and for ores size below 3 mm. The apparatus is known as “Sarkar-Manchanda” apparatus. The design and sell of the apparatus has been licensed to a foreign firm “W. Feddler and Co,” West-Germany. Some of the special

Table 2.8 Comparison of Indian and US coals

Properties	US sub-bituminous coal				Indian bituminous coal			
	Kemmer	Colstrip	Centralia	Glenmark	Bengal/Bihar	Maharashtra	Singarini	Singrauli
Moisture (%)	20.3	25.5	20	28	9	4.3	7	5.9
Volatiles (%)	34.2	27.72	34.4	26.3	31	18.76	21.5	25.9
Fixed carbon (%)	41.7	38.33	29.6	29.7	36	36.63	33.6	26.8
Ash (%)	3.8	8.45	16	16	24	43.31	38	41.4
CV (kcal/kg)	5400	4860	4500	3780	6000	4540	3600	3640
ID (°C)	1126	1121	1198	1160	1280	1240	1445	1480
ST (°C)	1165	1232	1254	1294	1380	1540	1500	1480
FT (°C)	1338	1287	1427	1350	1400	1540	1510	1480
Ash analysis								
Silica	55.5	36.4	42.5	51.3	61.8	64.15	68	63.1
Alumina	13.1	18.5	26.2	22.2	26.5	27.54	18	27
Ferric oxide	4.8	5.1	5.8	2.9	5.4	5.56	11.91	4.5
Calcium oxide	8.6	15.6	9.8	6.8	2.5	0.52	0.33	0.8
MgO	3.9	6.6	1	2.2	1	0.1	1.45	0.7
Sodium oxide	0.2	0.2	1.3	0.1	—	—	—	0.1
K ₂ O	0.5	0.4	0.4	1.9	—	0.41	1.13	1.1
TiO ₂	0.5	0.7	3.8	0.8	—	1.62	—	1.5
P ₂ O ₅	0.4	0.2	0.6	0.3	—	—	—	0.3
SO ₃	0.3	14.9	7.1	4.1	—	—	1.54	0.1
Not accounted	4.6	3.2	1.5	7.4	0.8	0.1	—	0.8

Source: Operational experience in utilization of coals in Indian power stations – H.N. Sharan and K. Vijaychandran; World Science News 15(2), 10–16 January (1978).

feature of the apparatus are as follows:

- (a) Entire operation (including separation and discharge of float-sink) is affected inside a closed system, and the evaporation of volatile liquid used for separation is almost eliminated, as a result of which the worker is exposed very little to the toxic vapor of the oil.
- (b) The experiment can be completed in half the time of a conventional method.
- (c) Results are more accurate and have good reproducibility factor despite shorter time required for the experiment.
- (d) Chances of personal error are minimized.
- (e) Special arrangements in the apparatus allow direct discharging of separated product into the closed filtration system connected to water filter pump.
- (f) Unlike conventional systems, there is no limit to the lower size for this apparatus.

On completion of the float-sink test, the fractions are dried, weighed and ash determined. The percent yield of total coal which is within ± 0.10 specific gravity range in the most effective density range of separation is known as "near gravity material." Such an experimental curve can be derived from yield-gravity plots. For easily washable coals, the near gravity material curves not only show a tendency to decrease both at lower most and higher most density ranges of cut but becomes maximum in the intermediate density range of cut, which generally vary from 1.45 to 1.55.

In general, specific gravity range important for industrial scale beneficiation which can be effected by these techniques can be categorized as follows:

- (a) Specific gravity 1.30–2.00 – involving separation of coal from shale or other refuses.
- (b) Specific gravity 2.60–3.00 – separation of gangue minerals such as silica or silicate and calcite from oxides or sulfides.
- (c) Specific gravity above 3.00 – separation of clean metallic mineral concentrate from the middlings or one metal-sulfide from another.

As a general rule, concentration of near gravity material varies directly with fixed ash content and varies inversely with free dirt content. But again exact yield of near gravity material depends on the conglomeration of the specific gravity fraction around the desired separation density range. According to Bird (USA), following washability criteria was proposed in 1931 for various specific gravity ranges:

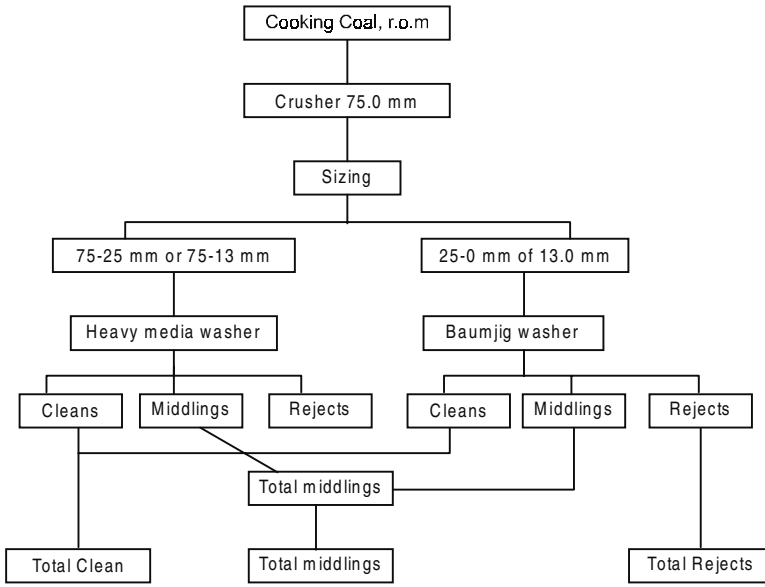
+0.10 Specific gravity distribution present	Washability characteristics
0 – 7	simple and any process can be adopted.
7 – 10	moderately difficult
10 – 15	difficult
15–20	very difficult
20 – 25	exceedingly difficult
Above 25	formidable.

Most of the Indian coals fall under formidable category mentioned above, whereas most of the American coals fall under simple to moderately difficult category. Indian coals (except the Assam variety), the near gravity material hardly come down to below 25–30% at 15–17% ash level, as against 10–12% usually obtained in the separation of American and continental coals at the clean coal ash level of 7–8%. Most of the inferior coals at Jharia, Bokaro, Raniganj, Ramgarh, Karampura, and central Indian coal fields exhibit much more cleaning characteristics as they often contain 60–80% near gravity material at the desired density operation. Assam coal, as mentioned above, being friable in nature, generates a large amount of fines (especially after storage) and its ash percentage with time has increased (Boragolai mines) from average 4 to 12% recently. Indian coals are of drift origin and thus difficult to wash.

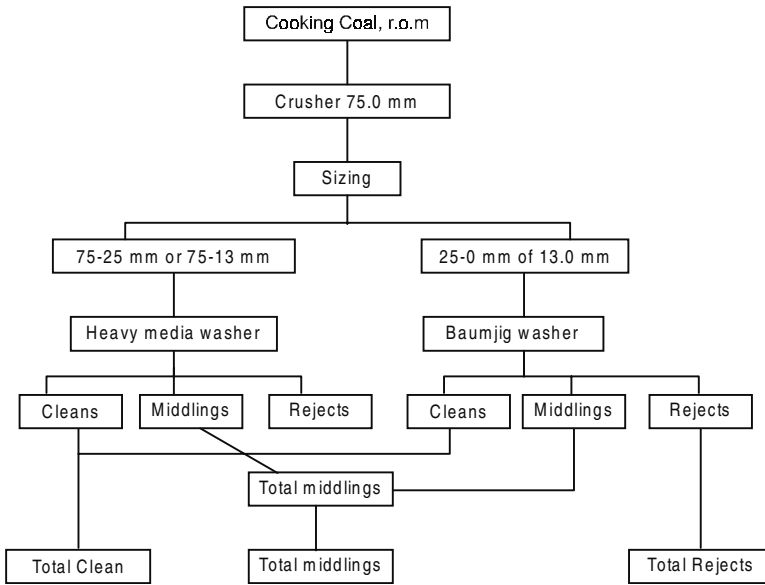
Three groups of washing techniques have been evolved which best suite our ROM coals:

- Group I – washeries designed to wash coal of easy to medium cleaning characteristics. Figure 2.3 illustrates washing scheme for such group of coal. The washeries at Bojudih, Durgapur (HSL), Kargali and Gidi conforms more or less to this category.
- Group II – composite washing scheme for coking coal under this category with prewashing is shown in Fig. 2.4. Both Dugda-I and Pathardih washeries are of this category.
- Group III – this includes washeries schedule to wash coal of difficult cleaning characteristics. Figure 2.5 shows the washing scheme of this group of washeries. Washeries installed at Kathara, Swang and Durgapur (DPL) as well as Dugda-II falls under such category.

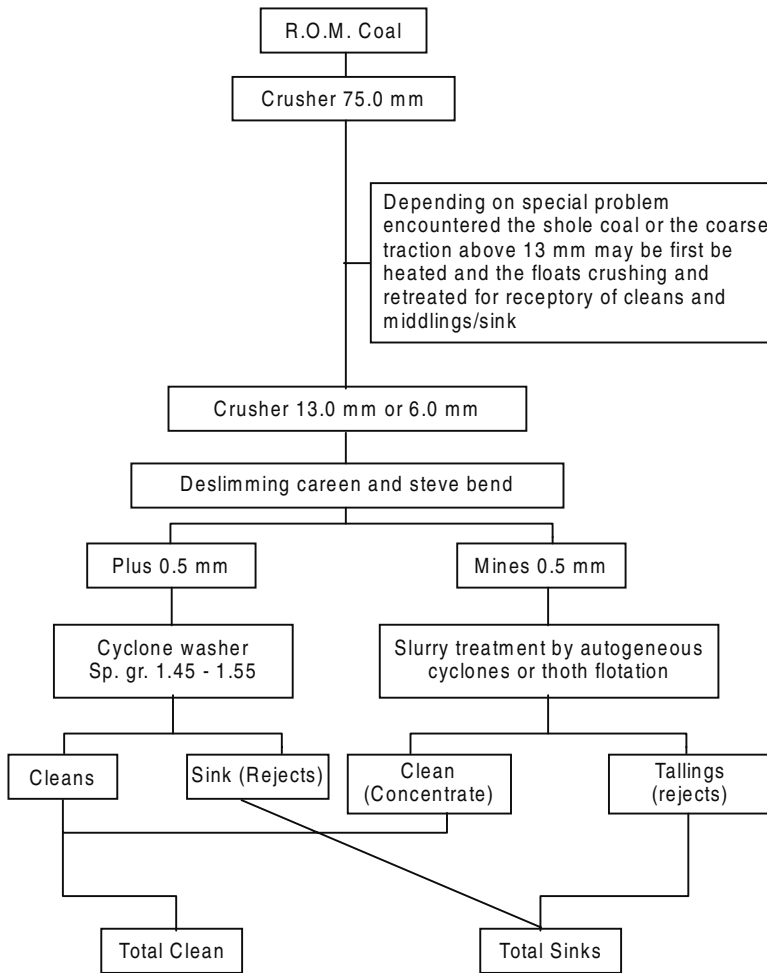
As mentioned earlier, for determining suitability of a particular type of washing for a specific batch of coal, first washability curve is established in small scale. Depending on the quantities plotted in the abscissa and



2.3 Composite washing scheme of coking coal (without prewashing).



2.4 Composite washing scheme of coking coal (without prewashing).



2.5 General washing scheme for upgrading of interior coking coal.

ordinate of the XY curve, they can be classified into following four categories:

- The characteristic curve or fractional yield versus ash curve.
- Total floats versus ash curve or cumulative float curve.
- Total sink versus ash curve or cumulative sink curve.
- Yield versus specific gravity curve.

The characteristic curve in above series is regarded as the parent curve from which other two curves (i.e., total float vs ash and total sink vs ash curves) can be derived by direct calculation or graphical plotting. The fractional yield in such case is expressed in percentage of the total coal. Total float vs ash curve directly shows the recovery of clean coal, and for

this reason this particular curve finds more frequent use in practice than the characteristic curve. Similarly the total sink vs ash curve is obtained by plotting cumulative yield of sinks at any specific gravity. The curve is complementary to the total float vs ash curve, and show directly the ash content of the total sink at any yield level of sinks or clean floats. In contrast to above three curves, the gravity-yield curve shows that the relationship between the specific gravity of separation and the total yield of clean coal which floats at that specific gravity. Thus the desired specific gravity of separation corresponding to any yield level of clean coal can be provided by this curve.

Due to near linear relationship of ash with specific gravity of a coal upto the 40% ash level, the yield-specific gravity curve when drawn on a proper scale and in a regular manner, becomes roughly parallel with the characteristic curve, specially for specific gravity less than 1.60. If the characteristic curve approaches a straight line (i.e., without any concavity) the coal becomes more difficult to wash and this is all the more true when the curve approaches vertically (i.e., becomes nearly parallel to the vertical axis). On the other hand, if the characteristic curve lies mostly near the vertical axis and then takes a sudden turn towards horizontal axis, the coal becomes very easy to wash. Thus the characteristic curve indicates optimum level for separation but also construct directly the total float ash or the total sink ash curve by means of area integration. However the chief limitation of the standard washability curve is that the yield of middling of any stipulated ash content cannot be directly read from them. In order to circumvent this difficulty, middling curves have been developed by CFRI (Dhanbad), India whereby direct reading of the yield of middling of any specified ash content is possible for any particular level of ash for the cleaned coal. Thus once the ash content of the primary cleans is made known, the middling curve or more specifically the secondary float curve, can be derived from the characteristic curve following the principle of area integration. The great advantage of the middling curve is that it can be drawn along with the standard curve in the same diagram and from it one can set at once what will be the middling of various stipulated ash content.

CFRI (Dhanbad), India in 1968 also proposed (in 4th International Coal Preparation Congress, Harrogate, UK), a new scale known as "Washability Index" for comparing washability characteristics of different coals. This index represented by a number ranging from 0 to 100, is independent of the overall ash content of the raw coal or the level of ash in clean coal. Lower the index value, more difficult it to wash. In such case the Meyers curve (ash unit curve explained in following section), is redrawn by expressing the cumulative ash unit at different yield levels as percentage

of the total ash in the raw coal. For any coal this yield-ash distribution curve originates at zero yield (corresponding to 0 ash) and terminate at 100 yield (corresponding to 100% ash). For any hypothetical coal, which is absolutely non-washable, this curve has to take the form of straight line running from zero yield (with zero ash) to 100 yield (with 100 ash). On the other hand, the greater is the concavity of this curve, the better is the cleaning characteristics of the coal. When the area bounded by the curve and the diagonal through the zero yield and 100% ash is expressed as the percent of the total area bounded by the two axis and the diagonal, we get the “washability index” in terms of pure numbers lying between zero and 100. Comparison of such indices for Japanese, Australian and South African coals show the index to range from 20 to 49, which resembles that of Indian coals.

CFRI (Dhanbad), India has also offered another simple criterion, known as “yield reduction factor,” for defining cleaning characteristic of coal. This is achieved by simply expressing the percent reduction or the sacrifice in yield for each percent reduction in ash content at any selected ash level of the clean coal (i.e., the factor = % yield/% ash reduction). It has been observed that the yield reduction factor for any particular coal seam remains reasonably constant so long as the size grading of the coal and its ash level do not undergo appreciable level of change. The lower the yield reduction factor, the better is the washability characteristic of the coal. This method is very useful in day to day operation of a washery, receiving supplies from various mine heads.

2.4 Representation of washability data

Washability data can be represented by two methods:

- (a) Block diagram (representing performance), and
- (b) Graphical method (for comparing the performance data).

2.4.1 Block diagram

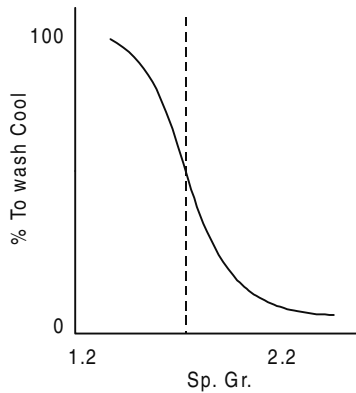
There are three types of block diagrams used regularly and these are – distribution diagram, mirror diagram, and Hancock diagram. In the distribution diagram, yields obtained at various density levels for a number of screened sizes are displayed. The width of each curve show the relative proportion of each size fraction floating in a series of liquid with increasing density. The mirror diagram, on the other hand, is prepared for the same coal before and after the washing. The diagram for the washed coal is drawn above that for the unwashed coal but in inverted form. If separation is ideal, one diagram is the mirror image of the other. And the difference

in the measure of the inability of the washing plant to make clean cuts on the coal tested. In the Hancock efficiency chart, weight fractions of refuse corresponding to several intervals of specific gravity (in terms of percent raw coal) are marked on a square with shaded area. Thus the total shaded area represents the total amount of refuse. The area of the square indicate the weight of the raw coal. Among above three methods, the distribution diagram give a simple overall picture of the nature of the separation affected. While the mirror diagram give a comprehensive visual indication of the difference between ideal and practical washing processes for most practical purposes the simpler Hancock chart is sufficient. In cases where more detailed information are required, graphical method with associated formulae is suggested.

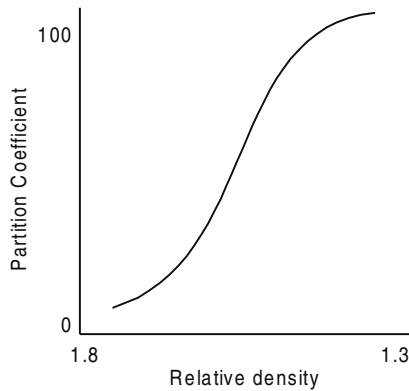
2.4.2 Graphical method

In actual practice, no commercial washing process result approach very close to the ideal washability curve, because of the difference in effects of the factors of particle shape and size on the result. This deviation of performance may be represented and evaluated by plotting the proportion of material included in the wrong product (at any specific gravity level), against the difference between that specific gravity and the specific gravity of separation for the coal. These values, from float-sink test data or from washing practice, may be plotted conveniently as mentioned by Yancey, Gear and Shinkowsky. Here coal of low density and refuse of high density are obtained as washed coal and refuse, respectively. As the specific gravity of separation is approached, the proportional of material obtained in the improper product increases rapidly. The curve thus obtained resemble a Gaussian Error Distribution Curve and washing performance can be assessed from such error curve (partition or distribution type). These curve represent practical results against float-sink data and thus shows deviation between practical and theoretical results. The results may also be expressed by three mathematical coefficients such as – Tromp error curve (Horsely and Vhetan) and the Meyer curve (Fig. 2.6 and 2.7).

In Tromp Error Curve, specific gravity is plotted as abscissa and percent sink as ordinate. Ordinate indicates the probability that a particle will be found in the sink. The value of the density (specific gravity) corresponding to 50% particle appearing as clean coal or dirt. Ordinate is called the partition density which shows the equal chance If the upper half of the curve is inverted the area under the curve measures the deviation of the curve from ideality. The smaller the area (Tromps area or Error area) the more closely does the washing process conforms to the ideal. The performance of two washers can be compared by determining the areas obtained with each when washing the same coal. With perfect separation,



2.6 Typical distribution curve.



2.7 Partition curve.

the area would be zero; the curve running at zero ordinate to the point D, then rising vertically to the value 100. The error area is the first coefficient deduced from the curve. The probable error is the half of the densities between two ordinates, which determines the width of the error area, so is also the measure of the separation error. Probable error is the second coefficient and imperfection in the third coefficient, mentioned above. Imperfection is the probable error divided by partition density minus one. Imperfection varies little with partition density and expresses the performance of the washer. It should be noted that the error curve is a function of particle size. Larger is the particle more close is the separation. Hence coal of certain size grading should be used when comparing performance of different washers. The Meyer Curve (Dell), on the other hand, represents three standard washability curve by a single one and is similar to the ash unit curve independently developed by CFRI (Dhanbad),

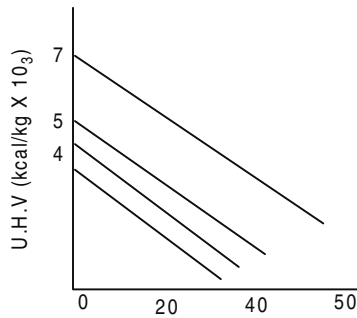
India. The curve expresses cumulative ash content of the floats as a percentage by weight of the coal feed against cumulative percent yield of floats over a range of specific gravity intervals. Thus the recovery of clean coal is directly read from the yield axis while the direction of the vector represents the percent ash. The specialty of this curve is that, the yield of middling for any stipulated ash content, for all ash levels of clean coal, can be readily obtained from it. To find out the yield of middling at any predetermined ash level, a straight-line is drawn to connect the ash content with zero yield. Then from the point of intersection of the curve with the straight-line joining the desired ash percentage of clean coal and zero yield, a parallel is drawn to the aforesaid middling line to cut the curve at a second point. The corresponding yield percentage is noted and by deducting from it the yield of cleans, the yield of middling is finally obtained. In a similar way, yield of ash content of the rejects or sink can also be determined from above plotting.

Considerations also have been given in the past by various organizations for effective beneficiation of different Indian coals and their recommendations are as follows:

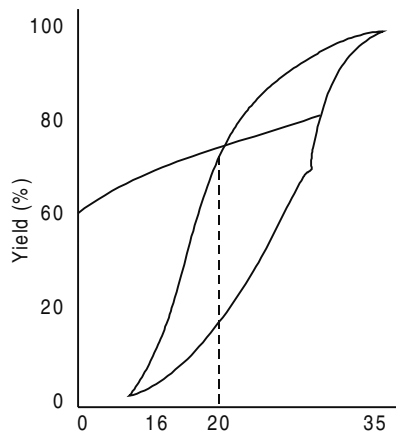
- (a) Deshaling of coal to 30% ash is economical for power stations situated at 1000 km and more from the coal source, considering transportation charge (ref: Report on cost effective beneficiation of non-coking coal for thermal power station – Subcommittee on Coal Beneficiation, SSRC, Govt of India, May 1988).
- (b) A 5% reduction in ash from 35% ash coal (in a 210 MW unit) would result in a saving of Rs 40 million per year (ref: Report on Trial with Beneficiated Non-coking Coal from Nandan Washery at Satpura Thermal Power Station, National Productivity Council).
- (c) The investment of Rs 500 million in setting up a plant to beneficiate 2.64 million tons/year containing 37% ash to 25% in a 450 MW plant would be paid back in 5 years due to benefits of using beneficiated coal (ref: Coal Beneficiation for Power Generation at Talcher (RRL-BBSR and Mecon (Ranchi), 1989).

All above considerations are limited to deshaling and deashing of coal at sizes above 10–25 mm. However, the coal in the power stations are subsequently ground to 80% passing 75 micron for use in boilers. But below 100 micron, the liberation characteristic of two coals studied indicate that ash could be reduced to around 20% without any sacrifice to the useful heat value (Fig. 2.8 and 2.9).

The known technique of beneficiating (viz. conventional floatation, oleo floatation, column and spray floatation, oil agglomeration, selective flocculation, etc.) can be adapted to realize such results in practice. The cost of beneficiation is to be accounted against – grinding, separation and



2.8 Useful heat value vs ash.



2.9 %ash versus ash content of coal.

dewatering. While grinding is anyway necessary and would not be an additional cost, the cost of separation is relatively less as compared to dewatering. It is in this context that the concept of high concentration coal slurry is being considered for adoption in place of pulverized fuel firing and could eliminate an expensive dewatering step.

2.5 Efficiency of a washery

Three different formulae have been put forward by three different investigators for representing efficiency of a washery. These are as follows:

“Fraser and Yancy Efficiency” = $(\text{Yield of washed coal} / \text{Yield of float with same ash content}) \times 100$

“Drackeley Efficiency” = $(100 - \% \text{ float in refuse} \times \% \text{ refuse}) / (\text{percent float in feed})$

$$\text{“Modified Drackeley”} = \frac{(\% \text{ recovery} \times \% \text{ sink in washed coal})}{(\% \text{ sink in the feed})}$$

2.6 Economics of coal washing

The cost of clean coal has direct bearing on the raw coal cost, plant operation and maintenance cost, and on loss in washing. Loss in ashing depends whether it is a two or three product washery. In a three product washery where clean coal, middling, and rejects are produced, the reject percent is a direct loss whereas middling forming a certain percentage of ROM feed, has to be sold at a much lower cost than the input price of raw coal. Where two product washery is in operation, washing loss may be less as compared to a three product washery, depending on the price and yield of the middling produced. The cost of clean coal is therefore depends on following factors: type of feed coal, type of product desired, type of washing used, and washery utilization factor. The first factor includes wide variation in size distribution in ROM coal. The second actor (product type) includes yield of various products either in a two product or three product washery. Here the near gravity material plays an extremely important part and if the operation between clean coal and middling can be achieved to a high degree of efficiency, cost per ton of clean coal can be brought down considerably. This is possible to the extent permissible as per washability characteristics of the coal fed to the washery. Depreciation of the plant also plays a vital role in the final cost of clean coal. Washeries can build pithead or can be installed in a centralized location in the midst of a number of collieries, depending on the pits output, infrastructure facility, by-product disposal, etc. From initial capital investment point of view, units of large capacity are preferable to smaller ones. Wear of chutes, launders and generation of fines are less with high capacity machines as there are less transfer points. It has been found that jigs and screens are economical when their individual feed rate is more than 400 ton/h. Filters and floatation machines are economical when their capacities are not less than 40 ton/h. With above considerations one has to decide upon the right size of individual machine which will produce maximum economy. In last three decade, mines targeted output is being achieved increasingly through more and more mechanization which, in turn, gives rise to more and more fines. ROM coal is accordingly loaded with more of free dirt and increased percentage of moisture. Present trend of washery design involves construction of modular (so that capacity can be increased in steps) and small portable (75–150 ton/h) unit. Though the conventional crushers (single or double) are still in use for pretreatment of washery feed, common practice in some of the major coal producing countries is to reduce all the

ROM coal to below 150 mm by means of rotary breakers which combine in a single operation – screening, crushing and packing. For non-coking coal such simpler dry methods are used for separating rared stone and abrasive minerals. Integrated circuits incorporating simple jigs and oil-agglomeration units which has been developed in India, have shown great potentiality for use in the beneficiation of high ash difficult to wash coking coals. Apart from the fact that much higher recoveries of metallurgical grade coals can be ensured by the application of this integrated process, its operation and maintenance problem will be much simpler as the use of expensive vacuum filters and thickeners can be kept at the minimum.

Jigs are still the most common coal processing units closely followed by heavy media systems. Heavy media processes are rapidly gaining ground, particularly for low density separation and for coals containing high percentage of middling of near gravity materials. There appears to be new equipments in the market, although there are various modifications and improvements already incorporated in existing models. These improvements are generally brought about in Baum jigs or various configurations of heavy media vessels. Increased interest is being paid now to Humboldt Wedge Batac jigs. For cleaning small size coals, generally down to 0.5 mm or cinders, Vorsyl centrifugal separators and Deister tables are used. A centrifugal separator, developed by Soviets, uses a true heavy inorganic liquid as media (calcium-chloride), while Otisea process recently introduced in USA, uses a dense organic liquid as media. Froth floatation continues to be the most widely accepted technology for the treatment of slurry forming fines of coking coals. Cells as large as 36 cu. m, are now entering in the market. Another development in this field, is column floatation which consists of vertical cell upto 1.8 m² in cross section and over 18 m in height. Some of the newer plants are turning to small diameter hydroclones or water only cyclones particularly for treating fines (of about 0.5 mm diameter) which do not respond to floatation. Several plants are also experimenting with the use of heavy media cyclones treating down to zero size. Other solutions in this dircion include the use of Betac fine coal figs of Deiser tables for treating fines. Oil agglomeration technique, which is still at pilot plant trial stage, can provide the ideal solution for treatment of fines when it is fully commercialized.

2.7 Coal mining

Mining of coal is divided into two broad categories – surface mining and underground mining. Choice of either method depends on the geographical formation and subsidence occurring in the coal in coal mining area. While coal exploration in India is mainly done by Geological Survey of India, Coal Survey Laboratories (CSIR) and state bodies in India analyses

borehole samples collected from mines. Commercial production of coal is done in India by agencies (Table 2.9):

2.7.1 Bhaska method of mining

It is almost a hundred year since coal mining started in Makum coalfield of North Eastern region. It is almost a hundred year since coal mining started in Makum coalfield of North Eastern region. Bhaska system of mining has been followed for extraction of coal from different mines of India for decades and this method alone has been responsible for the whole production till 1976. In highly inclined thick seam with weak strata as well as friable coal in absence of stowing material, no other satisfactory method than Bhaska method would work. The development is carried on board and pillar pattern along the floor of the seam in this process. The level developments are done following the contour of the seam and the dip-rise diverges along the main inclination. The main levels are 18 m apart and dip-rise at 5.5 m interval. All developments and splitting work are done only by pick mining. For starting extraction, first a few inclined holes are made above 3 m from safety props to get a funnel like shape and blasted. Some widening and heightening is carried out along dip and rise for the convenience of operation and a few supports are put up if required. The heightening and widening process is then started from one split junction. The above process is continued only with hand drilling and blasting operation. After each blasting proper dressing by light pipe and attachment is carried out, and thus coal is obtained. The process of recovering coal by Bhaska method is a skilled operation. The method basically founded on the principle of stress distribution in enlarging domes and depends entirely on the skill of the person engaged. In the skilled region GI-pipes are preferred over others. Stainless steel pumps, their

Table 2.9 Organizational set up of coal industry in India

Company	Subsidiary	Jurisdiction
Coal India Ltd.	Eastern Coalfields Ltd	Raniganj/Rajmahal coalfields
	Bharat Coking Coal Ltd.	Jharia coal fields
	Central Coalfield Ltd.	Coalfields of Bihar, Orissa and Singrauli
	Western coal fields Ltd.	Coalfields of MP and Maharashtra
	Central Mine Planning & Design Institute	Specialises in exploration, planning and consultancy services
Singareni Collieries Ltd (Andhra Pradesh)		Coalfields of Andhra Pradesh
Tata Iron and Steel Ltd.		Own captive mines for steel plants
Indian Iron and Steel Co.	-do-	

repair, employing expensive pipe, etc, makes the process costly and hence always there was a search for a better and cheaper process to substitute it.

In recent time, attaining the twin objective of accelerated production and lower cost for the Indian coal industry is a challenging task as compared to the traditionally labor intensive nature of the industry. These objectives can only be achieved through greater mechanization which results in higher productivity and lower cost of production. In practice strategies adopted by mining industries to achieve these objectives are:

- (a) Greater application of mechanized surface mining.
- (b) Introduction of mechanized longwall mining method wherever possible.
- (c) Adoption of special mining technique specific to local condition. Needless to say, the success of this strategy is dependent upon the development of capacity for indigenous manufacture of equipment and ensuring supplies of spares and services.

2.7.2 Open-cast mining or surface mining

In this method, the mine is opened from top completely and the process is also termed as “quarrying.” In this case, the principal factor to be considered before adoption of open cast mining is the overburden to coal ratio, the physical characteristics of the seam, topography, and continuity of operation. With increasing overburden to coal ratio, the cost of removal of overburden (known as stripping cost) adds considerably to the cost of mining the coal beyond economic limit. To develop a mine, the break even stripping ratio (at the surface of the final pit) must be established. It is found from the formula:

$$B = (R - P)/S$$

Where B = breakeven stripping ratio (overburden per ton of coal) in meter³, R = market price of coal per ton, P = production cost, including cost of mining and preparation but excludes stripping cost per ton of coal, and S = stripping cost per meter³ of overburden.

Coal mining in under Indian scenario, the above ratio is given as 2.5:1 at present rate. Physical characteristics of the seam such as its inclination, presence of dirt or waste bands, variation in thickness and quality of coal influences the decision on adoption of open-cast mining. With dipping seams, the quantity of overburden to be removed rapidly increases as the coal is followed down the dip until a stage is reached when open cast mining becomes uneconomic, where potential reserve of relatively poor quality coal must be sold at a reduced price.

With limited reserve of coal, as compared to other major producers like

China, USA, and USSR, India's endeavour has been to convert as large as part of the resources is feasible to mineable reserve. With its high percentage of extraction, surface mining has always been attractive from the angle of conservation. Near large surface deposits, high grade deposits under deeper cover, deposits under adverse geological conditions occurring within economic depth of operation and pillars left in shallow underground workings, are all proposed to be extracted by open cast mining. Additional welcome features associated with surface mining are the higher productivity levels, lower costs and shorter gestation period. Share of open cast mining in India could be increased in large mines by working upto greater depth (upto 480 m). This in turn has necessitated development of larger and more powerful equipments. Most of the equipments proposed for open-cast operation are being covered under indigenous manufacturing. It is proposed to deploy draglines is also envisaged where a single dragline cannot deal with the full thickness of overburden. Walking draglines of 24–32 m, bucket capacity with 96–75 m, boom length (which are being manufactured in the country), are being planned and develop for bigger projects. In these projects, where dragline application is not feasible due to high overburden cover, haul back system with 10 cu. m rope shovels working in conjunction with 120 ton rear dumpers are standardized for application. In case of projects with high stripping ratio like at Amlori and Khadia, equipment sizes for haul back system have been enhanced to 20 cu. m shovels and 170 ton rear dumper. Hydraulic excavators are also being introduced for coaling operation as their selective mining is expected to be advantageous for working of the banded coal seams and relatively thinner seams which cannot be mined with rope shovels thus achieving better coal recovery. Non-diesel transport with crushing and belt conveying of coal and overburden are being envisaged to save on oil consumption. Cheaper blasting agents like site mixed slurry, are being introduced to reduce the cost of blasting.

Large reserve of good quality coking coal is locked up in developed pillars in thick coal seams in Jharia coalfield. There are, besides, multiple problems of fires, inundated workings, goofed out areas and crushed strata conditions. This coalfield has as many as 30 contiguous coal seams contributing to the complexity of mining operations. In order to maximize recovery of the scarce coking coal, large scale open cast mining of these developed workings is proposed. The master plan drawn out for Jharia coalfields, provide for 9 such open-cast blocks with strike length of 3 to 4 kilometers to extract the already developed pillars. Open-cast mining in this area is going to be a big challenge demanding meticulous planning and highly skilled innovative mining techniques.

2.7.3 Underground mining

The methods of recovering coal by underground mining can be categorized under two broad heads – board and pillar method and the longwall mining. The choice between pillar and longwall method, depends on rock pressure condition, nature of coal and adjacent strata, thickness and uniformity of seam, folding and faults, presence of dykes and flexibility of operation. In India, extraction of thick coal seam by square pillars is the usual practice adopted. However, the recent trend is shifting toward longwall process parallel to roof and floor. Hydraulic mining is also likely to find good application with our friable and moderately soft coals. The advantages of hydraulic mining are – winning of coal is not hindered by bringing of face support, the system is not very sophisticated to warrant complexity of adoption, higher output per working face results with steeply inclined seams. With increased emphasis on Open-cast mining to secure rapid increase in coal production, the share of coal won by underground mining has steadily decreased from about 80% in 1970–71 to about 54% in 1983–84. In absolute terms, however, underground coal production rose from 58.27 million tons in 1970–71 to 74.76 million tons in 1983–84, and is expected to reach a level of 150 million ton by 1999–2000. The early years of Indian coal mining saw the adoption of the board and pillar system of underground mining. While the European coal mining industry switched over to longwall mining earlier in this century. The manual board and pillar system continued hold away in India, because of relatively shallower depths. With mining conditions becoming more arduous due to increased depth of mining operations, the quantum jump projected in underground production could not achieve higher output without adoption of more efficient and productive mining technique.

2.7.4 Mechanized longwall mining

A concerted effort was made to introduce longwall mining in India in the post nationalization period. Field trials with different levels of mechanization with caving/stowing have been carried out since then. There has been a greater stress on caving method due to scarcity of suitable stowing material near coal mining areas. The initial trials were based on use of friction props/ranging drum shearer combination for stowing with 100 ton hydraulic chocks as goaf edge support for caving faces. The results from use of ploughs for thin seams (0.9 to 1.5 m) and double ended ranging drum shearers for moderately thick seam (1.5 to 3 m) appear to be promising. It is anticipated that longwall mining would contribute about 10% of the total underground coal production by the end of nineties. With greater application of longwall mining, it is proposed to step up its

contribution to about 25 % of the total underground production by the turn of the century.

2.7.5 Mechanization of the board and pillar working

Where the strata condition or the already developed working do not permit the introduction of longwall mining, it is proposed to increase the productivity of the board and pillar mining system by increased mechanization. The strategy adopted has been to mechanize loading and face transport operation since this would eliminate manpower engaged in manual loading tramming, thus contributing to higher productivity. Seaper loaders, aide discharge loaders and load-haul-dumpers have been introduced for board and pillar development and de-pillaring. Of these, load-haul-dumpers have given better results for the board and pillar mining condition.

2.8 Adaptation of special mining techniques

While the above technologies are suitable for ordinary condition, a special mining techniques are being adopted to deal with specific local conditions. Since most coal seams in India are thick, these cannot be exploited by single slice method. The choice here is mainly restricted to multi-slice longwall mining either with stowing or caving. Due to problems of lower productivity, poorer advances, higher costs scarcity of stowing material associated with stowing, the thrust has been towards perfecting caving techniques. Due to the fact that Indian coals are harder, the roof is stronger and the depth of mining shallower in these cases. Techniques perfected in France and USSR cannot be applied directly and are being modified to make them fully successful in Indian environment.

Other especial methods of mining under consideration or application, are hydraulic mining and shield mining to extract soft coals in the thick and steep seams of Assam. Schemes are also being worked out in collaboration with various agencies for dealing with special problems like caving under massive sandstone roof, caving under water bearing strata, working coal seams developed on semi-horizon method, etc. It is anticipated that with the implementation of above programmes, the share of under-ground coal production won by mechanized methods, which is currently 7% will increase to about 35% by the early part of next decade.

2.9 Conservation of coal

While India's total coal resources are estimated at around 112,000 million tonnes, the mineable reserves may amount to only about 60,000 million

tonnes. It is estimated that these reserves would be sufficient to sustain the coal requirement only for another 150 years, even assuming a lower rate of growth in coal consumption beyond this century. The position regarding coking coal is even more depressing the probable life expectancy being around 80 years. The need to adopt suitable conservation measures in coal production and utilization cannot be over emphasized in this context. Greater conservation is sought to be achieved in coal mining by maximizing the percentage of extraction of coal. Measures proposed for this purpose involve greater application of open cast mining, extension of such mines to greater depths, increase in the size of underground mines (to reduce loss of coal in barriers), adoption of longwall mining on a larger scale and extraction by stowing in thick seams and below surface features. Fires and spontaneous heating in Jharia coalfields, which would otherwise have led to substantial loss of prime coking coal reserves, have been successfully controlled. Coal Industry is also interacting closely with major coal consuming sectors such as steel industry and power generation authorities, research institutions and BHEL, to develop coal utilization processes which would promote greater conservation of coal. In August 1986, Department of Energy (Govt. of USA) selected steeply dipping bed underground coal gasification/steam injection gas turbine demonstration plant with hot gas clean up and direct reduction of iron ore, as the major national thrust area programme, considering both commercial viability and energy conservation requirement.

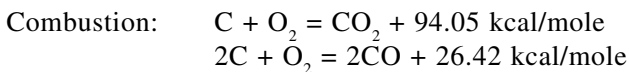
2.9.1 Harnessing coal by under-ground coal gasification

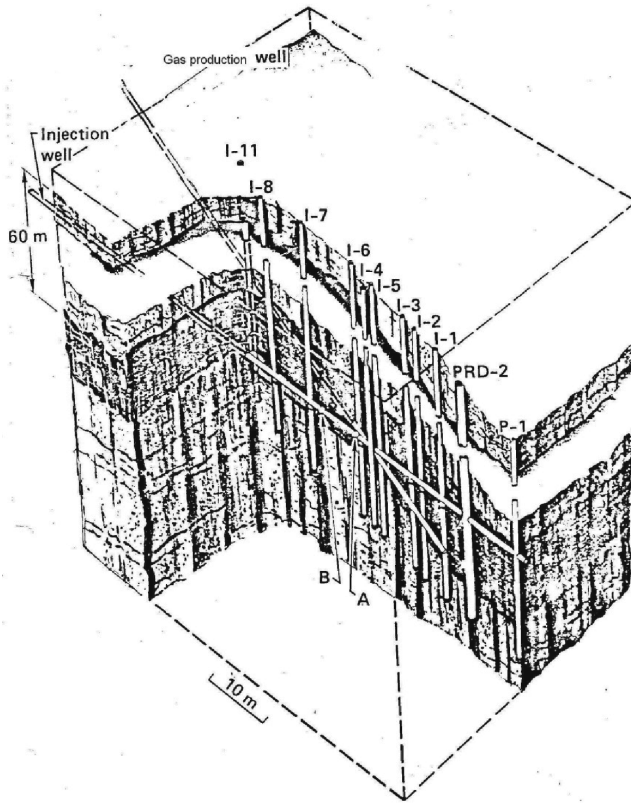
Underground coal gasification, in short called UCG, has the attractive feature of potential use of unusable energy resources like coal lying in deep and thick beds. Conventional mining of these coal beds is difficult if not impossible; at best less than 20 ft of the coal in a deep bed whose total thickness is 50–100 ft is extractable by underground mining. For UCG, low rank coals such as sub-bituminous and lignite are preferred to bituminous coals because the former shrink upon heating, whereas bituminous coals swell, and typically occur in thinner seams. It is estimated that minimum depths of 60 m for a seam of 2 m thick and 90–120 m for a seam of 6–9 m thick are required in order to avoid surface substance during gasification. The maximum depth is determined by the cost of drilling. The Soviets and early US experiments in UCG encountered severe problems when attempting to gasify coal seams 2 m thick or less. Heat losses are considerable in such thin seams, leading to low thermal efficiency and poor product gas quality. A coal seam overlain by a strong, dry roof rock with a tendency to plastic failure, seems desirable in order to minimize heat losses and escape of gases to the overburden. The coal seam should

not be a major aquifer, nor should major aquifer occur above the coal for at least twice the stable cavity height associated with the burn.

The UGC process was first suggested by Siemens in 1868 and was outlined technically by Mendeleev in 1888. Lenin studied accounts of British field testing and proposed applying the technology in Russia in 1913. A major field test was initiated in USSR in 1931 and after world war II, there were field programmes in several Western nations. By the early 1950's the Soviets had evolved a successful UGC system which was applied in – (a) flat lying beds in coalfields at Tula and Schatska (near Moscow) and later at Angren near Tashikent, and (b) steeply deeping beds at Lisichansk in the Donets coal basin and at Yuzhno-Abinsk in Siberia. The results at Tula, Lisichansk and Yuzhno-Abinsk were sufficiently encouraging to plan for increased UGC production from 0.7 billion m³ to over 40 billion m³ per year. However these plans were not implemented. Production peaked in 1966 at 2 billion m³ per year and declined to 0.7 billion m³ per year by 1977. Production of 0.7 billion m³ of low heating value gas (80–100 Btu/cft) is equivalent to 300,000 tons of coal consumed. Apparently the only station presently in operation in USSR is Angren and Yuzhno-Abinsk. The reasons for decline in production may be due to very low heating value, closer well bore spacing, and/or higher product gas losses, e.g. at Angren. Such results would produce unfavorable economics under US condition. UGC technology in USSR also faced stiff competition from increasing natural gas production and efficient open cast coal mining. It is unfortunate that Soviets made little use of underground diagnostics and modeling, and apparently ignored several innovations which were suggested in their own literature. Some of these, like linking by directional drilling, are now being used in USA. US program (sponsored by DOE), in contrast to more natured Soviet program, which emphasizes modeling and subsurface instrumentation in an attempt to understand and hence to achieve better control of the underground process. Perhaps because of the success of these attempts to understand the process, that the US results have been more encouraging.

In UGC process coal is gasified in the underground seam by burning in place underground. If the burn geometry is properly arranged, the combustible gases are illustrated schematically in Fig. 2.10. The most useful product gas is formed by injecting oxygen and steam instead of air to burn the coal so as nitrogen is not introduced as a diluent. The steam provides hydrogen necessary to complete the reaction and also to provide a means of lowering the reaction temperature. The steam, oxygen/air reaction in UGC process is as follows:





2.10 Gas production well in underground coal gasification.

Gasification: $C + H_2O = CO + H_2 - 31.0 \text{ kcal/mole}$

$C + O_2 = 2CO - 41.2 \text{ kcal/mole}$

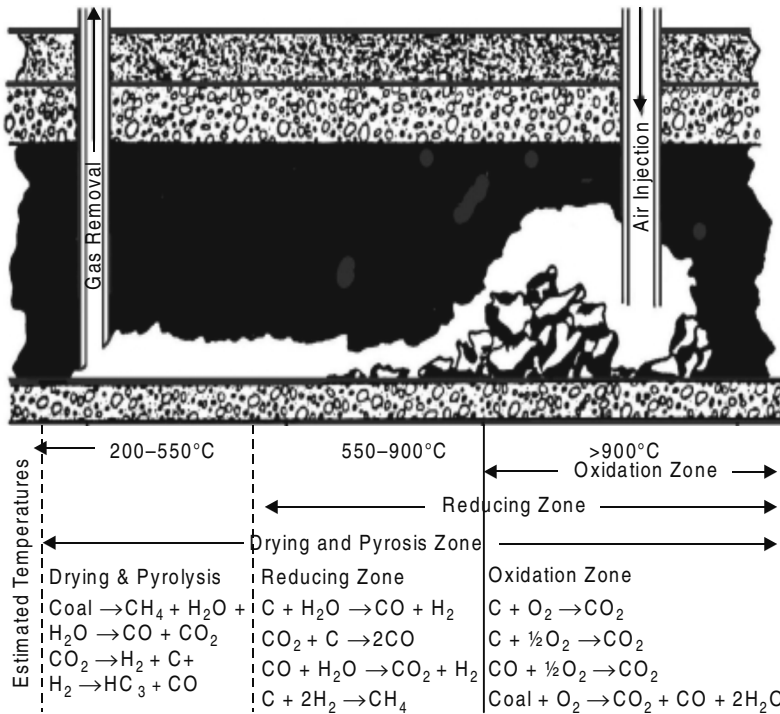
Water-gas shift: $CO + H_2O = CO_2 + H_2 + 9.8 \text{ kcal/mole}$

Methanation: $C + 2H_2 = CH_4 + 17.9 \text{ kcal/mole}$

$CO + 3H_2 = CH_4 + 49.3 \text{ kcal/mole}$

$2CO + 2H_2 = CH_4 + CO_2 + 59 \text{ kcal/mole}$

Air gasification yields low Btu gas of about 125–160 Btu/cft, whereas oxygen gasification produces about 250–300 Btu/cft (medium Btu) gas. During in-situ gasification, the above oxidation, reduction, and pyrolysis reaction takes place in three different reaction zones. Figure. 2.11 also grows towards the roof laterally as well as along the axis towards the production well. The oxidation zone goes on growing, while the reduction and pyrolysis zone remain constant or reduce in size. The product gas can either be burned directly to provide process heat or the generate various materials like SNG, methanol, ammonia, etc.



2.11 Procedure for making injection well.

Coal, in its natural state in the seam is usually a material with low permeability. It is formed in layers under great pressure, and only by supplying oxygen at high pressure can sufficient flow be forced through the natural cracks or “cleats” and pores, to sustain combustion. Gasification under these conditions is difficult, if not impossible and certainly uneconomical. Several processes have been used at various times to raise the permeability of the coal between the steam and oxygen injection and gas production points high enough for effective gas flow rates. These methods include – hydraulic fraction, electro-linking, reverse combustion and directional drilling. Of these methods, only the later two have proven to be practical. The reverse combustion process involves injecting air into the seam through one well at a high enough pressure to produce a small air flow through the seam to another well a igniting the coal at the base of this second well. The burn front moves back against the flow by conduction following the path of maximum flow. This process produces channels about a meter in diameter, filled with loose coal char and rubble. Reverse combustion has been used to link wells upto 20 m apart and at medium depth, has always produced a link. However there are some drawbacks to the method. At substantial depth (over 300 m), the pressures required are

so high that spontaneous ignition of the coal can take place near the injection well which makes the link impossible to complete. Even at moderate depths, there is no control over the path taken by the link and undesirable gasification geometries may result.

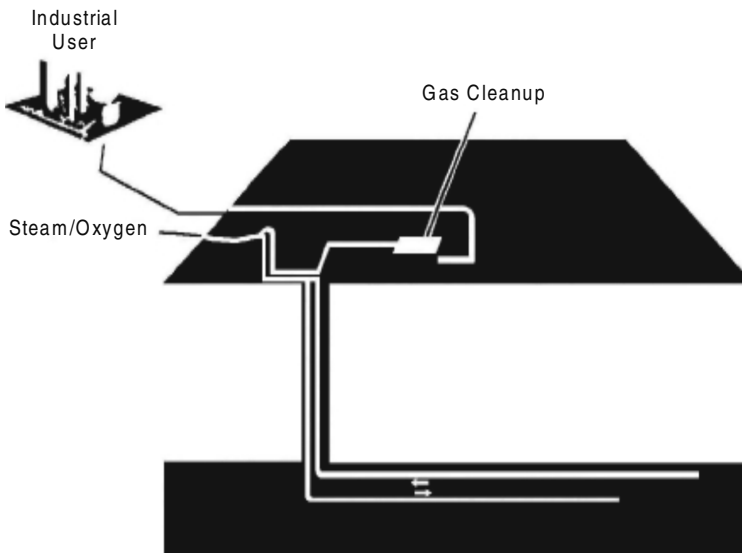
Directional drilling has been used successfully to physically link wells upto several 100 m apart. The drill controlled from the surface, can be made to follow a predetermined path through the coal. Special rotary drilling technique that utilizes variable stabilizer placement and bit pressure to control cutting direction have been used as well as down hole hydraulic mud motors that can be tilted to change hole direction. Several gasification tests have been done using directionally drilled links but not without some difficulty. Although there is no fundamental reason why directional drilling cannot become a reliable and economical linking method, the direction control requirements are at the present state-of-art and current costs are high. Since directional drilling offers the possibility of greater control of the process geometry and also allows greater flexibility in choice of method, it is the linking method of choice under most circumstances.

After the wells are connected by directional drilling, the coal at the bottom of the injection well is ignited and gasification is started by injecting oxygen and steam into the coal seam. The coal burns around the base of the injection well and the fire slowly moves upward and outward creating a pear shaped cavity with the long axis proceeding toward the production well. As the cavity grows, the coal on the walls and roof of the cavity collapses as it is weakened by the heat, forming a rubble pile around the injection point. The product gas composition is best at this stage of the process since the burn zone is small and compact and since the only true heat loss is to the vaporized water in the coal that exists as steam. Eventually the cavity reaches the roof of the seam and the falling coal is replaced with falling roof rock. The burn zone then begins to move away from the injection point toward the unburned cavity walls. As the cavity gets larger, the burn zone tends to move to the top of the seam since ash and fallen roof impede the flow of oxygen to the lower part of the cavity. Oxygen bypassing can occur, with flow going through the inert rubble and with the burning of downstream product gas. The hot gases formed lose heat to the inert rock in the roof and to the water in both coal and the roof rock. Thus the heating value of the product gas begins to decline because of lower efficiency of the process. This continues as the burn cavity gets larger and larger, and more and more inert material is available for heat loss. Eventually the burn zone reaches the production well or the heating value drops to an unacceptable limit. In either case a transition is then made to the next well pair in order to continue the process.

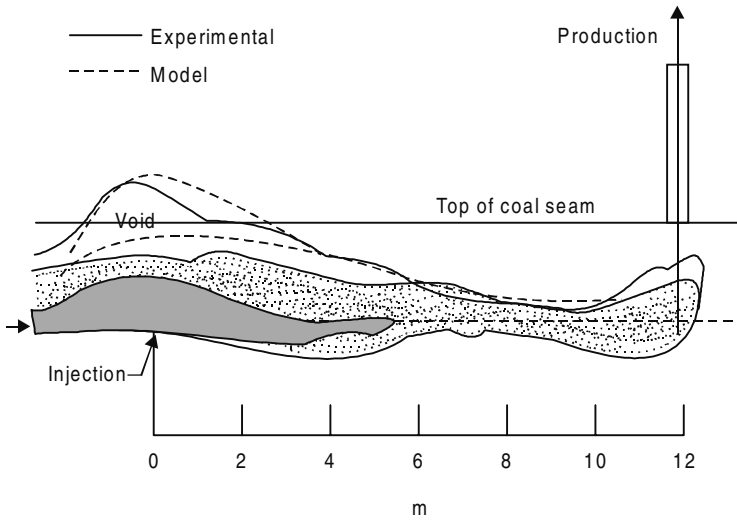
In UCG, the degree of decline in heating value of the product gas is a function of the water content of the coal, the roof material, and the strata

above the roof that are affected by the collapse as the cavity grows. Strong, dry materials are less of a problem than weak, wet rock; low permeability coals with little or no free water are preferred. Also the thicker the coal seam, the smaller the fractional heat loss to the roof for the same size cavity.

With fixed injected and production point, little can be done to control the heat loss effect except to shorten the distance between wells to keep the cavities small enough to have acceptable loss. However, well drilling and surface piping can be major expenses items, and the process quickly becomes uneconomical if the well spacing is too close. The Controlled Retracting Injection point (CRIP)¹² method was developed to minimize the effect of the heat loss and to add another control parameter to the process. The concept requires a drilled hole for linkage, as shown in Fig. 2.13. A steel liner, inserted through the casings of the injection well until its tip reaches a position near the interaction point with the production well, and carries the injectant – either air or oxygen/steam. As the burn cavity grows larger it eventually interests the roof of the seam and roof collapse begins. At some point heat loss to the roof material begins to significantly degrade the gas quality. When this happens, the injection point is retracted in the upstream direction by burning off a section of the injection liner with the igniter. The coal opposite to the burned zone ignites and a new cavity starts to grow. Since the high temperature zone is once again entirely within coal, the heating value of the product gas will rise to its original value. The CRIP concept involves a repetition of this process



2.12 Deep mine scheme for UCG.



2.13 Placement of production well.

and thus draws the burn step by step, in controlled manner, upstream from the original injection point. In UCG process it is also important to locate the connecting channel between the injection and production wells near the bottom of the seam. Low rank coals such as sub-bituminous and lignite, shrink and fall apart on heating so the coal immediately above the gasification zone falls to the bottom, creating an underground packed bed of coal. Thus the burn consumes the bottom as well as the top of the coal bed, utilizing almost all the coal.

With the CRIP process, the maximum burn width becomes a function of the minimum acceptable product gas heating value for the designed end use. Almost all of the coal, along the long injection channel can be utilized, but to get the highest possible heating value the parallel modules would have to be separated by about one seam width in order to access all of the coal. This still involves much less drilling and surface piping than a corresponding vertical well array.

If gas heating value is of no concern, then the only limitation on the ultimate burn width per channel when the transport of oxygen to the walls drop so low that the heat generated by the reactions per unit wall area is equal to the heat loss. At this point, the fire goes out and that oxygen is then available further downstream. Thus for burns in extremely wet coal such as the Hoe Creek mine, the cavity was long and narrow and eventually burned out the production well. A commercial UCG operation using CRIP would employ a larger number (upto 100) of injection production well pairs operating simultaneously in a system. Each well pair would consume about 100 tons of coal per day, producing some 5 million cubic feet per day of medium heating value gas (250–300 Btu/cft).

Uncontrolled burns in a UCG can be prevented by utilizing only those coal seams which lie below the natural the natural water table. In this instance, stopping the injection allows water to invade the reaction zone and extinguish the fire. A certain amount of underground water is desirable for the steam-char reaction; however, most UCG sites contain so much water that control of the influx is a problem. Steeply deeping beds which seems difficult to mine by conventional technique, can be harnessed easily by UCG process.

First UCG test known in USA was carried out by US Bureau of mines in 1950's at Gorgas, Alabama. The results were not encouraging and thus was abandoned. It was only in 1973 (the year of oil embargo) that US Govt. renewed its interest in UCG and since then upto 1986, twenty- one tests have been carried out. Results of these are shown in Table 2.10. Sixteen of these tests are govt. sponsored and the results indicate that sites with relatively dry strong overburden and at least moderately thick coal (e.g., Hanna, Rawlings, and Centralia tests) produced the best results to date. Sites with thin coal or wet and weak burden (e.g., Howcreek and Texas tests) produce less favorable results. Table 2.15 shows the tests conducted by private sector. Basic Resource Inc. (a subsidiaries of Texas Utilities) purchased the technology from Soviets in 1975, conducted tests with Texas Lignites for a 7 MW (e) power plant. Gulf Oil concluded 2 s successful tests in a steeply dipping coal bed near Rawlins, Wyoming, and is presently considering plans for commercialization. World Energy Inc. has developed plans for a 25 MW (e) generating facility near Rawlings, Wyoming. Applications have been made to the US Synthetic Fuel Corpn., Lawrence Livermore National Laboratory, in cooperation with two US utilities, Washington Water Power Co. and Pacific Power and Light, have completed two field tests using the CRIP method (controlled injection point method). In this process (tried at Centralia, Washington, in 1983), the injection well was drilled following the seam some 90 ft. from the exposed coal face where it was intersected by a vertical production well drilled from the surface. A second slant production well as drilled to cross over the injection well near the vertical well. This well was designed to test the effect of producing hot gas through a long open hole in coal as a possible economic alternative to vertical production well. (Fig. 2.14 and 2.15)

Oxygen and steam were the major injectants; air was used briefly during occasional outages. A vertical production well was used for the largest part of the first burn; a switch was made to the slant production well for the rest of the experiment. Shortly after the production will change, the movable ignitor was used to burn-off a section of the injecting tubing in order to move the location of the main site of coal gasification. As a UCG cavity initially develops, the product gas heating value, chemistry, and

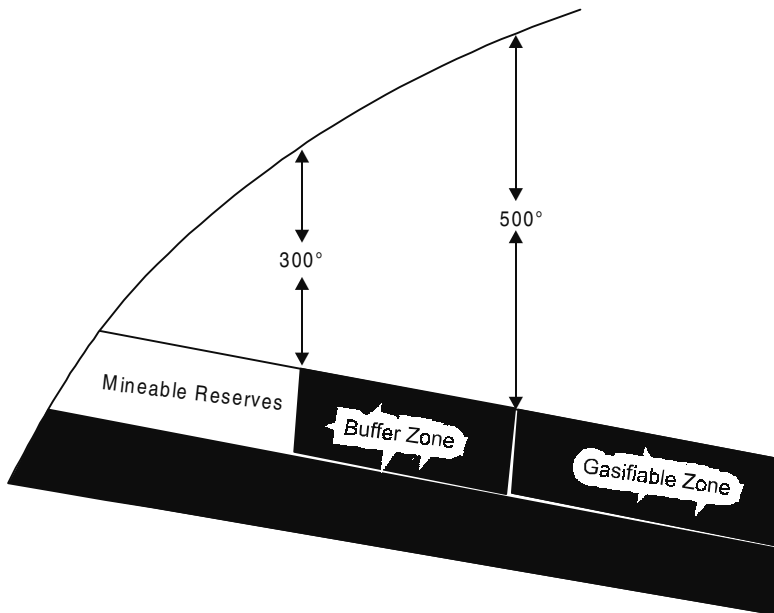
Table 2.10 Summary of US government sponsored UCG field tests. (Forward gasification method)

Test	Year	Duration	Coal consumed	Gas quality		Cold gas thermal efficiencies
Laramie Energy Technology Center (Hanna, Wyoming site)						
I	1973–74	168 days	2720 tons	126 Btu/cft	4.7MJ/m	77%
II-A	1975	37	962	137	5.1	85%
II-IB	1975	38	780	143	5.3	86%
II-II	1976	26	2201	168	6.3	92%
II-III	1976	39	3414	132	4.9	77%
III	1977	38	2663	138	5.1	77%
IV-A(a)	1978	7	294	109	4.1	78%
IV-B(b)	1978	48	3184	102	3.8	73%
IV-B(a)	1979	7	468	149	5.5	95%
IV-B(b)	1979	16	663	122	4.5	83%
Lawrence Livermore National Laboratory (Hoe Creek, Wyoming site)						
I	1976	11	123	101	3.8	82%
II (air)	1977	13	286	108	4.0	80%
III (O ₂)	1977	2	47	263	9.8	88%
II (air)	1977	43	1155	104	3.9	74%
III (air)	1979	7	256	113	4.2	81%
II (O ₂)	1979	47	3251	212	7.9	73%
Centralia, Washington site						
LBK (O ₂)	1981–82	20	140	262–294	9.8–10.6	80%
LBK(air)				140	5.2	
CRIP (O ₂)	1983	28	1500	248	9.2	74%
Morgantown Energy Technology Center (Pricetown, West Virginia site)						
	1979	17	234	149	5.5	97%

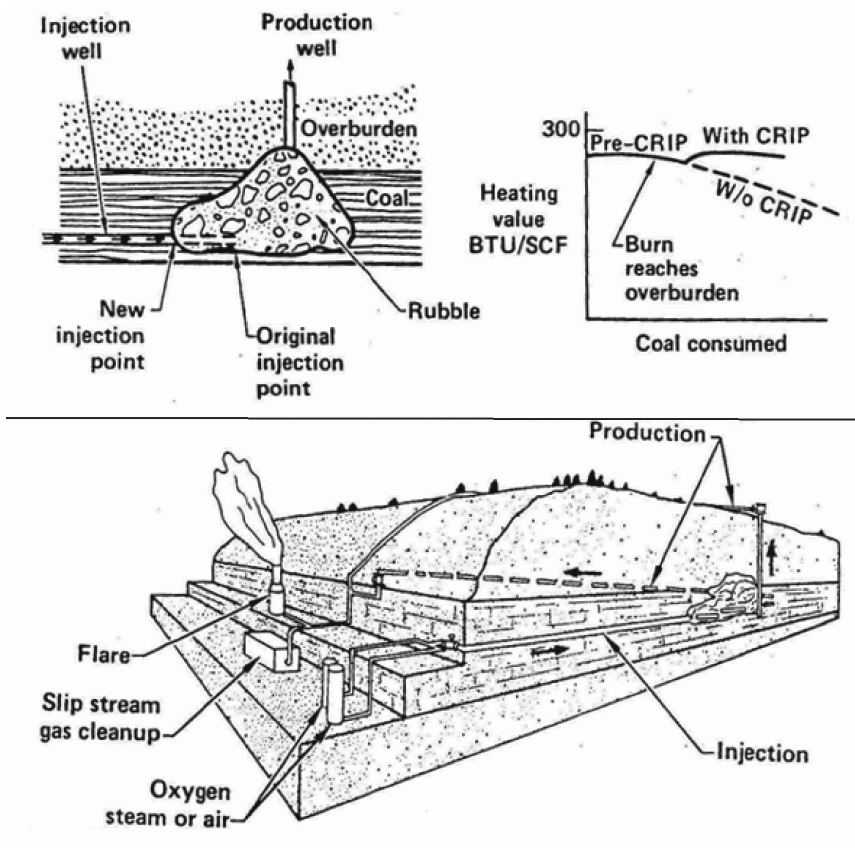
thermal efficiency are all excellent. When the burn reaches the roof, heat losses begin with a corresponding decline in gasification indicators and in economics. The decline is acceptable at sites with strong dry roof material, but is less acceptable at sites with a wet weak overburden. Hill and Shanon proposed a new concept for underground coal gasification, the CRIP method, in which the operator can control heat losses. The concept requires a drilled hole for linkage. A liner inserted through the casing of the injection well until its tip reaches a position near the intersection point with the

Table 2.11 Privately sponsored UCG field tests in USA

Test cold gas	Year	Duration	Gas quality		Coal gasified	Thermal efficiency
Basic resources Inc.						
Fairfield, Texas	1976	26 days	126 Btu/cft.	4.7MJ/m ³	–	–
Tennessee Colony (air injection), Texas	1978	197	81	3.04	1000–5000 ton	–
Tennessee (oxygen injection)	1979	10	230	8.6	212	–
ARCO Coal Co.						
Reno Junction, Wyoming	1978	60	200	7.4	3600	94%
Texas A & M University (with industrial consortium)						
College station, Texas	1977	1	35–114	1.3–4.2	2	–
Bastrop county, Texas	1979	2	85	3.2	–	–
Bastrop county, Texas	1980	–	35–150	1.3–5.6	–	–
Gulf Research & Development Co. (Rawlins, Wyoming site)						
I (with air)	1979	30	1207	151	5.6	91%
I (with oxygen)	1979	5	125	250	9.3	74%
II (with oxygen)	1981	66.0	8550	330	12.3	88%
Ratio of heating value of gas to heating value of coal used in deriving the gas.						



2.14 Coal resource development at Centralia.



2.15 Planned layout of the Centralia partial-seam CRIP test.

production well, carries the injectant, either air or oxygen/steam. As the burn cavity grows larger, it eventually intersects the roof of the seam and roof collapse begins. At some point the heat lost to the roof material begins to degrade the gas quality. When this happens the injection point is retracted in the upstream direction by burning-off a section of the injection liner with the igniter. The coal opposite burn zone ignites and a new cavity starts to grow. Since the high temperature zone is once again entirely within the coal, the heating value of the product gas will rise back to its original value. The CRIP concept involves a repetition of this process over and over again, drawing the burn step by step, in a controlled manner, upstream from the original injection point. Steam/oxygen gasification have been employed in seven of the US field tests since 1979. This method produces a more valuable, versatile product. Tables 2.12-2.14 compare the gas qualities obtained by these tests. The chemistry in these tests were not similar, yet the heating values are comparable. Tables 2.6 and 2.7 show

Table 2.12 Partial seam CRIP test summary (Av. value steam O₂ gasification, 1983)

Dry product gas heating value		248 Btu/cft (9.2 MJ/m ³)
Coal gasified		2000 tons
Dry gas composition (vol%)	H ₂	36.1
	CH ₄	5.4
	CO	18.5
	CO ₂	36.1
	C _n H _n	1.0
	H ₂ S	1.6
	N ₂ and Ar	1.3
Thermal efficiency		74%

Table 2.13 UCG produced gas composition compared to SASOL (dry N₂ free basis)

	Average UCG gas (vol%)	SASOL (vol%)	Angren, USSR (vol%)
Synthesis gas (H ₂ + CO)	60.4	60.8	59.5
CH ₄	6.7	9.7	2.4
CO ₂		32.9	29.3

Table 2.14 Comparison of field gasification test (LBK 1) with modeling result

	LBK-1 test	Model
Dry product gas		
H ₂	0.42	0.44
CH ₄	0.035	0.026
CO	0.25	0.22
CO ₂	0.28	0.30
Ratios to injected O ₂		
Produced dry gas (mol/mol)	2.2	2.1
Heat of combustion (kJ/mol)	890	820
Cavity volumes (m ³)		
Void	8	7
Char rubble	19	21
Ash rubble	6	6
Total	33	33

the gas compositions obtained site select ion, steam/oxygen gasification, extensive instrumentation and laboratory pre-burn modeling. The Washington Irrigation and Development Co. (Centralia, Washington), plans to take the strategy in a little different way. They have divided the coal reserve into three categories as per depth i.e., mineable, buffer-zone, and gasifiable reserve. They plan to adopt CRIP method for UCG, first from the coal face exposed in the base of the final highwall in surface-mine and would access and recover the coal from the area designated as the buffer-

zone. The reserves targeted for UCG development are those designated as gasifiable reserves.

Under the Indian scenario a modest initiative has been taken to conduct experiments at pilot plant level at Mehasana district of North Gujrat. Oil and Natural Gas Commission, Govt of India, while drilling for oil discovered huge reserves of coal intermingled with oil bearing formations in North Gujrat at 800–1700 m depths in 1979. These coals have been estimated at in order of around 63 billion tonnes. It is estimated that in the form of gas about 37 billion tonnes can be recovered by UCG process, USSR, USA, France, UK, Belgium and West-Germany have reported their success at lower and medium depths. However, so far, experimentations at deeper depths has not been so successful. The maximum depth at which the present experiments going on, it's around 860 m (at Thulin, Belgium under a joint Belgo-German agreement). Keeping in view a number of basic factors like, topography, sub-surface geology, hydrology, depth, thickness, continuity of coal seams, recoverable coal reserves, environment aspects, etc, above site was selected. In above site the coal seams occur at depths of 700–1000 m and with thickness 10–40 m. There is no stream or riverlet except Khari Naudi which is not prennial. The area is unpopulated flat terrain with few hillocks here and there upto height of 50 m. Drill hole samples are moderately hard, black, brittle, and dull luster. The coal seams are heterogeneous, inter-bedded with shales, sand, and silt stones. It is evident from CGWB data that deepest ground water aquifer is at the depth of 542 m. The coal seams proposed to be gasified in Mahasana city area, are encountered at depth of about 700–800 m whereas the maximum depth from which tube wells.

Therefore, the danger of contamination of ground water aquifers due to UCG experimentation in the area is ruled out. The total geological coal reserves in Mehasana city area is expected to be around 974.5 million tonnes and the coal reserves are considered to be of “B” category.

Establishing linkage in a UCG system is a major task, and the major techniques currently used for establishing linkage between process well (i.e., injection/production wells) through the coal seam are – (a) reverse combustion linkage (RCL), (b) fracturing followed by RCL, (c) directional/horizontal drilling, (d) electro linking, (e) shaped charges, and (f) cornering water jet drilling. Since in the case of deep coal seams having negligible permeability, the (b) and (c) techniques mentioned above are more applicable. These two methodologies are also contemplated for the Mehasana (Gujrat) test for achieving linkages. Other techniques mentioned above are not fully developed and have many limitations, especially for deep lying coal seams. It has been observed in course of oil/gas well hydraulic fracturing that above 700– 800 m depth, normally horizontal fracture are formed, and below this vertical fractures are formed. However

it varies from bed to bed, depending on mechanical properties of the rock. In this place, probability of vertical fracture seems to be more from experimental results. With continuous injection of air of required composition at required pressure and flow-rate, the reverse combustion front will propagate rightly toward the injection well. In the present study, the pressure and flow rate requirement is assessed around 200 kg/cm^2 (i.e., of the order of fracturing pressure) and $400\text{--}500 \text{ m}^3/\text{h}$, respectively. The propagation process will be constantly monitored with the help of pressure and temperature measurements in the injection as well as production well, and the chromatographic analysis of the product gases. As the well spacing is around $30\text{--}40 \text{ m}$ and the propagation rate is normally expected to be $1\text{--}2 \text{ m/day}$, the RCL process may prolong for about $20\text{--}40$ days. The depth and thickness of the seam being 700 and 10 m , respectively, the angle of inclination required to achieve 30 m spacing in the seam is about 70° which is very difficult to achieve. Alternatively, two inclined holes with about 55° angle of inclination meeting in the coal seam which enables us to achieve total 30 m spacing in the coal seam, have to be drilled. The approximate amount of coal expected to be gasified per day will be about $60\text{--}70$ tons between the two process wells during pilot plant test. When the reverse combustion front reaches the injection well successfully as indicated by the casing thermocouples and the reduction in injection pressure, the flow rate of oxygen, or oxygen enriched air or air only, will be increased gradually to the tune of 10 moles/s of O_2 only (i.e., at the rate of around $800 \text{ m}^3/\text{h}$ in case of pure O_2 only). When combustion starts at large scale, the oxidation zone will be enlarged in order to increase temperature of the zone to the order of 1000°C or more; the injection of steam is initiated and gradually increased to the order of $30\text{--}40$ moles (i.e., equivalent to $2000\text{--}2500 \text{ kg/h}$ of water). Since the temperature of the reaction zone is sufficiently high, it will be possible to inject simple water instead of steam with required quantity of oxygen or oxygen enriched air or air only. The injection rate of oxygen and water will further be increased to $45:15$ mole concentration per second of water and oxygen which is equivalent to about 2916 kg/h of water and $1210 \text{ m}^3/\text{h}$ of oxygen. However, the injection rate of water/steam and oxygen /air will also be restricted by the flow capacity of the linkage established between the two process wells.

If air is injected the gaseous products are basically N_2 , CO_2 , CO , H_2 , CH_4 , water vapor, and low level of higher hydrocarbons to produce a low-Btu gas. Steam/oxygen injection allows production of an essentially nitrogen free medium-Btu gas. Low or medium Btu gas is suitable for burning to produce process heat or to generate electric power, while medium-Btu gas can also serve as chemical feedstock for upgrading to a suitable product such as SNG (Synthetic Natural Gas), methanol, ammonia,

and diesel fuel. All the economic assessment by various sources term UCG between competitive to highly attractive. These calculations show over last two decades with changing dollar value and inflation, has shown these fixed results – UCG product costs are comparable to imported natural gas, about 25% lower in cost than the slagging Lurgi gas and 50% lower in cost for chemical feedstock than the price for synthetic gas produced by reforming natural gas. But inspite of all these studies degree of risk frequently asked by industries, still needs to be addressed in order to attract a much larger capital investment. If for example, we look to the reverse combustion linking steps, most widely adopted, two wells are drilled into the coal, high pressure air is injected into one well until production flow is achieved at the second well. The production well is then ignited and a narrow-burn front drawn to the source of oxygen at the injection well leaving behind a high permeability char zone (hence the term “reverse combustion”). As soon as the high permeability zone reaches the injection well, the pressure drops dramatically, the high pressure low volume injection is replaced by low-pressure, high-volume injection and a wide combustion/gasification zone moves back through the coal to the production well. This process, while very successful in many coal seams, proves very unreliable or unpredictable in others. Cost effective operation requires that easily applicable, non- invasive characterization technique be developed and made available to industry. Inexpensive and effective site integration technique would not only improve process economics but will serve to lower the overall risk of applying the technique and might lead to earlier commercialization. Material balance is not generally considered as diagnostic, but when used either with a sweep model or with prior knowledge of sweep geometry they provide surprisingly accurate resolutions of the burn front. Vertical process well run the risk, sometime, of the burn rising up past the well and destroying the well thermally or failure of complying due to thermal cycling. Horizontal injection facilities have more chances of survival. Till 1960, the industrial philosophy was to go for higher and higher plant size to decrease ultimate product cost. The cost estimating thumb-rule was that unit size could be doubled with only 50% increase in capital cost. This was based on a 0.6 scaling exponent in the equation.

$$(\text{Capital cost A/Capital cost B}) = (\text{size A/size B})^x$$

where x is the exponent. But these methods have changed in last two decades due to low availability of capital, unit operating cost, system reliability and investment risk. Investment risk can be lowered by unit-size reduction. UCG effectively decouples the producer from many of the non- measurable risk parameters because of the manner in which a plant of any size could be built with a very rapidly decreasing level of risk. Data

from various sources indicate that capital requirements for a UCG plant to produce the energy equivalent of around 4000 bbl (640 m³) per day of methanol might be around \$300 million. However, UCG will be developed in such a manner that the money “at Risk” would really only be the first module which would cost between \$10–20 million. If this relatively high risk module operates satisfactorily indicating no geological anomalies, a step-wise scale up to a full plant over a short period could be performed at a very low risk for the gas generator portion. Synthesis gas cost from UCG calculated in 1984 showed a value of \$3.50–4.0 / million-Btu. As compared to the same gas reformed from new natural gas at a cost of \$8.0/ million-Btu. Methanol generated from UCG can be used in vehicular traffic which will cause lower cost per unit volume compared to petrol. However, current cost of methanol for stationary energy use (i.e., for power production) \$10 per million-Btu is almost twice that of natural gas and fuel oil (\$5/million-Btu) and it is, therefore, not cost competitive. Construction of methanol plants, at sites of flaring or otherwise unusable natural gas production site, promises to lower the cost; but except in remote locations methanol from natural gas may not be the most cost effective fuel to power generation in near term. Methanol from coal, in the long term however, may prove to be cost competitive for power production or in special circumstances, for example where pollution is a critical concern.

Cost estimate, in terms of 1982 dollar, for some products made using UCG as a feedstock include (30% equity and 20% DCF basis):

Medium heating value gas (250–300 Btu/MCF)	\$4.35 /106 Btu
Pipeline quality synthetic gas	\$5.19/106 Btu
Methanol	\$0.52/gal or \$9.19/106 Btu
Gasoline	\$1.39/gal or \$10.20/106 Btu

Cost estimates for medium heating value gas, methanol, and gasoline were obtained assuming a 30% equity and a 20% discounted cash flow profit. The pipeline quality gas estimate assumed a 35% equity and a levelized cost based on historical real returns as capital by the natural gas industry. The pipeline quality gas estimate includes the \$0.45/106 Btu process development. These estimates include producer’s profit but do not include transportation, excise taxes, or retail profit.

The estimates for medium heating value gas and methanol derived from UCG compares favorably with costs of the same products from existing sources. The pipeline quality gas estimate exceeds the present average wellhead price of natural gas (Figs. 2.15 and 2.16).

In the USA, UCG is projected to be competitive with natural gas in the 1999–2009 time frame. The GRI estimate that UCG-derived substitute natural gas at \$5.19/10⁶ Btu compares very favorably with equivalent

Table 2.15 Cost estimate for 24000 x 103 Btu /day

	SNG	SNG	SNG	MBG	MBG
Type of gasification	Surface	UCG	UCG	UCG	UCG
Type of bed		Horizontal	SD*	Horizontal	SD*
Plant cost (million US\$)**	\$350	\$270	\$165	\$170	\$95

* SD = Steeply dipping bed.

** UCG data by P.R. Bruggink and B.E. Davis of Gulf. Surface data from unpublished sources. Surface investment do not include cost of supporting coal mines.

SNG = Synthetic Natural Gas. MBG = Medium Btu Gas. UCG = Underground Coal Gasification.

Table 2.16 Cost estimate for a 1000 ton / day methanol plant

Type of gasification	Surface	UCG	UCG
Type of bed		Horizontal	SD*
Plant cost (million \$)**	400	316	280

* SD = Steeply dipping bed

** UCG data by P.R. Bruggink and B.E. Davis of Gulf. Surface data from unpublished sources. Surface investment do not include cost of supporting coal mines.

estimates for production using the Lurgi (\$5.96/10⁶ Btu) or Westinghouse (\$5.74/10⁶ Btu) process.

The estimated gasoline price using UCG feedstock also exceeds the present market price of \$1.18/gallon without tax or \$10.20/10⁶ Btu. However, the mid-range projection of the US Department of Energy shows crude oil at \$57/Bbl by 2000 (in terms of 1982 \$). Gasoline price will then be in excess of the UCG estimated price.

Table 2.17 SNG from coal: Plant investment breakdown

Coal handling	8%	28% saved by UCG
Gasification	20%	
Shift conversion	3%	
Purification	20%	
Methanation	6%	Some foul water used for gasification with savings in purification
Oxygen plant	11%	
Steam / power supply /distribution	18%	
Water supply / cooling water	5%	For steam generation and water supply
Site development	9%	
Total	100%	

Source *: L.E. Swabb, Exxon. USA.

Environmental effect from UCG has both positive and negative side. Subsidence is the main problem but can be dealt with. Phenol which is the principal organic contaminant in the coal aquifer, exhibited quite high concentration immediately after the burn, but these concentrations have steadily decreased due to coal sorption. Other organics also strongly sorbed

by coal. A minimum depth of 200 ft for a 6 ft thick seam and 300–400 ft for a 20–30 ft seam appears reasonable to avoid surface subsidence during gasification. The maximum depth is more of an economic question than a technical one but practical considerations would seem to limit the depth of gasification to perhaps 2000 ft. Mobil Corpn. has developed the technology of converting methanol to a premium unleaded petrol. This product produced by UCG is estimated to cost approximately \$1 per gallon at the refinery (the price does not include transportation, retail profit or taxes). This is the same price as that for petrol produced from OPEC oil, again at the refinery.

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3.1 Introduction

As mentioned earlier, evolution of coal is a continuous metamorphic process influenced by geological condition and during this course, composition of coal (e.g., volatile matter, fixed carbon, inherent moisture, etc.) keeps on changing. This later phenomenon requires classification of coal into different groups in order to find out better conversion processes, which will enable us to utilize the coal more effectively in various industrial processes. Thus we see how coal is classified into various groups and then look more in detail into three-dimensional structure. Here the reader should note that while degree of metamorphism account for rank of coal, the range of impurity in it determines its grade.

3.2 Classification of coal

If we try to follow the evolutionary path of coal, we find coal first as a colloidal substance at the first formative stage (which is known as lignite), and this character progressively changes and become crystalloid at the intermediate stages and then turn into almost crystalline substance at the end of the evolutionary series. Thus its hydrophilic nature changes to hydrophobic property at the end of the series. Various forms of coals obtained at these different stages of metamorphic path is classified as follows:

Anthracite coal – These coals are hard in nature, have little porosity and hence low reactivity as well as low volatile matter content. Fixed carbon present in these coals ranges as high as 92–98%. It has a semi-metallic luster. It ignites with difficulty and burns with short flame without smoke.

Semi-bituminous coal – These coals have higher percentage of volatile matter (up to 16%) and fixed carbon in the range 89–91%. It falls between anthracite and bituminous coal in its properties.

Bituminous coal – It is relatively soft and dark black variety of coal, having volatile matter content 15–20% and fixed carbon around 65–85%. Due to high volatile during burning it gives large flame and is sometimes

called long-flame coal also. The coal has higher reactivity and vitrain content. These coals are of carboniferous age and also known as soft coal. It is brown to black in color and burns with a smoky flame.

Lignite or brown coal – These coals are friable and has a dull black to brown appearance. Their volatile content is about 35–40% and fixed carbon about 47%. Hydrogen content of these coals is high and their reactivity is also higher. Rank wise they fall between sub-bituminous coal and peat.

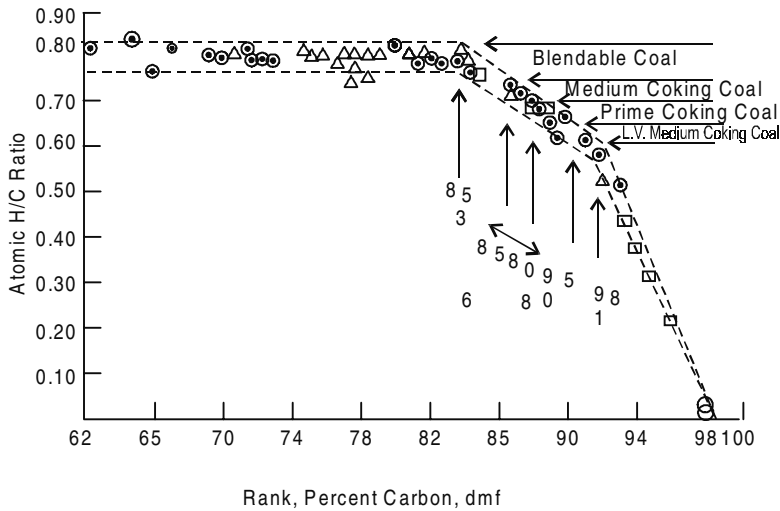
Peat – These are the coals at the lowest rank of the coal series. They still remain some structural similarity of plant material (lignin and cellulose). Their moisture as well as oxygen (30%) and hydrogen content are very high but calorific value and fixed carbon are much lower than bituminous coal. In terms of heat value, coals can also be categorized as shown in Table 3.1.

It should be noted here that there exists a correlation between the hydrogen and volatile matter, closest for the coals rich in carbon but observable throughout the bituminous coals down to 84% carbon or possibly below. The caking power is related to the amount of hydrogen (and consequently volatile matter) for the coals rich carbon, probably down to 87% of carbon. For the coals rich in oxygen the caking power does not appear to be related to the amount of hydrogen. Thus in terms of carbon–hydrogen content, Mazumder (*Fuel*, 51, 1972, p. 284) has shown the division of coal with increase in rank bound by clear-cut planes (Fig. 3.1).

Above-mentioned rank classification of coal plays an important role in selection of coal for particular use. For example, combustion studies of pulverized coal have shown that rank has a larger influence on the overall combustion process than the maceral composition. Bituminous coals of higher rank, especially those rich in inertinite were found to have large combustion period, to avoid high residual carbon levels in the fly ash. Similarly reactivity of coal, as shown above, which increases with decrease in rank position, found to be more suitable for gasification purpose. Petrographic composition also found to influence both the liquefaction behavior and the properties of the liquefied products. The presence of cations and pore size distribution in coal macerals contribute to the maceral distribution and to the formation of carbonized residue. Determination of

Table 3.1 Calorific value of various carbonaceous material

Coal type	Calorific value (kcal/ kg; dmaf basis)
Cellulose and wood	6500–7800
Peat	7800–11500
Lignite (brown type)	11500–13000
Lignite (black variety) and semi-bituminous coal	13000–14000
Bituminous coal	14000–16000
Semi-anthracite coal	15500–16000
Anthracite	15500–16500



3.1 Status of different categories of caking/coking coals in the metamorphic path of coal (position superimposed in the earlier correlation).

the proportions of reactive and inertinite macerals found to help in predicting, more accurately, coke strength from various coals used in steel plants.

3.3 Coal structure

As we know by now, coal is a heterogeneous substance and contains both aromatic and aliphatic structure in different sizes and different kinds along with hetero-atoms like oxygen, nitrogen, sulfur, etc., and thus makes its structure extremely complicated and variable. Nevertheless, attempts have been made by several researchers for last couple of decades to elucidate structure of coal and although their influences are varied and contradictory sometime. Here we see some of these results to get an idea of 3D structure of coal. As we know coal is composed of mainly carbon and hydrogen network, but it also carries some hetero-atoms. Our first discussion is on these hetero-atoms, their nature and detection, followed by discussion on the main carbon–hydrogen frame work.

3.4 Sulfur in coal

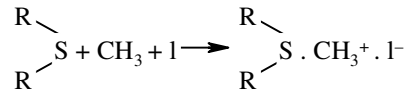
Sulfur in coal occurs either in inorganic or organic form. Inorganic form is the pyritic sulfur, and organic form is in thiophene, thiol, or disulfide configuration with the carbon-hydrogen skeleton. The time honored, tested, and accepted ASTM method for total sulfur (Method D-3177) and for

sulfate and pyritic sulfur (Method D-2492), are still the standards with which ultimately all other methods are compared.

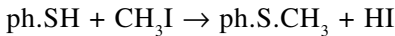
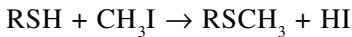
According to these procedures, the sulfur forms in coal are obtained by determining sulfate and pyritic sulfur in one sample and subtracting their sum from the total sulfur content obtained in another sample, to get the organic sulfur by difference. Currently, there are two alternate ASTM procedures for determining total sulfur in coal. One involves igniting the coal sample with Eschka mixture (contains 2 parts of magnesium-oxide and 1 part of anhydrous sodium-carbonate), leaching the sulfur from the residue with hot water and determining the sulfate gravimetrically as barium-sulfate. In the alternate procedure, the washings from an oxygen bomb calorimeter, used to measure the heating value of a coal sample, are collected and the sulfate content in them is determined gravimetrically, as above. The ASTM method D-2492 for sulfur forms in coal poses many challenges. The initial step consists of extracting a sample of coal with boiling dil. HCl to dissolve all sulfates. The finish is again the gravimetric determination of sulfates discussed above. Besides inerrant uncertainties in gravimetric analysis (like incomplete precipitation) loss during filtration, reduction of sulfate to sulfide during ignition, etc.), there are several other sulfate or sulfides during ignition etc, there are several other considerations in this step. First of all, it is important that all of the non-pyritic iron forms are completely dissolved while none of the pyritic is solubilized. There are occasions when these requirements possibly are not met. For example, samples of coal which have been treated chemically or subjected to HCl. Even air oxidation of pyrite in coal results in many different types of iron sulfates, some of which may not be readily acid soluble. Also coal which has been through a preparation plant may have incorporated significant amounts of magnetite from the heavy media circuit which may not dissolve rapidly enough in the 30 min allowed. Finally, there is some evidence that certain pyrites, especially after chemical or thermal treatment, may also dissolve to a small degree in hot dilute HCl. All of these possibilities will have an effect on the next step, determination of pyritic sulfur. In this step, the residue from the HCl extraction is leached with HNO₃ (diluted 1:7 with water) to dissolve all the pyrite. Either boiling for 30 min or standing overnight is acceptable. The extract is then analyzed for total iron by titration or by atomic absorption spectroscopy, and pyritic sulfur is calculated assuming the 1:2 stoichiometry of FeS₂. There is a growing discomfort about this stoichiometry which is documented more easily for mineral grade pyrite, but which is difficult to obtain for coal derived pyrites. The reason that iron and not sulfur is measured is based on the concern that HNO₃ may dissolve some of the coal and thus some of the organic sulfur. But if in the previous steps all the non-pyritic iron has not been

extracted or if some of the pyritic has been dissolved, as discussed above, the results of pyritic iron are affected. The importance of careful dissolution in these sequential extraction steps is thus obvious. There is some evidence that cold and hot HNO_3 leachings give different results for dissolution of minerals in coal and thus may affect the value of pyritic iron. If some of the coal is dissolved by the HNO_3 and if the organic matter is not properly decomposed by the recommended H_2O_2 treatment, then subsequent oxidimetric titration of the iron will also be affected. Finally, there is some controversy whether all the pyritic is extracted by the HNO_3 leaching. In at least one documented case, there were significant amounts of pyritic left in such residue. With such difficulties, it is not surprising that the ASTM reproducibility (i.e., the difference between the averages of duplicate determinations carried out in different laboratories) for a coal containing at least 2% pyritic sulfur is 0.04 for sulfate, 0.40 for pyritic, and 0.20 for total sulfur. Although no reproducibility is given for organic sulfur, it is obvious that it can be substantial since all three sulfur values must be obtained first (and each has an error associated with it) to calculate the organic sulfur value by difference. But the uncertainty in the organic sulfur values is not only due to mathematical propagation of errors. There are several other factors which can affect the determined value of organic sulfur in coal. One of them relates to the presence of elemental sulfur. Since S is not extracted by either of the acid treatments, it will not be included as sulfate or pyritic sulfur. But since it appears in the total sulfur determination, it will add to the so called organic sulfur content. Usually coals contain a few tens to a few hundreds ppm S, but some have as high as 1000 and 2080 ppm (i.e., 0.10 and 0.21%, respectively); Also, weathered coals can contain significant amounts of elemental sulfur. Another source of error could be due to the presence of sulfide minerals. During the initial HCl extraction, they can decompose and sulfur can escape as H_2S . Again, since such sulfide content will be included in the total sulfur, it will eventually be counted as organic sulfur. The Illinois (USA) basin coals are especially prone to such errors because they can contain considerable amounts of sphalerite (ZnS). Finally, during severe treatment or high temperature processing, various jarosite species containing iron and sulfur can form which are intractable to leaching with HCl or HNO_3 . Thus for such coals, organic sulfur may appear to increase at the expense of pyritic sulfur. Other unexplained chemical transformations during high temperature chemical treatment may have the opposite effect, showing an apparent decrease in organic sulfur while the pyritic sulfur is apparently increased. Further researches in recent times have made it possible to differentiate between various forms of organic sulfur containing functionalities. One of the latest methods revealed by TRW, USA is low temperature ashing. Here selectively, sulfur compounds are cut from coal

by radio frequency generated plasma. The sulfur compounds thus released in the gas phase are cryogenically trapped in low temperature bath and estimated. Leco Corporation (USA) introduced high temperature combustion of coal and estimation of evolved SO_2 by I.R. technique to arrive at total sulfur in the coal sample. Similarly, Fisher Instruments introduced endometrial titration followed by amperometric detection technique. Still others reported complicated instrumental techniques like ESCA, Mossbauer Spectroscopy, EXAFS, and electron microprobe, scanning electron microscope with energy dispersive X-ray analysis, TEM, and various X-ray methods for determination of sulfur in coal. The IR-bands of sulfur are not very strong and are rarely well resolved. Because Raman spectrometry is relatively more sensitive to sulfur containing groups, it has some potential for sulfur group analysis, even though the dark color of coal samples, degradation of coal under laser beam and chemiluminescence may be severe problem. Although Raman spectra of coal have been obtained, no specific work for sulfur compounds have been mentioned in the literature. The reaction of sulfur functional groups with selective reagents has been used with moderate success in solid coal analysis. Methylation by methyl-iodide was used by Postovski and Harlampovich to estimate the amount of sulfide sulfur as per following reaction:



Determination of the amount of I^- left in the sample is a measure of the concentration of organic sulfides. Mercaptans and thiophenols release HI when reacted with CH_3I :



The HI released thus can be used to estimate the amount of $-\text{SH}$ groups in the sample. Non-destructive extraction of coal, by various solvents through depolymerization technique, has shown that the ratio of the total carbon to the organic sulfur, does not change as a result of extraction. But this does not necessarily imply that, the sulfur functional group distribution is identical in the solid state and in the extract. More studies have shown that the ratio of sulfur to carbon in an extract is different than in the original coal. Attempts to determine the sulfur functional group distribution in some bituminous coal extract by tetrahydrofuran, dimethyl-formamide, and benzene, showed the following distribution in Micke (USA) coal extract;

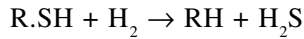
thiols ($-\text{SH}$) = 3–9%, disulfide ($-\text{S}-\text{S}$) = 6–13%, aliphatic - sulfide ($\text{Ar.S}-$) = 7–19% and, undetermined about 30%. The undermined sulfur is probably in condensed thiophenic structures. Moreover, since it is unlikely, that unstable groups like disulfides will survive the coalification process, these data should be extractability of compounds in different solvents with different polarities and the sulfur content and functionalities will be uniformly distributed in all the extracts, irrespective of the solvent polarity. Extraction with different polarity solvents also indicate that sulfur to carbon ratios vary with the solvent polarity. Attar and Dupeis⁴ have shown that a much larger fraction of the sulfur is thiolic relative to thiophenic in the polar solvent extract. The aromatic solvent extracted much more sulfur than the polar solvent, most of which is thiophenic (see Table 3.2). It should also be noted that thiophenic sulfur compounds are the major constituents of the sulfur compounds in shale oil.

Depolymerization of coal is accomplished by the hydrogenation, pyrolysis, oxidation and reactive solvents. Only the most stable sulfur compounds survive catalytic hydrogenation at high temperatures and pressures, Hydrodesulfurization of coal at a hydrogen pressure of 2000–4000 psi and temperature of 450°C, followed by examination of the product by mass spectrometry allowed the identification of 14 different organosulfur compounds. Carbonization technique has also been applied to identify sulfur compounds in coal. It is found that carbonization up to 1400°C will not desulfurize the coal completely. Sulfur will be retained both in organic and inorganic forms. Coking at 1600°C desulfurize the coal (95%) but substantial loss of material occur. Approximately 66% of the inorganic and 73% of the organic sulfur are retained in the coke. About 23% of the inorganic and 26% of the organic sulfur goes in the gas. Some researchers found 50% of the total sulfur retained in the coal, 3% going to the tar and 45% going to the gas phase. The exact ratio is believed to depend on the distribution of the sulfur functional groups in the specific coal. Increase in ash content, increases the amount of sulfur retained in the coke. Overall desulfurization that is achievable reaches a plateau at 800°C. Further increase in temperature does not substantially contribute to desulfurisation. Some of the pyritic sulfur reacts with the coal and forms H_2S and other compounds as well (e.g. CS_2). Some of the pyritic sulfur reacts with the coal to form very stable compounds that do not readily decompose. The

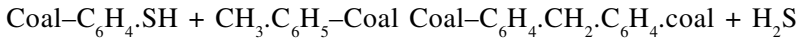
Table 3.2 Sulphur functional group distribution in super-critically extracted coal

Sample	R.Sh + f – SH	RSH	hiophenes
Coal	–	2.51	27
Polar solvent extract	2.85	3.08	34.6
Aromatic solvent extract	0.457	5.05	68.5

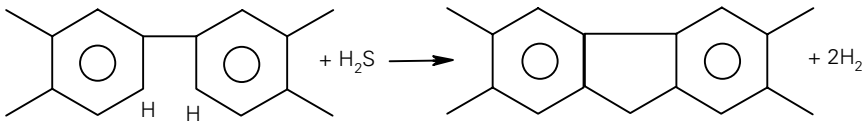
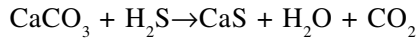
sulfate sulfur remains in the coal, probably as calcium-sulfide and H_2S that is released may react at high temperatures with the hot code or with CO to form CS_2 . Elimination of H_2S is less favorable thermodynamically since the Gibbs free energy of formation of H_2S is only -7.9 kcal/mole (compare that with H_2O being -54.6 kcal/mole). However, since sulfur stabilizes free radicals, H_2S elimination may be kinetically very fast. Attar reviewed chemistry and kinetics of transformation of sulfur functionalities upon processing. The primary transformation of sulfur functional groups during coal processing can be classified into two groups. Unifunctional reactions in which one sulfur group either decomposes or reacts with molecules of gases or solvents which are not part of the solid matrix, e.g.



and multifunctional group reactions between physically adjacent functionalities, which are part of the solid matrix, e.g.

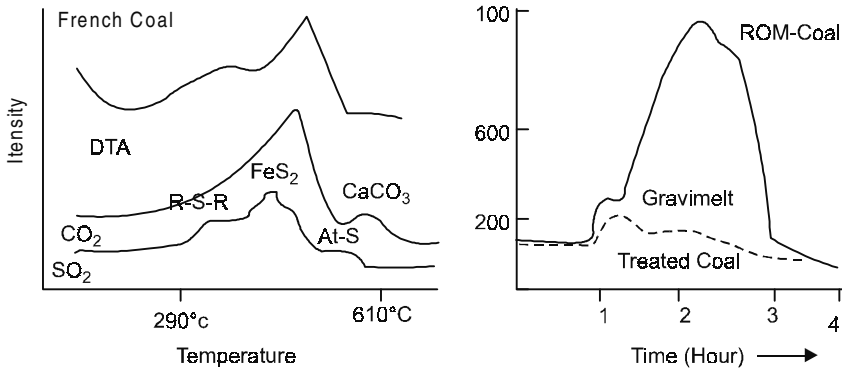


Limited data are available on the first kind of interaction and virtually none are available on the second kind. One very important secondary transformation which should also be considered, since it affects the distribution of sulfur and other groups, is the reaction between H_2S and the inorganic and organic components. For example,



The second reaction above is the free radical chain transfer with H_2S . The large difference in the activation energies (which determine the rate of unifunctional decomposition of sulfur in coal pyrolysis) between the decomposition of the model sulfides and sulfides in coal indicates that a different mechanism controls the rate of decomposition of sulfides in each case. Consequently, one must conclude that elimination of sulfides during coal pyrolysis occurs predominately by reactions of the sulfidic groups with the C-H-O matrix of the coal. Another observation by Attar et al was that the initial rate of volatilization of organic sulfur during coal pyrolysis is faster than that of the volatilization of the organic material. This observation was explained by the fact that no thiolic groups were found in coals pyrolyzed in vacuum for 25 min at temperature above 400°C . It

appears that thiols decompose rather rapidly even below the plastic temperature and yield H_2S . The activation energy for the decomposition of ethyl-thiol was estimated at 63 kcal/mole and 55 kcal/mole for t-butyl ethiol, and 53 kcal/mole for benzyl ethiol. It is believed that the alkyl-thiols and sulfides in the gaseous phase are products of the reaction of H_2S with organic compounds and that COS is formed by the reaction of H_2S with CO_2 . These gaseous compounds are also the dominant sulfur compounds in the product of coal gasification. The sulfur in coal tars is almost exclusively thiophenic, although some sulfides, thiols and others were identified in the light oils. It is believed that the latter are products of secondary reactions, whereas most of the thiophenes, because of their extreme thermal stability, are decomposition products of the original coal matrix. However, some thiophenic structures may be destroyed or produced during the pyrolysis since adding FeS_2 to coal changes the ratio of the various thiophenes in the tar. Experimentally, it has been found that the concentration of dibenzothiophenes, benzothiophenes, and alkylthiophenes in the tar decreases substantially when fine FeS_2 is added to the coal prior to the pyrolysis. Incorporation of pyritic sulfur into organic compounds during coal pyrolysis was noted by several researchers. The main sulfur compounds in liquefaction products are thiophenic. The thiolic sulfur decomposes during the preheating stage by a unifunctional reaction and releases H_2S . Part of this H_2S may react with solvent and with the mineral matter in the coal. During the early stages of the digestion of the coal some of the pyritic sulfur is reduced to pyrohotite with the approximate sulfur to iron ratio of 1:1.1. The organic-S is gradually removed from solution during digestion. In sub-bituminous coal (e.g. Provence, France and Muskingum-Meigsin USA) vitrinite was found to contain major part of organic sulfur and metals. Occurrence of the two things together suggests presence of organosulfur- metallic species. Programmed temperature oxidation (Chanterelle Method, first reported from Paris in 1967) and programmed temperature reduction (Attar's Method, USA, 1983) showed aliphatic thiols and sulfides as fragile compounds and aromatic sulfides as thermally stable compounds. It was found that free organic sulfur compounds and elemental Sulfur are not present here. Programmed Temperature Oxidation (PTO) is based on the concept that the difference in reactivity of sulfur, carbon, and mineral species can be made by following the evolution of SO_2 , CO_2 , and differential thermal analysis curve during combustion. In PTO studies DTA and CO_2 evolution curve represents three maxima (exothermal). The first two is due to decomposition of organic carbon and the third (less exothermicity) for decomposition of calcite. SO_2 maxima occurs in three temperatures [see thermogram (Fig. 3.2)] – 375°C, 460°C, and 500°C. The first and third peak was seen increase with addition of pure pyrite. Another small peak was seen at 580°C. Lacount



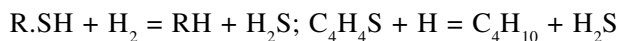
3.2 Release of various sulfur components at various temperatures.

et al (ACS, Fuel Chemistry Division, 1986) with less heating rate ($3^{\circ}\text{C}/\text{min}$) found additional three peaks at 320°C , 430°C , and 480°C . Model compound studies show the peak at 430°C is due to pyrite and 320°C peak is due non-aromatic sulfide while the peak at 480°C is consistent with thiophenic, aryl-sulfide and aryl-sulfone oxidation. Integration of SO_2 data up to 400°C and beyond 400°C reveals that 41% of the sulfur is associated with loss of non-aromatic carbon and about 59% is associated with oxidation of aromatic carbon. About 50% of the sulfur was lost up to 400°C .

Programmed Temperature Reduction (PTR) is based on heating coal samples and it is a hydrogen solvent mixture and a catalyst (Co-Mo-sulfide). At various temperature discrete H_2S peaks are detected and area of the peak is proportional to the sulfur amount in coal. PTR test (a representative graph shown below)6 showed that higher the organic sulfur content, the easier it is to convert to H_2S . Thiophenic compounds and high molecular weight sulfur compounds are less abundant in French coal than in US coal, as revealed by this study. This thermokinetic method as described by Attar used two hypotheses which are valid to a zero-order approximation in the case of the reactions of functional groups attached to large molecules and which react with the specific reagent:

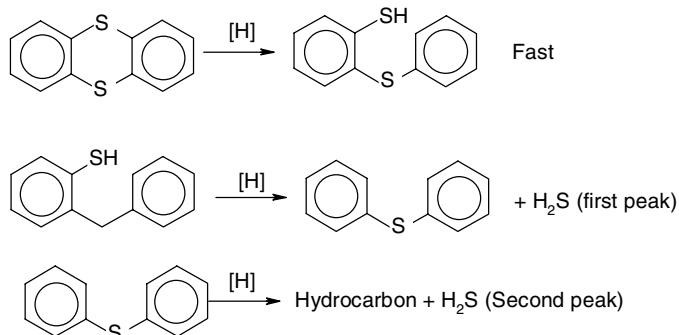
- (a) The activation energy of the reaction depends mainly on the reagent and on the functional group, but is almost independent of the next neighbour of the group.
- (b) The pre-exponential factor of the rate constant is almost independent of the functional group and depends mainly on the reducing agent.

Therefore one may assume that a one-to-one correspondence exists between a given activation energy and each functional group, when a specific reducing reagent is used. All sulfur compounds can be reduced to H_2S . However, different groups are reduced at different rates. For example –

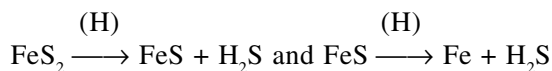


By controlling severity of reduction gradually, it is possible to reduce different groups at different steps and detect them accordingly. As an example, let us look at the kinetogram for reduction of thianthracene (shown in Fig. 3.3).

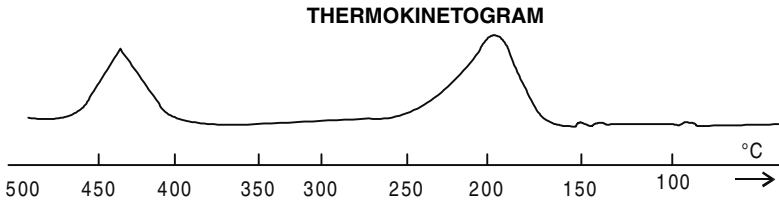
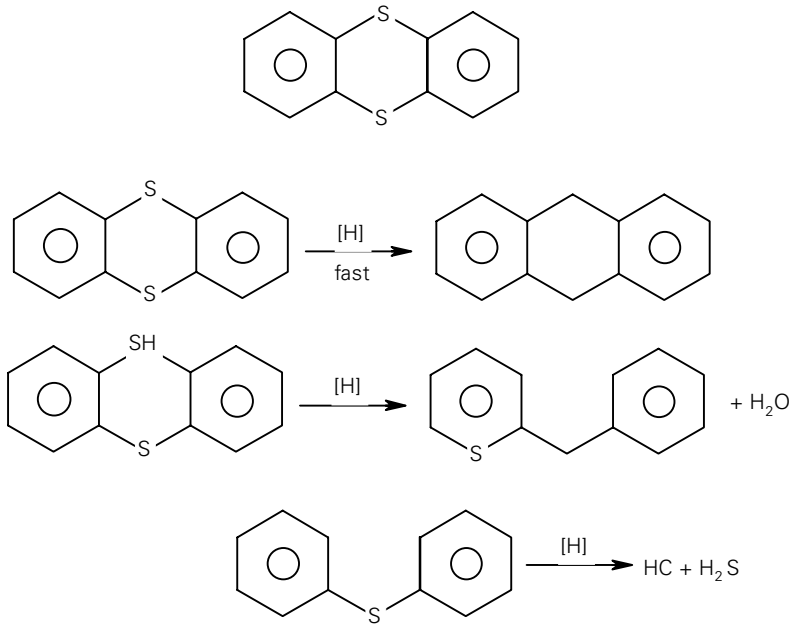
The reduction of the first sulfur (I) proceeds as if it were an aryl-thiol and the second as if it were aryl-sulfide. The corresponding process can be represented as:



Temperature maxima values, as standardized with polymeric sulfur model compounds, correspond as, aliphatic-thiols = 160–190°C, aromatic thiols and thiolates = 200–240°C, aliphatic sulfides = 240–280°C, alicyclic sulfides = 290–330°C, arylsulfides = 450–470°C, and thiophenes = 500–600°C. About 90% sulfur in model compounds is detected by this method; rest may have decomposed into other gases or condensed. Reduction of FeS₂ can proceed as follows:



However, while the organic sulfur is dispersed in the organic phase, most of the pyritic sulfur is present as small lumps of FeS₂ often result in the formation of a layer of F and S or Fe on the surface of the crystal which limits the rate of mass transfer of reducing agent to the core of the FeS₂. If the rate of the chemical reaction controls and a mild reducing agent is used, conversion of the FeS₂ to FeS would complete before conversion of the FeS to Fe would begin. However, when a very strong reducing agent is used, the rate of either reaction step or both can become diffusion controlled. When a Fe layer is formed on the surface of FeS, it blocks the diffusion and effectively stops the reduction process altogether. Experiments, in fact, has shown that reduction of pure iron pyrite (-60 to 325 BS mesh) with a very strong reducing mixture, never proceeds beyond 1–2% of the material. Thus all the analytical techniques (besides PTR) reported for determination of pyrite is unsatisfactory. The other inorganic



3.3 Thermokinogram of coal with hydrogen reduction.

sulfurs include disulfides and sulfates. The occurrence of sulfates of Ca, Ba, and Fe are in negligible amount while that of cubic pyrites or orthorhombic marcasite constitute almost all of inorganic sulfur.

Later in a modified experiment on PTR, B.B. Majchrowicz (Fuel Process Technology, 24, pp. 195–202, 1990) of Limburg University, Belgium, used an unique reducing solvent mixture which models a typical coal liquefaction solvent and contains components to swell the coal, acts as an aromatic solvent, and transfer hydrogen. Attar used only Co-Mo-sulfide catalyst in a hydrogen solvent, while Majchrowicz used a mixture of reducing solvents comprising phenanthrene, resorcinol, 9–10 dihydro phenanthrene, tetralene, and pyrogalol, tetralin liquefies coal and this helps in mass transfer. The case of reduction of sulfur functional groups is in the order:

thiols > aliphatic sulfides > aromatic sulfides > thiophenes.

A similar desulfurization sequence is expected in coal liquefaction processes involving hydrogen donor solvents. Characteristic temperatures at which different groups will emanate H_2S were found to be independent of reactor design. Both solid and liquid product can be used in the experiment.

While PTR and PTO both offer some degree of resolution and quantification leading to information about the structure and reactivity of the total coal organic sulfur, relation between structure and thermal stability of organic sulfur compounds in coal are difficult to establish. For various counter arguments, PTR thermokinetogram remains speculative. The thermo-reduction method can only provide us with a finger print of coal sulfur functionalities and reactivities. While aliphatic and benzylic sulfides, mercaptans and disulfides emanate H_2S and CS_2 , the thiophenes show little conversion even at $950^\circ C$. Benzene-thiols on the other hand are remarkably resistant to thermal reactions in absence of oxygen (up to $650^\circ C$).

We notice from above discussions that thiols and thiophenes are the most predominant sulfur compounds, and following reports concludes their quantitative abundance in coal:

- (a) Lngnasiak (*Fuel*, 1978) reported that high organic sulfur containing Raser coal contains 1/3rd of its sulfur in the form of sulfides, but no thiols at all. According to Jones (International Conference on Coal, USA, 1981), the vitrinite of high volatile bituminous coal mainly include sulfides and thiophenes rather than disulfides and thiols. Coalkins (*Energy and Fuel*, 1987) suggested that the aliphatic sulfur compounds in coal are sulfides.

However, thiol sulfur forms have frequently noted through poorly quantified. According to Attar, 18–30% of the organic sulfur in high sulfur coals is sulfidic and 10–40% thiolic. Wrongly thiol sulfur may also come in pyrite test by decomposition. Non-thiophenic functions might partly account for the high micro-metal content of coal (France origin).

- (b) Up till now no method gives quantitative estimation of thiophenic sulfur content in coal. It is determined by PTR where pure organic model compound is used as a reference or by difference supposed between non-thiophenic sulfur and total sulfur in coal. Preoxidation of coal, followed by XPS-spectrophotometry or FT-IR has shown that sulfides and thiophenes are the major sulfur species in vitrinite. X-ray absorption and XAS show that, coal sulfur is mainly pyritic and thiophenic. Recently P.H. Neil (*Fuel*, 1987) showed that coal thiophenic compounds are so abundant that they could introduce noise in aromaticity measurement using CP-MAS C^{13} -NMR.

3.5 Oxygen in coal

No direct method for determination of oxygen in coal has been accepted universally yet and thus oxygen content in coal is determined by difference. This causes large error in the evaluation process and results are difficult to compare in finer scale. The only direct method available for oxygen determination is via neutron activation analysis. However it is not used as a standard analytical technique. However some information available in literature in this respect is presented below:

- (a) The range of variation of oxygen content of coal on a maf basis is 0.5–18 wt%.
- (b) The oxygen content decreases almost linearly with rank of coal (as determined by neutron activation analysis).
- (c) The oxygen content of different macerals is different and depends on the rank of coal. For coals of the same rank, micrinite has the highest oxygen, vitrinite has an intermediate value, whereas exinite has the lowest oxygen content. The largest spread in oxygen content is observed in exinite.
- (d) For coals with same oxygen content, inertinites have the lowest hydrogen content vitrinite have intermediate hydrogen content, whereas exinite have the highest hydrogen content.
- (e) Drying coals with oxygen content high, is more difficult than drying coals with a low oxygen content. The interaction of organic oxygen with water or with other polar solvents (e.g. methanol) is strong and causes such coals to swell and heat up. L. Blom in his Ph.D. dissertation (University of Delft, 1960), divided oxygen functional groups into carbonyl, hydroxyl, carboxyl, methoxyl and “other” groups. Methoxyl groups and the other groups were reportedly present only in low rank coals. The amount of oxygen in carboxylic groups decreased continuously with the increase in coal rank until about 80% carbon, where the only oxygen group present were phenolic and carbonyl groups. Fresh bituminous coals reportedly contain virtually no aliphatic hydroxyl, carboxyl, or methoxyl groups. Aliphatic hydroxyl groups have been reported in brown coals, however according to this view, for coals of rank higher than lignites virtually all of the oxygen can be accounted for as carbonyls, phenols and carboxyls. Recent work also suggests that etheric oxygen is present and that the quantity of carbonyls in raw coals is small. It was also suggested by some authors that initial stage of coal liquefaction involved cleavage of etheric bonds. Rartle et al. (*Fuel*, 54, 226, 1975) measured aromatic ether oxygen in a concentration around 3.8 ether oxygen per 100 carbon atoms in a coal containing 83.1% carbon. This figure is close to the value of 2-ether connections per 100 carbon

atoms reported by Szaladow and Given (Am Chem Soc, Div of Fuel Chem, 23, 4,161, 1978) for a coal containing 83.47% carbon. It was also reported in some US sub-bituminous coal lignites, no more than 1/2 of the oxygen is free phenolic oxygen. Almost 1/2 is reported as etheric. The carboxylic acids present were postulated to have been derived from esters in the original coal. Furans, pyrans, and quinones have also been postulated to be present in coal.

Methods used to study functional groups distributions in coal can be divided into three main categories:

- (a) Direct investigation on coal.
- (b) Investigation of coal extracts.
- (c) Investigations of depolymerization coal (e.g. pyrolysis, hydrolysis oxidation and cationic depolymerization).

Most of the available data have been derived on products of coal depolymerization. However, such data must be interpreted very carefully since it is not always clear how the method of depolymerization influenced the structure of the resultant product. It is also true that many of the weakest bonds in the coal structure are destroyed by almost any depolymerization method. The rate of mass transport of degraded product from coal matrix is slow and thus to arrive at meaningful conclusion, most of the time becomes difficult. In short, we discuss below two such direct methods for evaluation of oxygen functional groups.

(1) **Infrared spectroscopy** – The main problem associated with IR-analysis are – (a) Inherent difficulties in the analysis of dark solids by IR, although thin sections of coal are red, (b) Sampling errors and sample preparation errors. Sample preparation for IR-analysis involves crushing the coal to a very fine powder or polishing the coal to a thin section. The surface of the coal is often oxidized during the process and this changes the oxygen functional groups on it. (c) The mineral matter in the coal interferes with the spectra. (d) Quantitative IR- analysis of coal powder is essentially impossible because it is very difficult to reproduce the spectra of solid pellets e.g. KBr pellets or mulls. (e) IR-analysis is not a very sensitive method and analysis of samples with a small concentration of a functional group is possible only using double-beam instrument. Such analysis cannot be easily accomplished with solid samples. The assignment of absorption bands to functional group was done in accord with what is accepted for low molecular weight compounds. Dilute finely crushed coal in KBr (about 2%) has been used to obtain the spectra of solid coal. There has not been much published data on IR-spectra of this coal section. Cryogenic crushing is being used today to reduce the level of oxidation of the surface of coal during sample preparation. The Fourier Transform

Infrared (FTIR) technique has the potential to improve the sensitivity or IR-analysis of coal and to allow quantitative determination of the distribution of organic functional groups in it.

FTIR-spectrum of coal has been found to be very similar to that of the corresponding coal tar. This observation must be viewed with care since the elemental analysis of coal and tar are very different, and because many functional groups cannot survive high temperatures, some differences in the functional groups distribution must exist between the coal and tar. The inability of IR-analysis to distinguish such differences suggests that even state-of-art FTIR cannot give a full description of the hetero-functional group distribution in coal. The main conclusion with respect to distribution of oxygen functional groups in coal, as derived from IR-data, are –

- (a) The total oxygen content decreases with an increase in coal rank or age. However the rate of decrease in the relative abundance of different oxygen groups is different.
- (b) The main group assignments are as follows: carbonyl and carboxyls (1700 cm^{-1}), hydrogen bonded phenol (3250 cm^{-1}), and hydrogen bonded carbonyls (1600 cm^{-1}), Olefinic bonds interfere with the latter.

Thus, quantitative estimation of the carbonyls can be done only if the concentration of the olefins is determined. It should be noticed here that IR-analysis can be used to determine quantitatively the ratio of different coals, by comparing the ratio of the molar extinction coefficients of different functions per gram of coal, for different coals.

(2) **By selective chemical reagents** – These specific reagents are selected to react with specific functional groups. After the reaction, the amount of reagent retained by the coal or by determining the amount of reagent left untreated, the groups are quantified. Some of these reagents are as follows:

- (a) Total OH – by esterification with $(\text{CH}_3\text{CO})_2\text{O}$. After reaction, the solution is hydrolyzed with standard $\text{Ba}(\text{OH})_2$ at 100°C for 4 h and excess $\text{Ba}(\text{OH})_2$ is titrated. Each OH releases one CH_3COOH .
- (b) Phenolic OH – Titration of the acidic-H with $\text{Ba}(\text{OH})_2$.
- (c) Aliphatic OH – By esterification with phthalic anhydride. The excess acid is titrated with $\text{Ca}(\text{CH}_3\text{COO})_2$ and the acetic released is determined by titration.
- (d) Carboxylic groups (COOH) – Ion exchange reactions. Acetic acid released is titrated with 0.01–0.005 NaOH.
- (e) Carbonyl group – By formation of oxime with hydroxylamine hydrochloride. The N-content of the coal before and after treatment is determined.
- (f) Ethers (total aliphatic ethers) – By hydrolysis with HI. OH added to

the coal after reaction is determined. In the second step, NaOH is added to above mixture and I incorporated or released is determined.

It should be noted here that in all conversion processes (like combustion, pyrolysis, gasification or liquefaction), these functional groups play a key role in coal degradation. The accepted mechanism for the initial stages of all these processes is the thermal decomposition of the organic matrix to free radicals. In combustion many of the free radicals react with molecular oxygen and form peroxy radicals which further decompose and branch. In pyrolysis, the radicals stabilize by binary collision and recombination. In direct liquefaction, the radicals react with molecular hydrogen, with the solvent hydrogen, or with each other and stabilize. The initial stage of gasification is thermal pyrolysis of the organic matrix. This proceeds in a very short time period, whereas most of the time in the reactor is needed for the gasification of char. Thermal decomposition of ethers, carbonyls, and phenols, proceed by free radical mechanism. Decomposition of carboxylic acids proceeds by hydrogen transfer or by radical-ion mechanism which results in the elimination of CO_2 . Decomposition of carboxylic acids proceeds by hydrogen transfer or by a radical ion mechanism which results in the elimination of CO_2 . Decomposition of oxygen functional groups, in general can be summarized as follows:

- (a) Thermal decomposition of small molecules containing oxygen functional groups, occur at temperatures which are in general above 450°C , except for carboxylation of acids the decomposition of quinones, and the decomposition of sterically hindered aromatic ethers.
- (b) The main oxygen containing products of the decomposition of oxygen group are H_2O , CO_2 and CO .
- (c) Except for the decomposition of some of the carboxylic acids, oxygen functional groups decompose by a free-radical mechanism.
- (d) Transition metals, acids, and bases catalyze the decomposition of oxygen functional groups.
- (e) Decomposition of polymers which contain oxygen proceeds in accord with the chemistry of the decomposition of low molecular weight analogs. Elimination of small stable molecules like H_2O depends on the Gibbs free energy and kinetic mass transfer of the process within coal matrix.

3.6 Nitrogen in coal

It is generally agreed that the nitrogen present in coal has come from plant and animal proteins, from nitrogen rich bacteria and from plant alkaloids.

Nitrogen in coal generally found in the range 0.5–2%. Most commonly in the 1.5–1.75% range in bituminous coals and less than 1% in anthracite coals. Total nitrogen in coal can be determined by modern elemental analyzers. But it is extremely difficult to determine nitrogen functional groups in coal. The two approaches which appear to have produced most of the available information are as follows – (a) analysis of coal extracts, and (b) analysis of the products of depolymerized coal (e.g. by pyrolysis, oxygenation, or hydrogenation).

Extraction of coal with mineral acids yields amides and amino acids. The acid extracts contained up to 80% of the total nitrogen in peat, 20% in lignite and down to about 3% in anthracite. Thus during coalification nitrogen compounds are converted to nonbasic, presumably heterocyclic forms, incapable of being extracted with mineral acids. Monoamino and diamino acids have been identified in peat, lignite, sub-bituminous coals, but no diaminoacids found in bituminous coals and anthracite. Most of the nitrogen in coal of tar and liquefaction products is found in pyridines, condensed pyridines, pyrroles and nitriles. Low temperature coal tars contain pyridines, quinolines, pyrroles, indoles and carbazoles. Thus it is generally believed that most of the nitrogen in coal is incorporated in heterocyclic rings, such as pyridines and pyrroles, with possibly small amount of nitrogen containing side chains. But this view again is not universally accepted because such evidence in coal is derived from destructive pyrolysis or oxidation.

Traditional accounts of nitrogen in coal extracts use the term-“basic” and “neutral” nitrogen. The former is that nitrogen present in acid-soluble fraction. The extract contribution of the nitrogen to the acid solubility during coal extraction is not uniform and depends on the hydrocarbon environment of the nitrogen. If the nitrogen in a molecule can form a quaternary ion, acid solubility of the molecule increases. The main importance of classifying nitrogen compounds according to their acid solubility is that more basic molecules can be hydrotreated more easily by using common hydrodesulfurization catalysts. However, characterization of nitrogen in coal products by solvent extraction alone does not provide information on its form in coal. Depolymerization studies have led us to following conclusions:

- (a) The majority of the nitrogen compounds in coal tar are cyclic, predominantly pyridine and quinoline derivatives. Limited amounts of anilines were also found in coal tar.
- (b) Basic nitrogen compounds constitute an integral part of the coal solid matrix and are responsible for the anion exchange capacity of the coal.

However, crude estimates indicate that the bases in coal are insufficient to account for the bases in coal tar. Consequently, one must conclude that at least some of the bases in the tar were formed during pyrolysis of the coal. In summary it appears that, 50–75% nitrogen in coal are present as pyridine and quinoline derivatives.

The presence of cyano and amino groups has never been fully proven or disproven. The quantity of aniline in coal is probably small because they are very reactive and could have not survived the coalification process. The source of the elemental nitrogen upon pyrolysis is probably secondary gas phase reaction which involves ammonia.

Studies by author has indicated that pyrolysis at 700°C of N–E coals, followed by pitch recovery by distillation of resultant tar at 360°C, results in accumulation of about 75% of total nitrogen of coal in the pitch itself. This indicates association of nitrogen in original coal in three or more membered heterocyclic rings.

3.7 Structure of coal

In last few decades various workers tried to find correlation between carbon, oxygen and hydrogen (the major constituents of coal) in order to establish structure of coal. Aims of these correlations were basically to find a link between different rank coals and their carbon content. Example of some of these are Hicklings plot (percent carbon vs. percent oxygen), Seyler's chart (percent hydrogen vs. percent carbon) and others like Ralsstem Rose correlation, American ASTM standard plot for coal ranks and grades etc. But one of the inherent problem with these plots is that they took the variables on percent basis and not on molecular or atomic basis. As a result, these correlations could not trace the genetic path of coal evolution. We can see this by means of an example – if we plot hydrogen content on percent weight basis for phloroglucinol (trihydroxy benzene), resorcinol (dihydroxy benzene), and phenol (monohydroxy benzene), and benzene, as a function of percent carbon we find a linear increase in hydrogen with corresponding increase in carbon content. But if we plot on molecular basis (i.e., atomic hydrogen is to carbon ratio) hydrogen content through the series is same. This is because the genetic transformation between one coal and the other is completely masked as coal data and is considered on percent weight basis. On the other hand, H/C ratio truly represent the hydrogen status in various rank coals. This phalacy was first pointed out by Mazumdar (Director, CFRI, Dhanbad, India) and the plot of H/C vs carbon content (Fig. 3.1), put forward by him, revealed three clear cut class of coal generated in the genetic mutation of coal. As shown in Fig. 3.1, these three categories are bound by three carbon segments of 62–84% C, 84–92%, and beyond 92%C. Above author

has put forward his explanation for such divisions as follows. It is well known that, coal is essentially an aromatic substance and that aromatic character progressively increases with increase in rank of coal, thereby conferring to it progressive thermal stability. In lignite stage it is about 3–4 benzene rings, around which are present hydroaromatic and aliphatic (mostly methyl) groups as conferred from its precursors. Progressive decarboxylation and dehydroxylation from this rank onward, lead to rank enhancement.

Without any basic change in the carbon-hydrogen skeleton of coal from 62–4% carbon level. Beyond 87% carbon level (when caking and coking coals begin to appear), dehydrogenation of hydroaromatic structure accompanied by demethylation starts, causing aromatization of the hydroaromatic structure and consequent aromatic ring growth. This process is believed to be almost complete near the 92% carbon level. Beyond 92% carbon level, there appears to set in a very fast dehydrogenation process causing carbon-hydrogen skeleton to almost bare carbon skeleton (as in graphite). These theories were proved on the basis of aromaticity and hydroaromaticity of different rank coals, and also the volatile matter obtained on low temperature pyrolysis (which breaks hydroaromatic part and emanates a star and gas), also confirmed with test of enhancement (linearly) of tar and gas content with increased reduction (increasing hydroaromatic content) of starting coal. It is remarkable that irrespective of the rank of coal, at least in the bituminous range (i.e., C = 80–92%, pyrolysis give char/coke of practically same composition (e.g. C = 97–97.4%, H = 0.4–0.6%, N = 1.4–1.6%, S = 0.4–0.5% and O = 0.2–0.5%). This was further confirmed by D. Joseph and A. Oberlin, CNRS, France (Carbon 1983) in their experiments with a number of carbonaceous substances like anthracene oil, mesophase pitch, some natural compounds like sporopollenin and kuckersite, as well as coal and lignite. The elemental analyses (Fig. 3.4) of the raw starting products were plotted on a Van-Krevlin diagram (H/C versus O/C; ref. Coal, Van-krevlin, Elsevier Publication, 1961). Samples were then oxidized at 200°C for increasing period of time and results plotted on the same diagram (see Fig. 3.5). Results obtained by Van-Krevlin for coal shown in right hand diagram. As can be seen in above diagram, slope of oxidation path differs notably between products and depends on the elemental composition of the initial material. But the ultimate point of the oxidation curve is same for all carbonaceous compound. They named this end product as “oxychar” in analogy with the ultimate oxidation residue of coal known as “oxycoal.” They also tried to plot atomic ratio parameters similar to B. K. Mazumder’s work mentioned earlier, i.e., $D(H/C) + D(O/C)$ and (O/H) against time and obtained stepwise split curves of oxidation. They explained these phenomenon by – first stage involving dehydrogenation when oxygen content do not change

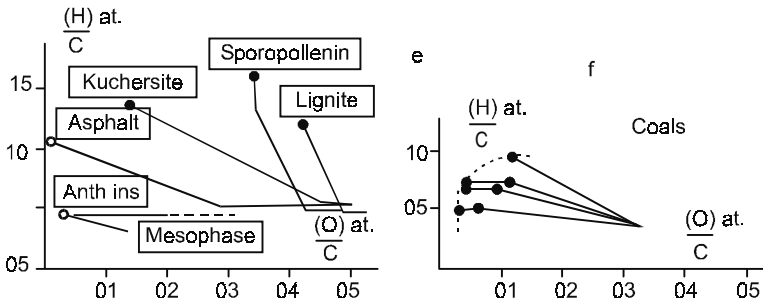
or hydrogen is released and the oxygen content increases. The second step always involve dehydrogenation accompanied by increase in oxygen content; And in the third stage only slow increase in oxygen content. Oxychar was found to have elemental composition of $H/C = 0.5$, $O/C = 0.5$, i.e., $O/H = 1$.

Figure Evaluation of genetic path of coal (from H/C vs. % C diagram put forward by B. K. Mazumder, mentioned earlier) reveals that the abundance of non-caking coal against scarcity of high caking or coking coal (having $C = 84\%$). This is because during first stage of coalification (i.e., formation of low rank coals) involves deoxygenation which require low temperature ($T < 80^\circ\text{C}$) and milder geochemical forces (which are easily available and thus their occurrence in nature so plentiful). Next higher coalification step involves dehydrogenation reaction which calls for stringent geochemical conditions which depends on depth of burial (hence temperature gradient) and are not available. This makes high rank coal a scarce commodity. Above author also has shown that high volatile coals are a class by themselves in contrast to high rank ($C = 84\%$) coals and exemplified when calorific values are plotted against air dried moisture content. Relevant plots show occurrence of linear relationship for $C = 62\text{--}84\%$ but beyond 84% there is a sharp break (hydrogen variations also show similar trend in these coals). It is further evident from above results that coalification is a unique continuous process, as various mathematical equations can apply equally well to all coals of the world. Thus the whole exercise is very systematic. Both reflectance and density variation studies also attest to all above facts.

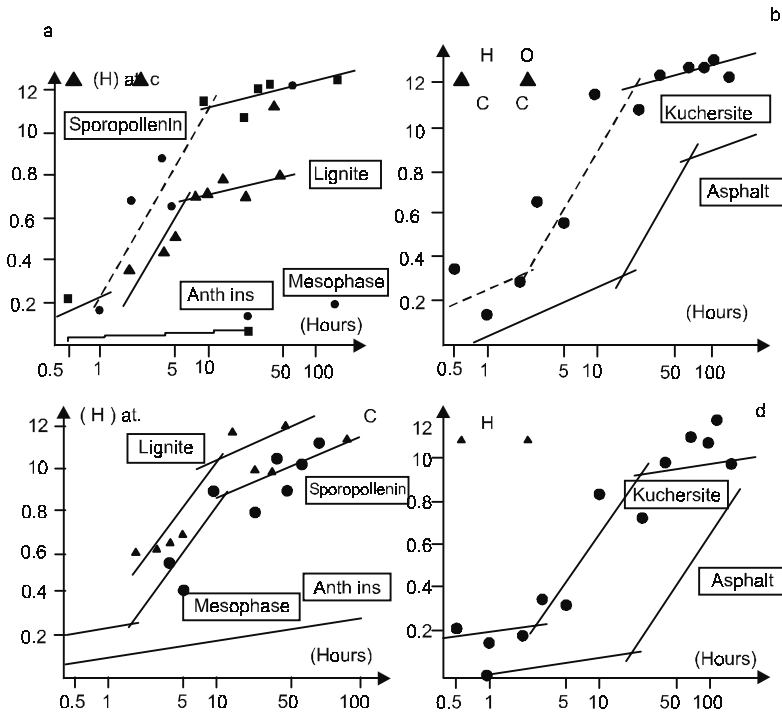
Prof. B.K. Mazumder has studied extensively the vitrain samples in order to follow genetic path of coal evolution, as this particular phase has accrued minimum contamination during its evolution. His studies resulted in the following relation for the hydroaromaticity of coal:

Hydroaromaticity (f_H) = $(H/C - 0.55)$ workers in last few decades.

First three-dimensional model structure of coal was offered by Given in 1959. Almost at the same time B. K. Mazumder (CFRI, Dhanbad, India) offered his model. Subsequently a number of models appeared in literature which were proposed by Hill, Van-Krevlen, and recently by Heredy and Wender in 1980. Here we discuss the most prominent three models offered namely by Given, Wender and Mazumder. Figure 3.6 shows the typical three-dimensional coal structure proposed by Mazumder (CFRI, Dhanbad). Specialty of the CFRI model is that it made an attempt to visualize the structural genesis of coal through sequential reactions, right from lignite to anthracite, whereas all other models depict structural pattern and particular rank level. Secondly, it is also important to see that the detail hydrogen distribution of the non-aromatic part of the coal structure is

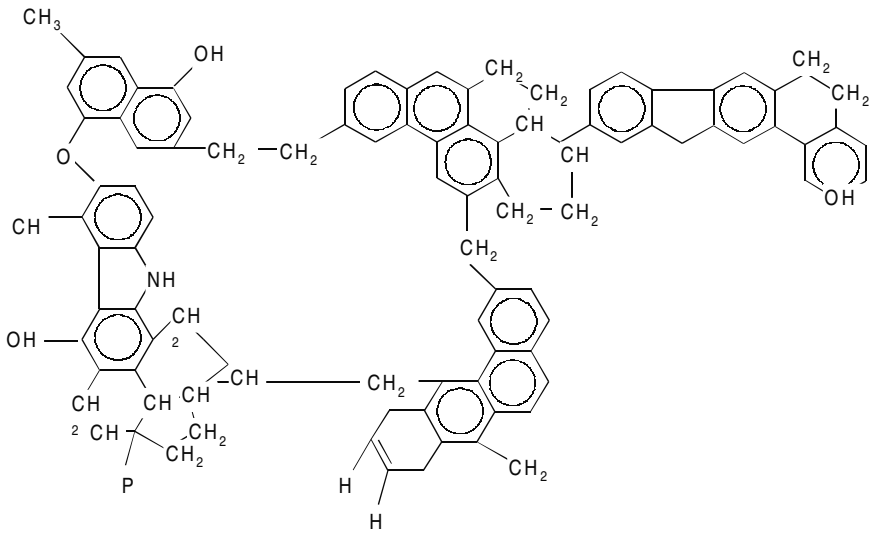


3.4 Van Krevelan diagrams showing oxidation path at 200°C, (i) lignite, (ii) sporopollenin, (iii) kuchersite, (iv) asphalt, anthracene-oil insoluble fraction (anther. Ins) and mesophase, (e) summary of the data, (f) coal from [9].

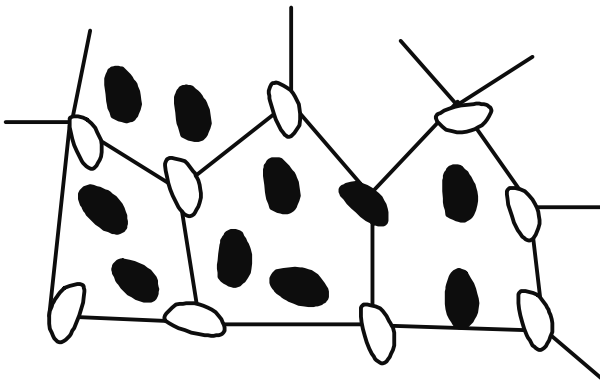


3.5(a, b) $\Delta(H/C) + \Delta(O/C)$ plotted versus the logarithm of time; (c, d) $\Delta(O/H)$ plotted versus the logarithm of time.

governed by the ratio of NMR result of $(H-CH+H-CH_3)/(H-CH_2)$ which is consistent only with CFRI model but not with Given or Wender model. Another important point to observe is the nature and disposition of the hydroaromatic structure. Both the Given and Wender model depict this structure as fused to the aromatic nuclei and not as side chain as visualized by CFRI model. The tetralin, decalin, or dihydroanthrane or



3.6 Molecular structure of bituminous coal.



3.7 A two-component structure of coal (aromatics, aliphatic, small molecules).

dihydrophenanthrene type of hydroaromatic structure as indicated in the Wender and Given model, seems to be incompatible with some chemical reactions like the stabilization of hydroaromatic structure during pyrolysis, consequent on prior dehydrogenation to the extent of hardly 10–15%, compared to 20–35% of the total dehydrogenation possible either by sulfur or catalytic method. Scholl's reaction has shown to stabilize the hydroaromatic structure along with aromatic carbon fraction during subsequent pyrolysis. Possibility of such reaction cannot be explained by either Given or Wender model. The CFRI model concludes that hydroaromatic structure which constitutes 70–75% of the non-aromatic part, is present as side chain to the aromatic nuclei of coal and the

stereochemistry between the two thus permits cyclo-dehydrogenation, aromatization, and coalescence with aromatic nuclei as is observed in actual experiments. Geochemical evolution leads to the growth of aromatic nuclei with progressive disappearance of the hydroaromatic structure to about 92% carbon level. The aromaticity value (at 81–85% carbon level, $f_a = 0.7$) deduced from CFRI model is same that later adopted in Wender's model. The hydroaromaticity value ($f_H = 0.24$, i.e., 24% of total carbon occurring as hydroaromatic) in Wender's model was also advanced by CFRI experiments involving sulfur induced dehydrogenation reactions. Difference in Given and Wender model with that of CFRI-model is that, the former model show hydroaromatic structure fused to the benzene ring whereas CFRI model predicts hydroaromatic structure as attached to benzene ring as side chain.

Author of this book has experimented with less matured tertiary coals of North Eastern region of India, which are unique in its nature, as mentioned earlier. Additive carbonization experiments with these coals⁷ which show that, $ZnCl_2$ causes dehydrogenation of large hydroaromatic moieties in these coals (as compared to Gondwana coals), and thus abruptly increases coke production rate during additive carbonization⁷. Occurrence of high hydroaromatic structure in these coals is further exemplified by large tar production during pyrolysis.

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4.1 Introduction

Coal, as we have known it by now, is a heterogeneous substance and characterized by different maceral compositions, here in this chapter our discussion thus focuses on both proximate/ultimate analysis of coal and maceral/thermal/pore analysis of coal. We will get acquainted with associated analytical instruments used in modern time. We basically divide our discussion on topics – coal maceral composition, sampling technique for coal analysis, proximate and ultimate analysis, thermal analysis, pore and other special analysis and analysis of flue gas emanating from coal combustion.

4.2 Coal maceral analysis

Differences in the plant material and the extent of its decomposition during the first stage, largely determines the different petrographic types in coal, also known as “macerals” and the subsequent action of pressure and heat during the geochemical stage caused the differences in coalification or maturity of the coal, usually known as the “rank” of the coal. Thus we differentiate between “grade” and “rank” of a coal, saying grade of coal as the divisions based on impurities (inorganic) associated with it, whereas rank indicates its advancement on the metamorphic path. Macerals (so called by analogy with the word minerals in inorganic rocks) are commonly grouped together under the names vitrinite (highest density), exinite and inertinite (mostly inorganic deposits). Bonded structure of coal containing different macerals can be identified as follows:

- Vitrinite – Brilliantly glossy and vitreous in appearance. It occurs generally in thin bands of 2–10 mm thickness.
- Clarinite – Bright coal less brilliantly glossy than vitrinite but with a satin luster and a clearly striated structure.
- Durainite – The banded dull coal. It is hard and gaseous granular, matt surface. Normally it is gray in color, exceptionally it may occur as sooty black which becomes brown when scraped.

Fusain – Powdery, dull black. It occurs as thin path or wedges in the bedding plane.

Vitrain and clarain together make-up the bulk of a normal coal seam. The difference in properties of the banded constituents may cause two coal seams of the same rank but of different petrographic composition (i.e., different proportions of vitrain, clarain, durain and fusain). Fusain is always entirely non-coking in nature. It is noteworthy that the vitrinites of low rank coals, contain up to about 15% oxygen and 5% hydrogen and that with increasing rank the oxygen decreases first with little change in the hydrogen content, but later the hydrogen content decreases to about 2.5%. Exinite contain more hydrogen and less oxygen than the corresponding vitrinites, whereas the reverse is true for micrinite (one form of inertinite). In a given coal, exinite has a higher volatile matter content than vitrinite, while inertinite has a lower value. High volatile matter corresponds to little low rank and vice-versa. While volatile matter forms the primary basis of coal classification, it is found necessary in practice to use at least one more parameter in order to characterize the behavior of coal when heated, because two coals may have the same volatile content but differ from one another in the extent to which they swell or cake together. Microscopic study determines rank of a coal. In a given coal, the reflectance of the exinite and inertinite are lower and higher respectively than that of vitrinite. Coal is not a crystalline substance and the molecular structure cannot be deduced from X-ray analysis. X-ray analysis has on the other hand has provided very useful information on the arrangement of carbon atoms. The results of X-ray analysis of vitrinite may therefore be summarized in terms of three types of structure: (a) in low rank coals, an open structure of small, condensed aromatic layers randomly oriented and cross linked, (b) in medium rank coals, a “liquid structure” with fewer cross-links, a moderate degree of orientation and reduced porosity, (c) in high rank coals, a structure of larger layers with a higher degree of orientation and oriented pore systems. Comparison of vitrinite reflectance with sporinite fluorescence in relation to coal properties showed that, the vitrinite reflectance is more closely associated with volatile matter content than sporinite fluorescence; but sporinite fluorescence is more closely associated with calorific value and maximum fluidity than vitrinite reflectance in different coal ranks as well as in the same coal rank. Separation and characterization of macerals in a Chinese coal showed that density gradient centrifugation provides a good separation into maceral fractions. The almost continuous variation in chemical and physical properties with density is remarkable. Transmission Electron Microscopy (TEM) has been used to describe and quantify the microtexture of coals and cokes. An attempt to analyze microscopic components of coal

(macerals) with laser microprobe has recently (1989) been described by Layouts of US Geological Survey, Cheston, Ya and Hercules (Department of Chemistry, Univ. of Pittsburgh, USA). Their technique involved finger printing coal macerals. The instrument they used, a LAMMA-1000 produced by Leybolds-Heraens, had a spatial resolution of a few micrometers, high selectivity and ability to analyze hydrocarbons with mass number up to 2000 daltons as well as all of the elements and isotopes, including hydrogen. It uses Nd-Yag laser whose fundamental wavelength (1060 nm) is frequency quadrupled to 265 nm. The laser beam has a power density ranging from 10^5 to 10^8 W/cm². Ions are separated by a 1.8 m time-of-flight spectrophotometer. An entire spectrum can be collected in a few microseconds, and both positive and negative mass spectra can be obtained for more complete chemical information. Vitrinite from a medium volatility bituminous coal gives reproducible spectra and fingerprints of the vitrinite. Trace elements such as Li, F and Ti characteristic of bonded vitrinite are absent from non-bonded type, indicating the different origins of the macerals. Those with trace elements probable formed from woody tissue and those lacking them more likely came from humic gels. Another type of maceral called resinite, also can be fingerprinted by the vitrinites. Thus the technique can be used to classify macerals and micro-volume determination. It can also be used to detect maceral source of sulfur and genesis of coal.

4.3 Sampling procedure for analysis of coal

Coal is a heterogeneous material and therefore sampling procedure is of utmost importance in order to get a reproducible result. We generally think greater is the sampling volume better is the result. But modern automatic analytical instruments take samples in milligram quantities (e.g. Parking Elmer elemental analyzer). Accuracy of the results in such low level of sample is argued on the following points. The analysis of coals by instrumental methods where sample size used are in milligram range, require considerations for – preparing the samples for analysis and specify procedure for the analyzer. The question of moisture is to be understood first. The sample may be analyzed on an as received basis, after air drying, after extensive dehydration or on a dried basis. It is recommended that all analysis should be made on moisture-free samples, since coal that contains moisture is considered unstable and heterogeneous. The dried basis method is recommended for all higher ranked coals. These coals generally do not oxidize when dried. Lower ranked coals, which can oxidize when dried, should be analyzed on an air-dried basis. Next, the question of obtaining a representative sample from a heterogeneous substance in always of concern with any analytical method. The degree of heterogeneity would

require a corresponding homogenization of the samples substance. In other words, the greater the degree of heterogeneity, the more demanding is the homogenization requirement. Coal is a classic example of this problem, because it consists of complex organic structures which are intimately mixed with mineral matter. The degree of its heterogeneity is directly related to its mineral matter content. The problem in analyzing this substance is, as stated above, concern of obtaining a representative samples with the method employed. Standard testing methods exist for the analysis of coal such as the American Standard Testing Methods D-3178, procedure for the determination of carbon and hydrogen. This method prescribes a sample of 200 mg which is sized to pass through number 60 mesh (250 micro-meters) screen. Specified methods for homogenizing and pulverizing coal samples to this particle size are detailed as ASTM D3176. Still other methods which employ still smaller samples, such as that with Perkin-Elmer Model 240C elemental analyzer, optimally use samples from 1 to 3 mg, which is ground and mixed further to pass a 200 mesh (75 micro-meters) screen. It is recommended to use a Vibrating Mill because this is readily done and the particle size found is actually finer than 325 mesh (45 micro-meter) size; or for grinding a larger volume sample rapidly, a larger capacity mill should be used such as the Pitchford Blender Mill Model 201, which is obtained from the Pitchford Scientific Instrument Division, Hankinson Corp, Canonsburg, PA 15317 (USA). The obvious concern is – does this smaller sample give an acceptable representation of the heterogeneous substance. The answer is “Yes” (Fujimori and Ishikawa, Fuel, 51, April 1972). Not only is it representative, it actually contains more particles than the larger samples used by the standard method. The proof of this is simply done by computing the mixed distribution of the organic and mineral matter of the coal – which essentially determines the degree of heterogeneity. This could be done mathematically by separating each in compliance with the binomial distribution which postulates that: “a particle that occurs with a given probability among the members of a population will occur a certain number of times in a succession of samples of the population.” Therefore, for the purpose of estimating a true mineral matter (ash), yield (M) in coal at a probability of 95%.

- (a) $1.96 [M(1 - M)/n]^{1/2}$ greater than/equal to $B = 1.96 SM$ where, SM = repeatability shown as standard deviation and B = confidence interval (prob. of 0.95). The number of particles (n) required for the analysis can be calculated from –
- (b) n greater than/equal to $M(1 - M)/SM^2$, the number of particles (n_0) contained in the sample of every particle size and any sample weight used can be calculated from the following equation.
- (c) $n_0 = \text{sample weight (g)} / 4/3 \pi [D \text{ (CM)/2}]^3 \times d$ where, D = mean

diameter of the sample, d = density of the coal (1.3). By using the above equations, the theoretical number of particles required to obtain a representative sample is determined by equation (b). The results obtained – theoretical number of particles present, for various mineral matter (ash) contents and corresponding expected error is shown in Table 4.1.

By using equation (c) the number of particles that would be found in various sample weights with corresponding particle sizes is computed and is shown in Table 4.2. What is immediately realized is that the smaller sample with its corresponding fine mesh provides more particles than the larger samples used in conventional methods and would by comparison be more representative. For comparative purpose, Table 4.3 shows how many more particles are present in the smaller samples used with the 240 when comparing to the larger samples used by conventional methods. The validity of obtaining a more representative sample of 3 mg at 325 mesh (45 μm) when comparing against a 25,100, or 200 mg sample at 60 mesh, is true only if the original sample used for grinding to 325 mesh or finer is 0.5–2.0 g.

4.4 Demineralization procedure for coals

This method (Communication from Nixon and Nandi, Department of Energy, Mines, and Resources, Ottawa, Canada) is designed to remove mineral matter from coal in a two-step acid treatment procedure. The coal is first treated with HCl to remove all metal salts. Then this is followed by,

Table 4.1 Theoretical number of particles

Mineral matter (%)	Error (%)	Number of particles
5	0.05	190,000
	0.10	47,500
	0.20	11,875
	0.30	5,278
10	0.05	360,000
	0.10	90,000
	0.20	22,500
	0.30	10,000
20	0.05	640,000
	0.10	160,000
	0.20	40,000
	0.30	17,777
30	0.05	840,000
	0.10	210,000
	0.20	52,500
	0.30	23,333

Table 4.2 Number of particles present in various sample weights

Sample weight (mg)	Particle size (mmm)	Number of particles
2	45 (325 mesh)	32,244
3	45	48,366
4	45	64,448
25	25 (60 mesh)	2,350
100	250	9,402
200	250	18,804

Table 4.3 Particle comparison between 240 and alternate method

(240) wt (mg)	Alternate method (SW) mg	Factor greater
2	25	13.7
	100	3.43
	200	1.7
3	25	20.6
	100	5.1
	200	2.6
4	25	27.4
	100	6.9
	200	3.4

a HF treatment to remove all silicates and silica from the coal. Procedures adopted for this is as follows:

Step 1:

1. Several grams of coal are ground to -100 mesh.
2. The coal is then placed into a 250 ml beaker containing 100 ml of 50% HCl soln.
3. Add a Teflon stirrer bar, then place the beaker on a stirrer hot plate.
4. Activate the stirrer to a reasonable speed and then heat the mixture approx to 80°C.
5. Heat (and stir) the mixture for 2 h.
6. Filter the mixture with a Whatman #40 filter paper.
7. Wash the coal residue with warm deionized or distilled water until the filtrate is free of chloride ions (check with 5% silver-nitrate solution).

Step 2:

1. Transfer the coal residue to a 100 ml Nalgen or Platinum beaker.
2. Slowly add 50 ml (40%) of HF to the beaker.
3. Place the beaker on a steam bath for 30 min.
4. Then transfer the beaker to an ultrasonic vibrator bath and allow it to agitate for 25 min.

5. Filter the mixture with a Whatman#40 filter using a plastic funnel.
6. Wash the residue several times with warm deionized water.
7. Dry the residue in a vacuum oven at 75°C for 2 h. The vacuum should be filled at conclusion with an inert gas (argon is preferred).
8. Store the sample in vacuum desiccators filled with argon.

Statistical method of coal sampling constitutes an important step in all coal estimations. There are three statistical procedures, namely – random sampling stratified sampling, and systematic sampling. These are detailed below:

(a) Random sampling – This is the most commonly adopted practice whereby each unit of a population has an equal chance of being selected in the sample. Mean (range) and variance (square of standard deviation, S^2) gives an estimate of population parameters. The random error (defined by, variance / standard deviation) is due to different set of random sampling of the estimate of these samples average is given by the equation: Variance of the sample average, $V(x) = (N - m)/(N - S) \cdot (a^2/n)$ where, $x = x_i / n$, a^2 is population variance which measures the deviation from the average value and is obtained as the sum of square of the deviations from average value divided by the number of samples. n in above equation is the number of units in the sample. a^2 in turn, is given by the equation:

$$a^2 = (N - 1) / N \cdot S^2, \text{ where } S^2 = (1/n - 1) \sum x_i^2 - N \bar{x}^2$$

In such collection procedure, after drawing a random sample unit from population, it is removed from the population before drawing next sample. This procedure is also known as “sampling without replacement” and is a common practice in industry.

(b) Stratified sampling – As has been mentioned earlier, in case of heterogeneous material like coal, increasing the sample size will decrease the variance or the error in result. But in large volume the cost of sampling also increases in this method and there is a limit beyond which we cannot increase sample size. In the alternative method of “stratified sampling,” the entire population is divided into several groups or strata such that units within a strata are more or less homogeneous. From each strata, then a preassigned number of sample units are collected by random sampling process. Stratification procedure is useful only when population is heterogeneous and there is possibility that it could have been divided into a number of groups relatively more homogeneous. It has two special advantages over others, like – all the different groups have equal chance of representation in the sample of analysis, variation of the result from true value is reduced. In stratified sampling the mean of the units in the population is given by the expression – $\bar{X} (av) = \text{Summation of } N_i X_i /$

summation N_i where x_i = estimated mean of the i -th strata, N_i = number of units in the i = the strata, and K = total number of strata.

(c) Systematic sampling – When the population of samples are available in an orderly manner, the random sampling procedure is simplified. The method consists of first selecting at random a single sample item from the population of N items at regular predetermined intervals of space or time in order to make up the desired sample size “ n ” so as to cover the entire period of sampling operation. In this method, selection of the first item determines the subsequent units of sample. The method has been widely used in coal sampling for its simplicity of operation and spread of sample units all through the population. In general sampling procedure of Indian coals, a combination of stratified and systematic procedure is applied in collection of increments. All these procedure aim at the common goal of achieving a sample from stockpile (population) where each unit gets equal opportunity for inclusion into it. Experiments have revealed that variability of ash in Indian coal depends mainly on the size of coal and if all the sizes of coal particles are not properly represented in the sample, it will not be representative of the consignment. It has also been observed that for Indian coals there is no well defined relationship between the average ash and its standard deviation. In most cases standard deviation of ash was found to be ± 1 independent of average ash content. The magnitude of error has therefore been fixed at $\pm 2\%$ from true ash for the probability being 0.95. Above consideration have lead to the evolution of Indian standard method of sampling coal and laid down in IS-436 of coal sampling (Part-I, 1964, Govt of India, ISI, New Delhi). Under this instruction, Indian coals have been divided into three size groups – run of mine coal (nominal size 23–0 cm), large coal (nominal size 15–5 cm) and, small coal (nominal size 5–0 cm). The ISI specification recommends division of a “lot” into a number of sub-lots depending on the weights, irrespective of whether sample is to be collected from wagons, conveyors, trucks, stockpiles etc as per following chart:

Weight of the lot	No. of sublots gross
Upto 500 metric ton	2
501 to 1000 ton	3
1001 to 2000 ton	4
2001 to 3000 ton	6

Sampling from wagons – During loading and unloading ISI specifies collection of minimum weight of gross sample for different size group of coals from railway wagons, for each size group corresponding weight of increment and the number of increments are as follows:

Sample	ROM	Coal (large)	Coal (small)
Weight of gross sample (minimum)	350 kg	175 kg	75 kg
Weight of increment (approx)	7 kg	7 kg	5 kg
Number of increment (minimum)	50	25	15

It also recommends collection of increment from at least 25% of wagons in a sub-lot. The increments shall be evenly distributed over the selected wagons and to be drawn at regular intervals of time and space. This procedure can be extended to sampling from trucks, tubs, etc.

Sampling from conveyor – The weight of gross sample for each size group is same as that recommended for sampling from wagons, but the approximate weight of increment is 5 kg in all cases; Subsequently number of increments are different being 70, 35, and 15 for ROM coal, large coal, and small coal, respectively. The increment shall preferably be taken from the full cross-section and thickness of the stream in one operation. Precaution need to be taken in manual sampling from a running belt. The limit suggested by the International Organization of Standards (ISO) are – minimum speed of 1.5 m/s, height of coal maximum 25 mm, flow less than 200 ton/h. When the coal is in motion, the most reliable method of obtaining increments is to sample where the coal is being discharged from the belt. If it is practicable to stop the belt, increments may be collected from the entire cross section by sweeping coal lying between the sides of suitable frame placed across the belt. The material collected from all the increments in a subplot shall be mixed together and shall constitute a sample. For reasons described earlier, sampling from stockpile or from a loaded wagon is to be discouraged. However, under certain unavoidable situation following method has been recommended for sampling from a stockpile. The principle is the same for sampling from loaded wagons, trucks, etc.

Sampling from stockpile – The entire stockpile of coal is to be divided into sublots of approximately equal weights as specified. The surface of each subplot shall be leveled and one point for every 250 metric tons (approx.) of coal in the subplot shall be chosen at random. The first two digit random number may be considered as abscissa and next two digits as the ordinate of the point in any units of measurement (cm, meter, etc). In case height of the stockpile is not more than 1.5 m, the material shall be collected at every selected point by taking the whole section of coal from top to bottom over the area of a circle of 30 cm diameter. When the height of the stockpile is more than 1.5 m, the sample shall be collected at every selected point by taking the material over an area of a circle of 30 cm diameter and up to a depth of 1.5 m.

4.4.1 Reduction and analysis

As stated earlier, a gross sample of coal or any other mineral, has to be reduced in size and weight and ultimately only 1 or 2 g of the material is analyzed in the laboratory for quality assessment. IS-specification recommends reduction of gross sample of different upper size in stages to about 1.5 kg in the size of 3 mm and ultimately to 212 micron size, for analysis in the laboratory. The reduction of the sample is as much important as collection and a little negligence on the part of the worker may vitiate the result. The space where reduction is done should be clean, closed, and roofed over and care should be taken against loss of fines and contamination with foreign matter. Some size reduction equipment such as Jaw-crusher, Coffee-grinder, Palmac-mill, Raymon-mill, etc., may be used. The size reduction stages recommended by the IS-specification should strictly be following otherwise reduction errors may be considerably higher than the error in sample collection.

Reporting of results:

When only two gross samples are collected, the individual ash % should be reported. When more than two gross samples are collected and analyzed, the average ash content (X) and range (R) of the test results shall be reported; as for example for four gross samples with ash content X_1 , X_2 , X_3 , and X_4 percents, the results shall be reported as: $X = (X_1 + X_2 + X_3 + X_4) / 4$ and, range = difference between maximum and minimum ash content values of the 4 individual gross samples. The limits of the variation of the average quality (X) in the "lot" under study shall be reported as $X \pm hR$, where "h" is a probability factor with differing values for different size of sample and are available in the IS-specification or any standard statistical table. IS-specification also provides a method for rejecting a test result which is under suspect. The ISO has also recommended detailed procedure for collection and preparation of samples under different conditions of production, preparation and use and provide methods for calculating accuracy in sampling. The specification also provides essential description of different types of automatic samplers.

4.5 Statistical quality control (SQC)

The SQC technique is considered to be a management tool like cost accounting, time and motion study and budget control. Its contribution lies in improving the product quality and in reducing cost. A statistical approach to the behavior of the variable quality is a pre-requisite to the adoption of SQC technique and this is done by drawing and analyzing

sample at regular interval of time or space or any production sequence. If a large number of sample is taken, the results can be grouped in the form of a frequency distribution or histogram. If a production process is subjected to systematic variation only, then the frequency distribution invariably depicts a predictable pattern. Collection of data on quality characteristics of coal samples could lead to a sampling distribution with a mathematical basis which can be related to the underlining distribution of the production process. Statisticians have developed formulae mentioned earlier for describing pattern of variation exhibited by quality characteristics normally encountered in any production process. Some fundamental statistical parameters are computed from the data to represent the distribution. The common parameters are – (a) for central tendency, i.e., the value of the variable around which the individual values are scattered, is the arithmetic mean (\bar{x}), and (b) for measures of dispersion, i.e., the measure of degree of variation of individual value from the arithmetic mean is the “standard deviation” (s), standard error (\bar{x}), range (R), and mean range (\bar{R}). The property of the normal distribution that 95% of its area lies between the arithmetic mean and ± 2 standard deviation that 99% lies between the arithmetic mean and ± 3 standard deviation, is of paramount importance to a SQC unit. In order to adopt SQC technique in any industry (e.g. coal industry), the operating engineers and technicians must have the technical knowledge and familiarity with the conditions under which coal is produced. There must be a record of quality assessment by collecting samples at regular intervals. Calculation of statistical parameters mentioned above from the recent available data should then be done. The record is to be maintained on – (a) actual measurement of quality characteristics (e.g. ash content is case of coal), (b) number of samples collected at each time and (c) frequency of sampling, (d) lot size etc.

4.5.1 Different types of control charts

We shall consider control charts for continuous variable only. There are generally three types of control chart used – (a) \bar{X} and R chart, (b) \bar{X} and S chart, and (c) for \bar{X} or for R or s alone.

Starting SQC scheme

Following steps have to be gone through before adopting SQC in any industry:

- (i) Choice of quality characteristics.
- (ii) Specification, if any, of the quality characteristics.
- (iii) A laying out of data sheet – for individual observation and for statistical parameters.

- (iv) Sampling and inspection – Select “n” number of samples (in case of coal more than two from a lot) in sequence of time or space, and test each sample for chosen quality characteristics; record the “n” observed data in the sequence in which they are selected.
- (v) Lay-out the form for control chart record on a standard cross-section or graph paper (preferably in millimeter graph paper) and spaces for recording quality characteristics, specified maximum and minimum limits and consignment/lot number should be provided. The control chart consists of a “central line” (CL) denoting average value of the characteristics and two control limits on either side of central line which are called “upper control limit” (UCL) and “lower control limit” (LCL). The control limits are computed from probability distribution of the statistical parameters.
- (vi) A horizontal scale for data and time of collection of samples may also be provided.
- (vii) Two vertical scales on the left hand margin of the paper – one near top for plotting \bar{x} and one below for plotting R is to be used.
- (viii) Plotting of values of \bar{X} , R, etc. are then done in a sequential manner⁸.

4.6 Preliminary analysis

Collection and analysis of some preliminary data covering a period, say at least 6 weeks to calculate control chart parameters may be made. If, however, some reliable and representative past data are available, they may be used for calculating the parameters. We shall consider a case where a producer dispatches 50 wagons of coal produced from a seam to a consumer. It is observed that data collected daily and analyzed for ash and daily average ash (\bar{x}) was recorded. From these \bar{x} given by sum of daily average ash divided by 42 were computer and was found to be 32.5% and after the 42 daily average are plotted on the chart, a solid line through \bar{x} (in the present case through 32.5%) is drawn.

The control limit:

On the assumption of “normality of distribution of ash content,” control limits (dotted lines) for \bar{x} is given by $\bar{x} \pm A_2 R$ where the value of the factor A_2 is available in standard tables for different sample size. In the present case, it was found that –

$$\bar{X} \pm A_2 R = 32.5 \pm 2.0$$

The next step is to check and review whether preliminary as to how good the control is, then only \bar{X} or R may be taken as representing the quality of coal supplied from the colliery, otherwise fresh sample are taken

covering at least 6 to 10 weeks production / supplies and parameters calculated and plotted as described above. The control chart may then be placed to the manager in-charge production/quality control and plotting of the values of the parameters made. When any value of X or R fall outside the control limits, this generally indicate variation due to assignable causes for which necessary action should be taken for the “lot” which indicated lack of control. After the assignable causes of variation have been eliminated or minimized, the standard (32.5 ± 20) may be reviewed or revised in the light of the new data. The control, charts, if preserved, shall give a definite idea of quality of coal obtainable from the source for a reasonable period of time, i.e., so long the production and preparation process or the characteristics of coal in the seam does not undergo any drastic change.

4.7 Proximate and ultimate analysis of coal

Guidelines for proximate analysis is covered under ASTM D3172. This is the combination of three determinations and calculation of a fourth. The proximate analysis is defined as an assay of moisture, ash, volatile matter, and fixed carbon as determined by above prescribed method. Various methods of proximate analysis of coal are described below and ultimate analysis described thereafter.

4.7.1 Moisture

Equilibrium moisture in coal is defined an amount of moisture contained in coal at 30°C in a relative humidity of 96–97%. No absolute method for determining the true moisture content of coal by heating has been devised because of the wide variation in temperature at which different forms of moisture (including surface, inherent, chemically combined moisture in coal) and water of hydration in clay minerals are liberated. R. F. Abernety et al stressed empirical method for determining moisture in Coal. In one method weight loss of coal was measured after heating to 106°C in a flow of dry oxygen free nitrogen. In other methods weight loss measured at the same temperature but nitrogen atmosphere always gives higher results because heating in air sometime oxidizes coal and offsets the moisture loss through addition of oxygen. Measuring indirect weight loss after heating in nitrogen at 130°C for 30 min, with a flow of nitrogen, was judged the most convenient method. Moisture loss during pulverization depends on maceral composition. Losses are least for vitrain and increases in order of vapor of moisture (e.g. clarain durain fusain¹⁰). To determine moisture in coke, temperature must be increased to at least 300°C. Temperature of 100–110°C is not enough to remove all moisture. Low

rank coals are more reactive to oxygen and thus pose a problem. Two methods have been considered for determination of moisture in low rank coals – first through measurement of weight loss caused by drying in a tube subject to vacuum which reportedly gives a sharp moisture cut-off¹¹ and by measurement of electrical capacitance, which has been related to moisture content of brown coals containing up to 27.3% moisture (relative error 6.6%). M. Hampel has reviewed seven methods for continuous measurement of moisture in coal. These are electrical conductivity, dielectric constant, microwave attenuation, neutron scattering, NMR, IR, and thermal conductivity. Continuous measurement of moisture in bituminous coal has been accomplished using a capacitance method, in which coal moves between the plates of a capacitor. The lower plate has a keel that extends into the stream. The dielectric constant which are very different for dry coal and water, change in proportion to the moisture content of a particular coal. When calibration curve is prepared for each coal tested, the accuracy for moisture content is $\pm 1\%$ absolute. Results of laboratory studies of microwave attenuation for continuous moisture measurement are coal warrant further testing of this method in plant trials¹⁵. Although the calibration curve varies from one type of coal to another, a useful relationship between microwaves and moisture content (wave absorption) of coal has been found. Changes in characteristic microwave absorption in different coals are rank dependent and are probably associated with petrographic composition and pore structure. R. F. power absorption method has also been tried for determination of moisture in coal. The general analytical technique suggested for moisture determination is through ascertaining loss during air drying (by ASTM D3302) followed by co-distillation of moisture with xylene¹⁷. Two chemical methods suggested for determination of moisture in coke are (a) extraction of coke using anhydrous methanol and addition of CaH_2 from which the amount of heat released is measured, (b) extraction of coke using anhydrous dioxane and measurement of the refractive index of the solution to determine its water content. Only the first method was found to be suitable for practical purposes. (Neser and Kaloe, *Sb Ved Pr Vys Sk Banskedtrawe, Roda Hutn*, 19, 129–140, 1973). Moisture can also be determined using a thermogravimetric balance as in a proximate analyzer. Although many above methods have been tried for moisture determination, the universal standard method adopted is through weight loss determination at 100°C . ASTM D1412, D2961, and D3302 further distinguish three types of moisture. ASTM D1412 defines “equilibrium moisture” as the moisture of coal at 96–97% relative humidity and at 30°C ; which is an estimate of the bed moisture content of coal in the seam before mining. ASTM D2961 defines another moisture content known as “single stage total moisture” which

includes both surface moisture and the residual moisture remaining in the sample after determining the air-dry loss. For this estimation, coal reduced to No. 8 top sieve size (500 g sample) is dried at 107°C for 1½ h. The third ASTM D3302 defines “two stage total moisture” which is the standard general method of moisture determination and determines the total moisture in coal as it exists at the site, at the time of sampling. For its determination the coal sample (under 0.5 mm size) is first dried to constant weight (to 0.1% constant per hour) and then the sample is ground to 60 mesh and the residual moisture determined. The total moisture is then determined from the formula:

$$M = R (100 - A) / (100 + A)$$

Where M = total moisture (%), A = loss at air dry basis (%), and R = residual moisture (%), ASTM D3173 prescribes “residual moisture” determination for both coal and coke. Here the coal is crushed to pass a 250 micro-meter (No. 6) sieve and moisture of 1 g sample determined.

4.7.2 Ash

ASTM D3174 defines the ash determination procedure. In this procedure the coal sample is burnt in free air at 700 to 750°C and the ash determined gravimetrically.

4.7.3 Volatile matter

Volatile matter determination has been covered under ASTM D3175. This method determines the weight percent of gaseous products, exclusive of moisture, which is released upon heating the sample under specified conditions, in absence of air. Specifically, 1 g sample (–72 BS mesh) is introduced into a preheated furnace and held at 925°C for 7 min. This value is used, as mentioned earlier, classification of coal by rank, for estimating coke yield, and for an indication of burning characteristics.

4.7.4 Calorific value

Heating value of coal can be determined either of the two specified methods – ASTM D3286 or D2015. ASTM D3286 specifies heating value determination by isothermal Jacketted Bomb Calorimeter (whose accuracy depends on the operator) and ASTM D2015 specifies determination of the same by Adiabatic Bomb Calorimeter, which is automated and most widely used. It should be noted here that C.V. determination by either method condenses the generated steam in-situ and thus boiler engineers in normal burning of coal (where steam generated escapes through flue) make necessary correction while using these values.

4.7.5 Fixed carbon

Fixed carbon is determined indirectly by subtracting the total value of moisture, ash, volatile matter from 100. In low volatile matter substances like coke and anthracite, this value approximately equals to the elemental carbon content of the substance. ASTM D388 classifies coal (as per rank) based on these value and volatile matter content.

4.7.6 Fusability of ash

ASTM D1857 describes standard method for the determination of fusability of ash both in coal and coke. For this purpose, first a cone is prepared as follows – moisten the ash with a few drop of 10% solution of dextrin containing 0.1% salicylic acid as a preservative and work it into a stiff plastic mass. The mass can be given the shape of a cone. The cone shall be 10 mm in height and 6.4 mm in width on each side of the base which is an equilateral triangle. Then the 4 ash fusion characteristics are determined as follows:

- (a) Initial deformation temperature – The temperature at which the first rounding of the apex of the cone occurs. Shrinkage or warping of the cone ignored if the tip remains sharp. At this temperature first rounding of the apex of the cone appears.
- (b) Softening temperature – The temperature at which the cone has fused down to a spherical lump in which cone height equals the base width.
- (c) Hemispherical temperature – The temperature at which the cone has fused down to a hemispherical lump, at which point the cone height equals the base width.
- (d) Fluid temperature – The temperature at which the fused mass has spread in a nearly flat spread-out in a nearly flat layer so that height of the melt layer has a maximum height of 1/16 inch. These values for a typical north-eastern coal (Indian) is –
Initial deformation temperature = 1320°C
Hemi-spherical temperature = 1400°C

4.7.7 Elemental sulfur

Reflux the coal sample with cyclohexane and then determine the elemental sulfur (%) by gas chromatography with the extract.

4.7.8 Organic sulfur

TRW (USA) has evolved a low temperature ashing process for direct determination of organic sulfur in coal, whereby a microwave plasma

radiation selectively breaks organic sulfur bond and release in gas phase as SO_x , SO_x is then cryogenically trapped and estimated.

4.7.9 Combined sulfur

Purnell and Doolan¹⁸ have recently suggested a process for rapid estimation of sulfide, sulfate, and pyretic sulfur in coal. In this process first “sulfide” sulfur is determined by reaction with HCl (evolved H_2S is estimated) while “sulfate” and “pyritic” sulfur are reduced at 210 and 270°C, respectively, by tin (II) – phosphoric acid solution (evolved H_2S in each step is determined by titration with 2-carboxyphenyl–hydroxymercury (II).

4.7.10 Swelling index

ASTM D720 specifies the method for determining swelling index through preparation of a coal sample in the form of a button, carbonizing in a specified silica crucible with cover for a fixed temperature and time. The remains of the button is compared with standard profile and assigned numbers from 1–9 in ½ unit increment. A value of zero is assigned to a residue that is non-coherent. The test is an indication of caking characteristics of coal burned in a fuel bed and also the state of weathering of coal mined near outer lines.

4.7.11 G.K. Assay and caking-index

Fusibility of cokes during its formation from coal is called its “caking property.” British coals having less than 83% carbon in the pure coal are non-caking. Caking property begin to appear at the level of rank associated with C = 83% and increase with increasing rank to a maximum at the rank level equivalent to C = 89.91%. As the rank increases still further, caking properties rapidly decline. This is just a general classification and exceptions do exist. Both brown coal (woody structures with 40–60% moisture and C = 60–65% daf basis) and lignite (20–40% moisture, 65–73% C daf basis and V.M. = 40–60%) are quite devoid of caking power. Lurgi gasifiers (with O_2 and steam under pressure) are suitable for making fuel gas from such low grade, non-caking coals. The lower rank bituminous coals are non-caking but the phenomenon of fusibility, which is caking power, appears for the first time among coals in this class. Caking power in this class of coals increase with increasing rank and the bituminous class includes the strongest coking coal know. With higher grade, higher carbon (C = 90–93% daf), so called “semi-bituminous” coal, caking power decreases. Caking power is assessed by “Gray-King Coke Type” test. This test discriminates between two types of non-caking behavior on

carbonization and between 14 levels of caking power from “very feebly caking” to “very strongly caking”. The other classification, based on volatile matter yield (daf basis) is as follows:

Coal type	Volatile matter
Anthracites	Less than 9.1%
Low volatile steam coals	9.1–19.5%
Medium volatile coals	19.6–32.0%
High volatile coals	more than 32%

Each of above four main classes is sub-divided according to the caking properties of the coals. The whole range of caking properties as measured by the Gray-King coke type test, is classified into six groups:

- Non-caking coals yielding Gray – King coke type A and B.
- Very feebly caking yielding Gray – King coke type C and D.
- Weakly caking yielding Gray – King coke type E, F, and G
- Medium caking yielding Gray – King coke type G₁, G₂, G₃, and G₄
- Strongly caking yielding Gray – King coke type G₅, G₆, G₇, and G₈
- Very strongly caking yielding Gray – King coke type G₉ and over.

In the British coal rank number system, each of the four volatile matter classes is known by a 3-figure system; as for example –

- 100 = anthracites, non-caking, V.M. less than 9.1% (daf).
- 200 = the low V.M. steam coals, non-caking to strongly-caking.
- 300 = medium volatile coals, either weakly or very strongly caking.
- 400, 500, 600, 700, 800, and 900 = the high V.M. coals.

The various main level of ranks indicated by the code numbers above involve properties suitable for following industrial purposes:

- 400 = suitable for carbonization in coke-ovens to produce first grade metallurgical cokes.
- 401 = include the best coking coals for coke ovens.
- 500, 600 = suitable for steam-raising; carbonization in gas works; carbonization in coke ovens to produce second grade metallurgical coke; blending with very strongly coking coals for carbonization in coke ovens.
- 500, 600, 700 = suitable for steam raising and for carbonization in gas-works.
- 700, 800, 900 = suitable for steam raising.

International classification system also expresses coal by 3-figure code numbers. The first figure indicates the volatile matter yield (and the

calorific value if the V.M. is more than 33%), the second figure indicates the British Standard Swelling number and the third figure and Gray-King coke type.

For practical purpose of coal characterization, two principal tests are at present used in Britain. In these tests, coal of 72 B. S. mesh size and air dried are heated in conditions in which they are free to swell and the appearance of the coke residue is used as an index of the caking power. These tests are known as –

- (a) British Standard Swelling Number test (No. 1–9, as explained above).
- (b) Gray-King low temperature coke type test.

British Swelling Number test

In this test the coal (1 g of –72 BS in a covered silica crucible) is violently heated and the heating is unidirectional. In these circumstances all coals except which are quite devoid of caking power soften and produce a coke residue which is, compared with original mass, to some extent swell (heating is for 2½ min or until no volatile matter is evolved).

Gray-King Coke type test

This test uses slow, all-directional heating. It is less simple than previous test to perform, but is probably the most information British test at present in use. In this test 20 g of –72 BS coal are arranged as a uniform layer 6 inch long in a tubular silica retort. The retort, mounted horizontally, is connected to a receiver for liquid products of carbonization (i.e., tar, aqueous layer etc) and to receive and burn gas. A horizontal electric furnace at 300°C is placed over the retort and the temperature is raised from 300–600°C at the rate of 5°C/min, i.e. in 1 h. A temperature of 600°C is maintained for 15 min and the furnace is removed. The coke residue in the retort is examined and evaluated. The coke residue in the retort may be a powder closely similar to the original coal or it may be fused but shrunken compared with coal, or equal in size and shape to the coal charge but well fused, or it may be swollen. If the coke is swollen, another test is made in which the charge is a blend of the –72 BS coal and –72 BS electrode carbon, an inert material whose presence will depress the swelling of coal. The object is to find the minimum number of grams of electrode carbon which must be contained in a 20 g charge of coal/carbon blend to give a coke residue which is well fused but is neither swollen nor shrunken. This quantity of electrode carbon is an index of caking power for coals which swell in this “slow heating test.” Very low B.S. swelling number are likely to mean very low values on the Gray-King coke type scale and very high

B.S. swelling numbers probably, but not is necessarily, reflect high values in the Gray-King coke scale. In assessing caking properties it is better to make both tests. Caking tests does not give complete carbonization behavior of coal. They must indicate likely suitability or unsuitability of coal for this purpose. As a rule, the strongly caking coals should be avoided for furnace work, except in large plant having very intensive combustion conditions. It is probably true that the smaller a combustion unit is and the lighter its duty, the more selective it tends to become. Most cases, high ash content of coal is a disadvantage, but on the other hand, low ash coals are also not desirable in most combustion techniques. Where the coal is to be burned on an industrial grate, it should contain enough mineral matter to form a layer of ash on the fire-bars which can act as a protective blanket and prevent the bars becoming overheated. Ash content of 7–12% is usually suitable for industrial scale combustion on grate. In combustion practice, caking properties should be considered in relation to the method of stoking and to the possible harm caused to the combustion conditions by the formation of large coke masses. The caking properties of coals intended for carbonization should be considered together with volatile matter yield shown by the proximate analysis. For the manufacture of coal gas, the main requirements are moderate caking properties (i.e., strong enough to cause the coal to form a good, coherent coke which will be easily removable from the plant without having swelled excessively). The yield of potential heat in the form of gas should be high in this industry so that the coals chosen because of their caking power should be on the low rank side (and hence high volatile matter yield) of the curve for variation of caking power with rank. In India, the general method followed for determination of caking index is to carbonize 25 g charge of sand and coal (both ground to definite size) in varying proportions at 900°C until a mixture is found which gives coke which will just support a 500 g weight and at the same time not give more than 5% in non-coherent powder. The lower ratio (whole number) is the agglunating value of the coal.

4.8 Hardgrove grindability index

ASTM D409 specifies procedure for determination of grindability index of coal by Hardgrove Machine. Grindability determines the relative ease of pulverization of coal. Standard coal samples are used for calibration of the instrument. High grindability index denotes easy to grind coal. It has been found that lower is the volatile matter in coal higher is the grindability index (GI). High volatile coals show GI value in the range 35–55 and low volatile coals 100 and above. GI value is also an indication of friability of coal, although the later property has been specified separately by ASTM

under D440 test (Drop Shatter test) and D441 test (Tumbler test for friability determination).

4.8.1 Micum test

These tests are designed to determine abrasion resistance and mechanical strength of cokes. A fixed size and amount of coke (50 kg, +5 cm) is rotated at an exact speed for definite time in a cylindrical drum (100 cm internal diameter and 100 cm internal length) and the fines passing through -10 BS mesh is reported as micum M_{10} value. This gives a comparison of abrasion resistance of the coke. Similarly (+40 mm) M_{40} value indicate strength of the coke and determines its suitability in blast furnace application.

4.8.2 Porosity

The fraction of the volume of a solid occupied by pores can be determined from measurements when the solid is immersed first in one fluid, which fills the pores completely, and then in another fluid which does not enter the pores at all. Helium and mercury are commonly chosen as the two immersion media. Graph of porosity against rank parameter show a minimum for the coking coals (89% carbon content). The size distribution of the pores can be investigated by immersing the coal in mercury and progressively increasing the pressure on the mercury. Because of surface tension, the mercury cannot enter pores with diameter smaller than a value "d" for any given value of pressure "p," where $p = 4 \gamma \cos \theta / d$; γ being the surface tension and θ the angle of contact. By recording the amount of mercury entering the coal for each small increment of pressure, it is possible to build up a picture of the distribution of sizes of pores. By using liquids of various molecular sizes it is possible to investigate the distribution of micropore sizes and a bimodal distribution is found with peaks corresponding to diameters of about 0.5 and 0.8 μ m. In recent time, pore volume has been studied by neutron scattering technique¹⁹. The access of solvents and reactants to the micro-void volume in porous carbons (Illinois coal, USA) studied by above workers found microvoids to be completely filled by aqueous soln. Whereas nonaqueous mixtures of cyclohexane can not fill the entire microvoid volume. Thus the surface of microvoids is predominantly aliphatic in character with the principal compositional variations being the presence or absence of acidic functionality on the surface. The porosity changes from a high value of 5–30% for lignite to 2–3% for coals having 87–89% carbon before increasing further to anthracite. This structural aspect also influences the total surface area of a particular amount of coal. The surface area generally tend to fall from a

value in the range of 100–200 m²/g among lignites and sub-bituminous coal to 50–100 m²/g in the bituminous coal range and the again increase to over 100 m²/g for anthracite. Over 90% of surface area is contained within a micropore system that represents between 50–80% of the total void-volume and microporosity predominates as the rank of coal keep on increasing.

4.8.3 Heaven test

This test is used to find the abrasion index of coke. Heaven machine consists of a steel drum of 9.15 cm internal diameter and 45.7 cm inside length. 10 kg of coke sample of +5 cm size are weighed accurately and placed in the drum and rotated at 24 rpm for a total of 1400 revolution (i.e. for 56 min). The coke is then removed, sieved, and percentage on 1 inch mesh is found out.

4.8.4 Shatter test

This test measures the resistance to shattering or the impact hardness, as distinct from surface hardness which is measured for abrasion tests. In this test a weighed quantity (50 lb or 22.7 kg) of +5 cm pieces of the coke is dropped four times on to an iron plate from a specified height (6 ft). The proportion of coke remaining on certain screens given a measure of the strength of the coke.

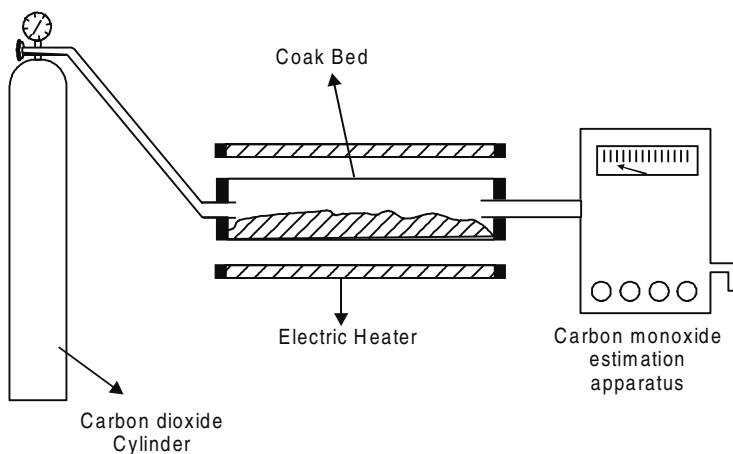
4.9 Reactivity of coal and coke

Reactivity of coal towards oxygen/combustibility under specified experimental conditions have been reviewed by Mitra et al²⁰. The experiments were carried out using a Staton Thermobalance. Under this test 1 g of coal (passing through 212 micron size) taken in a silica crucible and heated at a rate of 5°C/min. Oxygen is simultaneously passed at the rate of 50 cc/min. Progress of rise in temperature and change in weight of sample recorded. At a particular temperature, a sudden and very rapid rate of loss of weight occurs. This is the ignition temperature. This temperature is kept constant and the experiment is continued until 50% of the sample is burt-off. From this record time taken for 10, 20, 30, and 40% burn-off and cumulative loss (in mg) in 5, 10, 15 and 20 min are found out. The time taken for a particular burn-off (10, 20, 30, or 40%) and the cumulative loss in a particular time (say 5, 10, 15 and 20 min) is taken as a measure of combustibility/reactivity. As far as reactivity of coke is concerned, several studies have been reported for coke/char towards air, steam, carbon-dioxide and sulfur. Among these most frequently referred and the most

studied method is the reactivity towards CO_2 . The F.R.S. (UK) method widely used earlier has certain limitations like, horizontal coke bed, slow rate of passage of CO_2 through the coke bed and consequent inhibiting influence of CO on the reaction, the temperature gradient set up in the coke bed due to the endothermic heat of reaction and problems in measuring the reactivity of highly reactive samples. Accordingly an improved method was reported by Banerjee et al²¹ and now widely used in industries and steel plants. Here we discuss this later method in detail. Schematic diagram of the vertical reactor and other associated set up is shown in Fig. 4.1 below. Later the methods developed by Norwegian and Polish scientists also employ the same principle. In above case, however, the reactivity (K) is expressed as C.C. of CO_2 . A graph is then drawn with plots of rate of flow of CO_2 gas against (% CO_2) in the existing gas and from this graph, the rate corresponding to 75% CO_2 in the existing gas (i.e. 15% conversion), corresponds to the reactivity value of the sample. On analysis and comparison of results it is seen that, due to draw back of F.R.S. (UK) method mentioned above, two cokes made under identical carbonization condition from two different coals are very close to each other even though the coals differ widely in their ranks. CFRI method of reactivity determination on the other hand shows better correlation with other general properties of the coke. Accordingly CFRI method described above has won universal acceptability in industry.

4.10 Plasticity and dilatometric properties

ASTM D1812 and D2639 cover methods for determining plastic properties of coal. The first one is suggested for plastic properties determination by

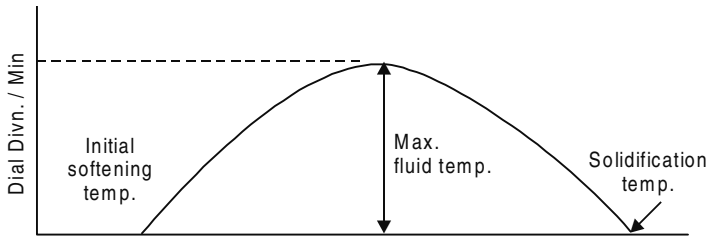


4.1 One method of estimating coke reactivity.

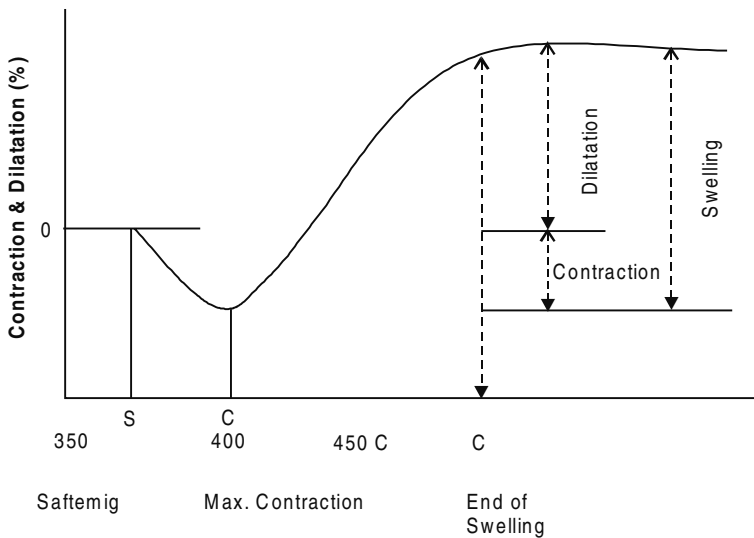
Gieseler Plastometer and the second for constant-torque Gieseler Plastometer. In these tests, the coal sample (–72 BS mesh size) is heated at a rate 2°C/min. A stirrer rotates through it and the torque measures the plasticity. A resultant typical curve is shown below (Fig. 4.2). Evaluation of metallurgical coal and coal blends used and in the production of coke for steel industries. Dilatometric test measures the expansion curve of coal and help us evaluate softening point, maximum contraction value, and swelling behavior of coal. A typical dilatometric curve of coal is shown in Fig. 4.3 below.

4.11 Ultimate analysis of coal

Ultimate analysis covers determination of elemental composition of coal (e.g., carbon, hydrogen, sulfur, nitrogen, etc) together with ash in the



4.2 Dilatometry of coal.



4.3 Dilatometry of coal.

material as a whole. We will discuss determination of nitrogen, sulfur and oxygen in detail in next section and carbon as well as hydrogen under modern instrumental method of analysis in subsequent sections. Reader may also refer standard ASTM D3176 method for general elemental analysis, D3177 for sulfur, D3178 for carbon, and D3179 for nitrogen and oxygen by difference determinations.

4.12 Thermal analysis of coal

Before we discuss actual thermal analysis techniques for coal, let us first look at the general thermal behavior of coal. This makes our comprehension of analytical techniques easier. In the temperature range, depending on rank of coal, 350–500°C yielding Gray-King coke type plastic, coalesce into a coherent mass which swells and then form a solid porous structure. In this series of transformation, two important temperature zones can be distinguished. The first is that in which the coal is plastic and the second is that at higher temperatures in which the resolidified material contracts. Prime quality coking coals have volatile contents in the range 20–30% (dmaf), become plastic before active decomposition occurs and are so named because they yield strong coke with good abrasion resistance. Viscosity and rate of devolatilization of the plastic mass are such as to minimize inter-granular swelling but enable neighboring coal particles to adhere strongly. The coke thus formed has fairly uniform pores of small diameters surrounded by relatively thick walls giving rise to a high resistance to abrasion. Coals with volatile matter content outside the range 20–30% undergo decomposition both before and during the plastic temperature zone. In many cases, strong, intragranular swelling occurs and the whole mass may foam, giving rise to high porosity and thin walled pores of large diameter within the coke. This product has a relatively low resistance to abrasion. It is clearly seen that the inherent strength and abrasion resistance of coke are determined by the behavior of the parent coal in the plastic zone. Post plastic temperature range contraction is non-uniform. The plastic stage involves the breaking of cross-linkages, comprising either oxygen or non-aromatic carbon bridges between neighboring aromatic groups, leading to mobility of some of the decomposition products. The lower molecular weight component can undergo further change to yield the gaseous volatile matter like H_2 , CH_4 and other hydrocarbons and the highly complex mixture of molecules found in coal tar. The higher molecular weight fractions remain and form semi-coke on solidification during which adjacent aromatic clusters join up through a free radical condensation mechanism. These free radicals are formed from the initial scissions and side chain broken-off through heat treatment. The normal behavior of coals undergoing carbonization may

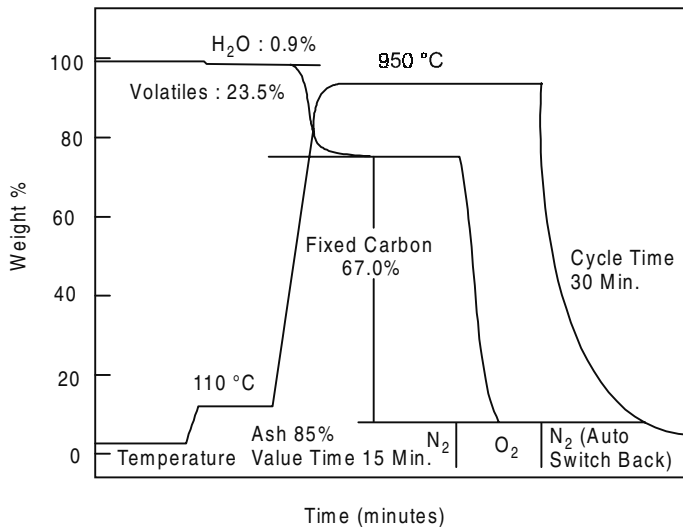
be affected by oxidation or hydrogenation of the coal, as well as by the presence of mineral matter (particularly sulfur) in the coal. Higher heating rate increase fluidity and swelling, and the temperature range over which the coal is plastic is extended. Some coals which show no softening when heated slowly, soften and may swell when heated more rapidly. Some authors have concluded that very fine grinding of coal reduces its plasticity, the effect being particularly pronounced with coals high in inert components. Crushing to the coarse sizes used in commercial plants have different effect with different coals, depending on its petrographic composition. Coals which soften, swell and form coke on carbonization under atmospheric pressure to not give a coherent coke when heated in vacuum. Reduced pressure decreases the degree of softening and swelling. On the other hand, if coal is heated under pressure the softening and swelling increases, and a firmer coke is produced. To obtain an appreciable effect, however, pressures of several atmospheres are necessary. The plastic properties of coal are affected markedly by even mild oxidation. In general, oxidation restricts the plastic temperature range and brings about a decrease in fluidity and swelling. Storage of coal, particularly those with higher volatile matter, may result in oxidation even at ambient temperature. Oxidation of the coal is harmful for normal coking practice but as noted previously, under controlled conditions it is useful in reducing the swelling of briquettes when these are carbonized. Mild hydrogenation of coal increases the swelling and the fluidity: The plastic range is also widened. The reaction of sulfur with coal is similar to that of oxygen. Thermal properties of coal are measured by modern instrumental techniques such as, Differential Thermal Analysis (DTA), Thermo Gravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC). These are discussed in detail in the following sections.

4.12.1 Differential thermal analysis system

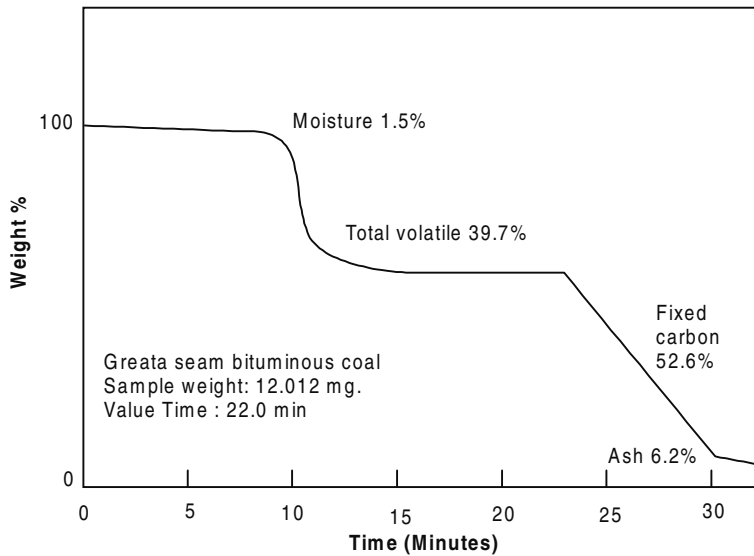
In DTA, the sample and a reference substance are heated together at a constant rate and the temperature difference between them is measured and recorded. This technique is now widely used for high sensitivity detection of various reactions caused by heating such as transition, fusion, solid–solid reaction, dehydration, decomposition, evaporation, and cross linking. In particular its application in coal, as shown in Fig. 4.6 below, is applied for evaluation and detection of various transforming parameters.

Note: In anthracitic coals, a value of $a = 82$ is employed and is considered constant. For coke samples, the value of $a = 0$ is recommended. In TGA, a sample is heated at constant rate and the change of the sample mass is measured. This technique is effective for quantitative analysis of thermal reactions that are accompanied with some mass change, such as

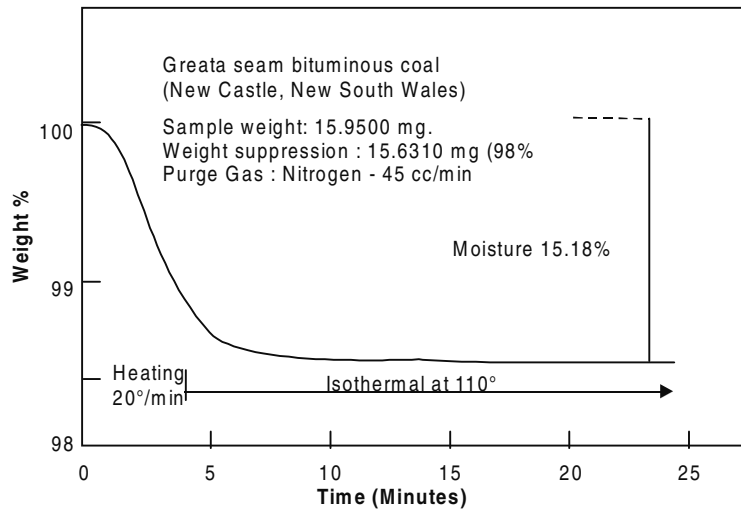
evaporation, decomposition, dehydration etc. Now a days it is widely used for rapid evaluation of proximate properties of coal. In carrying out proximate analysis of coal by this rapid and low mass furnace of a TGA, involves heating to 110°C and holding (programmed) is thermally for 5 min while the moisture is lost from the coal sample. The furnace is then heated at 80°C/min to 950°C and held for approximately coal. The purge gas is then switched to either air or oxygen and the fixed carbon content of the char is oxidized leaving the ash content as the residue. The value of these determinations are read directly in weight percent as shown in Figs. 4.4 and 4.5 below. This rapid instrumental analysis allows the operator to complete two analysis within a period less than 1 h. The moisture content of fossil fuels and coal products is determined mostly on an “as received basis.” Since moisture content decreases with increasing rank, the moisture capacity of coals may also be considered as a rank parameter. For such ranking the coal samples should be exposed to the same partial pressure of water vapor and sufficient time allowed for equilibrium to establish prior to analysis by thermo gravimetry. A saturated solution of K_2SO_4 in water which produces a relative humidity of 96–97% at 30°C is generally employed for this purpose. In cases of higher rank coals of low moisture content where a larger number of significant figures are desired, operator may have to exercise the ordinate scale expansion option. This procedure is shown Fig. 4.6 below. As can be seen in the figure, the moisture can be determined from the thermogram to two significant figure (1.5%) from the ordinate scale. However, by suppressing 98% of the original sample



4.4 A typical proximate analysis of coal by microcomputer controlled thermogravimetry.



4.5 TG proximate analysis of Greta seam bituminous coal.



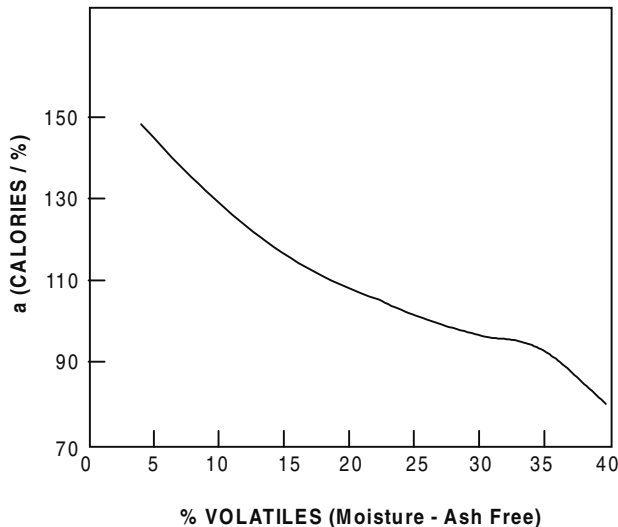
4.6 Determination of moisture by expanded ordinate TG.

weight by employing the weight suppression dial, one may expand the ordinate scale so that 2% weight loss represent the full 100 chart divisions of the ordinate axis. Thus as can be seen in above figures, moisture content of this coal may be determined to four significant figures (1.518%) on an “as received basis.” Since the heat of combustion of fossil fuels is primarily

the result of the oxidation of the volatile matter and fixed carbon, Goutal equation, as given below, can be used for calorific value determination of coal by TGA.

$$CV \text{ (cal/g)} = 82 C + aV$$

Where CV = calorific value (cal/g), C = % fixed carbon (moisture free basis), V = % volatile matter (moisture free basis), a = coefficient which varies with percent volatile matter (V) in the coal. Following table and graph (Fig. 4.7) shows the value of "a" as a function of volatile matter.



4.7 Goutal's coefficient "a" versus percentage volatiles (DAF).

Thus on completion of the proximate analysis of coal by thermogravimetry, the analyst should express the % volatile and % fixed carbon on a dry weight basis. This is easily done by multiplying the "as received" results by the factor $100/(100\% \text{ moisture})$. In order to select a value for the coefficient "a" from above figure, the % volatile matter should be calculated on a dry-ash-free basis by the equation

$$V' = (V/V+C) \times 100$$

Once the value of the coefficient "a" is obtained, the calorific value of the coal may be calculated in cal/g using Goutal equation mentioned above. This value may be converted to the more common units of Btu/lb by the equation.

$$CV/ \text{ (cal/g)} \times 1.80 \text{ Btu.g/cal.lb} = \text{Btu/lb}$$

Above calculations are shown by an actual calculation in following table.

	ASTM-values	TGA Results
% ash	7.51	7.38
% volatile	25.08	25.82
% fixed carbon	67.41	66.80
Calorific value (Btu/lb)	14,439	—

Calculations using ASTM-values:

- The volatile matter first be expressed on dry-ash-free basis by the equation: $V' = (V/V+C) \times 100 = (25.08 / 25.08 + 67.41) \times 100 = 27.12\%$
- This value of V' is employed to establish the value of “a” from Fig. 4.7. For $V' = 27.12\%$ $a = 100.3$
- Now the calculation of the calorific value may be made as follows:
 $P = 82 C + 100.3 V = 82 (67.41) + 100.3 (25.08) = 8043 \text{ cal/g} \times 1.80$
 $= 14,477 \text{ Btu/lb}$

Calculations using values of Elder (V' equation above):

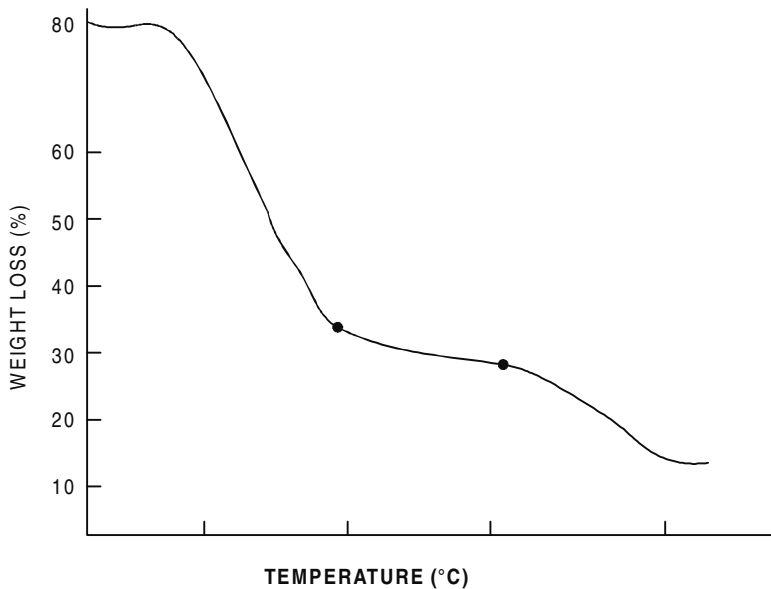
- daf basis, volatile matter is calculated as – $V' = V / (V + C) \times 100 = 25.82/(25.82 + 66.80) \times 100 = 27.88\%$
- From graph above (Fig. 4.13), value of “a” is – $a = 97.7 \text{ cal/\%}$ for $V'=27.88\%$
- Hence calorific value of CV is – $CV = 82 C + 99.7 V = 82 (66.80) + 99.7 (25.82) = 8052 \text{ cal/g}$ or $CV = (8052 \text{ cal/g}) \times (1.80 \text{ Btu.g/cal.lb}) = 14,494 \text{ Btu / lb}$

As one can see easily from above, both calculations give a calorific value which is in excellent agreement with that given in above table as ASTM-value in Btu/lb. The calculation above using the ASTM-values of total volatiles and fixed carbon differs only by 38 Btu/lb or 0.26% relative error. The value obtained from the TGA studies differ by 55 Btu/lb or 0.38%. Needless to say, this is in outstanding agreement. Obviously the method works best for coals having a daf volatile content between 5 and 35%, as can be deduced from the plot in Fig. 4.8. Provided that the analysis of the coal was accurately performed, the calculated calorific value will seldom vary more than 2% from the obtained data by bomb calorimeter. However, it should be noted here that the correlation chart for the assignment of the coefficient “a” should not be used for anthracite coals, coke, sub-bituminous coals, or lignites. Anthracitic coals and coke have low volatile content and high fixed carbon values. Obviously, in these cases the fixed carbon plays the predominant role in determining the calorific values. Thus the following modified equations were evolved for use:

$$CV \text{ (cal /g)} = 82 (V + c) \text{ for anthracitic coals}$$

CV (cal/g) = 82c (a = 0) for cokes.
 or CV (Btu/lb) = 147.6 c for cokes.

These equations found to give TGA results which are within 1% of that obtained from ASTM Bomb Calorimeter method. Similarly TGA can be applied to pitch for deriving many important result for its subsequent conversion to graphite through mesophase. Following diagram (Fig. 4.8) shows the TGA curve of pitch obtained by solvent extraction and treated thermally in nitrogen at 400°C. As can be seen in the diagram up to 200°C there is practically no loss in weight, indicating that the pitch is thermally stable even in air at temperature up to 200°C when subjected to heating at a rate of 10°C/min from an initial temperature of 40°C. There is gradual loss in weight when the temperature increased from 200 to about 450°C. The weight loss is about 60% indicating that most of the lower weight fractions present in the pitch have been removed as a result of interaction in the presence of oxygen. This also shows that this pitch cannot be used for binder or even for impregnation purpose in conditions where C₂ is present, even at temperature as low as 450°C. This is an important observation which clearly indicates that wherever a combination of higher temperature is desired the pitch may not behave as a pseudoplastic material. In the temperature range 450–650°C, there is practically no loss in weight probably because of the fact that coke formation has already been completed around 480°C and whatever the higher weight and fractions left over are not subjected to oxidation and there is no functional groups

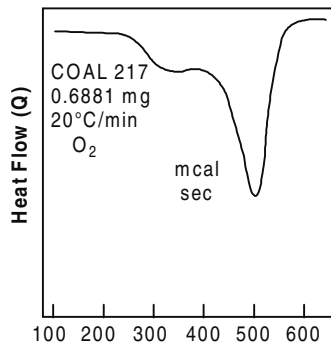


4.8 TGA curve for coal tar pitch.

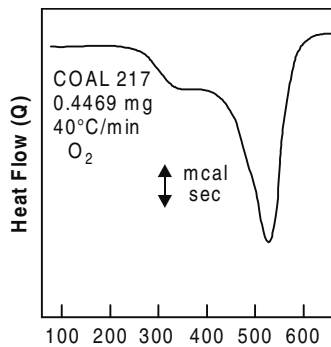
left in the pitch / coke residue. From 500–760°C there is substantial weight loss (accounting for about 40% of the initial weight). This is due to oxidation of coke to CO_2 which is a well known phenomenon. The entire amount of pitch is thus consumed at temperature around 680°C. The oxidation of pitch bonded composite material is an important use of the composite for application in electrodes and particularly in environments where it may not be possible to maintain inert atmosphere. These results thus have necessitated the use of surface coating of refractory material which does not impair the electrical properties of the composite electrode but gives a surface protection.

4.13 Differential scanning calorimetry

This apparatus in short known as DSC, measures heat flow as a function of programmed temperature. Thus it provides a rapid and continuous recording of sample activity. A typical thermogram generated by DSC is shown in following figures (Figs. 4.9 and 4.10). The two step decomposition is a characteristic of coal combustion. The first peak is

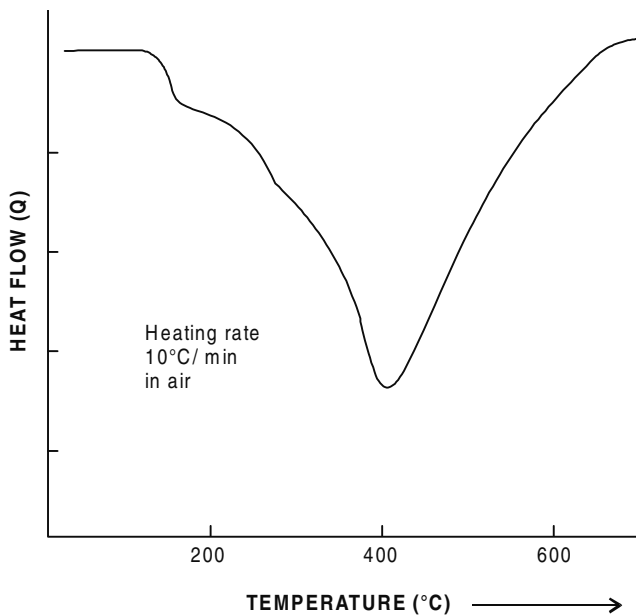


4.9 Typical DSC curve of coal (20% c/min).



4.10 Typical DSC curve of coal (40% c/min).

associated with the combustion of volatiles and the second with the combustion of fixed carbon. The total area under this curve is proportional to the heat of combustion. Moreover the ordinate displacement from an extrapolated base-line to the curve at any temperature is a measure of the reaction rate at that temperature. Thus DSC can also be used to measure the effect of catalyst on the rate of combustion of coal. Calorific value determined by DSC (20°C and 40°C per min heating rate) shown agreement within $\pm 3\%$ to ASTM values. It also shows excellent repeatability. Like TGA, DSC also been applied to coal tar pitch for deriving valuable information regarding its conversion to industrial compounds. Figure 4.11 shows the DSC curve of a solvent fractionated pitch at 400°C in nitrogen. The experiments were carried out in air in the temperature range 28°C to 550°C with heating rate of 10°C/min. The curve depicts temperature versus heat flow and it may be noted in above figure that there is a slight change in exothermal heat flow in the range 50–260°C which shows that there is no exothermic reaction. Some trend towards heat increase is observed in the temperature range 260–340°C. An abnormal curve shows that fast increasing trend from 260–380°C. This indicates that the particular temperature of 390°C may be best suitable for mesophase formation (a precursor to graphite formation). When mesophase formation first starts, the aggregation of lower and medium molecular weight components in the form of spherules takes place and this process is characterized by

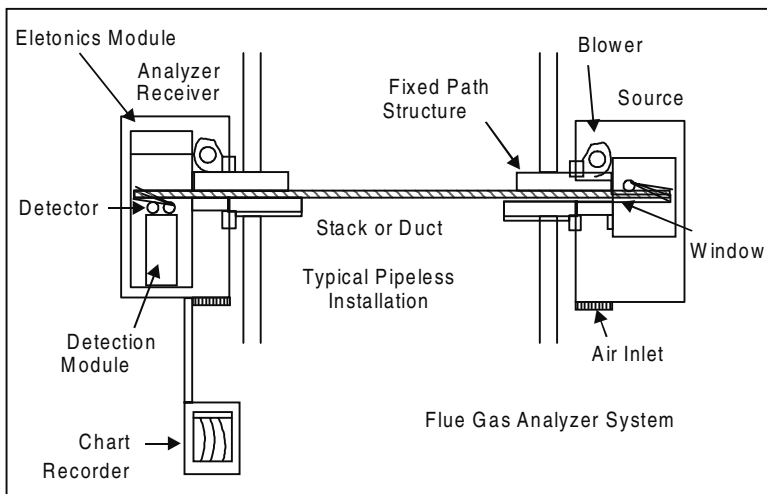


4.11 Typical DSC curve of a pitch fraction distilled at 400°C.

endothermicity. Above 390°C continuous exothermicity is observed which presumably due to oxidation of carbon and decomposition of pitch components.

4.14 Analysis of gaseous component

Combustion of coal gives rises to gases like CO_2 , CO , H_2S , SO_2 , NO_x , O_2 , etc. These gases are generally vented off to the atmosphere by tall chimneys and their concentrations monitored by automatic on-line stack gas analyzers. Particulate materials (e.g. inorganic oxides and unburnt carbon) also escape through these gases and quantitative estimation as well as their arrest is important from environmental regulation point of view. Basically there are two types of instruments used as stack gas analysis. The first type detects gases (e.g., NO_x , SO_2 , CO_2 , CO and H_2O) by spectrophotometric means. Absorption spectroscopy in UV (for NO_x and SO_2), infrared (for CO_2 , CO and H_2O) and visible range (for opacity or particulate concentration) is used. These instruments can be mounted on a stack, duct or other gas stream. A polychromatic beam of light from a source in an enclosure on one side, collimated and then passed through the gas, to an analyzer on the opposite side (see following Figure 4.11). Signals proportional to gas concentrations are transmitted from analyzer to recorder. In such instrument, the signal is insensitive to particulate level in the gas stream, dust on the windows, intensity degradation of source lamp, and sensitivity of the detector. Reductions in total light transmittance of greater than 80% can be tolerated without appreciable error. Most gases absorb energy in only certain spectral region. The analyzer isolates the

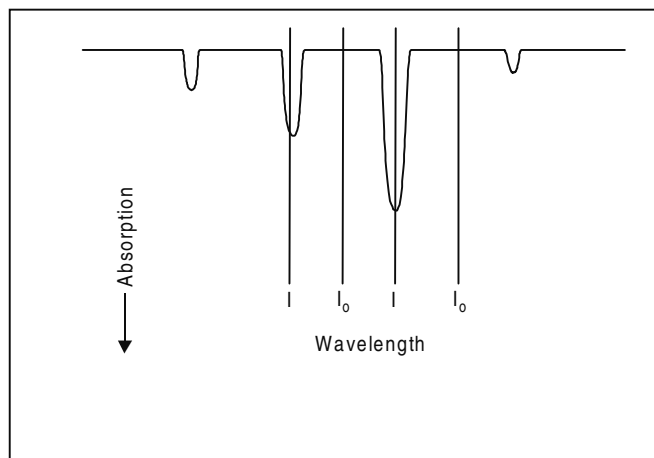


4.12 In-situ stack gas analysis system.

wavelength characteristic of the gas of interest and measures their individual intensities. Most gases approximately obey the Beer's law:

$$I = I_0 \cdot e^{-lC} \text{ or } \log I/I_0 = -lC$$

Therefore, concentration $C = (\log I/I_0)/l$, where l = absorption coefficient (known), as shown in above figure (Fig. 4.13), both the intensity at a specific region where the gas uniquely absorbs (I) and the intensity at an associated region where the gas is non-absorbing (I_0) are alternately measured with a single detector. This occurs 40 times a second. The "I" wavelength (s) are selected to be at absorption locations unique to the gas of interest. Any light level change, whether due to source decay, darkening of the window, scattering by particulates, water drop or aerosols in the gas stream, affects both I and I_0 equally, leaving the ratio unchanged. Thus the ratio of I and I_0 produces a reading that is free of interference, instrumental drift and gain effects. In the second type of instruments, the stack gas is sucked through a probe / filter system and diluted by air to a fixed ratio (called sample conditioner) and then the diluted gas goes to separate detectors where NO_x is determined by chemiluminescence, CO_2 by thermal detector, SO_2 by UV and CO by IR detectors. An in-situ solid electrolyte, sulfur-dioxide flue gas sensor is presently marketed. This device is claimed to be free of error which is likely to arise because of dirt in flue and determination of SO_2 by spectrophotometric method (UV or IR region). This in-situ method is also superior as it has no moving parts like light choppers, spinning gas cells, or power pressurization at the filter window as this is a spectrophotometric determination. Following figure shows one such assembly along with the solid-electrolyte sensor. These solid electrolyte sensors consist of stabilized zirconia (ZrO_2) for oxygen and



4.13 Sample high resolution gas spectrum.

potassium-sulfate for SO_2 . The K_2SO_4 -cell is composed of two half cells. The process side pellet and potassium electrode is exposed directly to the flue gas and is trapped between the end cap and the support tube. Holes at the end cap allow the flue gas to diffuse to the process pellet. The impervious barrier support tube provides the leak free barrier between process gas and reference gas. It also provides an ionic conduction path between two half cells. The second half cell is formed by the reference pellet with its platinum electrode. The voltage developed across the electrodes is the result of potassium-ion flow thru the half cell as well as impervious barrier support tube. Thus like zirconium sensor, the output of the potassium sulfate sensor follows a modified version of Nernst Equation which is as follows:

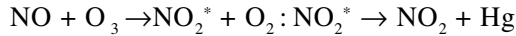
$$E = RT / 2F \ln (P''_{\text{SO}_2} / P'_{\text{SO}_2}) + \ln (P''_{\text{O}_2} / P'_{\text{O}_2}) + C$$

where, F = Faraday constant, R = gas constant, T = absolute temperature, P''_{SO_2} = partial pressure of SO_2 at sensing electrode, P''_{O_2} = partial pressure of O_2 at reference electrode, P'_{SO_2} = partial pressure of SO_2 at sensing electrode, P'_{O_2} = partial pressure of O_2 at sensing electrode, C = cell constant. Following above Nernst equation if the partial pressure of oxygen (P'_{O_2}) and the partial pressure of SO_2 (P''_{SO_2}) at the reference electrode portion of the sensing cell are held constant, the output of the K_2SO_4 -cell is a function of the partial pressure of oxygen and the partial pressure of SO_2 in the flue gas. Where the oxygen partial pressure is constant, such as in air, the probe output varies only with SO_2 partial pressure variation. But for stack gas analysis, the oxygen partial pressure must be considered. The oxygen partial pressure in the flue gas can be measured by a ZrO_2 excess oxygen sensor. The E_1 output from the K_2SO_4 cell and an E_2 output from ZrO_2 cell produce an E_3 output voltage as follows:

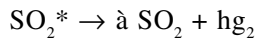
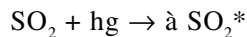
$$E_3 = E_1 - 2E_2$$

Thus, the voltage E_3 is converted to a 4–20 mA signal representing the SO_2 flue gas content. These calculations are best accomplished via digital, microprocessor based electronics when other functions such as automatic calibration of the analyzer and computations of pounds of SO_2 per million Btu of fuel burned, are required. A solid electrolyte operating at high temperature, is capable of outputting voltage that is inversely proportional to the logarithm of the oxygen present in the combustion flue gas. The logarithmic output of the analyzer provides a major advantage since the accuracy of the measuring cell can be defined as a percent of reading rather than a percent of full scale. Since the cell operates at high temperatures, it has an additional advantage that it can survive the flue gas attack temperature environment avoiding fouling condensation common in sampling flue gas. The NO/NO_x analyzer based on

“chemiluminescence” principle, operates on following reaction mechanism.



The hg in the second step above, is being detected by photomultiplier tube. This operation is based on two functional modes – in the NO mode only NO concentration is detected through the conversion of NO₂ an subsequent emission of radiation and in NO_x⁻ mode the sample is passed through a NO_x⁻ NO converter where all NO_x (NO_x = NO + NO₂) is converted to NO. In other words, in this latter mode the instrument responds to total oxides of nitrogen. The difference between the NO and NO_x mode is the amount of NO₂ in the sample, since NO₂ is usually the only higher oxides of nitrogen found at the pollution source. The light signal given-off by the excited NO₂ delay, passes through an optical filter to a photomultiplier. The optical filters serve to limit the spectral region viewed by the detector, thus eliminating possible interference due to other chemiluminescent reaction. The response is linear and fast (1.5 s for NO mode and 1.7 s for NO_x mode). The ozone is produced internally from dry air entering through the oxygen regulator and high voltage ozone generator. The CO-analyzer is generally based on gas filter correlation analysis system (US Patent RFCA to Thermo-Environmental Instruments Inc) where a rotating filter wheel contains two gas cells – one filled with N₂ and the other high concentration of CO. When the optical beam passes through the CO-cell on the filter wheel all the light energy of the individual absorption light is removed and CO in the sample chamber does not alternate energy. The beam therefore generates a reference signal. Alternatively, when the optical beam passes through the N₂ cell of the filter wheel it does not absorb energy at the CO-absorption line but CO in the sample cell does attenuate energy. The beam now generates a measured signal. The net difference between the reference and the measured energies is proportional to the amount of CO in the sample. The “Pulsed Fluorescence SO₂ Analyzer” measures SO₂ concentration in the flue gas based on following principle (note here that, SO₂ is also measured by IR-spectrometry principle). The reaction involved in such case is:



The absorption takes place in the region 230 nm to 190 nm, where it is free from quenching effect by air or most other molecules that occur in air. To stimulate the characteristic fluorescence, the pulsed technique permits the use of a small source of light with a life time in excess of 10,000 h. Continuous source of UV-energy will consume large power supply and results in substantial degradation and failure after only a few

100 h of operation. Pulsating UV-light is focused through a band pass filter into a fluorescent chamber. Here it excites the SO_2 molecule which gives off this characteristic decay radiation. A second filter allows only this radiation to fall on a sensitive photo-multiplier tube for proper detection and output of which is directly proportional to the concentration of SO_2 . Besides liquid chromatography, gas chromatography is also used for detecting low boiling components of coal derivatives. Interested readers may consult references 50–55 in this regard for further information on the subject.

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5.1 Introduction

When we say ‘cleaning of coal’ we mean cleaning of coal from extraneous inorganic materials or from harmful elements like sulfur which otherwise will pollute air during combustion and other coal conversion processes. Removing sulfur from coal can be effected either by chemical method, by mechanical means, or by bacterial leaching. If we bypass these cleaning processes, sulfur must be scrubbed out from the flue gas. We discuss all these process in terms of their technical and economical feasibility, but first let us discuss cleaning of coal from inorganic matters by general washability method.

5.2 Float-sink and washability tests

Wet cleaning processes take advantage of the relatively large differences in particle density between pure coal and dirt associated with it. Very clean bituminous coal has a specific gravity of approximately 1.3, very pure anthracite 1.6, shales usually have values around 2.4 and iron pyrites 5. The behavior of raw coal in a wet washer can be predicted from laboratory simulation tests known as float and sink test and washability test. A sample of the coal to be cleaned is immersed in a liquid of specific gravity 1.6 which may be either CCl_4 or an aqueous solution of CaCl_2 . Dirt will sink and can be removed and weighed. The material which floats at specific gravity of 1.6 is treated in a bath of liquid of a lower specific gravity, 1.5 for example, when a further portion will sink and can be recovered and weighed. The progress is repeated until the original raw coal has been resolved into fractions of different specific gravity and hence of different ash content. The yields of sink at each specific gravity stage are plotted as a graph against specific-gravity. The ash contents of the floats or the sinks (or both) at each specific gravity stage are also plotted against specific gravity or against yield. In this simple way the graphs show for any desired specific gravity the yields of clean coal (floats) and of dirt (sinks) and their ash contents. Such graphs are known as washability curve.

Petrographic compositions also affect specific-gravity and hence its knowledge helps us in predicting the effectiveness of washing such coals. With decreasing particle size, the practical feasibility of gravity separation diminishes because the efficiency of separation drops-off. Particularly in low volatile coals, a substantial portion of the coal may be lost in these fines if other means are not applied for separating them from slimes (clay matter) and recovering them.

Froth Floatation Technique is used for this purpose. This involves bubbling air through a suspension of fine coal and water to which various chemical agents have been added to improve the process. Surface properties greatly influence floatability of fine coals and the separation occurs due to preferential physical attachment of air bubbles to the coal. The coal particles float to the top and are removed. Selected silicones have been found to perform better than kerosene when used as collector in the cleaning of fine coal by froth floatation. The main action of the silicone is to get adsorbed on the coal grains and render their surfaces more hydrophobic. Agglomeration of low rank coals and coal fines using oil agglomeration technique has been developed by CFRI, Dhanbad. Floatation cell in this case uses 20% kerosene and 80% furnace oil as optimum mixture. The oil can be recovered and used again. Consumption of oil in this technique could be reduced to 25% when some additives are used in the deoiler bath which recovers oil by heat treatment. The impact of the oil agglomeration is a significant decrease in moisture content, an increase in heating value, a small decrease in ash content and almost 100% recovery of coal and bridging liquid and a decrease in moisture capacity of coal. Cost calculation under Indian conditions show that to bring the ash level of coal from 23% to 17% by above physical method, causes the cost of coal go up by 2.5 times. With higher ash coals, the cost could go up by about 4 times. This necessitates finding alternate route which will be more efficient, relatively more simple and economical. Selective crushing to various sizes and proper blending, chemical combination and beneficiation, and oil agglomeration technique have shown the possibility of beneficiation, but not found to be economically viable. However, the impact of the study on the petrographic constituents and corresponding selective crushing may perhaps make this technique useful in the petrographic beneficiation of coal, for use as high quality blend in coke making. Dry beneficiation techniques, such as heavy media cyclone separation (using sand or magnetite in water), microwave treatment and selective crushing, density separation in hydroclones, may perhaps, one day prove to be a viable solution in commercial scale. On comparative basis, technology of dry cleaning of coal is more attractive as compared to wet method, simply because of the advantages of dry handling of coal and retention of higher calorific value. Air dense media in fluidized bed separator is one such technique adopted for dry beneficiation of coal.

5.1 Summary of major chemical coal cleaning process (with approx cost)

Process and company	Method	Type of S Removed	Problems	Annual operating cost (raw coal cost \$25/ton) (Including raw coal cost)
'MAGNEX', Hazen Research Inc, Golden, Colorado (USA)	Dry pulverized coal treated with Fe(CO) causes pyretic sulphur to become magnetic material and removed magnetically	Upto 90% pyretic	Disposal of S-coaining solid residue, continuous recycle of CO to produce Fe(CO)s requires demonstration	40.7
'SYRACUSE', Syracuse Research Corporation, NY, USA	Coal is commuted by exposure to NH ₃ vapour. Conventional physical cleaning separates coal / ash	50–70% pyretic	Disposal of sulphur containing residue	37
'MEYORS', TRW Inc., Redondo Beach, CA, USA	Oxidative leaching using Fe ₂ (SO ₄) ₃ plus oxygen pyretic from water	90–95% pyretic	Disposal of acidic FeSO ₄ and CaSO ₄ . Sulphur extraction step requires some demonstration	43.4
'LOL', Kennecott-Copper Co, Ledgemont, MA, USA	Oxidative leaching using O ₂ and water at moderate temperature and pressure	90–95% pyretic	Disposal of gypsum sludge; acid corrosion of reaction	46.9
'REDA' (PERC), Bruceton, PA, USA	Air oxidation and water leaching at high pressure and temperature	About 95% pyretic and up to 40% org.	Gypsum sludge disposal; acid corrosion at high temperature	51.6
'GE PROCESS', General Electric Co, Valley Forge, PA, USA	Microwave treatment of coal permeated with NaOH solution forming soluble S ²⁻ .	75% of total sulphur	Process condition not established; Caustic regeneration process not established.	41.8

It utilizes the key factor such as density difference between heavy inorganic and organic carbon to affect the separation process. Trial at RRL-Bhubaneswar (report no. T/MPT/436 dated October 2003) with Talcher (Orissa) coal indicate a drop in ash content from 40% to 30% with about 60% yield using this technique. In such pneumatic dense media separator (which is considered the most cost effective route to beneficiate high ash coal), the dense medium is created by suspending solid particles in an upward flow in a vertical straight column. This causes the clean coal to float at the top which is continually being scooped out, and sinking of the heavy density ash at the bottom of the separator. Archimedes principle although applicable to some extent in these dense separators, but dynamic condition existing inside the separator warrant consideration of other factors such as frictional force operating between the particles and the up going fluidization air, the drag force, association of small particles forming large clusters and consequent change in dynamic properties, etc. These factors in-turn specifies fractional void in the bed, mean harmonic size of the particles, effective density of the bed, etc., which are essential to define fluidization parameters and characterize the bed (see Chapter 6 for more details on fluidization engineering relevant to the present subject).

5.3 Chemical coal cleaning

In this section we learn the techniques of removing inorganic materials by chemical treatment and then removal of sulfur by both physical and chemical methods. Demineralization of coal with chemicals, remove inherent mineral matter that is inaccessible by physical methods. Results have shown that ash levels can be brought down by this method to as low as 0.5% (dry basis). The hot alkaline treatment of coal results in the conversion of clay minerals to various sodium-dydroaluminosilicate and simultaneous extraction of quartz. Hematite was found to be the solid conversion product of the pyrite. Extraction of the alkali leached coals with hydrochloric acid, removes hematite, calcite and various sodium-hydroaluminosilicates. Mineral matter remaining after the combined treatment consisted mainly unreacted pyrite, illite and amorphous silica. The other important element needs to be taken out of coal before its use is sulfur. As mentioned earlier, North-Eastern coals of India contains high amount of organic sulfur (not the other inorganic variety like pyrite or marcasite or elemental sulfur form). Occurrence of different varieties of sulfur in coal can be classified as follows:

- (a) Epigeneric – mostly coarse crystallites, above 50 micro-meter size.
- (b) Syngenetic – fine crystallites with sizes 5 to 50 micro-meters.
- (c) Finely intergrown and ultrafine pyrites – crystallites smaller than 5 micro-meters in size.

Inorganic sulfurs include sulfates and sulfides, as well as sometimes elemental sulfur. Inorganic sulfurs can be separated either by density (float-sink method) or by surface properties mentioned earlier, or by magnetic separation technique. The success of the magnetic separation method depends on the size distribution and again crushing of coal to desired size adds to the total cost of coal cleaning. Potential methods for removal of organic sulfur from coal have been classified into six groups, these are solvent partition, thermal decomposition, acid-base reaction, reduction, oxidation and displacement. These mechanisms all have the common feature of being potentially capable of removing organic sulfur content of coal as small soluble or volatile molecules. Following are the general representation of these processes:

- (a) Solvent partition – $R_1.S.R_2 + x \rightarrow R_1.R_2S_x.X^-$
 (b) Thermal decomposition – $R_1.S.R_2 \rightarrow R_1.R_2 + S$
 $R.CH_2.CH_2.SH \rightarrow RCH=CH_2.H_2S$
 (c) Acid-base neutralization – $RSH + OH \rightarrow RS^- + H_2O$.
 (d) Reduction – $R_1.S.R_2 + 4H \rightarrow R_1H + R_2H + H_2S$
 (e) Oxidation – $R_1.S.R_2 + 2R_3.H_2 \rightarrow R_1H + R_2H + H_2S + 2R_3$
 $R_1.S.R_2 + R_1SO_3H + R_2SO_3H \rightarrow R_1OH + R_2OH + 2H_2SO_4$
 (f) Nucleophilic displacement – $R_1.S.R_2 + Nu \rightarrow R_1.S.Nu + R_2$
 $R_1.S_n.R_2 + Nu \rightarrow R_1.S_{n-1}.Nu + R_2S^-$
 $R_1.S.R_2 + Nu \rightarrow R_1.S^- + R_2Nu$
 $R_2.S^- + R_1S_{n-1}Nu \rightarrow R_1S_{n-1}R_2 + Nu$

Low ash coals can be separated from sulfur of the bulk coal by Gravi-float method where a solution of coal in iron sulfate (sp.gr 1.3–1.4) is float-sink separated and washed with water. 3–4% ash coal is thus washed from a 12% ash sample. Organic sulfur to the extent 77% have been found to be removed. In Gravi-Melt Process where the coal is fused with molten alkali, results in 100% removal of inorganic sulfur and up to 80% removal of organic sulfur. But the progress completely destroys caking property of the coal. Author of this book have experimented with a new technique for desulfurization where along with 100% removal of sulfur in a very short time and also retains 60% of its caking property. The process involves treating the coal with an organometallic compound (sodium salt) and since caking property of the coal is related to the hydroaromatic and aliphatic chains, substitution of such group with the organometallic compound helps in retain the caking property while sodium effectively removes all sulfur in a short time. Mild hydrogenation also removes organic sulfur to the extent 30–60% are oxidation with hydrogen-peroxide, hydrothermal treatment of coal with sodium-hydroxide, chlorinolysis followed by hydrolysis, etc. Table 5.1 shows some of the results of desulfurization by

these processes. It should be noted here that thiophenic-sulfur is the most difficult organic sulfur to take out. Most organic sulfur removal involves breaking carbon-hydrogen skeleton either in aromatic, hydroaromatic or aliphatic structure and thus all these chemical desulfurization process makes the coal pulverulent. The processes are costly and as a result no chemical cleaning process till this date has been commercially viable.

5.4 Economics of coal cleaning

As mentioned earlier if coal is not cleaned from sulfur prior to its use, we need to take care of it through flue gas desulfurization. Stack gas scrubbing is reported capable of removing in excess of 5% SO₂ in the flue. Chemical coal cleaning, on the other hand, removes varying amount of sulfur, depending on the coal and the leaching variant, but seldom resolves removal of more than 70% sulfur removal. SO₂ scrubber, which is appropriate at a full scale power plant, will require design and thus highly capital intensive. Because the fixed charges must be distributed over the actual kWh generated, the cost of scrubbing in mills per kWh will be high for plants with low load factor. Coal cleaning, on the other hand, is coupled from boiler operation and thus cost of coal cleaning in mills per kWh is independent of load factor. Coal cleaning costs, within the most common load factor range, should clearly be comparable to scrubbing costs. It may be noted that approximately 74% of all 1976 US coal fired utility fall within the 35–65% load factor range, approx 56% of US capacity fall within the 40–60% load factor range. Chemical coal cleaning has the potential of constituting, in many cases, an economically viable alternative to stack gas scrubbing and the purpose of low sulfur coal. The greater the hydrophobicity of coal surface, greater is the response to floatation and separation from mineral matter because the latter is largely hydrophilic. The rate constant (thru kinetic study of coal cleaning by floatation technique) were found to correlate well with the atomic O/C ration of coal. This is of course, expected because atomic O/C ratios are indicative of presence or absence of oxygen groups in coal, which in turn, indicate the lyophobic or lyophilic character of coal surface. It is obvious that higher is the O/C ratio, higher will be lyophilic character of coal surface and hence lesser would be amenability of such coal to floatation. Petrographic analysis show that in case of low rank coal floatability varies as follows – Inertinite > Vitrinite > Exinite > Fusinite > Micrinite. Whereas the order in case of medium and high rank coal is – Vitrinite > Inertinite > Exinite > Micrinite > Fusinite. Higher efficiency in floatation method using silicones (e.g., methyl-isobutyl-carbinol) is due to the fact that it is absorbed on the coaly grains and thus renders their surface more hydrophobic. Alkali treatment (such as Na₂CO₃ and NaOH) at 250–350°C brings about full

decomposition coal mineral such as kaolinite and elimination but not so with pyrite or the illite. Further some silica which goes into solution as silicates gets precipitated as amorphous silica on sudden cooling after alkali treatment. Calorific value is not a primary control function in coal cleaning. It has an approximately linear relationship to ash and moisture content. But after gross rock dilution in a raw coal has been removed, the yield in terms of thermal efficiency of recovery with ash content becomes non-linear and an increasing penalty in thermal recovery for unit decrease in ash content becomes the rule. It has been observed that, for all levels, capital charges account for the more than 50% of the total costs of preparation. As a general rule of thumb, a decision to proceed with cleaning depends on (discounted coal flow vs. return on investment) of at least 15% per year and more commonly 20% per annum.

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6.1 Introduction

In this section we will learn different ways of coal utilization adopting various coal conversion techniques. As we will see soon, one thing common to all these conversion processes is to derive calorific value of the coal for combustion or conversion to value added products like chemicals or gases. A recent development in this conversion process have been direct conversion of these hydrocarbons to useful electrical energy through a device called “fuel cell.”

6.2 Coal combustion

Combustion of coal in air is one of the most important coal conversion/ utilization process widely used in our day to day life. In this process the heat released during reaction of carbon with oxygen (exothermic) is utilized to raise steam either for process application or for power generation. This combination of carbon and oxygen may sometime be spontaneous and this give rise to mine fire. This aspect of spontaneous combustion is an important issue and we will discuss this first along with measurement of spontaneous combustibility of a coal and prevention, before we go to conventional commercial methods of coal combustion/utilization.

Spontaneous combustion – The oxidation which occurs in a stockpile is not related to laboratory oxidation which occurs at temperatures higher than those found in the stockpile coals. This difference could be due to the temperature dependence of competing reaction pathways or due to the temperature dependence of a particular reaction change. Observation of spontaneous stockpile fires, show that dehydration reaction occurs first resulting in the disintegration of lumps, followed by release of steam from inside the stockpile. The passage of steam and airflow causes oxidation hydrolysis and hydration reaction inside the stockpile causing increase in the temperature from the heat of reaction, leading to partial distillation of low temperature combustible gases such as methane and ethane. The

oxidation of coals were studied using gas-desorption, acidity measurement, PAS-FTIR (Foto Acoustic Fourier Transformation Infrared) and NMR-spectroscopy. Relaxation time obtained from the C13-NMR spectra of stockpiled coal indicates a loss of molecular mobility in the oxidized sample, consistent with the formation of cross-links. These multi-technique approaches have shown that anhydrides are the early and significant oxidation product and marks one pathway of oxidative attack. Oxidation occurs through and radical-mechanism, leading to the emission of hydrocarbon gases and formation of anhydrides and carbonyl functionalities. A model which considers simultaneous measurement of oxygen concentration and heat evolution has shown that such results from calculation and conclusions can give a better insight into the various mechanism of oxidation. Besides theoretical modeling practical measurement also proves the cause. When exposed to air, all coals absorb oxygen even at room temperature and release heat. The decomposition of metal-coal-oxygen complex is thought to give rise to this exothermicity and moisture plays a vital role in this process. Besides coal particle size, rank, temperature, moisture and humidity, petrographic constituents also play a vital role in spontaneous heating of coal. The case of oxidation of different petrographic constituents follow the following order – Vitrain > Clarain > Fusain > Durain. Therefore, the coking coal having more of vitrain and clarain are more prone to oxidation compared to non-caking coals. Further the ash content increases from vitrain to fusain, which decreases susceptibility and thus explains above observation. However, if ash contains pyrites, increase in ash content may increase susceptibility to spontaneous combustion up to a certain limit. In addition, silica also found to have catalytic effect on spontaneous combustion. The heat generated during oxidation of pyrite to FeSO_4 and consequent swelling leads to the crushing of coal matrix and increases surface area which later helps in spontaneous oxidation. The main function of the inhibitor used for spontaneous oxidation is to form a layer on the pore surface and thereby preventing oxidation to take place. Generally boron-compounds are considered good inhibitors (10% solid ammonium-hydrogen tetraborate). Calcium-chloride is also a good inhibitor and 10% CaCl_2 is approximately equivalent to 5% ammonium-hydrogen-tetraborate. It is good inhibitor below 150°C. Certain compounds like “Moutan Powder,” containing both an inhibitor and a surface active agent are giving an effective performance up to 200°C. Other inhibitors tried are NaCl, calcium-bicarbonate, and calcium carbonate in water. Air drying of brown coal is also found to decrease its reactivity towards oxygen and hence reduces the auto-oxidation tendency. It is observed that a careful “free swelling index” determination provides a rapid and reliable assessment of the weathering status of high

volatile bituminous coals and sub-bituminous coals. Low-rank sub-bituminous coals and lignite, which contain 20–60% of inherent moisture, are often highly susceptible to spontaneous ignition. This moisture plays a vital role in these spontaneous ignition processes. Coating of a coal derived tar on the surface of the carbonized coal reduces the oxidation rate by reducing oxygen in volatile-matter released by carbonization and plugging of the coal pores by the tar coating. The assessment and chemical inhibition of self-heating in coal using a calorimeter which measures the total heat generated by coal under controlled oxidation condition, show that chemical surfactants such as emulsified oil can inhibit the oxidation reaction. Under stockpile conditions, the range of heating rates for safe coal, treated and untreated coals have been found to be 0.20–0.25, 0.88–1.30 and 0.46–0.56°C/day respectively. Spraying of stockpile with inhibitors like lime + Na_2SiO_3 (0.1–0.2%) also prevents self-ignition. It is interesting to note that the treated coals were observed to stop heating once the stockpile temperature reached approx 60°C. Above (Na_2SiO_3 + lime) mixture is suggested to be sprayed at the periphery up to 1 m height and depth of stockpile with compaction, would help in storage of coal for a reasonable period of time. Studies on spontaneous combustion results in determination of risk factor index of various coals towards self ignition. Factors which have significant effect on self-ignition of coal are:

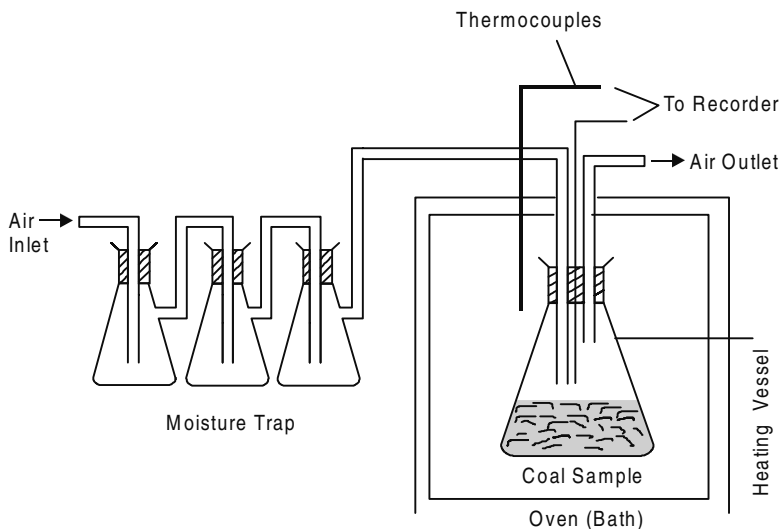
- (a) Pyrite content may accelerate the spontaneous combustion process.
- (b) Changes in moisture content i.e., drying or wetting of coal have anapparent effect in the process.
- (c) As the particle size diminishes and exposed surface area increases, the tendency of coal toward spontaneous combustion increases.
- (d) It is widely recognized that low rank coals are more susceptible to spontaneous combustion that higher rank coals. The abnormalities in this relationship may be attributed to the petrographic constituents of coal. However, this phenomenon has not yet been fully understood and requires further study.
- (e) Ash content, generally diminish the liability of coal to spontaneous heating. Certain parts of the ash such as lime, soda and iron compounds may have an accelerating effect, while others such as alumina and silica produce a retarding effect. Oil shale bands adjoining the coal, play an important role in mine fire.
- (f) Temperature of underground atmosphere is a direct factor.
- (g) Presence of faults and zone of weakness around faults may contribute to the process by allowing air leakage into the coal mass.
- (h) Mining methods with partial extraction in which part of the coal seam is being left in the goaf and pillars, can contribute to the potential for spontaneous combustion.

- (i) Air flow rate is a complex factor. Because an air supply provides oxygen while it carries away the heat produced. There is a critical air quantity which allows the coal to oxidize and also allows the generated heat to accumulate. Therefore it favors the process.
- (j) High ventilation differentials and changes in ventilation system also affect development of the spontaneous combustion process. Many laboratory test methods have been described to determine these risk-indices of self ignition. Some of them are as follows: (a) Static isothermal method (b) Chemical method (c) Adiabatic oxidation method (d) Dynamic oxidation method (e) Crossing point temperature method.

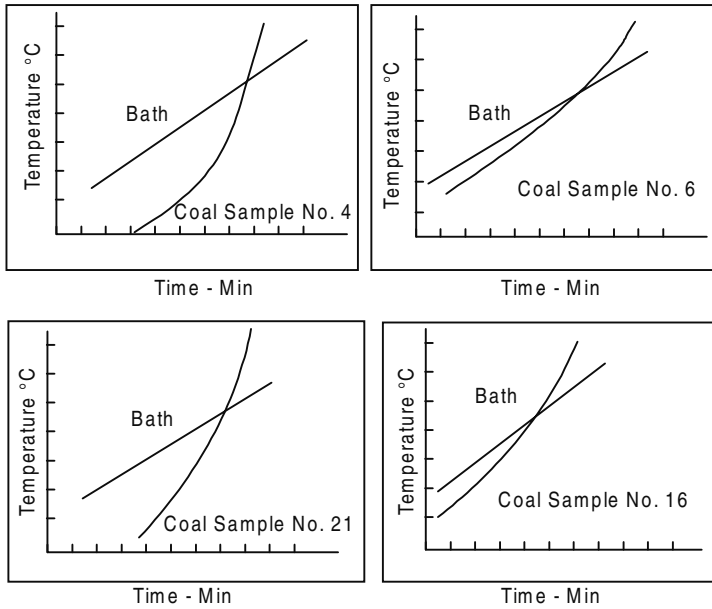
Of all above methods, the last one seems most practical and widely used procedure. "Crossing point Temperature" is the temperature at which self-ignition of the coal takes place. Figure 6.1 shows such an apparatus schematically, and Figure 6.2 depicts a set of typical curves obtained in crossing point test with this apparatus. In such an apparatus, heating rate is varied between 0.8 and $0.9^{\circ}\text{C}/\text{min}$. In between self-oxidation (just described above) and free burning (oxidation) of coal here exists a process for controlled oxidation of coal. This controlled oxidation of coal gives rise to various important products like fertilizer, special plastic precursors etc. This methodology is explained below.

6.2.1 Controlled oxidation of coal

Coal can be oxidized by oxidative chemical reagents. In course of nitric-



6.1 Laboratory set-up for crossing point temperature tests.



6.2 Typical curves of crossing point temperature tests.

acid oxidation (refer pioneering works done at CFRI, Dhanbad, India), irrespective of its rank, coal passes through an intermediate product called nitro-humic acid prior to its conversion into water soluble aromatic acids. Nitro-humic acid thus formed could be extracted with acetone. Substitution reaction, such as sulphonation followed by phosphonation could fix more phosphorous in coal and 3–4% phosphorus, 3–4% nitrogen, and 2–2.5% potassium can be fixed in the coal depending on its rank. Multipurpose nitrogenous organic fertilizer thus can be obtained from coal. Field trials have proved that coal acids are more effective in nitrogen utilization than urea. Process mentioned above is the two stage conversion (coal to nitro-humic acid and nitro-humic acid to water soluble polycarboxylic acid), but this can also be affected in single step provided the optimum concentration of HNO_3 in the reaction vessel is maintained throughout the reaction period. It has been found that 40% of the nitric acid is consumed in oxidation for the non-aromatic part of coal structure without producing any tangible amount of coal acids in the first stage of the reaction. If the hydroaromatic structure of coal is preoxidized by air/oxygen, then about 40% of total requirement of HNO_3 in the first stage of the reaction could be effectively cut down. This oxidation step can be carried out in a fluidized column. Similarly oxidation of aromatic carbon matrix in processed coal (or anthracite) generates mellitic acid (benzene hexa-carboxylic acid) which is important compound for metal casting, as a fire extinguisher,

smoke screen, etc. The hexa basic acid derives its name from the occurrence of aluminium salt ($\text{Al}_2\text{C}_{12}\text{O}_{12} \cdot 18\text{H}_2\text{O}$) as the mineral mellite (honey-stone) found in brown coal. Mellitic acid has melting point 288°C in sealed tube and the hexamethyl ester having melting point 188°C . Sealed tube mellitic acid yields a stable trianhydride that sublimes when heated at 200°C at 3–4 mm pressure. Acid dissociation constants of mellitic acid are $\text{pK}_1 = 1.40$, $\text{pK}_2 = 2.19$, $\text{pK}_3 = 3.3$, $\text{pK}_4 = 4.8$, $\text{pK}_5 = 5.89$ and $\text{pK}_6 = 6.96$. Further controlled oxidation of the benzene ring gives rise to pyromellitic acid (structure shown below) which is an important precursor for special grade high class plastic like polymer and have great industrial demand. Japan has the monopoly of supplying this compound to all industries round the world and most probably they synthesize it from petroleum derivation.

6.2.2 Combustion of coal for power generation

Oxidation phenomenon of coal with gradual rise in temperature has been studied extensively. These results have been important in drying coal which sometime give rise to fire without our proper knowledge of the oxidation phenomenon. Solar drying of coal has been found one of the best methods preventing fire and taking out moisture at about 50°C . The chemical reactions that occur with predried coal at 100°C with oxygen have been studied by in-situ FT-IR. Spectroscopic study shows that vacuum drying at 100°C resulted in the decomposition of carboxylic-acid species to form a variety of new carbonyl species and decarboxylated or decarbonylated coal. Oxidation of predried coal at this temperature range leads to formation of new carbonyl species. Thus the assumption that drying does not either the chemical composition of coal is not correct. Overall chemical changes at this moderate temperature zone in presence of O_2 or air depends upon sample pretreatment, drying and storage. The principal spectroscopic changes indicate significant changes to the carboxylic acid species present. The spectroscopic changes were observed in the IR-band of 1000 to 1800 wave-number. It has been found that change in carbonyl stretching intensity is an accurate determinant of oxidation only if the coal has been thermally pretreated prior to oxidation. Increase in broad intensity at 1670 (and 1020 cm^{-1} for other) indicates wide variety of carbonyl species formed. Based on these studies, if drying time is determined for powdered coal in the laboratory, the time necessary to dry a bulk sample is approximately equal to the gaseous diffusion time through the coal. Drying time 1000 times longer than those used with thin section laboratory sample (about 3 h) might be required to achieve complete drying of powdered sample. Such an increase in scale implies that several months drying time is needed in all but the most finely ground coal. Thus it is likely that some thermal-chemical change will occur along with bulk drying at moderate temperature.

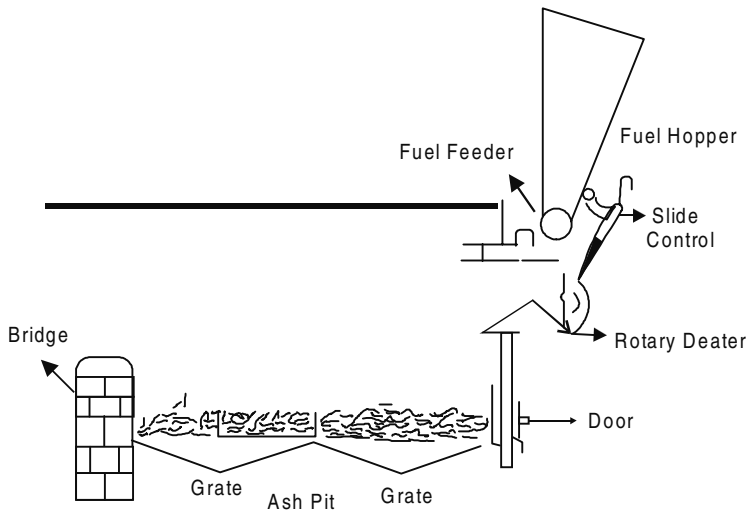
These reactions are mainly reaction of carboxylic acids to form other carbonyl containing species such as ketones, aldehydes, and/or esters. The carboxylic acids are most probably aliphatic since most of the spectroscopic changes observed in the CH bending mode region occurring at frequencies attributable to aliphatic (1540 cm^{-1}) rather than aromatic (1600 cm^{-1}) species. Additionally the lack of an intense absorption less in the 1290 cm^{-1} region indicates that, unlike the carbonyls, the carbonyls are not dimerized. The carbonyl absorption band occurs at about 1700 cm^{-1} . The most probable oxidation products of carbonyl are ketones, aldehydes, esters and others. A hydroperoxide reaction pathway is the principal mechanism for oxidation of coal at moderate temperature. It may be noted here that North Eastern coals of India, becomes very much friable on storage and catches fire due to weathering. Next comes, high temperature oxidation of coal a phenomenon found inside high temperature furnaces, and also in the form of fine powders oxidation using pulverized fuel (PF) burner. Pulverized fuel, in the form of fine particles dispersed in primary air, is supplied through a burner, secondary air is being provided under pressure around the burner in a way which ensures turbulent mixing. Until recently, the main mode of burning coal at high temperature for power generation and steam raising through a boiler was the use of stoker furnace. There are various different designs of stokers in existence and selection that are done primarily with the consideration of following capacity ranges:

- (a) Hand firing grate (up to 5 t/h capacity).
- (b) Vibrating feeder furnace (up to 10 t/h capacity).
- (c) Travelling grate stoker furnace (up to 75 t/h capacity).
- (d) Spreader stoker (up to 150 t/h capacity).
- (e) Pulverized fuel burners (for large capacity utility boilers).

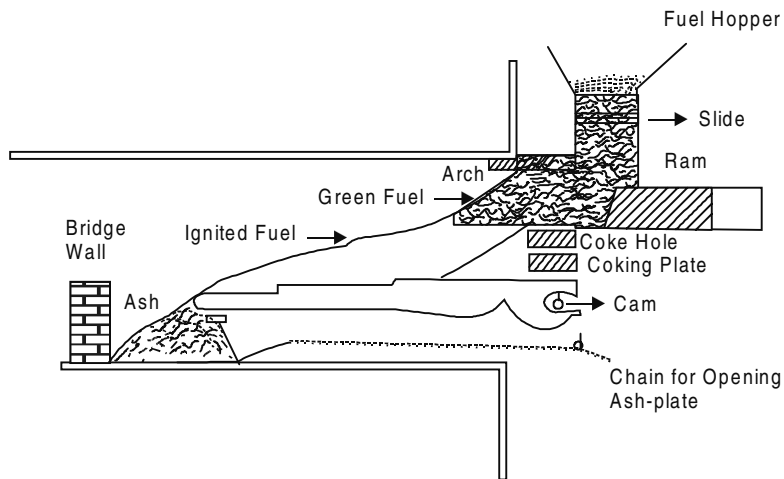
These different types of stokers are discussed in some detail below.

1. *Sprinkler type stoker* – Sprinkler stoker are rarely used now a days since their popularity has declined because of the tendency of such stoker to cause grit and smoke emission. As the name implies the stoker imitates the sprinkling method of hand firing. The sprinkler stoker operates with natural or forced draught, responds quickly to steam demand, and has an easily controlled rate of fuel feed and distribution, but when the boiler is shut down quickly and later restarted, smoke and grit emission are difficult to avoid. Burning rates up to $195\text{ kg/m}^2\text{h}$ are possible but grit emission is serious above $145\text{ kg/m}^2\text{h}$. Fire should be 70–100 mm thick. (see Fig. 6.3)

2. *Ram type coking stoker* – This stoker (see Fig. 6.4) imitates the coking method by hand firing. There are several different types but in each one the fuel is fed from an overhead hopper to the front of a reciprocating piston or ram. The ram pushes the fuel on to a coking plate where it ignites and finally is moved towards the ash discharge and through reciprocating



6.3 Rotary type sprinkler stoker.



6.4 Ram type coking stoker.

action of the fire bars. Volatile matter released early in the travel of the fresh fuel is ignited and burned without smoke as it passes over the incandescent fuel at the back of the grate. The length and frequency of the ram stoke can be altered to vary the amount of fuel fed to the furnace. The main advantages of coking stoker are:

- (a) It can burn a wide range of coal, except those having high caking quality.
- (b) It needs little attention apart from infrequent slicing of the fuel bed.
- (c) If care is taken with the air supply and the fuel bed left undisturbed,

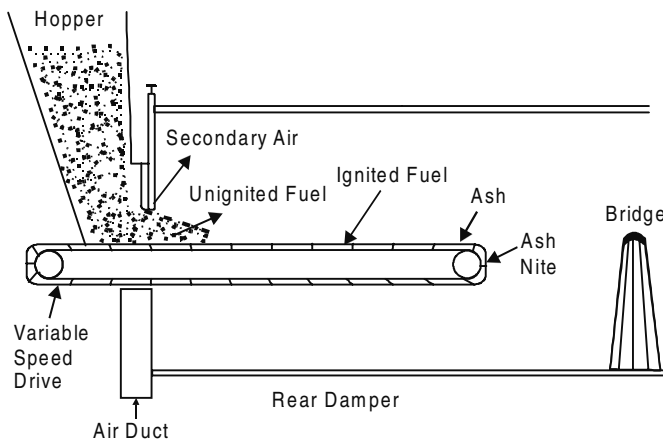
smoke is unlikely.

- (d) There is little risk of grit emission even when the coal contains large amount of fines.

The fire should be 300–350 mm thick at the front of the grate, tapering-off towards the back with the whole grate covered.

Coking stokers are usually designed for a maximum burning rate of 170 kg/m^2 but rates of 244 kg/m^2 or more have been obtained with shortened grates when using certain specific types of coals. Control is difficult if the burning rate is less than $58 \text{ kg/m}^2 \text{ h}$. Induced draught is generally used but the thick fuel-bed and small area of air passages through the grate make draught requirement high. The coking stoker with its thick fire is slow to respond to changes in steam demand.

3. *Chain-grate stoker* – This stoker has no counterpart in hand firing. The grate is an endless chain fed with fuel from an elevated hopper via a guillotine door. The chain carries the fuel under an ignition arch; where it starts to burn and ash as well as clinker are discharged over the back and into the ash pit. These stokers usually work best under balanced draught conditions. A wide variety of fuels can be burned but the most suitable are small or small graded coal. Coke breeze can also be burned. Ash content should be not less than 8% to ensure that a sufficient thickness of ash rests on the chain links to prevent overheating. It is usual to have the fuel-bed of about 100–130 mm thick and level across the width of the grate. The burning rate in such system varies from as low as $73 \text{ kg/m}^2 \text{ h}$ to well over $170 \text{ kg/m}^2 \text{ h}$. Both coking and chain grate stokers fitted to shell boilers can incorporate automatic combustion control equipment, where the fuel/air ratio once set for a given fuel, can be maintained. (see Fig. 6.5)



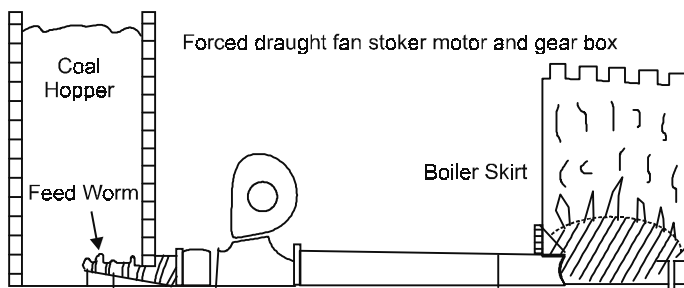
6.5 Chain grate stoker.

4. *Under feed stoker* – Here fuel is delivered from a hopper or outside bunker by a conveyor screw or ram to a retort. As the fuel passes up through the retort area, combustion air is supplied under pressure to jets or tuyers placed near the top or upper side of the retort, at which level combustion takes place. Volatile matter from the fresh coal rises through the incandescent coal on top of the retort, reaching ignition temperature as it meets the air supply. This ensures smoke free operation. Combustion air is delivered under pressure to the tuyers by fan and controlled by dampers. Over-fire draught requirements are only about 0.12 m bar negative. (see Fig. 6.6)

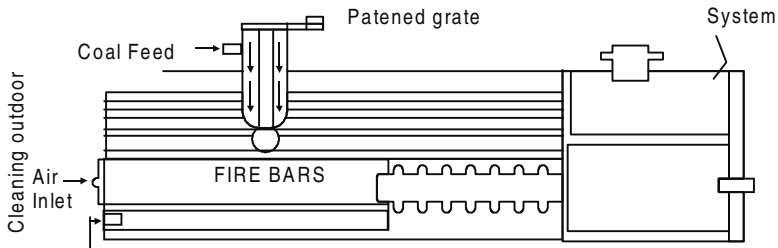
The best fuels are free-burning graded coals with low proportions of fines and moisture, since both these characteristics increase the tendency of the fuel to arch-up in the hopper or block the screw-conveyor. Coking coals are unsuitable. Underfed stokers can be fitted to sectional and central heating, vertical steam and other horizontal shell boilers. Coke is not generally used on an underfed stoker because it causes abrasion of the feeder gear and tube.

5. *Vekos Automatic Auxilliary Furnace / Stoker*: The Vekos furnace or stoker, as fitted to a Lancashire boiler, economicor Cornish boiler, consists of a cylindrical, water cooled combustion chamber connected to the boiler furnace tube or tubes by a refractory lined steel duct, with a close fitting door at the end of the furnace for cleaning purpose. Water for cooling the combustion chamber is taken from the bottom of the boiler to the front end of the water jacket and returned from the top rearend of the jacket to the boiler at a point just below normal water level. By this means, radiation losses are reduced & water circulation within the boiler improved. The Vekos stoker has been successfully built into packaged boilers. The grate is fitted at the bottom of the combustion tube and has no moving parts. Coal is fed from the top of the furnace into a whirling chamber (see Fig. 6.7).

6. *Spreader-fired air-cooled oscillating grate* – This type of stoker furnace can effectively burn low ash fusion, highly coking coal. It provides the compact thin fuel-bed needed and adequate over-fire turbulence is



6.6 Hopper model underfed stoker.

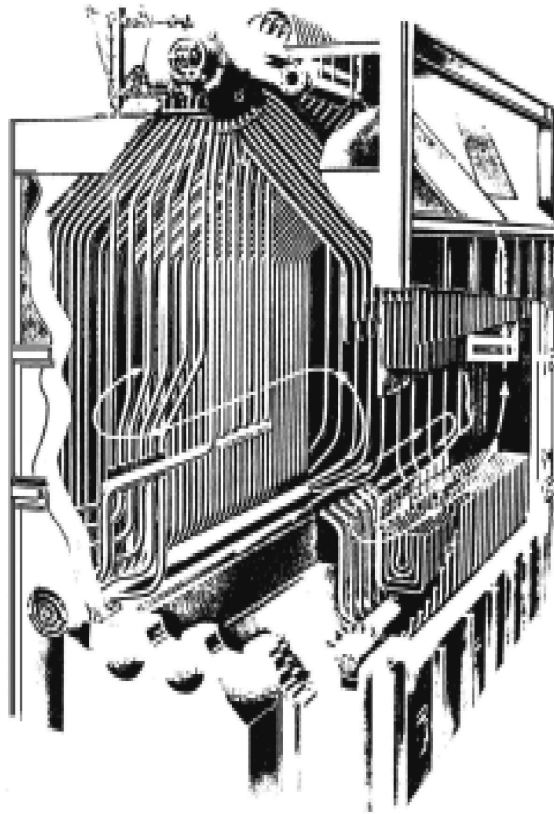


6.7 Vekos automatic auxiliary furnace/stoker.

provided for eliminating smoke. Fig. 6.8 shows the cut-way view of such a boiler. Improvement in performance can further be affected by water cooling the bridge-wall so that it may be used as a target against which large coal particles may strike without stitching and building up to a large coke or clinker mass. Highly coking coals require burning in thin fires. With spreader firing and continuous ash discharge the optimum fuel-bed thickness is 2–3 in. Thin fires normally overheat the grate but zoning dampers are effectively limiting device for this tendency. Thus overheating is controlled by distribution of combustion air and in this way the rate of combustion according to the ash thickness. The grate surface consists of pinhole type pinhole type bars (3 in. wide and 24 in. long) bolted to a grate of rigid steel grid. The air opening is 2.6% of the effective grate area. The grate is inclined slightly downward to the front. The grate drive or oscillating mechanism consists merely of an eccentric shaft mounted on the grid, driven by an electric motor at the natural frequency of the grate, which is about 1200 rpm. This oscillating motion bounces the ash over the grate surface into the ash-pit at the discharge end. The amplitude (usually less than 1/8th in.) and the time of oscillation are adjusted to suit the coal. At full boiler load, time of oscillation is only about 5 s/20 min.

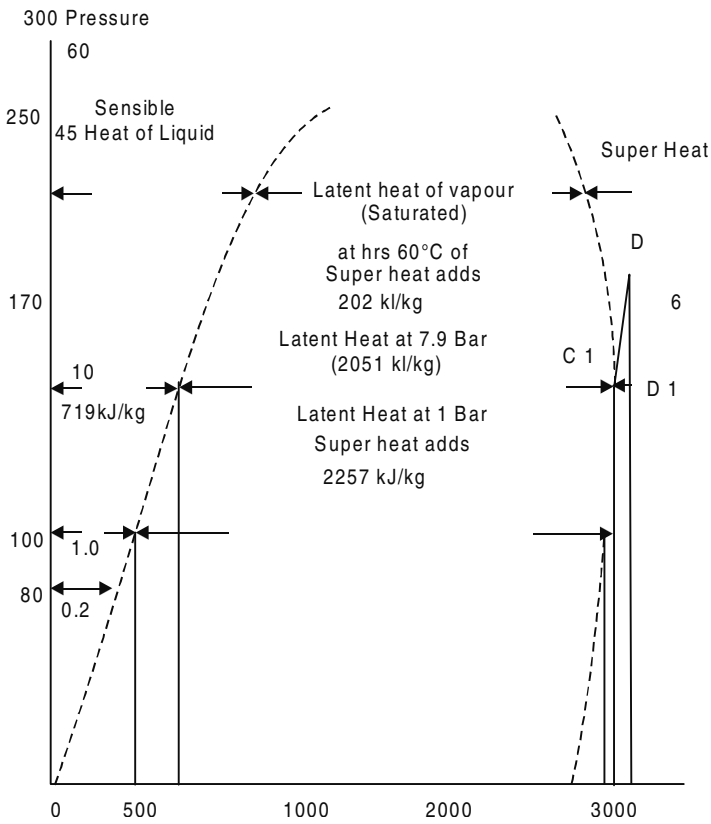
6.2.3 General comment on grate-firing

Steam raising in boilers, using stoker furnace show that while the value of the latent heat becomes less as the pressure rises, the value of the sensible heat increases, so there is a steady increase in total heat up to pressures of around 400 lb/in² (27.6 bar), after which the total heat begins to fall off. When the steam is formed and all water have evaporated, the addition of heat will raise the steam temperature. This further increase in heat is known as the superheat of steam. It is emphasized that superheaters must be fitted externally to the boiler or water container in order to raise the steam temperature at any given steam pressure. These are seen in following Fig. 6.9. In above figure the horizontal straight lines are shown as additions of latent heat at atmospheric pressure and 100 lb/lm² respectively, while



6.8 Cutaway view of the foster wheeler SA boiler.

the sloping line on the left of the diagram shows the rise in water temperature with pressure and the addition of sensible heat. The sloping line C1D1 shows the added superheat temperature and C1D1 the gain in heat due to superheating by 60°C at 7.9 bar. If hot water is available to the boiler at 82.2°C (180°F) from condensate return, only 374 kJ/kg (161 Btu/lb) would be needed to raise the temperature to its boiling point at 100 lb/in^2 (6.9 bar.g); whereas if no such supply were available 719 kJ/kg (309 Btu/lb) would be required, assuming that the initial water temperature is at freezing point, which in practice would be most undesirable. However, there are many boilers using feed water at a considerably lower temperature than 82.2°C so that a potential exists for fuel saving, since so much less heat has to be applied to the water boiler when an external source of hot water is available. The sum of “latent heat” and “sensible heat” is known as total heat or Enthalpy of steam. When pressure is reduced boiling point is lowered.



6.9 Properties of steam at various temperatures.

Boiler thermal efficiency

It is the ratio of the “useful heat output in steam” to the heat input in the fuel i.e., thermal efficiency = heat in steam above feed temp (kJ/kg) × (wt of steam/kg fuel)/calorific value of fuel (kJ/kg). The heat in the steam can be obtained from steam tables, whilst the heat in the fuel must be determined in laboratory (calorific value). The thermal efficiency may be expressed on the gross or the net calorific value of the fuel, i.e., thermal efficiency = 100 – total heat loss (in %).

Gross calorific value

All fuels contain some hydrogen. When hydrogen is burnt it combines with oxygen to form water vapor, which normally leaves the boiler as steam in the flue gases at exit gas temperature. However, while determining calorific value in the lab. The products of combustion are allowed to cool the original temperature of the fuel before combustion occurred. That is,

the steam gives up its heat and condenses to water, which itself is allowed to cool. All the potential heat in the fuel is therefore accounted for and is known as the “Gross Calorific value.”

Stack loss

Flames may be luminous or non-luminous. Oil and coal produces luminous flame, whereas natural gas burns with non-luminous flame. Luminous flames have greater radiating power when compared with non-luminous flame (e.g., on switching from oil to natural gas firing, less heat is transmitted in the furnace tube resulting in a higher flue gas temperature in the region of the tube plate). Sensible heat lost in the flue gas is given by the expression:

$$\text{Stack gas loss} = K (T_1 - T_2)/CO_2 (\%)$$

Here, T_1 is the flue gas temperature ($^{\circ}C$) leaving the boiler, T_2 is the ambient temperature and K is a factor dependent on fuel and is as follows:

Fuel oil	$K = 0.56$
Anthracite	$= 0.68$
Bituminous coal	$= 0.63$
Natural gas	$= 0.38$
Coke	$= 0.70$

Above calculations in practice show a loss in thermal efficiency of 1% for every $22.8^{\circ}C$ rise in flue temperature. At boiler efficiency around 75–80% the increase in fuel consumption is approximately 1% for every $18^{\circ}C$ rise in flue gas temperature.

Radiation and other losses

Every boiler will lose heat by radiation and convection but the heat loss will be reduced if the boiler, its shell or the steam and water drum are effectively lagged and the lagging is kept in good condition. Table 6.1 gives an indication of the magnitude of losses under this heading even from reasonably insulated boilers:

Table 6.1 Radiation & other losses in various boilers

Type of boiler	Radiation & other unmeasured losses
Modern package boiler	2.0
Water tube (modern) boiler	1.5
Water tube (WIF type) boiler	3.5
Economic wet back	3.0
Economic dry back	4.0
Sectional boiler	5.0
Cornish, Lancashire, Vertical boiler	6.0
Lancashire with economizer	7.0

However, it should be noted that the “radiation losses” quoted referee to MCR (maximum continuous rating) and if the boiler paint works on low output the percentage loss is proportionately increased. The maximum attainable thermal-efficiency of a boiler depends on its type and design. Table 6.2 shows the typical efficiency values.

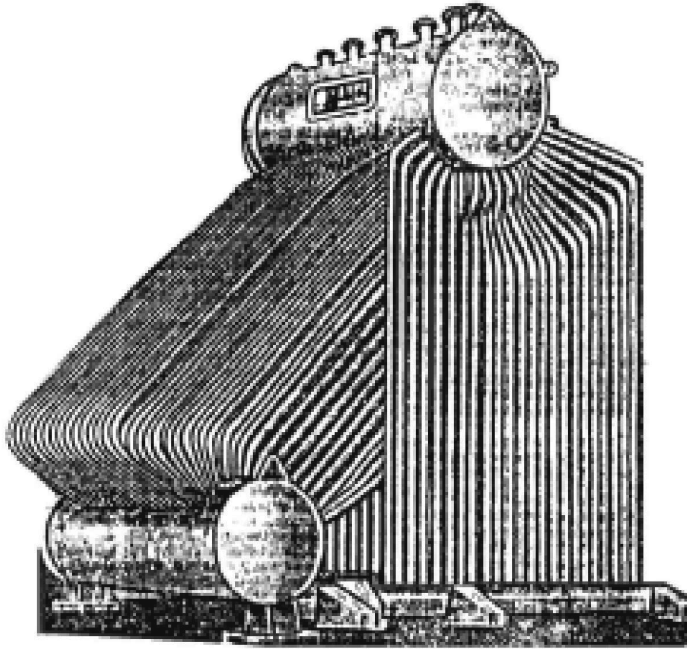
In the furnace tube of a shell-boiler, radiant heat is the predominant factor in heat transference. The flue gases are relatively slow moving in the flues of Lancashire-boiler and in order to abstract as much heat as possible, the heating surface area and hence its length is quiet great. In order to recover still further quantities of heat a secondary heating surface is added in the shape of an economizer. The size and space requirement of Lancashire type boilers presented many problems and as the value of velocity of gases in improving the rate of heat transfer was established, boiler designers took advantage of the fact by replacing external flue passages with tube bundles inside the boiler shell (see Fig. 6.10).

Superheaters

Steam produced from a boiler without superheater will either be trying saturated, or more likely wet. In works where steam is transmitted over long distances, the inevitable heat less from pipe surfaces cause the steam to become even wetter at the point of use unless a superheater is fitted to the However, it must be remembered that coal was the principal fuel available in Great Britain at the time when the economic boiler, as it was known, came into being and the designer had comprise between heat transfer requirement and the practical one of coping with grit and ash build-up inside the tubes. It was decades later when clean liquid and gaseous fuels became more abundant that high combustion rates and high convective heat transfer in tube nests also became a decisive factor in the design of shell boilers. Now, the so called modern package boilers are characterized by being smaller in size, having smaller tube diameters to affect high velocity convection heat transfer compared to the boilers of

Table 6.2 Efficiency of various type boilers.

Type of boiler	Efficiency (net) %
Vertical smoke tube	72
Lancashire	65
Lancashire with economiser	75
Lancashire with economizer & superheater	78
Economic: Two pass	75
Three pass	80
Packaged shell	82
Water tube boiler	83
Package (low pressure hot water)	80
Sectional boiler	67



6.10 Package water-tube boiler.

the earlier generation and of like output. The term “package” ready refers to the fact that the boiler because of its relatively small size compared to its predecessors can be conveniently sold and delivered complete with its burner and controls boiler plant. This is a separate bank of tubes placed near the boiler furnace through which steam passes to receive additional heat by convection or radiation. The superheater increases the surface area capable of accepting heat and the production of superheat, also increase the thermal efficiency of the boiler. Steam flow must be maintained through the superheater to prevent the tubes burning-out and a thermometer should be fitted on the outlet header so that the operator can determine the steam temperature. In a few cases, superheated steam is provided by using a superheater which is fired separately. The maximum steam temperature possible in a shell type boiler is approximately 343°C but this figure can be increased to over 537°C in a water tube boiler.

6.3 Combustion air

In fuels, carbon and hydrogen occur together and so burn together. When they burn together completely, the hydrogen combines with some of the 21% oxygen in air to leave water and nitrogen and the carbon combines with the remainder of the oxygen to form CO_2 and N_2 . If therefore, exactly

the right amount of air is provided to burn the fuel completely, the waste gases will contain less than 21% CO₂. There are two possibilities – the water in the combustion product will remain as steam or it will condense. In both cases, the percentage of CO₂ in the products will be less than 21%, but will be lowest in the first case because of the volume occupied by steam. The theoretical percentage of CO₂ in the waste gases, measured on the dry basis varies with different fuels but figures for the more common fuels, together with largest figures for practical purposes are given in Table 6.3. The figures are approximate but the operator should aim for the maximum figure obtainable with CO and with only a faint haze of smoke in the waste gases.

For one or more of the following reasons, it is possible in practice for combustion to be incomplete even though there is enough, or even too much excess air. In the absence of CO, the percentage of CO₂ in the waste gases indicate the amount of excess air used for combustion and it is essential for an instrument giving this information to be provided in the boiler house. If there is excess air in the waste gases, oxygen will also be present and an instrument which measures the O₂% can be used instead of a CO₂ recorder. In this case, the aim must be to keep the O₂% as low as possible while avoiding the presence of CO and smoke. The O₂% gives a direct indication of the amount of excess air in the waste gases. However, it may be noted that all stoker firing requires excess amount of air for efficient burning on grate (consequent loss of thermal energy through sensible heat of flue) and pulverized fuel burning necessitates fine grinding of coal which is expensive. In all these cases, furnace bed temperature is high (about 1200°C) and experience show that operation at this high temperature simultaneously makes coal ash soft, fuses and hence abrasive. This results in excessive wear of tubes and choking of grate. Also, combustion is not uniform over the grate area provided and results in uneven temperature pattern within the furnace. Due to lower heat release rate in conventional boiler, furnace volume required to burn low grade fuel is too large and hence economically unattractive. Moreover coals with high sulfur cannot be used in conventional stoker grates as it will emanate corrosive SO₂ and eat up the metal parts of the furnace as well as pollute

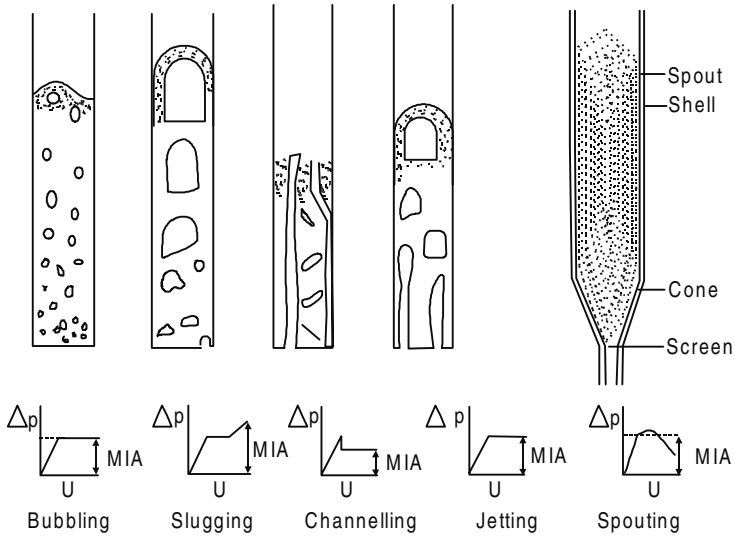
Table 6.3 Flue gas composition with various fuels

Fuel	Theoretical CO ₂ % (dry basis)	Target CO ₂ (dry)	Target O ₂ (dry)
Bituminous coal	18.6	12.0	7.4
Dry steam coal	19.2	13.0	7.9
Coke	19.5	13.0	7.0
Anthracite	19.5	13.0	7.0
Fuel oil	16.0	13.0	3.9
Natural gas	11.7	10.0	3.2

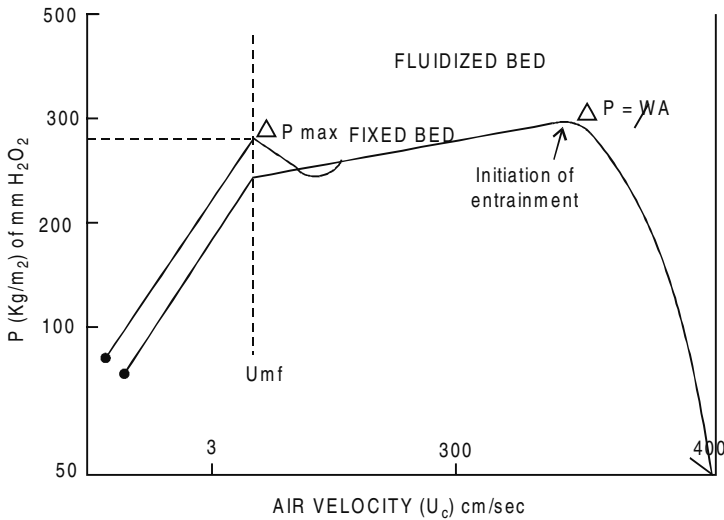
the air. Switching over from oil to coal firing also caused reduction (10–15%) in steam output. These furnaces cannot work when moisture content in fuel is high. In fact, conventional firing methods are not suitable to handle coal with ash content higher than 40%. All these inherent drawback of hand firing and stoker method was solved through design of the present new generation of coal firing known as “fluidized bed combustion.” In India fluid bed combustion (in short know as FBC) was first developed in authors institute (RRL, Jorhat), CMERI-Durgapur and CFRI-Dhanbad. These unique high efficiency methods of coal firing are discussed in detail in the following sections.

6.3.1 Fluidized bed combustion of coal

The very term “fluidization” implies fluid like behavior of the coal air mixture. In this situation where air is forced through fine coal particles a tubular vessel, the mixture of air and coal shows properties like maintaining horizontal surface on tilting, the mixture can be poured like a liquid and equalizes height when connected to two vessel of different fluid height, and a solid mass floats on the surface of the mixture. Such a situation is affected when air is forced through small holes at the bottom of a cylinder containing coal powder. Friction between air inside the tube and coal particles (called slip velocity) suspends the coal particles in air and the system behaves like fluid. If the cylinder is not transparent (as most boilers are made of metal container), the situation inside the cylinder is monitored by pressure drop across the bed. If we plot these pressure drops as a function of increasing air velocity of the air five very distinct curves corresponding to three distinct physical situations inside the reactor is obtained. In the beginning as we keep on increasing air velocity, the coal particles mere adjust among themselves and the bed expands (see Fig. 6.11). But after a certain velocity, first bubble appears and pass through the bed thus now the bed becomes fluid and pressure remains constant up to a certain limit. Velocity at which the bed becomes fluid like is called “minimum fluidization velocity (U_{mf}).” Further increasing velocity of the air brings the bed to a point when pressure drop starts declining and the fine particles carried away by the flue gas. This turbulent region extends to the velocity at which a sharp increase in the rate of carry-over of solids takes place; this is called “Transport Velocity.” For fine particles the transport velocity may be over ten times the individual “terminal velocity” (see Fig. 6.12). In practice bubbling region of the bed is called atmospheric fluidized bed. In this condition if we investigate by taking out coal particles elutriated with the flue, we find elutriation becomes constant at a particular height. This minimum height at which elutriation of coal particles become constant is known as “transport disengaging height” and important to boiler



6.11 Characteristic pressure drop curve for various types of fluidization (Δp - mass of particle above area of reactor).



6.12 Pressure drop vs. fluidization velocity diagram.

manufacturers for fixing height of the boiler. At high velocities mentioned above, boiler manufacturers construct “circulating fluidized beds” when the elutriation is recirculated into the reactor again. Fluidized bed combustion has a lot of advantage over fixed bed conventional firing. Some of these advantages are

1. Input fuel flexibility – Wide varieties of fuels like municipal refuses, rice husk, cold-water slurry, saw dust, lignites, industrial wastes and coals up to 85% ash (theoretically as well as practically up to 70% ash successfully burnt at TATA-Jamadoba power plant using washery rejects in India and Keeler-Dorrolivers Shamokin plant in USA). Peat oil-shale and any other carbonaceous material can also be used.
2. FBC does not require oil support for start-up or low load stabilization.
3. Considerable reduction in boiler size due to achievement of high heat transfer rate over small heat transfer area immersed in bed.
4. Low temperature and better distribution of fuel in the fluidized bed results in control, minimal fouling and slagging potential, thereby eliminating need for soot blower and wall blowers; thermally homogeneous combustion and hence lower possibility of local hot or cold spots, prevention of vitrification of ash particles (thus causing them to be less aggressive to abrasion than ash from stoker or pulverized coal fired units).
5. In-situ sulfur capture by limestone injection and thus permits use of high sulfur coals without polluting air. Moreover, relatively low temperature operation (800–850°C) does not give rise to NO_x in flue. These advantages save huge capital expense in the down-stream scrubbing of flue gas.
6. Wide turn-down ratio (1:5): Plant runs efficiently with 20–100% load variation.
7. Heat retention in bed allows fast restart.
8. Better load response than other combustion devices. Thermal lag in coal (coal is a bad conductor of heat and this drawback eliminated through fast heat transfer of coal burning particles).
9. FBC generates non-agglomerated solid wastes product which is easier to dispose of.
10. FBC requires less maintenance compared to pulverized coal and stoker fired units due to absence of pulverizers and moving grates.
11. Instrumentation and control requirements for FBC are minimal. No flame monitoring systems are required.
12. FBC operation is much cleaner on the shop floor than other modes of coal firing.

However, FBC also possess some draw-backs well, although they may be very few. Some of these are

1. The difficult-to-describe flow of gas, with its large deviations from plug flow and The bypassing of solids by bubbles, represent an inefficient contacting system. This becomes especially serious when high conversion of gaseous reactants is required in some fluid-bed chemical reactions.

2. The rapid mixing of solids in the bed leads to non-uniform residence times of solids in the reactor. For continuous treatment of solids this gives a non-uniform product and lower conversions, especially at high conversion levels. On the other hand, for batch treatment of solids this mixing is helpful since it gives a uniform solid product.

Table 6.4 Comparison of fluidized-bed boiler with spreader stoker & PF- boiler

Characteristics	Fluidized-bed	Spreader-stoker	PF-boiler
1. Fuel quality (ash, CV, MM, size distribution)	Has no effect on the operation	Output affected by coal quality.	Output affected by coal quality.
2. Maintenance	No moving parts, less maintenance require maintenance due to pulverisor use.	Moving grate at high Temp. zone	Frequent
3. Efficiency (for typical Indian coal with 45% ash)	About 86%	Around 76%	86-87%
4. Efficiency at low load :	Better	Poor	Less
5. Soot blowers :	Not required	Necessary	Necessary
6. NO _x Formation:		Low	High High

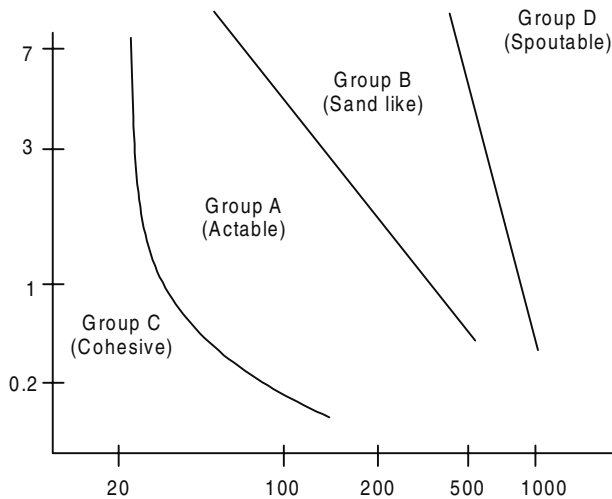
As mentioned above gross behavior of the solid particles in a fluidized bed depends on the basic inherent nature of the particles such as size, density, cohesiveness, etc. Accordingly Geldart and Bayens (1973) suggested the classification of all solid particles used in fluidization into four groups as they present density difference against the fluidizing gas and mean particle size. The properties observed in one powder in a particular group then can be extended to other similar group of solids. These four groups are –

Group A – These powders have a small size and a low density (d_p less than 1.4 kg/m^3). Beds of powders in this group exhibit a particulate expansion before bubbling occurs; in other words U_{mb}/U_{mf} is greater than 1. A maximum bubble size does appear to exist in these cases and most bubbles rise more rapidly than the interstitial gas. A typical example in such category is the cracking catalysis.

Group B – These materials are mostly of medium range size and density, sand being a typical example. For these powders, bubbling starts at the incipient fluidization ($U_{mb}/U_{mf} = 1$). In this category there appears to be no maximum bubble size and most bubbles rise quicker than the interstitial gas. At equal bed heights and ($U - f$) values, bubble size seems to be independent of both particle size as well as size distribution.

Group C – This group consists of all cohesive or strongly physically adhering powders which are difficult to fluidize.

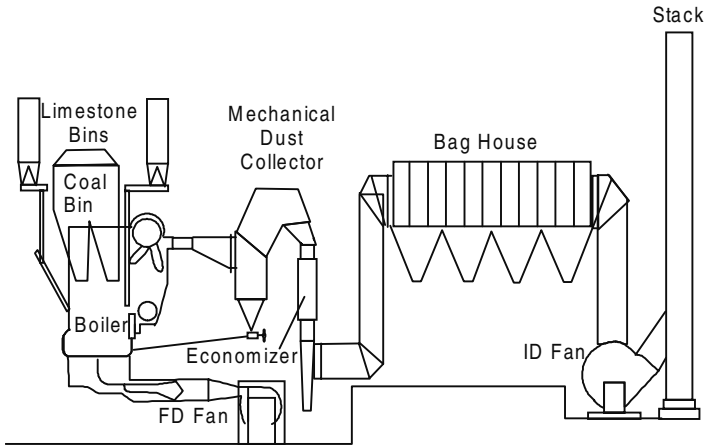
Group D – This group consists of large and very dense particles. In such beds, all but the largest bubbles rise more slowly than the interstitial gas. If gas is admitted through a central orifice, powders of group-D can be made to spout. Thus classification of powders by Geldart appears to be very simple and easy to use – it only requires knowledge of particle diameter and density difference (see Fig. 6.13).



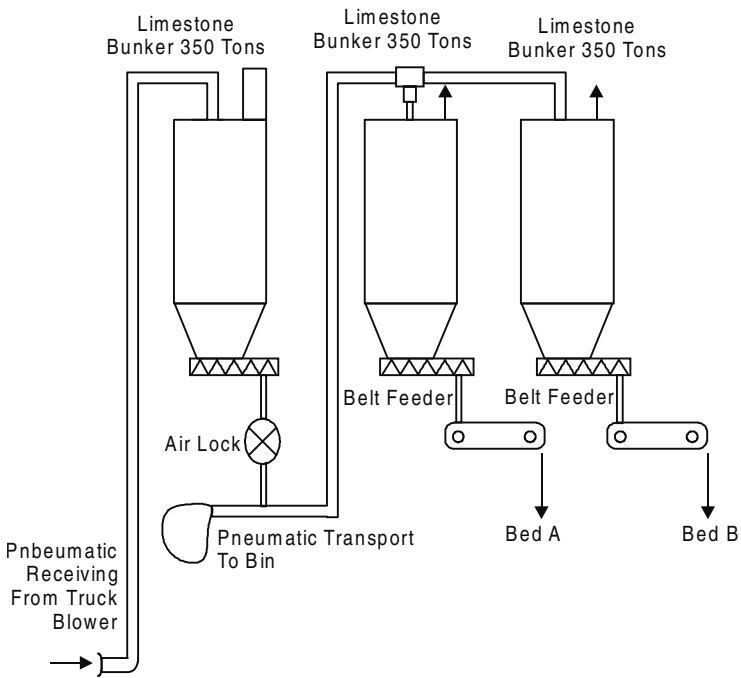
6.13 Geldart's classification of solids.

6.4 Total FBC system (Design aspect)

A special advantage of fluidized boiler is that it requires very small carbon inventory in the bed to sustain heat in the bed for later start up (slump bed) and offers a large turn down ratio not achievable by conventional fixed bed boilers. Upper operating temperature of a fluidized boiler using coal is fixed as per sintering temperature of the ash in the coal. Sintering of coal makes it difficult to remove ash from the boiler. Similarly lower temperature of operation of a fluidized bed is determined by the adiabatic furnace temperature in the furnace using a particular fuel and determines extinction temperature of the bed. Adiabatic furnace temperature is calculated by means of enthalpy and mass balance in the boiler. These calculations indicate that a fluidized bed boiler is capable of burning up to 85% ash coal (theoretical) and 75% ash coal (e.g. washery rejects) in practice. These figures are not achievable by conventional fixed bed boilers. While designing a fluid bed boiler, commercial manufacturers consider following parameters to design the total fluid bed system. (see Fig. 6.14 and 6.15)



6.14 Total fluidized bed boiler system.



6.15 A typical fuel feed system.

(a) *Minimum fluidization velocity –*

Minimum fluidization velocity (U_{mf} can be calculated theoretically using characteristic parameters like density, drag coefficient, viscosity, etc. In

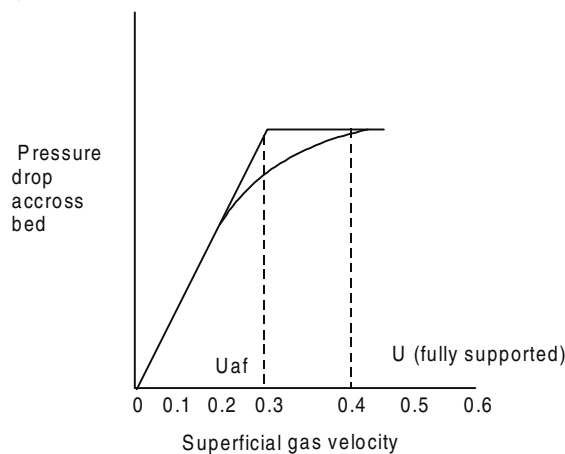
practice minimum fluidization velocity is determined by a plot of superficial velocity versus pressure drop in the bed for a particular fuel. For all practical purpose minimum fluidization velocity at which the boiler has to be operated is taken as 1.5 times that obtained by above means. Boiler height as mentioned earlier is fixed by transport disengagement height and this TDH value for a fixed fluidization velocity rises with increase in vessel size. Heat loss from the boiler is determined by excess air (above theoretical requirement of air for complete combustion of the coal particles). In a conventional fixed bed boiler complete combustion and minimum heat loss through flue is balanced by measuring carbon-dioxide gas content in the flue gas whereas in a fluidized bed boiler this balance is set by fixing excess air input in the fluidization air. Generally speaking all fluidized bed boiler using coal operates at 2–5% oxygen in the flue, corresponding to an excess air factor of 1.1 to 1.3 (i.e., 10–30% excess air) (see Fig. 6.16 and 6.17). Excess air factor (E) can be calculated using the expression:

$$E = 21 / (21 - \% \text{Oxygen})$$

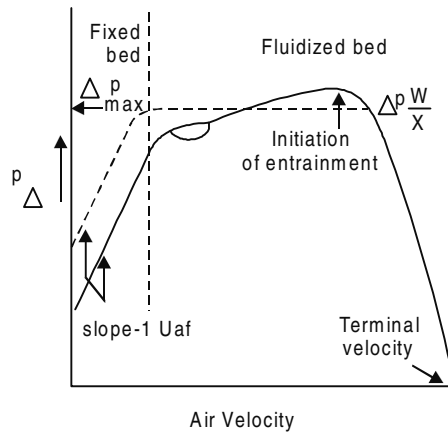
Emission of oxides of nitrogen gas at 20% excess air is typically of the order of 0.4% per MBtu. Interdependent of CO and NO_x is shown in Fig. 6.18. Concentration CO in the free board space (above fluidized bed) decreases with injection of small amount of air in overfire region of the bed.

(b) Designing distributor plate

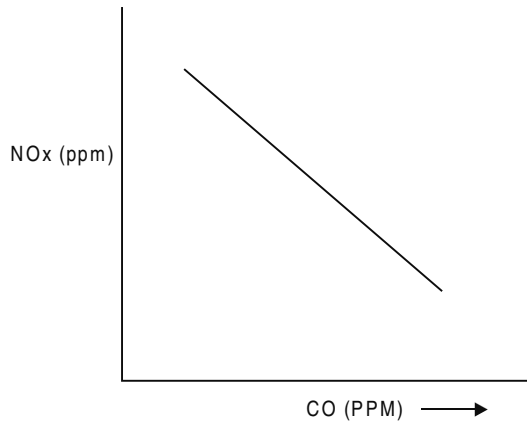
Distributor plate is the perforated plate at the bottom of the boiler through which air enters into the coal bed. Since atmospheric fluidized bed boilers generates large amount of heat (0.3–3 MW/m² bed area with 1.5–6 mm



6.16 Practical fluidization velocity.



6.17 Complete fluidization diagram.

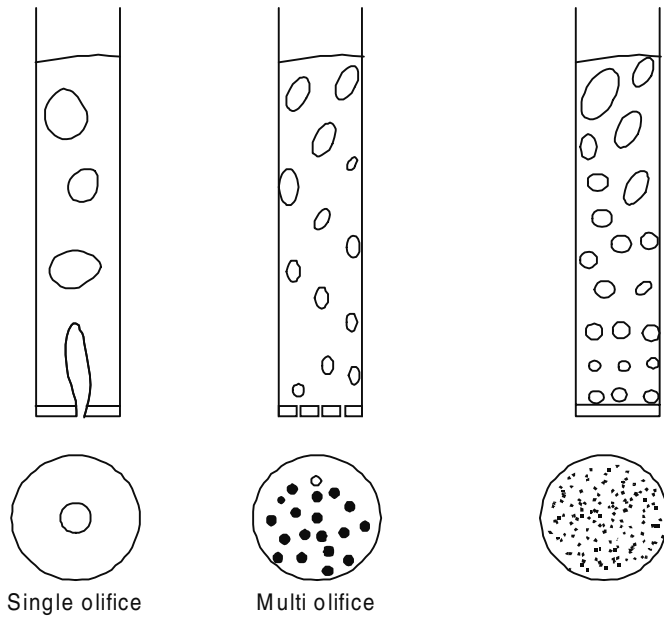


6.18 Interdependent of CO and NOx in the glue.

coal and fluidizing velocity of the order of 0.6–4 m/s) it is important to insulate the distributor plate with a thick cover of ash or other inert material. Generally there are two types of distributor plate in use nowadays and these are either perforated/standpipe nozzle or bubble cap nozzle. Pressure drop at the distributor plate is controlled in the design of distributor plate in order to maintain total pressure drop in the system within limit which is important for maintaining the bed condition. Most of the boiler manufacturer allows a pressure drop of about 100 mm as a thumbs rule for above purpose (see Fig. 6.19 and 6.20).



6.19 Water cooled flat plates distributor at CWS Marden.

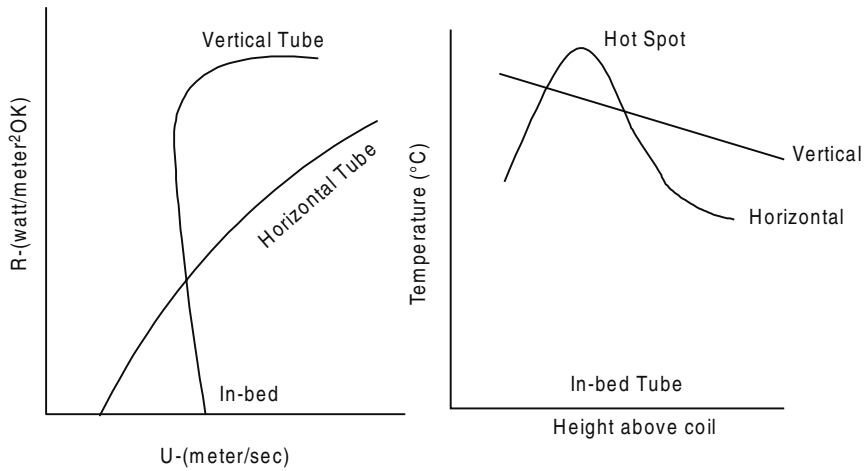


6.20 Quality of fluidization as influenced by type of gas distributor.

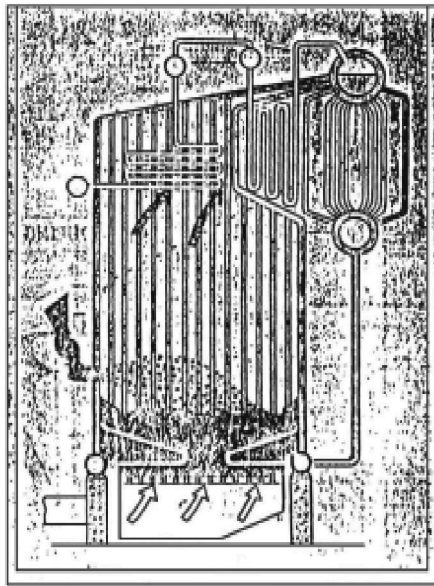
(c) Design of heat exchangers

Useful heat generated by a fluid bed boiler are taken out by a specially designed heat exchanger tube and header system (the later is required for separating superheated steam from water). These heat exchanger tubes

are placed both in the bed and the convective pass of the boiler. Water wall created around the boiler external wall also works as a large heat exchanger. Direct impingement of burning particles cause corrosion (black spots) to the inbed tubes. Accordingly vertical and horizontal placement of bed coils have been studied in order to minimize above corrosion effect vis-a-vis heat exchanger efficiency. Figures 6.21 and 6.22 shows these effects. It may be mentioned here that conventional tube boilers operates at a heat flux rate of the order of 50 to 75,000 kcal/h/m² whereas fluidized bed boilers heat exchanger tubes are exposed to a heat flux of 300 to 375,000 Kcal/h/m². Heat transfer coefficient (h) generally varies as a square root of T where T is the contact time in seconds, while h remains constant throughout the bed. However h varies exponentially with height in the freeboard region of the fluid bed boiler. Percent heat release rate (both in bed and over bed) goes down exponentially with recycle ratio of feed in coal fired FBC boiler. Heat transfer coefficient (h W/m²°K) also varies exponentially with mean particle diameter of coal but above 1.6 mm the decrease in h is less and thus for atmospheric operation a useful compromise is to use coal crushed to 3 mm top size (Umf = 2.5 m/s). It may be mentioned here that fine particles works like a lubricant to larger particles during fluidization and thus improves operation of the boiler. For this cut size 3 mm to dust is chosen as right feed material rather than a narrow cut band cut size. Convective heat transfer coefficient is also highest at Umf of a fluidized boiler. The value of convective heat transfer coefficient varies widely but generally lies in the range 15 to 350 W/m²°K which is significantly more than that of conventional water tube boilers (50 to 70 W/m²°K). Interestingly radiant heat flux varies as a power of 4 to the radiant temperature (T) in the bed. Typically, the value of radiant flux of a bed at 900°C and tube temperature of 250°C is about 80 kW/m² and under similar condition, the convective flux is about 200 kW/m² (see Fig. 6.23). Fuel (coal of about 0–6 mm size) are fed into the FBC-boiler through a 4 in. diameter pipe either from below (called “under-bed feed system”) or above the bed (called “over-bed feed system”). Rotary screw-feeder moves the coal from bunker through the feed pipe. Fuel feed point is judiciously located in the bed in order to avoid localized fuel concentration and proper burning of volatiles as well as CO within the bed. When requirement demands higher fuel feed rate, multiple feeding systems can be used. In view of the performance gain (like improved combustion efficiency, acceptability of more fines etc) achieved with under-bed system, the later is being generally used. However, for fibrous materials, like bagasse and straw, over-bed feeding is the only choice. Further comparison of these two feeding system are tabulated in Table 6.5 below.



6.21 and 6.22 Heat curve in vertically and horizontally placed cooling water coil.



6.23 Convection pass in FBC.

To optimize crusher power and also to maximize carbon burn-up, a top size of 6 mm is preferred for coals. The coal-air mixing nozzles hard faced to minimize erosion. Under-bed feed system is also helpful for friable coals, like that of N.E. region of India.

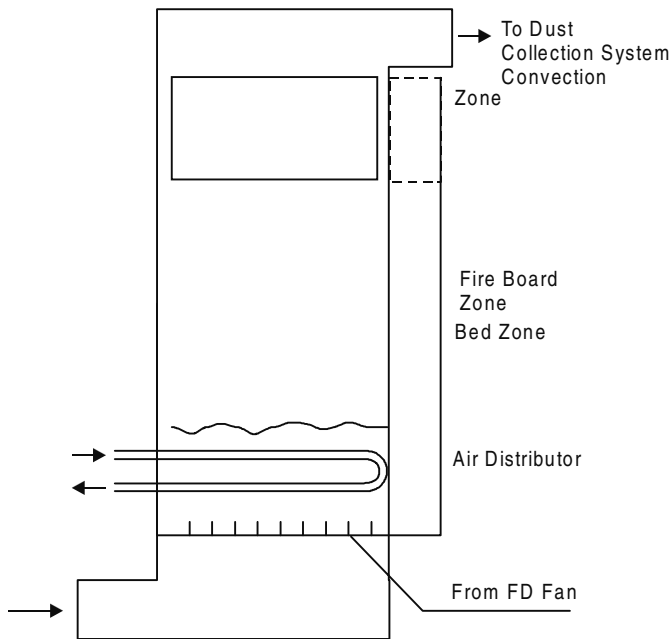
(d) Air delivery system

Air is delivered at the bottom of the boiler by forced draft fan. Position

Table 6.5 Comparison of over-bed & under-bed-feeding systems

Description of feed	Over-bed	Under-bed
Distribution of fuel and air	Poor	Good
Unburnt carry-over of fines	High, Needs double sieving	Low
Combustion efficiency	Base	More by 7%
Recycle requirement	High	Very less
Power requirement	Base	Marginally higher
Part load operation	Warrants segmentation above distributor plate	Segmentation only in air box.
Start-up	Complicated	Simple

displacement roots-blower can also be used. The boiler fans are sized with liberal reserves on the operating point viz. 20–25% on flow and 30–40% on head requirement. Air is introduced into the boiler through perforated plate, known as “distributor plate.” The fan power is thus directly related to pressure drop at the distributor plate and static bed height. The bed height is determined by the need to submerge the heat exchanger tubes and for high sulfur coals the volume requirement (i.e. residence time) for effective sulfur capture, is higher. The expanded bed height is normally set so that the in-bed tubes are fully covered which assumes the maximum use of sub-merged tube surface. For most Indian coals a shallow bed (less than 1000 mm) is adequate (see Fig. 6.24).



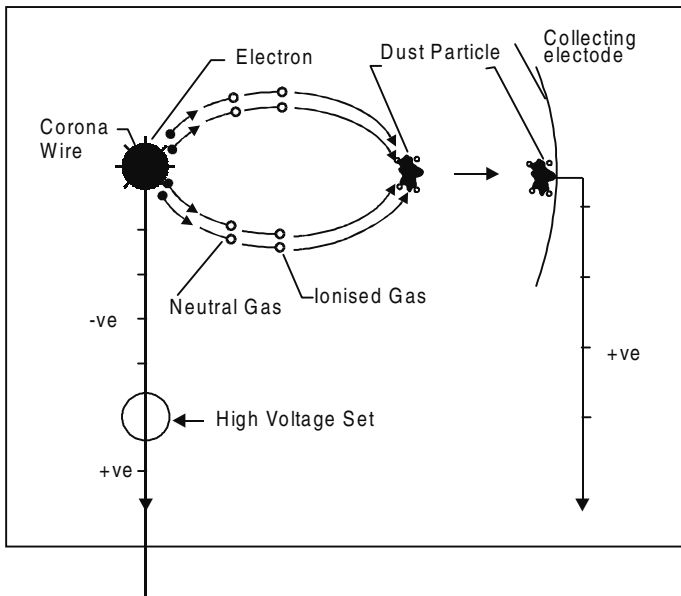
6.24 Fire board region in FBC.

(e) Particulate Removal System

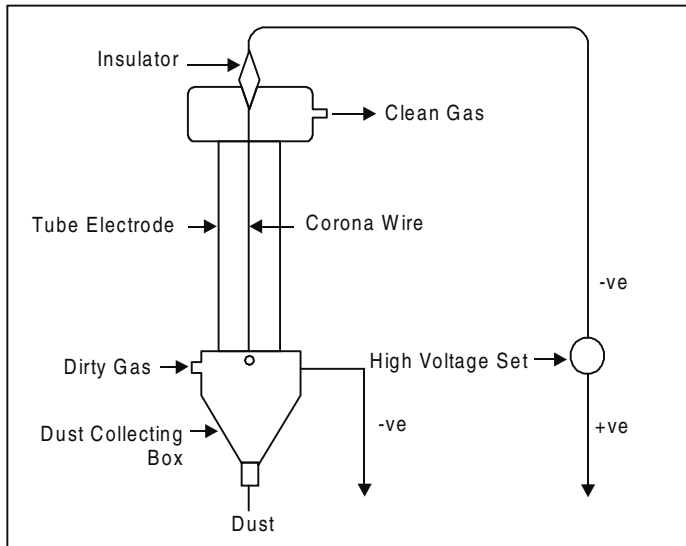
As mentioned above, as the gas leaves the boiler it carries with it fine dust particle. These dusts can be removed by either of the following means—

Cyclone separator, or water scrubber, electrostatic precipitator and bag-house filter system. Dry cyclone separator can remove up to 100 micron size particles. But particles smaller than this escape. Dust loading in the flue of a FBC is of the order $50\text{--}75\text{ g/m}^3$. Present author found through improvised experiments that incorporation of a water scrubber after the cyclone effectively removes all dust particles. In a commercial unit both ESP and bag-house filter systems are used. Cost of bag-house filter system is 30% more than ESP and also ESP is capable of controlling particulate emission to 150 mg/m^3 rate, whereas the maximum control available with bag-house is 250 mg/m^3 of particulate material. The efficiency of ESP is ensured by adopting optimum migration velocity and providing higher specific collecting area. The electrostatic precipitator is based on the simple principle that a charged body attracts ne oppositely charged. Construction and principle of operation of a ESP is shown in Figs. 6.25 and 6.26. Electrostatic precipitators are of two types – the dry or plate type, and the pipe or tube type wherein the collected material is removed as a dilute slurry. Efficiency of ESP is given by Deutsch-Anderson formula, which can be written as:

$$h = 1 - e^{-WA/Q}$$



6.25 Principle of electrostatic precipitator.

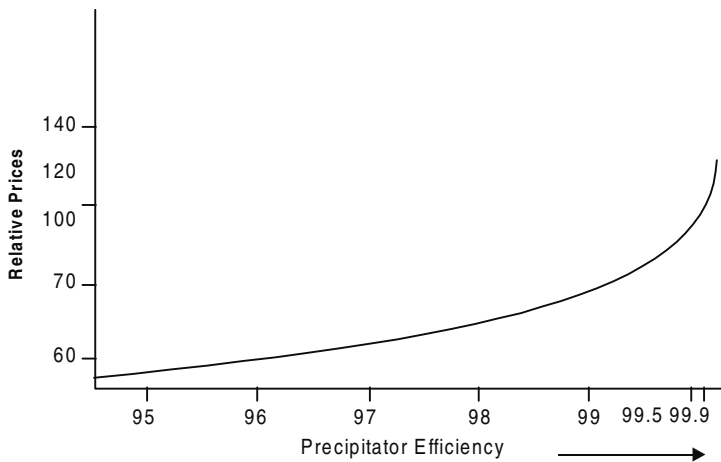


6.26 Elements of electrostatic precipitator.

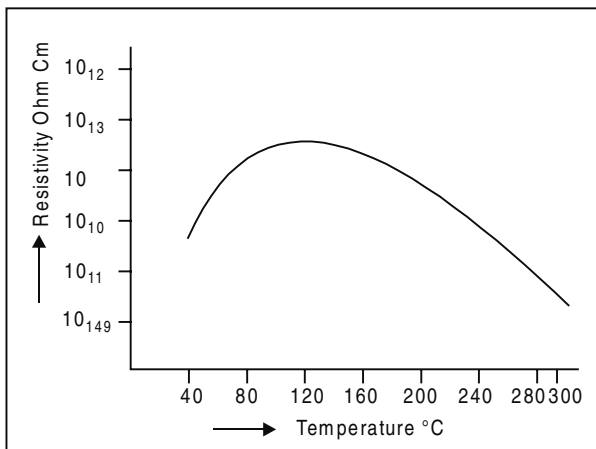
Where h = efficiency, A = collecting area of the electrode, e = Napierian log base, Q = gas flow rate, and W = migration velocity. Figure 6.27 shows the relation between relative cost and precipitator efficiency. It is an exponential curve, rapidly increasing above 98% efficiency. Resistivity of the dust is the main factor controlling efficiency of an ESP (higher the resistivity, lower is the efficiency of ESP). Addition of SO_3 , NH_3 is reported to increase efficiency of ESP. Besides this, lowering temperature, increasing humidity, and also found to increase efficiency of ESP. Relation between flue gas temperature and resistivity (hence efficiency) is shown in Fig. 6.28.

(f) Ash Disposal System

FBC-boiler is equipped with ash overflow pipe in the grate, through which burnt material (ash) is removed continuously (for underbed feed system) or batchwise (in case of over-bed feed system). Since the fluid bed operates with less than 1% carbon inventory at any time of operation, ash removal do not carry much unburnt carbon. However, the ash temperature corresponds to that of the fluidized bed and thus sensible heat is to be removed before its disposal. Ash coolers can be incorporated for recovering the sensible heat if the ash generated is high. Otherwise submerged belt conveyor or other wet ash disposal systems can be adopted. Ash removal by this method ensures constant bed height in continuous operation of the boiler



6.27 Air pollution at different precipitator efficiencies and relative prices.



6.28 Typical temperature - resistivity relationship.

(g) Start-up and load Control Systems

Generally the start-up procedure involves simple burning of charcoal to heat up the bed and when the bed reaches ignition temperature coal flow starts. These fresh coals then sustain the temperature. However, oil or gas fired start-up systems are also used. Burning charcoal or over-bed, dissipates heat and sometime submerged tunnel burner's help. Load control can be achieved by manipulating some of the principal bed parameters like – bed height, bed temperature and fluidization velocity. Segmentation of the bed allows partial slumping and partial load separation. This later method also helps in quick restorations of bed when needed. The wind box also in such case segmented into a few section depending on the

turndown requirement. Dampers on the fluidization air-line and in coal transport line are activated from the control room to cut-in or cut-out certain part of bed-segment desired. The response to load fluctuation is found to be excellent. The boiler efficiency practically does not reduce with reduction in load. Previous work at CMERI, Durgapur has shown that in approx, 70 s after lighting up the charcoal, the top part of the bed reaches 610°C whereas bottom part is at 130°C. Thus exact time and mode of supplying fluidization air is an art of starting up a fluidized boiler. If this is not followed properly the top part of the bed will reach up to 1200°C (while inside part of the bed will) remain cool) and clinker formation due to ash fusion will result.

(h) Boiler configuration

For small capacity boilers up to 5 t/h capacity, square configuration is found to be adequate for boiler design. A flue shell boiler with the fluidized combustion chamber located inside the flue tube, is offered up to 15 t/h steam capacity and for relatively low pressure steam. An external membrane wall fluidized bed combustor exhausting its gases into a shell type boiler to absorb the convective heat forms next grade of FBC-boiler in the range 15–30 t/h. A bidrum bottom supported natural circulation FBC-boiler is offered for capacities up to 100 t/h and for medium pressure range up to 65 atm. A box type top supported FBC-boiler with horizontal evaporator coils in the bed on forced circulation is offered for capacities beyond 100t/h and for medium and high pressure (Table 6.6).

6.5 Sulfur retention

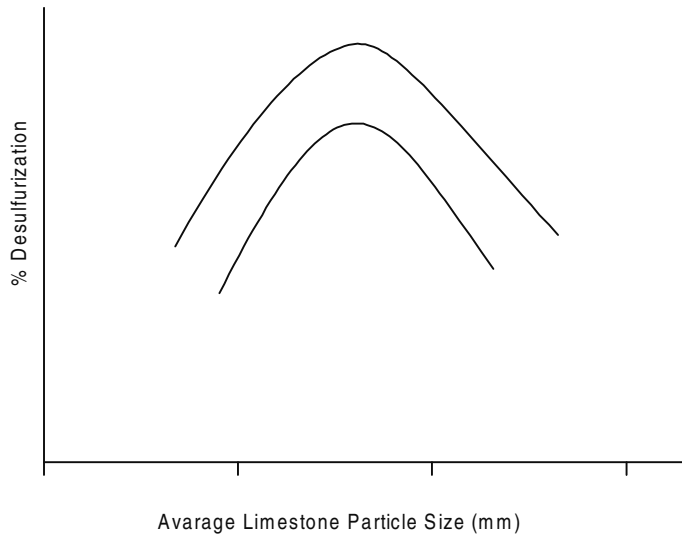
If the coal contains high sulfur, it is necessary to mix limestone with feed coal in order to capture sulfur as CaSO_4 in the bed and discharge it as ash. Several workers reported that at initial stage the combination of sulfur and calcium of limestone is fast but soon the limestone becomes coated with hard CaSO_4 and the reaction becomes to some extent diffusion controlled. Ultimately due to formation of impervious (as CaSO_4 molecules are larger in volume than CaO) coating of CaSO_4 , mass transfer limitation arises and the reaction stops. Depending on the lime content as well as composition and porosity, each grade limestone has an optimum size for maximum sulfur capture. Fig. 6.29 shows the phenomenon graphically. Another parameter which is important for bed sulfur capture is bed height. Bed height determines the residence time of the gas in the bed and thus bed height should be sufficient to allow capture of sulfur within the bed.

Thus high sulfur coal is never operated with a shallow bed. A typical curve for sulfur capture versus bed height is shown in Fig. 6.30. As can be

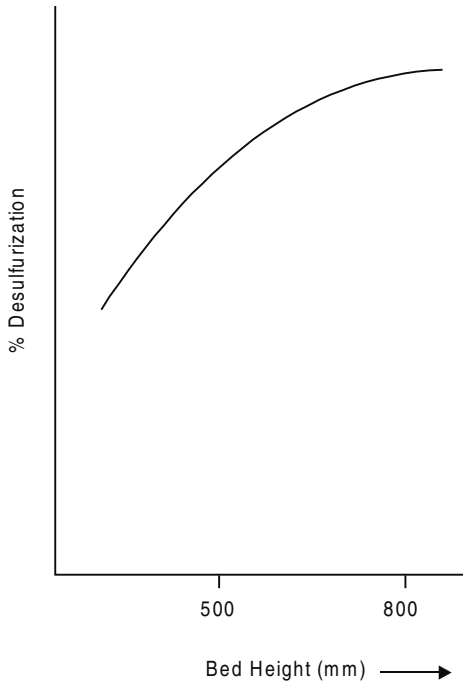
Table 6.6 Various methods of conventional turndown achievement in FBC. Design figure for turn-down ratio in FBC system is 5:1 (max). Note, control of coal flow while trims the bed temperature but can't control it fully. In practice, air control quickly changes boiler temperature. A FBC can operate to as low as 30% its capacity.

Method	Principles	Disadvantage
Bed temperature reduction	In-bed heat transfer area is kept constant. Temperature driving force kinetics.	<ul style="list-style-type: none"> • Temperature change is limited by combustion and desulfurisation is reduced.
Partial bed slumping	Active in-bed heat transfer area is reduced by partial bed slumping technique	<ul style="list-style-type: none"> • Air leakage to the slumped side causes agglomeration. • Splash cause bed material transfer to the slumped side and makes the restart difficult.
Velocity turn-down	In-bed heat transfer area is reduced by bed contraction and reduction in the velocity.	<ul style="list-style-type: none"> • Erosion of the tubes in the splash zone. • Bed height change is insufficient for a large margin of turn-down
Bed material discharge	In-bed heat transfer is reduced by discharging bed materials	<ul style="list-style-type: none"> • Erosion of tubes in the splash zone. • Troublesome particle handling is required.
Wing panel type	Heat transfer coefficient is changed by independent aeration at separated bed section (wing panel).	<ul style="list-style-type: none"> • Heat transfer coefficient is insensitive or too sensitive to velocity change • Limited only to small units.

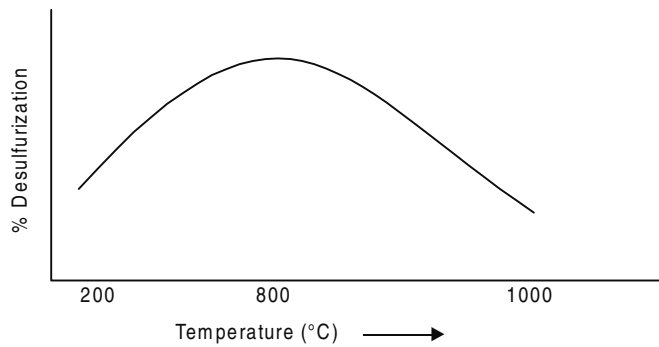
noticed in the figure, in later stage of desulfurization increasing further bed height brings about very little change in sulfur capture. In fact, generally it has been found that only 2–5% desulfurization is observed with increasing bed height between 500 and 100 mm. The reason being, probably increase in gas bubble size with coalescence reduces gas/solid contact with increase in bed height. Further excessive increase in bed height necessitates use of higher fan power and consumption of more electricity, and thus a cut-off limit is set as to maximum height of bed for necessary sulfur capture. The third important point with respect to sulfur retention in the bed is the operating temperature. It has been observed that bed sulfur capture increases with increase in bed temperature but after a certain temperature limit (Fig. 6.31) the amount of sulfur captured decreases. This temperature range is usually between 780 and 850°C. Further increase in



6.29 Extent of desulfurization of flue gas with limestone size.



6.30 Progressive desulphurization with the bed.

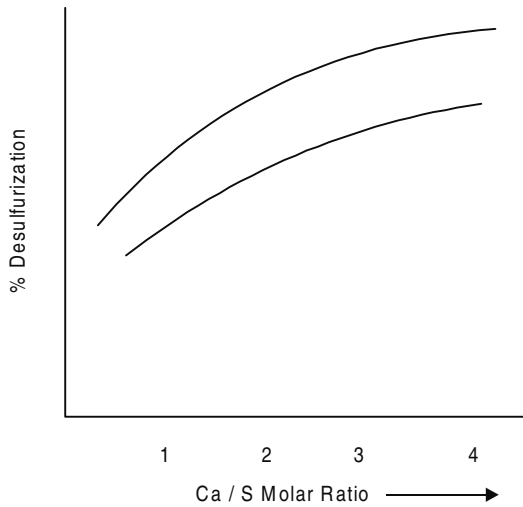


6.31 Sulfur in flue with increase in bed temperature.

temperature beyond this range, causes CaSO_4 to dissociate in reducing atmosphere and thus gives rise to additional SO_2 in the flue. The fourth important parameter to consider in desulfurization by limestone in FBC system is the right amount of coal to limestone ratio, so that the system operation at optimum condition. Due to variation in lime content from mine to mine and sulfur content in various coals. Ca:S ratio is an important parameter for effective desulfurization. Typical experimental curves for variation of (%) desulfurization on Ca:S ratio is shown in Fig. 6.32. In most cases this optimum ratio is between 2.5:1 and 3:1.

6.6 Economics of FBC

Viable economics of FBC boiler has been attested by the fact that in last one decade enumerable number of organizations in India and abroad have either newly installed or retrofitted existing boilers with FBC. Although situation India is little different than USA, as in India conservation of power (kW) is cheaper than generation of power per kW while in USA growth and demand pattern is slow and thus generation is cheaper. Because of this later reason, many feel that under present India condition FBC will be a stand-by technology rather than a substitute for large conventional power plant. International price for a retrofit FBC boiler (installation plus equipment cost) come to about \$554/kW while that for a new FBC plant is \$1000/kW; the same for a pulverized fuel fired boiler \$600/kW (the latter difference is mainly due to construction time). FBC has been found to be economical up to 60 MW range while above 60 MW, CFBC seems to be cheaper. We should also note that FBC is mostly used for power generation rather than for process steam alone, and in this respect most of the designs involved several separate FBC boiler in order to achieve desired control and turn-down. The design studies indicate that AFBC with a conventional steam cycle would give savings of about 10% in boiler capital



6.32 Rate of desulfurization with changing Ca: S molar ratio.

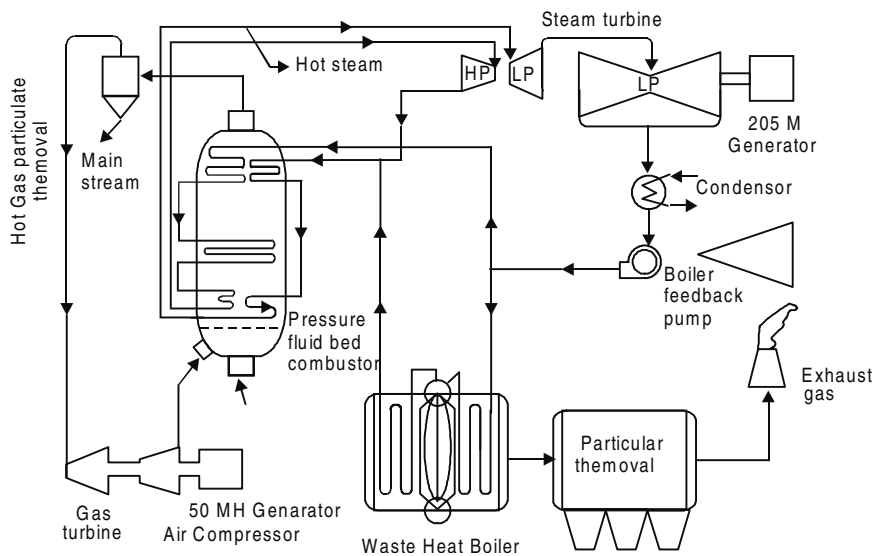
cost and power generation cost in comparison with a conventional plant both for 140 and 660 MWe units. For a pressurized combustor with a mixed steam cycle and open cycle gas turbine, the gas turbine driving the air compressor and producing about 25% of the power, the design indicates slightly increased savings at 140 MW and savings of about 20% in boiler capital cost and 10–14% in power generation cost at 660 MW. Complex cycles involving both open and closed cycle gas turbine have also been considered, particularly for sites where availability of cooling water is limited. Recently Bruce St. John of MUS Corporation, Gaithesburg, Maryland, USA has given a simple economic comparison of FBC with other boilers. From capital cost point of view, as per above author, an oil fired boiler will always be less than that of conventional solid fuel boiler or AFBC; and an AFBC will always cost more than a conventional boiler. Choosing a solid fuel boiler involves a trade-off between lower fuel cost and higher capital cost. In general, if the steam loan is small (less than 10 t/h steam) or the annual capacity factor is low (less than 40%) the life cycle cost of the oil fired boiler will be lower, the stoker boiler (low sulfur fuel) and AFBC (with high sulfur fuel) maximum. Thus a small capacity AFBC-boiler may be difficult to justify. This conclusion is confirmed by the fact that the medium size AFBC water tube boilers currently in operation is over 50 t/h steam capacity. Comparing a 50 t/h AFBC and a 125 t/h CFBC we find AFBC produces steam at a cost of \$17/t steam whereas CFBC produces \$13/t steam. These costs are calculated on conservative figures and steam costs may slightly be less also. These estimates include the cost of coal, limestone, ash storage and handling equipment, feed water

treatment plant, boiler cost, dust collecting device, economizer, FD and ID fan, gas analyzer and pulse-jet bag-house filter system. AFBC boiler (50 t/h steam) along with cogeneration facility (topping turbine) generates about 3700 kW of electricity (at a net heat rate of less than 6500 Btu/kWh, over 50% thermal efficiency) i.e., more than conventional electric utility system with steam turbine of overall efficiency maximum 38%. The CFBC unit (125 t/h steam capacity) generates approx. 11,600 kW of electricity (at a net heat rate of 6000 Btu/kWh), i.e., over 55% thermal efficiency, because of higher steam pressure). In all cases, cost of the coal is the largest component in annual operating cost. Steam cost varies linearly with fuel cost. Boiler capital cost (i.e. capacity of the boiler) and operating cost varies exponentially (Fig. 6.37).

6.6.1 Pressurized fluid-bed combustion (PFBC)

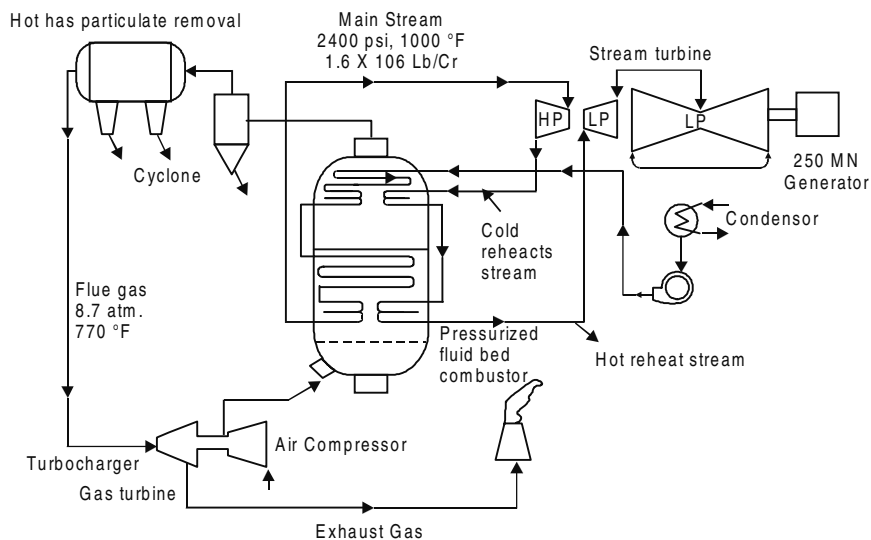
As the name implies, this is another version of FBC where pressure inside the reactor has been increased, as a result, due to higher concentration of oxygen available per unit volume, the reaction rate (and hence capacity of the boiler) increases. From economic point of view, interest in pressurized fluid bed combustor is based on the recognition that as combustion pressure is increased, the size of the combustor is decreased, as is the heat transfer surface requirement, thus reducing investment cost. Also above combustion pressure of 4 to 6 atm, a gas turbine can be driven by the combustion gases to compress the combustion air and generate electric power. The bed cooling surface can be steam cooled, resulting in a combined steam-gas turbine cycle, or the bed cooling surface can be closed, gas-cooled loop (He-air-CO₂). The desired result is to obtain improved power generation efficiencies. In a pressurized combustor the Ca/S mole ratio required for sulfur capture was less and than that had been found in ambient pressure combustor and the emission of NO_x was even less than that found in ambient pressure systems. Bed sulfur capture by dolomite in pressurized combustor has been found to be superior to that by limestone because with limestone (CaCO₃) the calcination reactions do not precede at temperature levels of 750–850°C and several atmospheric pressure. With dolomite (CaCO₃, MgCO₃), however, endothermic decomposition and half calcinations occur at temperature several hundred degrees lower than calcinations for CaCO₃, even at higher pressure. Thus PFBC-boiler burns coal in a fluidized bed of dolomitic limestone, operating at 6–16 times ambient pressure. When compared to AFBC, PFBC has several additional advantages like-compact boiler system, shop floor fabrication of boiler, modular technology, reduced construction time, economical in small size, higher thermal efficiency. Yet development of PFBC had been slow because of the following reasons. Pressure in the vessel with high temperature

requires development of special grade metal in order to prevent corrosion. Outlet valves are especially susceptible to erosion and the gas requires high temperature elaborate cleaning process which is difficult. Operation at elevated pressures reduces the size of the combustor and improves SO₂ capture relative to an AFBC. The compact combustor size will make it possible to shop fabricate the steam generator and other modules in factory in sizes up to about 250 MW, which improves quality control, reduces erection time and final cost, and provides the capability of rapidly installing small increments of capacity or converting oil-fired plants to coal. The smaller unit size increases the flexibility and reduces the risk of adding capacity to meet uncertain futures and other costs of new capacity. These two factors were found after evaluation that the benefits of modular technologies such as PFBC are worth a capital cost premium of about 25%. Several conceptual designs have been developed for commercial PFBC power plant. Although further development work is necessary to define the preferred configuration all concepts include a high temperature particulate removal system (cyclones or cyclone/filter combination) that cleans the flue gas before it is expanded through a gas turbine. In the combined cycle design (Fig. 6.33), the flue gas from the PFBC boiler enters the hot gas clean-up system at about 1600°F. After passing through the hot gas clean-up system and expanding in the gas turbine generator, the flue gas passes through a heat recovery steam-generator and conventional bag-house or ESP filter. Steam generated by the generator and PFBC-combustor drives a conventional steam-turbine generator. In this configuration, 2/3 rd

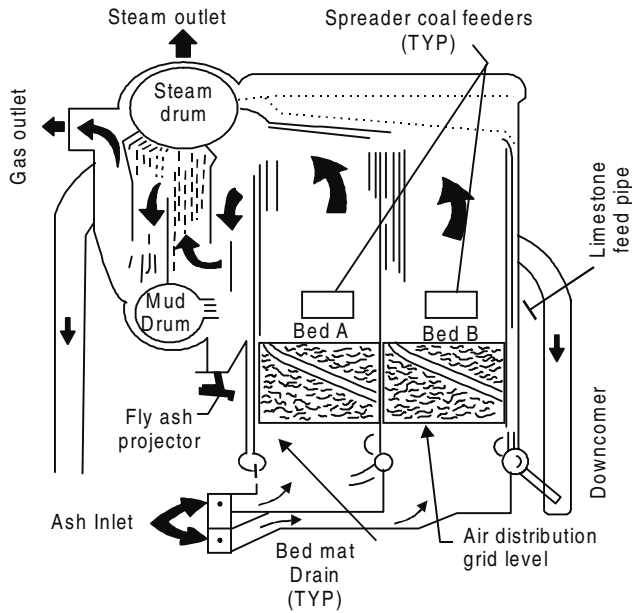


6.33 Conventional PFBC combined cycle.

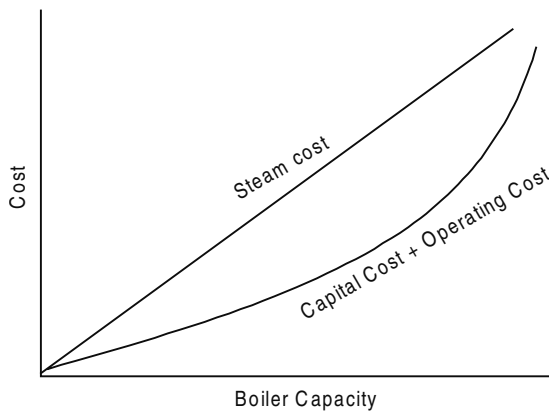
to 3/4th of the energy output is generated by the steam turbine. Although more complex than AFBC or conventional PC-plant, the PFBC/combined-cycle configuration has a higher overall thermal efficiency. A key PFBC technical issue is the design and performance of the high temperature particulate removal system and the reliability of the down-stream gas-turbine. In the combined cycle configuration, the particulate removal system must operate reliably at 1600°F and remove sufficient particulate to protect the gas turbine. Because the 1600°F operating temperature of the hot gas clean-up system is beyond the ability of today's technology to meet the EPA particulate standard, a second clean-up system is needed after the turbine which increases the complexity and cost of the system. As a result, EPRI is currently examining a simplified "PFBC configuration called PFBC turbocharged boiler" (see Fig. 6.34). Additional steam is generated in the combustor to reduce the flue gas temperature to about 800°F, which greatly reduces the technical problems in the hot gas clean-up device, the hot gas piping and the gas turbine, allows existing hot gas clean-up technology to be used. In addition, the gas turbine only produces sufficient power to run the air compressor and is decoupled from the synchronous electric generation system, which simplifies the control system. Because the technical risks are reduced and the system is simpler relative to PFBC-combined cycle, the PFBC turbo-charged boiler could become commercially available earlier to respond to the needs of the industry. Currently, PFBC pilot plant facilities are located at the International Energy Agency facility in Grimethorpe, U.K. and the DOE



6.34 PFBC Turbo-charged boiler.



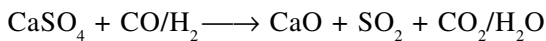
6.35 MW shallow FBC boiler (CRE, UK).



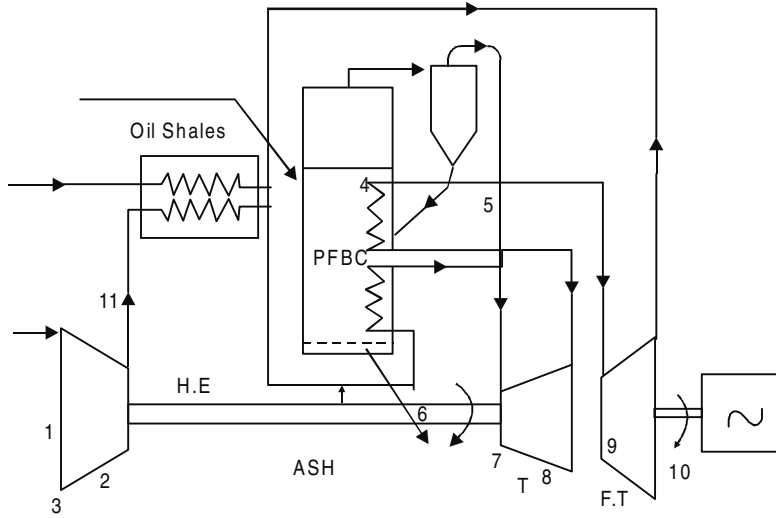
6.36 Variation of total cost of FBC boiler and steam cost with boiler size.

Curfiss-Wright Facility at New Jersey, USA. The later facility has a combined cycle configuration but so far has not been operated. The next logical step is to construct a prototype PFBC/turbo-charged boiler, most likely to repower an existing oil or gas fired plant. Due to complexity of the process, commercialization of PFBC/combined cycle configuration will occur late. For high sulfur coals the PFBC technology operates at about 1.8:1 Ca/S ratio (molar). The AFBC and PFBC boiler costs are not sensitive

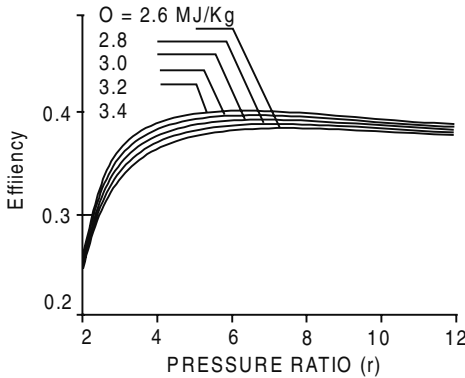
to fuel quality as the pulverized coal (PC) boiler. Y, Levy (Israel Inst. Of Tech, Haifa, Israel) in 1988 reported (J. Inst of Energy, Sept. 1988) application of PFBC for gas turbine operation using oil shales. Due to the fact that shales in Israel occur far away from any large cooling water reservoir, a Brayton cycle (which includes only gas turbine) with reheat and heat exchangers were found to be an economically viable proposition for electric power generation. A Brayton cycle has the additional advantage of not needing to have the heat exchanger installed within the bed (required for steam generation), as this is likely to suffer badly from erosion. In this PFBC boiler, the special technique adopted was to improvise mechanism for removal of large ash from flue gas and bed (ash is 60 to 80 times more than that for coal fired PFBC). Thermal efficiency value in the range 30% obtained. This relatively large value indicates the potential of using this technique commercially. Figures 6.37–6.40 show schematics of the Brayton cycle the PFBC boiler, ash recovery system and the PFBC set-up. Variation of cycle efficiency with calorific value of the shales are shown in Fig. 6.38. Schulte et al (Bergbau-Forschung GmbH, Essen, Germany) in 1987 reported in International Coal Conf. That pressure has a marked effect on ignition temperature and burning time (changing almost exponentially) and increasing pressure also inhibits the swelling of the particles which leads to smaller values for external surface here the heterogeneous reaction with oxygen takes place. PFBC system the spent lime (CaSO_4) can be regenerated at about 1100°C as per following reaction:



Sulfur-dioxide in the regenerator off-gas is at a sufficiently high concentration to be recovered as sulfur in a by-product plant. PFBC has been more attractive in power generation than AFBC for the simple fact that pressure energy available in the off-gas can be utilized by expanding through a gas turbine which drives the air compressor and also generates power. The combination of steam turbine, driven by steam raised in heat exchange tubes in the bed and gas turbine driven by the off-gas, gives rise to an increased efficiency in power generation. As the combustion rate increases with increased in proportion to pressure and the bed is consequently deeper in order to submerge the extra tubes. Pressure has no significant effect on heat transfer characteristics in the bed or on combustion efficiency. Typically a 2 m diameter pressure shell burns 500 kg of coal per hour at a pressure up to 6 bar. The off-gases after cleaning passes at the speed of 125 m/s to a cascade gas turbine. The dust burden in such cases is generally about 200 ppm and most of the dust is less than 20 micro-meter in size. Sulfur retention may also be achieved at the elevated pressure where it is preferable to add dolomite rather than limestone (reasons explained earlier). Emission of NOx in PFBC is still lower than



6.37 Schematics of Brayton cycle with reheat and heat exchanger incorporation a PFBC.



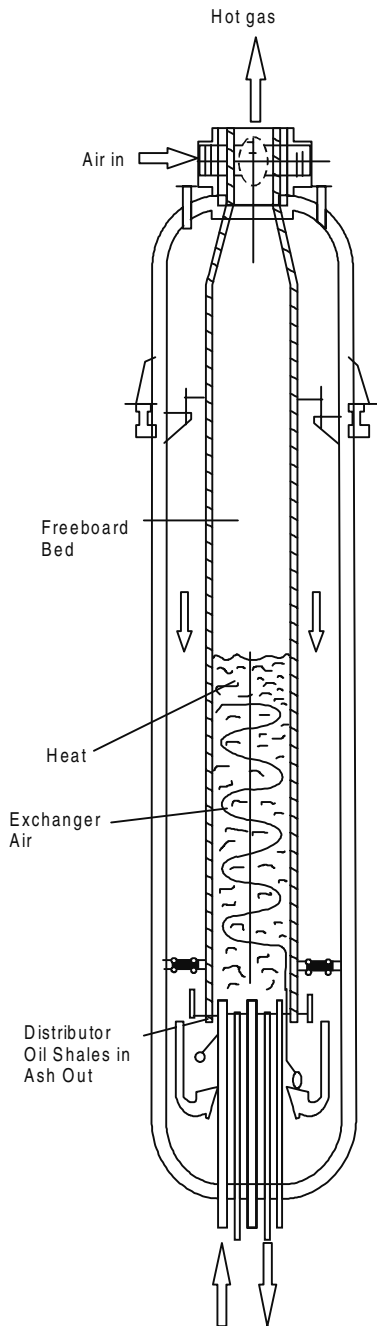
6.38 Variation cycle efficiency with the effective calorific value of the oil shales.

AFBC. Cost comparison of different coal burning systems with that of PFBC are shown in Table 6.7 (1984 price line):

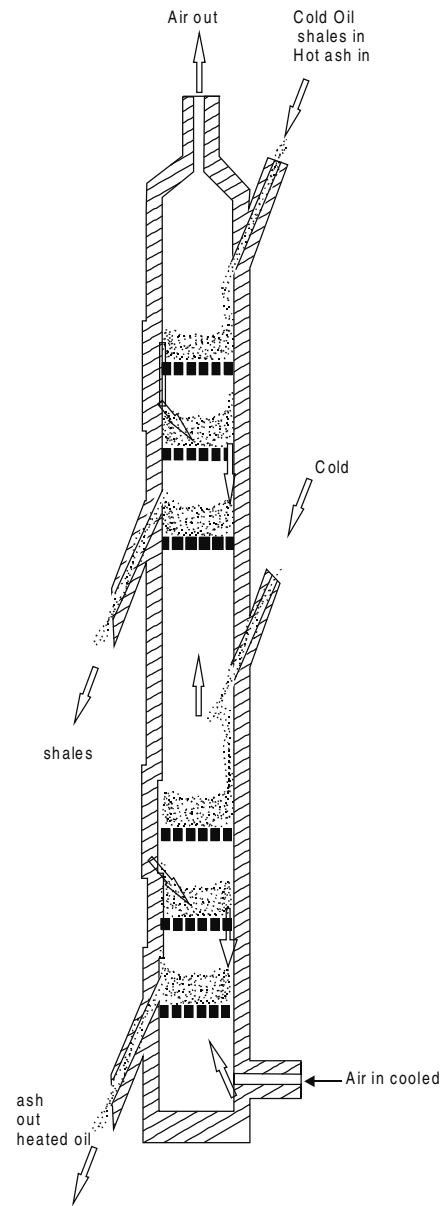
On the basis of above figures, it seems that AFBC will be advantageous if interest rates are high and fuel costs are low. In circumstances where interest rates are low and fuel costs are high, PFBC will be preferable.

6.6.2 Circulating fluidized bed technology

The operating velocity range of circulating fluidized bed boiler (CFBC) is much higher and distinct than bubbling fluidized bed or AFBC. The



6.39 Schematics of a typical PFBC.

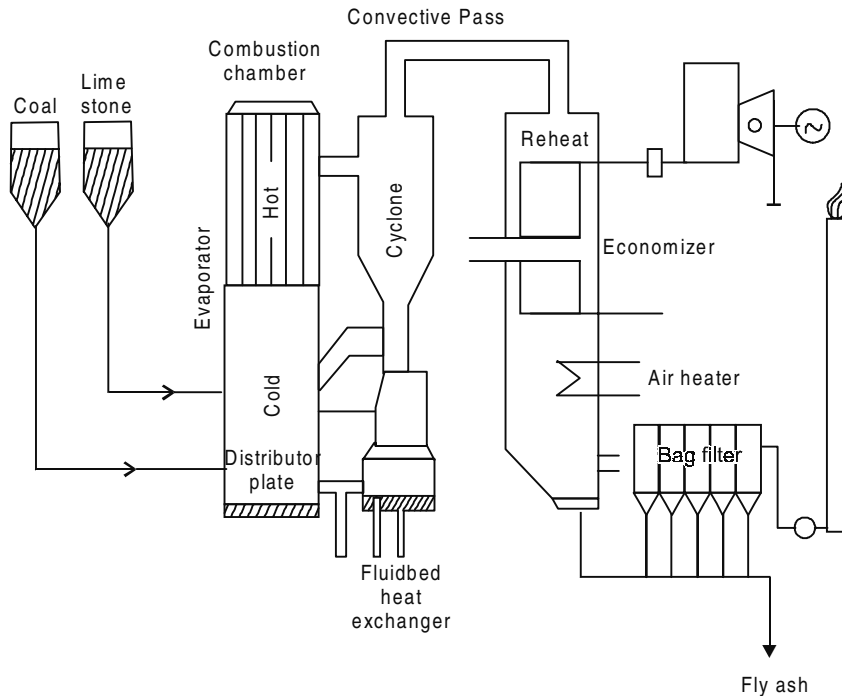


6.40 Schematics of ash recovery systems.

Table 6.7 Comparative costs of PC, AFBC & PFBC boilers

	Capital cost (\$/KW)	Efficiency (%)
Pulverised fuel burner (PC)	620	36.2
AFBC	632	35.8
PFBC	723	39.2

reason behind evolution of CFBC technology lies in the effort to overcome some of the inherent problems of AFBC, like – the later has relatively low combustion efficiency, low utilization of sorbents, difficulty in turn-down, etc. In AFBC, the specific thermal load per unit cross-sectional area of the combustor is limited to 1.4 MW/m² for the low volatile coal in order to maintain high combustion efficiency under the staged air firing for NO_x emission control. The maximum gas velocity in bed used in CFBC ranges from 6 to 8 m/s, corresponding to maximum thermal output per unit cross section of furnace to be 3–5 MW/m². In such combustor the fraction of heat recovered at the convection pass ranges from 30 to 40% and the major part of heat is recovered either through the furnace wall or by the external fluidized bed heat exchanger. Because of high gas velocity, the conventional in-bed heat transfer tubes are not employed in CFBC, the ratio between the heating surface in the combustor wall and the combustor volume is reduced with increased unit capacity. Accordingly, the scale-up of the boiler requires the installation of increased heat transfer area by use of either external fluidized bed heat exchanger or recently developed erosion resistant tubes (bundles) hanging within the furnace. Another advantage of CFBC is relative ease of fuel feeding (it can take any type fuel) and in case of high sulfur coal the consumption of limestone is cut to almost 1/3rd of that of AFBC. A schematic drawing of CFBC system is shown in Fig. 6.41. The first commercial CFBC-boiler was installed by Ahlstrom in its own board mill in Pihlava, Finland, with a steam capacity of 20 t/h. Since then Ahlstrom and Pyro-power, its US subsidiary, have put up 18 additional boilers, the largest of which produces 120 t/h steam. Colorado-Ute Electric Association is testing a 420 t/h (steam) CFBC unit to generate 110 MW (e) of electricity. Lurgi has put up a 270 t/h (steam) CFBC unit at Stadwerje Duisburg to generate 96 MW (e). In USA, Lurgi is collaborating with combustion engineering to put up CFBC boiler. The plant in Lunen, West-Germany, supplies process heat in the form of molten salt to Vereinitge Aluminium Werks, for generating high pressure steam for electricity generation. The thermal capacity of the facility is 84 MW(th) or about 110 t/h of steam. Sudvik Energiteknik of Sweden in collaboration with Babcock and Wilcox (USA) put up eight CFBC boilers in the range of 100 t/h of steam capacity. In USA, Strutters Wills Corporation and Riley Stoker Corporation, under license from Battelle Corporation sells CFBC boilers from 23 t/h to 70 t/h steam capacity. Keeler Dorr Oliver, also in



6.41 Lurgi type circulating fluidized bed boiler schematic of total system.

USA, has sold CFBC units of 193 t/h and 217 t/h steam capacity similar to Ahlstrom design. Babcock Power Ltd. (U.K.) and Multi fuel Boiler (their affiliated company in USA) are selling solid circulation boiler of the size 110 t/h steam capacity. In India both Isgec Thomson and BHEL has got into the market of CFBC. Theoretical back-up work and pilot plant trials are being conducted by IIT, Kharagpur (in association with Technical University of Nova Scotia, Canada), CMERI (Durgapur), CFRI (Dhanbad), and RRL-Jorhat. General advantages of a CFBC system are as follows (compares other FBC's):

- (a) *Fuel flexibility* – any carbonaceous material like tree bark, wood, peat, petroleum discards, etc., can be utilized.
- (b) *High combustion efficiency* – superior mixing capability & large reaction space enables CFBC attain a combustion efficiency over 98% in all commercial boilers.
- (c) *Efficient sulfur removal* – better contact & long residence time brings about good desulfurization at a lower Ca/S ratio.
- (d) Low NO_x emission (100–300 ppm).
- (e) Similar fuel handling & feeding system – requires one or few feed points.

- (f) High heat release rate – at a velocity of 6–8 m/s, causes high heat release rate of the order of 5 MW (th) /m² and requires small floor area.
- (g) *Capability for a good turn-down and load following* – the relatively high fluidizing velocity and the use of staged combustion permit a fairly good turndown ratio by simply reducing proportionately the amounts of the fuel and air. Gotaverken, Lurgi and Ahlstrom report turn-down in the range 3–4:1. Ahlstrom also reported operating its Kemira-Oy boiler in Finland, continuously for 2 months at 15–20% of the load, CFBC boiler is capable of responding to quick load changes and can accommodate rapid increase in steam demand by virtue of the large amount of heat stored in its solids. Gotaverken reports a load following capability of 4% per minute in its Avesta plant. Ahlstrom claims that 50% change within 3 min have been demonstrated in their plant.
- (h) *High availability* – figures in excess of 90% being quoted by most of the manufacturers. TVA (USA) at present going up to 500 MW(e) unit. AFBC has certain advantage below 30 MW(e) capacity. CFBC seems economically better off beyond 60 MW(e). Suitability of CFBC beyond 150 MW(e) is yet to be ascertained. Other areas of CFBC application are ore calcinations, dry scrubbing of power plant waste gases, etc. High slip velocity (up to 10 time free falling velocity) is used in such application. Because of high specific surface (10 times higher for a 0.1 mm particle than for 1 mm diameter particle used in AFBC), no reliable method is available today to calculate heat and mass transfer coefficients. However, orders of magnitude of these parameters can be accessed from the relevant equation for a single particle.

$$N_{up} = (h_{pd}p/l_g) = 2 + 0.6 Pr^{1/3} Re^{1/2}p$$

$$Sh_p = (B_{pd}p)/D = 2 + 0.6 Sc^{1/3} Re^{1/2}p$$

Heat and mass transfer coefficient are positively influenced by a high Reynolds number:

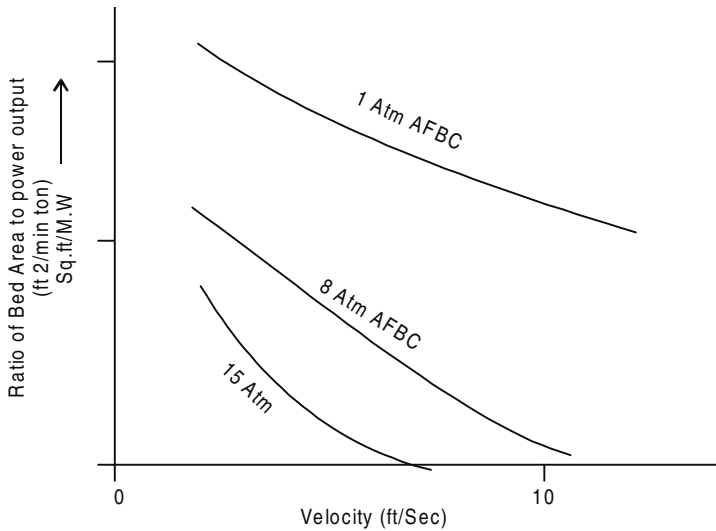
$$Re_p = (U_g \cdot dp)/\nu$$

which is formed with the relative velocity U_g between gas and particle. The optimum regimes of circulating fluid-bed reactors are found in the boundary between fluidized bed and transport conditions at low Archimedes Number (Ar less than 100). Furusawa and Shimizu (University of Tokyo, Japan) has shown (second Intl. Conf. On CFBC, March 1985) relationship between combustor height required for heat transfer and thermal output. The average heat transfer coefficient 200–250 W/m² °K

was estimated from both the capacity and the combustor height by conceptual design of 500 MW (e) plant (110 Mwe, Colorado plant, 1987). This value is much larger than that reported by Stromberg (1982), $100 \text{ W/m}^2\text{K}$. This strongly suggests that the heat transfer was enhanced by either the layer of falling solids close to the wall or the increased concentration of solids in the lower part of the bed. The heat recovery of CFBC can be characterized by the positive control of heat transfer rate through the wall. Both the longitudinal concentration profile of solids and concentration of solids in the vicinity of the wall can be controlled adjusting the amount of primary and secondary air. The objectives of air staging can be considered not only to modify the combustion for NO_x reduction but to control positively the heat transfer rate corresponding to the change of load. Staged supply of air also results in reduction of power consumption, by form. Thus the concentration of solids within the furnace must be controlled not only for the combustion and sulfur retention but also for heat transfer. The inert solids employed for the combustion of fuels with ash or low sulfur contents can be considered as heat transfer promoters dependent on the relative importance of external circulation rate of solids through cyclone and internal circulation rate (back-mixing) of solids. (see Fig. 6.42) Reduction in particle size of sorbents for effective sulfur retention results in enhanced external circulation rate of solids. Combustion of char does not always requires the external circulation, namely sufficient residence time required for complete combustion of char can be achieved by internal circulation of char. The optimal rates and the relative importance of external and internal circulation rates of solids must be determined taking account of sulfur retention, carbon bur-up and heat transfer. The effect of reduced circulation rate of solids on heat transfer and emission controls of SO_2 and NO_x should be intensively investigated. It may be noted here that the hydrodynamic properties of CFBC (i.e. concentration and circulation rate of solids and supply of air), differs significantly from those of fast fluidized bed concept. In some cases, in order to increase heat transfer area, external fluidized bed heat exchanger (FBHE) has been installed which required smooth circulation of controlled solids between combustion chamber and FBHE. Heat recovered from FBHE reported to range from 16 to 52% of the total recovered heat. Circulation of solids required to realize desired heat transfer rate reported by Kobro (1985) to be $10\text{--}15 \text{ kg/m}^2\text{S}$. This rate corresponds to approximately, 100 times the fuel feed rate. This solid circulation rate is much smaller than that used for "fast bed" (e.g. up to $200 \text{ kg/m}^2\text{S}$).

6.7 Cyclone furnace

A cyclone furnace is an efficient system of energy generation using high



6.42 Ratio of bed area to power output versus fluidizing velocity in fluidized bed combustion.

ash coal. Compared to conventional pulverized coal fired furnace, a cyclone furnace has the advantage of operational flexibility with respect to coal size (no fine grinding is necessary), ash content, and moisture content. Such a furnace can also achieve high combustion intensively, temperatures in the range of 1600–2000°C and handling of ash in the form of molten slag. Cyclone furnace has wide range of application as supplier of high temperature heat and in many cases can be used as a substitute for oil firing system. With time its importance is gaining ground as the source of coking coal is fast depleting. R. R. L. (Bhubaneswar) set up an experimental unit of 100 kg/h coal burning capacity with medium and high ash coal, and achieved a temperature of 1800–2000°C and satisfactory slagging condition for high ash coal (ash about 30%), where the silica ratio was as high as 80%. Heat loss through the molten slag is limited to the range 2–4% of heat input. The pilot plant study (1 t/h capacity) envisaged at Orissa Industries, Barang (near Bhubaneswar) for firing chamber kiln for the manufacture of refractory bricks, currently uses coal with 40% fine where the ash content vary 15–25% to generate sufficient heat for firing the bricks. These fines have no market at present and thus can be effectively used by cyclone furnace either under slagging (high temp) or non-slagging (moderate temp) conditions. A cyclone furnace of 1 t/h coal burning capacity will generate around 4.5×10^6 kcal/h heat (CV of coal taken as 5000 kcal/kg) heat loss in the furnace assumed to be 10%. The generate the same amount of heat; an oil firing system will need a capacity of around 500 l/h. The capital cost of the oil firing system would be in the range of

Rs. 3 lakh, whereas the same for cyclone system is around Rs. 15 lakh. A comparison of operating cost for both the system (with assumption of operating-h/year as 6000 h) is shown in Table 6.8.

The cyclone (1 t/h) since produces 4.5×10^6 kcal/h heat, then the cost of heat generation – $(65.5 \times 10^5)/(600 \times 5.23) = 209$ Rs/kWh

Same for oil-firing system = $(182 \times 10^5) / (600 \times 5.23) =$ Rs. 580/kWh

Thus saving by replacing oil-firing by cyclone-furnace is = $(580 - 290) / (580) \times 100 = 64\%$.

Note in these calculations, cost of coal is taken as Rs. 1000/t which includes the transportation as well as grinding charges; and cost of fuel oil per 1000 l is taken as Rs. 6000/-.

6.8 Coal carbonization

General effect of heat on coal has been discussed earlier with respect to DTA and TGA studies. Application of these results in commercial scale, i.e. coal carbonization at low and high temperature will be discussed in detail in this section. First we should note that results and products of carbonization not only depends on quality of coal but also on the rate of heating, mode of heating (e.g., fixed bed, fluidized bed or entrained bed) and the range of carbonization temperature. Accordingly, we will discuss the subject in following sequence:

- (a) Fixed bed carbonization (like beehive coke-ovens).
- (b) Fluidized or entrained bed carbonization.

Table 6.8 Comparative costs of Cyclone & Oil burning (Rupees, lakh)

	Cyclone	Oil burning
Interest on capital (at a rate 10%)	1.5	0.3
Depreciation (@10%, annually)	1.5	0.3
Labour cost	2.5	1.4
Fuel cost	60	180
Total operating cost	65.5	182

Table 6.9 Capital cost break-up of a cyclone furnace

Cyclone chamber and components	Rs. 4.5 lakh	
Ignition burner with accessories	2.0	
2 air-blowers	2.0	
1 air compressor	1.0	
Coal grinding & handling-feeding system	1.5	Total Capital Cost = Rs. 20 lakh
Air pre-heating system	4.0	
Instrumentation & control of flow, temperature sensors & gas analysers	3.0	
Erection charge	2.0	

- (c) Low temperature carbonization (i.e. carbonization up to 650°C).
- (d) High temperature carbonization (i.e. carbonization up to 1100°C).
- (e) Flash pyrolysis (fast heating of coal).
- (f) Products of coal carbonization.

At the end we will discuss economics of various above carbonization routes. But before we go to the technicalities of coal carbonization, let us look at the benefits of coal carbonization first. By now we know that thermal energy causes scission of hydroaromatic and aliphatic structure of coal from its aromatic counterpart and the resultant breakdown products according to their boiling range forms gas, liquor or tar. The last product tar, if further distilled at 360°C, leaves behind a thick viscous product known as pitch. So when we talk of carbonization products we mean all above products and the solid residue left in the distilling retort known as coke. Both cement plant and steel industries heavily depend upon these cokes for their production. While the former depends (especially where vertical shaft kilns are used) on powdered coke the latter industries depend upon lump coke generated through temperature carbonization. Carbonization at different temperatures leaves behind different amount of volatile matter in the coke residue and thus there are specific requirements of V.M. content for different uses. More the V.M. in coke, more smoke it will generate during burning. Interestingly North-Eastern coals of India contain very high volatile matter (about 35–40%) and the author has evolved a technique for using these cokes in cement making using VSK-technology despite its high sulfur content. In blast furnace operation the percentage of large size coke must be limited to the minimum, because coke in the large size fraction has less strength and is likely to generate more fines in the blast furnace (thereby changing permeability) ultimately resulting in a situation which is detrimental to its proper functioning. The increase in rate of heating carbonization improves strength of coke as indicated by M10 value and also shifts the softening and resolidification points. Since these latter two properties do not increase to the same extent, there is usually a widening of plastic temperature range. Rapid heating also causes internal stresses and thereby formation of fissures in the lump leading to production of smaller size cokes. With decrease in mean-size the resistance of coke to abrasion as represented by M 10 value is improved although there is slight reduction in M10 value. In our country, of the 140 million tons of coal mined annually, about 23 million tons is used for manufacturing metallurgical coke and gas. The tar generated in the process (called “coke-oven batteries”) is estimated around 0.4 million tons per annum. Unfortunately until recently most of these tars are not processed for chemicals but rather burnt in the steel plant as fuel. This is a tremendous loss of revenue for our country indeed. As a statistical comparison, we

may note that while in India 90% of the tar at present is burnt the same only 25% is burnt as fuel in other countries and rest processed for valuable chemicals. Recently set up "Dankuni Coal Complex" in West-Bengal (near Janai Road railway station) has taken a giant step towards this valuable saving. Dankuni Coal Complex (Coal India Ltd.) has already started producing some high value chemicals, like xylenol, meta-para-cresol, o-cresol, and phenol from tar. Tar produced from non-coking coal by subjecting it to a process of destructive distillation in medium temperature retort. Above chemicals extracted from tar are sold as base chemicals to industries manufacturing polymers, bakelite, laminates, resins, plasticizers, pharmaceuticals, disinfectants, tanning chemicals, electrical insulations, wire enameling, etc. Phenols and cresols are produced in India only by synthetic process from other chemicals such as benzene and toluene. Xylenol produced by Dankuni Coal Complex is 92% pure (with less than 1% neutral oil contamination) and purity of meta-para cresol is also 92%, with as high as 49% meta isomer and less than 1% neutral oil. In India due to dwindling source of good coking coal, prime coking coals are being increasingly imported from Australia and other countries. Coals of N-E region have high caking index and blending 10–15% of these coals with non-coking variety as tested by Bhilai Steel Plant, produces good coke and sulfur also comes within limit. "Formed-coke" technology with non-coking coal also useful proved in such case. Durgapur Project Limited, West-Bengal, have five coke oven battery for supplying 50,000 m³ of gas everyday to the city and private sector (the price tag for the gas is Rs. 3 per therm). The gas is also supplied to DVC for power generation (15 MW). Gas generated by similar means also is utilized by fertilizer plants in India at Ramagundum, Talcher, Sindri and Gorakhpur (all belonging to F.C.I.) for production of urea. The Ramagundam plant at Andhra Pradesh broke even in 1985–86 and established and Talcher plants were commissioned in 1980 based on coal technology (K-T gasification route) and abroad there is only one such plant in South Africa (Moderfontein) employing this process, which took 7 years to stabilize at 80% capacity utilization. The latest of carbonization plant (LTC type) Dankuni Coal Complex, in West-Bengal as mentioned above, was installed on 29th December, 1981. The project was completed in association with Babcock-Woodall-Duckham Ltd. (Crawley, Sussex, UK) by Coal India Ltd. Other Indian counterparts who helped executing the project is Heavy Engineering Corporation, Ranchi. HEC hooked up with Chemical and Thermal Engg. Ltd. (UK) for constructing coal in tar distillation. The project came to full operation in 1985. In this plant non-coking coal is carbonized in continuous vertical retort. Coke inside the retort is quenched by steam/water injection system. Steam reacts with coke to generate water gas which when mixed with carbonizing gas increases the gaseous thermal output. The plant carbonized

1500 t of non-coking coal brought from Raniganj collieries and carbonized in 100 continuous vertical retort. Following are the outputs of this plant.

Domestic coke (tones/year)	=	351,450
Town gas (million/day)	=	18–20
Tar products (tones/year):		
	Oil various grade	= 13,000
	Pitch	= 11,073
	Phenol	= 434
	D-cresol	= 189
	M, P – cresol	= 402
	Xylenol	= 603
	H.B.T.A	= 520
Other products (tons/year):		
	Ammonium sulfate	= 5,500
	Sulfur	= 580
	Calcium carbonate	= 5620
	Coal fines	= 83,780

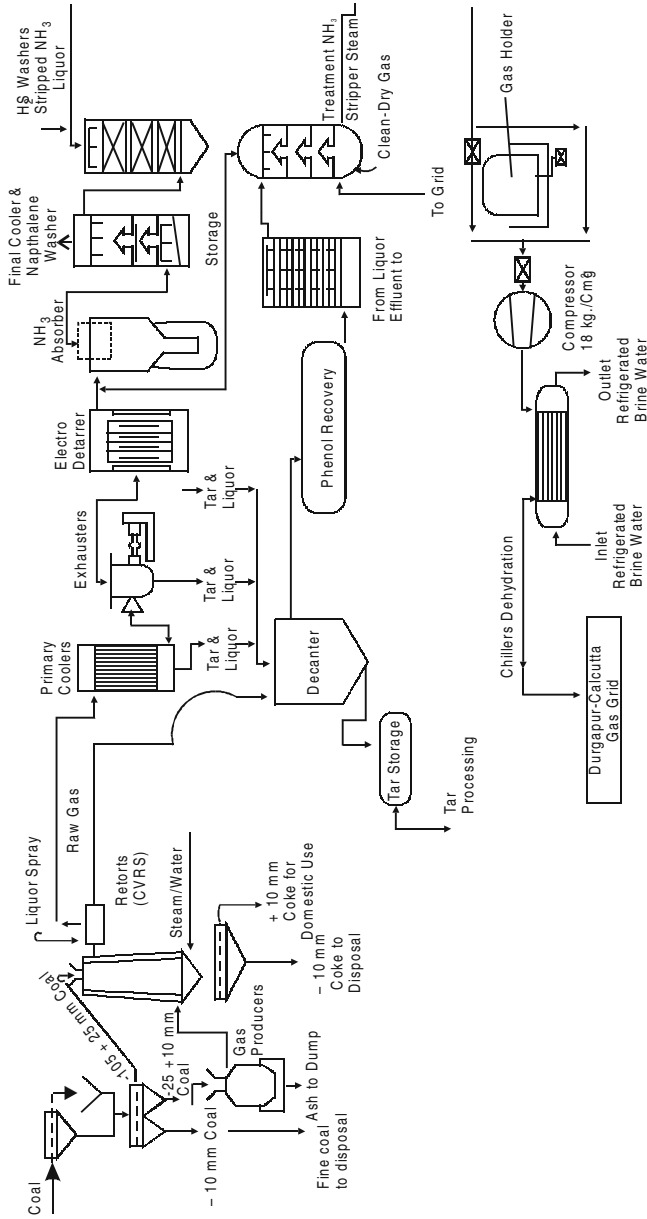
Coke and gas (twin fuel) is dispatched to Calcutta for use in the domestic and industrial sector. The project provides substitution of oil to the tune of Rs. 30 crore per year (at present rate) and open up many ancillary industries like salicylic acid, aspirin, paracetamol, phenol–formaldehyde resin, phenyl, insecticides, carbon-black (from oil/pitch), etc. Another such plant is likely to come up in Kanpur soon. A low temperature carbonization plant (Lurgi-Spuelgas retort) was set up in 1965 at Neyveli Lignite Corporation, Tamil Nadu, which has an installed capacity for carbonizing 768,000 t of lignite from South Arcot district every year. But due to short supply of lignite from mines, the plant operates at 25% capacity. Another LTC plant is operation at present (commissioned in 1979) is at Ramakrishnapuram (Singareni coalfields, UP) Installed capacity of this plant is 900 t/day of non-coking coal. It produces 50 t of tar/day. This plant was made with IICT, Hyderabad (a CSIR Laboratory) know-how. Similarly, about 16 million tons of coal is carbonized annually in India in various “high temperature carbonization” plants (coke oven batteries) to produce about 400,000 tons of tar annually. These are situated at various steel plant complexes in India. Places where distillation of tar facility exists indicated below along with their installed capacities (Table 6.10).

Besides these, there are two small units in private sector – Synthetic Asphalts, Bombay and Lloyd Bitumen, Madras and Lloyd Tar Products, Bhilai. Width of these coke ovens are generally 14 in, 16 in, or 18 in (18 in is also the international standard). The ovens are generally 7–15 ft high and carbonization time 18 h. In such carbonization unit, bed thickness is important for tar yield (temperature has no effect on this parameter). High temperature carbonization processes produce a low reactivity coke reflecting itself in slow rate of change in its combustion then a peak demand

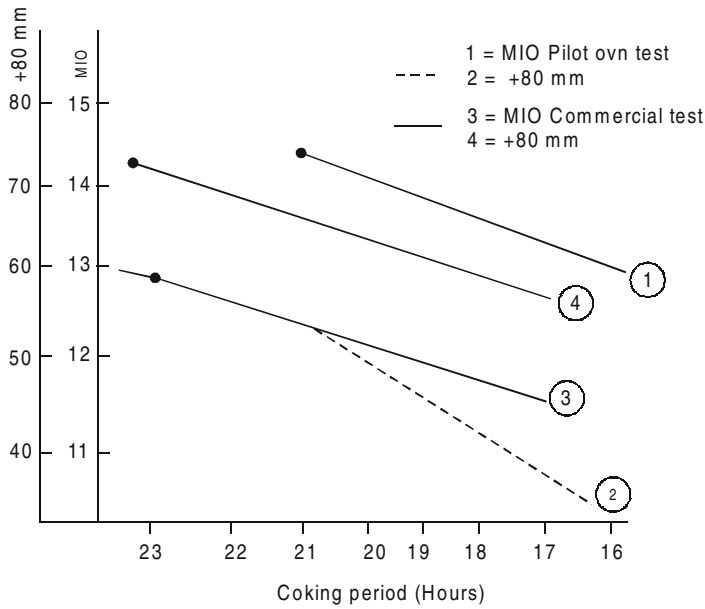
Table 6.10 Various tar processing plants in India

Name of the plant	Location	Capacity
Bokaro steel plant	Bihar	450 ton /day
Bhilai steel plant	Madhya Pradesh	350 ton /day
Rourkela steel plant	Orissa	300 ton /day
Durgapur steel plant	W-Bengal	200 ton /day
Durgapur Projects Ltd.	W-Bengal	100 ton /day
Shalimar Tar Products	Bihar	100 ton /day
Barare coke oven plant	Bihar	20 ton /day
Entracost Pvt. Ltd.	Bihar	13 ton /day

has to be met. The product of the low temp carbonization processes, the smokeless coke, has a high rate of reactivity and this coke is still used in central heating plant where the rate of change in load is not rapid. Town gas, the product of HTC and LTC, is still used mostly within the manufacturing area, e.g., steel works and any sulfur produced is used in related industries. The LTC unit mentioned above, at Hyderabad is of Lurgi-Spelgas type having a throughput of 25 t of coal per day and was set up in 1954. There are some coals at Madhya Pradesh and Maharashtra which disintegrate during carbonization forming coke fines below 1.3 cm size (about 25%). These coke breezes can be used in newly developed VSK method of cement making. For production of steel, the coals are selected on the basis of low sulfur and phosphorus. Coals of Raniganj have been found to contain high phosphorus while that of M.P. are high in both sulfur and phosphorus. Coals obtained from lower seams of Talcher mines, Orissa, have comparatively low ash as well as low phosphorus and sulfur, thus making it suitable for ferro-alloy making. It has been observed that increasing rate of heating during carbonization, improves strength of the coke as indicated by its M10 value (see Fig. 6.44) According to ISM norm, metallurgical cokes (especially those meant for steel plant) should have a maximum sulfur content of 0.70%. Tests conducted by CFRI, Dhanbad with 4% sulfur Makum coal blended with 30% medium coking Raniganj coal and 10–15% non-coking Jharia coal, resulted in good coke with maximum tolerable 1% S and good coking property. The acceptance of slightly higher sulfur limit and economic transportation of Assam coal to eastern steel-plants are, therefore, vital issues for utilization of North-Eastern coals of India Various coal carbonization data has been utilized by Mazumder (ref: Fuel, London) as a tool for indirect determination route for coal structure determination. For example, he has shown from coal pyrolysis data up to 600°C, that quantitative hydroaromatic content in a coal is directly proportional to the tar and gas yield. Inversely, it was shown that if hydroaromaticity is generated in coal, the extra tar generated is directly proportional to the percent aromatic carbon rendered hydroaromatic. Experiments conducted by the author of this book with



6.43 Flow diagram—Dnarakuni coal complex



6.44 Dependence of quality of coke on coking period.

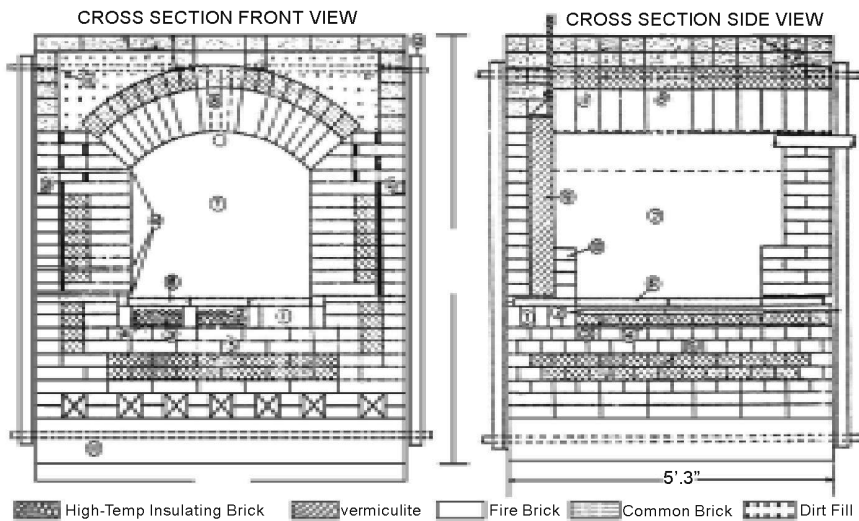
N.E. coals, by pyrolysis with additives like $ZnCl_2$, H_3PO_4 , ethylene-diamine etc has established hydroaromatic and aromatic content quantitatively in these specialty coals. On the other hand at the end of coalification series, anthracite which is almost a bare aromatic skeleton on pyrolysis (carbonization) do not yield any tar but converts to only char. Pyrolysis of chlorinated coals have been found to produce tar which are devoid of chlorine. HCl gas was generated in this experiment with reduced amount of volatile matter indicating that the reagent promotes condensation and molecular growth through elimination of HCl rather than degradation reaction. Additive carbonization has also been used to suppress SO_2 emission from high sulfur coals during free burning. In this regard NH_3 gas has been found effective in controlling above toxic emission. Sulfur in the coal was reduced after carbonization from 75% to 27% of initial sulfur. Carbonization of high sulfur coal $MgCO_3$, CaO , Al_2O_3 , NH_4Cl , $CuCl$, crude oil, thiourea, pyridine and aniline, do not reduce sulfur in the resultant coke. Coal carbonization with addition of pitch found to decrease tensile strength in the resultant coke. The blended charges gave (ref: Manual J. Gonzalez-Cimas, Fuel, Vol. 66, Aug and Nov 1987) low porosity coke with low strength, implying change in pore structure and lack of mutual fusibility. Now-a-days non-recovery coke ovens (where the product gas is burnt in-situ, unlike high temperature carbonization with tar recovery) are preferred and in India metallurgical hard coke is produced in by-product coke ovens (mostly located in integrated steel plants). Non-recovery coke

ovens utilizes 80% of its heat content through direct thermal radiation from gases over coal bed and balance 20% goes through exhaust gas, which is passed through cavity in coke oven walls and through under sole level refractory to heat coal indirectly by conduction. In non-recovery coke oven where no external heat is required, heat transfer is in vertical direction as against horizontal direction in case of slot type by-product oven design. Further a non-recovery coke oven operates under negative pressure while conventional high temperature carbonization ovens operate under positive pressure. Non-recovery coke ovens have arch roof and thus heat transfer takes place by radiation from top inside the oven and conduction from the flat bottom. A one lakh thirty thousand tons/year non-recovery coke oven producing 12 MW of power costs around Rs 50 crore under present Indian condition. It may be mentioned here that 85% of the world coke production is utilized for iron making through blast furnace route. Now a days composite materials (like ceramic-metal, ceramic fiber with polymer etc) are used in lining doors, and ceramic fibers for lining roof of non-recovery coke ovens with advantage.

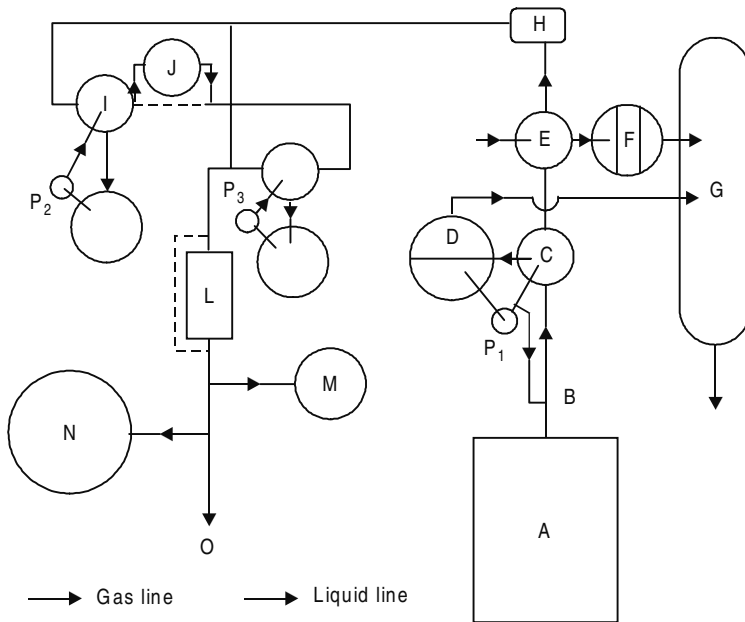
6.8.1 Low temperature carbonization

Low temperature carbonization implies coal carbonization in the range 500–650°C. Carbonization from 700 to 900°C is regarded as medium temperature carbonization, and carbonization above 1000°C is known as high temperature carbonization. Above difference in temperature range leaves behind different range of volatile-matter in the resultant coke. Consequent production of tar and gas also varies accordingly. Higher the volatile matter in the coke, it is easier to burn it in domestic appliances (but then with consequent smoke and long flame of fire). The blending of high and low volatile coal, is a common practice in order to obtain a strong coke, relatively free from shrinkage cracks and a minimum coke breeze. The major industrial use of coke and char produced by LTC technology, for blending with metallurgical coking coal as a substitute for low volatile coals and for gasification for production of synthesis gas for chemical purposes. If the coal is heated rapidly under conditions that prevent decomposition of the primary products, 68 to 87% of the net heat in the raw coal is left in the char and 10–23% of the potential heat appears in the primary tar. Fixed gases represent approximately 2% of the heat and approximately 2% is lost or dissipated in the reactions of decomposition. Depending on the rank of coal, the yield of tar will vary from 0 to 44 gallons per ton; therefore it is important that each coal be carefully considered if it is to be carbonized for industrial use. Because of the possible high value of the tar as a chemical raw materials and because of the smokeless quality as well as high heating value of the coke, LTC has

attracted many researchers attention. Authors own experience with N.E. coal (LTC) has shown that the coke is suitable for cement making by VSK technology. The coals were carbonized in a horizontal retort with external heating system. Frank Reed and Harold Jackman of State Geological Survey, Urbama, Illinois, USA has invented an unique sole heated LTC oven (see Fig. 6.45; Ref: J. of Industrial and Engg Chemistry, 36(4), 1944), whereby 175 kg coal under conditions approaching commercial practice can be carbonized. The oven is also provided with condensing equipment (shown in Fig. 6.46) for recovery of by-products and with apparatus for determining heating value and quantity of gas. The oven is heated by superkanthal wire (electrically) and has a top plate of SiC (which is not cemented) for expansion contraction of the heated surface. Substitution of SiC tile with silica floor tile, reduced the heat gradient across the floor and ensures more even heat distribution. In the operation of a commercial coke oven battery, the heat once attained remained fairly constant and fresh coal is charged into an oven kept at approximately the same temperature at which coke was previously pushed from oven. ##The coal generally gives an initial chilling effect when charged. In all carbonization tests, coking is continued until gas evolution drops to a rate of 10–15 cft/h and the heating value of the gas decreases to approximately 400 Btu/cft. Internally heated carbonizers are suitable for non-coking coals and lignites while externally heated systems are suitable for coking coals. Some processes were also developed based on carbonization of coking coal slacks to produce shaped fuels (like Disco, Coalite process, etc.). Processes were also developed to carbonize sized non-coking coals. With the growing



6.45 Sole-flue coke oven, electrically heated.



6.46 Flow diagram of coke oven and By-product recovery system.

Bacrity of coking coals, processes which could utilize non-coking coals gained ground (like Rexco process in UK, Lurgi-Spelgas in Germany, India, as well as in other countries). The internally heated system gives a comparatively lean gas ($CV=1600-1800$ kcal/m²) and the excess gas is used within the plant for steam raising or in the tar distillation plant. The total heat available as surplus is more or less same in externally and internally heated system. Externally heated LTC process yields a rich gas with calorific value of about 4000–4500 kcal/m². The quantity of gas available after meeting the requirement for carbonization may not be appreciable. A 1500 t/day plant may give about 4 million cft/day of surplus gas. However, it is desirable to have an external source of heat like producer gas for providing the heat required for carbonization and divert the entire gas from LTC for domestic purposes. By this, a 1500 t/day plant may require about 13 million cft gas output per day. Using this gas for domestic purpose is possible only if a network of distribution system exists, as is the case in Bombay and Calcutta. The LTC plants at Calcutta and Bombay using externally heated retorts have been chosen from this consideration. This gas, on account of high hydrogen content (about 46%) can also be used for synthesis purpose. In India only Bombay Gas Co. is employing horizontal retorts coupled with producer gas and water gas plant, for production of town gas. Externally heated processes used for medium caking and coking coals, is similar to the coke oven in the sense that coal

is carbonized in narrow vertical retorts and heat is transferred to the coal across metallic or refractory walls. The retorts are made up of cast-iron or refractories. The internally heated system which is more suited for lignite briquettes and non-coking bituminous coals, involves heat transfer by convection and conduction from hot gases rising through the coal bed and is therefore more efficient. The capacity of individual carbonizer is large. For coking coals that is not suitable. This process uses lumpy coals; while in externally heated processes, coking variety fines or non-coking lumpy coals can be used. While comparing “internally heating” versus “externally heated” we find, in the low temperature carbonization by external heating the limit set to the thickness of charge is well recognized, owing to poor thermal conductivity of coal. Thus the weight of coal which can be carbonized in a static retort heated by outside flue is relatively small. To overcome this limitation for static retorts, some means of internal heating of the charge is required. Internal heating also ensures rapid carbonization. Nayvelli Lignite Corpn’s LTC unit is an example of internally heated unit in India. LTC-coke has been found suitable for both domestic and electro-metallurgical industries. It may be noted that the term retort is used for the chamber used in the manufacture of fuel gas using coal tar and generally classed as either horizontal or vertical. The retorts are characterized by small cross-sectional areas and small coal capacities per charge, as compared with full size metallurgical ovens. Usually 3–16 retorts are grouped symmetrically in a unit called “bench.” Retorts are heated by the combustion of producer gas. Gas is the primary product recovered from the operation of the retort: coal tar and coke are by-products. High volatile coals (v. m. = 30–40%) are generally used to obtain maximum gas yield. The coke from a gas retort plant is unsuitable for metallurgical use and is therefore sold for domestic use or gasified. Govt. of Orissa (through IPICOL) has proposed to set up a plant at Talcher for production of ferro-alloy coke. Internally heated retorts are more suitable for such coke making, as the capacity of the plant is likely to be small and rich gas may not find economical use. In UK a reactive coke named “clean-glow” was produced in the conventional high temperature continuous vertical retort using non-coking coals similar to those available in the Raniganj coal-fields. Gas produced was used as town gas. Thus the concept of production of solid smokeless reactive fuel found a definite shift and selection of the process became more flexible. Operation of retort above 900°C results in decomposition of methane gas and the reaction of methane with water² vapor, which is undesirable from fuel gas quality point of view. It has also been observed that non-coking coals even when carbonized to yield coke having low V.M. (as low as 1.5% in the coke), produces highly reactive coke suitable for domestic and industrial use. Even at a high flue

temperature in the retorts, yield of tar from coals having 30 to 40% V.M. ranged from 6 to 7% (against 2.8% in coke ovens). Gas obtained has calorific value of 4200 kcal/m. The gaseous thermal output was also high (40–50 therm per ton). Till 1960, main interest in LTC was to convert various fractions of tar to motor fuel, aviation fuel, and diesel oil, and coke for generating electric power and for gasification by water-gas reaction. Since low temperature tar is complicated from composition point of view, it did not have any ready market and accordingly it was hydrogenated to make liquid motor fuel earlier. There is no development in the retort design for last three decades. All development in carbonization apparatus now centers around fluid-bed and entrained-bed carbonization. Retort system, whether horizontal or vertical, batch or continuous, are unsuitable for construction of huge capacity units that may be required to achieve the economics of the scale necessary to make synthetic fuel from coal a viable operation. Vertical batch process is generally used for coking (both by direct and indirect heating) and vertical-continuous process (both direct and indirect heating) for non-coking coal. Horizontal continuous process is used for coking once attained remained fairly constant and fresh coal is charged into an oven kept at approximately the same temperature at which coke was previously pushed from oven. The coal generally gives an initial chilling effect when charged. In all carbonization tests, coking is continued until gas evolution drops to a rate of 10–15 cft/h and the heating value of the gas decreases to approximately 400 Btu/cft. Internally heated carbonizers are suitable for non-coking coals and lignites while externally heated systems are suitable for coking coals. Some processes were also developed based on carbonization of coking coal slacks to produce shaped fuels (like Disco, Coalite process, etc.). Processes were also developed to carbonize sized non-coking coals. With the growing scarcity of coking coals, processes which could utilize non-coking coals gained ground (like Rexco process in UK Lurgi-Spielgas in Germany, India, as well as in other countries). The internally heated system gives a comparatively lean gas ($CV = 1600\text{--}1800\text{ kcal/m}^3$) and the excess gas is used within the plant for steam raising or in the tar distillation plant. The total heat available as surplus is more or less same in externally and internally heated system. Externally heated LTC process yields a rich gas with calorific value of about 4000–4500 kcal/m³. The quantity of gas available after meeting the requirement for carbonization may not be appreciable. A 1500 t/day plant may give about 4 million cft/day of surplus gas. However, it is desirable to have an external source of heat like producer gas for providing the heat required for carbonization and divert the entire gas from LTC for domestic purposes. By this, a 1500 t/day plant may require about 13 million cft gas output per day. Using this gas for domestic purpose

is possible only if a network of distribution system exists, as is the case in Bombay and Calcutta. The LTC plants at Calcutta and Bombay using externally heated retorts have been chosen from this consideration. This gas, on account of high hydrogen content (about 46%) can also be used for synthesis purpose. In India only Bombay Gas Co. is employing horizontal retorts coupled with producer gas and water gas. Till 1960, main interest in LTC was to convert various fractions of tar to motor fuel, aviation fuel, and diesel oil, and coke for generating electric power and for gasification by water-gas reaction. Since low temperature tar is complicated from composition point of view, it did not have any ready market and accordingly it was hydrogenated to make liquid motor fuel earlier. There is no development in the retort design for last three decades. All development in carbonization apparatus now centers around fluid-bed and entrained-bed carbonization. Retort system, whether horizontal or vertical, batch or continuous, are unsuitable for construction of huge capacity units that may be required to achieve the economics of the scale necessary to make synthetic fuel from coal a viable operation. Vertical batch process is generally used for coking (both by direct and indirect heating) and vertical-continuous process (both direct and indirect heating) for non-coking coal. Horizontal continuous process is used for coking coals. Highly coking coals are unsuitable for LTC furnace. Generally speaking, coking index in the range 8–10 is the maximum limit for LTC. Very high coking property causes the coal to agglomerate within the shaft of the furnace and stops its downward movement. It is important to note here that pure coal having heating value of less than 500 kcal/Lc are non-agglomerating and as the heating value increases above 3500 kcal/lb, the coal becomes more and more strongly coking. This is an important division of coals, because the higher rank coking type coals are relatively very difficult to carbonize rapidly at low temperature. Generally it has been found that it is difficult to carbonize at low temperature in a fluidized-bed any coal having a heating value over 7100 kcal/kg without excessive recirculation of char or oxidation of coal. On the other hand, it is not difficult to carbonize, the lower rank coals which have no coking property and requires no dilution with char. Rank-wise up to high volatile bituminous coal, are suitable for rapid carbonization in a “fluidized-bed” or “entrained-bed” (at low temperature) and all coals (despite their great variation in physical and chemical property) produce the same quality char having a calorific value of 7000 kcal/kg. Out of some 250 LTC processes developed so far, only the following ones have been commercially successful:

Rexco Process – Rexco is the most commercially successful internally-heated system. In this process, hot gas derived from the incomplete combustion of part of the carbonization gas is used for internal heating. Each retort is filled with lump coal. The top of the charge is ignited and

the volatile product made are drawn through the retort from the top to bottom and passed to a series of condensation and purification train. Part of the clean gas is then returned to the combustion chamber attached to each retort where it is incompletely burnt with air and passed into the top of the retort to continue the carbonization. In Rexco process (a batch process), internal heating takes place by gasifying part of char. But it does not operate mainly by gasifying the charge but a part of the gas made in carbonization being incompletely burnt in a separate chamber and the products then being passed through the coal charge to continue the carbonization. Steam-carbon reactions do occur, however, to a minor extent. Temperature gradient in the retorts is 700°C at the top and about 550°C at the bottom. Excess gas can be used for other works like, steam raising in boiler. Rexco process gives true LT-tar (9.5%) as compared to G.K. Assay tar (9.9%) for weakly caking coal (NCB No. 801 type). Total time for one cycle is 17 h.

Coalite process – In the externally heated coalite process, cast iron retorts each containing a nest of 12 tubes (9 ft high and 4.5 in. diameter) are used. Each tube holds approximately 0.5 cwt of weakly caking coal. The retorts are heated by radiation from a thin refractory surrounding wall heated on its opposite side by the combustion of coal gas, causing rapid heating of tubes. CFRI, Dhanbad plant (1960) is the modified version of the Fuel Research Station (UK) model which is similar to coalite process in that externally heated narrow chambers are used for carbonization. But it is a continuous process (unlike “coalite”) and uses firebrick chambers instead of iron metal. Gas yield depends on the V. M. content of the coal. While carbonizing coal with 28–29% volatile matter, the gas was just sufficient for heating up the retort.

Lurgi-Spuelgas process – The term “spuel-gas” in German language means “not gas.” In this process raw brown coal of size less than 2 cm is dried first to 15% moisture and then processed into briquettes. Regional Research Laboratory (Hyderabad) has one Luxri-Spuelgas unit which is an internally heated LTC plant with 25 t/day capacity and uses 3–8 cm coals. Drying, carbonization and burner chamber are mild-steel lined inside with refractory brick.

Disco process – In USA, this is the only commercially successful LTC process. In this process certain coals in pulverized form is heated in air in an externally heated revolving steel retort to about 300°C a carbonized to lumps of coke that are spherical in shape. The agglutinating value of a strongly coking coal must be reduced by preheating and partial oxidation with air. On the other hand, a poorly coking coal is merely preheated rapidly in the absence of air to so that the plastic properties will not be affected.

Krupp-Lurgi process – Coal is cooked in narrow cells with steel walls. Coke produced by this process is highly reaction of easily ignited. In the

Koppers outer heated surface by hot gas (Spuel gas) process, both external and internal heatings are adopted. Again depending on the type of furnace/oven used, LTC processes are grouped as follows:

a) *Static furnace* – Lurgi-Krupp process (LTC) is based on carbonizing coal in static bed in metallic chamber, heated externally to 500–600°C to produce reactive semi coke used in gas producers for production of synthesis gas.

b) *Rotating furnace* – This furnace made by koppers produces from fat coals (more client resulting in increase capacity of the reactor, V. M.) a semi-coke which is used for domestic fuel. Carbolux (UK) sales such product under the trade name “Coalite.”

c) *Fluidization furnace* – This process considerably increases heat transfer coefficient resulting in increased capacity of the reactor, V.M. of coke diminishes rapidly with increase in temperatures and complete distillation, is obtained without having to raise the temperature beyond 700–800°C. Slack coal can be carbonized in fluid-bed for getting char fines. Further coke generated by this process has anti-fissure property similar to coke dust. Depending on the design details of the plant, material of construction, operational details and type of material to be used for carbonization, these processes can be further sub-divided as:

- (a) Vertical, horizontal, or inclined retorts.
- (b) Moving or stationery retorts.
- (c) Metal or brick retorts

Appropriate coal plant for a particular type of coal is selected with following consideration.

1. *Fine coal (at rest)* – can be best carbonized in external heating system. Here the heat penetrates from the wall to the center of the charge relatively slowly and the product is discharged after carbonizing as a lump-fuel. The coke produced is used for special purposes, such as metallurgical coke or smokeless domestic fuel. Coke produced from this class of retorts could not be used economically for industrial fuel purposes, such as steam raising and would have to find market where “form value” is important.

2. *Lump coal (at rest)* – is carbonized in internally heated retorts. This has been used to carbonize coal at low temperature before gasifying the coke or char in standard water gas machine. The heat for carbonization is derived from the sensible heat in the gases leaving the gasification zone at 750–800°C. The gases are drawn through the retort to effect carbonization. This method of carbonization has been proposed for treating boiler plant fuel or for carbonizing coal to make char for electric furnaces: coal charges up to 2500 kg (120cft) with such retorts have shown that the capacity is in the range of about 5–6 kg of coal per hour and per cft of retort volume

when using 800°C gases for carbonization. Maximum yield of primary tar have been obtained by this method and lump coking coal can be carbonized if sized to about 2 × 4 in. lumps and mixed with 15% of recirculated coke. Retorts of this type cannot be used for carbonizing fine coal because of the resistance to passage of the heating gas through the column.

3. *Fine coal (in motion)* – can be carbonized in externally heated retorts. This is, as mentioned earlier, also known as Disco Process, where coal is introduced into one end of a revolving retort and heated by contact with its heated surface. Hot gases at about 800°C circulate through the double outer shell and furnish the heat for carbonization. The normal capacities of these retorts ranges from 5.5 to 6.5 t/h when making lump coke suitable for domestic fuel, but the capacity may be somewhat higher if coke quality is sacrificed. The unit capacity ranges from 1.37 to 1.62 lb/h/cft of retort volume or 3.1–3.7 lb/h per sq ft of heating surface. Retorts of this type could not be used economically to produce char for boiler plant fuel because of the relatively low capacity and higher investment cost. The coke or char from this process has special form value and reactivity and can demand a premium market. In this process, the fuel potential primary tar yield from coking coal is not obtained because of the necessity of oxidizing the coal to control coke structure. Oxidation reduces the yield of tar to about 60% of the potential yield. The “Hayes Process” is also in this category. Here the retorts are small in diameter (about 18 in. compared to 9 ft for Disco Process) and a heated length of about 20 ft. The externally heated retort is rotated slowly in one direction and the fine coal is propelled through it by a screw, which rotates forward and backward to move the coal at the desired rate. The capacity of the retort when heated in a furnace operating at about 800°C and producing char of about 17% VM is 6–7 lb of coal/h per sq. ft of heated surface or approximately 15 lb/h per cft of heated surface or approx 15 lb/h per cft. The char produced from this operation has no particular form value. It is used in briquettes for domestic fuel and blended with coking coal to improve the structure of coke. The char could not be used economically as a power plant fuel. The yield of tar by this method is very high.

4. *Continuous externally heated vertical retort* – It was designed by Woodal Duckham and Glover West, having silical or firebrick refractory wall. The retorts will carbonize coking and non-coking coals at relatively low capacity which is limited by the rate of transfer of heat through the refractory walls. Such retorts will transfer heat to the coal at a rate of 2000 to 3000 Btu/h/ft². The newer ovens of this type uses alloy steel or carbonandum lining for containing the coal, and these transfer heat at a rate of 5000–10,000 Btu/h/ft², depending upon the design and the method of combustion. Ovens of this type are in operation with non-coking coals developing heat transfer rates of about 7000 Btu/h/ft² and carbonizing

low rank coals at rates of 10 lb/h/ft² or 24 lb/h/cft. Retorts of this type require fuel of about 1.5x0.25 in. size to favor circulation of gas through the coal and attain maximum capacity of course, still the capacity is limited by the rate at which heat can be transferred through the walls of the retort and to some extent by the recovery of heat inside the retort. If combustion occurs in the flue next to the lining of the retort, heat transfer rate of 6000 to 10,000 Btu/h/ft² can be attained, but if the heat is derived from hot gases produced in a Dutch oven or at a point separated from the wall of the retort, the rate of heat transfer and not exceed 4000 Btu/h/ft² because little heat is transferred by direct radiation from the gas. This is an important distinction in oven and retort design.

5. *Continuous, Internally heated vertical retort* – also known as “Lurgi-Spelgas” system, is used for distilling oil-shale. In this system, hot gas or combustible mixture of fuel gas and air is introduced into a combustion arch near the base of the column and percolate upward through the descending material to heat it to carbonizing temperature. The carbonized material is cooled by a counter current circuit of gas below the hot gas Inlet. Air and combustible gas may be introduced into a combustion arch inside the retort and excess air may react with the material being carbonized to generate heat for the process. The coal or shale distills as it is heated to the range 400 – 500°C and the vapors move forward through the charge as a mist. Such retorts can operate with relatively low off-take temperature, below the b.p of water because of persistence of the tar or oil mist; for this reason, the thermal efficiency is relatively high and minimum equipment for condensing the vapor after leaving the retort is required. Retorts of this type operate best on closely sized materials that will encourage even distribution of the heating gases. They will not operate satisfactorily on slock and they cannot operate on cooling coals. The capacity of such system is 200 – 300 lb/h/ft² of cross sectional area.

6. *Carbonizing coal in fluidized-bed with 100% internal heating* – There are three general concept in fluid-bed carbonization –(a) fine raw coal is charged to one side of the bed and air is jetted (2 ft/s) in for fluidization, while carbonized char is withdraw from the top or bottom of the other side of the bed. In this system air reacts only with char and develops heat and hot gases as well as products of distillation leaves the bed at 500°C. The char retains 15–25% V.M. This method do not have commercial success as it can only work with reactive fuel like preheated and dried lignite, but will not work for higher rank coals. Capacity of such system is about 365 lb/h/sq ft of the bed area. (b) A more complex system similar to above would be one in which products of combustion and air at about 800°C are jetted into a fluidized bed to carbonize the bed at 500°C. The bed is heated by both sensible heat of in-going gas and by combustion of excess air. Such a system is thermally stable but requires equipment to preheat air

and pre-combustion of the process gas. Capacity of such system is about 365 lb/sq ft. at a superficial velocity of 2 ft/s. (c) Another version is a moving burden technique, where heat of carbonization is derived from the sensible heat of char preheated in a circulating fluid-bed. The raw coal is added to the hot char and carbonization is attained by exchange of sensible heat in the char. When coal is carbonized with circulating hot char, approximately 1 kg of char or coke at 1000°C is required to carbonize 0.5 kg of dry bituminous coal to 500°C and the capacity of the carbonizer to could be 300–400 kg of coal/h/ft² of the bed area when superficial velocity is limited to 3 ft/s. One difficulty with this method of carbonization is the pre-heating of char to 1000°C without excessive formation of CO. The minimum CO has been obtained by rapid combustion in the entrained state (discussed in following sections) employing relatively high superficial velocity. Char produced by this technique has low V.M. and this may not be suitable as power plant fuel. The heat of carbonization of coal is normally endothermic below 650°C corresponding to decomposition reactions and is normally exothermic above 650°C, corresponding to condensation reactions. The net heat of carbonization is exothermic by 58–158 kJ/kg (25–68 Btu/lb). Carbonization time in minute is given by (i) for flat retorts, Carbonization time (min) = $9.2 W^2/T^4$ (ii) for round retorts, externally heated system (fine coal at rest), Time = $18.4R^2/T^4$ where, W=width of the first retort, R = Radius (inches) for round retorts, and T = average temperature of retort wall adjacent to coal in °K/1000. The evolution of volatile matter is approximately given by Gregory and Little-John correlation as follows. $Q = 3.162 (109/T)^{3.914}$. The next important thing to consider in carbonization is the heat required for the carbonization. For all practical purposes related to engineering design, the heat required for carbonization can be taken as equal to the sensible and latent heat in the products of carbonization at the temperature they leave retort. No credit should be given to exothermic heat of reaction. The following example illustrate a simple calculation procedure as adopted for fluid-bed carbonization at 500°C using Texas lignite and Utah bituminous coal.

(a) Texas lignite – Btu/lb (maf) = 12900 (=7260 Btu/lb total), moisture = 35.2%, V.M. = 28.2%, fixed carbon = 28.2%, and ash = 8.4%.

Yield on carbonization – Char = 45.7%, Tar + 1.0 = 7.3%, gas = 7%, and water = 40%. Potential heat distribution: Char = 76%, Tar + L.O.I = 17%, and gas = 5%

Heat required (Btu/lb of raw material)

Char	=	0.457 (900–60) 0.25	=	107
Tar	=	0.073 (900–60) 0.75+0.075×135	=	56
Gas	=	0.070 (900–60) 0.391	=	23

Water	=	0.40 (900-60) 0.047×10+0.40×1060	=	582
Total			=	768

Heat required (btu/lb of raw coal)

Char	=	0.65 (900-60) 0.28	=	153
Tar	=	0.196 (900-60) 0.75+0.196×135	=	149
Gas	=	0.058 (900-60) 0.59	=	29
Water	=	0.096 (900-60) 0.47+0.096×1060	=	140
Total			=	471

b) Utah bituminous – Btu/lb (maf) = 14,430 (i.e. 13100 Btu/lb overall), moisture = 4.6% V.M. = 44/4%, fixed carbon = 46.4%, ash = 4.6%. Yields on carbonization: Char = 65%, Tar + L.O = 19.6%, gas = 5.8%, water = 9.6% tar = 44 gallon /t. Above calculation show that, the heat required to dry a carbonize lignite is about 65% more than the heat required to carbonize bituminous coal. This difference is due to the large amount of water that must be expelled from lignite. The heat required to remove moisture from lignite amounts to over 75% of the heat required for carbonization. Therefore, when lignite is processed, drying and pre-heating should proceed the carbonization step. When processing a bituminous coal, the two step operation may not be necessary and all the heat for carbonization might be supplied in one operation. If this can be accomplished with the high volatile non-coking coal, such as those produced in Carbon County, Utah and Western-Wyoming, from which 30 to 44 gallons of tar/ton can be extracted, the fuels could be processed profitably some distance from the mine. Comparison of brown coal and lignite, vis-à-vis other grades of coal in terms of heating value (maf) is correlated against the proximate and ultimate analysis and the ASTM classification (according to rank), as well as coking properties, are shown in Fig. 6.94. Generally speaking, all coals having an ASTM classification up to and including high volatile bituminous coal can be considered suitable fuel for rapid carbonization in low temperature in a fluidized-bed or entrained state^{36,37}. When such coals are carbonized, the heating value of the pure char is approximately 14000 Btu/lb from any of the fuels considered, because all of the water and much of the oxygen have been evolved during carbonization. Despite the great variation in physical and chemical properties of the different lower rank coals in their raw state, the pure chars produced therefore are substantially of the same basic quality. They are characterized by their high reactivity and ease of ignition. Pyrolysis of lignite has been studied in depth by Sunberg et al at M.I.T. Cambridge, Massachusetts (USA), where they varied the rate of heating from 10² to 10⁴ °C/s in 150–1100°C range and obtained results which are

shown in Figs. 6.75–6.79. Examination of Fig. 6.75 reveals that there are apparently five principal phases of devolatilization. The first occurs at very low temperatures (about 100°C) and is associated with moisture evolution. The second phase at 1000°C/s heating rate begins at about 450°C and is associated with a large initial evolution of CO₂, probably from low activation energy decarboxylations. The loss of carboxyl groups as CO₂ at relatively low temperatures has been reported for lignites. A small amount of tar is also evolved at this stage. This material may contain not only real tar (e.g. asphaltene and heavy oils) but also small particles of lignite broken off the parent particles by the escaping gases as mentioned above. The third phase involves evolution of water chemically formed in the range 500–700°C where the only other significant product is CO. It can be seen from figure that carbon, nitrogen and sulfur during this phase remain largely in the char while the oxygen and hydrogen contents of the char sharply decreases. The fourth phase involves a final rapid evolution of carbon containing species. Carbonoxides, tar, hydrogen and hydrocarbon gases are all rapidly evolved in the temperature range 700–800°C where little water is produced. The fifth phase is the previously discussed high temperature formation of carbon-oxides. Chukanov believes that coal pyrolysis involves three stages – evolution of carbon-oxides and water (at 450–550°C) then formation of tar and hydrocarbon gases, and finally degasification of the residue. Since coal is always “hydrogen-starved” in the sense that its empirical formula is usually CH_{0.6} to CH (lignite is roughly CH_{0.9}) while the desired products are in the range CH to CH₄, it is desirable to use the coal hydrogen as efficiently as possible. The oxygen in the coal removes most of the hydrogen at temperature below those at which the principal hydrocarbon forming reactions can occur; thus, by the time the coal is hot enough for the latter reaction to occur, there is above methods of control, however, are applicable only within relatively narrow limits. Besides these, large scale actual tests have demonstrated their adequacy in determining the relative expansion behavior of coal charge. The more common used are:

- (a) The Fussell movable wall oven, heated from two sides, for determining expansion pressure at constant volume.
- (b) The Brown-type sole heated oven, for determining volumetric expansion and contraction at constant pressure. It is to be noted here that, reduction of such testing technique to bench scale or laboratory expansion testing methods have yielded either incomplete or misleading results.

A critical analysis of the development of expansion pressure show that the fundamental determinants involved are rate of gas evolution and

resistance to the escape gas. The significant resistances to the escaping gas are:

- a) The capillary structure, which governs the swelling of individual coal particle.
- b) The plastic layer which determines the pre-peak pressure.
- c) The plastic envelop which govern the peak pressure.

The problem of directly measuring the rate of gas evolution and of determining the values of the resistances by laboratory methods which would simulate coke oven conditions remain to be solved. Since it is of paramount importance to the coking industry, that the dwindling supply of premium coking coal can be effectively utilized, increased knowledge of expansion behavior and simpler and more accurate methods of predicting such behavior from lab tests of physical and chemical properties of coal and coal blends are sorely needed. The problem of selecting coals for control of expansion pressure during carbonization is not one of distinguishing between coals of different rank or of widely different chemical composition as measured by proximate and ultimate analysis, but one of differentiating between coals of the same rank and apparently identical chemical compositions, which exhibit widely divergent expansion behavior. Russel has shown the characteristic relationship between coal rank and plasticity (Table 6.11) as measured with the Geisler plastometer for typical coals to be:

Besides rank of coal, other factors that influence the fluidity include:

- (a) Decreasing the rate of heating shortens the temperature of plasticity and decreases the fluidity.
- (b) Oxidation of the coal has a similar effect.
- (c) High concentration of anthraxylon, translucent attritus and channel coal structure, increases the fluidity.
- (d) High concentrations of ash, opaque attritus and fusain decrease the fluidity.

Most of the low, medium and higher ranking high volatile coals show

Table 6.11 Plastic temperature range of various coals

Typical coal Rank	Plastic temperature range (°C)			
	Volatile matter	Initial fusion	Maxm. Fluidity	Solidification
Low volatile	17	440	480	500
Medium volatile	22	395	475	505
High volatile	34	370	450	480
High volatile	38	380	440	465

the expected inverse relationship between fluidity and expansion pressure. The coals at the limits of coking band are anomalous in that they show both low fluidity and low expansion pressure. It is probable that the swelling of the later coals is insufficient to form continuous plastic layers. The regions of maximum rates of gas evolution corresponds with those of maximum fluidity. Comparison with expansion pressure curves of the coal indicates that expansion pressure is due to liberation of relatively large amount of volatile matter while the coal mass was in a viscous condition. Coal in general, is built up of aggregation of molecules (micelles) separated by capillaries whose average diameter is of the order of 40. When porosity is plotted against volatile matter, the same type of curve was obtained as for surface area.

Since coal in natural condition contains moisture adsorbed on the capillary surface, it would be expected that moisture content curve would resemble those observed for surface area and porosity. This was actually found in all cases whether moisture is reported on the total, air-dried or 50% humidity moisture basis. From these observations, it appears that the poorly coking and non-coking coals are characterized by a comparatively open type of capillary structure whether judged by surface area, porosity or constrictions. Studies at various temperatures showed that capillary persisted throughout carbonization and therefore complete fusion of the coal do not take place. According to one theory, the swelling of particles of coking coal is due to the entrapment of gases of decomposition within the capillary structure described. The rate of diffusion of these gases to the exterior of the particle will be governed by the pore diameter and constrictions. In case of coking coals, the restrictive nature of the capillary structure causes a build-up of gas pressure within the pores. As the temperature is increased, the coal softens and the pressure of the interior gases distends the particles. In confirmation to this theory, tests have shown that slow rate of heating ($0.5^{\circ}\text{C}/\text{min}$) will greatly suppress swelling and rapid rates will produce coke like residues from normally non-coking coals. On the basis of internal structure, the anomalous fluidity-expansion behavior of coals at the limits of the coking bond are accounted for, since these coals would not be expected to swell sufficiently to form continuous plastic layers. According to Koppers, expansion pressure is due to the entrapment of gases of decomposition within the plastic layer, the pressure being dependent on the viscosity of the layer and the rate of gas evolution. After the pressure compress the charge to its maximum bulk density, the full expansion pressure must be exerted on the oven walls. If only a slight coke shrinkage occurs, pressures on the walls is maintained as the plastic layer progresses toward the mid-plane of the oven. At the time of

meeting of the plastic layers, nearly all expansion curve show a peak. Russel assigned the cause of expansion pressure to the entrapment of gases within a continuous plastic envelop formed by plastic layers moving in from walls, floor, roof, and doors.

Near the end of the coking period when the plastic seams are meeting at the centre of the oven and with the envelop still entrapping the gases, the rate of heating increases sharply (due to pre-drying and pre-heating prior to gas evolution and to the effect of heating from both walls), thus increasing the amount of gas evolved with the net result that the pressure rises rapidly. Expansion owes generally shows the extent of peak pressure in case of low and medium volatile coals. For high volatile coals, the envelop is relatively permeable and this together with the large coke shrinkage. These explanations indicate that a number of simultaneous, separate processes are involved in the build up of gas pressure within the plastic coal and the net pressure is transmitted to the walls. Effect of each of these variables upon coal expansion are outlined below.

(a) *Compressibility of charge* – The probable effect of this factor is the reduction of expansion pressure during the early part of the carbonization period. The pressure within the plastic layer during this period may be relieved by expansion of the layer and compression of the uncarbonized coal between the layers. However, there is no possibility of pressure relief in this manner with charges of high bulk density and after maximum bulk density has been attained with charges of low bulk density. Although no experimental evidence is offered, coals of the same are considered to have similar compressibility characteristics. Consequently, while this factor may partially explain the course of pressure during carbonization, it does not account for the wide difference which have been observed in the expansion behavior of different coals.

(b) *Coke shrinkage* – Coke shrinkage for various coals indicate that this factor remains more or less same (10–12%) for all coals, and tends to relieve gas pressure developed in the plastic layers and envelop throughout carbonization period. However, comparative gas and wall pressure measurement show that the coke piece is pushed out to the wall during he expansion process, thus minimizing any possible effects of differences in coke shrinkage.

(c) *Formation of plastic layer and plastic envelop* – Widening the top of the oven and reducing the top flue temperature eliminated the peak expansion pressure by permitting the easy escape of gases from the interior of the charge. The peak pressure is due to gas pressure within the plastic envelop.

(d) *Gas pressure within the charges* – Pre-peak wall pressures were due to gas pressures within the individual plastic envelop. The expansion

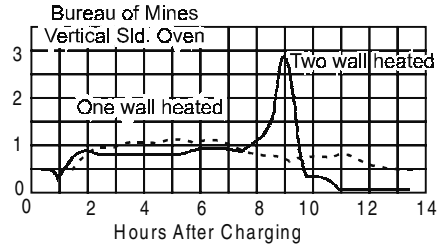
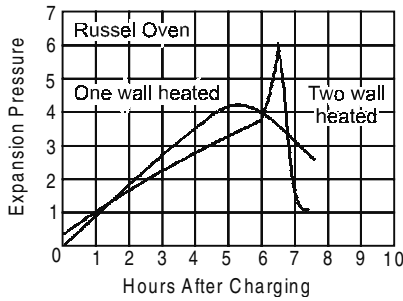
pressure of the plastic layer was transmitted on one side of the coke to the oven walls and on the other side was neutralized by a similar force, from the opposite plastic layer, transmitted by the compressed coal particles. The relationship between gas pressure at the middle of the charge and peak wall pressure is given by the following equation-

$$\text{Gas pressure} = 1.95 \times \text{wall pressure} - 0.83$$

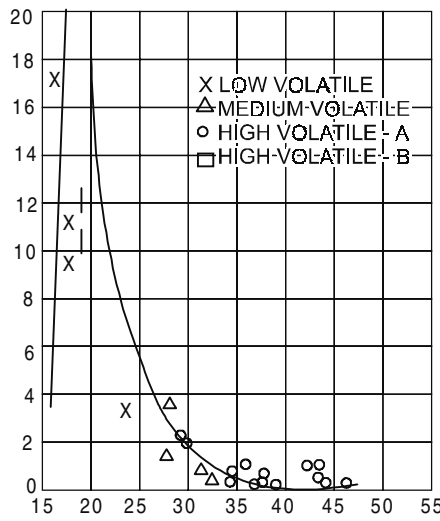
(e) *Thickness of plastic layer* – The thickness of plastic layer is defined as the distances in the charge corresponding to the upper and lower temperature limits of plasticity and is calculated by the equation:

$$\text{Thickness (in.)} = \text{Plastic range (}^\circ\text{C)} / \text{Temperature gradient in plastic layer (}^\circ\text{C / in.)}$$

(f) *Theory of the mechanism of development of expansion pressure* – As coking coal passes through the range of carbonization temperature, the occurrence of the simultaneous processes of rapid volatilization and softening of the coal substance, causes swelling of the particles. The force causing swelling is the pressure of the internal gases, which are partially constrained by the capillary structure of the coal. For coals forming continuous plastic layers, the restraints imposed by the walls, floor, and the weight of the super-incumbent coal permit this internal pressure to deform the softened particles into a plastic layer, which entraps bubbles of gas. The pressures within these bubbles must rise to a value high enough to enable upon oven walls. For low-volatile coals (Figs. 6.46 and 6.47), the gas pressure within the plastic layers increase as the layers progress toward the middle of the oven possible due to the thickening of the layers. At meeting time of the layers, the rate of temperature rise increase sharply, with a consequent increase in the rate of gas evolution. Since the area of escape for the gases within the plastic envelop is now greatly restricted, these factors cause a rapid increase in the mid-plane gas pressure, with an accompanying increase in wall pressure. The higher ranking high volatile coals (Figs. 6.46 and 6.47) produce highly fluid plastic layers which at no time offer any substantial resistance to the flow of gas. Typical blends of low volatile and high volatile coals (Figs. 6.46 and 6.47) produce plastic layers in which a pressure of about 1 psi is developed during the pre-peak period. The pressure rises to about 2 psi only under the exaggerated conditions (high rate of gas evolution due to drying and preheating the axial coal mass during the earlier carbonization period and to the accelerated temperature rise from the effect of heating from two sides) present at the time of meeting of the plastic layers. The coals which form non-continuous plastic layers (coals at the limits of the coking band, oxidized and high-inert charges, and their mixtures) develop maximum pressure during the early part of the coking period and little or no peak



6.46 Influence of type of heating upon expansion pressure.



6.47 Expansion pressures of unblended coals in russel oven.

pressure (Figs. 6.46 and 6.47). Since these coals are characterized by low fluidity, poor swelling ability and poor fusion, it is not probable that carbonization pressure results from gas pressures within either the plastic layers or plastic envelop. The comparatively open physical structure of these coals permit only slight swelling. The usual result is low wall pressures, whose source as gas pressure within the coal particle themselves.

Other factors which influence expansion behavior during carbonization are as follow:

(a) *Bulk density* – The effect of bulk density upon volume expansion may be accurately represented by the following expression.

$$E_x = W_x / W_t (100 + E_t) - 100$$

Where E_x = volume expansion at W_x bulk density (in %), E_t = volume expansion at W_t bulk density (%), W_x = standard bulk density (pcf), and

W_1 = test bulk density (pcf). Size distribution is the dominant factor governing the bulk density (the highest bulk densities obtained with the widest distribution of sizes). Surface area is the significant factor in changing bulk density when coal is wetted. Calculations of the relative surface areas showed that the minimum bulk densities were reacted at a moisture content of approximately 0.13% moisture/unit surface factor. If the bulk densities of packed coal in the oven are not uniform, the region of maximum bulk density corresponds with the regions of initial wall failure.

(b) *Plastic size* – At constant bulk density, finer pulverization may lead to slight increase in expansion pressure. The volume expansion generally increases by 2% for each 10% increase in the percentage of -4 mesh coal.

(c) *Rate of heating* – In general, faster rates of heating increased expansion pressure and volume expansion, with some indication of the pressure reaching a maximum at flue temperature of about 2300°F. From a theoretical standpoint, faster rates of heating should increase the rate of gas evolution, which would tend to increase the expansion pressure at the same time. The thickness of the plastic layer would be decreased and the fluidity increased, both of which would tend to decrease the expansion pressure.

(d) *Oven width* – The expansion pressures of the more highly expanding coals decrease as the oven width is increased from 6 up to 10 to effective in reducing the bulk density variation effective in reducing relative influence of the other factors.

(e) *Heating conditions* – Comparative expansion pressure tests with one wall and two opposite walls heated, show that the two methods of heating gave substantially identical expansion pressures during the pre-peak period. One-wall heating failed to give the pressure peak observed with two-wall heating, since the conditions necessary for the development of peak pressure are not present when heating is from one wall only.

Finally, the last but not the least important factor governing expansion behavior during carbonization is the properties of the coal itself. Figures 6.46 and 6.47 show the influence of type of heating and volatile matter on oven wall expansion pressure. The volume expansion plot shows that a maximum is reached at 17% VM content with a lesser peak at 27%. The major effect of ash content is on bulk density, with only a slight independent influence upon expansion. Expansion pressure reduces with increased amount of oxidized coal. From the view point of petrographic composition, bright fraction (macerals) show greater expansion than the corresponding dull fraction. This is probably due to the fact Vitrain has smaller capillaries than durain or fusain.

6.8.2 High temperature carbonization (HTC)

High temperature carbonization are carried out between 900 and 1200°C. The main aim of this process is to generate hard uncreative coke suitable for metallurgical applications. More specifically cokes generated at 900°C are suitable for foundry applications. While, blast furnace cokes are produced between 950 and 1050°C. Still at higher temperature 1100–1200°C, cokes are produced by Beehive Coke Oven method and reserved for some special applications. Table 6.12 below shows the ISI-specification of cokes obtained by HTC process.

In practice coals of different varieties are blended together in order to get coke with above specifications. This requires knowledge of coking characteristics of various coals. Generally coking properties of coal deteriorates on storage and unless adequate precautions are taken to prevent oxidation, the coke generated by HTC process are found to be inferior grade.

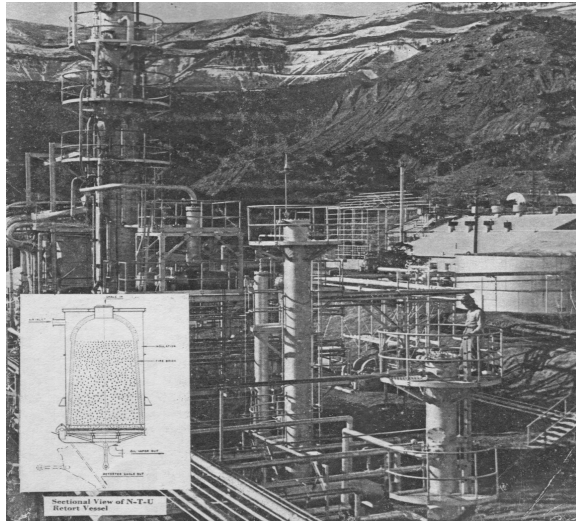
Dilatometric studies in the post-plastic zone reveals the presence of two contractions rate peaks related to primary and secondary fissure producing influences. The principal fissure forming force tends to control the size of pieces on discharge from the coke oven. The second affects the less severe system of fissures which only become manifest when subjecting the pieces so formed to more severe stresses, as in the shatter test; hence the relationship between the height of the first and second peak in the contraction rate curve and the size of the coke and shatter strength respectively. Neither coke breeze nor anthracite exhibit any contraction in the region of the first contraction peak while at or around the temperature of the second peak, anthracite does contract. If the above relationship are valid, then the addition of anthracite or breeze to a coking coal should reduce the first peak and increase the mean size of coke produced from such a mixture. Similarly reduction of the second peak by addition of breeze should bring about improvement in the shatter index of the coke. Anthracite however which can not affect the second peak to the same degree, should have a noticeable effect. All these postulates have been verified experimentally. Furthermore, it was shown that calcining anthracite

Table 6.12 Properties of coke (ISI specification)

Volatile matter	2.0%
Sulphur in coke	0.70% (maximum)
Phosphorus in coke	0.30% (maximum)
Porosity	35 – 48%
Micum-index on 40 mm	75%
Micum-index below 10mm	14% (maximum)
Shatter index on 38 mm	85% (maximum)
Shatter index on 12.5 mm	97 (minimum)
Haven stability factor on 1 inch	40 minimum

and reducing its volatile matter content, progressively reduced its second contraction-rate peak. Comparison of cokes made without any addition, with untreated anthracite and with calcined anthracite, showed that untreated anthracite influenced only the mean size, whereas the calcined anthracite increased mean size to a greater extent and improved impact resistance, thus confirming the suggested relationship. However, the amounts of breeze and anthracite which can be incorporated in a blend may be limited by their effect on abrasion resistance; both cause deterioration after certain levels of addition depending upon also grading. With high volatile coals the more fluid, low-volatiles steam coals can help to compensate for this, and where control of size, strength, and abrasion resistance are necessary, these steam coals have an important function. The size grading of the coking modifier is important and usually it is finely ground. Large irregular inert particles build up stresses and propagate cracks as the semi-coke contracts around them, weakening the coke product and reducing its resistance to abrasion, thereby worsening factor than improving properties.

HTC pilot plant study by Dasgupta et al (CFRI, Dhanbad) has identified critical design and operational parameters. Figures 6.48 and 6.49 show the view of this pilot plant while Fig. 6.50 show the schematic of by-product recovery. In this plant the battery of ovens have three ovens 14 in., 16 in. and 18 in. average width, 4 ft height and 9 ft length. The ovens are built with pure silica bricks and have capacities of 980, 1100 and 1180 kg of coal per charge. The ovens are still compound regenerative type with common gas run heating and each oven is provided with 8 heating fluses, 4 on the ram and 4 on the coke side, and 2 self-scaling doors, 2 charging holes and 1 ascension pipe (for exit of gaseous products). Each heating wall is provided with a regenerator chamber built in two parts to facilitate heating of both gas and air in case of lean gas firing. The heating gas reversal mechanism is mainly operated and reversing is done every 30 min. The waste gases from the regenerators enter the undersigned waste gas flue through the waste heat boxes and are led to the atmosphere. The daily throughput of the battery on dry basis is about 3500 kg by top-charging and 3850 kg by stamp-charging with flue temp. of 1250°C. The carbonization time for the 14, 16 and 18 in. ovens are about 14, 17 and 19 h, respectively. An electrically driven ram car provided with a door extractor pushes the charges out of the ovens to a brick-lined coke wharf through a coke guide. The red hot coke is quenched by means of water from a hose pipe. The ram car is also provided with a leveller and a device for stamping or compression of the charge. The stamped charge is introduced into the oven from the side. The coke from the wharf may either be carried to a coke screening system for being separated into fraction of +38 mm, 40–



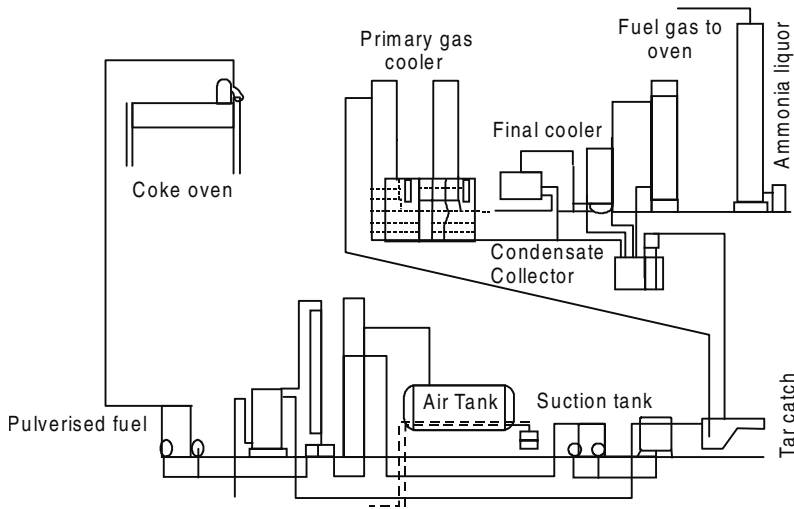
6.48 View of pilot battery from pusher side.



6.49 By-product plant.

13 mm and 18–13 mm sizes or may be hand screened to greater ranges of size from 6 to 0.5 in., as is usually done.

The gaseous products of carbonization pass through cast iron ascension pipe and foul gas mains (4 in pipe) to primary coolers (vertical tubular condensers with 400 mm diameter, 600 mm height and 30 m² in cooling surface for each, with material circulation inside the tubes) one for each oven, for condensing tar and liquor in the gases. The exit gases from the



6.50 Flow sheet by-product section of the high temperature carbonization pilot plant.

primary coolers mix together and pass through a conventional electrostatic detarer for the removal of tar fog still remaining in the gas. A voltage of about 30,000–40,000 V is applied in the detarer. The gases are then sucked by a radial flow exhauster (one standby is also provided) which delivers about 250 mm WG to a final cooler (vertical tubular condenser, of 4000 mm diameter, 5000 mm height and 25 m² cooling surface) when the gases pass through an ammonia scrubber with 1 in. berl-saddles in two sections; water being sprayed from the top at a rate of 25 gallons/h (400 mm diameter, 10000 mm height and has 260 m² surface).

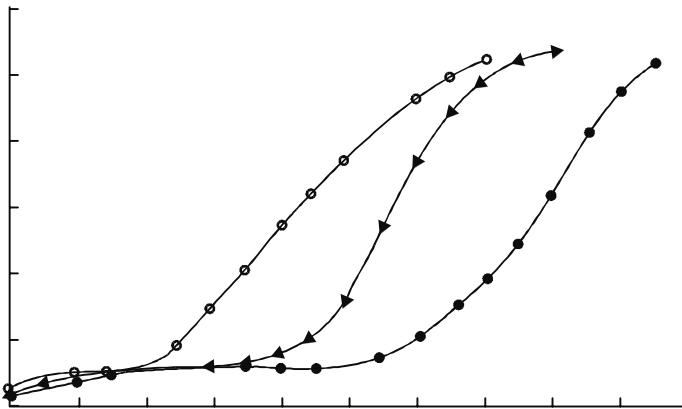
The NH₃ and part of H₂S contained in the gas is absorbed in the water and this scrubber water goes to the drain. Finally, the gases pass to a 150 m³ capacity gas holder from which part of the gas is fed back to the ovens for heating. There is provision for circulating part of the gas to the main gas stream before the exhauster to control the exhauster suction. The condensed tar and liquor from the gas mains are collected in a tar catch tank. The condensate from the coolers, electro-detarer and the exhauster are collected in a low level tank and pumped back to the tar catch tank, from where they pass to a suction tank (1000 mm diameter, 1200 mm height) and are pumped to a decanter in which tar and liquor are separated by gravity. The decanter is 800 mm diameter, 6500 mm in height. The thick tar from the bottom is collected in a cylindrical storage tank and the liquor from the top of the decanter overflows into an intermediate vessel, where a constant flow returns to the suction tank and joins the main condensate stream. The excess liquor from the intermediate vessel may be drained out. Part of the liquor from the top of the decanter is heated by

recirculation at the conical bottom portion before being pumped to the ascension pipes for spraying. Figure 6.51 shows the results of carbonization in three ovens. Progress of the carbonization is indicated by the coke mass temperature versus time for the three ovens at a flue temperature of about 1250°C. The center of the coke mass remains at about 100°C for 4, 6 and 10 h for the 14, 16 and 18 in. wide ovens.

More or less same practice is followed in actual coke ovens operation in steel plants, but for the by-product recovery in the initial stage a wash-oil is used for recovering the “benzole” or light-oil fraction (boiling up 170°C). This fraction is dominant in benzene (70%), toluene (20%) and xylene (4%). and have commercial important for recovery of these chemicals occurring in high concentration in the first step. Wash oil has the property of dissolving BTX and it can be regenerated and used again. Standard wash-oil is a petroleum 7distilleries, 230–300°C fraction. Different types of oils have been proposed for the recovery of benzole by absorption. Thus tetralin, coal tar oil (creosote fraction), green anthracene oil and various petroleum fractions have been proposed, but of these only creosote oil and petroleum oil have gained universal use. Work at CFRI, Dhanbad also resulted in choice of selected fraction of HTC and LTC tar for benzole recovery. HTC tar oil fractions found more effective than petroleum oil for absorption of benzenes (90–95% of the gas) in latter studies. Performance of LT-tar oil is comparable to that of HT-tar oil with respect to benzene absorption characteristics.

6.8.3 Beehive coke oven

Discussion on HTC relates to another type of coke oven (known as “Beehive Coke Oven” because of its similar shape and form) which



6.51 Rate of carbonization in the three ovens.

although practiced to a much lesser extent these days, still did not disappear from the carbonization scene as it also produces a very special type of coke very much in demand in foundries. In advanced countries like Germany, England and USA have installed beehive coke-ovens but were largely replaced by product recovery ovens which has larger capacity for hard coke manufacture and simultaneous tar recovery facility. Even today, in spite of above facts a certain quantity of coke is being prepared by beehive method by above advanced countries mainly for foundry application. Table 6.13 shows the number of beehive coke plants in operation in USA in the recorded period of 1900–1970.

The downward trend towards number of oven can be traced to the basic weakness of the beehive coking process which are as follow:

1. The process can not recover valuable by-products, including energy in the form of gas.
2. Low efficiency (product yield is about 50% max). Coal to coke ratio for a properly operated beehive should be 1.5 as against 1.4 for the by- product ovens. This difference is unavoidable but the ratio can be maintained at that level if the beehive work efficiently.
3. Cause extreme pollution to the environment.

Other plants under non-recovery category include the rectangular Mitegell oven, which is heated through a side flue and the Curran-Knowels oven. Neither of these achieved great popularity, although they possess many advantages over the beehive oven. In India, coke was first manufactured in beehive ovens for the iron and steel works at Kulti toward the end on the 19th century. In 1950 the production of beehive coke in India was about 150,000 tones out of a total of 2 million tonnes of hard coke produced at that time. In the last 4 decades, the production of coke from the beehive ovens had registered a small annual increase, though production of coke from by product ovens (HTC) has increased almost 4 folds (largely in steel industries).

In foreign countries the beehive ovens had often been operated as an alternative means for the manufacture of hard coke so as to fill in the gap in the production and the market demand of coke. In fact beehive coke production can help to create the new market for coke so that when the

Table 6.13 Beehive coke ovens in USA (1900–1970)

Year	Number of plants	Number of ovens
1900	387	57,499
1910	548	100,362
1920	347	75,298
1930	121	23,907
1940	93	15,150

demand becomes adequate to warrant installation of by-product cokeovens, a battery of by-product ovens of economic size is installed and operation of some of the beehive ovens is discontinued to balance production. It is chiefly on this ground that we find the need of beehive ovens to co-exist in India with by-product ovens as they do in many other countries of the west. The point in favor of the beehive coke oven lies in its relatively low installation and operation cost compared to that for a battery of by product ovens. Unlike by-product ovens, beehive ovens can be brought into operation from the cold state in a very short time and again be cooled down without any material damage to the furnace, so that the ovens can be operated at will depending upon the market demands of coke. This is not possible in the case where the oven not to be cooled down without serious damage to them. The other reasons for manufacture of hard coke by beehive coke ovens are that they produce very lumpy and dense hard coke, low in reactivity which very often is the first choice by foundry men. With speciality North Eastern coals of India, in 1988 Mahavir Coke Industry has set up beehive coke oven batteries at Gwahati (Assam), output of which is entirely used by Hindusthan Electrographite, Bhopal for production of graphite anodes for Acheson furnaces. The beehive coke oven design emanated from the charcoal kiln process practiced earlier. Beehive process is a self heating process where the volatile matter is burnt over the coal charge under restricted and directed air supply, and the radiant heat bounces back to the charge from its arch shaped roofs. A battery of ovens is constructed side by side as well as opposite facing rows with common wall at the back, in order to minimize heat loss and simultaneously maintaining a uniform thermo profile within the ovens. The burnt gas escapes through the oven to central stack and vented into the atmosphere. Thus the coking process starts at the top and proceed downward. Coking time varies between 36 and 48 h in a commercial size unit (the time depends on depth of charge). The ovens are initially heated up with charcoal or gas burning before placing the charge into it. The ovens are made up of fire brick (alumina brick) and insulated by 2–3 layers of brick one above the other. The charge is placed on a metal grate car which can be easily pushed in and taken out. The ovens when reaches to its desired temperature, the coal particles are fed through the conical feeder from the top on the grate and levelled off with a manual spreader. Holes are placed in such a way that air enters by natural draft to the volatile off gas, the oven reaches maximum temperature within a short time. Gas evolution then slowly decreases and the passage of air closed accordingly to preserve heat.

6.8.4 Fluidized and entrained baed carbonization (LTC)

By now we are able to differentiate between bubbling fluidized bed and

entrained bed. In carbonization industry fluidized bed is employed with 100% internal heating while in entrained bed external heating technique to employed. We will discuss these two modes of carbonization along with their merits and demerits in following section.

If the primary purpose of carbonization is to produce a readily ignitable smokeless lump fuel, its size shape, volatile matter content and reactivity are major consideration, then fixed-bed process is the choice as they enable us to take advantage of the coking property of the coal for compensating any relative low heat transfer rate. Nevertheless, fluid bed carbonization (as developed by NCB, UK) can be used for the first stage of manufacture of smokeless lump fuel. If on the other hand, the product is not required in lump form, fluidisedbed processing offers the great advantage of high heat transfer with consequent saving in capital and operating cost. Moreover, for metallurgical coke making and firing of large boilers, char in granular or powder

form is preferable to lumps. Development of LT has been retarded by the fact that coal has a low thermal conductivity and therefore the heat transfer rate in the carbonizer has tend to be poor, with consequent adverse effects on thermal efficiency and plant throughput, low thermal conductivity greatly restricts the rate of heat transfer by conduction, by following Fourier equation.

$$\frac{dQ}{d\theta} = KA \frac{dt}{dx}$$

where, $dQ/d\theta$ = rate of heat transfer (Btu/h), K = thermal conductivity (Btu/h. ft²). A = cross sectional area of the heat path (ft²), and dt/dx = temperature gradient (°F/ft). The efficiency of LTC process is restricted also by the fact that, to keep within the required temperature limit, it is necessary to work at a low temperature gradient. As can be seen from above Fourier equation, in system where the heat is transferred mainly by conduction, the rate of heat transfer may only be increased by making “A” as large as practicable and x , the length of heat path, as small as possible. Supplementing conduction with convection gives a more uniform temperature as well as improved heat transfer. Convection may involve – (a) forced movement of gases through the coal and /or, (b) movement of the coal particles themselves. Of these, (a) may be applied the fixed beds of lump coal and both (a) and (b) occur in fluidized beds, Whereas the value of convection lie in maintaining temperature uniformity throughout the bed, best heat transfer into each individual particle can occur only by conduction. Fourier’s equation show that conduction into small particles under fluidized bed conditions can be quite rapid, because “A” then corresponds to the total surface area of the particles is large; whilst x

corresponds to the nominal radius of the particles and is small. The heat required for fluidized-bed carbonization may be supplied either by direct combustion of a portion of the char or tar within the bed (internal heating) or by heat transfer from some source of energy outside (external heating). With internal heating, air is used as the fluidizing gas and it is possible to adjust the flow rates of air and coal so that the heat generated by combustion equals to the heat required for carbonization plus the heat losses from the carbonizer. Fluidized carbonization with 100% internal heating can be discussed by considering three general concepts for heating coal in a fluidized state. These are

- (a) The simple classical system of this type is one in which air at atmospheric temperature is jetted into a fluidized bed to effect carbonization in the bed at 500°C. The air reacts only with the char in the bed to develop heat for carbonization, and the products of partial combustion and the distillation gases /vapors maintain the bed in a fluidized condition. Fine raw coal is charged to one side of the bed, and the carbonized char is withdrawn from the top or bottom of the other side of the bed. The products of distillation and the heating gases leave the bed at 900°F and are stripped of most of the entrained dust by suitable cyclone mounted above the bed. In this simple fluidized distillation system, the char is heated only to 900°F and retains 15–25% volatile matter. To the best of author's knowledge, no commercial operation presently employing the system, and no successful pilot plant operation has been so far demonstrated. Such a system might operate successfully on a reactive fuel such as preheated, dried lignite, but it is important to note that it can not be used with higher rank coals. A fluidized bed of the type considered would require a superficial gas velocity of about 2 ft/s (average velocity of gas excluding volume of solids). At this rate, the capacity of a fluidized carbonizer of this type would be approximately 365 lb/h per sqft of bed area.
- (b) A more complex system similar to above would be one in which products of combustion and air at about 800°C are jetted into a fluidized bed to carbonize the bed at 900°F. The bed is heated by both the sensible heat in the outgoing gases and by combustion of the excess air. Such a system would give more assurance that a 500°C fluidbed could be maintained, but auxiliary equipment will be required to preheat air to carry out the precombustion of the process gas. The carbonization capacity of carbonizer of such unit is around 365 lb/h/sq ft at superficial velocity of 2ft/s.
- (c) Another version is the moving burden technique wherein heat for carbonization is derived from the sensible heat of char preheated in

a circulating fluidized bed. The raw coal is added to the char (hot) and carbonization is attained by exchange of sensible heat in the char. A pilot plant using this system for carbonization and gasification of coking coal has been operated successfully in England.

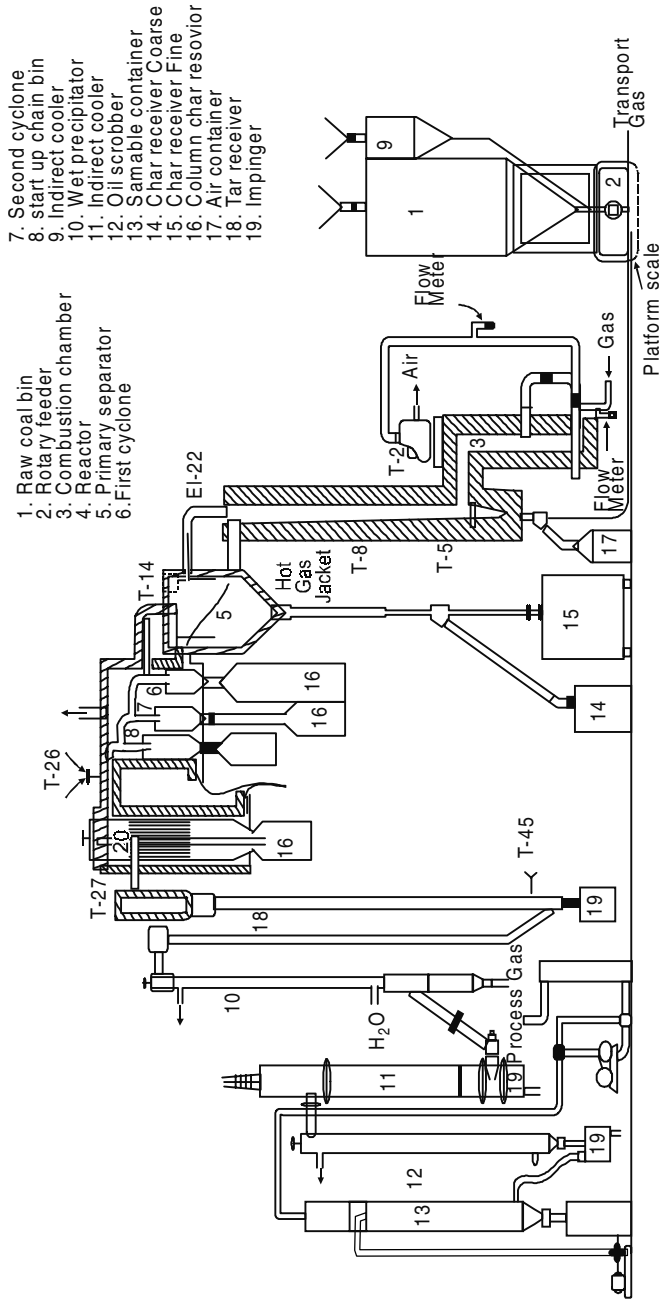
When coal is carbonized with circulating hot char, approximately 2 lb of char or coke at 1800°F is required to carbonize 1 lb of dry bituminous coal to 500°C, and the capacity of a fluidized-bed carbonizer could be 600–800 lb of coal per hour per square feet of bed area when the superficial velocity in the bed is limited to 3 ft/s. One difficulty with this method of carbonization is the preheating of char to 1000°C without excessive formation of CO. The minimum CO has been obtained with rapid combustion in the entrained state employing relatively high superficial velocity. The pilot plant referred earlier employ this method. Char thus produced with the moving burden technique is characterized by low volatile content and relatively low reactivity, and for this reason may not be suitable as power plant fuel. By appropriate adjustment of carbonization condition, either the char or the tar may be used as the principal fuel for internal heating. At 460–500°C the char does not burn readily and the air (O₂) is used up in burning tar. At 550–600°C char burns so easily that O₂ is largely consumed in the char recycle line and little oxygen remains for reaction with the char.

External heating is necessary when gases other than air are used for fluidization; for example, fuel gases from other processes or gas from the fluidized bed carbonization itself, recycled after purification. Gas from external heating is essentially a matter of economics based on local requirements. If the production of char is the main interest and the other products are of marginal value, internal heating with preferential combustion of tar is the most suitable arrangement because it demands only the simplest of plant and yields the maximum char and the minimum by-products. Sengupta et al has shown, however, that the nominal residence time of the fluid reactants taken conventionally as basis for predicting performance of fluid-bed reactors above is inadequate for the scaling up of fluid-bed LTC plant, although residence time greatly influence yield and product distribution pattern in such case. In these cases the nominal residence time (NRT), is generally calculated by driving the solids trapped in the fluidizer with the solid feed rate. Here the above author proposed to use average residence time (ART) instead which is found but by referring to the data of batch carbonization studies (obtained in the same reactor under identical conditions) and then extrapolating the same for the present data. Difference between NRT and ART is generally high but narrows down as the temperature rises. In the case were the coal is agglomerating in nature, prior oxidation of coal or external recirculation of char is

necessary. Coking coals has also been carbonized in fluidized beds using sand as heat carrier.

But highly coking bituminous coal can be carbonized successfully in entrained bed carbonizer using air as all or part of the transport gas, without prior coal oxidation or external recirculation of char. In the 500–700°C carbonization range, the air to coal ratio appears to be the variable controlling the formation of agglomerated char. Studies indicate that there exists a region where bituminous coal cannot be carbonized in the entrained state. This limit appears to be defined by air to coal ratios equal to or less than 6.75 cft/lb (maf basis). It is quite probable that an intermediate area exists where incipient char agglomeration occurs and plant geometry may act to hasten a serious build-up of agglomerated char. The upper limit of air to coal ratio is defined by the quantity of air necessary to react with the coal at a given feed rate, to produce the desired carbonization temperature with enough external heat supplied to offset radiation losses. A greater quantity of air supplied to the reactor operating under approximately adiabatic conditions, would result in higher temperatures. As a representative figure, carbonization of bituminous coal by entrained bed technique leaves 8.7% (dry basis) at 500°C. The yield of tar plus light oil ranges from 26 to 44 gallon /ton and char yield ranges from 550 to 650 kg/ton. Heat in the gas ranges from 900 to 3000 Btu/lb (maf coal). Figure 6.52 shows a typical set-up of entrained bed carbonization plant.

Carbonization of coal powder with air in a externally heated reactor involves, moving the coal with air to the base of an externally heated vertical retort. Heat is transferred from the wall of the reactor to the suspended mixture, and the air reacts with the coal to supply a substantial portion of the heat required for carbonization. All products of reaction, including char, tar vapor, and gas, leave the top of the reactor, and the products are separated in suitable equipment. This system has been selected for processing lignite at Rockdale, Texas (USA). In this system of carbonization, gaseous products inside the reactor move upward at a superficial velocity of 6–8 ft/s near the top of the reactor. 30–40% of the heat required for carbonization is transferred through the wall of reactor and 60–70% is derived from combustion of air and carbon inside the retort. Approximately 80 Btu is transferred to the coal from such cubic foot of air introduced with the coal; consequently, 2– 4 ft³ of air is required for each lb of dry lignite carbonized. Reaction can be controlled automatically by regulating the heat transferred through the wall and by changing the air–coal ratio. This method has certain advantages – the capacity and efficiency are high and product gases have higher heating value owing to the external heat. Compared to other systems of carbonization, fine coal is heated in a minimum time, and the capacity of the reactor is high. About 12 min is required to carbonize the coal, and the capacity of a reactor is



- 1. Raw coal bin
- 2. Rotary feeder
- 3. Combustion chamber
- 4. Reactor
- 5. Primary separator
- 6. First cyclone
- 7. Second cyclone
- 8. start up chain bin
- 9. Indirect cooler
- 10. Wet precipitator
- 11. Indirect cooler
- 12. Oil scrubber
- 13. Samable container
- 14. Char receiver Coarse
- 15. Char receiver Fine
- 16. Column char reservoir
- 17. Air container
- 18. Tar receiver
- 19. Impinger

- 1. Raw coal bin
- 2. Rotary feeder
- 3. Combustion chamber
- 4. Reactor
- 5. Primary separator
- 6. First cyclone

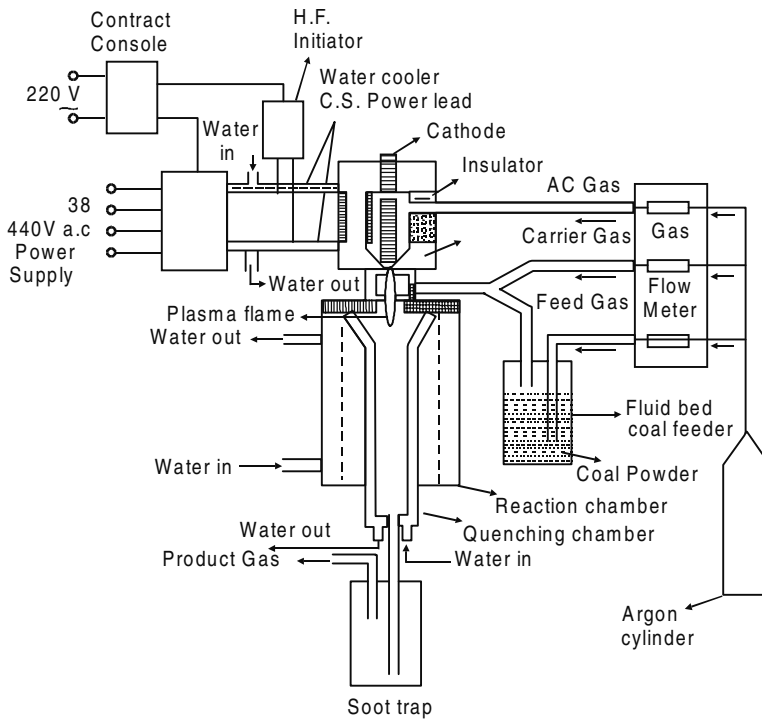
6.52 Pilot plant for carbonization fine coal.

60–90 lb/ft³ of reactor volume per hour, depending upon diameter and volume of reactor. The ratio of heating surface to reactor volume has to be a properly balanced to permit upto 40% of the required heat to flow through the wall of the reactor. By suspending fine coal in a gas stream moving upward, fine particles which take short time to carbonize, are swept through the reactor rapidly, and the larger particles move through the system at a rate inversely proportional to their size. Thus carbonization of all sizes is attained in minimum time depending upon the superficial velocity of gases. The reactor is suspended in a furnace and is heated by combustion of process gas which is burnt in direct contact with the retort, giving rapid transfer of heat to the reactor by direct radiation from the gas.

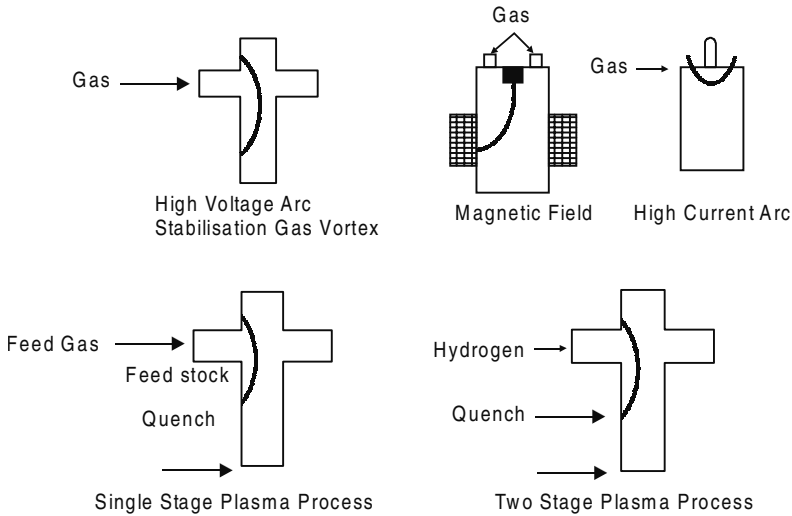
6.9 Flash pyrolysis

This is a special case of carbonization where the coal is heated at a very rapid heating rate. At very high heating rate (10^5 °C/s) upto 70% of the coal can be volatilized, much of it as pitch even though standard laboratory tests show that the coal contains only 40% of volatile matter. Thus flash pyrolysis can be employed for deriving enriched by-product by carbonization of low rank and medium caking coal. Fast pyrolysis of coal showed that the apparent overall activation energy increases with the rank of coal. Flash pyrolysis is found to be independent of reactor size and residence time and sub-bituminous coals have been successfully converted into refinery feed- stock grade oils using red-mud as a slurry phase catalyst and using fused beds of steel-wool and Ni-Mo catalyst. Pyrolysis at high heating rate, need not be necessarily yield high amount of liquids. Besides heating rate, pressure and gas atmosphere, the particle size and temperature influence liquid yields from primary thermal decomposition at high heating rates with optimum conditions for fast hydrogen access to the coal particles and the released volatiles at high pressure and reaction temperature. Catalytic hydro-pyrolysis of coal under fast heating conditions using a small fluid-bed reactor, showed the feasibility of catalytically promoting the vapor phase hydrogenation of coal volatiles at atmospheric pressure. In the absence of externally added hydrogen, flash heating of a ZnCl₂ impregnated low rank bituminous coal was found to yield large amounts of tar products than the untreated sample. This is the reversal of the trend observed in slow pyrolysis. Flash pyrolysis of coal with reactive and non-reactive gases showed increasing yield of gaseous hydrocarbons. Chars produced from flash pyrolysis of two bituminous coals show high reactivity to oxygen, burning at rates upto 10 times than those for bituminous coal char and petroleum coke. Muller of Chemische Werke Huls Aktiengesellschaft, Marl, West-Germany disclosed a single stage plasma process (in 1985) for commercial production of acetylene. This process

was first started by BASF in West-Germany in early 20s. The first commercial unit was put up by Chemische Werks GmbH in 1940. Above author has further improved upon the process and now the production of acetylene and ethylene by this process amounts to about 180,000 ton/year. The process is competitive with that of ethylene production by petrochemical process because of its unique wide range of flexibility towards raw material. The basic principles of plasma generation by various methods are shown in Fig. 6.54. The arrangement shown in the upper row differ in the voltage/current ratio. Smaller the ratio for a particular electric power, shorter is the burning arc and easier to stabilize the arc on an intended discharge path. However since the current intensity increases with decreasing voltage/current ratio at constant power burning off on the electrodes also increases, so that a compromise must be found. High voltage arcs of lengths upto 1.5 m can be stabilized in practice only by means of a gas vortex which needs sophisticated control of the flow; however, the comparatively low current intensity allows the use of cheap long lived electrodes. Although special stabilization measures are in general unnecessary for high-current arcs of a length of a few centimeters, for arc length upto about 50 cm, stabilization of the arc can also be obtained by



6.53 Schematic diagram of "plasma reactor" (CFRI, Dhanbad).

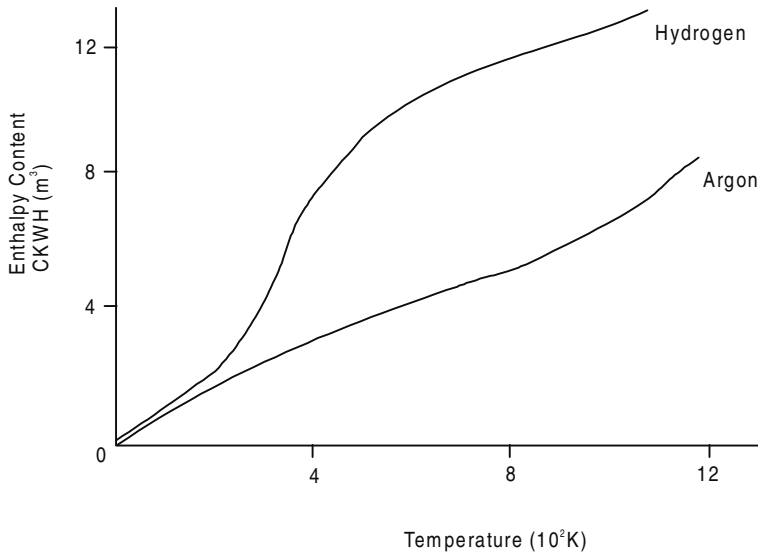


6.54 Plasma process arrangements in principle.

a magnetic field arranged concentrically around one or both electrodes. If the earthed electrode is located outside the actual arc furnace, this is called “transferred arc.” Since electrode burn-off does not present a problem in this case, even relatively long arcs can be operated without special stabilization measures in the region of this electrode.

Temperature within the arc zone is between 9700 and 20,000°C causing the gases to exist in plasma state. Although plasma state occurs within a small part of the reaction space, it is an important effect and resulted in design of two different arrangements of the system:

- (a) The one stage arrangement in which the feed material to be converted to gas, flows through the electrical discharge zone as the carrier gas or with a carrier
- (b) The two stage arrangement in which a carrier gas flows through the zone and the feed material is injected into the “hot plasma jet” and converted into desired product (e.g. C_2H_2 or NO). In the two stage plasma process, the carrier gas serves as a store for the energy of the electrical discharge. For chemical reactions the energy density should be as high as possible at the lowest possible temperature. As shown in Fig. 6.55 (comparison of hydrogen and argon yield) shows that other polyatomic gases which dissociate at relatively low temperatures and thus capable of storing large quantities of energy and can be released again when the temperature is lowered are particularly suitable.



6.55 Change in hydrogen and argon yield.

6.10 Acetylene production

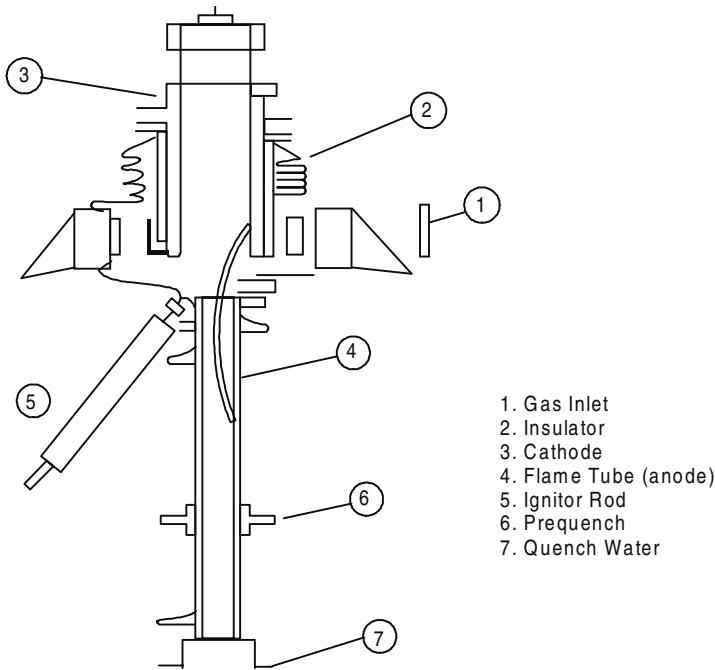
The formation of acetylene from hydrocarbons require a large quantity of energy which, on one hand is determined by the high enthalpy of formation and which amounts to 4–5 kWh/kg of C_2H_2 , depending on the hydrocarbon employed. Furthermore, C_2H_2 is formed to a significant extent only at temperatures above $1700^\circ K$, accordingly approximately a further 2.5 kWh/kg of acetylene are additionally required for heating the feed material. If this energy is to be generated by combustion of hydrocarbon, then between 30 and 40% of the feed material must be burned. This portion now can be made available as electrical energy by means of the plasma process. Since the formation of acetylene in industrial processes is in general above the equilibrium concentration and the reaction rate is very high at the temperature of formation, the residence time of the reactants at this temperature must be a few millisecond in order to obtain acetylene concentrations in the gas which allow an economical recovery of acetylene. This leads to the following requirements for the production of acetylene:

- Supply fo large quantities of energy at high temperature.
- Limitation of the residence time to a few millisecond, which requires high heat transfer rates in order to supply necessary energy within this short period.
- A high rate of quench in order to avoid decomposition of the acetylene into the elements during cooling process.

All these requirements can be met in a relatively simple manner in plasma process.

6.10.1 Single stage plasma acetylene process

Figure 6.56 shows a section through the plasma furnace. The arc burns between the water cooled cathodes and the likewise water cooled anode over a length of about 1.2 m at a current intensity of upto 1.2 kA. The cathode is at a different voltage potential of 6.7 kV and is separated from the earthed parts of the furnace by an insulator. This results in a power of 8.5 MW. The hydrocarbon to be cracked is tangentially fed via the vortex chamber, so that a gas vortex forms in the plasma furnace; the arc mainly burns in the “dead zone” of the vortex. The roots of the arc on the electrodes are forced into a rapid rotation by the vortex flow, so that the arc burns only for a fraction of milliseconds on any given point. In this way, immediate burning through the electrodes can be avoided and life time of electrode upto 1000 h can be obtained, even if the electrodes consists only of carbon-steel. Within the arc column, temperature of about 20000°K occur. Intensified by the vortex flow, the arc is surrounded by a coaxial temperature field with a steep gradient, which results in a wall temperature



6.56 Chemical Werke Huls AG plasma furnace.

of only 700–800°K. Heat losses from the arc furnace can thus be limited to about 10%. An axial temperature profile is superimposed by radial temperature distribution, since the gas is increasingly heated up as it flows through the plasma furnace, so that the radial temperature profile is flattened. Additionally, energy is increasingly consumed by the conversion of hydrocarbons, resulting in decrease of temperature again behind the anodic striking point. Maximum acetylene production is reached in the direction of gas flow just below the anodic base. At this point, gas still has a average temperature of about 1800°K. The enthalpy content of this gas stream can be utilized in the conversion of more hydrocarbons, especially for the production of ethylene. The liquid hydrocarbon is injected for prequenching into the hot gas stream in less than 1 ms. The hot gases (1300°K) is then quenched with water to about 500°K. The rate of quenching is thus 10^6 °K/s or more.

Due to large variation in temperature within the entire plasma furnace, it is not possible to define an exact reaction temperature. Rather this space can be conveniently divided into different temperature/reaction zones, size of which is governed by:

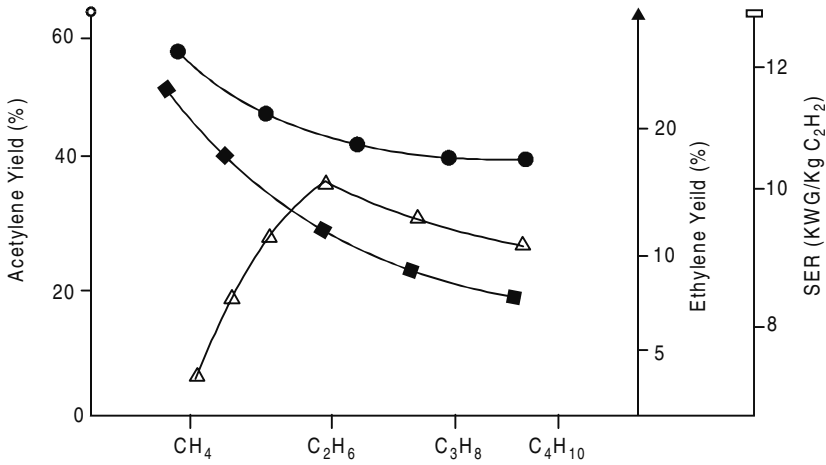
1. geometry of the plasma furnace, specially the electrodes.
2. electrical parameters of the plasma furnace, which fixes temperature of the arc column.
3. velocity distribution of the gas stream, and
4. nature of the hydrocarbons produced.

6.10.2 Reaction and yield

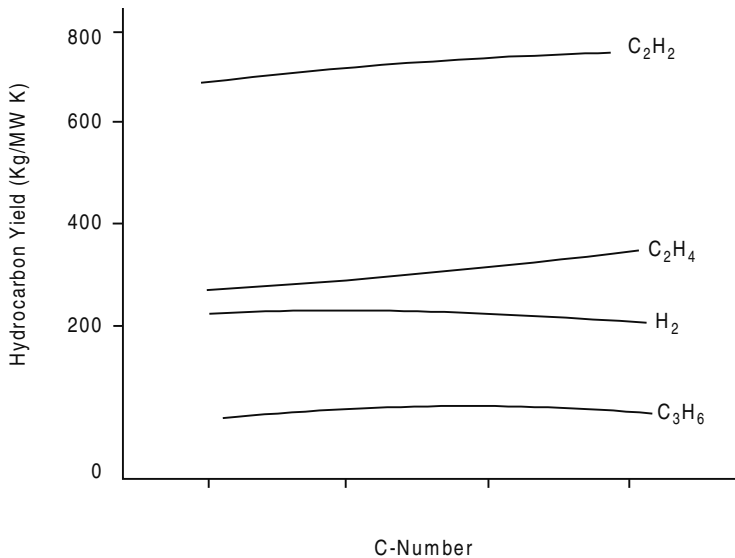
Due to the complex inter-relationship among above four parameters affecting high temperature zone, it is difficult to ascertain production of acetylene and ethylene either by thermodynamic or kinetic method. Although it seem that due to occurrence of high temperature acetylene yield could be governed by thermodynamic equilibrium, but the fact is that 40% of the cathode and anode space which provides the direction of reaction is located at a distance of about 2 cm from the wall where the temperature is relatively low. Thus one may only roughly calculate the yield and energy consumption in such case. In yield calculation the parameters mentioned above for high temperature zone becomes important. We will discuss also the result of the process in terms of hydrocarbon yield, in following section.

Figure 6.58 shows the yields of acetylene and ethylene, and specific energy requirement for various saturated hydrocarbons under a fixed reaction condition without prequenching. Methane shows the highest yield of acetylene and the lowest yield of ethylene, but simultaneously it has

the highest specific energy requirement (SER); ethane gives the highest ethylene yield. With increasing chain length, the acetylene yield, the ethylene yield, and SER decreases. This implies decreased reaction enthalpy for the formation of acetylene from a particular hydrocarbon. When mixtures of different hydrocarbons are used, the results can be well represented as a function of C-number (mol fraction of bound carbon in the gas). Fig. 6.58 shows the result obtained for a mixture of methane and propane can be represented as a largely linear function of C-number.



6.57 C₂H/C₂H₄ yield and energy consumption for various hydrocarbons.



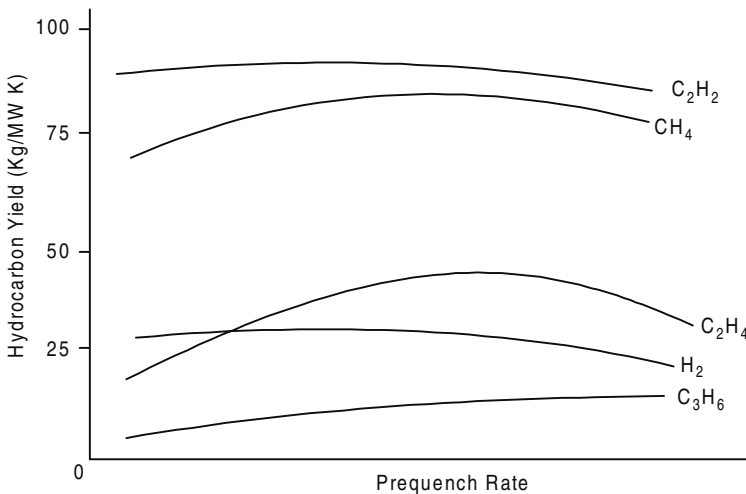
6.58 Specific product yield as a function of C-number of CH₄/C₃H₈ mix.

Virtually similar yields are obtained when mixtures of methane and n-butane are used. Marked deviations are found, however, when unsaturated or branched hydrocarbons are used as feed material; but even in the later case an analogous relationship between yield and C-number can also be found which will help calculating yield of product spectrum for any gas mixture by progression model analysis.

Methane, unsaturated C_4 compounds and higher acetylenes are also found to form as by-products in these reactions along with others (Fig. 6.103). The great flexibility of the plasma furnace makes it possible to recycle these components into the cracking process, after they have been separated off. As a first approximation, the cracking of the hydrocarbon used as the prequench takes place analogously to the ultra-short time cracking in the steam cracker.

Fig. 6.59 shows the yield of various hydrocarbons relative to electric power, with natural gas as the plasma gas and propane as the prequench. Whilst the acetylene and hydrogen obtained remain virtually constant, the ethylene obtained passes through a flat maximum with increasing quantity of prequench.

The reason is that, in the region of small quantities of prequench, more ethylene can be formed initially with an increasing feed rate. At the same time, the reaction temperature falls due to the greater quantity of prequench. When it falls below a certain value, the temperature is then no longer adequate for the formation of sufficient ethylene during the given residence time. In addition to ethylene, propane is also formed increasingly with a rising quantity of prequench, but the propane/ethylene ratio, which is 0.25



6.59 Specific product yield as a function of prequench rate.

as a maximum is substantially lower than in the case of the ethylene production in steam crackers: this indicates the substantially greater severity for cracking. This is also confirmed by the methane yield. Froment has carried out experiments on the ethylene and propylene yield for different hydrocarbons and cracking severities in steam crackers. If the methane yield is taken as the indicator of the cracking severity, the quantities of ethylene and propylene formed in the prequench are in good agreement with the value obtained by Froment. The structure of the hydrocarbon has a great influence on the ethylene yield. The relative ethylene yields of various hydrocarbons are compared in Table 6.14.

Above discussion confirms that a wide variety of feed material can be used in arc process without any further modification of the system (plasma furnace). With the aid of reaction model, optimum feed rate and reaction condition for various hydrocarbons can be predicted. Depending on the various yields a definite proportion of the electrical energy supplied can be stored in the form of "chemical energy."

Distribution of the electrical energy fed (for generating ARC)

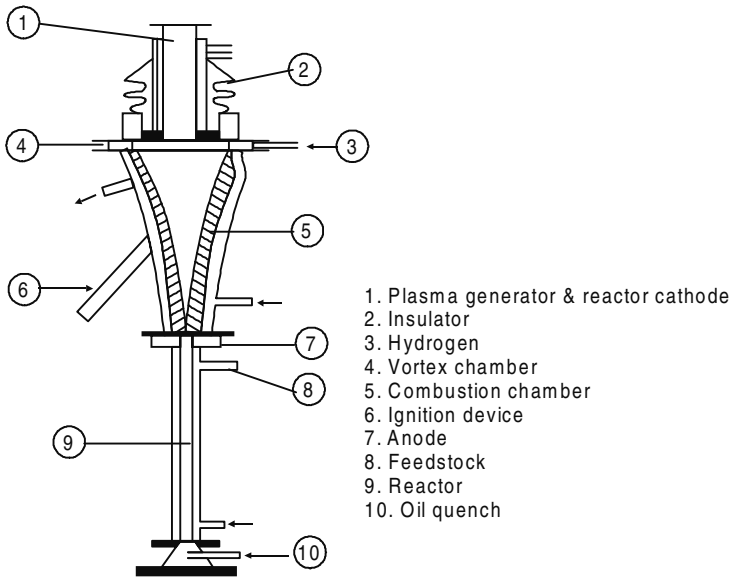
Losses in cooling water	10%
Enthalpy of the gas	40%
Chemical energy	50%

Separation of cracked gases: In addition to the components mentioned above, cracked gas also contains a large number of other components such as soot and higher acetylenes. A typical cracked gas analysis obtained is as follows:

H_2	= 59.5% by volume
C_2H_2	= 15.5
C_2H_4	= 6.0
C_3H_6	= 0.9
C_3/C_4 acetylenes	= 1.3
C_3/C_4 dienes	= 0.3
Butenes	= 0.1

Table 6.14 Relative ethylene yield with various hydrocarbon used as prequench

Hydrocarbon used for frequency	Relative ethylene yield (%)
C_2H_6	100
C_3H_8	52
n- C_4H_{10}	72
i- C_4H_{10}	24
n- C_4H_8	27



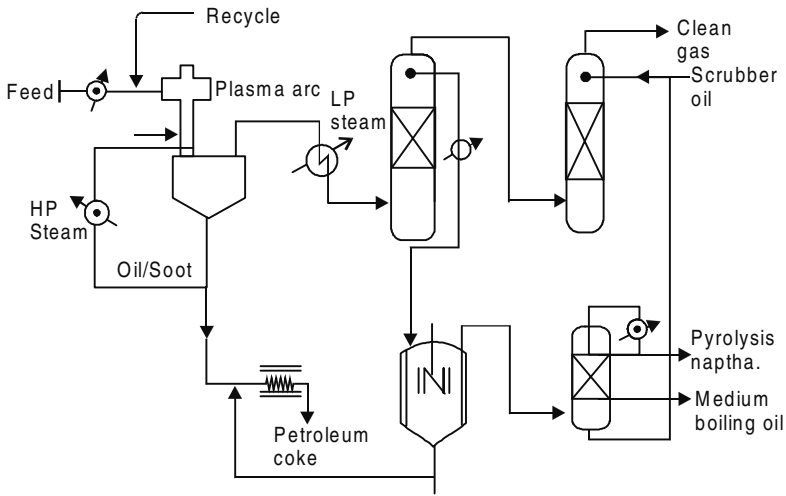
6.60 Plasma generator and reactor.

C_5C_6/C_6H_6	=	0.6
CH_4	=	12.5
Saturated C_3/C_4	=	0.9
N_2	=	1.0
CO	=	1.1

The cracked gas is separated in two stages, namely a low-pressure stage for separating off soot and higher hydrocarbons, and a high pressure stage for separating and purifying gaseous constituents.

Low pressure purification: If the cracked gas is quenched with water, the enthalpy content of the gas which amounts to about 40% of the total electrical input, can not be utilized for heat recovery. If, however, a high boiling oil is used for quenching, about 80% of the enthalpy can be recovered in the form of steam. Based on large scale preliminary tests, a new separation scheme was developed and shown in Fig. 6.61.

Here the soot is taken out by high boiling oil along with quenching procedure. The soot /oil mixture thus obtained is then processed for making petroleum coke free from sulfur and ash, a high value product. After repeated cleaning of soot in several oil-scrubbing steps, the high and medium boiling fractions are separated by a select scrubbing oil which is also being regenerated continuously. Aromatic hydrocarbons thus separated can be utilized after necessary stabilization (e.g., in motor fuel sector).



6.61 Low pressure purification of cracked gas from plasma furnace.

High pressure separation

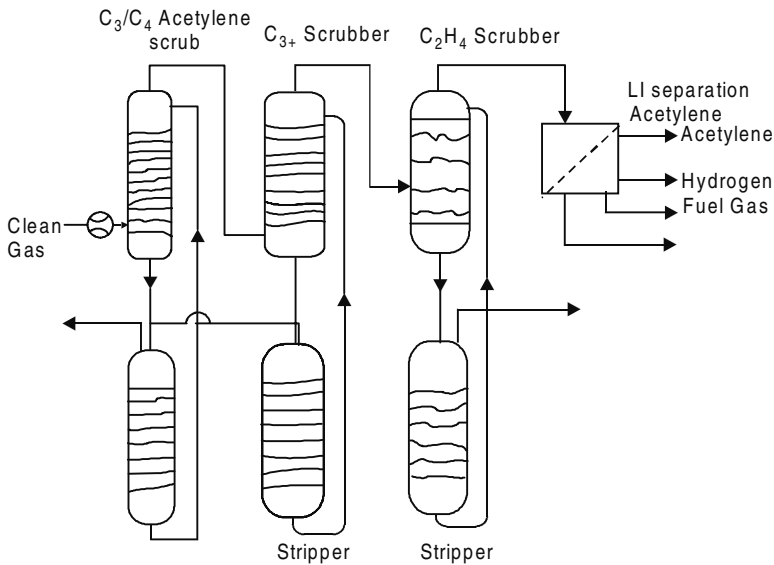
After the gas has been compressed to 15–19 bar, the acetylene is separated by a solvent. Production plant at Huls, West-Germany uses water as solvent for this step. Linde-AG has developed another process where selective solvents are used for this purpose which gives lower investment cost. The separation takes place in four steps (Fig. 6.62):

- Separation of the higher acetylenes.
- Separation of C_3 hydrocarbons.
- Separation of acetylene to a purity of 99.7% (by volume), necessary for further processing at later stage.
- Separation of residual gases into hydrogen, ethylene, methane, and fuel-gas category in a low temperature plant.

The methane along with exit gases from stages (a) to (c) above, is recycled to the plasma furnace. The hydrogen obtained is of hydrogenation quality and the ethylene obtained is of polymer grade. To adjust the optimum C- number, a small part of the hydrogen can also be admixed to the feed hydrocarbon. Fig. 6.62 shows the high pressure separation according to Linde AG.

6.10.3 Economics

Average consumption figure of the raw gases and by-product yields with gas mixtures of saturated C_1 – C_3 hydrocarbons as plasma gas and LPG as prequench medium are shown in Table 6.15.



6.62 High pressure separation unit (according to Linde A.G. Plant).

Table 6.15 Consumption figures & by product yields for single stage plasma C₂H₂ process

Consumption / by product yields	Unit	Figures
Hydrocarbon consumption	tonnes/ ton of acetylene	2.5
Energy required for cracking	KWH/tonne of acetylene	9800
Energy required for separation	KWH/tonne of acetylene	2500
By-product yields : Ethylene	tonnes /tonne of acetylene	0.42
Hydrogen	tonnes /tonne of acetylene	0.28
Soot	tonnes /tonne of acetylene	0.50
Pyrolysis gasoline	tonnes /tonne of acetylene	0.08
Residual oil	tonnes /tonne of acetylene	0.12
Fuel gas	KWH/tonne of acetylene	500

Table 6.16 shows that there is a low raw material consumption especially with C₂H₂ and C₂H₄. This can be further seen from the competitive process such as partial oxidation route for production of acetylene and naphtha cracking for production of ethylene, as shown in Table 6.16.

As the figures in Table 6.16 show, even the cost of electricity required for arc generation can be covered by the difference in raw material consumption or by a modern efficient power station, equalising overall cost. However, special advantage of plasma process is that electrical energy can be obtained from low grade fossil fuel or even from non-fossil energy sources. With respect to spectrum of by-products, arc plasma process has the special advantage in that the most of cracked gas components are recyclable, finally generating only a small number of by-products, which

Table 6.16 Comparison of raw material consumption in other C₂ production processes

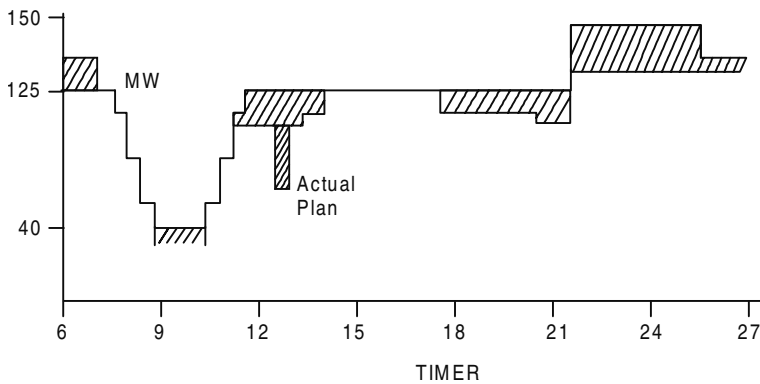
Process	Raw material consumption (tonnes / ton of C ₂ H ₂ + C ₂ H ₄)
Plasma process	1.6
Partial oxidation	4.4
Naptha cracking	4.4

results in less problem with respect to marketing by-products. Also the hydrogen generated is of high purity and has a large demand in the market. After necessary treatment, some of the soot can be used in rubber sector or as a high-grade carburising agent. Remaining small amount of residual oil can be used for the production of synthesis gas. This kind of economics for raw material and by-product sale results in a balanced investment. A further advantage of the plasma arc process is that the plasma furnace can be started a brought to full load within a few seconds. This enables to run the system with: “off-peak” energy of a power station.

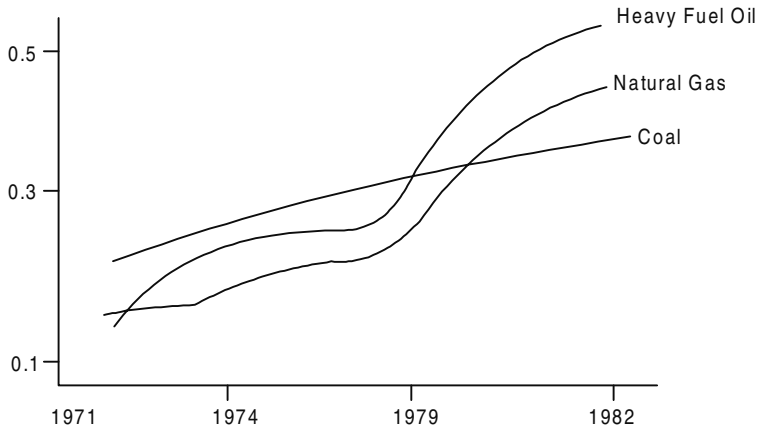
This technique is followed in the plant at Huls: Fig. 6.63 exemplifies this daily schedule. This also implies flexibility of the schedule (change over) at a short notice. To isolate the down-stream gas separation from rapid fluctuations, gas holders are installed for 200,000 m³ of cracked gas and 150,000 m³ of recycle gas, and there is also an acetylene gas holder. Thus a total of 440 MWh of electrical energy can be stored. In this way in certain regions favorable power contracts can be utilised.

Furthermore, relative energy cost of various energy forms, have favored with time electrical power use in recent days in West-Germany as well as in other industrialised nations (Fig. 6.64).

Many forecast assume that this development will continue in near future although there may be some variation and this gives rise to bright prospect



6.63 Plasma furnace day schedule.



6.64 Trend in price ratio of various energy carriers to electrical energy in Germany.

for plasma process in the years to come. With these incentives, research in plasma process has been directed mainly in two direction –

- (a) Widening of the raw material varieties that can be used in the process.
- (b) Application of the technology in other industrial processes.

Above points are exemplified by the case study of acetylene production from coal in the following section.

6.10.4 Acetylene production from coal

In plasma process only a small part of the hydrocarbon can be fed in liquid form (as discussed above). If this shortcoming is to be avoided, a two stage arrangement (described above) must be used. As early as 70s Chemiske Werke Huls AG, designed a commercial plant based on two stage process for cracking crude oil and residual oil. Hydrogen was used as plasma gas in such case for following advantage:

- (a) Hydrogen is capable of storing greater amount of energy at a relatively low temperature.
- (b) Hydrogen is obtained as a pyrolysis by-product itself.
- (c) Do not form any undesirable by-product.
- (d) Has a positive effect in the reaction which results in increased yield from same feed-stock.

Plasma generator used for acetylene production from coal (8.5 MW capacity) is also operated with gas vortex stabilization as described above for one stage plasma furnace. However, for lower density of hydrogen more attention needs to be paid for flow conditions. Here the arc is generated between an iron cathode and an iron anode at a current density

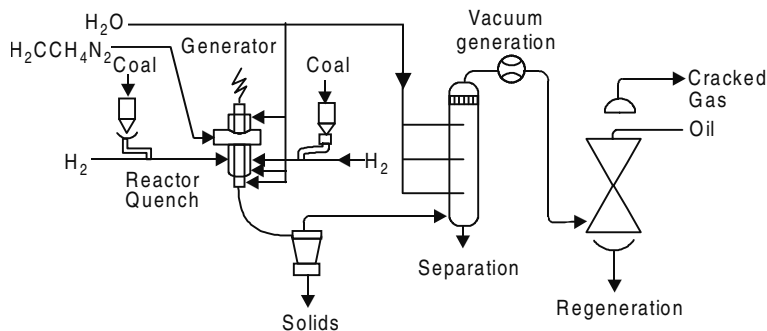
of 1.2 kA and a voltage of 7 kV. At the plasma generator exit hydrogen has an enthalpy density of 3.3 kWh/m³ which corresponds to a mean temperature of 3300°K. Hydrocarbon, either in gaseous, solid or liquid form, then can be introduced into this hot gas and reacted for a suitable residence time in order to form acetylene and some by-products. They are then quenched with oil or water. Chemische Werke set up this plant in 1980 and a pilot plant later at the end of 1982 which optimized – reactions, reactor design parameters, recovering heat and separation procedure.

Schematic diagram of this plant is shown in Fig. 6.65. Core of this plant as shown is the plasma generator with electrical power of 500 kW. The dry and pulverized coal is injected into the system by means of a carrier gas consisting of hydrogen or a recycled gas. The coal gets heated up to about 2000°K in a fraction of second emanating volatile matters which then are cracked to acetylene. After a residence time of order of milliseconds, the gas/coal mixture is quenched with water down to a temperature of 200°C. After separating coke/soot the gas is cooled further and purified by several oil-scrubbing stages. A vacuum of about 0.3 bar is generated in the delivery line by a pump. If water quenching step is replaced by other quenching methods, it will be possible to recover the sensible heat in the form of steam.

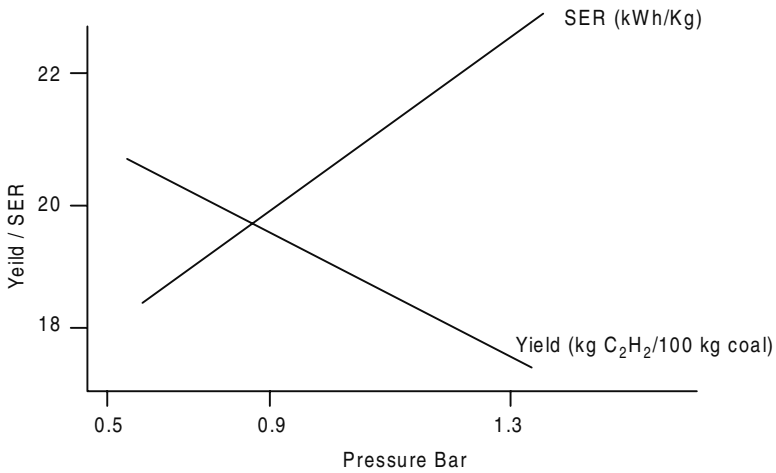
Optimization of react or size requires consideration of followings:

- (a) Coal particles need mixing with hot plasma jet as fast as possible in order to achieve rapid heating and consequent devolatilization of coal in short period necessary for acetylene formation.
- (b) Coal particles must be volatalized to the maximum extent before they strike the reactor wall; this will avoid cake formation.

Reaction design for continuous run of several hours was achieved from above considerations but thermal losses was relatively high in first design. Secondly pressure in the system proved to be an important parameter as the yield of acetylene markedly increased with rise in pressure (Fig. 6.66)



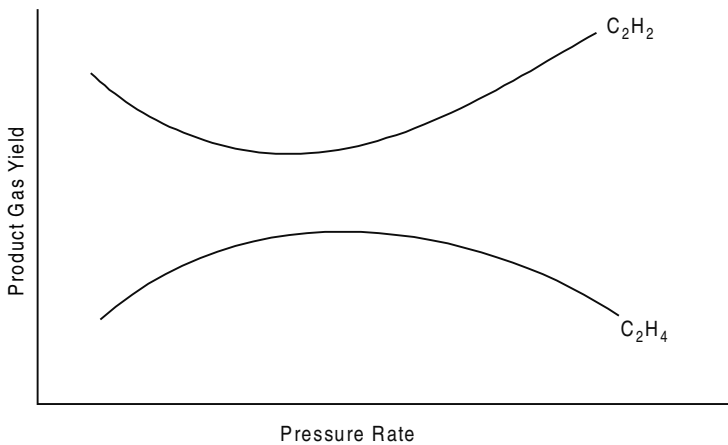
6.65 Acetylene from coal (pilot plant schematic) Germany.



6.66 Pressure dependence of the acetylene yield in coal pyrolysis.

and the specific energy consumption decreasing with the fall in pressure. Thus the pressure effect indicates that transport processes within coal particles have a marked influence on pyrolysis efficiency. Similarly, coal particle size also have a marked effect on the yield of acetylene. Further more, volatile matter content and oxygen% in the coal also plays an important part on acetylene yield.

Exit gas temperature before quench found to be 1800°K, which shows like one stage process liquified gas can be used in this case also as prequenching medium (Fig. 6.67). Besides acetylene, ethylene also forms in this process and thus the ratio of acetylene/ethylene is adjustable in this technology.



6.67 Sketch of the acetylene and ethylene yields as a function of the prequench rate.

Ethylene produced simultaneously as a by-product contributes high in the economics. Semi-commercial plant based on this pilot plant is scheduled for 1987 and will appropriately generate data for commercial set-up by 1993. This pilot plant programming at present optimizing – minimum coal requirement as feed, conversion to other basic chemicals, etc. Since the process has advantage of low investment cost, the break-even size for a profitable plant is also low.

Following are some enquiries put forward by the author and reply by Muller of Chemische Werke:

Question and Answers:

1. How the economics of the process of C_2H_2 generation from coal could be justified using large amount of electricity at the processing media? Electricity is a prime value and off-peak use may not be justified all the time especially in a continuous plant. Whether raw material saving offset other costs?

-With reference to comments by Chakraborty (Acetylene from coal by plasma – Chakraborty, CEW. 14 (11), pp. 65–68) electricity is available in India at favorable price and infrastructure facility for utilization of product gas in steel industry (sponge iron making) exist in India and thus the process is suitable for Indian conditions. Moreover, it is observed that electricity cost rises less rapidly than raw material price. Plasma process is thus economical in India and has been found so in last four decades in West Germany.

2. More details of the construction of pilot plant unit requested. Whether other electrodes can also be used.

In April 1984, paper written by R. Muller gives detail of 8.5 MW unit (discussed above) and 0.5 MW plasma generator is just a scaled down unit of 8.5 MW. In this generator, the arc burns between two cylindrical water-cooled steel electrodes. As a result of the vortex stabilization, stationary arc roots are not formed; instead, the arc roots rotate over the inner surface of the tube electrode. Apart from steel, other electrode materials also have been tested and found to have no influence on the result of acetylene cracking. Selection is based on compromise between cost and life of the electrodes.

3. How much soot is generated by this process? - Solid products generated by the process are coke and carbon-black. The latter strongly adhere to the surface of the former and we were unable to separate these two.

4. What is the size of coal used in this process? Grinding to extraordinary fine size may affect economics of the process.

You are right. Size of coal particle is an important parameter. Our

experience show, finer the coal particle better is the production of C_2H_2 . According to our estimate (as also being used by other European countries), coal size 90% below 100 micro-meter (same as used in pulverised fuel burner) are suitable.

5. What are the limiting factors in scaling-up the process?

There is no limit in this case. At Huls, plasma reactors of arc power 6–10 MW are used. Depending upon requirement appropriate number of reactors are arranged in parallel to meet demand.

6.11 Economics of coal carbonization

Economics of coal carbonization depends upon a number of factors, such as

- (a) Quality and use of the end products.
- (b) Market cost of the main product and thereby contributing to overall economics.
- (c) More specifically, on the single largest product for which the plant is meant.
- (d) Total cost of the project.
- (e) Site specificity of the project.
- (f) Basic property of the raw materials.

The last parameter is not of least importance, as can be seen from following experience obtained by the author while working with speciality coals of North Eastern India. These coals have very high volatile matter and consequently their carbonization yields relatively high amount of by-products like tar and gas. with very high rise in by-product prices (pitch, creosote oil, etc.) in past couple of years and also possibility for use of these cokes for cement making by VSK-technology (compared to economics of using coke breeze from Bihar and other countries). Broadly areas where gas has no market, it may be advisable to install internally heated furnace as the capital investment with such carbonizer is much less than conventional continuous vertical retorts and the loss in revenue due to non-utilization of lean gas produced in the internally heated type retorts, gets largely compensated by their low capital cost. Continuous vertical retorts are designed to produce optimum quantity of twin fuel – coke and gas. By appropriate use of coal, these units are also capable of generating coke for ferro-alloy industry (besides domestic coke). In these type of plants, revenue earned from gas plays a significant role in project economics. Generally, coals suitable for CVR in producing domestic coke and town gas supply. This only LT- carbonization operation bordering on success in USA are those that produce a semi-coke or char that has improved form value and semi-coke is substantially greater than the value

of raw coal on heat value basis, value of tar may be only slightly more than the value of coke on the same basis. If the price of the coke were the same as the raw coal on heat basis, present operation of LT-carbonization in USA should not be commercially successful. The main reason for this is that the time of carbonization is too long and cost of processing is too high. But the situation in near future may change due to present oil crisis.

If coal is to be carbonized to produce a char for power plant fuel, the value assigned to the char cannot be much greater than the value of the raw coal on a heat basis because a power plant can burn almost any grade of fuel efficiently. Char may have superior value because of its improved physical and chemical properties and this must be considered in assigning a value to processed fuel. For example, a lignite of 7000 Btu/lb heating value containing 36% moisture definitely has less value for fuel, on heat basis, than a dry char of 11,000 Btu/ lb which can be made from the lignite by carbonization. The char can be burned at higher efficiency, higher temperature and with higher heat release/cft of furnace volume, and can be handled at a lower cost.

If a power plant is obliged to use lignite as fuel, cost of suitable facilities to partly dry and pulverise the lignite for efficient combustion is substantial and the combustion chamber of a conventional steam-generating unit has to be modified to burn the high moisture lignite efficiently. The cost of drying and carbonizing facilities for producing a high grade fuel of about 11,000 Btu/lb for combustion in a slagging type furnace may not be much greater than the cost of lignite pulverizing and drying equipment required for conventional pulverised fuel firing in a non-slagging type furnace; consequently, the net cost for processing may be quite low. The net cost is the difference in cost between the two methods of utilization in terms of fuel cost at the burner after the value of tar is credited. If coal is to be carbonized successfully for power plant fuel, the value of tar must more than pay for the net cost of processing. To accomplish this, the net cost of processing must be low and time required for carbonization as short as possible. This is a difficult technical and economical problem, and results show that power plant utilizing char as fuel must be at the mine head except when the yield of tar from the coal is very high.

If the coal is to be carbonized to produce char for blending with high-volatile coking coal to replace low-volatile coal in coke-ovens, the value of the char must be equated with the value of low volatile coal it may replace. In the western states and California in USA, the delivered cost of low volatile coal from Oklahoma is 35 to 100% higher than the cost of high volatile coal (coking), so in this case the margin available for processing costs is substantial and the economics of LT-carbonization for this purpose will be quite different than for power plant fuel. On the other side, Bureau of Mines (USA) has advocated drying and carbonizing lower

rank coals before burning the char as fuel for power production or before using the char for blending, because the value of tar from some fuels may be substantially higher than the cost of the coal and the lower rank coals can be dried and carbonized very rapidly at relatively low cost. Large plants for drying and for experimental work on carbonizing lignite, using the process developed by the Bureau of Mines at Denever, has been constructed by Texas Power and Light Co for the Aluminium Company of America at Rockdale, Texas (USA), where a 240,000 kW steam-electric power plant uses dried lignite and char to furnish electric power for the aluminium smelting works. This new development has created considerable interest in coal distillation and Bureau of Mines has received many enquiries as to the possibility of using LTC with various coals for making fuel for electric plants.

Generally in all processes production of char is avoided as it do not have a ready market. However, if the char is intended for use as us a power plant fuel, following economic relationship holds good between total cost and value of coal char and tar:

$$V = (C + P - RC) / T, C = (VT - P) / (1 - R), \text{ and } P = VT - C(1 - R)$$

where P = nett cost of processing and handling fuel to the burner, C = landed cost of coal at power plant, R = nett heat ratio (char/coal), T = tar yield (gallons/ton) V = break-even value of the tar (cents/ gallon).

A plant which is meant to supply special product like ferro-alloy coke having low ash, low sulfur, low phosphorus and high reactivity, may be economical even at low capacity. The reason is that such special cokes are not produced in the country and the ferro alloy producers use char coal in large quantities paying high price (Rs. 1800/- ton or more). Some ferro-alloy producers are also trying to import low ash coke. If the LTC-plant is captive to a ferro-alloy plant, the coking unit may be installed adjacent to the ferro-alloy unit to avail of common facility. Talcher (Orissa) coal is specially suited for this purpose whereas Raniganj coal is not as the later has high phosphorus content. All MP coals in India also have low P and S. In general, LTC gives a tar which is not subjected to cracking and therefore supposed to be primary in nature. This is particularly true for internally heated system due to flushing action of gases and short residence time in the hot zone. The yield of tar is also more in LTC. Simple compounds like benzene, phenol are present only in smaller concentrations. The tar contains more of hydroaromatic compounds and less of aromatic compounds than HTC-tar. The tar acids content is also high (30–35%) and the higher homologues of phenol are predominant. The main group of products from LTC tar is phenols. LTC- tar is the only sources for some of the xylenols. Processing pattern followed for HTC-tar is not suited for LTC-tar. When the capacity of LTC-plant is say 1000 ton/day which gives about 60 ton/

day tar, detailed processing for extraction and fractionation for phenols may not be economic. It is then preferable to process the tar for bulk products like creosote, pitch, etc. When sizable quantity of tar is available, the phenols can be extracted from the fraction upto 230°C and fractionated to compounds like cresols, xylenols, etc. The neutral portion after separation of phenols can be hydrogenated to middle distillates under mild condition. The hydrogen requirement will be low and this is more advantageous than hydrogenating the total tar oils with phenols, as the phenols have to be first hydrogenated to aromatic hydrocarbons and then to hydroaromatic compounds to get suitable middle distillates. The hydrogen consumption for neutral oil hydrogenation is about 300 m³ per ton while for total tar oil is 500 m³/t. A minimum economic size capacity LTC-plant for detailed tar processing with tar acids recovery and fractionation, is considered at a level of 10–12 million gallons per year of tar necessitating carbonization of 2400 ton /day assuming a tar yield of 7%. Even if a LTC-plant of this size is not installed at one place, it may be possible to pool the tar from different LTC-plants at one place and carry-out the tar acid extraction and fractionation and even hydrogenation. It is desirable to add HTC-tar from coke ovens at this stage and process it. Efforts should be made to divert the tar from coke- oven plants instead of burning them. HTC-tar processing is essential for overall economy as it will give valuable aromatic compounds like naphthalene, anthracene, and pyridine bases, phenol, and cresol. LTC-tar is highly phenolic, being predominant in the higher phenols which have limited use. Naphthalene and anthracene are virtually absent and the pitch obtained has to be given special treatment for use in road making. LT-tar is a good raw material for conversion to petrol by hydrogenation but its economic viability with the limited quantity of tar is poor. The Indian market condition would permit LTC-tar to be processed to obtain various oil fractions, the different type of phenols and pitch. The phenols boiling beyond 270°C need not be recovered from the heavy oil fraction along with pitch which can be used as raw material when fuel in the production of carbon black. It was also found that non-coking coals of India when carbonized (upto 1.5% VM in coke) yields highly reactive coke suitable for both domestic and industrial use. Gas obtained in such case has calorific value of 4200 kcal/ m³ and thus suitable for town supply. Gaseous thermal output is low in LTC range than in HTC range. Coals selected for internally heated (only coke yield) and CVR method f or twin fuel production has following specifications:

Property	Internally heated	Twin fuel CVR
Moisture	Upto 8%	Upto 8%
Ash	Upto 25%	Upto 25%
Volatile matter	25–35% (generally 28 and above)	(normally 30–32)

Caking index	Below 5	10 (max)
S.N.	Below 1.5	2.5 (max)
Free carbon (dmf)	81–83%	80–84.3%

Next comes the economic plant capacity. As Chakraborty mentioned, a plant meant to produce only coke and no rich gas, has to be of large capacity (900–1500 ton/day coal throughout) considering the lower price of domestic coke (Rs. 500–600/ton) in the market. Also prospect of marketing products are more near the consuming centre. Advantage of setting up such plants near the pit-head are often offset due to transportation problem (if the consuming centre is far from the coking plant) of coke, tar, etc., to the prospective markets. Moreover, coke made from non-caking coals do not possess adequate physical strength to withstand repeated handling and long distance transportation. It is appropriate to make such cokes near as possible to the consuming areas. It has also been observed that, delivered cost of coke at the consuming centre, which may be about 100 km away from the coke plant, is marginally lower compared to the cost of coke produced at the consuming centre. Generation of coke fines is a loss to the company as price of coke fine is about one-third of that of sized coke. The average price difference between sized coal and coal-fines is about Rs. 6 per ton. Coal fine has such better market than coke dust.

CVR (continuous vertical retort) is most suitable for producing twin fuel and tar products. These plants are capital intensive and the economic viability mostly depends on the assumed market of gas and coke. Capacity of such plants is mostly decided on the demand of town gas in the domestic and industrial sectors. Gas transmission system being very costly, it is suggested that such plants be located within a reasonable distance of the consuming point where both coke and gas can be marketed. The minimum economic size appears to be 750 tpd of coal input. A tar processing plant if included, should be simple to produce only oil fraction and pitch which have ready market. Phenol extraction and separation is very costly. An elaborate processing plant may; however be included if the carbonization capacity of the plant is 1500 tpd and above. The Dankuni Coal Complex (WB) carbonizes 1500 ton of non-caking coal per day to produce 100 ton of coke (smokeless domestic coke), 18–20 million ft³ of gas and 75–80 ton of tar chemicals, which includes phenol, cresol of different grade, xylenol and HBTA. In addition, 5500 ton (NH₄)₂SO₄ (fertilizer grade) made.

6.11.1 Comparative plant economics

It has been assessed that, one internally heated LTC-plant (with tar recovery facility) meant to produce about 190–200 ton of coke/day may cost Rs. 10–12 crore including all facilities. Cost of production of sized coke (plus

6 mm) may range from Rs. 600 to 650/ton and taking 12% return on equity, selling price of coke will be Rs. 700–750 per ton. Delivered cost of this specific coke at the consuming centre is likely to be Rs. 800/ton. The consumer will naturally be attracted to buy this coke after striking a balance between the cost of charcoal and special grade hard coke. If the LTC-plant is made captive to the consumer, cost of LTC-coke may be reduced and the user won't have to procure desired coke from open market.

For production of domestic coke (no rich gas), one 900 tpd LTC plant (internally heated) may cost Rs. 270–290 million. Annual production of LTC-coke will be about 23,500 ton. Cost of production of coke will range from Rs. 350 to 370 per ton. Taking 12% return on equity, selling price may vary from Rs. 425 to 450 and the consumer may not get it at a price less than Rs. 550/ton. However, cost of production of coke will be reduced if plant capacity can be increased to, say, 1500 tpd of coal, but marketability of 400,000 ton of coke within an area of 100–150 km distance has to be ensured. Cost of such project, along with elaborate tar processing facility may be about Rs. 500 million.

Cost of production of sized coke can be reduced maximum to Rs. 270–280 per ton and taking 12% return on equity, ex-factory price will be about Rs. 340/ton. Thus under prevailing coal price and increased plant cost, it will be difficult to sell processed solid fuel (domestic coke produced by LTC) at a lower cost than Rs. 340/ton (ex-factory), unless some new technology is adopted.

Setting up of a CVR for processing solid fuel to produce twin fuel (coke and gas) is tied up with the marketability of gas and coke in the area. Capital cost of CVR installation to carbonize 1500 tons of coal per day be Rs. 80–85 crore. Economics of such project will depend upon to a great extent on the assured outlet of gas, since the tar chemicals are to be sold at the prescribed price in the market and also price of coke will be required to be maintained at the optimum level for the consumption of the major section of people, including those living in villagers. Gas produced in CVR is meant to be consumed mostly by the industry and its price will be governed by the fuel oil price and also price of LPG in the domestic sector. LPG and natural gas are no doubt strong competitors to any coal gasification project. One CVR installation, of 1500 tpd capacity, may fetch an annual turn-over of Rs. 430 million to Rs. 450 million. At 100% production level, the plant may bring 10–22% profit on equity.

6.12 By-products of coal carbonization and their utilization

Besides coke, by-products of coal carbonization means mainly two products – tar and gas. Use of coke has already been discussed at length and as far

as gas is concerned its chemical components occur in so dilute form that its recovery is uneconomical: Gas is thus mostly used as a fuel or at best as reducing agent for iron ore fines for production of sponge iron. One ton of coal gives about 300 m³ gas which yields about 10–11 kg of (NH₄)₂SO₄. The coke oven gases are processed in developed countries for recovery of sulfur, thiocyanates, ferrocyanides and ammonia. (NH₄)₂SO₄ obtained by absorbing NH₃ in H₂SO₄ from coke oven gas was considered inferior to that obtained synthetically because of its tendency for caking. This has been traced to the wide range of crystals formed and the presence of entrained H₂SO₄. It has been shown that by careful control operations, it would be possible to get (NH₄)₂SO₄ similar to that obtained synthetically. On the other hand, tar obtained from carbonization is rich in various chemicals and accordingly we will limit our discussion at this stage to tar components and generation of tar chemicals. But let us first see the chemical constitutional difference between LTC-tar and HTC-tar. Table 6.17 shows the general characteristics difference between LT and HT tar (Note: While composition of LT-tar may vary with coal quality, composition of HT-tar remains same irrespective of coal quality).

It is interesting to note from Table 6.17 that, LT-tar is rich in phenols and aliphatic hydrocarbons while HT-tar contains more naphthalene, phenanthrene, anthracene (aromatics), and yields more tar. Total tar yield in case of low temperature carbonization is also much higher than high temperature tars. In case of high temperature carbonization, the high temperature causes pronounced aromatization and dehydroxylation. Neutral- oil fraction from LT-tar have less aromatics and contain very little naphthalene, anthracene, more of paraffinic, and naphthalenic bodies. Although, an appreciable portion of neutral oil may be better processed into diesel oil by straight distillation but it can still generate better value product by hydrogenation. LT-tar is very much complex in composition (more than 450 individual components identified so far by capillary gas chromatography) and thus do not have a ready market. HT-tar on the other hand has narrow range of different chemical constituents and easier to process. Predominant chemical constituents in HT-tar are shown in the table below:

Table 6.17 General characteristics of LT & HT tar

	LT-tar	HT-tar
Yield (related to coal input)	10%	3%
Aliphatic hydrocarbons	10%	Nil
Phenols	25%	1.5%
Naphthalene	3%	10%
Phenanthrene / Anthracene	1%	6%
Pitch (fraction above 3500C p.p.)	35%	50%

Predominant composition of high temperature tar

Boiling Range	Av % of tar	Major components
0–170 °C (Benzole or Light oil fraction)	0.5	Benzene, Toluene, o,m,p -xylene
170–210 °C Carbolic acid	1.5	Styrene, Indene, Hydroindene, Coumaron, Mesi-tylene Phenol, o-Cresol, m-cresol, p-cresol Pyridine, a-picoline, β -picoline, γ -picoline
210–230 °C Middle, creosote Or naphthalene oil	4.5	Naphthalene, Thionaphthene, a-methyl naphthalene, #-methyl naphthalene, 2,3-xylenol, 2,4-xylenol, 2,5-xylenol, 2,6-xylenol, 3,4-xylenol, 3,5-xylenol
230–270 °C Middle or Creosote Oil	11.5	Biphenyl, Indole, Quinoline, Iso-quinoline, Quinaldine
270–300 °C Heavy or Neutral oil	4	Biphenyl, Acenaphthene, Diphenylene oxide, Fluorene
300–350 °C Anthracene oil	13	Anthracene, Phenanthrene, Carbazole, 1-methyl fluorine, 2-methyl fluorine, 3-methyl fluorine, 4-methyl fluorine, 9-methyl fluorine Diphenylene sulphide, 1-methyl phenanthrene, 2-methyl phenanthrene, 2-phenyl naphthalene, 3-methyl phenanthrene, 9-methyl phenanthrene, fluranthrene, Pyrene.
Above 350 °C Pitch (crystalloid)	45.6	1,2 benzfluorene, 2,3-benz fluorine, 3,4-benz fluorine, Acridine, Phenanthredine, 7, 8-benzquinoline, Benz m,p,o-fluorethene, 3,4-benzfluoranthene, 10, 11-benzfluoranthene, 11, 12-benzfluoranthene, 1, 2-benzpyrene, 4, 5-benzpyrene. Perylene, 11, 12-benzperylene, Picene, Brazan, Triphenylene, Coronene

The average yields of by-products under Indian conditions through HTC (coke ovens) are shown in Table 6.18.

Tar goes with thermal condensation products, while benzol and liquor are collected separately. Coke is the ultimate residue and gas is the totally non-condensable part. These three condensation part – benzol, liquor and tar, are discussed in detail.

Benzol is recovered from the gaseous product of carbonization by absorption in wash oil, absorption on active carbon and by cooling, which results in condensation. Of these, the wash oil process is most widely adopted as it is suitable under a wide range of condition. Characteristics of wash oil, mentioned earlier and will not, thus, be repeated here but we will concentrate our attention more on recovery aspect of benzole.

Crude benzole yield is around 1% by weight of the coal carbonized, which means in terms of total weight, coke oven batteries has the capacity to generate 190,000 ton/year in the whole country. In addition to this another 5130 ton of benzole will be available if hydro-dealkylation of

Table 6.18 Average yield of byproducts from HTC(coke oven) plants

Product	% by weight
Gas	16
Benzole	1
Liquor	4
Tar	3
Coke	73

naphthalene-oil fraction (210–270°C) is carried out. Table 6.19 shows the benzole fraction composition as derived from various carbonization furnaces (figures are in percent):

Table 6.19 Yields of various chemicals from different type of furnaces

	Coke ovens (steel plant)	Continuous Vertical Retort	Intermittent Vertical Retort	Horizontal Retort
Benzene	65	45	45	68
Toluene	15	8	19	12
Xylene	5	4	8	2.5
Ethyl benzene	0.5	0.2	0.5	0.2
Trimethyl benzene				
Ethyl toluene	0.3	0.5	0.2	0.2
Tetramethyl benzene	0.1	0.2	0.1	0.1
Isopropyl toluene	Trace	1	1.5	0.1
Nephthalene	0.3	0.1	0.1	0.1
Paraffin	1.5	0.5	1	0.7
Naphthalene derivatives	0.3	20	7	5
Unsaturation	0.2	4	2	2
Indene	10	14	10	6
CS ₂	0.4	0.7	0.3	0.8
Thiophenes	0.5	0.7	0.4	0.4
Other components	0.7	0.4	0.6	0.5
Other components	0.5	0.7	1.7	1.4
Benzol / to coal	3-3.5 gal	2-2.5 gal	1.5-2.5 gal	2.5-3 gal

In India, at present we carbonize about 25 million ton coals annually. BTX is also derived from petroleum sources. Benzene, toluene and xylene are the main fractions of benzol (as can be seen in Table 6.19) and these are separated by acid wash, followed by distillation. In the new method, hydro-refining of benzol followed by distillation is practiced. One of the important compound that can be recovered from benzol forrunnings is cyclopentadiene (occurs upto 12% by weight). Cyclopentadiene is an important pesticidal intermediate (like Endosulfan, heptachlor, aldrin, dieldrin, chlordane, isoderin, etc.).

Ammoniacal liquor obtained from coal carbonization vapor contains 52% phenol, 2.4% cresols and 6% xylenols. The acid sludge obtained from this operation contains valuable organic bases like pyridine, quinoline,

etc. In Western countries these bases are separated regularly and constitutes a major source in those regions. In Russia phenol is recovered from coke-oven effluents, by steaming process. The mother liquor from $(\text{NH}_4)_2\text{SO}_4$ crystalliser contains 30–40 g of pyridine bases. In Russia 60% of the pyridine bases needed in that country is produced from this source. The crude bases recovered contain 60–70% pyridine, picolines, 10–25% phenolic compounds and 10% neutral oil. Western countries; however, do not extract pyridine bases from this sources.

In above discussion we have known general constituent of tar. In general in addition to above, it is found that tar contains about 10% of the heterocyclic oxygen, nitrogen and sulfur containing groups. Compounds containing more than one heterocyclic atom; however is rare and although poly-aryl compounds (like diphenyl, phenyl-naphthalene, etc.) are present, they are very minor in percentage occurrence. Compounds with partly saturated-ring systems are also present in small amounts but in most of the components containing ring $-\text{CH}_2$ in groups, the CH_2 is part of a five member ring. Thus only a very small number of the component chemicals in tar are present in an amount to warrant its economic extraction. Arguing on this line, Mc-Neil has listed following compounds in tar that has possibilities of economic recovery.

Table 6.20 Important components (wt%) in coke-oven (HTC) and vertical retort (LTC) tar

Components	wt% of dry tar	
	Minimum	Maximum
Benzene	0.22	0.25
Toluene	0.04	0.06
O-xylene	0.07	0.13
m-xylene	0.03	0.05
p-xylene	0.02	0.03
Ethyl benzene	0.02	0.03
Styrene	0.02	0.04
Phenol	0.61	0.99
o-cresol	0.25	1.33
m- cresol	0.45	1.05
p- cresol	0.27	0.86
Xylenols	0.36	3.08
High Boiling tar acids (HBTA)	0.83	8.09
Naphtha	0.97	3.21
Naphthalene	0.12	0.25
Methyl-naphthalene	3.18	8.80
Acenaphthene	0.66	1.06
Fluorene	0.51	0.88
Diphenylene Oxide	0.68	1.50
Anthracene	0.26	1.00
Phenanthrene	1.75	6.30
Carbazole	0.60	1.33
Tar bases	1.77	2.09
Medium soft pitch	43.7	63.5

In India, out of 12 coke-oven plants associated with various steel industries in government as well as private sector, only 5 plants have tar distillation facility. Based on Table 6.20 and infrastructural facility available. Recovery of following chemicals from coal tar is recommended.

1. *Tar acids* – Phenol, cresol, xylenol, HBTA (high boiling tar acids).
2. *Pyridine bases* – Pyridine, beta and gama-picoline, high boiling tar bases, quinoline, indole, and carbazole.
3. *Hydrocarbons* – Naphthalene, anthracene, acenaphthene, and fluorene.

Rourkela Steel Plant is the only integrated steel complex in India which have full facility for recovery and purification of tar acids. Pyridine bases are not recovered from coal tar in our country. But the recovery of tar bases will yield (along with pyridine) picolines and quinolines which has long been proposed with the Bokaro Steel Plant. The Bhilai Steel Plant and Durgapur Projects Ltd have facilities for making only sodium-phenolate from which phenol, cresol and xylenols can be manufactured. With this vision, Durgapur Chemicals was set up in the mid-sixties mainly as a down-stream project of Durgapur Project Ltd. Thus Naphthalene and benzene (hydrodealkylation of 210–270°C coal tar fraction yields 15% benzene and 60% naphthalene) are two main products of DPL which are used by DCL as critical inputs. Naphthalene is processed into phthalic-anhydride which is used in paints, dyes, plasticizers, etc. Benzene is converted into phenol, mono-chlorobenzene or dichlorobenzene, dephenoloxide, etc. Plantwise availability of crude tar and tar products from various steel plants in India are shown in Table 6.16. Note in this table that figures for Neyvelli Lignite Corp. are not included as it is a LTC plant, whereas all plants listed above are of HTC type. Table 6.21 lists the by-products extracted and sold by Neyvelli Lignite Corpn, in the year 1976.

The light-oil is a fraction which constitute about 60% benzene, 15% toluene, 4% xylene (o,m and p), 1–5% naphthalene, 2.5–3% styrene-indene and small amounts of paraffinic naphtheneic hydrocarbons, thiophenes and CS₂. In LTC process light oil output is about 1.4% and that in HTC 0.8%.

Table 6.21 Composition of LTC tar phenols obtained from Indian coal and lignite

Material Fraction	Singraren coal tar B.P. upto 230°C	Neyvelli lignite tar B.P. upto 220°C
Phenol	11%	52%
o-cresol	12	8
m, p-cresol	23	32
Xylenols & ethyl phenols	54	8 (major are 2,4 xylenol & 4-ethyl ph)
of which 2,4 & 2,5 xylenols	16	
3,5 xylenol, 3-ethyl phenol & 4-ethyl ph.	16%	(ph = phenol)

The recovered crude tar is distilled in a continuous pipe still to give four standard fractions in order of ascending boiling range—light oil, naphthalene oil, creosote and anthracene oil plus pitch. Crude tar is first dehydrated and then fractionated in a distillation tower. Pitch and anthracene oil are separated in other columns. Light oil has a boiling point less than 195°C. Light oil is sometime added to benzole before refining

as it resembles crude benzole in chemical composition. Of the total pyridine bases formed during coal carbonization, about 40% is precipitated with coal tar and balance 60% remains in the coke oven gas. Pyrolenes bases remaining in coke oven gas are low-boiling bases like pyridines, pyrolenes and lutilines. Those precipitating with tar are the higher boiling ones like quinoline, iso-quinoline, quinaldine, etc. Naphthalene is separated by hot press method and has a crystallization point of 78–78.5°C and contains about 4% residual impurities. This naphthalene does not have the purity high enough for manufacture of alpha and beta-naphtholes. High purity products can be obtained by chemical treatment of hot pressed naphthalene.

Neyvelli Lignite Corporation has also done some unique experiments on production of plant growth stimulators on the basis of humatic matters. The lignite was digested in an autoclave (156–200)°C at equivalent pressure of 7–21 bar. By this process about 150–200 g of organic matter per liter of the mass was brought to water soluble condition (pH of solution being 9–10). The fixation of nitrogen in the lignite was done by air oxidation followed by ammoniation (with gaseous ammonia) in dry process, and in wet process first treatment with nitric-acid and then ammoniation with ammonium-hydroxide. The resultant compound was found to work excellent in promoting vegetative growth. Demand of coal chemicals in India, as surveyed in 1985, is presented in Table 6.22.

CFRI, Dhanbad, made a significant contribution towards our knowledge in tar chemicals in last three decades. This includes development of a novel method for recovery of lower phenol from ammoniacal liquor (1.7 to 3 kg acid/litre of liquor) by using dilute aqueous ammonia. Recovery of Indene-Coumarone resin from benzole fraction was successfully tested at Bhilai Steel Plant. Phenol-formaldehyde resin from tar acids (180 to 270°C fraction) for preparation of hard boards and epoxy resin (also polycarbonates and polysulfones) from bisphenol A and C (from phenol and o-cresol and also after hydro-dealkylation of HBTA) has been successfully carried out in the institute. Tar bases like quinaldine, lipidine and indole were separated from cresole or wash-oil fraction. 98% quinoline was obtained after fractionating naphthalene-oil fraction in 30 plate column and treating the appropriate out with 34–40% aqueous phosphoric acid (quinoline phosphate separated out by fractional crystallization) and subsequent decomposition of the quinoline-phosphate with caustic-soda

Table 6.22 Demand of coal chemicals by various industries

Chemical	User Industries	Demand ton/yr (1985)
Phenol	Resins including board and laminates	22,400
	Pharmaceuticals	5,000
	Enamels	2,200
	Epoxy resins	2,300
	Pesticides, weedicides etc.	6,600
	Total:	38,500
Cresols	Resins & agrochemical industries	10,000
	Disinfectants, agrochemicals etc	300
	Dyestuff industry	300
	Drugs and pharmaceuticals	1,266
	Agrochemicals	500
Total:	2,066	
Picolines	Drugs and pharmaceuticals	1,600
	Rubber, insecticides, textiles etc.	1,400
Total:	3,000	
B.T.X.	Insecticides, resins, polymers etc.	6,02,000
Naphthalene	Dyestuff, plasticizers, alkyd resins etc industries.	25,000
Anthracene (+90% pure)	Anthraquinone dyes	3,060

solution. Moth ball quality naphthalene was separated from naphthalene-oil out (210–230°C) by centrifugation or crystallization (cascade process) followed by hot pressing. For obtaining high purity naphthalene (99% pure) solvent refining with a wide variety of solvents from acetic acid, methanol to diacetone alcohol, and mixed solvents, followed by crystallization from such organic solvents, were successfully tried. However recrystallization failed to remove thionaphthalene which forms mixed crystals with naphthalene. Chemically pure naphthalene was obtained by – (i) sulfuric acid refining, (ii) hydro-desulfurization over cobaltmolybdate and alumina as catalyst, or (iii) treatment with formaldehyde in the presence of an acid. Of these, the last mentioned process is the choice for CdF CHIMIE, France and is based on preferential reaction of HCHO with thionaphthalene in the presence of catalytic quantity of sulfuric-acid to form methylene bridge polymers of low volatility, which can be separated by distillation. The catalytic vapor phase oxidation of naphthalene to phthalic-anhydride under fluidized bed condition, has been developed in pilot plant level with 80% yield. Further improvement of yield to 97–99% has been achieved in the laboratory by employing alkali promoted V_2O_5 - P_2O_5 catalysts in the fixed bed. The purity of the product is 95–96%. The beta-naphthol process developed by CFRI, Dhanbad has been patented and commercialized. A 650 ton/year plant is already in full production at Bokaro (Bihar) and a second plant having 1000 tpa production capacity has been commissioned at Cuddalore (Madras). The recovery of naphthalene from naphthalene oil in Indian steel plants seldom exceed 50% of the potential resulting in loss

Table 6.23 Chemical output from different steel plant coke ovens in India

Description Chemicals	BSP (400 MT/ day)	BSL (400MT/ day)	DSP (106 MT/ day)	RSP (108 MT/ day)	TISCO 100t/d (Burn- pur)	TISCO 400t/d Jamshed- pur	Total
Crude tar-% dry charge	3.02	3.2	3.0	3.0	2.89	3.0	
Production(t/y)	146140	165800	85.140	93.660	64.330	95.580	650920
Naphthalene	6140	11.500	3.400	3.750	-	-	24790
Crude anthracene	2,920	4.300	-	-	-	-	7,220
Crude phenol	1,170	-	-	-	-	-	7,170
Phenol	-	500	-	140	-	-	640
Cresols	-	600	-	230	-	-	830
Pitch	78,180	90,360	51,080	46,830	-	-	266450
Tar oils	53,340	56,700	28,950	17,230	-	-	156220
Pyridine bases	-	200	-	-	-	-	200

of considerable quantity of naphthalene with drained naphthalene oil (DNO). The DNO which is the mother liquor left over after naphthalene recovery contains about 50–60% naphthalene, 3.4% 1-methylnaphthalene, 10–12% 2-methyl naphthalene, 3–8% phenolics and 1.8–2% quinoline bases. Laboratory studies at CFRI have shown that the recovery and separation of the two isomeric mono-methylnaphthalenes can be accomplished in following manner: The DNO is first freed from phenolics and basified by extraction with 10% NaOH and 25% H₂SO₄ respectively. The neutral portion is then cooled and maintained at 15.5°C to crystallize some of the dissolved naphthalene and filter-pressed. The oil is then subjected to fractional distillation in a 30 plate column and a narrow cut in the range 238–246°C is collected. This fraction contains about 70–80% 2-methyl naphthalene and 20–30% 1-methyl naphthalene, 2-methyl naphthalene is separated from this cut by cooling it in two stages first at 0°C and then at –20°C. The crude is filtered under suction when about 70% of 2-methyl naphthalene is obtained as white crystals of 90% purity. The crude is recrystallised from methanol to obtain 2-methyl naphthalene of 99% pure.

Phenanthrene is the second largest constituent of coal tar, its percentage being around 5. Anthracene, phenanthrene and carbazole occur together and on an average constitute about 75% of the lower boiling fraction of anthracene oil (i.e., 300–330°C). Crude anthracene cake having composition – anthracene 25–30%, phenanthrene 30–40%, and carbazole 12–20% together with some acenaphthene, tetracene, diphenyl-sulphide, fluorine, etc., is recovered from this fraction by cooling followed by centrifuging or filtering under reduced pressure. The so-called 40% anthracene is obtained by recrystallizing this cake from hot anthracene oil which retains most of the phenanthrene without altering the anthracene:

carbazole ration. Methods have been developed at CFRI to upgrade the purity of anthracene upto 95% in 90% recovery by use of selective solvent systems designated as Arosolve, which have low solubility for anthracene but high solubility for the contaminants. Chemically pure anthracene can be obtained by removing impurities (mainly tetracene and carbazole) by azeotropic distillation with ethylene-glycol. The mother liquor obtained after anthracene crystallization can be worked up further for the recovery of phenanthrene and carbazole. The carbazole content can be taken out by alkali fusion followed by hydrolysis. The more polar phenanthrene having greater affinity to polar organic solvents can be purified by treatment with sulfuric-acid prior to recrystallization.

Alternatively, it is treated with sodium and maleic-anhydride which removes impurities like diphenylene-sulphide and carbazole. Among the trio, only pure anthracene has been established market for the production of anthraquinone, an intermediate in the production of vat dye. A process for the oxidation of anthracene (purity 90–95%) to anthraquinone containing less than 1% anthracene has been developed at CFRI, in the semi-plot plant level. The catalyse employed is V_2O_5 - MoO_3 supported on silica-gel and promoted with alkali metal sulphates, bi-sulphates, Ni_2O_3 , Fe_2O_3 , etc. The reaction has been studied in the vapor phase under fluidized condition to yield 100–105 wt% of product acceptable to the dye-stuff industries. In contrast to anthracene, phenanthrene and carbazole do not have immediate commercial outlet. However, it is known that the oxidation products of phenanthrene, namely diphenic acid as well as phenanthraquinone have shown considerable promise as raw material for resins, plasticizers, and agricultural chemicals respectively. The demand for carbazole, on the other hand, is gradually picking up with its recent application in the production of carbazole-indene resin.

Regional Research Laboratory, Hyderabad has shown a unique way of deriving many important chemicals via methanol, while the later is obtained from coal by high pressure (275 atm) ZnO - Cr_2O_3 catalysis method or by low pressure (50–100 atm) 200–300°C pressure developed recently using Cu - ZnO - Al_2O_3 catalyst. The routes considered for producing ethylene and other low boiling olefins from coal are via Fischer-Tropsch synthesis. This will be discussed in greater detail in the coal gasification chapter later. In the same institute, scientists have worked on rapid pyrolysis process of coal for deriving coal chemicals. A suggested strategy is to adopt an entrained flow hydro-pyrolysis process by utilizing H_2 obtained from by-product char gasification. Yield of gaseous and liquid by-product (quantitatively) by rapid pyrolysis is controversial. It seems the key factor is the stabilization of released intermediates and subsequent hydrocracking to produce liquids in high yield. Other reactive gases like CO_2 and steam

showed a distinct positive effect on pyrolysis products under moderate heating conditions ($103^{\circ}\text{C}/\text{s}$)

presumably due to similar stabilizing effect. It was shown that pyrolysis of coal in shock tube, laser irradiation, and flash irradiation gives a predominant product – acetylene. Besides these static conditions, coal can also be rapidly pyrolyzed under flow condition like in fluidized, down-flow, and entrained flow reactor (COED process). The later flow process has commercial feasibility but not static or batch process. In fluidized bed reactor (heating rate $104^{\circ}\text{C}/\text{s}$, the contact time 0.5–1 s) at 854°C yields a variety of olefins (ethylene, propylene, butadiene, etc.) which can be used as starting material for several chemicals. Mostly C_1 – C_3 hydrocarbons are generated by this method (both liquid and gaseous state). In the third method, by plasma technique (mentioned earlier) highest acetylene production is obtained (95%). There appears to exist a linear relationship between fraction coal converted to acetylene and volatile matter (daf basis) in various coals. A notable feature of all plasma pyrolysis (AVCO process) studied is the complete absence of liquid products. Commercially COED method for fluidized bed, Hydrane method for Free-fall and Garrett method for entrained bed are used. Recently, a multi-tubular entrained bed reactor (36 tubes, each of 40 ft length and 6 in. diameter) proposed by cities services (a RandD Co.), USA, and has been preferred over earlier method. Entrained flow reactors provide economic and trouble free operation. In this laboratory cracking and hydrogenation of low temperature coal tars and alkyl phenols have also been studied. The main purpose of these thermal cracking and hydrogenation is to break down larger molecules by catalytic cracking and hydrocracking. Thermal cracking of LT-neutral oil (175 – 275°C BP) and petroleum gas oil gives gases of some thermal value. Under pressure (100 psig and 426°C) LT-tar gives 34% petrol containing 35% tar acids or an acid free yield of 22% petrol. But it causes corrosion in the cracker than petroleum cracking as the latter gives less acid. With rise in pressure and temperature, the yield of petrol from LT-tar increases. The derive fuel gas (low Btu gas) from LT-tar, solid heat carrier system was considered as the best method for tar cracking. The cracking is carried out at 800 – 900°C in fluid-bed over high temperature coke. Over 900°C methane dissociate in presence of water and thus temperature above 900°C was found undesirable for generation of fuel gas. Olefinic gases (ethylene) can also be obtained by thermal cracking (400 – 800°C) of LT-tar and neutral light oil (d.p 120 – 360°C). Fractions having low C/H ratio gives highest production of olefins. Contact time in such cracklings are 0.1 to 1 s. But yield in all these cases are much less compared to petroleum based processes and thus was uneconomical. Cracking of volatile matter to BTX was favorable on activated carbon than on silica. HBTA above 207°C or alkyl-phenols can thermally be cracked to lower phenols in presence of

steam at 675°C with an yield of 54%. Recycling further improves the yield. Cu, Fe, Ni, coke, silica gel, charcoal, and clay has been used as catalyst for thermal cracking. Low boiling aromatic hydrocarbons (aviation spirit) was obtained from neutral oil fraction (B.P. 100–280°C). The product contains 17% normal paraffin (C_{12} to C_{17}), 9% iso-paraffins, 10% monocycles, 40% bicycles and 20% polycycles. Tar acids boiling above 230°C when cracked in vapor phase (700–850°C) gives 30% low boiling phenols. V_2O_5 promotes dehydroxylation of high boiling phenols. The yield to lower phenols increases with temperature rise when activated carbon is used, whereas the same decreases with silica as inert material. Dealkylation was further affected with Fe_2O_3 (5%) with tungsten and vanadium-sulphides. Hydrocracking (hydrogenation + cracking) of heavy oil fractions generates light oil fractions. The resultant petrol has a octane number of 75 with molybdenum catalyst. LT-tar hydrogenated at 4410 psig pressure and 460°C with iron catalyst yield products with diesel index of more than 45. In hydrogenation of LT-tar, iodine was found to be more active than cobalt-molybdate or nickel-tungsten catalyst.

At NCB (UK), Bernhardt et al. has studied extensively non-catalytic vapor phase thermal cracking of coal-tar to BTX and ethylene. BTX yield upto 27% and ethylene 24% reported by above authors. Above results were obtained with hydrogenated coal-tar. Experiments by above authors have showed that product yields could be predicted closely from the cracking pattern of the components and the composition of the mixture. Chakraborty et al at Calcutta University studied thermal cracking of LT-tar and found that yield of pyrolytic carbon increases with temperature and gas shows an increase and then a decrease in yield with temperature. Percentage of CO, CH_4 , and H_2 increases with increase in temperature while that of ethane and ethylene decreases with increase in temperature. Above 700°C due to breakdown of CH_4 , amount of H_2 increases abruptly. Increase in residence time also increases amount of pyrolytic carbon deposited on solid inert surfaces in the cracker.

LTC-tar on the other hand, are more complex in nature and they reflect the nature of the parent coal to a greater extent. Broadly speaking, LT-tar may be classed as coming nearer to petroleum crude with respect to aromatic type (except for high oxygen content). Choudhury et al have carried out some excellent piece of work which aimed at obtaining data useful for designing plants for their treatment and also for further upgrading to increase their product value. Their results show total oils distilling to 360°C vary between 64.2 and 73.5%. The tars do not contain naphthalene and anthracene. The residue on distillation consists of 23.40% pitch of softening range 86–150°C (RandB). While distilling at various temperatures (160–350°C), the rapid increase in distillation rate above 310°C (100 mm) is due to the incipient cracking of the higher boiling

components. A comparison of the distillation curve at atmospheric pressure shows the occurrence of cracking at temperatures above 330°C. At 100 mm pressure the distillate obtained upto 270°C corresponds to that of 360°C at atmospheric pressure for various LT-tar, ranging from 42 to 52% whereas by atmospheric distillation the distillate obtained for the same range of temperature was 65–77%. This higher distillation yield at atmospheric pressure could be explained as being due to the cracking of the higher boiling components present initially in the LT- tars to lower molecular weight components. Thus yield of distillate at various pressures can be correlated to following equations.

$$Y = 0.36 - 66.25 t \text{ (at atmospheric pressure) and}$$

$$Y = 0.33 - 37.50 t \text{ (at 100 mm Hg pressure).}$$

where, Y = yield of the fraction and t = temperature (°C). Distillation of phenol and cresol (cut of B.P. 210°C) was found to be similar in a wide number of LT- tars, but distribution of higher tar acids show wider variation and is a characteristic of the individual tars. The total distillate (pitch free) contains 22–39% of tar acids, 2.2–4% tar bases, and 57–75% of neutral oil. Analysis of the distribution of tar acids, bases, and neutral oil in various 10 degree cut show that tar acid content of the fraction show a steady rise reaching the maximum value at about 230°C. These tar acids are predominantly monohydric as confirmed from their boiling points. Above 230°C, the tar acid content of the fraction decreases to a constant value. The neutral oil, on the other hand, show the reverse trend of tar acids distribution pattern. The distribution of aromatics, olefins and saturates show a similar trend in all LT-tar studied. Toluene and xylene accounts for the higher aromatic content at temperatures below 200°C whereas the higher alkyl-aromatics are responsible for the peak in the temperature range 250–300°C. The mean distillation curve of neutral oil can be represented by a similar type of equation.

$$Y = 0.5 t - 95$$

where, Y = % cumulative yield of fractions (v/v) and
t = temperature in °C.

The neutral oil fraction was found to contain following components:

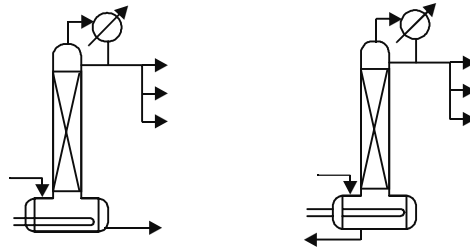
Carbonyls	= 0.9%
Aromatics	= 72%
Naphthalenes	= 9.3%
Paraffins	= 11.7%

The aromatics (above found to be made up of following:

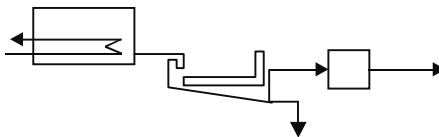
Alkyl pyrenes and higher aromatics	= 23.6%
Alkyl naphthalenes	= 17.0%
Alkyl phenanthrenes and alkyl anthracene	= 13.1%
Alkyl benzenes	= 9.5%
Alkyl fluorenes	= 5.5%

Further studies have shown, composition of the LT neutral oil fraction resembles closely to that of petroleum. Thus the neutral oils could be subjected to hydrogenation to produce diesel oil, or fuels for manufacture of carbon-black. This fraction can also be used as wash-oil for benzole recovery in HTC process mentioned above. The distillation residue (28–32% of the tar) known as LT-pitch have low specific gravity and free carbon, and contains more phenolic bodies and solid paraffins. Further it has high viscosity-temperature susceptibility and low oxidation resistance. It contains less aromatic than HT-pitch and appears to be mainly composed of alkylated aromatics and straight chain hydrocarbons. A schematic detail of separation of LT-tar is shown in following flow diagram.

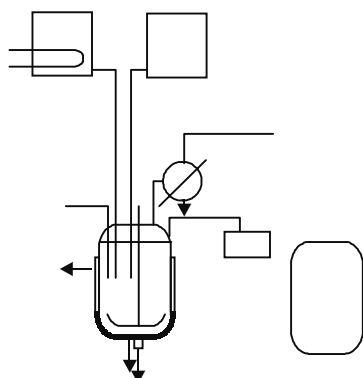
Before winding up this section, let us acquaint our self with some of the industrial processes for converting tar components to various industrial products. Some of these processes are shown schematically in Figs. 6.68–6.72. In India, tar and benzole recovery is poor, thus we need to improve upon this first. Modern tar distillation plant with distilling capacity 60,000–70,000 ton tar/year, will cost about Rs. 20 crore and comparing annual investment of all steel plants, this expenditure can be absorbed to recover these valuable by-products. Recovery of Indene-Coumarone resin from high boiling fraction of crude benzole or solvent



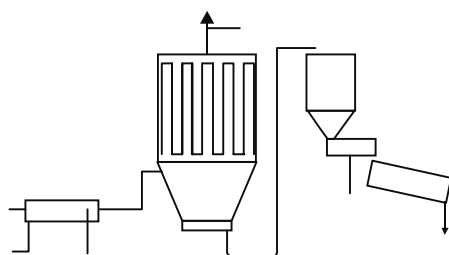
6.68 Light oil distillation for BTX recovery.



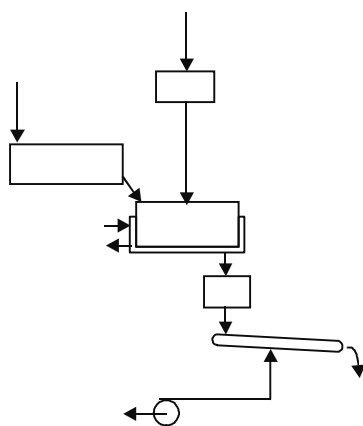
6.69 Naphthalene recovery.



6.70 Phenol formaldehyde resin plant.



6.71 Carbon black manufacture.



6.72 Coke briquetting plant.

naphtha has been successfully tried in the commercial production trial at Bhilai Steel Plant in 1982 and the technology generates grade-I quality IC-resin for paint industry. Quinoline has also been recovered in the same plant from naphthalene-oil fraction by SAIL-R&D. At Bokaro Steel Plant, similar technical feasibility of recovering light crude pyridine bases (second

grade) from coke oven gas has been demonstrated. Along with these, feasibility of extracting H_2S and HCN from same source has also been demonstrated in lab scale. It was also noticed that volume of gas can be increased (but yield of coke and tar do not change) by increasing coke oven temperature from 1200 to 1350°C. If the coal is highly caking it can be rapidly carbonized in entrained bed.

6.13 Coal gasification

Although our theoretical chemistry knowledge tells coal gasification a simple process of reaction of coal carbon with H_2O to form CH_4 , CO and H_2 the later two again combined in a methanator to form CH_4 , but in practice the situation is complicated due to low contact possibility between coal carbon and gasifying agent. This lead to development of process utilizing proper size non-caking and pretreated coal (which lowers caking tendency). Further improve in the gasification technology came from application of catalysts and substantial increase in overall system efficiency through integrated gasification cum combined cycle power system (IGCC). These gasifications can be carried out either with steam or hydrogen or with restricted supply of air. Based on the technique of gasification used, the process can be classified as atmospheric pressure or elevated pressure gasification.

Compositiion of the gas and its calorific value varies from process to process. In steam gasification at 1 atmospheric pressure, the amount of steam which does not react with the carbon and which is therefore left as a component gas, decreases with rising temperature as also does the formation of CO_2 and CH_4 . Thus the gas consists almost completely of H_2 and CO at temperature beyond 800°C. At a pressure of 20 bar qualitatively the same trend is found but in the range of 800–1000°C there are significant amounts of H_2O , CH_4 , and CO_2 . It can be concluded that a high conversion of the carbon and the steam into gases require high temperature exceeding at least, say, 700°C and that high pressure favors the formation of CH_4 . Simultaneously, during the course of heating pyrolysis brings about formation of coke. Coke itself is a porous solid and gasification reactions take place at the inner surface. Therefore, the steam first has to penetrate (or permeate) through a film of formed product gases. Then it has to diffuse into pores before reactions at the wall with carbon takes place.

In steam gasification, it is known that any of these three steps, which occur successively, may determine the rate of the overall reaction, depending on temperature. At normal pressure and at temperature below 1000°C, the chemical reaction is slowest so that enough steam molecules are always offered to the reacting surface. Thus in these range of

temperatures, the rate cannot be influenced by accelerating pore diffusion, for instance by increasing the pressure of film diffusion for example by turbulent mixing. This means, however, that the process can be successfully applied at temperatures above 1000°C, where pore diffusion become rate determining or above 1300°C where film layer diffusion determines the rate. Also it should be noted that the rate of steam gasification rise with temperature and can be described by an exponential law. At a given temperature the reactivity remains essentially constant with increasing carbon burn-off.

It has been found that a big difference exists between lignite and hard coal: but it should be mentioned here that there is no marked difference between different hard coals (anthracite) over a wide range of rank from anthracite to high volatile bituminous coal. The difference in reactivity between lignite and coal can partly be ascribed to different ultimate analysis and to the differences in physical and chemical structure of the two solid fuels. In the case of hydro-gasification, no great differences exists between lignite and hard coal, the reaction rate is less temperature dependent than in the case of steam gasification. Another difference between the two processes is that the rate of reaction during hydro-gasification decreases with carbon burn-off. For steam gasification, only the range between 1 and 10 bar does have pressure influencing the rate of reaction. Beyond 10 bar, the effect of pressure is negligible. This is because, the surface of the coke is already saturated with water molecules, thus rendering negligible effect of increasing pressure. The strong dependency of hydrogasification reaction rate on pressure upto and beyond 100 bar is due to the fact that hydrogen is less strongly adsorbed on the reaction surface than steam, resulting in an unsaturated reacting surface in this pressure range. Liquor formation during gasification can be avoided by passing the hot gas over activated carbon, thus promoting carbon-steam reaction and results in increased calorific value of the gas. It can be predicted from the unique of Assam coal that high pressure gasification will give high methane yield as the VM and consequently aliphatic hydrocarbon content of these coals may also be suitable for the same above reasons.

Various coal gasification processes differ from one another by the way heat is added to the gasifier. In autothermic coal gasification, the reaction heat is generated in the gasifier itself by using a mixture of oxygen and steam as gasifying agent, whereby a certain amount of coal is burnt and the remainder with steam reacts. In other processes heat is generated outside the gasifier by burning either coal or its by-product in a separate combustion chamber with air. This heat can be transferred to the gasifier either by super-heated steam, steam-gas mixture or by solid heat carriers. As the reaction heat is not generated in the gasifier itself, these processes are called "allothermic." In some allothermic process nuclear reactor is used

as a heat source. Heat is transferred to the gasifier here by hot helium. Autothermic processes have already been operated on an industrial scale and further divided into three category – fixed bed, fluidized bed, and entrained bed. We have already acquainted ourselves with these terminologies earlier, which is purely based on the type of fluid-dynamics occurring inside the reactor. Further we may note that in a “fixed-bed” gasifier, a bed of coal particles is moved here during gasification downward in the presence of counter current flow of oxygen and steam. In order to attain reasonable gasification rates the gas velocity must be high and the pressure drop low. This, in turn, implies two limitations with respect to the feed coal – particle size should be more than 5 mm and caking capacity low. In such process, the product gas leaving top of the generator contains pyrolysis product which are formed in the upper layer of the fixed bed. Most systems under this category, adopts a dry ash removal procedure and thus the reaction temperature must be below the sintering point of the ash. The best known process of this kind is the Lurgi which operates at pressure upto 35 bar presently being used in commercial sizes. In the “fluidized bed” gas generator, the velocity of gasifying agent (oxygen and steam) is just high enough to suspend coal particles. Coal can be continuously fed whilst ash is withdrawn from the other side. The avoid agglomeration effect, the operating temperature of conventional fluidized bed gasifier must be below the ash sintering point (i.e., about 1000°C). Commercial Winkler process is an example of this category and found specially suitable for lignites and highly reactive hard coals. The third process “entrained-bed” gasification involves feeding coal in the form of dust with high linear velocity of oxygen and steam. This results in temperature of about 1500°C and corresponding high reaction rate. At this temperature the ash is discharged as liquid slag and withdrawn continuously through the bottom of the reactor. A major advantage of entrained bed reactor is that caking coals can also be used and that the reaction temperature is not limited by the composition of ash. Moreover, the product gas do not contain any tar. Koppers-Totzek gasifier used for making synthesis gas used in production of ammonia and fertilizer is best example of this type. Fig. 6.83 shows the schematics of the three types of gasifiers mentioned above and Table 6.24 shows the composition of gases obtained by above three processes. Gree et al. have shown that coal thermoplasticity and coke structure plays a decisive role in determining reactivity of coal towards hydrogen. His theory was confirmed through experiments with K_2CO_3 and ferric-oxide on the thermoplastic properties of a weakly caking coal which decreases swelling of the coal (effect being maximum at 1–2 Mpa pressure). It was observed that potassium carbonate did not increase the reactivity substantially except when the char was initially carbonized at atmospheric pressure. All the chars prepared with ferric-oxide as additive showed higher reactivity than

that from coal carbonized alone under identical conditions. The greater reactivity observed for the chars carbonized initially at atmospheric pressure was due to their surface areas being higher than those of chars prepared at higher pressure. It is well established that small quantities of certain inorganic compounds and minerals can modify the behavior of coal during gasification, affecting – (a) the rate and quantities of products formed, (b) the caking and swelling proper properties and (c) the coke/char structural properties. Considerable interest has been shown in the use of additives for modification of coal behavior during gasification. The two areas of current investigations are (a) and (b) above. In (a) the possibility of catalytic effect leading to lower process operating temperatures can benefit overall efficiency and reliability of operation. One of the problems in this direction is to obtain a catalyst which is cheap enough for doing away with expensive recovery process. In the case (b) operational difficulties can occur with high swelling coals in both fluidized and fixed bed gasifiers. Various methods proposed for the modification of coal behavior can involve a partial oxidation step, and are accompanied by an economic penalty and/or operational problems. There is scope for dry mixing of additives with fines to produce briquettes of the required properties and when the coal additive contact and mixing need to be intimate. Alternatively, the additive could be added directly with the coal or as a solution. Still potentiality exists for developing a cheap catalyst which could confer in both areas, be economic and in addition provide greater operational flexibility with high swelling coals. In case of the product gas composition, a comparison of a typical series of steam/oxygen gasifier that cover the main types of gasifiers show that they can vary greatly with the following ranges being found: CO about 10–55%, CO₂ about 5–20%, H₂ about 10–45%, H₂O about 15.50%, and CH₄ 5–20%. Even within gasifiers of a similar type, for example, fixed bed gasifiers, large differences in product gas composition can occur. At British Gas/Lurgi, slagging gasifier, high temperature (2000°C) are produced in the raceway. These temperatures lead to this region being under mainly thermodynamically controlled rather than kinetically controlled. The steam/oxygen ratio is low, there is little or no excess steam resulting in low concentration in the gasifier bed. The raw gas composition at the top of slagging gasifier is typically – CO about 50%, CO₂ about 2%, H₂ about 25%, H₂O about 15%, and CH₄ about 7%.

At the temperatures prevailing at the top of the gasifier bed, the reactivity of steam and hydrogen are of interest. In comparison the raw gas composition in the dry ash Lurgi gasifier is typically – CO about 12%, CO₂ about 16%, H₂ about 23%, H₂O about 42%, and CH₄ about 7% and the reactivity of the char towards steam is much more important in this case. The caking and swelling of coal is a physical phenomenon but its

origins are chemical. The interactions between coal and inorganic compounds involve both physical and chemical processes. The thermoplastic process is influenced strongly by the release of volatiles which in-turn is affected by the operating conditions such as heating rate and pressure. High heating rate also tend to raise fluidity. Increasing pressure reduces the volume of gas evolved; it also decreases the volatility of decomposition products and increases their residence time in the plastic phase, so enhancing secondary reactions and leading to an increase in gas and coke yield but with decreased tar yield. Factors which influence rates of reaction of chars with gases are the following – surface area of the char available at reaction temperature, concentration of active sites on the available surface, diffusion of gases to the active sites, structure and crystallinity of the char and the presence of catalytic inorganic species. The catalytic activity of a series of sodium-salts in steam gasification has been studied. Low cost inactive catalyst raw materials of mineral origin like KCl and K_2SO_4 has been found to yield the same effect as active catalyst if the activation is accelerated. Effectiveness of K_2CO_3 and nickel catalysts in steam gasification of a number of coals showed that effectiveness of K_2CO_3 was considerably large, irrespective of the coal type and that of nickel strongly dependent on the coal type and it was extremely large for the low rank coals. A new catalyst formulation has been reported recently for converting synthesis gas into a highly aromatic gasoline using a single fixed-bed reactor. When an intimate mixture of precipitated Fe-K catalyst and of the ZSM-5 zeolite is used, no formation of the aromatics in the liquid phase is observed. But large quantities of olefin and heavy hydrocarbons are recovered. The selective production of a highly aromatic gasoline from synthesis gas is possible in a single fixed-bed reactor using an appropriate mixture of Fischer-Tropsch catalyst with an acid ZSM-5 zeolite.

6.13.1 Various designs of gasifiers

Table 6.24 shows the major coal gasification processes and the corresponding heating value of the product gas. Processes are categorized as per the classification described earlier and processes which uses both fluidized and fixed bed like – coed, cogas and other types (not fitting to above classification) like ATGAS-PATGAS, molten salt and gasification by electric means is not listed but discussed later.

While fixed bed can use non-caking to weakly caking coal and fluidized bed non-caking to medium caking coal, there is no limitation with respect to caking property for entrained-bed gasifiers. In India, at Talcher (Orissa) and Ramagundam (AP) synthesis of gas for fertilizer plant is made by employing Koppers-Totzek process, while the Winkler Fluidized Bed

Table 6.24 Summary of major coal gasification process

Reactor type / Process name	Heating value (Btu/ft ³)
Moving bed:	
Lurgi	294
Wellman-Galusha	268
Willputte	300
Bureau of Mines (stirred reactor)	164
Woodwall-Duckham	160
Fluidized-bed:	
Winkler	294
Exxon	—
ECR	153
C ₂ -acceptor	374
Char oil energy demonstration	—
Synthane	405
Battelle-Carbide process	—
Westinghouse process	136
U-gas process	153
U-gas process	104
Ignifluid	—
Entrained flow:	
Koppers Totzek process	290
Garrette	700
H.R.I. Process	—
Babcock and Wilcox	286
Bigas process	378
Heating by recirculated solids:	
Toscoal	600
Lurgi Ruhrgas	512
Molten media heat carrier:	
Patgas	315
Kellog	329
Otto-Rumel	284
Hydrogenation:	
Hydrane	826
Hygas	495

gasifiers have been adopted by Neyvelli Lignite Corpn for a same purpose. Lab scale pilot plants are existing at CMERI (Durgapur), 18 ton/day 10 atm pressure steam/air fluidized bed gasifier at RRL, Hyderabad (BHEL make), 19 ton/ day Lurgi gasifier at CFRI, Dhanbad, 24 ton/day Lurgi gasifier at RRL- Hyderabad and 150 ton/day fluidized bed gasifier at BHEL-Tiruchirapally (for combined cycle power generation of 6.2 MWe). The last one is in collaboration with Westinghouse Electric Corporation (USA).

It may be noted here that gasification is mainly carried out by controlled reaction of coal with steam and since this is a heat consuming process (endothermic), oxygen is added to supplement the same. Pressure also helped in the gasification process; as for example Lurgi pressure gasifier favors methane formation. As of now 90% of the commercial gasifiers around the world employ Lurgi process and 8% Koppers-Totzek process.

Table 6.25 Summary of coal gasification reactors and typical operating conditions

Reactor Type	Reaction Temp (°F)	Reaction Pressure (psig)	%CH ₄	C ₂ H ₆
Moving Bed:				
Lurgi (H ₂ =39%, CO=18%)	1150-1600	450	9.6	1
Welman-Galusha	100-1200	Atm	—	—
Wilputte	—	—	—	—
Bureau of Mines (stirred reactor)	1000	100	3	—
Woodl-Duckham	—	Atm	1.7	—
Fluidized Bed:				
Winkler (H ₂ =36%, CO= 45%)	2000-2200	Atm	3.2	—
Exxon	1300-1800	25-45	—	—
BCR	2100	250	—	—
CO ₂ -acceptor	1500	150-300	—	—
Char oil energy demo.	650-1600	Atm.	—	—
Synthane	1100-4500	600	24.4	0.8
Battelle-Carbide	—	—	1.1-6.9	—
Westinghouse	2100	300-450	2.7	—
U-gas	1900	300	4.7	—
U-gas	1100	1000	7.8	—
Ignifluid	2000	300	—	—
Entrained Flow:				
Garrette	—	—	—	—
HRI process	1700	450	4.3	—
Kopper-Totzek and H ₂	—	—	—	—
Heating by Recirculation solid:				
Toscoal	800-1000	Atm	—	—
Molten Media Heat Carrier:				
Patgas	2600	1000	—	—
Kellog	1750	1200	7.5	—
Hydrogenation:				
Hydrane	1400-1650	1000	73.2	—
Hygas	1000-1500	1000	18.7	—

The residence time of coal grain for good performance of the reaction at desired gasification temperature (700–900°C) is about 30 min or more. Typical gas composition from an Otto/Saaberg pressure gasifier, which uses all types of coal, pulverized to less than 3 mm, with moisture content 2% and using 1 ton of oxygen and 0.1 ton of steam per ton of coal (pressure 25 bar and temperature 850°C) is as follows (all figures in vol%): CO = 57– 61%, H₂ = 29–33%, CO₂ = 6.5–8.5%, CH₄ = less than 0.2%, and O₂ = less than 0.4%, cold gas efficiency = 73%, overall thermal efficiency = 88– 92%, and carbon conversion = 99.5%. Description of other processes mentioned in Table 6.25 is mentioned in the following sections.

(a) *Moving or Fixed Bed gasifier:*

This type of gasifier produces low Btu gas and mainly meant for town gas

supply. There are two types of fixed bed gasifiers exist in the market – single and two stage. In single stage, Wellman-Galusha and Wilputte gasifiers, where the gasifier shell is either brick-lined (former type) or water-jacketed (later type) are used. In the Wilputte gasifier, heat is supplied from an external source whereas in water jacketed system (Wellman-Galusha type), the process is self-sufficient in steam requirement. Wellman-Galusha is at atmospheric pressure gasifier and accepts only anthracite or coke and bituminous coal with an agitator. Typical coal sizes (with upto 30% fines acceptable) are 32–50 mm for bituminous, 5–15 mm for anthracite and 6–16 mm for coke.

In stage II gasifier (Woodwall-Duckham, Wellman Incandescent and Poster Wheeler Stoic type) have independent control for distillation for VM and gasification of carbon in the coal. These are counterflow type, primarily designed for low temperature distillation and gasification of high volatile weakly caking coals. The gasifier is shaped like a vertical cylinder and has two distinct sections – the refractory lined drying/distillation retort and water jacketed gasifier section. It can be operated both with lignite and bituminous coal (but not anthracite as it has low VM). Air requirement here is about 2.3 kg/kg coal and steam 0.25 kg/kg coal. CFRI, Dhanbad has 2- stage gasifier of capacity 17 kg/h coal (air 25 m³/h and steam = 4.6 kg/ h).

In “Lurgi Process,” crushed coal is introduced into the gasifier from top and gasifier is operated at 615–760°C and 2.4–3.1 Mpa pressure. It has a revolving grate at bottom for continuously removing ash (also to support charge) and to insert O₂/steam from bottom. Product gas contains both tarry material and low BTU gas.

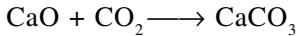
(b) Winkler process

This fluidized bed gasifier (operating 800–980°C) produces gas rich in CO and H₂ at atmospheric pressure. Most of the ash (about 70%) is carried with the gas and rest 30% removed through bottom. Carbon conversion here is about 60% with medium Btu gas throughput. Presently 16 plants (36 gasifiers) have been installed in whole world.

(c) CO₂ acceptor process

This is one of the most widely adopted process, which uses both lignite and other more reactive coals to produce high Btu gas. The process, developed by consolidation coal Co, utilizes lignite and dolomite for producing pipeline quality gas. The process operates at 800–1000°C (1–2 Mpa) and is unique in the sense that heat for the endothermic steam-carbon reaction is supplied by the reaction of dolomite with CO₂ (i.e., no

oxygen supply is required), as per following reaction:



The CO-shift and methanation is enhanced by CO₂ removal. Spent dolomite is regenerated in an external required at 1038°C. The gas received from the gasifier after purification has a H₂/CO ratio of 3:1. A plant to this effect has been installed at Rapid City, South Dakota (USA).

(d) COED process

COED, known as “char-oil-energy-development” process, is one of the most efficient process for coal gasification. In this process coal is converted to synthetic crude oil, gas and char multi-stage. In this process coal is converted to synthetic crude oil, gas, and char by multi-stage fluidized-bed pyrolysis. In each stage the coal or char is brought to fluid state. In these stages, dried and crushed coal is shock-heated to successively higher temperatures. The optimum temperature of each stage and the number of stages vary with coal quality. The staged temperature are selected to be just below the maximum temperature to which the coal can be heated without softening and agglomerating into large particles. Typical operating temperatures are 600–650°F for first stage, 800–850°F in second stage, 1000°F in third stage, and 1600°F in fourth stage. The residual char is available as fuel for power plant use or material for gasification. COED plant has been tested at Princeton, New Jersey (USA).

(e) Synthane process

Bureau of Mines (USA) developed this process for converting bituminous coal, Sub-bituminous coal and lignite to substitute natural gas (SNG). The process involves gasifying coal in a fluidized bed (816–982°C) upto 1000 lb/in² pressure to a raw gas containing CH₄, CO, H₂, CO₂ and water vapor. The raw gas is methanated to about 100% methane or SNG. Compared to other SNG processes being developed, the synthane process has several unique features, principally in the means of handling caking coals and methanating purified gas. Coal is first contacted with a steam/oxygen mix at 500°C in a fluidized bed preheater (7 Mpa pressure) to destroy the caking property of raw coal. Decaked coal from the preheater enters the gasifier at the top and a mixture of steam-oxygen is introduced through the bottom of the fluidized bed. The gasifier operates at a pressure as high as 1000 lb/in² and 1800°F. Product gas (synthesis gas) leaves overhead and unconverted coal or char is withdrawn at the bottom. Thermal efficiency of the process is 68%. The char can be burnt to generate all the steam required in the process. After removal of tar and solids, the gas passes

through two conventional processing steps – CO shift and acid gas removal. Finally, the product gas goes to the methanator for conversion of CO and H₂ to CH₄, a step that increase the heating value of 500 to 900 Btu/ft³. In this liquid phase methanator, an inert liquid (such as mineral oil, C₁₅ to C₂₁ molecules) is pumped upward through the reactor at a velocity sufficient to both fluidize the catalyst and remove reaction heat. Synthesis gas when passed through the reactor is converted to 100% CH₄. The inert liquid phase absorbs the large exothermic heat of reaction through latent heat of vaporization.

(f) Koppers-Totzek process

This is a high speed entrained steam-oxygen gasifier operating at atmospheric pressure. The gasifier operates at 1815–1930°C and exit gas temperature of about 1510°C. At this high temperature, CH₄ and other volatiles from coal are cracked and most of the gas consists of CO and H₂ only. Thus there is no tar, phenols, condensable hydrocarbons or CH₄. An intimate mixture of oxygen and dried pulverized coal (less than 0.1 mm size) is introduced through a pair of opposing coaxial burners arranged so that their discharges converge. It can use any type of coal and world's 85% coal based ammonia plants use this technology. The ash is removed in the form of molten slag at the bottom. In case of bituminous coal, the process consumes about 0.9 kg oxygen and 0.3 kg steam per kg of coal. Thermal efficiency referred to the crude gas is about 70%. The main disadvantage of this process is that it consumes high oxygen which leads to high cost. In India, Talcher and Ramagundam plant (each of 900 ton/day capacity) operated by FCI uses this technique. Present cost estimate for the two projects (four burner type) are about Rs. 1700 million each. Each plant has three gasifiers with independent stream. Each gasifier has a throughput of about 35,000 m³/h of crude gas and can handle coal upto 22 ton/day. The Talcher plant operates at a free flow of ash temperature of about 1400°C. Fig. 6.83 show in block diagram essential features of Kopper-Totzek plant as supplied to TVA (USA).

(g) Westinghouse process

This is a single stage pressurized fluid-bed gasification system. Because of its simplicity and absence of tar in product gas, the system has low capital and operating cost. Coal ground to 3/16th of an inch to 0 in., are fed to the gasifier through a lock-hopper-cum-rotary feeder system. The coal reacts with oxygen (or air) fed through the central feed tube, resulting in production of H₂ and CO. As the bed of char circulates through the jet, the carbon in the char is consumed by combustion and by gasification.

Molten agglomerated char migrate to the annulus around the feed tube and are continuously removed by a rotary feeder to lock-hopper. Recycled product gas or steam is used to partially fluidize the ash and cool it as it is withdrawn. Product gas has a composition – $\text{CO}/\text{H}_2 = 21$ and $\text{CH}_4 = 10\%$ on dry basis. The gas is quenched to its adiabatic saturation temperature at 600 psig to increase moisture content of the gas prior to shift conversion. A side stream of the quenched gas is further cooled (but not shifted) and is recompressed for use in transporting solids or fluidized portion of the gasifier.

(h) Exxon gasification process

In this fluidized bed gasifier, operating at $816\text{--}927^\circ\text{C}$, all types of coals can be gasified. For steam-coal reaction, the necessary heat is provided by a stream of recirculating char when it is partially burned with air. The process is unique as no oxygen plant is required for producing high calorific value gas (because O_2 is replaced by air). After separating the flue gas from hot char, it is returned to the gasifier. The medium calorific value gas obtained can be upgraded to SNG.

(i) BCR/OCR bi-gas process

Jointly developed by British Coal Research Establishment (BCR), UK and Office of Coal Research (OCR) of USA, this process uses both fluidized bed and entrained bed gasification technique. The process can utilize all kinds of coal. Gasifiers consist of an upper entrained flow vessel operating at $760\text{--}927^\circ\text{C}$ and 6.89–1034 Mpa pressure and lower vortex-flow operating at 1538°C at same pressure. Synthesis gas moving upward from this lower section volatilizes pulverized coal as it comes in contact with it and undergoes partial methanation at $760\text{--}927^\circ\text{C}$. Char and product gas mixture is then fed into the bottom gasifier section where it gasifies with oxygen and steam at $1482\text{--}1649^\circ\text{C}$ leaving a slag. Upward passing gas through the top stage is led to cyclone and shift conversion, purification and catalytic methanation.

(j) Garrette process

This is an entrained bed coal gasifier which uses pulverized coal and is being fed to the pyrolysis reactor with a recirculating stream of hot char. The process operates at 593°C and atmospheric pressure. The hot char from heater circulates to the pyrolyzer and provides the heat for pulverized coal pyrolysis. The pyrolysis gas is separated from entrained char in a series of cyclones and sent for purification, shift conversion and methanation.

to upgrade the gas from its raw state (22.38–24 MJ/m³) to pipeline quality (26.11 MJ/m³). In entrained bed gasification the caking coals need no pretreatment as the small coal particles gasifies rapidly and do not get any chance to agglomerate. Energy produced per unit volume is much higher than fixed bed or fluidized bed gasification (no tar forms in this case).

(k) ATGAS-PATGAS process

This process involves molten media gasification where both caking, high ash and high sulfur coal can be gasified. The crushed coal is injected into a molten and iron bath, followed by steam lancing. The process operates at 1371°C. Volatile matters crack at this temperature and both CO and H₂ are formed. Oxygen is also being purged through the molten metal which reacts with fixed carbon and forms CO, H₂, ash, and sulfur of the coal forms a slag on the molten metal and is being continuously removed. The gas produced has a medium calorific value. If only ATGAS process is used, the product gas is upgraded by shift-conversion and methanation to form SNG. But in PATGAS, the synthesis gas is used to produce chemicals.

(l) Molten salt process

Invented by M. W. Kellogg Co, NJ (USA), this process gasifies coal at 990°C and 2.89 Mpa pressure. Dried and pulverized coal is fed to the salt gasifier along with steam and oxygen. The process is based on catalytic properties of molten alkali carbonate (Na₂CO₃) to enhance steam-carbon reaction. Due to catalytic action of Na₂CO₃ the reaction proceeds at lower temperature and thus when this catalyst is used caking coal do not need any pre-treatment. Reactor lining is made up of fused cast, high alumina material, to resist attack of molten salt on it. A bleed steam of molten salt containing coal-ash in solution, is withdrawn from the top of the gasifier and is contacted with water to dissolve Na₂CO₃. Ash is separated by filtration. Bicarbonate and calcining it to restore the carbon salt, it may be recycled to the gasifier. Heating value of the gas is 12.31 MJ/m³.

(m) Hy-Gas process

This is a hydrogenation process in which coal is first pretreated to destroy its agglomeration tendency by mild surface oxidation. Non-agglomerating coals such as lignite and sub-bituminous coals are processed directly without pre-treatment. The coal is then slurried with a light oil (a by-product of the process itself), pumped to the required hydrogasifier pressure level of 1100 lb/in² and fed to the top of the hydrogasifier vessel (135 ft tall). In the first section of the hydrogasifier, the slurry oil is driven-off and

recovered for recycling. The coal then falls through the reactor and passes through a low temperature (1200–1400°F) devolatilization step where methane is generated from the volatile matter in the coal. The devolatilised coal then progress to the high temperature reactor sector (1700–1800°F) where the coal is hydrogasified to methane through contact with hydrogen and steam. The large amount of methane produced under these conditions is then removed at the reactor top. The product gas at this point consists of methane, CO₂, H₂, CO, SO₂, and some impurities. CO₂ and SO₂ is removed and SO₂ is converted to elemental sulfur. The purified gas then passes through a Ni-catalytic methanator (1000 lb pressure and 550–850°F temperature of the coal fed to the hydrogasifier, approximately ½ is gasified to methane. The remaining ½ is removed at the bottom of the reactor and is sent to the 2 MW electro-thermal gasifier. In the electro-chemical gasifier (a unique facet of HYGAS-process), the hot coal char reacts with steam to produce a mixture of synthesis gas and steam at 1000°F and 1100 lb pressure. Energy for sustaining this reaction is supplied by the electric resistance heating resulting when current is passed between two electrodes immersed in the coal-char bed. The gas from the electro- thermal gasifier then passes into the hydrogasifer to provide the hydrogen needed to produce methane. The remaining unconsumed char is removed from the electrothermal gasifier and could be burnt completely to produce the electric power required for the electrothermal gasifier and other plant equipment. Such a plant has been tested at Chicago, Illinois, USA.

(n) Electrofluidic gasification process

Here, reaction of steam and char in a reactor produces a mixture of H₂ and CO, as well as CH₄ containing mixtures, which can be upgraded by methanation to SNG. Process operates at 816°C and 1034 Mpa pressure. An electrofluidic reactor is heated by passing an electric current through the fluidized-bed of conducting particles. The bed itself serves as resistor between electrodes placed in contact with the bed. The process is useful for carrying out reaction which require substantial energy inputs and are favored by high temperatures.

(o) Arc-coal process

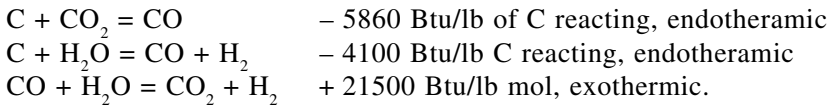
Production of acetylene by this process is much more economical than any other process involving direct conversion of coal to gas. Details of this process has been outlined earlier and accordingly will not be detailed here.

(p) Hydrane process

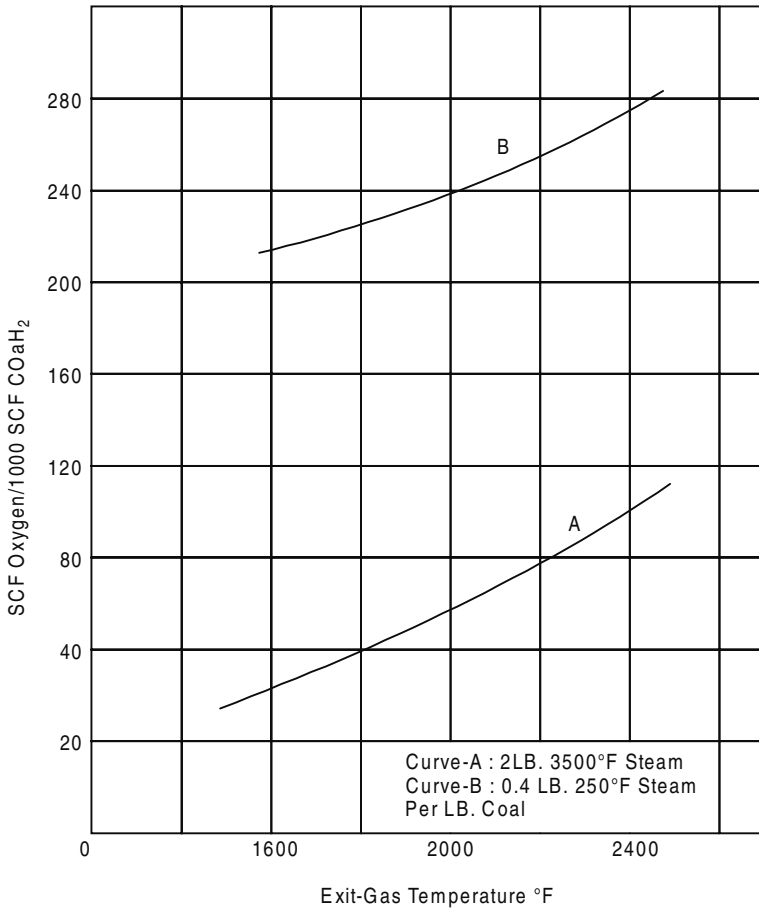
Invented by the US Bureau of Mines, this hydrogasification process operates on crushed raw coal fed to a two-zone hydrogenation reactor operated at 1000 psi and 1650°F temperature. In the top zone, the coal falls freely through a hydrogen rich gas containing some methane from the lower zone. About 20% of the carbon is converted to methane. The char from the top stage falls into the lower zone where hydrogen feed gas maintains the particles in a fluidized state and reacts with about 34% more of carbon to make methane. Char from the lower zone is reacted with steam and oxygen to generate the needed hydrogen.

In all process mentioned above, the general mechanism of gasification can be summarized as follows. First, the physical picture of gasification of pulverized coal completely entrained in a gasifying agent may be obtained by following the mechanism of gasification of a single particle. If the particle and its surrounding gas are considered to be spherical, then the ratio of dia of gas-sphere to that of the particle is about 37:1 at atmospheric pressure. Hence the gas space surrounding the particle is large and good mixing is an important factor in promoting the reaction. If the coal contains 70% carbon and 10% ash, if all volatile matter and 90% of the carbon are gasified, and if the volume change is proportional to the weight change, then the ratio of the diameter of the particle after the reaction to that before the reaction would be expected to be 0.55. For a 200 mesh particle falling through its terminal velocity in a gas (CO, CO₂ and H₂O) at 2000°F, the Reynold's number is approximately 0.2 so that Stoke's law applies. The terminal velocity or the maximum relative velocity between the gas and the particle falling under the influence of gravity is 0.14 ft/s. Meyers has shown that the major resistance to the reaction between carbon and CO₂ is diffusional below relative velocities of 0.7 ft/s and chemical in nature above that when the reaction temperature is 1800°F. The major resistance to reaction in entrained coal gasification, may be diffusional and therefore an increase in temperature will not produce a large increase in reaction rate. Since the relative viscosity between coal particle and gas is low, turbulence is of doubtful value in promoting the reaction, as the coal particles are moving with the gas. One effective method of obtaining a high relative velocity between the coal particle and the gas would be to cause the particle to move in a spiral path so that a centrifugal force several times that of gravity is obtained; that is, a much greater relative velocity is obtained than caused by turbulence only. When a 200 mesh coal particle enters a region at 2000°F, it is heated rapidly through the plastic range, the volatile matter being distilled-off and forming an envelop around the particle. Hence the initial reaction with oxygen is combustion of the volatile matter. Most bituminous coals contain enough

volatile matter to react with most of the oxygen; and since gaseous combustion reaction are rapid, most of the oxygen disappears in a short length of the reactor. Consequently, reactions occupying most of the reactor space are those of steam and CO_2 with the fixed carbon of coal. Very high initial temperatures are not observed, because the steam present limits this temperature as in the usual operation of a fixed-bed gas producer if external heating is used and high heat transfer rates are sought by use of metal walls, the reactions are slowed down, since temperature of the metal must be kept comparatively low under 1000°C . Heat release by various related reactions at 1000°C are



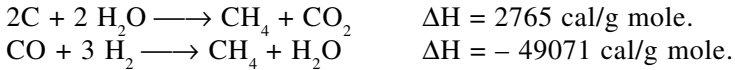
As above equations suggest, heat is required in the system and this heat may be supplied by preheating the entering system steam. To supply all the heat for the reaction by the entering steam, will necessitate either an excessively high steam temperature or steam in an excessively large amount. The water gas shift reaction reaches equilibrium at the exit gas temperature. The reaction of CO_2 and steam with carbon, however, is far from equilibrium in all coal gasification systems. In general, if a low steam/coal ratio is used, the gasifying agent is almost exhausted at the exit end of the gasifier. If a high steam/coal ratio is used, however, the exit gas still contains a fairly high concentration of gasifying agent. It would be expected from mass-action effect that a greater carbon gasification and a lower exit-gas temperature would be obtained with high steam/coal ratio in entrained coal gasifier. The exit gas temperature is strongly influenced by the reaction rate at the exit end of the reactor. In a concurrent gasifier with entrained pulverized coal, the exit end of the gasifier contains lowest concentration of fuel and gasifying agent and also lowest temperature, all of which tend to decrease reaction rate. Thus it is expected, equilibrium will not be reached and considerable amount of energy which could have been converted to chemical energy as per equilibrium reactions will actually be left as sensible heat with the exit gas. Fig. 6.73 shows calculated oxygen requirement for various exit-gas temperature when a standard coal is used. The graph indicates that lower the exit-gas temperature, more efficient is the gasification process. The exit gas temperature can be influenced by the shape of the gasifier. If the reacting mass progressively flows through a tube, a temperature gradient is established along the tube as the reaction proceeds, resulting in a lower exit-gas temperature, and hence a greater extent of the reaction. If the reacting mass is mixed with turbulence inside the reactor, however short circulating will raise exit-gas temperature and decrease extent of the reaction. Oxygen requirement per unit of $(\text{CO} + \text{H}_2)$



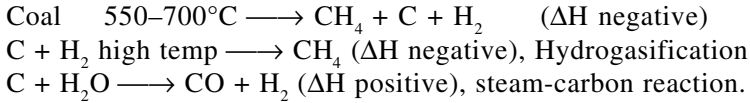
6.73 Calculated effect of exit gas temperature (°F) on oxygen requirement.

mixture produced increases with increase in heat loss through radiation from the gasifier to the surroundings. Since heat loss by radiation is proportional to surface area, it will increase with the increase in ratio of surface area to volume or length to diameter of the designed gasifier. Thus a balance need to be obtained between shape and size of the reactor for proper progress of the reaction with minimum heat loss.

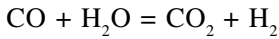
Reaction of oxygen with coal approaches zero order in the 550–1550°C range. External mass transfer and more diffusion rate of oxygen are the two limiting parameter in coal-oxygen gasification reaction. Devolatilization of coal on the other hand is described as first-order kinetic. Following are the ΔH values for methane formation during coal gasification reactions



Following devolatilization reactions are exothermic in nature (but subsequent reaction with steam is endothermic in nature):



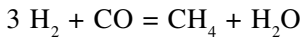
The relative concentration of CO, H₂O, CO₂ and H₂ are nearly maintained in chemical equilibrium by the fast water gas shift reaction:



Depending on the magnitude of H₂: CO molar ratio, two different routes of methanation reactions are adopted:

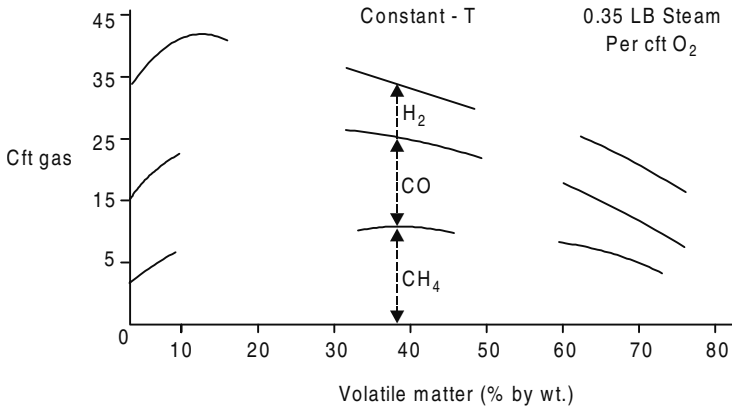
- Catalytic shift conversion (for H₂: CO less than 3)
- Catalytic methanation (for H₂: CO ratio greater than 3).

Catalytic shift conversion increases the hydrogen concentration and involves the chemical reaction shown above: while catalytic methanation increases the methane concentration as result of following reaction:

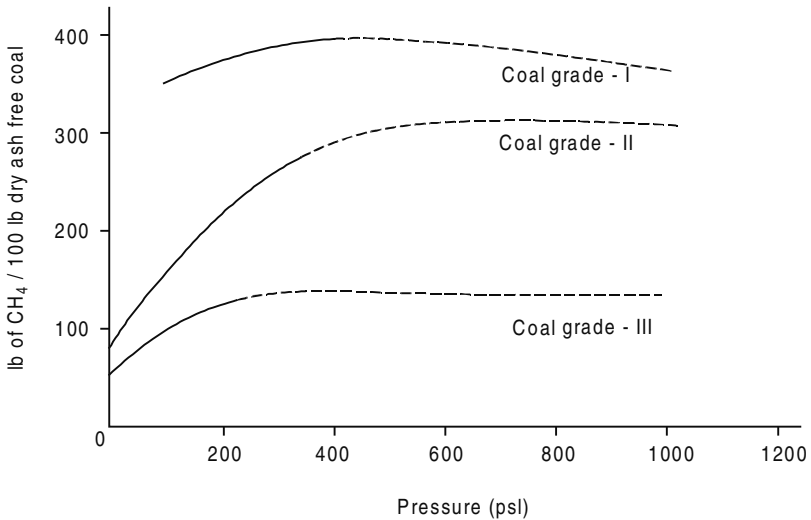


Catalytic methanation can not be accomplished effectively in the presence of sulfur compounds or of large water concentration. For this reason, water is first removed from the gas mixture by condensation and then H₂S, organic sulfur compounds and other sulfur containing materials, along with CO₂. Catalytic shift-conversion increases H₂/CO ratio to values larger than 3. Reaction products formed after catalytic methanation are treated for water removal and then the methane rich is used as pipeline product. To summarise the whole gasification process, we can say different reactions participate simultaneously and the equilibrium concentration of individual components are not reached as the concentration change is kinetically controlled.

Rate of formation of CO, which is endothermic in nature, becomes rapid above 900°C. Thus initiation of the process requires an external heat source. Variation of gas composition with coal grade shown in Fig. 6.74. It has been found that yield of methane, expressed in standard cubic feet of CH₄ per lb of dry-ash free coal, is a fairly constant figure for each type of coal. For sub-bituminous coals, the methane yield is approximately 3.9 cft /lb dry ash-free coal at an operating pressure of 350 psig. Although pressures have a direct effect on gas quality (CH₄ content), but the yield is also dependent to some extent on coal quality as shown in Fig. 6.75.

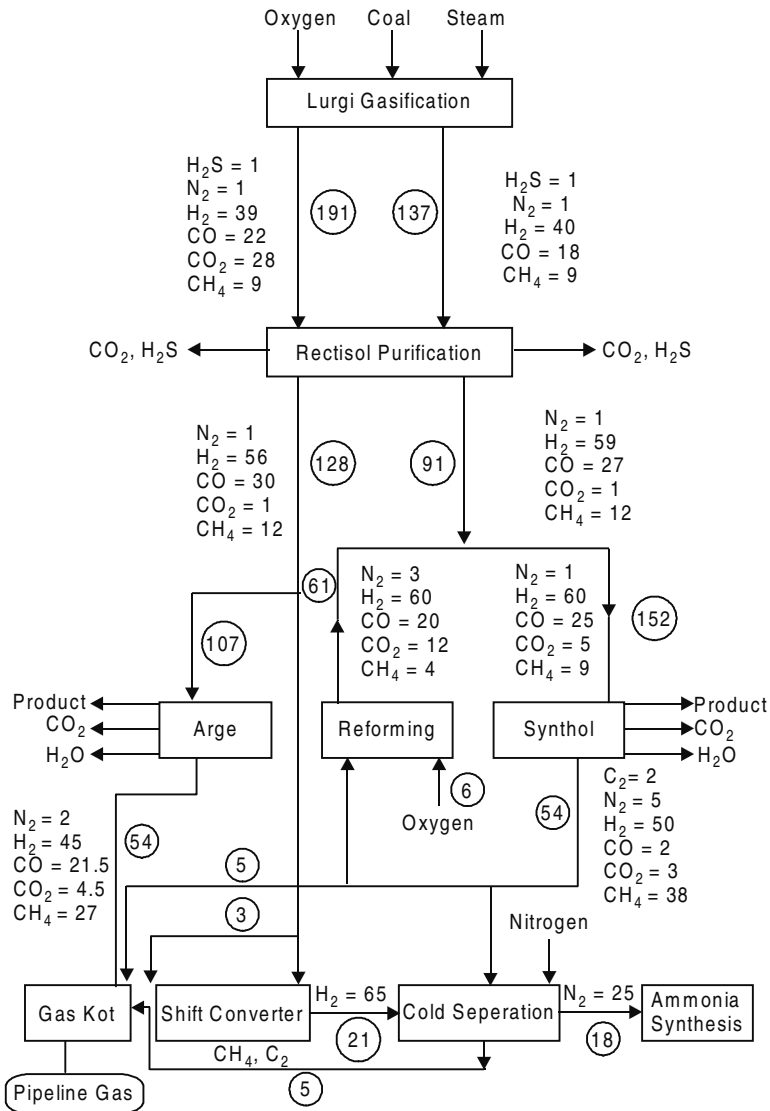


6.74 Variation in gas composition with coal grade.



6.75 Steam gasification of different coal at various pressure.

Essential feature of SASOL (South African Coal to Oil Plant) plant, world's largest commercial gasification of coal unit, is shown in Fig. 6.76. In the block diagram, all composition have been indicated in volume% and with circles are indicated by gas volume of the order 10^6 cft/day. As far as efficiency is concerned, town-gas generation gives highest followed by SNG production. (Methanol + SNG) is not much different from production technique than just SNG unit. Fishcher-Tropsch synthesis has been found to have lowest efficiency; however the value of the product may justify, as it has proved in practice by above described SASOL plant. Investment cost is inversely proportional to efficiency and it is interesting



6.76 South Africa coal to oil plant (block diagram).

to note that a coal fired power plant is more expensive and less efficient than a gas production plant from coal.

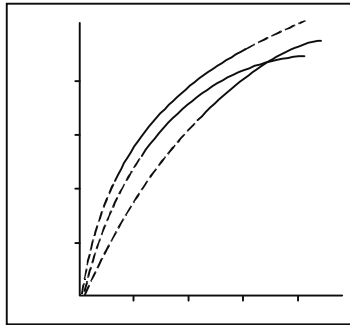
6.13.2 Choice of process

First of all, if the requirement of gas is for town-gas supply dilution of the product gas with nitrogen is no problem and air blown processes can be

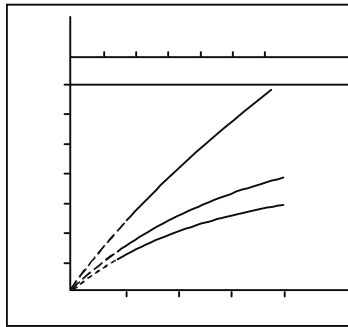
chosen. But if the gas is required for hydrogen production or chemical synthesis, CH_4 and N_2 is undesirable and oxygen blown processes are preferred. Thus product gas composition plays an important role in deciding the process to be adopted. Table 6.26 shows the approximate gas composition from various processes.

Table 6.26 Gas quality from various gasification processes

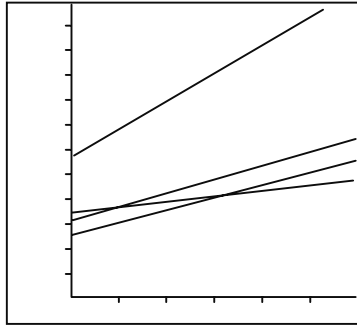
Gasification process	CH_4 (mole%)	CO (mole%)	H_2 (mole%)	CO_2 (mole)	H_2/CO ratio
Hydrane	73	4	23	—	5.9
CO_2 -acceptor	21	17	54	7	3.2
Lurgi	9	19	40	30	2.2
Synthane	24	17	28	29	1.7
Molten salt	8	34	45	13	1.3
Winkler	19	24	30	25	1.3
Koppers-Totzek	3	33	42	21	1.3
Bigas	—	56	37	6	0.7
Atgas	16	44	24	14	0.6



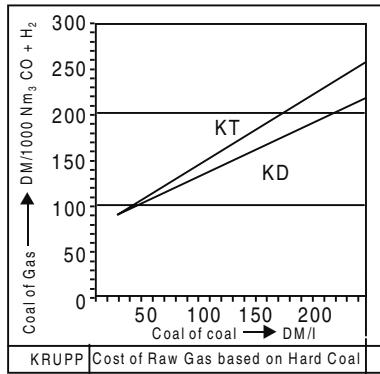
6.77 Investment for complete plants (NH_3 , CH_3OH , sponge iron).



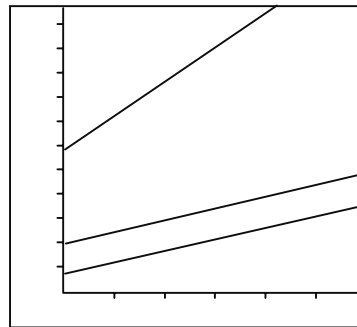
6.78 Investment for complete plants (SNG, H_2 , fuel gas).



6.79 Cost of F.T. primaries, (NH₃, CH₃OH, sponge iron).

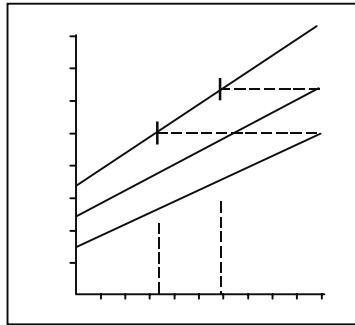


6.80 Cost of raw gas.



6.81 Cost of CNG, H₂ fuel gas.

Besides gas composition, choice of gasifier depends on how the gas is to be used, gasification by-products and on the desired scale of operation. For production of fuel gas to be used in small scale (about 70,000 to 350,000 ft³/h or 2000–10000 m³/h) a fixed-bed air blown producer or

6.82 Production cost of NH_3 .

fluidized process may be considered. For large scale demand (over 1000,000 ft^3/h or 30,000 m^3/h) a Lurgi fixed-bed or Winkler fluidized bed process using air and steam may be considered. Availability of proper coal is also a selection criteria at a specific site. For non-caking or weakly caking coals, fixed-bed process has the advantage of moderate exit gas temperature and good thermal efficiency. Use of oxygen and pressurized operation in Lurgi process enable high throughout capacities and production of medium calorific value gas. Since the volume of oxygen is only 1/7th the volume of gas produced, pressurized gasification reduces the required compression when the gas is to be used for synthesis or transmission. Furthermore, the gas velocities and fines carryover are reduced. High ash and moisture content coals can be successfully gasified provided the ash has sufficiently high fusion temperature. The Winkler fluidized bed process is insensitive to variations in ash content of fuel and has very high throughout capacities. Fuel preparation is also minimal. The process is limited by ash fusion temperature and fuel reactivity. The range of outputs is limited by limitations placed on blast velocity; gasification is also incomplete, resulting in inert char which can be burned under a boiler. Koppers-Totzek process is basically very reliable and has high on-stream availability. Any type of coal can be used, but it requires drying and grinding. Ash fusion temperature and viscosity are the most important features of the fuel. The exit gas is very hot and contaminated with dust. For modification of existing units to medium-CV gas generator, calls for little change in design. As mentioned earlier, gas composition varies from gasifier to gasifier and is directly related to its use and thus K-T process is appropriate for the chemical synthesis (ammonia or methanol) whereas Lurgi process is good for fuel production.

6.13.3 Economics of gasification

In general, economics of coal gasification by a particular process is linked

directly to its efficiency. Thus first generation Lurgi plant is still considered good. Comparison of Lurgi with Kopper-Totzek is demonstrated through following data. In these calculations, life of the unit is taken as 25 years, DCF return 10%, SNG cost 22–27 pence/therem, synthesis gas cost 18–22 pence/therm, and coal price 6–11 pence/therem):

Process	Effeciency (%)	Capital cost (\$/ton coal)
Lurgi	56%	140
Koppers-Totzek	50%	133

In above calculation, annual operating and maintenance costs were taken as 7% of the capital cost, and plant size of 250×10^6 ft³/day. Koppers-Totzek process is more expensive than Lurgi for SNG but is preferable for synthesis gas manufacture, except at high coal prices. These results show that CH₄ content in Lurgi gas has the economic advantage. In last 14 years since the above calculations were made, the price levels have changed, but the relationship remains more or less same as of today (this is due to escalation of coal price and capital costs to the same extent). The second generation gasifiers (Bigas, Hygas, CO₂-acceptor and Synthane processes) all aimed at more fuel flexibility, elimination of oxygen and minimizing methanation requirement, by encouraging hydrogenation in the gasifier to obtain a direct high yield of CH₄ (e.g. Hygas), and finally increase the gas yield. Comparison of economics of these plants at the same scale (i.e. 250×10^6 ft³/day SNG) at 1976 price level has brought out following results.

Process	Efficiency (%)	Capital cost (\$/ton coal)	Coal consumption	Product Price \$ per 1000 ft ³
Bigas	62	98	5x106 ton/yr	1.1
Hygas	64	102	5x106 ton/yr	1.15
CO ₂ -acceptor	66	119	30,000 ton/yr	1
Synthane	64	1.8	15,000 ton/yr	0.95

As can be seen in above table, the average efficiency has improved little over past systems but the savings of capital investment are now about 20%. In all these calculations, efficiency and carbon utilization are calculated as follows:

$$\text{Overall plant thermal effeciency} = \frac{\text{Btu of product gas leaving the plant}}{\text{Btu of raw coal feed to the plant.}}$$

$$\text{Carbon utilization} = \frac{\text{mole of carbon in the product gas}}{\text{mole of carbon fed to the plant}}$$

It will be interesting here to compare the cost breakdown of the first generation Lurgi plant and a modern Westinghouse SNG plant as is used in recent time (Table 6.27):

Table 6.27 Cost breakdown of Lurgi and Westinghouse plant

% Cost breakdown of Lurgi process (1976 level)	
Coal preparation	4
Gasification	18
Oxygen plant	19
Shift purification & sulfur removal	25
Methanation and compression	12
Utilities and general facility	22
Cost breakdown of Westinghouse SNG plant (1979\$)	
Engineering equipment	658.2 MM\$
General facilities	72.4
Home office cost and fee	80.4
Contingency at 15%	121.9
Total plant investment (MM\$)	1183.3
Initial catalysts and chemicals	17.4 MM\$
Funds during construction	157.4
Royalties	7.5
Start-up cost	38.0
Working capital	30.0
Total capital requirement (MM\$)	1183.3
Nett operating costper year	179.3
Average gas cost (per million Btu)	\$4.40

Above figures indicate total plant cost and do not include social amenities laboratories, building etc. Figures 6.81 and 6.82 show sensitivity of product gas with changing raw material (coal) price. As the figures show price of coal is the chief item which represents about 50–70% of the total operating cost. Thus to make the gasification product competitive with alternate fuels, the raw material price has to be low enough to compensate for the high processing costs shown earlier. Fortunately uptill now rise in coal price (in last 4 decades) had not been so fast as petroleum price; but the situation may change in near future and the whole economy of coal conversion has to be reevaluated. Transportation cost of coal are not considerable upto a distance of 200 miles. Cost of production of low-CV gas is lowest and that of medium-CV is highest and thus the transportation charge of low-CV gas is twice that of medium-CV gas and 7 times that of high-CV gas. Thus long distance transportation is economically feasible only for high-CV gas. Local availability of coal or natural gas highly influence competitiveness of gasification at a particular site.

6.13.4 Use of gasification product

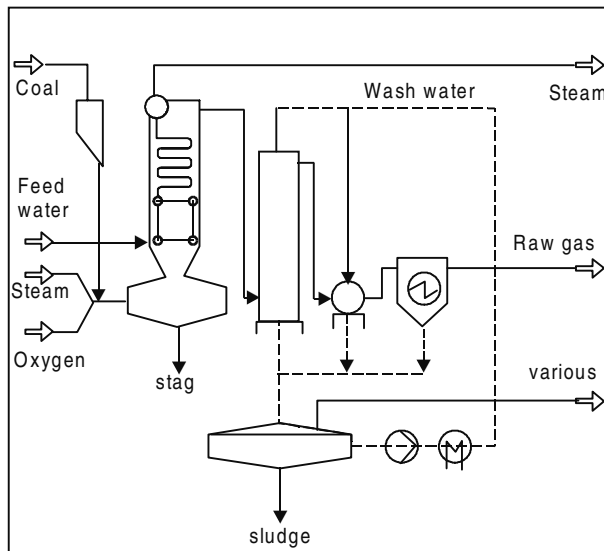
As mentioned earlier, depending on composition gasification products can either be used as town-gas, starting material for chemical synthesis, or as fuel for power generation. Use of gas as town supply is a well known phenomenon and thus we discuss more about the later two possibilities –

use as synthesis gas (Fischer Tropech process) and use in recent innovations of power modules (integrated gasification combined cycle power system).

(a) Integrated gasification combined cycle power generation

In short known as IGCC, involves burning the gases to drive a gas-turbine instead of conventional method of gas burning to raise steam in a boiler and driving steam turbine which is uneconomical. When the former process is combined with a steam raising operation, driving a steam-turbine, we have a combined cycle. By this means efficiency of power generation can be improved. In combined cycle operation (e.g., Steag-Lunen plant in West-Germany), where Lurgi fixed-bed gasifiers are used, in order to match operating pressure of the gasifier (about 20 bar) with super-charged boiler and gas-turbine (operating at 10 bar), it was necessary to install an expansion turbine and booster compressor. Thus pressurized gas is burnt in the boilers to generate steam and the boiler waste expanded in the gas turbine.

The overall efficiency of Lunen plant (165 MW) is 37% at full load. A steam turbine alone will operate at a maximum efficiency of about 33%. Attempts have been made to improve this efficiency by taking steam from the first stage of the turbine and returning it to the furnace to be reheated before passing to the 2nd stage. By this method it is possible to raise the

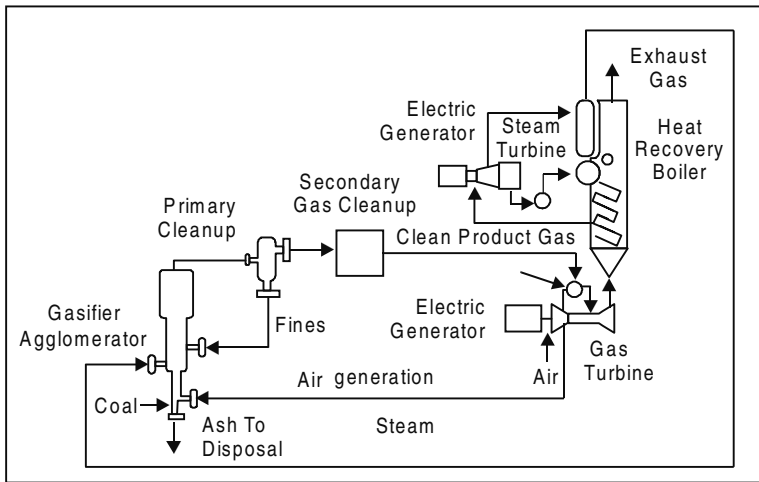


6.83 Flow diagram of Koppers-Totzek entrained bed gasification.

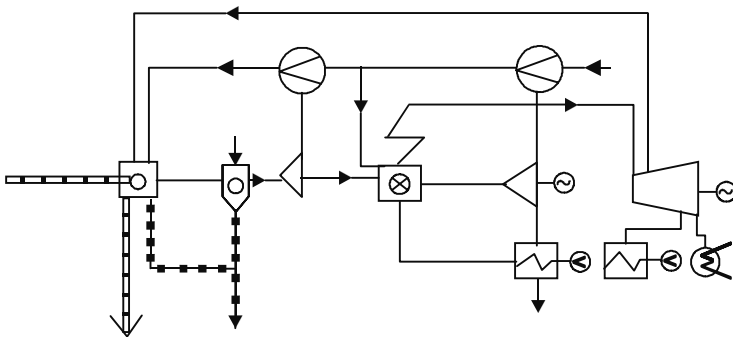
efficiency to about 38%, but it is unlikely that it can be further improved until the material of construction is changed to withstand higher temperature. However, gas turbine work at higher gas inlet temperature and use of a gas turbine in conjunction with steam-turbine (combined cycle) will possibly achieve higher efficiency, as is shown in following case.

In the first waste heat recovery combined cycle stage, the reject heat (600°C from the gas turbine is utilized in a steam cycle to generate more electricity. If the efficiency of individual cycle is 30%, then the overall efficiency now will be $0.3 + 0.7 \times 0.3 = 51\%$. In this design, the waste heat from the gas turbine passes to a heat exchanger where steam is raised. In the subsequent improved system (known as exhaust-fired combined cycle), supplementary fuel is burned in the steam raising equipment to improve the efficiency of the steam cycle. In still an improved version later (known as super-charged combined cycle), the fuel is burned under pressure in the boiler system and then the exhaust gas passes through the gas turbine. Here the rejected heat from the gas turbine may be used to preheat the working fluid. Currently, industrial gas turbines have a limitation on the inlet gas temperature of about 1000°C. The use of pressured fluidized bed combustion in a combined cycle giving an efficiency of 40% or more is therefore a real possibility. In near future industrial turbines will become available which have maximum inlet temperature of 1200°C or even higher. Efficiency in later case will rise to about 45–50%. Fig. 6.84 show the general layout of a coal gasification combined cycle electric power station.

The capital cost of a combined cycle power plant is likely to be of the same order as conventional pulverized fuel fired plant. Even when the westinghouse gasification technology is proven and SASOL plant is in existence for more than 10 years, it will still remain unproven in regard to combined cycle power generation. It is well known that the interfacing between a gasification plant and the power generation system possess serious difficulty, the Westinghouse combined cycle power system experience is not with coal gas. Pressurised fluid-bed reactors are not amenable to up-scaling to the order of 45–50 times from pilot plant size and thus possess real challenge in commercializing IGCC. BHEL (India) is making an effort to operate bed at high pressure unit in which coal is gasified with steam and air at 10 atmospheric pressure. While comparing different gasification options, Lurgi seems to be the most costly because of low gasifier capacity and production of liquid by-products. If oxygen-steam is used instead of air-steam, there is little difference in overall efficiency to a super-charged combined cycle (170 MW capacity). It has five high pressure (20 bar) Lurgi gasifiers. The general lay-out of the plant is shown schematically in Fig. 6.85.

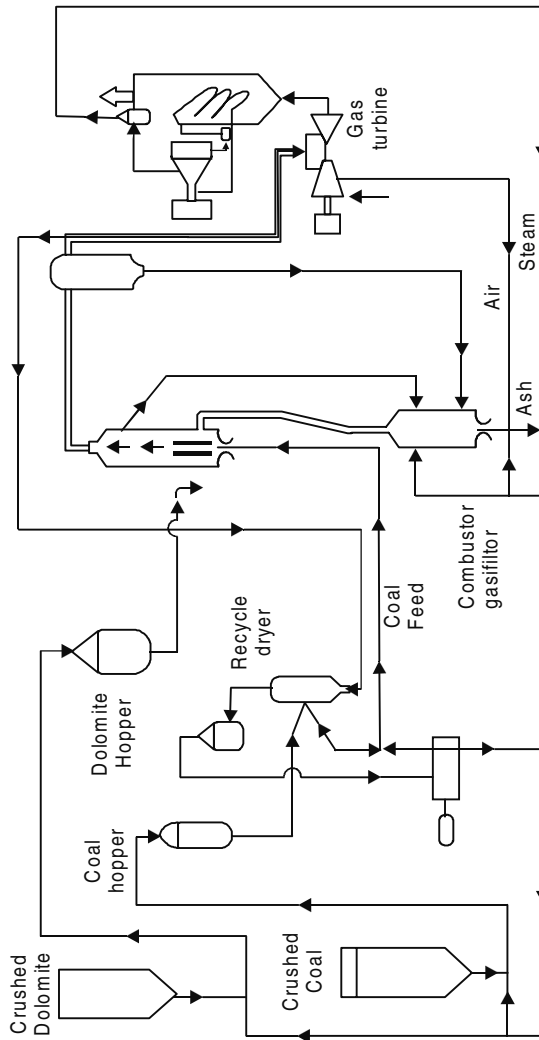


6.84 Coal gasification combined-cycle system for electric power generation.



6.85 Configuration of steam plant.

Configuration of the Westinghouse fluidized bed gasifier (0.5 ton/ h) cum combined cycle plant tested at the same place is shown schematically in Fig. 6.86 below. In this plant, the burned hot gas is first expanded through a gas turbine, then a steam-turbine. Capital cost of a combined cycle plant is likely to be the same as conventional PF-fired power plant. In Westinghouse system, the burned gas after passing through gas turbine goes to a waste heat recuperator to produce steam for the steam turbine. About 1/2 of the gas turbine output is used to drive the air compressor supplying the air for gasification and combustion; the other 1/2 goes for electrical output. About an equal amount of electricity is also provided by the steam turbine. A forced upward circulation through the gasifier prevents coal particle from agglomerating. This sticky nature of coal has been found with non-caking coals also.



6.86 Westinghouse IGCC process.

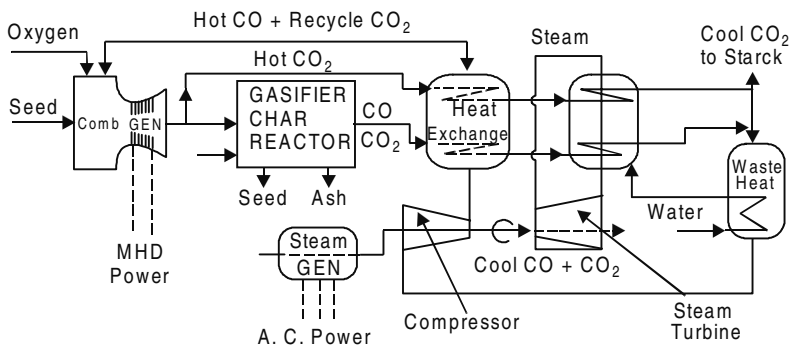
In line with these considerations aiming at more efficient power generation system, trials are underway to generate electricity from coal gasification product using Magneto-hydrodynamic principle, in short called MHD. In a MHD-generator, pulverized coal is burned with air to produce a plasma – a gas whose electrons have been stripped from its atom. Plasma temperature reaches some 2538°C. Plasma is an excellent conductor of electricity. The MHD-plasma is made an even better conductor by seeding it with metal fines. This mixture is fired at supersonic speed down a channel lined with electrodes, through which electricity in the plasma is drawn

off. The channel itself is inside the poles of a plant superconducting magnet. A successful MHD-generator would be far more efficient in converting energy in coal into electricity than conventional coal-fired power plants because of its high temperature. A basic law of physics say, you run a heat engine at higher temperature more efficiently it will operate. The waste heat from the MHD-generator can also be used to run a standard turbine to generate additional power. Fig. 6.87 shows the schematic diagram of MHD-power plant.

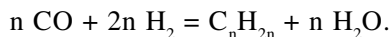
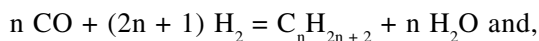
In India, Bharat Heavy Electricals, Trichurapally and Bhaba Atomic Research Centre Trombay, Bombay, are engaged in development and testing of MHD power stations. Pilot plant trial have already been conducted but many technical problems need solution before possible commercialization.

6.13.5 Fischer-tropsch synthesis

Gasification of coal results in production of CO and H₂. In the presence of a catalyst, CO and H₂ react to form gaseous, liquid, or solid product which may be either hydrocarbon or oxygenated compounds (like alcohol) and the process is known as FT-synthesis. Thus FT-synthesis is an indirect method of coal liquifaction. The other competitive method for producing liquid hydrocarbon is liquefaction. The other competitive method for producing liquid hydrocarbon is "Mobil M-Gasolin Process" (described below). Under high pressure (more than 100 atm) and at high temperature (around 400°C) the tendency of FT-synthesis is to form oxygen containing substances (e.g., $\text{CO} + 2 \text{H}_2 = \text{CH}_3\text{OH} + 57,000 \text{ Btu /lb mol}$). At lower pressure (1–30 atm) and lower temperatures (around 200°C), the products are mainly liquid hydrocarbon, although small proportions of oxygenated bodies are also formed. The reaction in its most general form is expressed as:



6.87 Proposed MHD power system.



Both the reaction are exothermic. The nature of resultant product is principally determined by three variables – pressure, temperature, and catalyst. Table 6.28 show the ef of these variables on product spectrum as is generally used in FT-synthesis.

Fischer-Tropsch process as a whole consists of four basic steps. The first step is to get CO and H₂ in proper ratio (3:1) through coal gasification and water-gas shift reaction described earlier. In the second stage, this synthesis gas is purified (dust and all sulfur-compounds removed). Presence of sulfur compounds even to minute amount will poison the catalyst. In the third stage, the actual synthesis reaction is carried out, either in a fixed-bed or in a fluidized-bed. As mentioned above, as all FT-synthesis reactions are exothermic, prompt removal of generated heat in the reactor is a key factor in designing the reaction vessel. One such system of temperature control involves, packing the catalyst between two water cooled surfaces, the evolved heat being utilized for raising steam. Another technique uses, suspending catalyst particles in a fluidized state in an upward moving gas stream. As the temperature of the bed rises, a portion of material is being constantly and automatically removed and simultaneously replaced by cool catalysts in order to maintain desired temperature level. Eventually in either case the activity of the catalyst charge begins to fall. Three month is said to be the normal life of catalyst in such process, in a static bed. At the end of which the catalyst can be again reactivated. In fluidized-bed reactivation proceed simultaneously so that the continual make-up supply of the catalyst which replaces the proportion withdrawn for temperature control is not

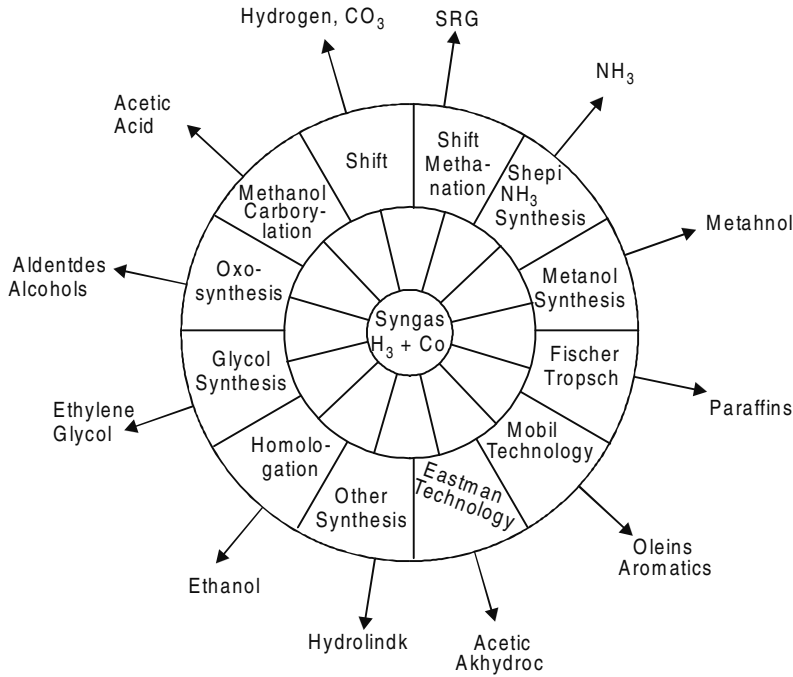
Table 6.28 Variables and products in FT-synthesis

Catalyst	Promoters	Temp(°C)	Pressure (Atm)	Products
Ni	ThO ₂ , MgO	250-500	1	Chiefly CH ₄
Fe, CO, Ni CH ₄ variables oxygenated	ThO ₂ , MgO, Al ₂ O ₃	150-350	40938	Paraffins & olefinic hydrocarbons from to wax plus amount of products.
Ru	—	150-250	100-1000	High mol wt paraffinic hydrocarbons.
ZnO, Cu, Cr ₂ O ₃	—	200-400	100-1000	Methanol.
ZnO, Cu, Cr ₂ O ₃	Alkali	300-450	100-400	Methanol & higher alc.
ThO ₂ , ZnO + Al ₂ O ₃	K ₂ O	400-500	100-1000	Saturated hydrocarbons.
Co, Fe	—	100-200	100-200	Oxygenated org. compds.

only cool but fresh. Recent laboratory work indicate nitrated fused Fe and Co – silica catalyst as being the most promising for FT-Synthesis. SASOL plant uses, fixed bed FT-unit with iron catalyst and Americal Kellog Co's Synthol plant (a fluidized bed FT-unit) again uses iron-catalyst but in powder form. A Co-ThO₂-MgO-Kieselguhr catalyst was used originally in the first commercial FT-plant in 1943 with a capacity of 1000 ton/year. These German plants had a output product distribution pattern of – 46% gasoline, 23% diesel, 3% lubricating oil, and 28% waxes, detergents, synthetic fat and oil. After Second World War, all these plans shifted to iron catalyst as Fe is cheaper than CO and also iron is found more stable and flexible with respect to product distribution pattern, SASOL-II (1980) and SASOL-III (1983) units were set-up based on fluid-bed synthol design. Products from fluid-bed synthesis units are mainly low-boiling hydrocarbons (C₁– C₄) and petrol with little medium and high boiling material. Above SASOL plant uses a local low grade bituminous non-caking coal with following average analysis: ash = 30%, VM = 21%, fixed-carbon = 49%. Gasoline (petrol) can also be derived via methanol route by this process using synthesis gas. Whereas for ammonia synthesis using coal gasification product, all CO must be converted to H₂, and for methanol synthesis a CO:H₂ ratio of 1:3 is first achieved. From normal 1:1 composition of synthesis gas to 1:3 ratio of CO to H₂, therefore, only a limited CO-shift conversion is needed as compared to NH₃ synthesis. Further, the complete removal of oxygen compounds necessary in ammonia synthesis can be omitted and a lower compression of gas will suffice. Plants have, in fact, been switched back and forth between NH₃ and methanol with appropriate adjustment of feed composition, catalyst and operating conditions. ICI have developed a low pressure technology operating

at 70–100 bar (Cu-ZnO-Al₂O₃ as catalyst) instead of 200–300 bar used formerly (with ZnO-Cr₂O₃ catalyst) for methanol synthesis. Lurgi has another version of the low pressure process, featuring a different catalyst somewhat lower pressure and tubular reactor instead of a staged fixed-bed internally cooled reactor where methanol is the only desired product. The Koppers- Totzek process of coal gasification is favored rather than Winkler or Lurgi, because of its optimum production of CO and H₂. On the other hand, Lurgi process producing significant yield of methane, has potential for production of SNG as well as methanol or ammonia. Possibility of synthesizing various chemicals via syngas route is shown in Fig. 6.88 below.

The “Mobil MTG-process” converts coal into high octane gasoline via methanol. This process involving the use of zeolyte catalyst (type ZSM-5) was preferred to convert methanol to gasoline (95% yield), as methanol has only ½ the energy content of gasoline per unit volume. Conversion of methanol to hydrocarbon and water is highly exothermic (1510–1740 kJ/kg).



6.88 Chemicals obtainable from Syngas.

To minimize this problem, the reaction is carried out in two steps in a fixed bed unit. In the first step, methanol is partially dehydrated for an equilibrium mixture of methanol, dimethyl-ether, and water in the dehydration reactor. In the second step, the equilibrium mixture is diluted with recycle gas and converted to hydrocarbons and water over the zeolite catalyst in the conversion reactor. The fixed-bed reactor is more suitable for small scale operation. The catalyst in the conversion reactor requires periodic regeneration. Cycle length for catalyst regeneration are typically 20 days. In the fluidized bed pilot plant test site at New Jersey, C_4 + gasoline yield was 88% of the total hydrocarbons. In Newzealand, Mobil Oil has made plant for converting natural gas to gasoline by this methanol process. It is operated since 1986 and produced about 12500–13000 barrel/day methanol and meet 35% of country's gasoline need. Badger-Energy at Cambridge, Massachussettes, is planning to convert 63000 tons of Applachaim coal per day to 167,500 barrels/day of 93 octane gasoline using Mobil Process. The other commercially important by-products of this process are liquid propane 91000 barrels, isobutene 14700 barrels, and sulfur 660 tons/day. The total capital cost of the plant was estimated at \$ 3.65 billion dollars in 1977 and full scale operation started in 1990. The cost of gasoline by this process will be between \$1.09 and \$1.46/ US-

gallon. The Mobil-Process provides better product selectivity and thermal efficiency (62%) with lower capital investment than the Fischer-Tropsch synthesis which is the only one in commercial operation at present for converting coal to petrol. Mobil-process also avoids formation of a wide range of co-products, in contrast to SASOL, for which market may not exist.

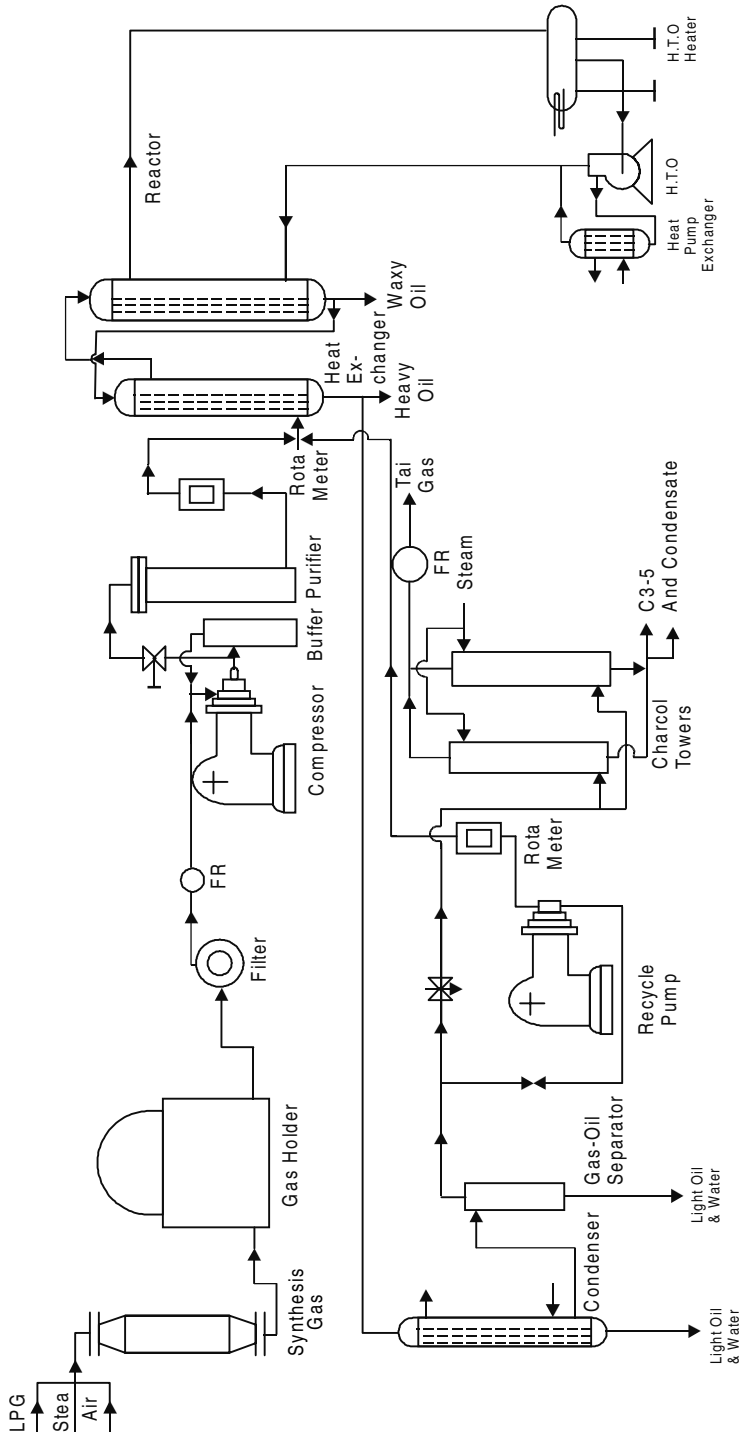
Of the various processes available for converting liquid fuel from coal (e.g., above processes as well as direct liquefaction of coal in presence of hydrogen and solvent extraction or supercritical extraction), coal gasification followed by FT-synthesis seems to be most appropriate for India on following grounds: FT-synthesis is better for making linear paraffin, linear and alpha-olefins and a good grade diesel oil (most needed in India) than Mobil process. The thermal efficiency of FT-process is low (40–45%) compared to direct hydrogenation of coal (50–55%). Yet this process by using a combination of ABGE and Synthol techniques, provide a full range of products normally derived from crude oils. In addition, it feeds the ancillary industries of a typical petrochemical complex (for which India has an established infrastructure facility) with ethylene, propylene, alcohols and ketones. Mobil process for converting methanol to petrol has advantage over the other processes with regard to product selectivity, thermal efficiency and low capital investment. Hydrogenation of tar (LTC tar) for deriving liquid and fuel is limited in India due to small availability of tar. If 10 LTC-plants are built (each 2000 ton/day coal throughput), the tar available will be only 400,000 ton/year. Further, hydrogen requirement can only be met through coal gasification and direct hydrogenation of coal, which requires coal with less than 10% ash which is rare in India. The solvent extraction of coal route (super-critical extraction or extraction with hydrogen donor solvent under pressure) may also not be suitable for high ash Indian coals. A plant to make 550,000 ton/year of petrol via coal gasification and methanol to petrol will return petrol price at Rs. 1780 crores and will require 2.85 million tonnes of coal annually. With petrol price at Rs. 4000/ton, the project is estimated to give more than 15% of internal rate of return. This process will also have limitation in India as the country needs more of middle distillate. Thus considering all possible five routes of making liquid fuel and considering the types of coal available in India as well as country's requirement, FT-synthesis seems to be the most viable option. CMPDIL, Ranchi in 1982 estimated that a one million ton per year liquid fuel plant based on KT-gasification and FT-synthesis will cost around Rs. 1611 crores as capital investment and \$35 per barrel as cost of production. The project will require 5 year to come to stream. At a plant construction cost of escalation 5% per annum, it is visualized that FT-process will be cost competitive against a new refinery coming up in 1990 operating with the crude oil price of \$48 per barrel. With reference

to studies carried out at RRL-Hyderabad where work was undertaken to obtain lower olefinic gases from synthesis gas, about 20 catalysts were tried and found that olefins obtained corresponds to 50% of the theoretical yield; however, olefinic content in the product being low, the process concluded as commercially not economical. The emphasis of work, therefore, was shifted towards middle distillate from olefins, taking into consideration the indigenous demand for diesel and kerosene, still there is need to develop suitable catalyst for obtaining middle distillate by this route. The process is also attractive from other angle that olefinic gases are obtained as by-product by this route. Since our coals contain more ash, it is more suitable for gasification and hence FT-synthesis is more in demand than direct hydrogenation. CFRI-Dhanbad is also working on FT-synthesis and installed a 5 litre/day liquid fuel pilot plant at the institute. Many other chemicals (other than those mentioned above) can also be obtained from synthesis gas (Fig. 6.88).

Table 6.29 shows as an example, various olefins that can be derived using ARGE fixed-bed and Synthol fluid-bed gasifier. It should be noted here that FT-synthesis process can not however, be considered for making olefinic gases alone. In 1983, Tennessee Eastman Co of USA became the first manufacturer to produce a modern generation of industrial chemicals by using coal as the feed-stock. They started commercial production of methanol, methyl-acetate, and acetic-anhydride by coal gasification (900 ton coal/day using Texaco gasifier). These acetic anhydrides are used for Eastman's photographic film base. Acetic anhydride is made from methane gas. The H_2/CO ratio in such case is especially suited for combined production of methanol and acetic-anhydride. Via carbonylation route although H_2 is not needed, is being used for decreasing hydrogen deficiency in methanol feed gas. This reduction minimizes the use of water gas shift reaction and increases the efficiency of coal utilization. The methyl acetate and acetic anhydride plants are highly energy efficient and they use medium and low pressure steam produced during cooling of the gasifier products. Elimination of the need for radiant heat section of the gasifier to produce high pressure steam reduced the cost and improved the reliability of the gasifier. The acetic anhydride is used in existing process to make cellulose acetate. The reaction with cellulose produces by-product acetic acid which

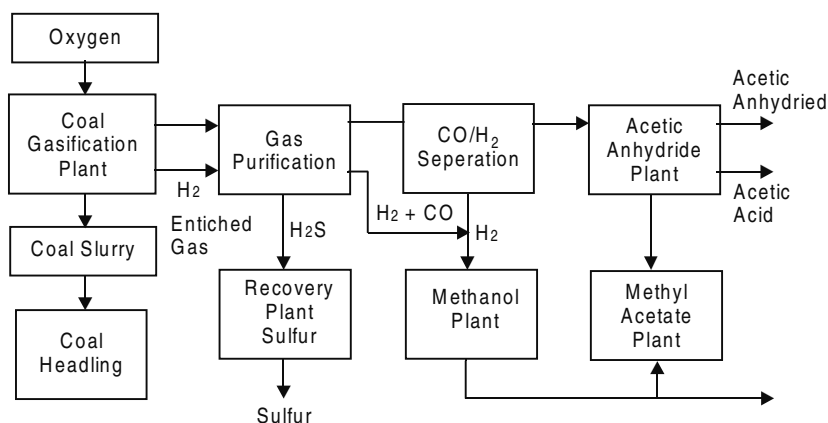
Table 6.29 Olefins from Arge and Synthol process

	% C converted	
	Arge Process	Synthol Process
C_2H_4	0.1	4.0
C_3H_6	2.7	12.0
C_4H_8	3.1	9.0



6.89 C.F.R.I. Fischer Tropsch process development unit capacity: 5.0 liter liquid fuel/day.

can be recycled to the methyl acetate plant to react with methanol. This combination of processes eliminated the need to construct an acetic acid plant. The operating cost of a coal based chemical plant (especially near mine head) is less than that for a natural gas or petroleum based plant. A flow-sheet of the plant is shown in Fig. 6.90. Here the gasifier operates under pressure and helps in reduction of gas clean up equipment and the need to compress the gas prior to its use as chemical feed-stock is minimized. The full recovery of heat in the form of low pressure steam from water scrubber as well as water-gas shift reactor, increases the thermal efficiency of the process and contributes towards its economics benefits. Conversion of the sulfide to elemental sulfur results in 99.7% of the sulfur originally contained in the coal being in molten form and sold as by-product of the operation. Methanol is produced from CO, CO₂ and H₂ by using catalytic, gas-phase reactor operating at elevated temperature and pressure. Proper feed gas composition for methanol production is formed by combing the hydrogen enriched syngas from the shift reactor and the H₂-CO stream from the gas separation unit. Methanol made from synthesis gas to form methyl-acetate by a Eastman patented process (US patent No. 4,435,595. This process has as its principal component a reactor/distillation column in which acetic acid and methanol flow counter-currently reacting and flashing simultaneously at each stage. The acetic acid serves the dual function of reactant and extractive agent to remove water and methanol from their methyl- acetate azeotrope. In addition to main reactor column, this process consists of two side-draw intermediate boiling impurities. In the final step of the process, purified CO from the gas separation plant is reacted with methyl- acetate to form acetic-anhydride by using a proprietary catalyst system developed by Eastman (Patent No. 4,374,070). Part of the acetic-anhydrides is reacted with methanol to co-produce acetic-acid. The



6.90 General description of coal gasification + acetic anhydride.

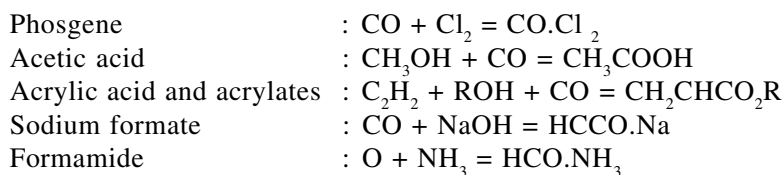
methyl-acetate resulting from this reaction is carbonylated in the acetic-anhydride reactor system. The acetic acid and acetic anhydride are refined in the distillation section of this plant. A reactor liquid purge stream removes high molecular weight by-products and a catalyst recycle process recovers and regenerates the catalyst from the purge stream (US Patent 4,388,217). The purification of methyl-acetate is difficult in presence of its azeotropes with water and methanol because the methyl acetate boiling point is very close to those of its azeotropes. Conventional refining schemes use evacuated and /or pressurized agents to remove water and methanol by extractive distillation. These schemes require numerous distillation columns and recycle streams. A novel approach was to conduct the reaction purification steps in a reactor/distillation column. In this combined single column, methyl-acetate can be made with no additional purification steps and with no unconverted reactant streams to be recovered. Since the reaction is reversible and equilibrium limited, high conversion of one reactant can be achieved only by having a large excess of other reactant. However, if the reacting mixture is allowed to flash, the conversion is increased by the removal of methylacetate from the liquid phase. If the reactants flow concurrently in a sequence of flashing reactor stages, the high concentrations of reactants at opposite ends of the column will ensure high overall conversion. In the new process developed by Eastman, the reaction occurs in the reactor column in a series of counter current flashing stages. Above the reaction section, water and methanol are extracted with acetic acid and the acetic acid is separated from methyl-acetate product. In the lower column section, methanol is stripped from by product water. Thus refined methyl acetate is the overhead product of the reactor column and water is the bottom product. Impurities are removed through a side draw system. This plant is highly heat integrated. Reboiler condensates are flashed to generate atmospheric stream to preheat the acetic acid feed, and the hot by-product waste water is used to preheat the methanol feed. The vapor side-draw provides most of the heat to run the impurity stripping column. Most important, the reactor column is inherently heat integrated. It can be thought of as four distillation columns, one on top of the other with the top and bottom of each column acting as the reboiler and condenser for the columns above and below respectively. Catalyst used for carbonylation (methyl-acetate and co-reacted with this homogeneous catalyst) was recovered and vacuum distillation units were installed in the refining section, to take advantage of the low pressure steam available from the gasifier. The control systems were required taking into account the broad range of time constants of the phenomena taking place in the reactor column and heat integration (salvation) devices. Elemental sulfur was recovered from sulfurous gases by the utilization of Claus-Process

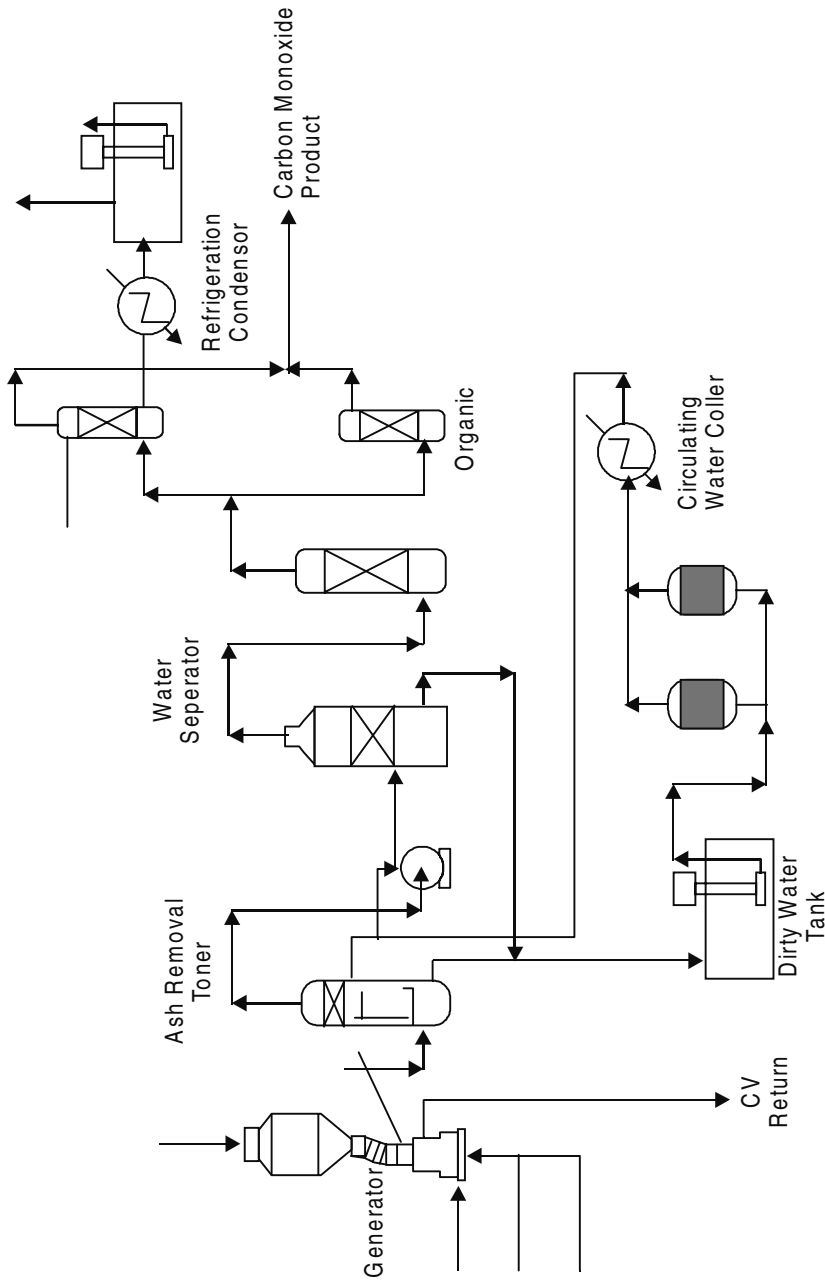
followed by a Shell-Clausen off-gas treating unit to meet all environmental standards.

All processes and chemicals we have discussed until now involves those steps whereby CO reacts under pressure with H₂ over a catalyst to form various chemicals. Economics of these processes is feasible only at large scale operation of gasifier and other reactors. But there are also some chemicals which is economically viable in smaller scale from pure CO. When relatively small quantities of CO is required, the IGT-CO generator provides a low cost simple procedure for such application. Flow sheet of a IGI-CO generator is shown in Fig. 6.91. The generator is made up of carbon-steel with a water jacket around it. No refractory lining is required. Metallurgical coke is charged into the generator from top and the generator is equipped with an alarm to indicate when it has run out of charge. Oxygen is admitted to the base of the generator by means of water cooled nozzles. Because of large excess in coke, no CO₂ is being formed. Typical composition of the gas leaving the generator is shown below.

Component gases	Vol% (dry basis)
CO	98.78
CO ₂	0.20
H ₂	0.40
H ₂ S	0.12
COS	0.13
CS ₂	0.07
N ₂ + ash	0.03
100	

The ash particles are removed by a water scrubber containing impingement plates and a mist eliminator. The residual ash is removed by a disintegrator which also boosts pressure of CO. All sulfur compounds then are removed by activated carbon. IGI-CO process Generator is available upto 600 m³/h capacity. If larger amount of CO is required (for a complex multi-product plant), say of the order of 2000 m³/h, air-blown coal gasifier with rotating grate can be incorporated. The gas in the later case will be dilute (less than 30%). CO in such case can be concentrated by using absorbers like cuprous tetrachloro-aluminate (COSORB process). Pure CO obtained by these processes can be used for the manufacture of following valuable chemicals at small scale:



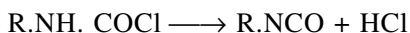
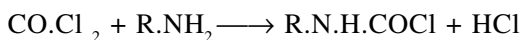


6.97 Production of CO using IGI generator.

Phosgene is prepared by reaction of dry and pure CO with Cl_2 (exothermic reaction) at 200°C in an iron tube packed with activated carbon. Phosgene is consumed to make other products as soon as it is made because of its high toxicity. Phosgene a highly reactive material is used to make following important materials.

(a) *Di-isocyanate*

The main use of phosgene is in the manufacture of di-isocyanate which are then reacted with polyether resins to form polyurethans (rigid foams). The most important di-isocyanates are TDI (toluene di-isocyanate) and MDI (methylene diisocyanate). TDI is product by mixing phosgene with toluene-diamine dissolved in an aromatic hydrocarbon or a halogenated derivative at $20\text{--}50^\circ\text{C}$. The resulting slurry reacted further with gaseous phosgene at 185°C when some HCl is liberated. The reaction is completed by blowing inert gas through the solution at 110°C .



The solution is vacuum distilled to recover the di-isocyanate. HCl produced in the the reaction is recovered and electrolyzed to derive Cl_2 which is returned again for phosgene production.

(b) *Polycarbonates*

Typical of the polycarbonates is bis-phenol-A-polycarbonate. This is prepared by the reaction between phosgene and bis-phenol-A $\text{C}_6\text{H}_4\text{OH-C}(\text{CH}_3)_2\text{-C}_6\text{H}_4\text{OH}$ in an inert solvent in the presence of pyridine. Bisphenol-A-polycarbonate is a high strength transparent plastic which competes with glass for glazing, bottle, electronic applications, small power tools, etc.

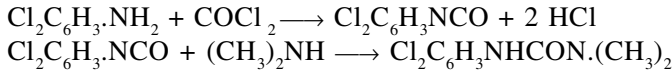
(c) *Other uses of phosgene are as follows:*

Product	End use	Intermediate for
Chloroformamates ($\text{ROH} + \text{COCl}_2 \longrightarrow \text{ROCOCl}_2$)	Solvents	Synthetic penicillin
Speciality isocyanates ($\text{RNH}_2 + \text{COCl}_2 \longrightarrow \text{RNHOCCI} - \text{RN.CO}$).		Special forms, herbicides.
Diethyl & Dimethyl carbonates ($\text{ROH} + \text{COCl}_2 \longrightarrow (\text{RO})_2\text{CO}$)	Solvents	Herbicides, synthetic penicillins.

As a typical example of highly specialized chemicals that may be produced using phosgene are the “Uron” family of herbicides. This family includes

Diurons	$\text{Cl}_2\text{C}_6\text{H}_3\text{NH.CON}(\text{CH}_3)_2$
Monouron	$\text{Cl.C}_6\text{H}_4\text{.NH.CON}(\text{CH}_3)_2$
Linuron	$\text{Cl}_2\text{C}_6\text{H}_3\text{.NH.CO.NCH.OCH}_3$
Fenuron	$\text{C}_6\text{H}_5\text{.NH.CON}(\text{CH}_3)_2$

As an example, diurons is produced by the reaction of 3,4-dichloro-isocyanate which in turn further reacted with dimethylamine:



Acrylic acid and acrylates

The reaction between C_2H_2 , ROH and CO is carried out at 30–50°C and 1–2 atmospheric pressure. Nickel-carbonyl is used as catalyst. To obtain higher acrylates, a modified version of the reaction mentioned earlier is used to obtain acrylic acid which is subsequently esterified directly. The main use of acrylates are in surface coating and textiles.

Sodium formate

The reaction mentioned earlier can be set as a by-product utilization from caustic soda. Sodium-formate is used in the manufacture of sodium-hydrosulphite, a major industrial reducing agent.

Formamide

The reaction shown earlier is carried out at 80–100°C and 100–300 atm pressure in presence of sodium-methoxide and methanol. A two stage process using methanol has been developed by BASF. CO is first reacted with methanol to form methyl-formate which in-turn reacted with ammonia to form formamide.

6.13.6 Ethanol from synthesis gas

In this last part of our discussion we see how ethanol can be synthesized from $(\text{CO} + \text{H}_2)$. Work on direct conversion of synthesis gas to ethanol has been carried out in bench scale using sodium cluster catalysts. The activity of the catalyst remained constant for a period of 1 month of operation (8 h a day). Work is being carried out at the Union Carbide Corpn (USA) using catalysts containing Rh and Fe. No commercial plant in this regard has been reported yet.

Gasification of coal by solar energy has also been attempted. The process is claimed to be cheaper than Lurgi process. Both moving-bed and fluidized

bed (coal + steam) route has been tried for gasification by solar energy. Interested reader is referred to the experiments by D.W. Gregg et al at Lawrence Livermore Lab., University of California, USA, for further information on the subject.

6.14 Coal to oil conversion

Earliest attempt to liquefy coal directly in presence of hydrogen, necessitated use of high temperature and pressure application. Coal was prepared as a paste with oil and reacted with a once-through cheap expendable iron-oxide catalyst. Efficiencies upto 70% was achieved but the limitation was that the technique was suitable for coals of low ash content (less than 8% ash), which most of the Indian coals do not have. Moreover the final products are aromatic, while India's requirement are more for paraffinic type of compounds. In the International scene, this earlier method was abandoned because of low grade catalyst necessitated use of very high pressure (700 bar) and thus the process was expensive. ICI later developed a better catalyst (tungsten-sulphide) which works in fixed-bed reactor and efficiently hydrogenates tar oils. Coal liquefaction product is known as "syncrude" or synthetic crude oil. There exists little prospect for the eventual commercialization of the following direct coal liquefaction process as SRC-I, SRC-II, Exxon donor solvent, Synthoil and H-coal process. Current research trend on coal liquefaction by direct hydrogenation are based on the concept of two-stage liquefaction. In the first stage coal is converted into a soluble intermediate – preasphaltene, and in the second stage this preasphaltene is catalytically converted to oil. For optimization of the first stage, short contact time and low severity conditions are being pursued. For the 2nd stage, there seems to exist ample scope for development of novel catalyst which hitherto was impossible in single stage operation. In June 1986, Sandia National Laboratory (USA) announced success of their bench scale trial of coal liquifaction at lower temperature and pressure. The process involves mixing crushed coal with a hydrogen rich solvent that flows into a reactor where it is heated to 450°C, depolymerizing the coal to yield the liquifaction product along with incompletely reacted coal solids and dehydrogenated solvent. The solids residue is sent to a gasifier to produce CO and H₂ which, together with steam and dehydrogenated solvent go to a catalytic reactor. In that reactor, water gas shift forms hydrogen that aids a simultaneous reaction rehydrogenating the solvent. Sandia figures that a single reactor for the later operation could be designed to operate at 125–175°C and 500 psi. Experimental results have shown that younger coals are more difficult to dissolve but produce excellent oil yield at relatively low hydrogen consumption. The use of H₂S as a promoter in processing Canadian coals

showed in general use of H_2S (5–15 wt%, on maf coals) results in higher coal conversion and distillate yield for sub-bituminous coal but little or no beneficial effect for lignites. H_2S was also effective in reducing coke formation during coprocessing. In fact, Sternberg at North Dakota University (USA) could use water and H_2S quite successfully substituting for organic vehicle liquid (operating temperature was 300–500°C in an autoclave). Some sulphide catalysts with water – H_2S system, were found to improve the yields. Selected Australian coals have been successfully liquefied in the presence of iron-sulfur catalysts at 20–30 Mpa and 400–465°C with recycling of solvents in a bench scale reactor. It is interesting to note here that North-Eastern coals of India (having high sulfur content) are easily amenable to liquefaction as determined by CFRI test. The solvent oil used in all such liquifaction process (which makes the slurry constitution before hydrogenating) plays a vital role in transforming hydrogen from gaseous to coal products. The hydrogen transfer ability was found to follow the following order – tetralin > decalin > naphthalene. The mechanism involves formation of an “adduct” between coal and donor solvent by the both hydrogen and covalent bond formation. Application of heat breaks the hydroaromatic sturcture more easily. The catalyst inhibits repolymerization reaction. The first liquefaction stage thus involves breaking down macro-molecules of MW about 5000 to sizes of MW 400 or less. The H:C ratio in coal is 0.8 to 1 and this is improved to 1.75 to 1 with resultant oil formation. The cost of production of hydrogen from coal is a major cost factor in the overall economics of coal liquefaction.

The first commercial coal hydrogenation plant was built at Leuna by IC-Farbenindustric in 1926. During second World-War, 12 coal hydrogenation plants were run in Europe with a total throughput of 4 million tons of oil per year. Most of these plants were located in West-Germany. In UK the first commercial plant was set up by ICI Ltd. at Billingham in 1935. It produced 30 million gallons of motor fuel annually. The plant was closed in 1958 due to cheap availability of petroleum oil. The US Bureau of Mines simultaneously developed their own coal to oil plants, notable of them is their 200 barrel of oil a day plant (1949) at Luisiana, Missouri. This plant was also closed in 1953. All these earlier plants were uneconomical for the reason that they operated at high pressure (3000–10,000 psig), high H_2 consumption (5000–10,000 cft H_2 per barrel of oil produced) and consequent high cost of voluminous H_2 production and its high compression needed for the process. Thus after 1960s, developments focused on catalytic hydrogenation and operating pressures at lower range. Notable of these are H-coal process and Synthoil process developed in USA and the German process.

6.14.1 H-Coal process

Developed by Hydrocarbon Research Inc. (USA), the process uses a ebullient bed catalytic hydrogenation unit where facility exists for adding or withdrawing the catalyst without disturbing the system. The design has additional advantage that ash and unreacted coal particles can pass through the bed without plugging the catalyst bed or causing large pressure drop. Since 1963, the process is perfected for two different modes of operations; one of these for distillate syncrude which is operated at low coal feed rate of 200 tons/day and the other for production of boiler grade fuel-oil at the higher coal feed rate of 600 tons/day. In addition to a higher throughput of coal, hydrogen consumption is reduced in the latter case. For further detail of the process literature cited may be consulted.

6.14.2 Synth-oil process

It uses a fixed-bed catalytic react or whereby the simultaneous desulfurization step converts high sulfur coal to a low sulfur, low ash synthetic crude. Coal crushed to 200 mesh is mixed with process derived oil and the slurry is fed only with H_2 to the reactor. The work was initiated by Pittsburg Energy Technology Centre, PA (USA) in 1969 and is being pursued in pilot plant level using using 2000 and 4000 psig pressure and $450^\circ C$ temperature. The process ended in July 1977.

6.14.3 German process

This is an improved version of earlier IG-Ferben process and adopted by Rubrkohle AG and Verga Oel Ag, in Nov 1977 in their 2000 ton/day pilot plant erected at Essen (Bottrop) West-Germany. In this process dried coal (less than 1% moisture and ground to less than 1 mm size) is mixed with a hydrogen- donor solvent, reground in a wet mill to a size less than 0.2 mm and passed through a reactor with Fe_2O_3 catalyst at 4500 psig pressure and $500^\circ C$. Contact time is 45 min. These results are being utilized for a commercial size plant set up.

In India we followed a less extensive and moderate programme since our independence for coal liquefaction process development. The proposal for synthetic oil was conceived as early as 1950. The Govt. after receiving the proposal invited Ms. Koopers Co. Inc. Pittsburg, USA, to prepare a techno-economic feasibility report for the production of syncrude using Indian coal. For this purpose, Govt. of India entered into an agreement with above company in May 1948. After necessary study, Koopers choose the site for the proposed plant adjacent to Raniganj coalfield (between Durgapur and Andal). Subsequent plants were

proposed at Ramgarh area on the north bank of Damodar river. The total investment at that time envisaged at \$72 million. Operating cost for the plant which includes coal price, chemicals, catalysts, labour and maintenance were estimated to the tune of Rs. 361 lakh per year. The production cost of aviation petrol at that price level turned out to be Rs. 0.81 per gallon with the throughput of 150,000 ton of the plant capacity. Coal cost at that time is taken at the rate of Rs. 7 per ton at plant site. Subsequently in 1954, a committee under the Chairmanship of late Sri K.D. Kalviya, the then Minister of National Resource and Scientific Research (Govt. of India), was set up. The committee accepting the need for coal based syncrude plant appointed an expert committee, known as Ghosh Committee in July 1955, to advise govt. on preparation of project reports and other matters relating to synthetic oil project. In this regard, a consortium of German firms made proposals for the production of motor fuel from coal of Jambed Bowla and upper- Kajora coalfields. The proposals were later abandoned because of reports of initial heavy losses sustained by South Africa's SASOL plant which went into operation just at that time and Govt. of India took this decision to set-up refineries based on imported crude and to explore oil deposits in the country. Later in the period 1965–1970 CFRI Dhanbad did some pioneering work on techno-economic feasibility study for conversion of upper Assam coal to oil, based on this report it was concluded that the economics of the plant depends on the cost of coal, cost of hydrogen, cost of catalyst and the sale value of the chemicals and by-products. With the price of coal Rs. 25 per ton (prevailing at that time) and natural gas price at Rs. 9 per m³, production of oil from coal alone can be competitive with import cost of middle distillates only in the scale of 100,000 barrel/day with partial chemical recovery. This will require 8 million tonnes of coal per year, 1500 MM m³ of natural gas per year and will produce 3.3 MM tons of middle distillates annually. The smallest unit, 30,000 barrel/day based on coal only, may not be fully competitive unless a substantial part is converted to chemical products. This is largely due to the higher per ton capital investment. The ideal combination, which calls for reasonable production of coal and availability of natural gas and at the same time reduces capital investment per ton of products due to scale effect, is a 60,000 barrel/day integrated plant with approximate equal liquid product yield from natural crudes. Additional advantages are – lower hydrogen demand from outside source, improvement in quality and quantity of saleable energy fuels from Assam crude, a better product pattern and quality, lower off-site and storage cost, reduction in foreign exchange in relation to capital investment, lower operation cost and greater flexibility of blending of products to meet market specifications. The disadvantage is higher production of naphtha crude. In such case, raw material required

are 2.6 million tons of raw coal, 1.5 million tons of natural crude, 2.03 MM m³/day (80 MM cft/day) of the natural gas, which will produce 1.74 MM ton/year middle distillate, 0.56 MM ton/year naphtha, 0.223 MM ton/year BTX, 150000 ton/year ashless coke, 61400 ton/year of phenol and cresol, 34000 ton/year of olefins, 95400 ton of ammonium-sulfate, 42240 ton of sulfur and 463400 ton/year of middlings and hydrogenation residue as boiler fuel valued at Rs. 980 million/year of which chemicals and by-products (excluding naphtha) constitute Rs. 612 million/year. Under these conditions, It was assumed that the return on equity capital investment is 33% (before corporate tax) and total return at 16% (before taxes) on plant investment (i.e., equivalent to an ROI of 8.8% after taxes on full equity) compared to American estimate of 4.5 ROI on coal-to-oil plant for gasoline production and upto 6% for 2/3rd fuel and 1/3rd for chemical plant. With 2/3rd as loan capital having 9% interest and 1/3rd equity and an average sale value of middle distillate at Rs. 165 per ton (compared to Rs. 180–200/ton for sale value existing that time), the total loan capital is expected to be repaid in 8 years. The difference in sale value (ex-plant) of middle distillate and market price prevailing during that period (Rs. 34/ton), enables a profit of 6% (before taxes) to be made on equity, even when full provision for repayment of loan capital is made from built-in profits on total investment. The plant investment for the combined refinery (both on and off site) will be Rs. 2200 million of which Rs. 1135 million will be foreign exchange (the prevailing import value for middle distillate will be at least Rs. 350 million per year). Additional investment for coal and power plant will be about Rs. 350–400 million. Although the prices of raw material and by-products has changed substantially since then, but the ratio of different items have escalated more or less to the same ratio which indicate that relationship among various cost estimates still holds good. Subsequent to this investment in February 1986. Coal India Ltd. submitted to the Union Energy Ministry a techno-economic feasibility report prepared by Flour Engineers, USA, for production of syncrude from coal at Jatgoria near Durgapur (W-B). The plant envisage to produce 1 million ton of kerosene, diesel, and petrol, LPG, Ethanol, methanol and sulfur at a plant investment cost of Rs. 2500 crores (800 crores of which will be in foreign exchange). A sum of \$500,000 was provided by the UNDP and UNIDO to above firm for this purpose. A national team comprising representatives from Union Ministry of coal and the coal processing consultant of UK along with WB Industrial Development Corporation and other appropriate India bodies were formed for the said purpose. The plant suggested will have a captive refinery to process the oil as conventional refineries to derive gas, the technology to be adopted will be Texaco Gasification Process which will again be synthesized by the Arge process to ensure maximum

output of middle distillates. Raniganj coal was found suitable for this purpose and a 1 million ton plant will require 6.6 million ton of such coal annually. The estimated cost include the cost of installing a 170 MW captive power plant. Govt. of India accepted this idea, the next step will be the preparation of a detailed project report. Later in January 1991, an expert panel from HRI (Hydrocarbon Research Inc. New Jersey, USA) visited India and estimated that petrol could be produced from Assam coal at a cost of \$18/barrel and taking mining of coal to a cost of \$6/ton, the overall cost of petrol will be \$24 per barrel at present price structure.

Besides direct conversion of coal to oil, there are four more possible routes for deriving liquid fuel from coal; these are –

- (a) Solvent extraction, followed by hydrogenation of coal extract.
- (b) Carbonization of coal and hydrogenation of the tar.
- (c) Super critical extraction (including gas phase extraction)
- (d) Gasification of coal followed by FT-synthesis.

The last process above has been dealt in detail in earlier chapter and thus we discuss the rest three alternatives in detail here.

6.14.4 Solvent extraction of coal

Various solvents can dissolve coal to different extent but without the heat dissolution is very small. Heat treatment at 350°C and above causes thermal degradation with consequent reduction in average molecular size and improves extraction by organic solvents. It is the prime objective of many such processes to stabilize and separate these species before they repolymerize. In this process, finely crushed coal is treated with anthracene-oil at a temperature of 350–400°C in a stainless steel autoclave whereby 85% of the coal substance goes into solution in case of higher rank coal and about 60–65% for lower rank bituminous coals. In case of supercritical extraction, the coal powder is treated with selected solvents at temperatures above their critical points which results in dissolution of about 50% by simultaneous catalytic hydrogenation and extraction. These processes basically rely on thermal breakdown of bonds in coal followed by outward diffusion/or active extraction of volatile matter thereafter. Coal extracts obtained by solvent extraction for long has been used to make carbon fibers. In the later process, the extract is made solvent free (7–8% solvent may be retained) and the mass is then aerated at a temperature below its softening point so that it does not form a lump again and it is then spun into fiber. These special process of conversion of mesophase pitch to graphite will be discussed in detail in a later section.

The five solvent extraction processes that has been tested successfully in semi-commercial scale are as follows:

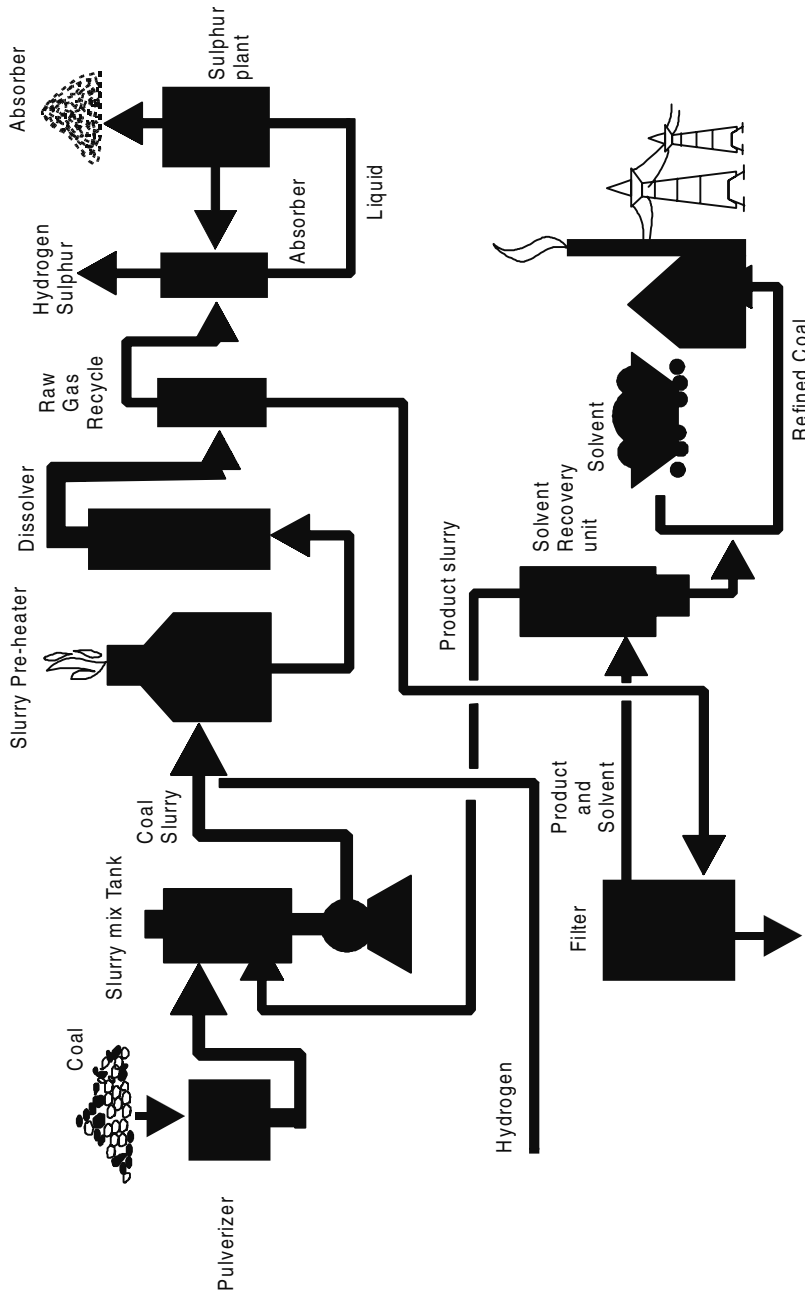
- (a) Solvent refined coal process (SRC). SRC-I was developed by Pittsburgh and Midway Coal Mining Co (USA), and SRC-II by Gulf Oil Co (USA).
- (b) Exxon donor solvent process.
- (c) H-Coal process; developed by Hydrocarbon Research Inc (USA).
- (d) Liquid solvent extraction (followed by hydrocracking) and supercritical gas extraction, developed by NCB's Coal Research Establishment', Stock Orchard (UK).
- (e) Coal-con process, developed by Consolidated Coal Co (USA).

All these processes from operational point of view, can also be grouped as

1. Solvent extraction without hydrogen gas addition.
2. Solvent extraction with hydrogen gas addition.
These are further subdivided into:
 - with catalyst (e.g., H-coal and Synthol process), and
 - without catalyst (e.g., SRC-I and SRC-II as well as Costream process of Pittsburgh Energy Technology Centre, USA).
3. Process with separate hydrogen treatment (e.g., Exxon solvent process).

6.14.5 Solvent refined coal process (SRC-I and SRC-II)

This process was developed by Spencers Chemical Co (1962–1965) and later a pilot plant (50 ton/day coal) was set up by Pittsburgh and Midway Coal Mining Co. Fig. 6.92 shows the entire process through block-diagram. In this process coal ground to 200 mesh is first dissolved in a heavy aromatic solvent (800–875°F) under moderate hydrogen pressure (1500 psig). No catalyst is added and the conversion is about 90%. The solution is filtered to remove ash and small amount of insoluble inorganic material or organic material, and fractionated to recover the solvent. Small quantities of hydrocarbon gases and light liquids are produced, along with a heavy organic material called “solvent refined coal” which has a melting point of about 350°F and contains about 0.1% ash and less than 1% sulfur. Its heating value is about 16000 Btu per lb regardless of the quality of coal used as feed- stock. This process removes all the inorganic sulfur and 60–70% of the organic sulfur in coal. This process later called SRC-I and further refined by Gulf Oil Co to eliminate filters (which are expensive and cumbersome) by a vacuum distillation unit. In this later SRC-II process deeper hydrogenation was affected (hydrogen consumption went up from 2 to 4.5 wt%) by longer residence time and product slurry recycle. Another development in this direction of solvent extraction without catalyst is the



6.92 Solvent refined coal.

“COSTEAM” process, in which 50% coal and water slurry reacts in synthesis gas ($\text{CO} + \text{H}_2$) instead of pure H_2 in a stirred reactor at 300 bar and 420°C . The residence time is 1 h and water is added to bring the steam/carbon ratio to 0.66:1. It specially suites to lignites.

All processes discussed above fall under category-II above. Category-I is similar to this but without hydrogen. Here coal is treated by physical method using a solvent like coal tar oil at temperature above 400°C ; small volume of gas is generated simultaneously. In such case, average molecular weight of dissolved coal is high (in average over 1000), there being little material soluble in benzene although usually it is all soluble in quinoline. The undissolved matter is mainly mineral matter and fusain. Different liquid solvents dissolve coal to varying degree the most efficient being naphthenic (i.e., saturated aromatic) compounds. Extracts produced this way are specially amenable to subsequent chemical treatment. In many ways the extract may be regarded as similar to crude oil although chemical compositions are different. Since the extract is clean, besides fuel oil, the extract is processed for production of high purity carbon whereby extracts are cooked and graphitized to make electrodes for steel and aluminium industry or carbon fibers. The Bojuntan process developed by Japan’s Resource Research Laboratory falls under this category of solvent extraction without hydrogen. In Japanese language pitch like bituminous substance is called “Bojuntan” and hence the name.

CFRI, Dhanbad also studied similar processes and a short summary of their findings are given below. Experimental work on solvent extraction of coal is being conducted in a 2-liner rocking (batch type) autoclave with hydrogen using anthracene oil (boiling range $300\text{--}360^\circ\text{C}$) as solvent. Insoluble from coal solution are separated on the basis of ash balance.

The studies on dissolution characteristics of Jharia (XIII seam) coking coal were completed. The effects of variables, like hydrogen pressure, coal to solvent ratio, temperature, residence time etc., were investigated varying one parameter at a time. Maximum conversion of 80% maf coal was obtained at 410°C .

Laboratory scale studies on the amenability of Samla non-coking coal to extraction have been undertaken. Effects of residence time upon conversion at different temperatures have been completed. It has been found that 62–65% of maf coal can be converted at 85 kg/cm^2 , 410°C and residence time of 120 min. Proximate and ultimate analysis of Samla coal and extract obtained are –

Table 6.30 Proximate and ultimate analysis of Samla coal and extracts

Coal/extract	M	Ash	V.M.	F.C	C	H	S	N	O	
Samla	4.2	11.2	33.0	51.6	67.28	4.63	0.31	1.95	9.41	all wt%
Extract (SRC)	1.2	0.2	67.8	30.6	85.56	5.42	0.27	2.23	4.58	all wt%

Material balance showed that hydrogen consumption in refining was about 1.2% of the maf coal under conditions of experiment. Considerable work also has been done at CFRI on solvent extraction without hydrogen. Assam coal in many respect differs from Indian Penninsular coal. Its vitrinite and exinite together amounts to about 94% and sulfur in organic form may be as high as 5%. Hydroaromatic carbon and hydrogen of Assam coal are also proportionately higher, being nearly 30–45% respectively. Ash content relatively though low, contains rare-earth elements like Ge which is believed to have catalytic effect in hydrogenation. The higher sulfur content is an advantage since it is considered to be effective in maintaining catalytic activity of mineral matter. All these factors are likely to be responsible for almost complete conversion of coal. Kutch lignite also gave 80–90% conversion under 80–100 kg/cm² hydrogen pressure. SRC is estimated to be economically favorable (although no commercial size unit cost is available) for coal to oil process primarily because of lower hydrogen consumption. A 30,000 bbl/day SRC plant is estimated (in 1974) to cost Rs. 150 crore (\$187 million) with coal price at Rs. 70/ton. Although extraction without hydrogen will have advantage from capital investment point, but actually the cost will be higher because of the requirement of fresh make-up solvent. CFRI Dhanbad has also recently successfully applied solvent extraction of coal in 7–10% proportion to increase coking characteristic of non-coking coal in steel production. In another attempt at CFRI, by Dwivedi, Sarkar, Prasad and Chakraborty, converted non coking coal and lignite to coking coal by hydro-extraction technique (hydrogenating 100 BSS mesh coal in anthracene oil at 400°C for 2 h and then boiling off the solvent along with light oil boiling below 300°C; the left-over material or the reconstituted coal has high caking index, 30–32). Furthermore, demineralization can be affected by this process and the product can also be blended with untreated coal to yield good coke. Since consumption of hydrogen by the process is the key factor for favorable economics, it was suggested that coke oven gas (containing more than 50% hydrogen) could be used instead. Mechanically this partial hydrogenation process eliminates more stable oxygen groups, hydrogenates unsaturated and produces spherical mesophase pitch.

6.14.6 H-Coal and synthoil process

These processes fall under second category, i.e., solvent extraction with added H₂ but in presence of catalyst and is used where more than 2% hydrogen is to be added or in other works when more of distillable hydrocarbons are required. In the H-coal process a slurry of coal and solvent oil is passed into an ebulliating bed (or violently fluidized bed) of catalyst. The reaction takes place at 2700 psi and 455°C. The catalyst cobalt-

molybdate settles below a point in the bed at which liquid product is drawn off to a hot atmospheric flash drum. The degree of hydrogenation can be controlled by this process. In Synthoil process, the catalyst bed is fixed and a coal- solvent slurry is pumped into the reactor with hydrogen at 450°C and 100–300 bar pressure. A high degree of turbulence is induced to minimize deposition of carbon and coal mineral matter. Similar yields are obtained in both Synthoil and H-coal process, i.e., 3 barrel of low sulfur oil per ton of coal (equivalent to 50 wt%, 65% thermal). Thermal efficiencies are high and costs are said to be low.

6.14.7 Exxon donor solvent process

It falls under the third category detailed above, i.e., process with separate H₂ treatment. In this process, the solvent is hydrogenated in a fixed bed reactor using commercial catalyst to increase its hydrogen donor power and thus it carries extra hydrogen back into the extraction stage. Simultaneous hydrogenation from solvent and hydrogen gas when present occurs during extraction but there is always significant hydrogenation from the solvent. The Exxon system finally distill out the product from the reaction products rather than filtering it out. The process gives 2.6 barrel of C₄+ liquid products from 1 ton of dry coal. In the NCB's (UK) liquid solvent and hydrocracking process, a hydrogen donor solvent (hydrogenated recycle oil) is used in a process similar to Exxon donor solvent process, to maximize the production of primary extract. The extract is first filtered then hydrocracked over special catalyst to give maximum yield of oils boiling below 400°C. Higher boiling oils are recirculated back into the system. Over 90% of the coal substance is converted to oil by this process and the product is suitable as chemical feedstock for aromatics production and a good blending material for internal combustion engine.

6.14.8 Super-critical gas phase extraction

Developed by NCB at Coal Research Establishment, Stoke Orchard, UK, the process involves extraction by a solvent like toluene above its super-critical temperature and pressure. The extract is separated from the solvent and hydrocracked to produce liquid distillates. It gives an yield of 14% gasoline and 35% diesel. Total yield of the extract ranges from 20 to 50% (by wt). The process has only been tried in small scale. Gas extraction affords a means of recovering the liquid products when they are first formed, avoiding undesirable secondary reactions. Other advantages of gas extraction are – gas extracts have lower molecular weight (about 500 compared to greater than 2000 in liquid extraction) and higher hydrogen

content and may therefore be more readily converted to useful products. Secondly solvent removal and recovery is simpler and more complete. Reduction of pressure precipitates the extract completely.

Of all the processes described so far, solvent extraction of coal has shown the maximum promise till this date. Thus it will be desirable to know some more detail about the process before we close the section. In general there are two key factors that determine the success of the process – solvent and catalyst. The later cause has been subject of detail studies especially after 1960, as from energy consideration it has the potentiality to bring down the operating temperature considerably as well as pressure. Hydrogenation of bituminous and sub-bituminous coal under mild conditions in absence of solvent, using an impregnated molybdenum – catalyst, show that the low rank coal was are more easily converted to liquids with a high oil to asphaltene ratio. Iron catalysts, in the form of ore and compounds like ferric-oxide, aerosols, ferric-hydroxide precipitated from iron-sulfate solution, has been successfully used in direct hydrogenation reactions. Hydro-liquefaction of coal using various metal carbonyls as catalysts have resulted in high coal conversion (above 90%) and high oil yield (above 32%). Hydrogenation of brown coal with molybdenum emulsion catalyst showed that it facilitates hydrogenation of complex aromatic structure without affecting the cracking of aliphatics. Hydropyrolysis of non-caking Indian coals at 800°C and 3 Mpa pressure have been reported by Chakraborty (CFRI-Dhanbad) as encouraging. Co, Ni, Cu, sodium-aluminate, sodium-silicate, and magnesium-acetate has been found to be good brown-coal liquefaction catalyst. In selecting a catalyst for coal hydrogenation, two factors which should be given primary consideration are the poisoning of the catalyst by coal sulfur and its thermal as well as chemical stability. Possibility for a large number of catalysts (see below), but selection of the most effective one pose challenge.

Possible Coal Liquefaction Catalyst

Oxides	Al_2O_3 , MoO_3 , $Mg_2Mo_3O_8$
Sulfides	V_5S_8 , $Al_{0.5}Mo_2S_4$
Carbides	WC, Pt_3SnC
Nitrides	Co_3N_2 , V_3Zn_2N .
Borides	MoB, $Co_{21}Hf_2B_6$
Phosphides	Co_2P .
Silicides	Mo_3Si
Alloy and intermetallic compounds	Ni-Cu, Zr-Pt ₃
Organometallic compounds	$Co_2(CO)_8$
Solid acids	Zeolites, Clays
Solid bases	CaO, $NaNH_2$
Molten salts	$ZnCl_2$

The last item above is a little different and recent concept. Shinn (Chevron Research, Box-1627, Richard, CA 94804 (USA) and Thooxlove Vermenlen (Chem Engg Dept, and Lawrence Berkley Lab, Univ of Californla, Borkley, CA 94720, reported good yield with molten salts. Major work on ZnCl_2 catalysts for hydrogenation and hydrocracking of coal was carried-out by Zielke, Struk, Evans, Costanza, and Gorin (Ind Eng Chem Proc Res Dev 1966, 158) at Consolidation Coal Co (now Conco Coal Development Co.) The emphasis there has been on a full boiling point range of liquid product, from treatment at temperature between 385 and 425°C and H_2 pressure of 140–200 bar. Working below 325°C requires addition of 10% water to ZnCl_2 alone melts at 317°C. This mix solvent (melt at 250°C) show increase in the pyridine solubility by 75% with addition of tetralin (without tetralin the solubility is 25%). Replacing water in the melt by methanol leads to large increase in pyridine solubility even without tetralin addition. Because oxygen removal from the coal occurs in parallel with solubilization, it was concluded that scission of other type C–O bond is the primary chemical reaction in either solubilization or liquefaction of sub-bituminous coal. The nature of the organic material in coal indicates that a reaction medium having a polar-organic character should be best able to penetrate the coal. Alcohols and phenols would appear desirable, particularly lower molecular weight alcohols which penetrate smaller pores. Methanol is likely to be important in aiding the ZnCl_2 penetration. Extractive solvents may interfere by blocking the pores. ZnCl_2 is an active catalyst in breaking cross-links (ethereal and aliphatic linkages) in coal. Addition of methanol enhance this activity whereas excessive solvent appears to dilute the catalyst. Solubilization increases almost linearly with hydrogen pressure, at constant temperature and methanol charge. There is a strong effect of temperature, leading to complete solubility at 275°C in less than 30 min. Incorporation is best limited by using lower methanol ratios and higher hydrogen pressures. Following activation the cleaned weaker bonds must be properly capped to prevent polymerization to char. Several mechanisms are available for such capping. First hydro-aromatic structure in the coal may exchange hydrogen with the reacted fragments. This type of donation may result in a net lowering of H/C ratio of the product as hydrogen is lost forming water upon oxygen removal. Two sources of the product as hydrogen is lost forming water upon oxygen removal. Two sources of external hydrogen are available for donor solvents and gas phase hydrogen. The contribution of gas phase hydrogen is normally small, but there is promise for enhancement of this effect through the use or additives with hydrogen activity. Finally, capping may occur also without hydrogen by alkylation or by alkoxylation with subsequent oxygen removal. Methanol appears important in this step, as its presence may prevent cross linking, subsequent

to ZnCl_2 attack. Extractive solvents (decane, perchloroethane, *o*-dichlorobenzene and pyrrolidines) reduce the solubilization while the donor solvents (reactive solvents like anthracene oil, indoline, cyclohexanol, and tetraline) increase it, but involves incorporation. While residence time is important with anthracene or phenanthrene oil, but not with hydrogen donor solvents as it suppresses repolymerization. It is important to differentiate between the ability of a solvent to prevent polymerization of the dissolved coal by hydrogen transfer and its ability to retain the dissolved coal in solution. For example, tetralin is frequently quoted as an excellent solvent for coals, but if the digest is allowed to cool, a large proportion of the depolymerized coal is precipitated. Anthracene oil do not suffer from this defect. Thus anthracene oil is likely to be the solvent for a commercial plant.

Dissolution of coal in different ionic medium has also been tried by Brimer and Salbut in Poland (using methanol and NaOH medium) and HF/ BF_3 catalyzed reaction studied by Olah et al at Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles (USA). In the former study methanol was chosen as it is the only alcohol not forming any non-volatile by product under reaction conditions which could contaminate the coal derived products. The main reaction is hydrolysis with dehydration and addition of hydrogen and ethylene produced from the reaction between the ethanol and NaOH. The higher yields with higher alcohols are attributed partly to alkylation but mainly to the contamination with by-products derived from the reaction between the alcohol and NaOH. The recovery of the liquid and solid products decrease with the rise in temperature due to the elimination of oxygen from the coal structure and (to a lesser extent) by the loss of volatile products. Analysis show, hydrogen and carbon in the products are greater than those in the parent coal. This is probably due to methylation reaction. The product yield at various temperature is not proportional to hydrogen intake. Decrease in humic acid content beyond 300 is due to decrease in oxygen functional groups (by dehydration and decarboxylation reactions). The second experiments with BF_3 , HF and H_2 catalyzed depolymerization and hydroliquifaction show that bituminous coal could be solubilized in pyridine to the extent of above 90% by treatment at 105°C for 4 h. At 150–170°C, cyclohexane solubility is 22% (distil ability upto 28%) and in presence of hydrogen donor solvent such as isopentane the efficiency of cyclohexane solubility still goes up. Thus use of acids like phenol as solvent in presence of BF_3 catalyst, the liquefaction temperature comes down drastically. Japanese workers have used *p*-toluene sulphonic acid along with the phenol for depolymerization of coal. Besides depolymerization a number of acid catalyzed reactions of coal have been reported. Among them are Friedel-Crafts alkylation of coal using AlCl_3 and alkyl chloride,

acid catalysed addition of olefins to coal and acylation reactions of coal. Lewis acids have also been tried for coal liquefaction. All these results indicate conventional solvents that are used for dissolving coal components can be grouped into following categories:

1. Non-specific solvents, which extract not more than a few percent of coal at a temperature upto 100°C, the extract being considered to come from resins and waxes which do not form a major part of the coal substance. Ethanol is an example.
2. Specific solvents, which extract 20–40% of the coal at temperature below 200°C, the most effective one being nucleophilic and having electron donor capacity. The nature of the extract is closely similar to that of the original coal. Here pyridine is an example.
3. Degrading solvents, which extract major amounts of the coal (upto more than 90%) at temperatures upto 400°C; the solvent can be recovered substantially unchanged from the solution. Their action is presumed to depend on a mild thermal degradation of the coal to give smaller and more soluble fragments. Phenanthrene is an example.
4. Reactive solvents, which dissolve coal by reacting with it. They are mostly hydrogen donors (e.g. tetralin) and their chemical composition is appreciably affected during the process; as a consequence of this reaction, the extracts differ markedly in properties from those obtained with degrading solvents.

In recent years considerable attention has been paid to the use of compressed gases as solvent as well in the extraction process. In order to achieve hydrogen concentration and a consequent favorable economics, current trends are towards short residence time coal liquefaction processes. Longaubach, Droege, and Chambam of Battelle Columbus Laboratory, Ohio, USA, developed a two step short residence time coal liquefaction process which substantially reduces hydrogen consumption compared to conventional solvent refined coal technology. Here the first step consists of a relatively low temperature, low pressure reaction of coal with a coal derived solvent at short contact time in the absence of molecular hydrogen. After removal of unreacted coal and mineral matter, the second step is a short contact time, high temperature and high pressure reaction of the soluble products, in the presence of molecular hydrogen. The main purpose of the first step is to dissolve the coal and purpose of 2nd step is to reduce the sulfur level of product and regenerate the solvent.

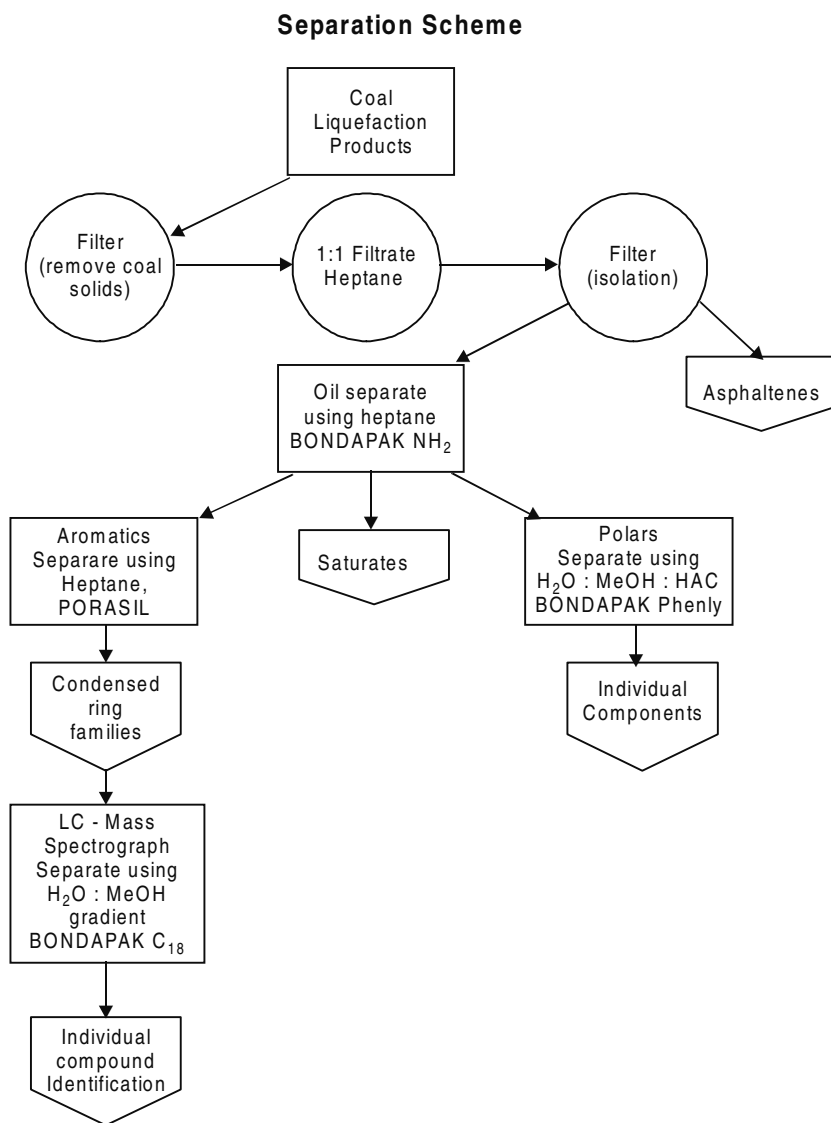
Decreased H_2 consumption should result from the short contact time, removal of mineral matter and pyretic as well as sulfate sulfur before the addition of the molecular hydrogen. These techniques are still in developmental stage. Reader may consult further literature for information in these developmental techniques. From energy point of view processes

which aim at minimum hydrogen utilization also looks at maximization of liquid yield and minimization of gaseous product. It should be borne in mind that although gaseous hydrocarbon by-products can be used to regenerate some hydrogen, the overall efficiency suffers as a portion of the gas must always be sacrificed due to thermal inefficiencies.

Low rank coals having high concentration of carboxylic acid groups and quinines, produce much more CO_2 gas than higher rank coals. As a result, less hydrogen is required to produce a given H/C mole ratio product than would be predicted from a straight forward stoichiometric calculation. The coproduction of methane increases the hydrogen requirement and will be a function of the particular process. Future commercial liquefaction plants will have to be hydrogen self-sufficient. Thus coal or one of its products, will be used to generate the needed hydrogen. In this regard, the preferable source of hydrogen undoubtedly will be coal liquefaction residue.

So far we have discussed the chemical aspect of coal liquefaction; but physical property such as viscosity, density, thermal conductivity, of coal and various solvents used in this process, are equally important for designing equipments for coal liquefaction. Due to limitation in space in this book, I will not discuss this part in detail here, but the reader is referred to literature on this particular aspect of coal liquefaction.

We conclude this section with the discussion on liquid chromatographic technique most commonly applied for the analysis of coal liquefaction products. General separation scheme by this technique is shown in Fig. 6.93. Under this separation procedure, "asphaltene" which has little commercial value, is determined as a class by simple gravimetric technique. After this isolation, rest of the compounds are determined by liquid chromatography. This later technique involves four steps. In the first step, the syncrude is broken down into saturates, aromatics and polar (mostly nitrogen and oxygen containing polar compounds in a commercially available column like Water's μ - BONDAPAK- NH_2 column with n-heptane as mobile phase. For quantitative estimation of the components, the following third step is followed. In the second step polar (resin fraction) are separated into individual components. Commercial columns (such as Water's μ - BONDAPAK phenyl column) are available for this purpose with a water/methanol/acetic and mobile phase. In the third step, aromatic fraction is separated as per number of condensed rings. In step-1 above, we get the idea of relative abundance of the different condensed ring families in the aromatic fraction. By collecting the material from the separation procedure and further separating them in appropriate column (e.g., Water's μ -PORASIL column) with n-heptane as mobile phase, it is possible to determine each of the condensed ring families. Results of these steps are shown in Figs. 6.94–6.97. Further separation of ring families into individual



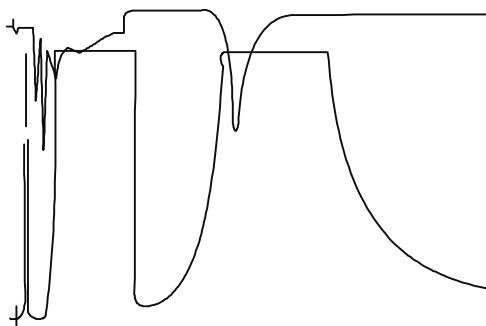
6.93 Separation scheme for coal liquids

components in fourth step will require interfacing liquid chromatogram with mass spectra.

6.15 Hydrogenation of coal tar

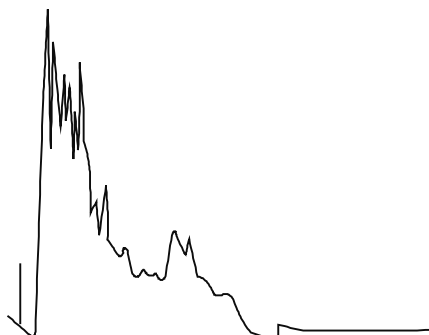
Tar occurs in the micropores of coal structure and comes out due to breakdown of hydroaromatic structure of coal during carbonization. Pressure

Step 1: Saturates, Aromatics, Polars



6.94 Separation into hydrocarbon groups is the first step in an integrated scheme for complete syncrude analysis.

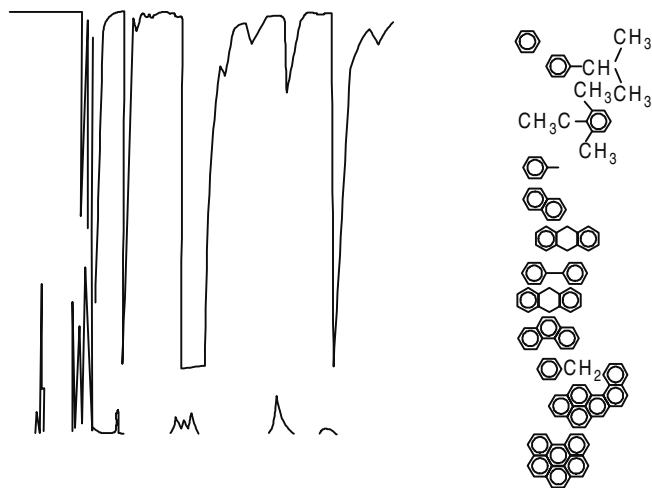
Step 2 Polar Fraction



6.95 The separation of polars gives the researcher the ability to collect fraction which can then be further analyzed, both by LC and by other techniques.

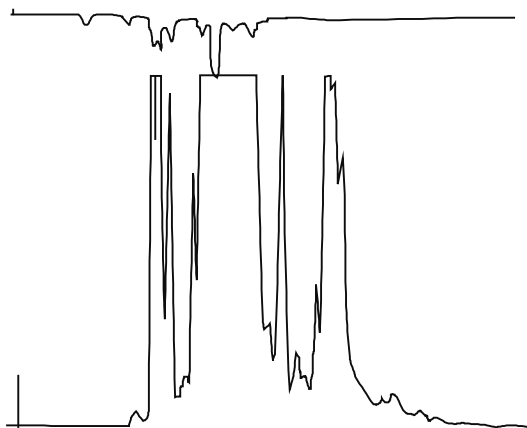
solvent extraction at 200–300°C gave yields of aliphatic and aromatic hydrocarbons approximating to the corresponding fractions in a low temperature tar from the same coal. Benzene in this case was used as the main solvent and tetralin was used in the final stage. In such case the main difference with corresponding group of hydrocarbons derived by direct solvent extraction of coal is that the aliphatics were nearly all saturated in the extracts, whereas about $\frac{1}{2}$ of those in the tars were olefinic and the aromatics in the extracts included some more highly condensed species than those in the tar. Other major differences between the tar and extract composition are the presence of complex benzene-insoluble oxygen compounds in the tar but not in the coal extract and the presence of a much larger amount of phenols of wide molecular weight ranges derived

Step 3: Standards



6.96 Separation of standards indicators that sample components are being selectively retained on the column according to ring size.

Separation of Aromatics



6.97 The chromatogram of an aromatic fraction gives an idea of what a real sample looks like in this technique.

from oxygen compounds in the parent coal, in tar. Liquid products are derived from coal by carbonization, thus by addition of hydrogen not applied here as mentioned earlier, but by H/C ratio in the liquid product is increased as carbon is removed from the system as a solid residue known as char. These processes of coal liquefaction is costly because capital investment for coke oven is high in relation to the unit cost of the oil produced. Nevertheless, if the tar can be obtained as by-product, the economics of tar hydrogenation looks good.

6.16 Economics of coal to oil process

Economics of coal to oil conversion under Indian condition (as estimated by CFRI, Dhanbad in 1960s) has already been discussed in earlier section. Subsequent to this, with change in various cost factors, a re-evaluation of the conversion process was carried out by Expert Committee appointed by Government of India under the Chairmanship of Chakraborty in 1977.

We discuss about this report here. Nevertheless it may be noted that we actually do not have a semi-commercial coal to oil plant in India and thus real hard data for evaluation of the economics is still not available. Accordingly the above expert panel borrowed basic data from American experience and extrapolated the same under Indian situation. The study considers following three possibilities.

- Case I – The product of the process is distillable synthetic oil. In such case vacuum still bottoms is sent to a fluid coker and H_2 is produced from the mixture of fluid coke and fresh coal, using a Lurgi coal gasifier.
- Case II – The product is syncrude. In this case, hydrogen is produced by partial oxidation of vacuum still bottoms containing solid residue.
- Case III – Product is a low sulfur fuel oil. Hydrogen is obtained from the solid separation residue.

Calculations were done on the basis of 25,000 ton/day coal plant and product credits were considered on the following basis – high Btu gas = \$1/MM Btu, sulfur = \$20/ton and NH_3 = \$33/ton. Summary of the results from above basis is shown in Table 6.31.

Table 6.31 Plant investment (in \$)

On-site	432,857,00	312,295,195	252,311,185
Off-site	86,111,110	54,816,101	44,180,000
Catalyst charge	401,111	3,420,000	2,000,000
Total	523,328,110	370,532,487	298,552,586

Table 6.32 Raw materials and utilities (\$)

	Case – I	Case – II	Case – III
Coal (ton/day)	33,200	29,180	25,000
Fuel	3,070	966	—
Total	36,270	26,146	—
Power KW	361,338	207,740	163,819
Water (GPM)	16,500	11,482	8,700
Method of solid separation	Coking	None	Settling
Feedstock for hydrogen	Coke & coalVac.	Bottom slurry	Settler
Hydrogen generator (type)	Lurgi	Texaco	—

Table 6.33 Annual operating cost (\$)

	Case – I	Case – II	Case – III
Coal (@\$8.36/ton)	105.15	76.14	73.33
Power (@ 0.6 C/KWH)	17.17	9.97	7.78
Catalysts & chemicals	10.91	4.49	8.91
Salary and benefits	5.95	4.46	4.46
Repair	7.54	5.36	4.31
Labour maintenance	9.21	6.38	4.82
Other services	0.60	0.60	0.60
Overhead & other expenses	2.00	2.00	2.00
Insurances & taxes (@2% investment)	10.46	7.41	5.91
Annual capital charge (@20% invest)	104.67	74.11	59.71
TOTAL OPERATING COST	273.66	195.92	171.89
CRUDE OIL COST (\$/Bbl, Indian condition)	7.55	7.08	7.38

Table 6.34 Annual revenue

	Case – I	Case – II	Case – III
Synthetic crude (\$ x 104)	204.06	157.57	—
Fuel oil, naphtha, & crude oil	—	—	153.70
High Btu gas (\$1/MM Btu)	57.49	39.67	11.25
Sulfur (\$20/ton)	8.71	6.45	5.79
Ammonia (\$36.4/ton)	3.40	2.23	1.65
	273.66	195.62	171.89

From above calculations, the Expert Committee concluded that a million ton synthetic oil plant will cost about Rs. 635 crore and the product crude oil Rs. 809/ton as against January 1977 imported crude oil price of Rs. 909–1200/ton. But definitely these calculations are based on linear extrapolation technique and casts some doubt about both technical and economic feasibility of a commercial plant even today. This is evidenced by the fact that besides South-Africa, no other nation has put up a single commercial plant as of today. But this technology will definitely be demanding in case of strategic requirement arise. Moreover, some international expert claim that production of synthesis gas and then oil by F-T synthesis, considering both overall efficiency, selectively, as well as ease of control of the process seems to be the cheapest and most economically viable option for coal-to-oil production. Whatever the argument may be, it is however universally accepted that the rate of increase in price of coal will be a dominant factor in determining the economic feasibility of coal-to-oil conversion irrespective of the process adopted. It has also been estimated that oil production either by direct hydrogenation or FT-synthesis are almost at par with respect to final product price.

In the International scenario, at 1978 price level, estimated cost of producing oil from coal by various methods, ranges between \$160/ton oil. Thermal equivalence of the products are almost same (costs in UK pound):

Process	Cost (1978 level)	Thermal equivalence of pdct.
Direct hydrogenation	72/ton oil produced	42700 MJ/ton oil
Pyrolysis of coal to oil and gas	82/ton of oil & 20 pence per therm of gas.	42800 MJ/ton oil
SRC method of coal liquefaction	80/ton oil	43200 MJ/ton oil
Methanol from coal	55/ton methanol	23000MJ/ton methanol
Liquifaction of cellulose to oil	24/ton oil	429000 MJ/ton oil

It is interesting to note in above table that, liquefaction of cellulose to oil closely compete with coal and that cellulose production is a renewable source of energy (heating value of the oil produced is same as coal). While calculating cost for coal to oil process, besides those factors considered above, inflation rate also plays a crucial role in predicting future situation. For example, as the above table shows production cost of oil from coal is roughly (UK pound) 8.30 per barrel. In a close inflation rate variation (5 to 8%), the price level of coal to oil will change in the years to come as follows (note we have kept coal prices same) (all prices in British pound).

Annual inflation rate	Price of coal-to-oil
5% on capital and labour cost and 2% on coal prices	19.60/barrel
6% on capital and labour cost, 2% on coal price	21.70
8% on capital and labour cost, 2% on coal price	28.00

So while directly using formula like follows⁹⁵, we have to carefully watch cut the inflation rate (or DCR rate) implicit in the equation:

$$\text{Product cost (L/GJ)} = (0.57 \times \text{relative capital cost} + \text{feedstock price L/GJ}) / (\text{Fractional efficiency}).$$

Implicit in the above equation are following assumptions:

1. The DCF rate is 5% per annum.
2. Capital cost of local based SNG-process is 140 L/kW thermal input.
3. Operating costs are 7% of the capital investment per annum for continuous operation and pro-rata for lower load factors.
4. The load factor for all process is 90%.

It may be noted here that an increase in DCF rate from 5% to 10% increase the gas cost (SNG-process) by about 12%. In these ensuing economic considerations, the final point is political consideration as well. Different nations have varying energy issues that estimate a process absolutely necessary in one country while the same economically not feasible being considered in another country. Nuclear energy is considered cheaper than energy produced from coal in most democratic countries. Coal to oil in large scale operation is also considered economically less

important than nuclear energy; but environmental activists demonstrates against installation of nuclear power as the final disposal of used fuel possess a great health hazard, while coal ash is completely safe in this regard. Technologies have now well advanced to offer completely environmental compatible flue gas emission from coal based plants. However the fact still remains that, relative abundance of raw material and price policy will definitely continue to play a key role in assessing these economics in the years to come. For example, in January 1991, an expert panel from HRI, New Jersey (USA) estimated that petrol could be produced from Assam coal at a cost of \$18/barrel, assuming cost of mining as \$6/ton and the overall cost of petrol will be \$24/barrel.

6.17 Hydrocarbon fuel cells

This unique hydrocarbon (coal gas or natural gas) to energy conversion device operates in static (noiseless) and pollution free manner. This is the most efficient way of converting fuel to electricity that we know today. The other coal gas to electricity conversion device, capable of competing with fuel cell technology is the magneto-hydrodynamic principle (in short known as MHD), a brief mention of which has been mentioned in earlier section.

In this section let us first review the MHD technology to a little more detail and then discuss fuel-cell technology in depth. In a MHD system the hot coal gas in the form of plasma is made electrically conductive by seeding it with alkali metal ions. After conversion the MHD flue gas contains CO_2 and other materials and thus is not completely devoid of pollution like fuel-cell. MHD system also requires water for heat transfer. Present RandD effort in this direction is aimed at increasing conductivity of the plasma (which is now of the order of 10 mho/m) and low electrical conductivity value of the plasma forces the use of super-conducting magnets of magnetic field around 5–50 tesla. The goal is to reach 200–1000 mho/m conductivity value for the plasma in order to make it commercially viable. Air pre-heat temperature of the order 1700–2000°C is required for a commercial MHD power plant. Although regeneration air pre-heater is used however according to the second law of thermodynamics, penalty is paid in regeneration. Efforts are therefore required to develop suitable recuperator. MHD-generator generates DC-power which necessitates use of very large inverter sub-station. Therefore development is necessary to evolve a cost effective inverter suitable for commercial size MHD-generator. Economics of the MHD generator also do not look very attractive until it is used with combined cycle-coal gasification unit using exhaust gas from MHD channel. Recently (1990) Russia installed a 500 MWe commercial MHD plant, data from which will answer to some

of the above queries and ultimately determine the fate of MHD power generation possibility at commercial scale. In India, a 5 MW(th) MHD test facility has been created at BHEL, Triruchirapally, Tamil- Nadu, by BARC, Trombay, Bombay, Rohatgi et al carried out the basic studies in this direction, and considered NO_x pollution from such units. At University of Tennessee, Space Institute, Nashville (USA), work is in progress to achieve a temperature of 2700–3000°C of coal gas using oxygen. Coal ground to 80% through 200 mesh and 50% through 325 mesh is used to burn in pressurized (3 atm) fluidized bed combustor (K with 1–2% concentration is used as seed material). The combustion chamber is made of 304 SS steel (0.125 in. thick plate). The time of residence is 45 ms and then fed to the channel at supersonic velocity (Mach 1.7 and 2). Coal used had average ash content of 14–16%. Heat from the high temperatures generator exhaust is used for gasification of coal. A two- stage and three stage cyclone furnace (stages are increased in order to reduce the carry-over, which should be about zero for MHD application) using 70%–200 mesh coal and N_2O_2 mixture (2:1) is used (similar to the one tested by Bureau of Mines, Pittsburgh. K_2CO_3 is used as seeding material at the rate of 15 lbs/100 lb coal. Molten-salt gasifier produces a clean fuel gas and the combustion products will be free of ash and sulfur impurities. Molten-salt reactor can either be placed before the MHD-generator (in which case the reactor gets an input from exhaust gas of the boiler heater placed after MHD and the reactor output to MHD generator) or after the MHD-generator (in which case the reactor gets input from MHD-generator exhaust and the generator output goes to boiler heater).

A fuel-cell on the contrary can be considered is the reverse of electrolysis cell. Thus it converts energy associated with a chemical reaction to electricity. Unlike a electrochemical corrosion process (where electrons are driven through the same electrode rather than through the external circuit), a fuel cell has to separate electrodes where gaseous reactants are fed and simultaneous occurrence of oxidation and reduction cause a potential difference that promotes the electron flow in the external circuit. Electrical power generating cells, accordingly, can be grouped under three categories.

1. *Primary cells* – like lead-acid battery, which becomes exhausted once the electrolyte gets used up.
2. *Secondary battery* – like rechargeable Ni-Cd battery where the cell can be recharged again by applying potential in the reverse mode.
3. *Fuel cells* – where the cell is inexhaustible and keeps on continuing as long as the fuel (gases) are supplied to the cell from external sources.

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7.1 Introduction

For long coal has served as an important source for various industrial carbon demand. Number and varieties of such products have increased with better understanding of its structure and thereby acquiring engineering capabilities to custom-tailor them as per the service needs. Such carbons varies from simple activated carbon, graphite electrode, glassy carbon, carbon composites, to molecular sieve and nuclear graphite. Greater varieties of carbon products have been generated by ordering carbon structure in coal to graphite form and thereby imparting to it special physical and chemical properties. Our understanding of micro and macro pore distribution in carbon matrix and gaining effective control over forming them, has opened up new vista for fabricating a number of fascinating industrial materials which hitherto was unknown in carbon chemistry. Insight into the physical changes associated with thermal treatment (like viscosity) has revealed another new dimension of controlling between vitreous and non-vitreous configuration; carbon molecular engineering, in essence, constitute these studies and helps us modifying a particular carbon matrix to a modified product with desired physical and chemical properties.

7.2 Carbon molecular engineering

Carbonaceous material as we know occupy special position between metal, polymers, and ceramics; and thus provide us an opportunity to produce materials from carbon, with properties common to both above extremities. Coal is also a microporous substance and Prof. P.L. Walker Jr at the Department of Material Science and Engineering, Pennsylvania State University (USA) who pioneered studies in this direction summarised coal into two types of carbon structure – the first being high micro-porosity (by micro-porosity we mean, pores less than 2 nm size). Material of this type have wide commercial applications and have a splendid growth potential. For example, activated carbon which is used to remove impurities

from gas and water streams; carbon as catalyst support and molecular-sieve also fall under this category. On the other hand there are carbons that have very small microporosity. These are represented by the graphitic materials – like carbon composites, electrodes used in production of steel and electrical motor brushes (known as carbon for sliding applications). The carbons are considered as polycrystalline materials. In the plane carbons are held by covalent bond, whereas between planes they are held by van der Waals force. One thing that distinguishes carbon from each other is crystalline size. But even more important is the crystallite alignment because this determines, for example, extent of micro-porosity in carbon. If these building blocks are very poorly aligned, they pack very poorly and porosity remains between these building blocks. If the crystallite size is small, the void size between these building blocks is going to be small, there will remain micropores. On the other hand, if we go to a very high crystallite alignment (e.g., in graphitised carbon fiber) we are not going to have any significant amount of porosity between the crystallites or building blocks. Therefore, the microporosity in the fiber will be very small. Looking at temperature – porosity diagram of coal, it happens to be in the range 400–600°C which will be of our present interest. This is the temperature range where most organic solids start losing hydrogen, produces free radicals which condense into large molecular units. It is this temperature range that crystallite alignment is going to be determined. Although final alignment to graphite structure takes place at a much higher temperature, but alignment at this temperature is most important of further high temperature alignment. Let us now consider first production of carbon matrix with high microporosity from coal. As the number of cross links in coal increases (mainly methylene and oxygen-ether linkages), apparent molecular weight of coal also increases. The coal changes from a thermoplastic material which softens as we heat up towards 600°C, to a thermosetting material as the number of cross-links in the original coal increase and as the number formed during thermal treatment increases. Additional cross-links are formed during thermal treatment as a result of condensation of hydroxyl and carboxyl groups in the coal.

Thus we find coal a really micro-porous material. Most of the surface area and most of the pore volume in coal (lignite to anthracite) are located in pores less than 2 nm size. Thus we certainly would like to preserve the micro-porosity in coal if we want to convert coal to micro-porous carbon. What it means is that we want the coal to behave as a thermosetting material. In other words, as we heat the coal up, we do not want it to soften. We do not want the building blocks to have an opportunity to thermally align and pack better, consequently lose much of the micro-porosity which existed in the original coal. The problem is, all bituminous coal is to a considerable extent thermoplastic material. In other words,

when heated they soften at about 400°C and begin to flow to a considerable extent, thereby are not showing to produce large micro-porosity which we desire. Some pre-treatment of the coal is necessary to convert it from thermoplastic to thermosetting precursor. We will see now some such possible pre-treatment. When we heat bituminous coal to 100–150°C (at this temperature carbon or coal gasification is insignificant) and expose it to air, there is an increase in weight as oxygen is added to the coal. It is thought that oxygen interacts primarily with some of the hydrogen to produce additional hydroxyl groups in the coal. Then as the pre-treated coal is heated to higher temperature in the range 400–600°C, we get condensation of these adjacent hydroxyl groups liberating water and leaving behind an oxygen atom which produces an additional ether cross-link in the coal. The coal is converted increasingly to a more thermosetting material as more oxygen is added. Let us see how effective this pre-treatment is. When coal is heated in nitrogen atmosphere it swells (sometime as high as 900%). The expansion takes place between 480 and 500°C. Now, if the same coal we keep in oxidizing atmosphere at 150°C and then swelling determined in N_2 . We find swelling decreasing. With increased amount of oxygen addition swelling is progressively reduced. Thus we can increase the thermosetting character of coal in very sensitive way. This approach is used for industrially converting bituminous coal to activated carbon. Treatment of bituminous coal with conc. HCL and conc. HF (at room temperature) by Polish workers (Fuel, 1983) resulted in reduction of swelling (and thus fluidity) of the coal upon heating. Addition of K_2CO_3 also markedly reduces the fluidity of bituminous coal upon subsequent heating. Thus addition of K_2CO_3 converts the bituminous coal to a thermosetting precursor – thereby retaining a high surface area in micropores upon heat treatment and also serves as a catalyst to enhance the rate of reaction of steam with char active sites located in these micropores during commercial coal gasification process. Most of the potassium can be ultimately removed from the char by under-washing. Now we have our char produced at about 600°C. There maybe some additional things we would like to do to the char to make it a more valuable commercial product. One possibility is to open up close micropores, because typically coals and their char not only have in them microporosity which is open but also a significant amount of microporosity which are closed in pores less than about 0.5 nm in size. These micropores are not useful because they are smaller than the size of most molecules. What we to frequently is to selectively remove carbon atoms from this microporous (low temperature carbon) by gasification with steam, CO_2 , or air. Removal of carbon atom have two effects. One, we increase the average size of the micropores which are already open to the adsorbate or the gas. Second we open up closed pores. Typically for coal chars, the surface area generated

goes through a maximum at a 40%. Coal chars are viable precursors for the production of "Molecular Sieves." If instead of gasifying a char to high burn-off, to produce activated carbon of relatively large pore size, we restrict burn-off to low level, we can produce a molecular sieve. At Union Carbide molecular sieves are generated to separate air components (N_2 and O_2). Another company Calgon Carbon Corporation (USA) is also producing such carbon molecular sieve by their own patented process. Other potential applications in this direction includes dehydration of alcohols (C_5 and lower) and separation such as CO_2/CH_4 , N_2/CH_4 , Ar/O_2 , H_2S/CO_2 , and C_2H_4/CH_4 . Readers further interested in the subject may consult Literature. Besides molecular sieves, carbon bodies of controlled pore size distribution have application as catalyst support material as well. In manufactured carbons, the porosity is typically about 25% by volume. In different types, however; it may vary from almost zero upto 50%, we can determine the pore volume open to helium by measuring a He- density by He-displacement and a particle apparent density by mercury displacement; surface area determined by N_2 absorption at $-196^\circ C$, present may be open or closed and may vary in size over a wide range. The amount of burn-off depends upon the molecules we wish to separate. Patel et al studied the effect of small levels of burn-off with anthracite char on the case of penetration (diffusion) of CH_4 into the micropores of the char. At a burn-off level of about 7%, CH_4 diffusion is activated, with an activation energy of about 28 kJ/mole. Upon additional gasification to about 8% total burn-off, there is a large increase in the rate of CH_4 diffusion into the char and a decrease in activation energy for the diffusion to about 12 kJ/mole. Another 1% increase in char gasification to total burn-off about 9% results in another substantial increase in CH_4 accessibility into the micropores. Diffusion is no longer activated since the pore size no longer closely approximates the molecular size of CH_4 . Rather diffusion is in the Khudsen regime, where the diffusion coefficient is proportional to $T^{0.5}$. Clearly small amounts of bur-off of a coal char can change its molecular sieving characteristics tremendously. This is an exciting part of molecular engineering.

Next comes materials with low micro-porosity. These are carbon materials with excellent crystallite alignment, like graphite. Graphite can be produced from coal tar pitch again by molecular engineering. Although this aspect, which gives rise to a host of graphite based industrial compounds and accordingly we will learn this technology in more detail in the next section, but here we will see how from molecular point of view, we can comprehend the phenomenon. Pitch, as we have seen earlier, is a mixture of large number of chemical compounds and to look at them all at a time will be fruitless from the point of view of our present objective; instead, we will first study the behaviour of some model compounds (like

anthracene, phenanthrene, biphenyl, and phenazine) which are also present in significant amount in coal tar pitch. Anthracene is a planar aromatic (linear) molecule. Upon heating to about 450°C (in an autoclave to prevent its vaporization), it commences losing hydrogen at the 9,10 positions forming free radicals. These radicals condense producing a large molecule (9,9'-bianthryl). Continued loss of hydrogen, free radical production followed by condensation, leads to increasingly large, planar molecules and eventually low temperature coke. Phenanthrene is also a planar molecule, but it is branched. It also undergoes loss of hydrogen and radical condensation reactions to ultimately produce large planar aromatics which are much less reactive than are linear aromatics. Thus, phenanthrene undergoes loss of hydrogen at a rate some 100 times more slowly than does anthracene; its carbonization rate and hence rate of formation of low temperature coke is much less than that of anthracene. Phenazine is a linear aromatic, like anthracene. However, nitrogen is substituted for carbon in the middle benzene ring (in the 9 and 10 position). Presence of nitrogen accelerates the loss of hydrogen, free radical production, and thus enhances the rate of carbonization over that of anthracene. Biphenyl contains two benzene rings which are not condensed but instead connected by a single carbon-carbon bond. It is a non-planar molecule with free rotation around the C-C bond. Hence, on its carbonization non-planar free radicals are produced which upon condensation lead to large non-planar molecules. As we see later, this has important implication as to the morphology of cokes and structure of carbons which can be produced, compared to the situation when the other three aromatics are used as precursors. Now consider the carbonization of a precursor which behaves as a thermoplastic material upon heating and forms planar intermediates (as does anthracene). We can observe the carbonization process in reflected polarized light. At some temperature the compound melts (128°C, the viscosity of the liquid decreases or mobility of the molecules increases). At about 450°C, hydrogen is lost from reactive positions in some of the molecules, free radicals form and condensation reactions occur. Eventually the planar molecules become large enough in size to realize sufficient Van-der-Waals attraction between them to promote their alignment. At this point anisotropic spheres known as "mesophase" appear in dispersed isotropic liquid. Interestingly, biphenyl which does not lead to planar intermediate upon carbonization is not a precursor for anisotropic mesophase. We can do molecular engineering using mixtures of compounds as precursors. For example, if we start with carbons of variable crystallite alignment and microporosity and find the results. The greater the phenanthrene content in the mixture, the better the crystallite alignment in the carbon, the larger its crystallite size, the higher its density and the smaller its microporosity. Graphical plot in this respect clearly shows how the addition of biphenyl to phenanthrene sharply reduces

crystallite growth in the low temperature carbon formed upon its heat treatment at 2800°C.

So far we have been talking about pure aromatic precursors, leading strictly to carbonaceous solids. However, we may want one or more metals to be dispersed in our carbon. We may want to produce such a composite. To do this, we simply add one or more organometallic compounds into our original recipe. Such addition can radically change all properties of the carbon. For example, addition of varying amounts of vinyl-ferrocene to furfuryl alcohol results in the production of variable crystallinity. The addition of 10% (by weight) of VF to FA converts non-graphitizable precursors to graphitizable precursor upon heat treatment to 2500°C. In the graphitized carbon fibers (derived from mesophase pitch) high crystalline alignment results in negligible porosity. Inorganic impurities in it, not only retard mesophase formation but also vaporizes at high temperature and leave behind unwanted voids. Upon drawing, the mesophase tends to align even better and now we want to preserve it. To achieve this, we heat it at lower temperature in air, adding a little oxygen to the fiber. The oxygen forms some cross-linkage so that later when we heat it at higher temperatures (for graphitization) the material does not soften and loose the good alignment which we achieved in the spinning step. It is then heated to high temperature to increase crystalline size and crystalline alignment. Most of these fibers produced commercially are of the size 5–15 micro-meter in diameter. Microscopic studies show, although in these fibers carbon crystallites have their basal planes running essentially parallel to the fiber axis, two extreme morphology can still exist – one with radial structure where the surface of the fiber composed of crystallite edges and the other onion like structure in which the fiber surface composed of predominantly basal planes. Young's modulus and tensile strength of these fibers are much higher in the basal plane than perpendicular to the basal plane. Carbon fibers of high crystallite alignment have Young's modulus approaching value that of graphite single crystal rather closely (about 900 Gpa). This is not true for tensile strength. Graphite single crystal has tensile strength of about 20 Gpa within the basal plane; best quality Union Carbide carbon fiber (P-120) has tensile strength of only 2.2 GPa in the axial direction. Further, the value does not increase much upon increasing heat treatment temperature from 1800 to 2800°C. Tensile strength is primarily determined by defects in the structure, that is the point of stress concentration. Its value is a function of length of fiber tested or probability of finding a flaw. This is why it is important to start with a clean precursor and the spin the fiber in an environment of low dust concentration. The selection of fiber heat treatment temperature depends upon the stiffness desired in the fiber and the composite. Since Young's

Modulus increases much more with increasing heat treatment than does tensile strength; strain at failure decreases with increasing heat treatment temperature. The fiber thus becomes more brittle. Also, as you increase crystallite alignment and Young's Modulus in the axial direction, you sacrifice some shear-modulus perpendicular to the fiber axis. In some cases, it may be desired to have somewhat higher shear-modulus and sacrifice some Young's Modulus. Again, this can be controlled by change in maximum heat treatment temperature of the fiber.

Pyrolytic decomposition of gaseous or vaporised carbon compounds also generates a host of very interesting industrial compounds; like use of pyrocarbon as coating and in the form of a compact self-supporting body under controlled conditions and hence with properties that could be varied as desired. Pyrocarbon coating and compacts are produced from gaseous or vaporized carbon compounds, which are decomposed pyrolytically on hot graphite supports (800–2800°C). Example of suitable carbon compounds are methane, ethane, propane, acetylene, benzene, and carbon-tetrachloride. The structure and properties of the pyrocarbon layers obtained depend mainly upon the temperature, pressure and residence-time, and nature of carbonaceous gas. The variability of pyrocarbon is extremely wide a ranges from almost isotropic, via granular, to the highly anisotropic laminar structure. These pyrocarbon structures have been examined in detail with respect to deposition in fluidized bed reactor. This deposition has gained considerable technological importance for the coating of fuel particles for nuclear reactors. Multiple layers are used having various mechanical properties, irradiation behaviour, and exhibiting good fission product retention. Another important application is the production of pyrocarbon coating on artificial graphite bodies the deposition then no longer taking place in a fluidized bed, but on fixed graphite objects. The pyrocarbon coating gives the artificial graphite a very smooth surface; it becomes substantially impermeable, its resistance to oxidation and erosion; it becomes substantially impermeable, its resistance to oxidation and erosion is greatly enhanced. If the coating is applied only to the outer surface of the shaped body, it provides only incomplete protection against slow selective oxidation, such as occurs e.g., in graphite components in nuclear reactors. If the protective surface layer is damaged, the oxidizing gas can pass through the pores of the graphite body and so destroy he material. To prevent this, it is necessary to deposit the pyrocarbon within the pores. This is possible at slow deposition rates (low temperature, low partial Pressure). Even after the surface of article coated in this way has been attacked, the protective action of the pyrocarbon in the pores persist.

Compact pyrolytic graphite bodies are produced at a constant

temperature and constant pressure at the lowest possible deposition rate. Crystalline order is obtained only within the layer planes; the material is turbostatic. Growth and ordering processes that lead also to extensive crystalline order in the C-direction, can be induced by additional heat treatment at temperature upto 3000°C. The growth rate, density, and micro-structure depend mainly on the deposition temperature. Whereas pyrolytic carbons having density of only 1.35 g/cc are obtained at 1600°C, the bulk density of pyro-graphite deposited at about 2100°C is between 2.20 and 2.23 g/cc. Because of the good alignment of the layer planes, pyrolytic graphite bodies like single crystals, are strongly anisotropic. Thus the ratio of anisotropy for the specific electrical resistance (perpendicular / parallel) is 1400; the parallel / perpendicular ratio for thermal-conductivity is about 440. As in the single crystal, the thermal expansion is negative parallel to the surface and strongly positive in the perpendicular direction (Table 7.1).

A crystallographically almost ideal graphite has been obtained by uniaxial hot compression of pyrolytic graphite followed by annealing at a very high temperature and low pressure. The ratio of anisotropy for the electrical resistance of this material at 300°K was 4000 and increased to 90,000 on cooling to 4.2°K. Owing to the high degree of alignment and the resulting strong anisotropy, pyrolytic graphite bodies can be produced only in limited thickness. The maximum thickness attainable for slab materials at present is about 10mm. In the case of tube it is proportional to the radius for curvature, i.e., maximum wall thickness/radius of curvature = 0.05. Bodies with sharp edges or thick walls can be produced by further matching or by combining thinner pyrographite plates.

The marked anisotropy of pyrolytic graphite, its increased resistance to erosion and oxidation, together with the high emission coefficient and high sublimation point of carbon, offer great advantages e.g., when used as rocket nozzle, as re-entry cones for space vehicles, for the nose cones and wing leading-edges of space gliders, or as a protective shield. Owing to the excellent conductivity parallel to the a,b plane of graphite crystal, the heat is well distributed over the surface, both radiation and ablation takes place over the entire surface. At the same time, underlying structural

Table 7.1 Properties of pyrolytic graphite

	Parallel to surface	Perpendicular to surface
Bulk density (g/cc)	2.20	2.20
Young's Modulus (kg/cm ²)	2.5×10^5	—
Flexural strength (kg/cm ²)	1×10^3	—
Electrical resistance (ohm mau ² /meter)	5	7×10^3
Thermal conductivity (kCal/m/h/deg)	350	0.8
Coefficient of thermal expansion (20-200°C/deg)	-0.5×10^{-6}	$+25 \times 10^{-6}$
Compressive strength (kg/cm ²)	1×10^3	4×10^3

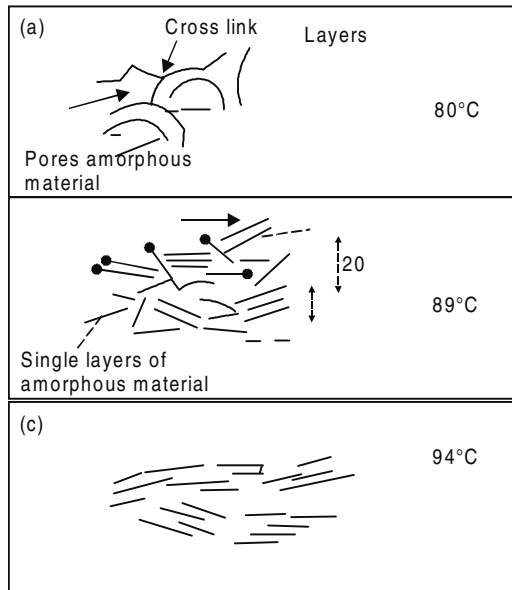
material is thermally protected by the insulating effect in the C-direction. Compact pyrolytic graphite plates are often used when a very uniform distribution of heat over a surface is desired. Pyrolytic graphite is also used to advantage in electronic tubes.

Pyrolytic alloys, e.g., with B, Si, Hf, and Co, are obtained when a vaporized organic compound of the alloying component is added to the gaseous carbon compound. A particularly well-known example is the pyrographite-boron alloy, which is characterized by higher elasticity, lower oxidizability, and greater insulation perpendicular to the layer planes and by an increase in the strength of the pyrographite which is high even in the unalloyed state. Franklin, as early as 1949, recognized that low rank coals (i.e., with high moisture, high volatile and non-caking in nature) having carbon below 84%, do not yield truly graphite carbon, even upto a temperature of 3000°C; whereas coking coals when heated even upto temperatures around 2200°C, yield synthetic graphite. Hirstch have thus distinguished coal as three types in terms of their susceptibility towards graphitization (Fig. 7.1):

1. *The open structure* – this structure is characteristic of low rank coals upto about 85% carbon content. The lamellae are connected by cross-links and are more or less randomly oriented in all directions, thus constituting the highly porous system.
2. *The liquid structure* – this is typical to the coking coals. Here the lamellae show some orientation which accounts for formation of crystallites comprising two or more lamellae. The number of cross links has decreased considerably and pores are practically absent.
3. *The anthracite Structure* – this type of structure is seen specially in semi-anthracite and anthracites, having carbon over 92%. In this region the degree of orientation of the lamellae relative to each other, appear to have increased.

Figure 7.1 shows above three structure schematically in different carbon % range as they occur in the coals. Low rank coals are abound by oxygen groups, in particular hydroxyl, and as a result undergo lots of cross- links reactions which appears as alignment and stacking of the aromatic lamellae. Due to absence of such cross-linkage in coking coals, it shows tendency towards graphitization at about 1700°C. But the same does not occur with anthracite. Most of the cross linkages breakdown at about 2000°C (hetero-atoms are removed between 1000 and 1600°C) and a crystallite alignment for graphite formation begins.

Accordingly, the yield and quality of pyrolytic carbon also depends on the nature and structure of the starting coal. Thus when carbon of low resistivity and high density is required (as for electrodes) obviously coking



7.1 Structural model of coal according to Hirshel
(a) Open structure (b) Liquid structure
(c) Anthracitic structure.

coal and anthracite is the material of choice. Conversely when carbon of relatively high resistivity is desired, as in the production of resistor coke, naturally non-caking coals are to be preferred. The speciality high volatile North-Eastern coals of India, on pyrolysis (in entrained bed) on the other hand yields char and volatile portion (on thermal cracking) a fine carbon particle known as carbon-black. The institute where the present author had been working earlier, has developed this technology and the process is as follows.

Carbon black is mainly produced by cracking of natural gas, petroleum hydrocarbon and coal tar oil. Prior to 1950, 95% of the world's supply of carbon black was based upon using natural gas as raw material and 75% of the world's supply came from USA. Today, however, the major amount of carbon black is produced by oil furnace process which allows location of the unit near the consumer. Carbon black produced from natural gas is of smaller particle size and a semi-commercial plant has already been tried by present author at Assam Gas Corporation Duliajan from stripped natural gas. The finer variety of carbon black is known as channel black as the material is deposited on iron channels placed about 2 in. above the flame (i.e., in the reducing zone of the flame). This channel process produced carbon black with high rubber reinforcing ability and colour intensity (thus suitable for printing purpose). These blacks cover a range of particle with

diameters from 100°A for most intensive colour black to a maximum of 300°A for easy processing rubber black. Table 7.2 shows properties of these different grades of channel black along with their usage.

Under optimized condition, these processes yield 27.3 kg of channel black/ 1000 m³ of gas. The proposed price (in 1989) for 1000 m³ natural gas is Rs. 2000 (as against present price of Rs. 300–1200/m³). Imported variety of channel black now cost about Rs. 300/kg. These natural gases contain 80–85% of methane and about 11% C₂-hydrocarbons. The flow of air through the hot house is regulated so that the excess air content of the exit gas does not exceed 40% which can be assured by analysis of flue gas. Excess air being calculated by the formula:

$$\% \text{ excess air} = 100 \text{ O}_2 / (21 - \text{O}_2) \times K$$

Table 7.2 Characteristic and application of channel blacks

Grade of Channel black	Average size (A)	Average surface area (m ² /gm)	V.M. (%) content	Application
Easy processing channel EPC	290	100	–	Fully reinforcing, easier processing & lowest hysteresis, used for tyre tread, making heels & soles of shoes & mechanical goods.
Medium processing channel EPC as	250	120	–	Fully reinforcing, medium for processing & other applications EPC grade.
High colour channel, HCC	100–140	90–400	16–5	Jetset carbon black used in lacquer, enamels & coloring plastics.
Medium colour coloring, channel, MCC	150–170	550–320	5 Oct	Used in enamels, plastic as a protection against UV-rays.
Regular colour newspaper channel, RCC	220–290	140–100	5	Used in plastic, paints, & book ink, carbon paper, utility paint, coloring nylon & other fiber
Medium flow channel, MFC	250	200	7	This black has good flow proportion in inks, used in paints coloring nylon & other fibers.
Long flow channel, LFC	200–280	300–360	12	Used for lithographic inks, letter press ink, carbon paper & type writer ribbon ink.

The value of K is 0.9 for natural gas. The second process uses high volatile Assam coal is a transport reactor to yield carbon black (of larger particle diameter) suitable for commercial production of carbon-black uses oil or tar as raw material for carbon black produced from coal are of SRF (semi-reinforcing furnace grade) used by tyre industries. Different particle size carbon-blacks produced commercially and their properties shown in Table 7.3.

Ash content of carbon-black from Assam coal (ash content of coal = 2.5 to 3.5%) is slightly higher which may act as a filler in the rubber without producing any adverse effect. Char and steam are the by-product of this process. Crushed coal of size – 72 BS mesh is used in the process and the partial combustion takes place at about 850°C, producing char and carbon-black from volatile matter. The former is first separated in a cyclone and the emerging gas containing carbon-black collected either by a bag-house filter system or with a water scrubber. Product quality varies with reaction temperature, the iodine number (m.gm/gm) is taken as a measure of quality, which varies linearly with temperature and thus iodine value can be adjusted to the desired level by adjustment of reaction temperature. Surface area (m²/g) has been found to vary almost exponentially with volatile matter (%) content of the feed coal. The yield of carbon-black was found to vary little (20–22%) with variation of ash content of the feed coal from 2.5 to 6.5%. Following is the list of the carbon-black producer (from furnace oil) in India with their licensed capacity in India.

Manufacturer	Location	Licensed Capacity (1981)
Philips Carbon Black year	Durgapur	36,000 ton/
Ureka Chemicals	Haldia	6,000 ton/year
Carbon & Chemicals	Cochin	2,000 ton/year
United Carbon (India) Ltd. year	Bombay	35,700 ton/
Ralson Ltd.	Ludhiana	3,000 ton/year
Oriental Carbon Black ton/year	Ghaziabad	18,000
Gujrat Carbon Ltd. ton/year	Baroda	10,000
Hi-Tech Carbon Ltd. (latest & most modern plant)	Renukoot	3,000 ton/year

Table 7.3 Particle size and surface area of Carbon-Blacks

Designation	Type	BET surface area	Particle size (A)
SRF	Semi-reinforcing furnace	22 m ² /g	200–800
GPF	General purpose furnace	50	—
HAF	High abrasion furnace	80	200–350
FEF	Fast extruding furnace	80	300–500
SAF	Super abrasion furnace	130	100–200
ASCOB	Carbon-black from Assam coal	—	390–600

In November 1988, Department of Scientific & Industrial Research (Ministry of Science & Technology), Government of India, prepared a study report under the aegis of National Register for Foreign Collaboration and the report brought out following observations and recommendation on carbon-black from petroleum feed-stock. The present installed capacity (based on indigenous carbon-black feed-stock) in our country is 181,000 ton/year and Planning Commission estimated 1990s requirement to be 159,000 ton growing to about 251,000 ton by 1994–95. The yield of carbon-black depends upon the “aromaticity” of the feed-stock. This is measured by the BMCI value (Bureau of Mines Correlation Index), after making adjustment for the sulphur content. Higher the BMCI value, higher is the yield of carbon black. The BMCI value for our indigenous feed-stock is about 85 (average). Carbon-black feed stock (CBFS), available abroad averages 122 and if this is made available to our existing indigenous units, carbon-black production could be increased to 216,000 ton per annum (as against present 120,000 ton annum production). This difference will attribute greatly to our future demand. There are, however; some impediments in import, such as – import duty, surcharge, and counter-weighting duty, which are high; modvat is not applicable to CBFS and there is lack of facilities for handling and storage of CBFS. There is also variation in BMCI value of indigenously available CBFS. These vary from 120 (IPCL and NOCIL) to 90 Barauni plant extract to 80 (HP and others). This is in contrast to the lower price abroad of 120–125 BMCI value of the CBFS, which is around US \$71–81/ton at port of shipment. Indigenous price has no correlation to BMCI value and varies from 3600/ton for Barauni to Rs. 2900/ton for Haldia (the price of carbon-black from Assam coal will be around Rs. 3200/ton). There is no freight equalization and CBFS distribution is not rational. The problem is further aggravated by erratic supplies. Indigenously manufactured carbon-black sells at Rs. 15,350/ton (SRF grade) to Rs. 32,520/ton (for SAF grade). International prices in contrast, are US \$650 – 800/ton (Rs. 10,000–12,000/ton) CIF. The import duty varies from 110 to 140% and even then, the imported black is competitive and thus substantial quantities are imported. Modern technology abroad has registered spectacular progress. Carbon black units are larger capacities (130,000 ton/year in contrast to 6000 to 36,000 ton/annum capacity Indian units). They employ longer furnaces (about 110–145 ft, compared to 21 ft or less in India), improved reactor and burner design, with more rapid and uniform feed-stock atomization, faster mixing, shorter residence time and higher capacities. Computer and microprocessor controls ensure consistent quality, lower surface area, higher tinting strength and narrower aggregate size of carbon-black, which results in enhanced surface polymer interaction (leading to higher tensile strength,

modulus, hysteresis and tread-wear in tyres and other rubber products). 98% of the carbon-black manufactured find application as a elastomer in rubber industry. There is also better energy utilization in the plants abroad. Air is pre-heated by tail-gas (to 600–815°C) and burnt tail gases are utilized for steam and power generation for drying carbon-black pellets. The above factors ultimately favors lower production costs and help maximization of output capacities. The report recommends more R&D involvement on our side to gain better control on carbon deposit formation mechanism and to broaden the CBFS spectrum. SAIL and other steel plants must be encouraged to switch over to furnace oil operations; this would ensure adequate quality of coal-tar to be released for the production of high BMCI CBFS.

Knowledge of chemical factors at surface of carbon-black helps us increase bonding with polymers (in rubber) and determine its usefulness as a reinforcing compound (elastomer) in tyre industry. Surface layers of carbon-black has been found to contain various functional groups mainly oxygen containing like, phenolic hydroxyl groups, aldehydes, quinone, carboxyl, and peroxide. Ether and several other groups are probably also present. Apparently these groups together with the concerns, edges and defects in the crystallites are important in the formation of vulcanisate. The free-radicals on the surface, i.e., unpaired electrons of carbon, oxygen atoms, and possibly also those of sulphur and nitrogen atoms linked by chemical bonds with the carbon atoms of the crystalline network are chemically active site. It can be assumed that the oxygen content of oxygen-rich carbon black is 3.5–4%, in other words there is on average one atom of oxygen per 10–1 Å of the surface of a black with 150 m²/g surface area. This indicates that the surface is about almost completely covered with oxygen groups. 11–12% of all the combined oxygen occurs in the form of carboxyl group, 3% as phenol and 2% as non-acidic groups. Experimental results have shown that upto 12% of the oxygen combined with channel-black occur as carbonyl groups which irreversibly combines with Grignard-reagent. This is the oxygen of quinone groups; rest oxygen belongs to the chemically inert ether groups and to the heterocycles. It is interesting to note that only a small proportion of the hydrogen which has combined with the channel-black occur in the active group (total hydrogen content in the black is 1.18%; one-fifth of it is active H). Most of the combined hydrogen is present as inactive group (e.g. C–H) apparently forming “seams” at the joint of the crystallites on the carbon-black surface. However HAF-grade black has been found rich in active hydrogen. Channel-black contains much active oxygen groups than carbon-black.

Another route to carbon molecular engineering with graphite is through incorporation of few metal atoms between the layers of well oriented

graphite crystals to give intercalation compound structure. Such treatments astonishingly brings about a new breed of materials, known as carbon foils and membranes. Examples are potassium-graphite, graphite hydrogen sulfate, and graphite oxide. In graphite oxide, oxygen and hydroxyl groups are located between the carbon layers. Luzi found as early as 1890, that graphite-oxide can be thermally expanded to more than 100 times its original volume. A more recent process for economical production of flexible-graphite foils is based on the compression of this expanded material. The starting material is generally coarsely crystalline, very pure natural graphite. The graphite is oxidized with fuming nitric-acid or with sulfuric acid/nitric-acid mixture, and then hydrolyzed. If the graphite-oxide after drying is heated, in a fraction of second to about 1000°C, it decomposes explosively. The gases liberated expand the graphite lattice normal to the layer plane by a factor of more than 100. The separated carbon layers of the graphite lattice are then firmly bound together by mechanical pressure; the resulting products are gas-tight, flexible, strongly anisotropic carbon-foils having a density of about 1.1 g/cc. Electron beam micrography of the product show pronounced layer structure of this material. These foils are produced without binders; they consist of pure carbon and can therefore be used up to a temperature above 3000°C in inert and reducing atmosphere or under vacuum. The strong dependence of properties on direction is again remarkable. The ratio of anisotropy for the specific electrical resistance is even higher than in pyrolytic graphite (Table 7.4 low). Incidentally, interlamellar compounds of graphite also can be prepared from "pyrolytic graphite," which then contains anions and cations regularly arranged between the layer planes of the graphite crystals, giving compounds with such formulae as C_8K , $C_{24}NO_3 \cdot 3HNO_3$. This also results in modification of the electronic property of graphite crystal and this technique gives us freedom to modify electrical and thermal conductivity of graphite and thus these materials are some time termed as "synthetic metals." It should be noted here that natural graphite flake is insoluble in oxide slags because of the inability of the covalent carbon to dissolve in the ionic media. In such carbon foils, the electrical conductivity parallel to the surface is comparable with that of well-ordered artificial graphite. Special emphasis must be placed on the impermeability of these foils to gases and lignites up to very high temperatures. Graphite foils are also

Table 7.4 Properties of carbon foils

	Parallel to surface	Perpendicular to surface
Bulk density (g/cc)	0.9	1.1
Electrical resistance (ohm.mm ² /meter)	8	4x10 ⁴
Thermal conductivity (k.Cal/m/h/deg)	150	3
Permeability in air (cm ² /s)	—	Less than 10-6

much more resistant to oxidation than artificial graphites. Their surface is very smooth and resistant to abrasion.

The flexible graphite is produced in the form of foils in thickness of 0.1 to 0.3 mm. These films are used directly or made into laminates several mm thick; the individual layers of which may be bonded together by carbonizable resin binders. Dense melded bodies can also be produced without binders. They are then equivalent to the foils in their resistance to corrosion and heat, and in their thermal and electrical properties. Owing to their greater thickness, however, they no longer possess high flexibility. Graphite foils and laminates have found their use in following fields:

1. as corrosion resistant seals (gaskets and packing) for very low to very high temperature; high thermal conductivity and hence good heat dissipation, self-lubricating, impermeable with and without cooling, long life, no maintenance, corrosion resistant;
2. for lining the press-moulds and casting-moulds; smooth surface, low friction, dense abrasion resistant;
3. as radiation shields in high-temperature furnaces; high reflection factor and good thermal conductivity parallel to the surface, combined with poor thermal conductivity normal to the surface.
4. in electrochemistry and electrical engineering, e.g., as a surface heater; high anisotropy towards electrical and thermal conductivity.
5. as linings for chemical equipment very flexible, corrosion resistant, impermeable to gases and liquids.
6. as films for bursting disks; impermeable to gases and liquids, corrosion resistant heat resistant.

Expanded graphite can also be made into "porous foam" (density 0.05–0.01 g/cc) by compression under a lower pressure and without a binder.

These foams may then be compressed further during use. Self-adhesive or plastic-coated graphite foils are already in the market. Carbon membranes only a few micro-meter thick have now also been developed. Though thin enough to be translucent, these membranes are, nevertheless, impermeable to gases and liquids. The membranes are again prepared from graphite oxide, which is made into a thixotropic gel in aqueous suspension. This gel is deposited on well-polished surfaces. Very careful drying gives a membrane of graphite oxide which is reduced in a stream of hydrogen above 500°C. The resulting carbon membrane, which has a highly imperfect graphite crystal lattice is graphitized above 2500°C; during this process, the density increases to 1.8–2.2 g/cc. Carbon membranes of this nature are used, as for example, as dialysis membrane for the desalination of sea water. Graphite ribbons has been made from graphite fiber by similar molecular engineering technique. Because of the novel morphology of

graphite ribbons, this material is attractive for improved composites and other applications. The graphite ribbons were formed by intercalation and exfoliation of Thornel P-100-4 (union Carbide) graphite fiber, which are pitch based fiber with a micro-structure such that the graphite layer planes radiate from the center of the fiber. These fibers are a production-type, non-standard material which differs from the commercially available Thornel P-100 fiber by having a V-shaped groove along the length of each filament. Intercalation of the pristine fibers by immersion in liquid ICI and exfoliation of the intercalated fibers by passing an electric current pulse through them along the fiber axis, under a vacuum of 200 micrometer Hg had been shown to cause the fiber diameter to increase by more than 100% and to cause surface corrugation along the fiber-axis. It is well known that pristine graphite fibers are so brittle that they can not be bent much before fracture. However, exfoliated graphite fiber can be bent and even be crimped. SEM of a crimped graphite-ribbon show that inspite of the very small radius of curvature at the crimp the fiber remains continuous. Thus graphite ribbons are less brittle than pristine fiber. The curved morphology and the surface corrugation of the graphite ribbons are expected to improve the adhesion between the graphite and the polymer matrix. In another attempt, thin carbon films (25–50Å) were graphitized after their formation by condensation in vacuum on cleaved NaCl substrate (at room temperature at a rate of 100–200 Å/S). After floating on water they were picked up on carbon grids and graphitized at 1000–3000°C in argon atmosphere. At 1000°C the layer consists of turbostatic (bi-periodic) elementary domains of 2–3 carbon layers thick and 4–12 aromatic rings in diameter. The carbon layers are practically parallel to the film surface. However, the elementary domains are separated by tilt and twist boundaries (zig-zag texture) thus forming larger wrinkled layers. During graphitization stage (1600–2000°C the elementary domains only grow in thickness. At 2000–2100°C, tilt and twist boundaries suddenly disappear by elimination of defects. The layer de-wrinkling allows progressive graphitization to continue (second stage occurs between 2000 and 3000°C). The diameter of the layers increases while the tri-periodic order improves until polycrystalline graphite is obtained. This carbon films deposited at room temperature have been found to be amorphous with a structure similar to silicon (i.e., mainly constituting of irregular tetrahedral). Upto 2000°C more than 80% of the material is still turbostatic but above this triperiodic order, leads to graphitization of the entire material. This demarcation of temperature scale at 2000°C is also an important point from electronic properly point of view. Below 2000°C the Hall Coefficient is positive and increases rapidly. But above 2000°C, it suddenly decreases and become negative. This indicates the disappearance of positive carriers (holes) owing to the sudden removal of the defect boundaries which causes the

dewrinkling of the carbon layers leading to one imperfect zig-zag structure. In the same way, the electrical conductivity slowly increases below 2000°C, while it increases much more rapidly above 2000°C. In this temperature range, the layers become entirely flat and thus the pi-electrons of the perfect biperiodic lattice acquire a semi-metallic character.

occupied by open pores of very uniform structure and can be produced from micro-crystalline cellulose without binders or from mesophase coal tar pitch. The homoporous carbons are used mainly as electrodes material for direct conversion of chemical into electrical energy in electro-chemical fuel cells. After a rapid increase, the diamagnetic susceptibility also becomes stable and equals to that of graphite above 2000°C. This result confirms that above- 2000°C the carbon layers have achieved a structure which is similar in perfection to that of graphite. Similarly at about 2000–2100°C the work function of the thin carbon film approaches that of graphite. This implies that the film surface is essentially identical to graphite surface. All these properties are also dependent on the presence or absence of defects in the carbon layer. After a rapid increase, the diamagnetic susceptibility also becomes stable and equals to that of graphite above 2000°C. This result confirms that above 2000°C the carbon layers have achieved a structure which is similar in perfection to that of graphite. Similarly at about 2000–2100°C the work function of the thin carbon film approaches that of graphite. This implies that the film surface is essentially identical to graphite surface. All these properties are also dependent on the presence or absence of defects in the carbon layer.

In graphitization of coal or pitch, cross-linkage hinders alignment of carbon planes to graphite structure. But if these cross-links are deliberately left on, the product does not graphitize even at 2800°C and the resultant product looks like and resembles glass (vitreous substance). These materials are called Glassy carbon and can be produced from three-dimensionally cross-linked synthetic resin. The structure of this carbon contains small regions of graphite-like layers, which are joined by numerous cross-links. These isotropic substances are hard, brittle and the density is very low (about 1.5 g/cc). Its impermeability to gases is nevertheless excellent, of the order of magnitude 10^{-11} cm²/s with He and thus of the same order of

Table 7.5 Properties of glassy carbon

Bulk density (g/cc)	1.45 – 1.50
Pore volume (vol%)	1
Young's Modulus (kg/cm ²)	2.6 x 10 ⁵
Flexural strength (kg/cm ²)	700
Electrical resistance (ohm mm ² /m)	50
Thermal conductivity (Kcal.m ⁻¹ h ⁻¹ deg ⁻¹)	3
Coef. of thermal expansion (deg ⁻¹)	3x10 ⁻⁶
Permeability (air), cm ² /g	10-11

magnitude as that of silicate glass and distance between layers of 3.44 Å as against 3.54 Å for graphite.

Glass-like carbon is much stronger and stiffer than conventional carbons and graphites. Its electrical and thermal conductivity are comparable with those of hard carbons. Owing to the small number of accessible pores and its high impermeability, glass-like carbon is very corrosion resistant. However, it is attacked by alkali metals with formation of intercalation compounds, as well as by carbide forming metals. To prepare glass-like carbon partially pre-condensed phenolic or furan resins are mixed with catalysts poured into moulds with very smooth surfaces and cured. The material is then removed from the molds and carbonized in accordance with a strictly defined heating schedule. The resulting shrinkage is pronounced, but quite definite and isotropic, so that moldings can be produced with a dimensional accuracy of $\pm 0.5\%$. Owing to its hardness, glass-like carbon can only be worked with diamond tools or by an ultrasonic technique. It is therefore preferable to work the cured resin before carbonization, taking the amount of further shrinkage into account. Glass-like carbon is produced as plates, tubes, crucibles, boats etc., with wall thickness of about 3 mm. It has found a number of applications, particularly in laboratory work. The similarity of its coefficient of expansion to that of many borosilicate glasses makes it possible to bond the two materials permanently. Since glassy carbon is not wetted by most molten metals it can be used in metallurgy for melting crucibles, and also for pipes for passing corrosive gases into molten metals and as vaporization dishes for the evaporation of metals. Glass-like carbon has a high resistance to erosion and is therefore also being tested as a rocket nozzle lining.

The last type of carbon we will discuss here is the "highly porous Carbon" (carbon foams). These carbon products have up to 75% of their volume occupied by open pores of very uniform structure and can be produced from micro-crystalline cellulose without binders or from mesophase coal tar pitch. The homoporous carbons are used mainly as electrode material for direct conversion of chemical into electrical energy in electro-chemical fuel cells. Owing to the uniformity of their pores, such electrodes can accept very high loads. Carbons with much greater pore volumes (carbon foams) are obtained by carbonizing foamed synthetic resins. The starting materials are open-pore rigid synthetic resin foams. Carbon foams obtained by carbonization are extremely light, having densities only about 0.05 g/cc. The percentage decrease in volume and in weight are the same, so that the carbon foams have the same bulk density as the synthetic resin foam. Carbon foam is composed of very thin carbon cells/walls. It can be used up to temperatures higher than 3000°C in an inert gas or under vacuum. Its thermal insulating qualities are outstanding; the thermal resistance of foamed synthetic resin is only slightly better

(thermal conductivity about 0.03 kcal /mole/h/°C). However, synthetic resin foams can only be used below their decomposition temperature (i.e., below 180°C).

7.3 Conversion of pitch to graphite

The liquid by-product obtained from coal carbonization is known as tar. More specifically components boiling below 350°C in above liquid by-product is termed as tar and those above 350°C is known as pitch. Earlier we have seen the properties of pitch and its chemical constituents; here we will learn more about its physical property-composition relation. Since pitch is a complex heavy residue, it was difficult to know its composition although rheological behavior of pitch was studied long ago. In last two decades or so, exhaustive and modern instrumental techniques have helped us elucidate its chemical composition to greater extent; this has resulted in turning out some very important industrial material through conversion of pitch to graphite via a mesophase.

Chemical composition of pitch is generally determined by following laboratory methods:

1. Solvent fractioning

This is one of the most commonly used method and varying the polarity of the solvent four resin types are separated – primary quinoline soluble (mesophase forming), toluene insoluble, quinoline insoluble (TI-QI), and toluene soluble. QI is also known as α - resin or α - particle (pure carbon particle of the order of 0.02 μ m) and is an indication of the level of cracking of tar during coking. QI part is rich in fixed carbon and reflected in the aromaticity (C/H ratio) value of the fraction. High QI with high aromaticity gives good dense material and imparts good mechanical property to certain finished products (like carbon electrodes). The difference between toluene insoluble and quinoline insoluble (TI-QI) is known as β -resin. β -resin therefore indicates components soluble in pitch or in quinoline which are

Table 7.6 Properties of carbon foams

Bulk density (g/cc)	0.055 – 0.065
Pore volume: total volume (%)	97
open (vol%)	95
Young's Modulus (kg/cm ²)	1200
Compressive strength (kg/cm ²)	4.8
Electrical resistance (ohm.mm ² /meter)	5500
Thermal conductivity (Kcal/meter/hour/degree)	0.04
Coefficient of thermal expansion: 20–2000C (degree ⁻¹)	2.1×10^{-6}
20–10000C (degree ⁻¹)	2.5×10^{-6}
Permeability (cm ² /g)	102

precipitated from toluene. β -resin are straight chain hydro-carbons, imparts great binding strength on solidification (see impregnation pitch), helps adhesion of coke particles during mixing and shaping. Nearly 85% of the coal tar supplied by our steel plants (in India), has QI particles below 15 micron. When pitch is heated at temperatures exceeding 380°C, mesophase spheres are formed. The primary QI particles present in the pitch stay at the periphery of the spheres and hinder their formation and coalescence. Table 7.2 shows the polarity index of various solvents used in solvent fractionation process. The five principal operations for fractionation available to us today are – distillation, extraction, adsorption, chromatography, and precipitation. Combination of these five basic processes are used in the various methods developed for fractionation of asphaltic bitumens. None of the five individual operations by themselves has provided separations satisfactory for determination of fractional composition. Thus the five schemes of separating pitches into smaller components are:

- (a) Extrography: It is a combination of extraction and chromatography. Analysis of the size fractions by size exclusion chromatography as well as high performance liquid chromatography has shown that extrography has a higher separation efficiency than solvent fractionation.
- (b) Size exclusion chromatography: This is also known as gel permeation chromatography or high pressure liquid chromatography. It separates pitch as per molecular mass distribution and by their ability to penetrate a porous-gel. It separates as per molecular mass distribution and detected by linear mass detector. But it is difficult to use it in large scale to produce sufficient amount for further experiments.
- (c) Charge transfer fractionation: Above three methods are physical separation method while this one is a chemical fractionation method. It is based on the principle that aromatic molecules are electron donors

Table 7.7 Polarity indices of various solvents

Pentane	0.0	Ethylene dichloride	3.5
Trichloro-trifluoro-ethane	0.0	Butanol-1	3.9
Cyclo-pentane	0.1	Propanol-2	3.9
Heptane	0.1	THF	4.0
n-Hetane	0.1	Chloroform	4.1
Petroleum ether	0.1	MTBX	4.2
Trimethyl pentane	0.1	Ethyl acetate	4.4
Cyclohexane	0.2	Dioxane	4.8
Carbon-tetrachloride	1.6	Methanol	5.1
Toluene	2.4	Pyridine	5.3
Benzene	2.7	Acetonitrile	5.8
Ethyl ether	2.8	DMF (dimethyl Formamide)	6.4
Methylene chloride	3.1	DMSO (dimethyl sulfoxide)	7.2

Table 7.8 %Solubility of pitches in common solvents with temperature

Solvent	92°C	100°C	108°C	127°C	180°C	Average
Quinoline	71	93	90	82	71	81
Nitrobenzene	66	88	84	67	57	72
Pyridine	61	88	82	67	59	71
Chloroform	52	68	68	55	46	58
Toluene	53	70	68	53	44	58
Benzene	50	67	66	56	40	56
CCl ₄	45	58	54	38	27	44
Acetone	44	56	50	31	28	42
Butyl-alcohol	33	40	39	27	19	32
n-Heptane	25	25	22	15	7	19
Isopropanol	20	27	22	19	7	17
Methyl alcohol	16	19	15	7	4	12
Petroleum ether	10	8	8	9	4	8

Note: (covalent + ionic) character increases in above table from bottom to top, while non-polar nature increases from top to bottom of the table.

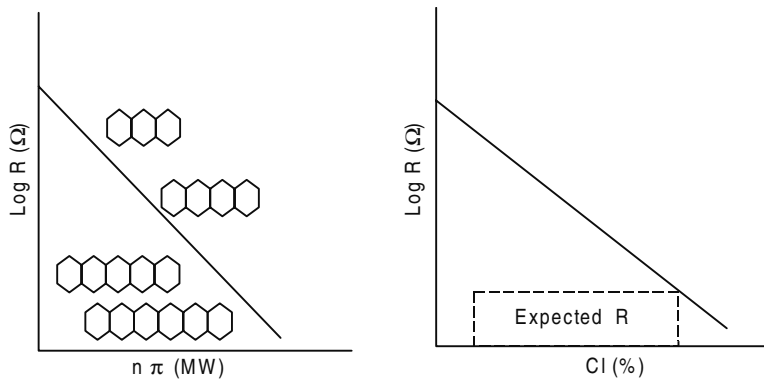
The table indicates % solubility of pitches with above mentioned softening points.

and form charge transfer complex with electron acceptors (like picric acid, indine etc). This reaction is reversible in nature. Since polar charge transfer complexes are virtually insoluble in the a polar or weakly polar solvents used, the yield in effect (with same acceptor) depends on first ionization potential of the aromatic donor. Charge transfer fractionation also separates a pitch according to the thermal reactivity of the constituents. Of the various known reactivity indices, Dewar 's reactivity number derived from Perturbational MO-theory is most commonly used.

- (d) NMR-spectroscopy (like used in organic chemistry).
- (e) Differential Pulse Voltametry.
- (f) Reaction analysis.
- (g) X-ray diffraction analysis (as in mesophase pitch). Average molecular weight of various pitch fractions range from 240 to 2350. Thus viscosity or ebullisopic method can be used to determine molecular weight of pitches.

In recent past, Maxilan Zander (at Rutger werks, FRG) studied Extensively pitch composition and his findings are quoted in condense form below. All the compounds so far detected in coal tar pitch can be classified under following groups:

- Polycyclic armomatic hydrocarbons (in short called PAH).
- Alkylated PAH.
- PAH with cyclopentene moieties (acenaphthalenes).
- Partially hydrogenated PAH.

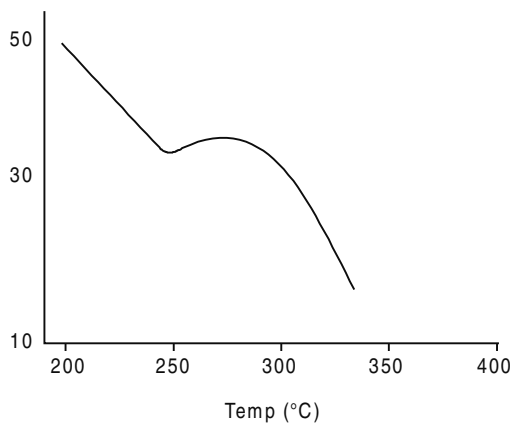


7.2 Electrical resistance as a function of molecular size.

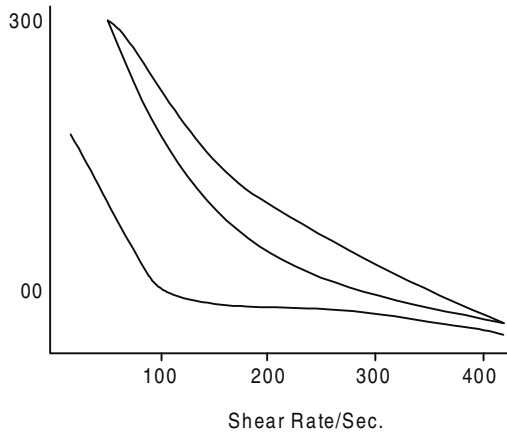
- Oligoaryls, oligoaryl methanes.
- Hetero-substituted PAH (with NH_2 and OH mainly), carbonyl derivatives of PAH.
- Polycyclic heteroaromatic compounds (benzologs of pyrole, furan, thiophene and pyridine).

In most pitches, polycyclic aromatic hydrocarbons (PAH) comprises the dominant class of compounds. These dominant class further can be represented schematically by Figs. 7.3–7.5.

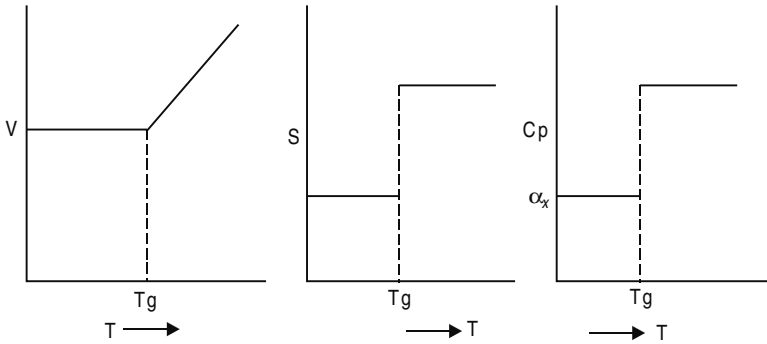
Partially hydrogenated PAH, mentioned above, occur in large proportions in petroleum pitches and much less in coal tar pitches. Oligoaryls (i.e., systems in aromatic moieties are joined by C – C single bond) have been found to occur in coal tar pitches and indications are that oligoaryls methanes are also present. Phenols and aromatic amines occur in pitches but concentrations are very low. Many polycyclic hetero-aromatic



7.3 Variation of viscosity of pitch.

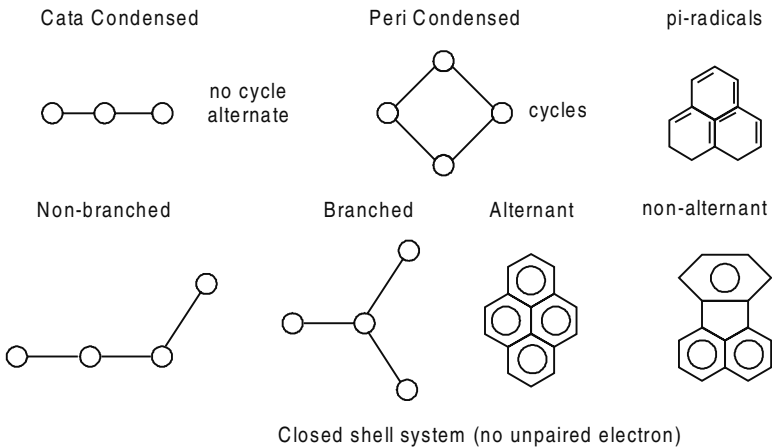


7.4 Variation of viscosity with shear rate at diff. temp.



7.5 Typical plot of temperature versus V, S, and Cp.

Building Principles of PAH



systems are also present in pitches although most of them are in very low concentrations. Successful pitch characterization is difficult because of the very large number of constituents present, but it is possible because the compounds belong to relatively few classes of compounds, as mentioned above. However, the enormous compositional complexity of pitches can be demonstrated for example by 2-dimensional chromatography. Thus GC with glass capillary / Mass Spectrometry allows detection of only 13 nitrogenous compounds in the molecular mass range of pitch. The column length was 92 m and the stationary phase was polyphenyl sulphonyl ether (poly-S 179). However, the tar was also separated by micro-preperative- GC in a narrow molecular mass range (210–235). The fractions were analyzed by HPLC using a specialized column which separate nitrogen compounds from polycyclic-hydrocarbons and about 35 nitrogen containing compounds were detected. Another difficulty in pitch characterization is the fact that various MW-range compounds tend to have same property. Correlation coefficients are high and makes interpretation of the results difficult. Take for example, solubility of following compounds in methylene-chloride (see Table 7.9)

Table 7.9 Solubility of various molecular masses in methylene chloride

Compound	Molecular mass	% Solubility in CH ₂ Cl ₂
Tetracene	228	2
Benz-a-anthracene	228	98
Pitch fraction	1050	94

The results are difficult to interpret, as can be seen above, because if solvent – fractionation is applied to pitches, the molecules are sorted out not only according to solubility, but solubility of PAH depends on three different structural features, namely molecular size, topology (as in above example) and degree of planarity. Effect of last factor is shown above where the solubility of a pitch fraction with a molecular mass of 1950 is comparable to that of benz(a) anthracene having a molecular mass of 228 because benz-a-anthracene is a planar hydrocarbon while the pitch fraction consists of non-polar oligo-aryl systems. Thus it follows that a mixture of above 3 components if solvent fractionated, the molecules can not be separated according to their molecular mass alone. Effect of topology on pitch component characterization has been well exemplified by above author with following example. PAH's after addition of small amounts of iodine, are electrical semi-conductors. In following graphs the left hand plot shows electrical resistance of polyacenes vs. molecular size which is exponential in nature. It shows electrical resistance decreasing with molecular size. Theoretically, this should apply to all materials if we neglect its topology. In the next experiment, fraction insoluble in chloroform (%CI)

which is comparable with the fraction insoluble in toluene (%TI), was isolated from various pitches, and the yield of CI plotted against electrical resistance after addition of 1% I_2 . In the right hand plot, log of resistance plotted against the yield of CI fraction. An exponential decrease of resistance with increasing yield of CI is observed. By analogy with the result obtained for the acenes, this means that with increasing yield of CI material the mean molecular weight also increases. Thus in conclusion, the statement that a pitch has say 10% TI and another 30% TI, in effect refers to different TI-material. Further, recent work at University of Tokyo, Japan (Kezuma et al., *Carbon* 1987) with FTIR-spectroscopy, X-ray diffraction, Raman spectroscopy indicates quinoline insoluble part of pitch has a higher aromaticity and lower graphitizability than those of quinoline soluble part.

Rheological properties of pitch has been studied by Rand at the University of Sheffield (UK) and his findings are as follows. Pitch shows glass transition temperature (i.e., the temperature where discontinuity in coefficient of thermal expansion (α), heat capacity (C_p) etc., takes place by extrapolation of viscosity value obtained to 10^{13} poise was estimated for the pitch at 10–15°C. Melting is a first order transformation, there being discontinuity in the first derivatives of the molar free energy, e.g., molar volume (V) and molar entropy (S): The sharp increase in these properties reflects the loss of positions order and the gain in molecular (and in case of polymers, conformational) motion. However, at the glass transition there is no discontinuity in these quantities by the second derivative i.e., the heat capacity (C_p), coefficient of thermal expansion (α) and isothermal compressibility (χ) show discontinuity. At the glass transition there is only a gain in mobility and in the case of the rigid molecules in pitch, the conformational effects are minimal being confined to alkyl side chain. Hence, the entropy change at this stage reflects only this gradual change in molecular mobility and it is small. Some pitches (like mesophase pitch), show Arrhenious type viscosity temperature correlation:

$$\ln \eta = \ln C + E/RT$$

Others follow Walther formula as follows:

$$\log, \log \eta = C - m \log T \quad (T \text{ in } ^\circ\text{C})$$

Above glass transition temperature (T_g), free-volume (i.e., that volume not occupied by the molecules themselves) change rapidly with temperature according for the relaxation time and the coefficient of thermal expansion. DSC apparatus can measure change in C_p and thus T_g can be found out. Surface-tension of pitch (having K and S softening point 65°C) was 26–45 dyne/cm in the temperature range 225–185°C; and that for a pitch

with softening point 145°C is 62–30 dyne/cm in the temperature range 270–335°C. Higher softening point pitches have a higher toluene-insoluble (TI) content. Molecular weight determined from viscosity using Kraemer's equation

$$\eta = K.M. \text{ (where, } \eta = \text{intrinsic viscosity)}$$

It has been found that vertical type retorts gives low aromatic tar whereas horizontal retort gives high aromatic tar. In horizontal retort and coke-oven tars the particles are comparatively large (0.5 to 1 micron) and infrequent, whereas in vertical retort tar particles are numerous but smaller. The particles in horizontal retort tar and coke oven tar appear to be clusters of small particles similar to the small dispersed particles of vertical retort tar. Viscosity of pitches between the temperature range of 180 and 300°C has been measured by Seth et al using a rotational (Reomat-30) viscometer. The uniformity of the impregnating pitch having softening point within the range 85–95°C is revealed by its viscosity variation in the range 180–300°C (Figs. 7.3 and 7.4). As the figures show, viscosity decreases with shear rate at all temperature on account of shear thinning and it shows a decreasing trend with temperature due to thermo-plastic character of the pitch itself. However, due to heterogeneous character of the pitch above changes are not uniform. Around 275–300°C pitch shows a tendency of decomposition and thus an anomaly in regular property change is observed in this region and onward.

Thus it is concluded that Indian pitches are fairly stable upto 275°C for impregnation purpose in carbon-carbon composites. Pitch decomposition which ultimately decides the life of the pitch standing several impregnating cycles is a function of its resinous constituents and can be predicted from its rheological behavior. Composition of alpha and beta resins content in pitch has further indicated (from contact angle studies with carbon-carbon composites and graphite fibers) that beta-resin content of coal tar pitch actually affects the wetting. Till now impregnating pitch is fully imported in our country. Performing pitches have high softening point and high secondary beta resin. They are different from conventional binder pitches which have lower softening-point. The increase in softening point of performing pitches is mainly on account of increase in secondary alpha-resin resulting from the development mesophase. The progressive increase in pyridine for fabrication of carbon-carbon composites. As softening-point in these pitches increase from 180 to 280°C, so do pyridine insoluble content from 7 to 53%. Now before switching our discussion to conversion of these pitches to graphite, let us look at a glance present state availability of this scarce commodity in India.

7.4 Graphite deposits in India

Appropriately graphite is considered a scarce and strategic material in India. The production of graphite is only 3000 tons per annum while the demand in 1987–1988 stood at 8300. Obviously this demand supply gap has to be met through costly import only. The reason for low production is because of the fact that although graphite is reported to occur in several regions of the country but majority of the deposits are of inferior quality (carbon content being only 15–20%). Regions where graphite with carbon content 35–60% available are located in the state of Orissa, Andhra Pradesh, Bihar, and Kerala. Good deposits are also indicated in Arunachal Pradesh. Deposits of lesser importance (carbon content 15–20%) are known to occur in Rajasthan, Madhya Pradesh, Tamil Nadu, Bihar, Gujrat, Karnataka and Jammu-Kashmir state. A total reserve of all these deposits (carbon content 15–60%) has been estimated at 173 million tonnes. Natural graphite of good quality occur in some of our neighbouring countries and Table 7.10 below show quantum of import from such countries.

Lower grade graphites are beneficiated generally by froth floatation technique (sp gr. 2.37 at 40°C) as explained in earlier chapter for coal, for upgrading the product. Table 7.11 shows the list of graphite beneficiation plants.

The price of graphite depends upon purity, variety (crystalline or amorphous) and size consistency. The price of run-of-mine till the end of 1980 was:

Table 7.10 Imports of graphite (natural) during 1980-81

Country	Quantity (ton)	Value (Rs. 000)
Belgium	—	47
France	3	18
Germany	66	1,366
Japan	3	83
Malagasy Republic	23	205
Sri-lanka	5	33
Other countries	Negligible	17

Table 7.11 List of graphite beneficiation plant in India

Plant	Locality
T.P. Mineral Industries	Sambalpur, Orissa
G.R. Graphite Industries	Sambalpur, Orissa
Agarwal Graphite Industries	Sambalpur, Orissa
Patna State Graphite Mining Co	Tittagarh, Orissa
Indian Plumbago Co.	Kovvur
East-Coast Graphite Industries	Vishakhapatnam
Chotanagpur Graphite Industries	Ranchi
Padma Graphite Industries	Kateru (via Rajahmundry)
Government Ceramic Center	Dowlaiswaram
Raja Crucible Works	Rajahamundry

Carbon content	Market	Price (Rs./ton)
Below 30%	Rajahmundry (Andhra Pradesh)	325
25–30%	Palamau (Bihar state)	400
30–40%	Do	500
Below 40%	Sambalpur (Orissa)	500
60–80%	Do	1100
Above 80%	Do	1500

Apart from carbon content and size variation, crystal size (flaky or non-flaky) is also an important factor for its valuation. As for example, graphite crucible industries require crystalline and flaky variety with carbon content about 85% and size range –20 to +80 BS mesh and priced at Rs. 7000–12,000 per ton (1980 price). Madagascar quality (crucible grade) were costing Rs. 10,000–12,000 per ton while that from Sri-Lanka Rs. 7000 to 12,000 per ton. In last 10 years the price has increased to very large proportion and some steel foundries importing flaky graphite from China at price Rs. 25,000 to 30,000 per ton (1990 price). Because of this sky-rocketing cost and meagre availability, graphite is considered a strategic material for India.

Nevertheless, our graphite industries (producing various graphite products from both synthetic and natural graphite) has expanded to such an extent that we should think now not only catering our steel industry (for making are furnace electrodes) but to export these graphite materials to neighbouring countries. Our steel industry still lags behind by about 15 years compared to the International scene. Take for example, Electric steel melting furnaces in India are of capacities 10–15 tons (almost 90% of them), whereas world standard product capacity ranges 80–100 tons. Such high capacity electric furnace requires special electrodes capable withstanding high electrode loading (25–30 amp/cm² vs. conventional electrode loading of 15 amp/cm²). These electrodes are made of needle coke which have a high degree of graphite order and is not produced in our country at all. Thus production of high quality graphite has become a dire necessity for our country. Presently we are making electrodes of 18 in. size (mostly) whereas 20–24 in. sizes are used in large size UHP electric furnaces all over the world. There is also demand of graphite electrode in phosphorus industry which presently meets most of its demand by import. Strategically also all our neighbouring countries imports all graphite materials from faraway countries like USA, Japan, Germany etc. Upgradation of our production will be able to win over these demands. Further, export potentiality exists for fast European countries where we have rupees payment facility as well.

Rare occurrence of natural graphite can be traced to the mechanism of its formation. Oberlin and Oberlin of CNRS, France showed that (1984–1988), extrapolation of Arrhenius plot for carbonization and

experimentally obtained results of progressive thermal graphitization indicates while carbonization can extend upto the completion stage in nature ($\Delta H \cong 65$ kcal/mole) but that for graphitization is thermodynamically unfavorable (having ΔH value of about 260 kcal/mole). These results indicate that since geothermal gradient energy is not strong enough for production of natural graphite, simultaneous additional shear stress will be necessary to form it in nature. Metamorphism and tectonic pressure supplies such additional energies. Anthracite not only have a necessary bare carbon skeleton for such transformations but also it has micro-pores which flattens along the horizontal plane under 5 K. bar pressure, thus giving a long range statistical order suitable for graphite formation. Unfortunately we do not have good anthracite deposits in our country and thus the shortage of graphites. The first step towards graphitization of coal is the elimination of volatile-matter and development of a somewhat ordered arrangement of carbon skeleton. This process is spread over a wide temperature range with simultaneous decrease in interlayer spacing. During this stage (1200–1600°C) flow of bubbles develop and whereas viscosity initially decreases but again increases at the end of tar release stage. The stresses thus created tend to align the aromatic molecules towards direction of horizontal plane and parallel to the flow. At this stage, thickness of individual stack increases as interstitial defects are eliminated. Activation energy at this stage, is about 65 kcal/ mole. Beyond 2000°C only CH_4 , H_2 are released (dehydrogenation only) and pore sizes remains constant. Maire and Mering in 1970 with their bromine experiment found that during graphitization the bromine occupies interlamellar position rather than going lamellar reaction. They concluded that graphitization is an ordering process of the internal structure of each layer. The ordering of layers and the development of a three-dimensional order is a secondary consequence of the change in the internal structure. Pauling in 1966 explained the graphitization process as a basic chemical transformation from the resonance structure of the benzene (aromatic) ring to a quinoid structure. In the quinoid carbon structure two of the bonds are single type and the third a double bond, while in the resonance structure all bonds are equal. Quinoid structure allows better packing of super-imposed layers and hence reduction of interlayer spacing observed during graphitization process. Pauling further noted that interlayer compressibility, magnetic susceptibility and certain X-ray diffraction results are consistent with his above theory. According to Runland's hypothesis offered in 1966, the graphitization process is a translation of distorted layers in the a-b direction. The unevenness of the process was considered as an annealing of defects between uneven layers. In 1984, Bragg et al offered a still different hypothesis based on his studies of graphitization of glassy carbons. Graphitization was found to be associated with thermal decomposition of

a graphite intercalating compound C_xH accompanied by diffusion of hydrogen. They found that the Hall Coefficient, which is the qualitative measure of the sign and density of majority charges carrier, changed sign for glassy carbons heated around 1900°C . They suggested that the change in sign was associated with the loss of a chemically bound intercalant species, hydrogen. The intercalated hydrogen plays the role of an electron donor and the material reverts to p-type as hydrogen is removed. Bragg and co-workers also found strong indications from neutron diffraction patterns that hydrogen is a ubiquitous chemical species. Kinetic and thermo-gravimetric analysis above 2000°C showed that the weight loss in diffusion controlled with an activation energy of 100 kJ/mole which is essentially the literature value cited for the diffusion of hydrogen in pyrolytic carbon. In recent time, carbonization phenomenon have been studied by Electron Spin Resonance spectroscopy. The reason for successful application of ESR is due to the fact that during carbonization (pre-graphitization stage) thermal cracking, cyclization and condensation reactions takes place; Many of these reactions are radical reactions involving neutral free-radical intermediates. ESR studies show radicals formed by the cleavage of bonds at the edge of condensed carbon rings and that these broken bonds could liberate electrons back into the ring system where they would become resonance stabilized. However, the effect of paramagnetic gases, especially oxygen ion, the ESR has to be taken care in such interpretation. Free-radical concentration in coal increases with rank or carbon percentage upto approximately 94% and then decreases. However, there is significant difference for different macerals and for their quantitative behavior with heat treatment (micrinite showing the highest and exinite the lowest free-radical concentration). With heat treatment, relaxation time for a typical coal (88.4% C) changed relatively little upto approximately 400°C and then drops sharply. The fact that for the carbonization of a pure compound like sucrose relaxation time (T_1) decrease with heat treatment temperature as soon as free radicals are observed, suggest that for a given coal there is a heat treatment temperature below which very little chemical and structural modification occur. In other words, there is a correspondence between structure and free-radical behavior for coal of a given rank and for a heat-treated coal of the same carbon content. Spins are associated more with aromatic skeleton (and not with chemical reactions like oxidation decarboxylation, acetylation, etc.,) and changes in aromatic skeleton (like by drastic hydrogenation) changes in spin concentration. Studies of carbonization with time show that below 350°C , electrons are observed while above 350°C temperature – electrons are observed. In the formation of anisotropic mesophase with pitch graphitization upto 400°C , very little change in radical concentration observed. Apparently, the most rapid increase in spin concentration

occurred above about 450°C, where coalescence of spherulitic to bulk mesophase was noted to occur. It is inferred that most of the condensation reaction proceeded concomitantly with these changes. Mesophase formation which involves recombination of molecular fragments into polynuclear compounds causes decrease in free-radical concentration (pyridine insoluble contain 4×10^{19} spins /g while pyridine soluble has been found to contain 0.5×10^{19} spin/g), but simultaneous dehydrogenation reaction will lead to increase in free-radical concentration. But later studies have contradicted this hypothesis and it was shown that free-radical concentration increases with mesophase formation.

Because of favorable C:H ratio, cross-linkages, etc., except anthracite, bituminous and sub-bituminous coal can not be directly converted to graphite. Anthracite having some long range order and favorable C:H ratio can be graphitized by directly heating to 3000°C, while for bituminous coal an indirect approach has been followed by Joro and Ladher (1988) at Coal Research Establishment (NCB), Cheltenham, England. We discuss this finding first and then conversion of pitch to graphite.

7.4.1 Graphitization of coal

In order to convert coal to graphite, first coal is digested (bituminous coal only) with high boiling solvent oil (a by-product of coal carbonization) at 400°C under pressure. This digestion causes certain amount of coal to degrade with evolution of gas. It is then filtered and bulk of the solvent removed by distillation leaving a solvent extract. Some solvent is deliberately retained in the extract so that its softening temperature is in suitable range (200–250°C). Strain graphatization was carried out continuously in an induction furnace consisted of graphite susceptor tube; the bore was increased along half its length, thus forming a step in the bore at the centre of the tube which acted as a target for sighting an optical pyrometer. The graphite tube was held axially at the centre of a quartz tube by two carbon discs and the annular space between them is packed with carbon black. The graphite tube is heated by a copper induction coil coupled to a Radyne radio-frequency generator. The furnace was purged with argon during graphitization of the coal extracted fiber. These studies reached to the following conclusions:

1. The properties of carbonized fibers are determined mainly by the processing conditions. They are relatively insensitive to the type of coal used.
2. Extracts of coal in the range: 82–91% carbon can be converted into carbon fiber.
3. Processing to 1000°C yields low strength (less than 1 GN/m²), low

modulus (40–55 GN/m²) carbon fiber with isotropic structure. Processing to 2700°C with strain, yields a high strength (upto 3 GN/m²), high modulus (upto 670 GN/m²) graphite fiber with anisotropic structure (concluded from X-ray and electron diffraction studies).

7.4.2 Graphitization of pitch

The other method is to graphite coal carbonization by-product – pitch (mainly tar fraction above 350°C). If we look at the graphite single crystal, it is a stack of (ABAB type) hexagonal rings whose covalent bonds are formed by sp² hybridization. The bonding between layers is of the Van-der-Waals type. The interlayer bond energy is only 1% of the C–C bond energy in the layers. Other properties of graphite single crystal are as follows: Table 7.12 Properties of graphite single crystal Graphitization process involves in the change in volume (due to change from short range random stack to long range stacked configuration) and a consequent change in density.

Commercial production of graphite electrodes involves graphitization of the green electrodes in an Acheson furnace where the central annular place of the muffle is filled with resistor coke for generating required resistance and consequent electrical heat while current is applied through two electrodes at two extremities. In such furnace the average power input is 4.5 KWH/kg material. Heating rate is 40–60°C/h and 3–4 days are required to bring the temperature to 2800–3000°C (before the furnace can be used for graphitization). After graphitization, 10–15 days of cooling period is allowed before the furnace opening.

Basically there are three types of pitches used in carbon industry. Because of their different processing step and source, these pitches have different physical properties. These three types are – binder pitch, impregnating pitch, and hard pitch. Binder pitch is a by-product of steel-plants coke-ovens. Bhilai Steel Plant supplies aluminium and graphite grade while Rourkela Steel Plant supplies only aluminium grade. The pitch obtained after vacuum distillation of tar by use of steam is subjected to thermal treatment or subjected to air blowing in hot condition in order to

Table 7.12 Properties of graphite single crystal

Property	Parallel to a-b plane	Perpendicular to a-b plane
Density (gm/cc)	2.266	2.266
Young's Modulus (kg/cm ²)	1 × 10 ⁷	3.5 × 10 ⁵
Electrical resistance (ohm mm ² /m)	0.5	1 × 10 ⁴
Thermal conductivity (Kcal/meter/hr/degree)	350	7
Coeff. of thermal expansion (20-200°C) (deg ⁻¹)	-1.5 × 10 ⁻⁶	+28.6 × 10 ⁻⁶

produce binder pitch of desired specification. Table 7.13 shows the characteristics of above two grades of binder pitch.

Factors which control the characteristics and thus suitability of a pitch for being binder grade are as follows. Softening-point as shown in above table should be within a particular range. Fixed carbon or coking value is important from the point of yield and cementing action. To ensure adequate wetting and binding properties free carbon (toluene insoluble part) should have an optimum value. Quinoline insoluble part wets the filler and then changes to binder coke. QI or β -resin is an indication of level of cracking of tar during coking. QI portion is rich in fixed carbon (reflected by aromaticity or C:H ratio). High β -resin with high aromaticity gives better densities and mechanical properties to the finished product. β -resin is the difference between TI and QI. α -resin therefore represents that soluble fraction of pitch or quinoline soluble but precipitated by toluene. It imparts great binding strength during solidification. It also gives green strength to the manufactured body. Another important parameter is viscosity which decreases with increase in QI. In India, from availability point of view, if the steel plants stops burnings tar, we should not have shortage of binder pitch. Present shortage of binder pitch is for this reason alone. Impregnating pitch have on the other hand different properties requirement as they are applied in hot condition on electrode surfaces in order to fill-up the surface holes. Table 7.14 shows the desired properties of impregnating pitch.

Table 7.13 Characteristics of binder pitch

Characteristics	Aluminium grade	Graphite grade
Softening point (&S) °C	—	88-94
Softening point (R&B)°C	90-100	101-106
% Fixed carbon	53 minm.	55 minm.
% Toluene insoluble	30 minm.	28 minm.
% Quinoline insoluble	10 maxm.	12-15 range
% Beta resin	20 minm.	18 minm.
% Ash	0.3 maxm.	0.3 maxm.
Real density (gm/cc)	—	1.32 minm.

Table 7.14 Properties of impregnating pitch

Characteristics	Typical value
Softening point (K & S) °C	70-74
Softening point (R & B) °C	80-85
% Fixed carbon	42-45
%Toluene insoluble	18-20
%Quinoline insoluble	3-4
% Ash	0.10-0.2
Viscosity	8-15 CPO

Pre-forming pitches are chemically solvent-fractionated and a special grade which forms anisotropic meso-phase liquid crystal. This meso-phase (developed as spheres at 380°C) have anion like structure and they have some long range order (turbostatic). Pre-forming pitches have high softening point and high secondary alpha-resin. They are different from conventional binder pitches which have lower softening point. The increase in softening point of performing pitches is mainly on account of increase in secondary alpha-resin resulting from the development of mesophase. The progressive increase in pyridine insoluble content gives pitch suitable properties for fabrication of carbon- carbon composites. As softening point in these pitches increases from 180 to 280°C, so do pyridine insoluble content from 7 to 53%. The term “asphalt” and “bitumen” in this regard are sometime confusing as in USA bottom residue in petroleum fractionation is called bitumen while in UK bottom residue of coal tar distillation is called bitumen (and asphalt the bottom residue of petroleum distillation). World Petroleum Congress proposed the term “naphtha bitumen” to cover all native bituminous products (petroleum, mineral waxes, asphalt, and asphalites) soluble in carbon-disulphide.

American Petroleum Institute (API) put forward following definition to “asphalts”: Black-to-brown solid or semi-solid cementitious material which gradually liquefies when heated and in which predominating constituents are bitumens. These occur in solid or semi-solid form in nature are obtained by refining petroleum. Asphalites are natural compounds similar to the asphalts but contain high percentage of n-pentane insoluble material (asphaltene) and consequent high temperature of fusion (115–330°C, R&B method). “Carboids” represent that part of the asphaltic bitumen which is insoluble in CS₂. “Carbenes” are soluble in CS₂ but insoluble in CCl₄. The carboids and carbenes are present in very small quantities and are therefore of minor importance. “Asphaltenes” are obtained after freeing asphaltic bitumens from carbenes and carboids by precipitation with light petroleum (86–88°C fraction). After drying they appear as dark brown to black powder and are soluble in benzene, CCl₄ and CS₂, but are insoluble in paraffinic hydrocarbons. They are highly aromatic and contain condensed rings. One general method of separating pitches which has gained favor in Great-Britain uses pyridine, benzene, and n-hexane as solvents. The fractions obtained are – (1) C₁, in-soluble in pyridine, a carbon like material which is suspended in the tars, (2) C₂ soluble in pyridine but insoluble in benzene, (3) resin- B, soluble in benzene but not in n-hexane, (4) n-hexane soluble material which may be further divided by vacuum distillation into resin A and oil.

It has also been observed that cross-linkage in anthracite coal is more than in petroleum coke; as a result both RPC (fixed carbon 87–95%, VM = 5–15%, and H = 4% approx, moisture = 0.5–2%) and CPC (calcined

at 1300°C and containing 97–99% fixed carbon, VM=0.3%, H =0.1%, and moisture = 0.1%) has been used by graphite electrode industries as raw material. Electrical resistance of RPC is in thousand ohms while that in CPC is about 0.05 ohm. CPC is manufactured in India by the oil refineries and some calcinations units like – Indian Oil (Barauni), Bongaigaon Refinery and Petrochemical (Assam), India Carbon Ltd. (Gauhati), Petrocarbons and Chemicals (Haldia) Goa Carbon Ltd. (Goa), and Universal Hydrocarbon (Barauni). Heavy bottom residue in such plants are coked at 500°C to derive RPC (volatile matter 2% max). CPC is used as the filler material in electrode making. Table 7.15 shows the general characteristics of CPC.

It may be noted here that RPC and CPC used in graphite industry are of petroleum origin, but a similar item “Pitch Coke” which is also suitable for same purpose, is still not feasible in India due to lack of tar availability. The feed-stock conventionally used for such coke manufacture (e.g., long and short residue, decant oil from catalytic cracker, extracts from lube plants, thermal tars from thermal cracker, aromatic tar/pyrolysis tar from steam cracking unit, or coal tar pitch). By the very basic nature of such raw material contains good part of sulfur in crude, essentially all the metals or ash forming components and bulk of the asphaltic materials. Normally, these materials are very aromatic, refractory, as well as contains variable amounts of ash components. There are three types of cokes used commercially for such purpose.

1. Delayed coking with multiple coking chambers and semi-continuous type coker.
2. Fluid-coking – Fully continuous where product can be withdrawn as fluidized solid. It is generally used with high sulfur (and metal) content feed- stock but yield of coke is less compared to above process (about 17% this case and 24% in above case).
3. Flexi-coking with gasification.

Table 7.15 Properties of calcined petroleum coke

Characteristics	Aluminium grade	Graphite grade
% Ash	0.45 maxm.	0.3 maxm.
% Volatile Matter	0.50 maxm.	0.3 maxm.
% Moisture	0.10 maxm.	0.10 maxm.
% Sulphur	0.70 maxm.	0.70 maxm.
Real density (gm/cc)	2.04 –2.07	2.06 minm.
Apparent density	50 lb/cft minm.	—
Resisivity (ohm inch)	0.04 ohm inch max	—
% Iron	0.035%	0.035 maxm.
% Silicon	0.03 maxm	0.030 maxm.
% Vanadium	0.02 maxm	20 ppm maxm.
% Nickel	0.01 maxm	—
% Boron	—	—

Generally rate of coke yield increases when rate of heating decreases; but gas yield also decreases with decrease in rate of heating. There is a delayed coker both at Gauhati and Barauni refinery. The Gauhati delayed coker has the capacity of 1000 tons/day (operates at 495°C, 2–4 kg/cm² pressure and a recycle to feed-stock ratio of 1:1.1). The Barauni refinery uses a combination of RCO (89%) and vacuum G.O. (11%), a feed-stock instead of only RCO used in Gauhati refinery and yields about 15.5% coke, 9% gas, 9.2% coke and gasoline, 16% kerosene, 20% coking gas-oil, 11.4% coking fuel-oil, 14.6% RFO residue and 4% as loss. Out of total coke thus generated, about 46% is consumed by aluminium industry alone, while carbide and foundry takes about 14%, carbon and graphite industry 9% and 31% is used as fuel (power plant, cement kiln, domestic use etc.) and other uses. Uses of RPC and CPC are shown in Table 7.16.

As can be noticed in above table, use pattern of RPC and CPC is dependent on its constituent elements and consequent gross properties. For example –

1. *Ash* – metal impurities in ash determines its ultimate application area. Like V acts as a catalytic agent in electrolytic cells and decomposes the amalgam and results in consequent formation of hydrogen causing, risk of explosion in the cell. Similarly, boron content acts as retardant to neutron yield in reactors and reduce efficacy. Thus it

Table 7.16 Uses of Raw Petroleum Coke (RPC) and Calcined Petroleum Coke (CPC)

Use of RPC:	
Low ash fuel:	- Power plants - Domestic fuel - Cement kilns
High purity reactants:	- Calcium carbide - Silicon carbide - Miscellaneous carbide
Ferrous metallurgy:	- High density foundry coke - Blast furnace coke
Calcination:	- Calcined petroleum coke
Use of CPC:	
Ferrous metallurgy:	- Recarburizing
Non-ferrous metallurgy	- Aluminium anodes - Titanium tetrachloride
Amorphous carbon products	- Electric furnace electrodes - Furnace liners - Carbonaceous cements & pastes - Carbon specialities
Synthetic graphite products	- Electric furnace electrodes - Electrolytic anodes - Graphite specialities - Nuclear application

can not be used in nuclear field. Other metallic impurities like Fe, Si, etc., decreases the oxidation resistance of the product, resulting in lower apparent density and low mechanical strength.

2. *Volatile matter* – higher the VM content, more porous will be the final product.
3. *Moisture* – higher moisture content makes it difficult to size and cause sticking during processing through various equipments.
4. *Sulfur* – it causes decrease in the current efficiency in aluminium industry and causes puffing at about 1400–2000°C with consequent crack in the electrodes.
5. *Real density* – it is the density of carbon product minus its porosity and is an indication of compactness of the coke. Lower real density causes higher porosity in the final product and consequently poorer mechanical strength. Real density also is a measure of the extent of calcinations process.
6. *Apparent density* – it takes into account both open and closed pores, they in-turn determines the binder content required for paste making in electrode industry. Higher the porosity, higher will be the need for binder content.
7. *Coefficient of thermal expansion* – lower the CTE value, higher is the thermal shock bearing capacity of the materials. This is important in applications such as arc-furnace where temperature shoots up to high degree in a fraction of second. Needle coke having high CTE value is preferred in such large size electrodes making (but CTE is of little significance in anode manufacture).
8. *Other mechanical properties* – final product (graphite electrodes) from much raw material should also meet specified flexural strength and Young's Modulus to make it fit for use in industries.

In India generation of such materials from coal and coal-tar has immense scope as in abroad. Commercial production of various filler materials are already on. Low ash coke can also be made into cathode blocks. Use of anthracite coal or some reactive coke also increases production of carbide by 10–15%, compared to conventional production of carbide with charcoal, Leco, and high ash coal blend. NML-Jamshedpur has developed both graphite based stopper-head (for tapping molten steel) and graphite crucible, graphite intercalation compounds have mobile electron which results in electrical conductivity even more conductive than copper. CFRI-Dhanbad has developed carbon-electrodes suitable for (H₂-O₂) fuel-cells application.

Preparation of this involves, determination of quality of pitch as binder, size fraction of coke particles, pressure moulding, baking, etc. The electrodes have crushing strength of 350 kg/cm² and apparent density of

1.5 gm/cc when impregnated with catalyst and formed into single cell, had open circuit voltage of 1.205 V (0.85 V current density 29 milli-amp/cm² in 5 M KOH, ideal being 110 milli-amp/cm² at 0.8 V).

Pitch coke is generally used in the manufacture of prebaked and Soderberg type electrodes. It is also used in foundries, in open hearth furnace and in manufacture of SiC. For core binding in foundries, a special grade pitch is used, known as core binder pitch. Core compounds contain high softening-point pitches. Sand clay and core binding compounds are intimately mixed, moisture with water and rammed into or around a pattern having the shape and dimension of the desired casting or cavity. The pattern is then removed from the mould or core, and the latter is baked to remove moisture, to melt, carbonize the core compound sufficiently to cement the sand and clay particles firmly together. After the mouldsand core have been used in the foundry, they are disintegrated and conditioned for reuse by addition of more core compounds. The suitability of coal-tar pitch for this purpose is due to its inherent binding capacity, which imparts strength to the molds and core prior to and during the casting of the metal.

7.4.3 Carbon electrode pitch

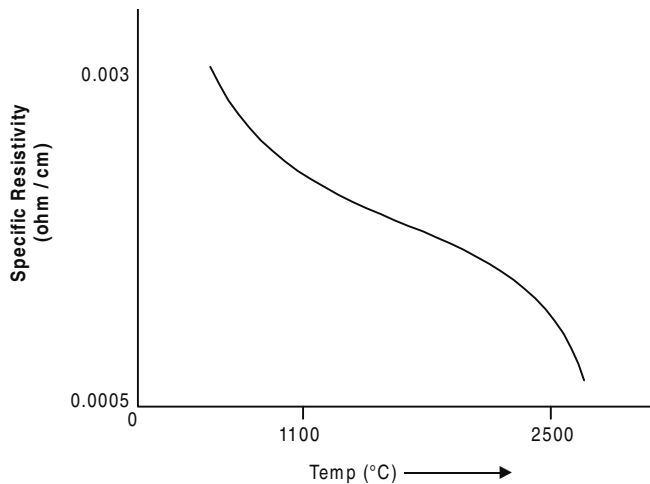
Coal-tar pitch is the preferred binder for use in the manufacture of amorphous and graphitized carbon electrodes, blocks and other shaped forms. The pitch is hot-mixed with sized petroleum coke, anthracite coal, carbon Black, scrap carbon, and the hot mix is moulded or extruded into desired shapes. These shapes are heated to 1000°C to form amorphous carbon articles or to 3000°C to give graphitized carbon forms. The pitch

	Tar	Soft Pitch	Briquetted Pitch	Hard Pitch	Electrical Pitch	Cultured Pitch
Composition (%)	A	A	A	A B	A	A
	B	B	B	C	B	B
	C	C	C	D	C	C
	D	D	D	E	D	D
	E	E	E		E	E

7.6 Solvent Fractions of tar and pitch: (A) Low molecular wt. tar oils (B) Middle - molecular wt. tar oils (C) Medium - molecular wt. tar oils (E) High - molecular wt. tar oils.

yields a coke during this heating which cements the carbonaceous aggregate together in a dense product of high electrical conductivity. Pitch from high temperature tar, especially from coke-oven tar, is found suitable for this purpose. Pitches from low temperature tar are unsuitable. In general, a high carbonization temperature in tar production correlates with a high coking value and high carbon/hydrogen ratio in the pitch there form. These high value correlates, in turn, with high electrode strength. The behavior of the binder during its transition from a liquid to a solid coke is important. Coke oven tar pitches gives less porous coke than does vertical retort tar pitch. Also coke oven tar pitches shrink less on transition from liquid to coke and thus, leave less free-space between the particles of aggregate, giving a denser product. Shrinkage is influenced by the decomposition temperature of the pitch. The lower the temperature at which decomposition occurs, the greater the temperature range of shrinkage on baking. In testing pitches, it is usual to perform a distillation test upto 360°C and then determine the softening point of the residue to ensure that decomposition does not take place at this relatively low temperature. The viscosity of the pitch is an important processing variable. Usually the critical adhesion range of viscosity corresponds with a temperature range of 30 – 40°C above the Kraemer-Sarnow softening point or 20–30°C above the ring-&-ball value. The actual softening point required depends on the mixing and forming facilities but should always be as high as permissible because the harder pitches have a higher coke value.

It is generally agreed among European electrode manufactures that a content of 30–35% free carbon ($C_1 + C_2$ resins) in the pitch binder is desirable, especially for Soderberg (continuous anode) paste. Continental



7.7 Change in resistivity with temperature.

European manufacturers specify a minimum of 20% beta-resin (C_2 resin). Free carbon has no wetting properties; the compounds which are benzene soluble contribute to this property. To ensure adequate wetting and binding property, it is usually specified that the coking value percent minus free carbon percent should not be less than 20. Charette and Bischofberger's characterization factors were used, to characterize pitches for electrode binder usage; namely – (a) the coking value times the C/H ratio of the whole pitch and (b) the percentage of benzene insoluble material times the C/H ratio of the benzene – soluble fraction. These factors gave a straight line relationship with the compressive strength of test electrodes made from 14 coal-tar pitches and 10 petroleum pitches. Results are available to show that vertical retort tar pitches give compressive strengths higher than horizontal retorts calculated by Charette and Bischofberger's criteria. They concluded that there is no unanimity in views put forward for the properties of the ideal binder pitch. Both the coking value and ratio of solvent fractions appear to be important. Chemical condensation, air blowing and thermal treatment can alter both values, but the results differ with different pitches and must be evaluated for each individual case. More recently, Dell has compared the aromaticities of a number of coal-tar pitches with characterization by the usual determinations such as coking value, C/H ratio, and solvent fractionation. He concluded that the quality of carbon anodes is related directly to the aromaticity of the binder pitch. The usual tests for pitches such as quinoline-insoluble, benzene-insoluble contents and coking value did not correlate with aromaticity. The more useful characterization for aromaticity include C/H of the CS_2 -soluble fraction, sulfonation index, and infra-red index of the whole pitch and the distillate fraction. The coke-oven tar pitch ranked highest in aromaticity of the pitches tested. Thus we find in conclusion that tars as per their composition variation becomes suitable for different uses; this is shown diagrammatically in Fig. 7.6.

Excellent reviews and original articles on high quality pitch based materials have been published by Zygmunt Stopel (Institute for Chemical Processing of Coal, Zabrze, Poland) and interested readers may consult above source. Indian manufacturers experience in production of electrodes at $500^\circ C$ states that above temperature is most critical is subsequent graphitization. Heating rate of $3-4^\circ C/h$ has been found to be most suitable with out pitches. During packing into the furnace, sand and coke ratio is generally kept at 1:1 (density of the packing material should be same as the density of the final product). The product after baking is hard and brittle and can not be drilled; Accordingly, necessary holes or other work should be performed before baking. In the subsequent phase, calcinations is done at $1300^\circ C$. Fortunately Indian cokes (petroleum origin) are non-puffing type and thus works well in these manufacturing processes. Earlier

works suggest that sulfur present in coke is responsible for puffing phenomenon, but recent studies contradicts above hypothesis and cites reasons as an inherent property of the particular coke. To suppress puffing action, where it occurs, some metallic oxides are usually added to the raw mix. Graphitization starts at as low as 450–500°C when mesophase first appear in the isotropic pitch. Activation energy in this respect keeps on increasing with temperature. It has been observed that coal based cokes give more puffing than the petroleum based cokes. It is believed that FeO in coke combine with sulfur to produce SO₂ and cause puffing. An optical pyrometer (with nitrogen passing through the graphite shielding tube) is used for temperature measurement in graphite industries. After the Acheson furnace reaches the temperature of 2600°C, it is held constant for 12–20 h for graphitization to be complete (during this step apparent density of the final product reaches 1.75). Value of real density at the final stage is not that important as is the apparent density. There is generally a 3% volume reduction while heating from 1700 to 2600°C. After baking, the porosity remains about 10–12%. Graphitized materials passes through the pseudoplastic stage between 2500 and 2700°C. In Acheson furnace generally AC-current is passed perpendicular to the length of the electrode to be graphitized But at Durgapur (West-Bengal) at the graphite India factory, DC-current (6000 KW capacity and 60000 amp rating) is being used which gives a better phase balance and improved power factor which results in considerable energy savings (in AC-heating large amount of current, about 80%, is lost during heat process). Once the graphitization is complete the furnace is allowed to cool for 12–20 days before discharging the product. In hot condition SiC heating elements can be taken out without any adverse effect, but then the graphitized product gas oxidized. It may be noted that although CPC is purer raw material but metallurgical coke is preferred in such work, as the former has low resistivity and produces low heat in the furnace (heat is proportional to the square of current, times resistance). It has also been noticed that 30–40% energy can be saved in such processes if the current is passed along the axis of the electrodes. Coke powder used as raw material for making the green electrodes, has been found suitable as packing material instead of sand and coke mentioned above. The furnace transformer used in such operations are different from those used generally as power transformer (the former one has 21 steps in the 80–300 V range and in each tap wattage is constant). 1170 kg of anthracite and 272 kg of coal pitch produces 1 ton of artificial graphite by this process. The tar pitch used for such purpose is first checked for its molecular weight range (by free point depression method and using benzene as solvent), softening point and three broad constituents – residue, oil and slurry phase. While the first (residue) forms mesophase during graphitization, the other two (oil and slurry) do not contribute to mesophase

formation but required for other physical parameters. It has been observed that while binder pitch containing QI in the range 10–12% and benzene insoluble about 30%, impregnating pitch contains less than 3.5% of QI. In India, binder pitch quality is controlled with following specifications – benzene insoluble = 24–33%, quinoline insoluble = 12–15%, and coking value about 65%. Quinoline insoluble phase containing carbon-black particles in the range 0.1–15 micron (the latter is the agglomerate) and 20 μ size constitute about 85–90% of total QI which hinders mesophase formation. After the electrodes have been graphitized by above method it is coated with impregnating pitch by carrying-out the operation in an autoclave.

Impregnation cycle practiced in India, is normally 10 h at a vacuum of 27 in. and pressure of 100 psi while in Japan this injection pressure is taken upto 250 psi. High pressure operation cuts down the impregnation cycle time to as low as 2 h cycle and thus boost the production to a great extent. For impregnating purpose only petroleum pitch is used. Benzene insoluble part in impregnating pitch should be low (about 7–12%) compared to binder pitch; but quinoline insoluble part is of the same range as binder pitch. Coking value is also maintained in such case at par with binder pitch. Generation of rejects in graphite industry is avoided as much as possible for the following simple reason. The 1986 price of CPC in India was Rs. 6700–7000 per ton while that of the rejects, graphite fines only, was Rs. 6500/ton. The price of average size standard electrodes were more as it involves more machining time and greater loss of material during processing. In India, anodes are dying market and is continuously being replaced by DSC. Projected graphite electrode demand in 1990 in our country stands at 30,000 ton/year. Recently M/s Travancore Electrochemicals have reported formation of needle like acetylene-black during its formation by thermal cracking of acetylene. This grade of carbon black has superior electrical conductivity and may open up new routes to make cokes for graphite industry. Present installed capacity of the plant is 76,000 ton/annum and the product in average sells for Rs. 25000/- ton. Pitch supplied by Indian Steel Plants to graphite industries are low in ash (about 0.18% and thus suitable for nuclear and anode graphite making) but they vary too much with respect to softening point (90–106°C) from consignment of consignment. For better product yield from such industries the raw pitch should have a variation of $\pm 1^\circ\text{C}$ in this respect. Softening point of the Soderberg carbon electrodes paste (used by aluminium industries) is 90–100°C. It is worth mentioning here that the main difference between aluminium, ferroalloys and calcium carbide industries is that in the former the electrode is not subjected to arcing, whereas in the latter the electrodes act as an arcing point with the charge. Thus due to the nature of industry and its requirement, aluminium grade anode paste is not suitable

for ferroalloys and calcium-carbide industries, which are “electro thermal” compared to the aluminium industry which is “electrolytic” in nature. Besides electrode industry, there is also a great demand for graphite in other industries and these are mentioned below.

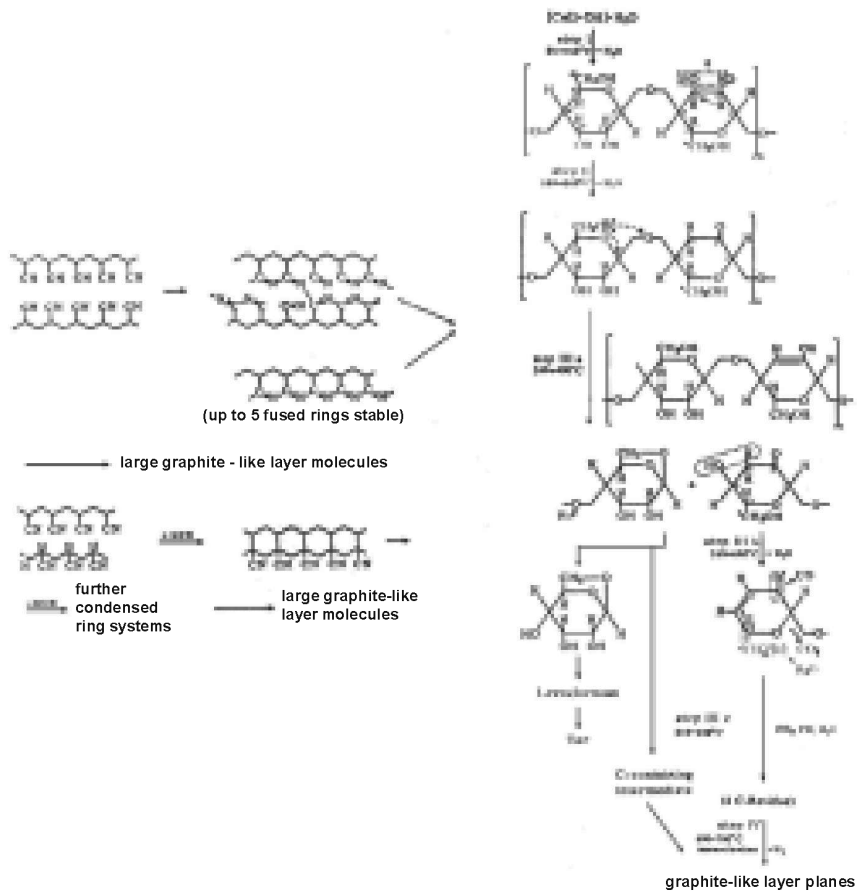
7.4.4 Carbon fibers

Graphitized carbon fibers are made either from Polyacrylonitrile (PAN) or from coal tar pitch. Our primary interest is in the later product and thus will discuss it in detail in this section. PAN-fibers has been developed earlier and used in “stealth” defence air-craft and the nose of space vehicles. Besides high temperature withstand capability, rocket nozzles made up of such materials allow uniform wearing and thus maintaining its dynamic equilibrium during space entry. Production of graphite fiber from pitch involves the first step of its refining. The average size of pyrolytic carbon (QI or alpha-resin) in pitches are about 1 micro-meter and impedes in the formation of pitch mesophase. If pitch is heated above 400°C, polymerization and condensation reactions proceed very rapidly with pitch until the product of these reactions are no longer soluble in pitch so that they form a detectable second phase known as “mesophase.” Mesophase spherules, if there is no alpha particles (free carbon) which adheres on the surface to the spheres, can coalesce with each other, form larger spheres, thus spread to the entire pitch and ultimately forms larger graphite flakes. After the pitch has been processed, it is extruded through a small diameter (about 0.5 mm) metal die and the fibers thus generated mildly oxidized in air so that semisolid crust is formed on the outer surface of the fibers and they do not stick to each other when stacked together inside the graphitizing furnace. Processed pitch has somewhat long range order and retains its memory of turbostatic flow order after extrusion process. Sometime graphite powder is also used to prevent sticking of these fibers in green stage and can be removed easily as they are loosely bound. Next the fibers are graphitized in an inert atmosphere at about 2800°C. Union Carbide (USA), uses a melt spinning process for drawing fibers from the molten pitch. Mesophase based carbon fibers are graphitizable whereas fibers derived from precursors such as cellulose, PAN and non-mesophase pitches are not. The densities of pitch based fibers are higher and after high temperature heat treatment approach the density of perfect graphite. They also have much higher electrical conductivity than the fibers prepared from other precursors. Gel Permeation Chromatography is used to determine average molecular weight of coal tar pitch and this in practice helps selecting the right cut (appropriate molecular weight fraction having desired number average molecular weight) for graphitization.

Electrical resistivity studies by Sharp indicate that upto 200°C the change in resistivity is consistent with viscosity controlled diffusion of current carriers. At 450°C which is the starting point for mesophase formation, the resistivity rises rapidly, then levels off, remains constant until the onset of mesophase coalescence and phase inversion takes place. The resistivity of the resultant mesophase pitch was found to be less temperature susceptible than that of the parent pitch. Once the mesophase are formed it becomes difficult to spun the pitch. Accordingly, spinning is done at less than 40% mesophase formation (for a particular molecular weight fraction), so that the melting point do not vary much between the isotropic and anisotropic phases. Spinning is always done well below 400°C to avoid rapid coking reactions. Singer has given the design of the extruding apparatus, SEM, X-ray and ESR picture of these fibers in above publication and interested readers may consult above source. Effect of extrudate diameter was studied by Jenkins and found small diameter fibers showing better orientation of the molecules. Above author further showed that by removing high fluidity component by an initial extrusion, it is possible to extrude pitch mesophase to produce a continuous rod of 3.8 mm diameter, which can be coked and graphitized, retaining much of the preferred orientation induced during extrusion. The coke thus produced has structural feature and physical characteristics in common with premium coke used in electrodes for steel-making (needle coke) where a low volumetric coefficient of thermal expansion is required for good thermal shock resistance. In such cases, the extrusion pressure could be supplemented by the gravity of the charge. A number of other workers has also studied deformation of pitch and flow through extrudate in a continuous fashion.

Oberlin and Geigon studied the SEM, mainly TEM micrograph of the transverse section of pitch based carbon-fiber and found that there are three different radial textures along axis of the fiber; outer most layer is polycrystalline graphite, next middle layer is porous structure (turbostatic) and inner layer has very similar structure to PAN fiber (i.e., partial graphitization). Thus pitch based fibers has approximately a lamellar sheet structure. Oberlin has followed this prospective graphitization by DTA and has shown that in the primary carbonization region (hydrocarbons are released) the DTA curve first peaks down to softening temperature (T_s), then again rises a little, falls to minimum at the mesophase sphere nucleation region (T_r), and then rises to a maximum at resolidification temperature (T_r). Gas released and secondary carbonization step starts after this. Lesser is the plasticity of the pitch narrower the difference between T_s and T_r ; correspondingly, the mesophase spheres become smaller, simultaneously their nucleation, growth and coalescence takes place within narrower temperature limits. All carbonaceous materials

follow the same graphitization process. Before the semi-coke stage, bulk mesophase made up of individual basic structural units (less than 20 Å in size) are formed. Then distorted and wrinkled layers appear below 2000°C. These layers stiffen rapidly and dewrinkle above 2100°C. With further increase in temperature, flat lamellae give flat polycrystalline graphite. Thus rate of local molecular orientation determines the graphitizability of any carbonaceous material. Jorro et al drew their carbon fiber from coal extract (by dissolution at 400°C in a solvent oil under pressure) by melt spinning, oxidation (at 250°C to make them infusible) carbonization (at 1000°C) and then by strain graphitization. Relatively low strength (upto 1 GN/m²) fiber are produced by carbonization to 1000°C while strain graphitization at 2700°C yields high strength (upto 3 GN/m²), high modulus (upto 670 GN/m²) fiber. The structure of the carbonized fiber is isotropic and that of the strain- graphitized fiber anisotropic. It should be noted that the modulus value of a product depends on its degree of crystallinity. Defect found in such fibers fall into two groups those which occur as a result of processing and those which are inherent in the feed-stock. All defects associated with the carbon structure, such as voids, blisters, etc., belong to the first group and it should be possible to avoid these by suitable design of spinning equipment and careful choice of processing conditions. Defects associated with inclusion fall into the second group and although these can not be completely eliminated, they may be reduced (e.g., by improved filtration). Chemistry of carbonization of such pitch, the first step towards graphitization has been studied in detail by Lewis. His work show, because of their complexity, pitches behave as eutectic mixture and exhibit glass like properties (T_g about 86°C). They soften over a wide temperature range to a relatively low viscosity liquid. As pitches are heat treated further, they undergo a series of physical and chemical changes, passes through the liquid crystalline mesophase and finally to infusible hydrocarbon polymer known as coke. During this process of carbonization, first the most volatile component distil, rising the average molecular weight and viscosity of the remaining pitch. Physical distillation is accompanied by thermal polymerization of the more reactive species of the pitch and the cracking of the substituent side chain from aromatic rings. Lewis showed by TGA and gas evolution data that the weight loss due to such process starts at about 250°C and reaches a maximum rate between 350 and 450°C. This weight loss is attributed largely due to physical removal (decomposition reactions) of low molecular weight volatiles. The gas detected during this evolution process is mainly H₂ and CH₄. Most pronounced is the abrupt evolution of H₂ at about 400°C which at about 450°C flattens out. CH₄ evolution maximizes between 480 and 520°C and follows a hyperbolic curve (dies down after 520°C and becomes very small at about 800°C). As pitches are further carbonized to about 1000°C,



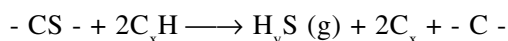
7.8 Thermal degradation of cellulose.

residual hydrogen is removed along with some of the other heteroatom. Hydrogen is removed mainly in the form of H_2 and CH_4 . This dehydrogenation process results in continued growth of aromatic molecular size and develops large concentrations of stable free-radicals. Between 500 and 1000°C when all hydrogen has been removed, further reaction that contribute to development of large aromatic moieties (isotropic or anisotropic, depending on the type of molecules present in the parent pitch) involves bond cleavage (C-C) and rearrangement among the various oligometric structure to form highly condensed and stabilized aromatic ring system. There is no evidence to support the development of extensive methylene bridge between aromatic units during pitch carbonization. The distinct feature of hydrocarbon free-radicals thus produced in the intermediate stage are, they do not undergo isomerization, hence no

branching in the molecules, no shift of unpaired electrons (only migration of hydrogen in special cases like in primary free-radicals) and these free-radicals do not involve in cyclization reaction (hence difference in product pattern with catalyst cracking). It may be noted here that C–C bond energy for primary terminal bond is 79, secondary is 75, and tertiary is 74 kcal/mol. For C–H primary bond energy = 75, secondary = 89, and tertiary = 84 kcal/mol, respectively. It is interesting to know that altogether different reaction involved in macro molecule development and ultimate graphitization by PAN fibers which has been used extensively until it is being replaced by pitch fibers. The reaction involved are shown in Fig. 7.8 along with that of cellulose fiber (which can also be graphitized into carbon fiber). Lewis also studied the role of heteroatom like sulfur which has been reported to facilitate to some extent in graphite formation during this pitch carbonization process. Catalytic effect of sulfur has been studied in detail and I will present the zest of this finding in following paragraph.

Catalytic effect of sulfur was first described by Christu who found a shoulder on the high angle side of the (002) X-ray diffraction profile when S containing carbons were heat treated above 1700°C. The shoulder indicated formation of well ordered graphite crystallites. This was later reported by Gillot et al (in 1968), Whittaker and Grindstaff (in 1969), Barilon et al, Fitzer and Weisenburger (1969, 1975, and 1976). Honda et Al (1969), Yannada et al (1977), Heinz (1978) and Sugimoto et Al (1985). Although still the exact role of S in graphitization process is not clear, but results indicates that release of S at high temperature causes “puffing” action to the carbon matrix and this in turn causes lowering of density, strength, electrical and thermal conductivity, increase in porosity and induces crack propagation which facilitates rearrangement of aromatic rings. The rapid irreversible expansion probably causes microstructural imperfections. Sulfur emanates in gas phase either as elemental sulfur or as H₂S. Irreversible puffing rises sharply with increasing heating rate for cokes having sulfur content above 1.5%, while for cokes below 0.8% sulfur content rate of puffing with heat is much less pronounced. According to some workers, escape of sulfur gas helps in the transformation from convoluted to a parallel ordered graphitic structure. While some workers maintain that sulfur atoms are preferentially located along dislocation lines within the lattice, where they cause cross-linkage and thus prevents formation of long-range graphitic order. The sulfur-carbon bonds are broken by excess thermal vibration energy and allow the dislocation line to move to the surface of the layer stack. Mechanism of sulfur induced graphitization below 2000°C is probably due to elimination of dislocation lines. Remaining sulfur above puffing temperature range is explained by Oberlin, occur due to their cross linked closed pores or trapped by

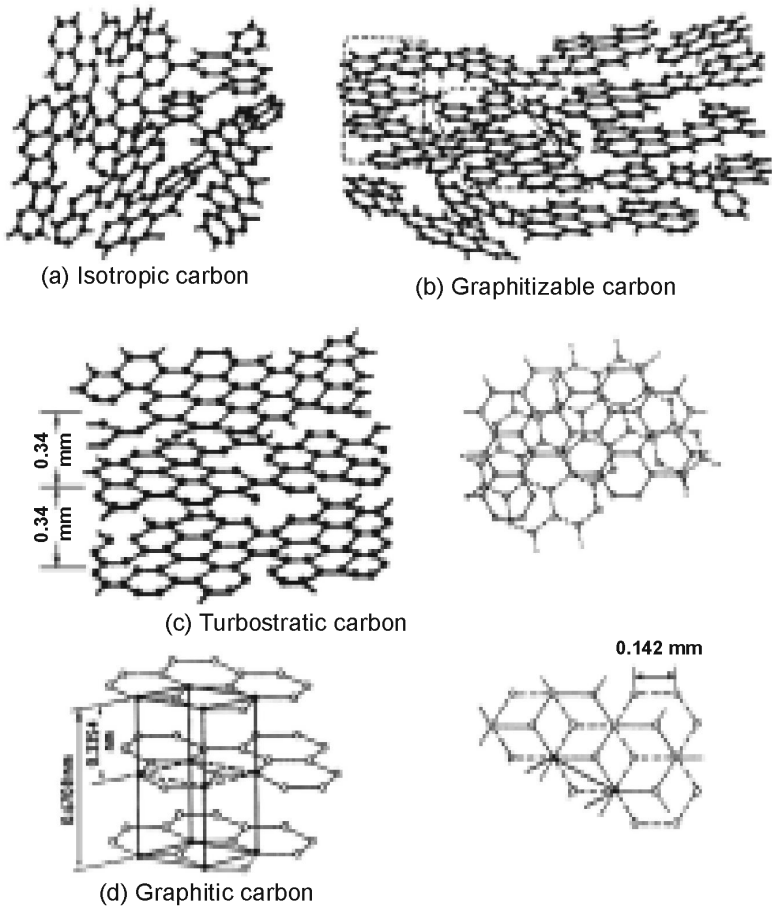
helicooidal structure. Morris et al also found that evolution of nitrogen parallels with sulfur release. Bradtzaeg et al worked on the hypothesis of intercalation of hydrogen between carbon layers. They inferred that a random but increasing removal of intercalated hydrogen will cause a continuous shift of the average interlayer spacing approaching the spacing in graphite. However, if sulfur enhances this process by reaction with hydrogen a discontinuous change in the development of the structure is likely. The stability of H_2S decreases with increasing temperature. Based on stabilities of various gases sulfur compounds, they proposed the following mechanism for sulfur induced graphitization:



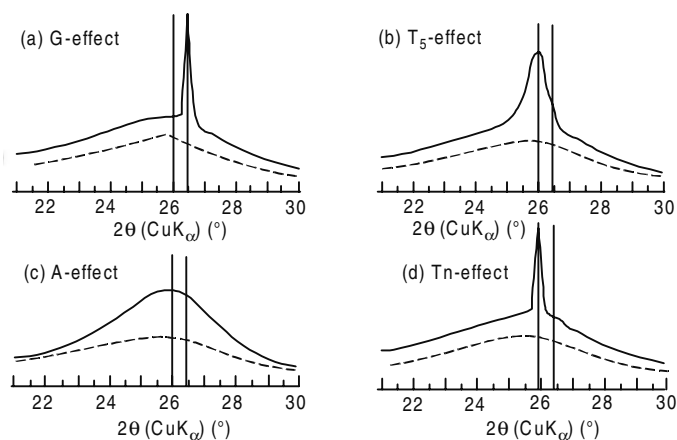
where $-CS-$ is the complex organic sulfur-carbon compound, C_xH is the intercalation compound with hydrogen and carbon, H_yS is the hydrogen-sulfur compounds (like HS , H_2S), C_x is the hydrogen free aromatic carbon layer, and $-C-$ sulfur free organic compound. Above equation shows, if diffusion of hydrogen is rate limiting in the sulfur enhanced graphitization process, formation of $CS_2(g)$ is preferred during rapid heating rates in the puffing region, while low heating rates will produce more $H-S$ compound. Formation of $CS_2(g)$ is thermodynamically favored at higher temperatures from where the Gibbs energy for the formation of CS is more negative. Thus puffing increases with increasing heating rate and a lower heating rate leads to less puffing but more enhanced graphitization. Longer the sulfur remains within the material in the requisite temperature range, more is the probability of reaction between sulfur and the intercalated hydrogen. But this theory of graphitization through intercalated hydrogen, at least for the graphitization taking place above $2000^\circ C$, was strongly argued by Bragg et al and Kamura et al on the ground that almost all hydrogen should vaporize off at much lower temperature. Other materials which may catalyse the graphitization process, effect of $AlCl_3$ was studied by Boero and Wargon. Their studies with model compound like naphthaline show that upto $300^\circ C$ mainly polymerization and disproportionation reactions occurring. At higher temperature $AlCl_3$ works as catalyst and gives rise to dehydrogenation reaction with evolution of hydrogen. This causes mesophase formation at a relatively lower temperature. When the catalyst is removed, the mesophase seems to be stable in a wide temperature range. Usually low C/H ratio and high aliphatic hydrogen contents were observed by above authors in the catalytically formed mesophase. These properties are probably responsible for the solubility behavior in conventional solvent. The first step of polymerization and disproportion reaction mentioned above lead to the formation of high molecular weight nearly planar molecules, which contain fully aromatic and tetralin-like rings in their structures. These molecules would then be able to enter into the stacking

process leading to the mesophase formation. Catalytic graphitization of carbon fiber, carbon black, and anisotropic mesophase spheres by chromia and chromium- compounds were studied by Mochida et al and found that catalyst addition as a liquid solution provided better dispersion than by solid powder mixing by grinding method. Sequential heat treatment below 2000°C were more effective for graphitization than high temperature treatment when the catalysts sublimed. Graphitization of both graphitizable carbon (processed pitch) has been studied by Mochida

- (a) Isotropic carbon
- (b) Graphitizable carbon
- (c) Turbostatic carbon
- (d) Graphitic carbon



7.9 Diagrams of structure of (a) isotropic, (b) graphitizable (c) turbostratic and (d) graphitic carbons.



7.10 X-ray diffraction (002) profiles of carbon before (dotted line) and after (solid line) catalytic graphitization.

et al with Cr, Mn, Mo – oxides and found two distinct stages of catalytic graphitization (1500–1800°K and above 2000°K). Higher temperature graphitization was attributed to partial dissolution precipitation process. Their theory was further conferred from studies with non-graphitizable carbons (like benzene insoluble fractions). The lower temperature graphitization occur only with graphitizable carbon and non-graphitizable carbons require a high dose (about 30% loading) of catalyst to bring about the graphitization process. Catalytic graphitization of cokes by indigenous mineral matter was studied by Oya et al and found smaller particles of mineral matter help in graphitization at lower temperature and found three types of catalytic effect by XRD. The same authors produced graphitic carbon from phenolic resin carbons by oxidation with Simon's Reagent and $\text{HNO}_3/\text{H}_2\text{SO}_4$ in presence of Ni-catalyst. Some excellent reviews on catalytic activity by various metals and their compounds have been published in recent times which I will mention in short, but readers may consult above literature sources for further detail on the subject.

At the outset it may be noted that catalytic graphitization do not have extensive industrial applications because of the undesirable characteristics of graphites containing significant amounts of residual catalyst material. From X-ray diffraction studies these catalytic phenomenos are put into four categories (a) the G-effect, (b) the Ts-effect (c) the A-effect and (d) the Tu-effect. Not only metals but also oxides and carbonates have been found to graphitize carbon. In the Periodic Table, Group IVb to VIIb metals have 2–5 electrons in the d-shell and forms strong chemical bonds with carbon to form metal-carbides. Hence elements of group IVb to VIIb, and VIII are graphitizing catalysts. Majority of graphitizing catalyst have an atomic number of less than 40 and a first ionization potential of 6–8 eV. Both

CaCO_3 and $\text{Ca}(\text{OH})_2$ produce G-component graphite. Fe_2O_3 is also an effective catalyst; as is some clay minerals (like elcrite). Finer particle size of the catalyst causes formation of Ts-component graphite. Formation of G-component, isothermally, results from the negative free energy of transformation of carbon to graphite. The less ordered is the carbon, the larger will be the value of $-G$ for the transformation into graphite. Mechanism of development of above four XRD effects are as follows – (a) the development of G-effect is explained by two theories. One is the solution of carbon into the catalyst particle followed by precipitation as graphite (this reaction proceeds isothermally because of the negative free energy change in going from disordered carbon to graphite. The second mechanism involves the formation and decomposition of carbide intermediates. (b) the Ts-effect involves formation of iron-carbide droplets, on the surface of which float detached elementary domains. On decomposition of carbide, a shell of carbon is formed which is graphitizable because the carbon lamellae are parallel to the external surface of the spherical hollow shell. (c) the A-component material is found to form on heating carbons in the presence of O_2 and CO_2 , the vapor of Ca and Mg and elements substantially bonded into the carbon lattice. Here defects within the crystallites develop during the graphitization process. Such defects prevent the growth of lattices. It is probable that such defects can react preferentially with an oxidizing gas and are removed. Thus the hindrance to further crystal growth is removed and the extended graphitization results. (d) the Tu-effect where heat treatment of a non-graphitizing carbon without catalyst occurs because of localized internal stresses set up by the anisotropic thermal expansion within the carbon crystallite. This stress is released by breakage of cross-linkages resulting in the Tu-component.

High performance PAN fibers are being marketed by Union Carbide/Torray (USA), Hercules and Stack pole (U.K), whereas pitch based carbon fibers are being made commercially by Union Carbide (USA) and Mitsubishi Chemical Industries (Japan) at their Saccade plant set up in 1985. In India, NPL (National Physical Lab, New Delhi) under the sponsorship of UNDP started its R&D work on carbon fiber in 1974. Although commercial production of carbon fibers has not started in India yet, but a number of private companies are already engaged in producing composites based on imported carbon fibers. In 1996 DRDO and HAL developed carbon-fiber based tail and guiding devices for Light Combat Aircraft in India, which now has gone into production.

7.4.5 Needle coke

Needle coke is highly structured, relatively more anisotropic, low metal,

low sulfur, premium quality carbon with large unidirectional elliptical slender pores interconnected at the major diameter. Because of its low thermal expansion coefficient it finds its major use in large diameter graphite electrode making industries. Table 7.17 shows the difference between needle-coke and other grade cokes like sponge and honey-comb coke.

Currently the need for needle coke in our country is about 6000 ton/annum. IIP, Dehradun have taken up a project on production of green needle coke from Indian crudest in joint collaboration with EIL, IOC, and NRDC. Presently entire demand in our country is met through imports only. Interestingly recently in the course of production of acetylene-black from acetylene, a needle carbon material is obtained by Indian industries which have high electrical conductivity and is being investigated as a source of new raw material for needle coke. In practice generally three types of feed-stock are used for producing needle in a delayed coking unit. These are – feed- stock derived from cracking processes, both catalytic and thermal (e.g., F.C.C decant/clarified oils, pyrolysis of processed tar); feed-stocks derived from coking of coal. Most of the commercial plants in operation today use the first type raw material as it is more aromatic (60–80%), low sulfur and low API with characterization factor around 11.4 or lower. Ethylene tar-slurry oil blend (pyrolysis of fuel oil) having low sulfur content is being used by Great Lakes Research Corporation (Elizabethtown,

Table 7.17 Characteristics of CP-needle coke and pitch coke

Characteristics	Calcined petroleum needle coke	Pitch coke
% volatile matter	0.3	0.30
% ash	0.2	0.30
Real density (gm/cc)	2.14	2.00
% sulphur	0.30 – 0.40	0.35

Table 7.18 Typical properties of sponge and needle grade cokes

Property	Raw coke	Calcined coke	Raw coke	Calcined Coke
Sulfur (wt%)	2.5	2.5	1.0	1.0
Ash (wt%)	0.25	0.50	0.1	0.15
Vanadium (ppm)	150	200	—	20-40
Nickel (ppm)	150	200	—	10
Silicon (wt%)	0.20	0.02	0.04	0.04
Volatile matter (wt%)	10-12	—	8	—
Resistivity (micro ohm -m)	980	—	—	965
particles-35 to +65 Tyler 0.49 to 0.23	—	—	—	—
Real density (gm/cc)	2.06	—	—	2.12
Bulk density (gm/cc)	0.80	—	—	0.88
Coeff. of thermal expansion (per deg, 30-100 °C range) 20×10^{-7}	—	—	—	5×10^{-7}

TN), USA. Singh at IIP, Dehradun (India) has shown that coke from vacuum residue contains more of asphaltic components and carbonize rapidly with negligible crystallite orientation. On the other hand, coke from more aromatic and refractory stocks, as in group one above, takes longer time to carbonize and there is high degree of crystallite orientation as the formation of coke proceeds through the condensation of polyaromatic compounds, which upon calcinations yields acicular structure. Only two plants in the whole world are commercially producing needle coke from coal tar pitch. One is located at Poland (Zabrze) and the other at Bergbau-Forschung GmbH, Essen, West-Germany. It is interesting to note that, coking of coal tar pitch in horizontal chamber oven yields isotropic pitch whereas discontinuous vertical chamber delayed coker yield anisotropic coke. The first step in the treatment of such pitch involves removal of QI as much as possible. In the above German plant, pressurized filter candle is used for this purpose and it effectively brings down QI to less than 0.1% while valuable beta-resin are kept intact. The filtered pitch then goes to a delayed coker through a pre-heater. The coke is then calcined in a horizontal (inclined) rotary furnace. This is a continuous operation and the liquid residue in the coker is recycled back to the feeder. The pre-heater operates at 400°C while the coker works at 400–450°C range. The mesophase formed settles at the bottom of the delayed coker which is discharged to the calcinations furnace by a screw-feeder. The calcination furnace operates above 1300°C where the mass behaves like plastic in warm condition. The output mass is extruded into desired shape and then heated to 2600–3000°C for graphite electrode production.

7.5 Graphite for nuclear application

Graphite is used as a moderator in CO₂ cooled nuclear reactors. Two processes occur within these reactors, which modify the graphite properties significantly. The first process is the creation of lattice defects by the energetic reactor-radiation, principally the neutrons and the second oxidation by the radiolytic species created by the radiation (beta, gamma rays, and neutrons in CO₂). As Kelly pointed out, the energetic neutrons (mean energy of about 2 MeV) produced by the fission process in the reactor fuel collide with the nuclei of the carbon atoms in the moderator and transfer them to a fraction of their energy (upto 0.284 MeV) which is much greater in general than the bonding energy of the carbon atoms in the lattice (about 5 eV). These carbon atoms, known as “primaries” are knocked out of the lattice and in-turn become energetic projectiles which displace further carbon atoms from the lattice in a cascade. Each initial neutron-atom collision produces several hundred displaced carbon atoms and of course vacant lattice sites. In a modern reactor, roughly one atom

in 10^4 is displaced per second and detailed analysis show that they can be assumed to occur at random, unlike the spike phenomenon in heavier atoms. The displaced or interstitial carbon atoms diffuse readily between the basal planes at all the temperatures of interest but the vacant lattice sites may be treated as immobile. Most of the diffusing interstitial atoms collide with vacant lattice sites and in spite of a small repulsive barrier, recombine with them. A few of the diffusing interstitials meet others and combine with them to form small interstitial groups. These groups appear to be two kinds, one which can grow by capturing further diffusing interstitial which have included annihilation by vacancies and the second which reaches a stable size of 4 ± 2 atoms is regularly broken up by the cascades of displacement (irradiation annealing). At small doses therefore, there are small groups of interstitial atoms in a field of single vacancies. As the dose progresses the density of the clusters of 4 atoms saturates but the other clusters grow as long as the vacancy concentration permits any interstitials to reach them. This model was based essentially on the combination of electron microscopy and lattice parameter measurements. For necessary dimensional stability, nuclear graphite thus should have thermal expansion coefficient within certain limits. Note that the coolant and graphite moderator are maintained below those (above 650°C) where the thermally activated oxidation of graphite by CO_2 is significant ($\text{CO}_2 + \text{C} \longrightarrow 2 \text{CO}$). The core of the AGR is a cylindrical graphite structure built from bricks of octagonal and square cross-section loosely keyed together with graphite keys. The structure is penetrated by channels parallel to the cylinder axis which contain the fuel elements, cluster of stainless steel clad pins in a surrounding graphite sleeve. The graphite structure which is the neutron moderator, is required to remain sufficiently strong, undistorted to permit loading, unloading of the fuel, the necessary movements of control rod and shut-off system for at least the design life of 25 full power years. The graphite employed in all of the AGR is manufactured from a special coke obtained from naturally occurring bitumen from the Uintah basin in the state of Utah in USA, known after its discoverer as "gilsonite." The use of this coke provides a finished graphite with desirable properties. The manufacturing process, except for the degree of purification necessary to reduce neutron absorption, is similar to that for conventional electrode graphite. The coke is ground to a maximum size of about 1 mm, mixed with pitch and formed into bricks by moulding. Calcination at 1300°C leads to a reasonable degree of rigidity. Further impregnations of pitch are made to give the desired density and this is followed by a final firing at approximately 2700°C in an Acheson furnace. The finished product has a density of about 1.87 g/cc and is highly isotropic. About one half (0.11 cc/cc) of the total porosity is open to the surface, the remainders being closed. Hutcheon with varied pore structure graphite found a linear correlation

between reaction rate (with CO_2) and open pore volume. This work therefore provides the information for the manufacturers with a firm basis for development of suitable materials on the production scale. Open porosity can be controlled by impregnation. Results also indicate that the reduction in pore diameter with resultant decrease in permeability and increase in surface area, was not particularly significant in this context. These considerations taken together indicate that a target of about 5 cc/100gm open porosity was a reasonable one at which to aim, having regard to the economic balance. The problem put to the graphite manufacturers ultimately lies in the production of graphite which is isotropic, has large crystal size, and has the highest available thermal expansion coefficient in order to achieve required accommodation factor (reflects the mutual orientation of the crystallites). The effect due to highly anisotropic nature of graphite crystal having a difference of CTE value by 1:18 in two directions (a and c). On this basis graphites have been obtained with isotropy ratios as low as 1.1 and with thermal expansion coefficient close to 5×10^{-6} (in between 27×10^{-6} and 1.5×10^{-6} for graphite single crystal in a and c direction).

Elements found to catalyze graphitization are – Li, Be, Mg, Ba; Ti, Zr, Hf, V, Ta; Cr, Mo, W; Mn, Re; Fe, Co, Ni, Cu, Ag, Au; B, Al; Si, Ge, and oxygen. Alloys, as graphitizing catalyst, behave differently from constituent elements. The lower the melting point (eutectic) of the alloy, lower will be the graphitization temperature. Because of the occurrence of good deposit of anthracite in USA (contrary to India which has none). Pennsylvania State University, University Park, USA, has worked on steam and air activation of anthracite (Ref: Chemistry & Industry, 1st April 1996, pp 253–257), a chemical modification route for graphitizing anthracite through removal of residual hetero-atom or aliphatic carbon in it that works as cross-link. Thus anthracite was directly reacted also with hydroaromatic compounds followed by high temperature graphitization at 2700–3000°C. The above investigators also found that in carbide catalyzed graphitizations, the efficiency of the catalyst is independent of the metal attached, indicating generation of highly active carbon by the graphite which voraciously react with the aromatic structure removing its defects and bringing about graphitization.

7.5.1 Graphites for sliding application

There are metal graphite composites used for both sliding and superior electrical contact in motor brushes. The other type of graphite product, without metal in it and used for non-electrical applications are the dry lubricant e.g., graphite powder or colloidal suspension of graphite. Let us

Table 7.19 Properties of nuclear graphite

Property	Anisotropic graphite	Isotropic graphite
Density (gm/cc)	1.71	1.82
Resistance (micro-ohm.cm)	7.35	1000
Tensile strength (Kpa)	9930	16550
Coefficient of thermal expansion:	2.2	3.8
with grain against grain	4.8	4.6
Anisotropy ratio (CTE ratio)	1.73	0.96
Total ash (ppm)	740	500
Boron content (ppm)	0.4	0.3
Neutron absorption coefficient ($\times 10^{-4}$ /cm) ³		-
Stackpole Graphite Grade 2020 (PA, USA):		
Maximum grain size	40 micro meter	
Specific resistance) (micro ohm meter	WG: 17.8	AG: 17.8
Fluexural strength (MPa)	WG: 37.9	AG: 33.1
Compressive strength (MPa)	WG: 89.6	AG: 65.5
Scleroscopic Hardness	50	
Total porosity	17%	
Tensile strength (MPa)	WG: 27.6	AG: 26.9
Thermal conductivity (Watt/m°C)	WG: 63	AG: 63
Sonic modulus of elasticity (GPa)	WG: 9.2	AG: 9.0
Ash	0.17%	

(WG = with the grain, AG = against the grain)

Note: Stackpole graphites are moulded dense, electrographite available in size upto 24" × 24" × 64". Maximum service temperature approximately 427°C; Maximum inert atmosphere service temperature 2760°C. Typical other application includes, continous casting dies, hot pressing molds, semiconductor jigs and fixtures, and as heating elements.

first look at the former variety which are metal intercalated compounds of graphite.

In sliding applications, the surface which undergoes friction is faced with high temperature due to friction as well as arcing, and thus requires intercalated metals which have both high vapor pressure at the generated service temperature and also provides molecular surface for sliding while performing as a good conductor of electricity. In such material the non-metallic component while providing necessary lubrication also prevents seizure or welding of the rubbing surface. These materials are generally made by copper, graphite sintered and shaped for required application. A third metal such as lead may also be added to further improve upon the properties. N.P.L. New Delhi has produced such materials with natural graphite, copper, tin, and lead powder intercalated by powder-metallurgical technique. A combination of such metallic and non-metallic phases used to yield a range of physical properties and further the composite material possess compatibility, conformability, embed ability required for thermal, electrical conductance and adequate lubrication behavior.

Other properties required with such brushes are carbon film transfer on the counter-surface, corrosion and oxidation resistance, commutation ability to suppress spark at the interface, ability to damp down vibrations and ride over the commutator surface even at high speed. The first carbon-brush industry was installed at UK (Morganites Inc) some 85 years ago. This company now has a collaboration with Assam Carbon Products Ltd., Gauhati (Assam), set up in 1963, to produce carbon blocks, brushes, current collectors (shoes, pads used in over-head cranes in steel industry and electric locos overhead wire slider) and special carbons (like scaling rings, gland rings, bearings, vanes, throughst pads, etc). The company later collaborated with Ringsdroff-Werke, West-Germany (in 1987) to make advanced moulded graphite products (for making continuous casting dies, pressure sintering dies, shaped electrodes for electric discharge machine, epitaxy for crystal pulling, jigs for glass to metal sealing, crucible for plasma coating and heating elements for semiconductors) by isostatic pressing technique with fine grained, large size graphites with isotropic properties. The company also collaborated with Sigri GmbH of West-Germany to produce high-temperature graphite materials (1300–3000°C) for metallurgical industries, iron and steel continuous casting, glass making, extrusion, and industrial furnaces making. Various such carbon products with their uses are shown in Table 7.20.

Carbon bearings are extensively used where contamination from oil/grease is undesirable, where temperatures are too high for conventional lubricants, and where operating conditions preclude use of other material.

Table 7.20 Typical applications of carbon bearing, sealing rings and gland rings

Product	Use	Wet/Dry	Shaft-speed	PV-factor	Max. Temp.
CARBON BEARINGS:	Chain grate stocker	Dry	0.2 rev/min	146 max	300°C
	Flue gas damper	Dry	Slow oscillating	—	350
	Furnace charging machine (10 ton)	Dry	24 rev/min	1820	500
	Veneer drying oven	Dry	7-108 rev/min	1720	160
	Rust proofing conveyor	Dry/wet	30 rev/min	785	225
	Submersible pump motor	Wet	1500 rev/min	36,400	—
	Vertical centrifugal pump	Wet	1450 rev/min	—	100
	Aircraft fuel pump	Wet	5000 max	2,400,000	—
SEALING RINGS:	Pump seal	Dry/wet	—	7-350 kgf/cm ²	—
Gland rings:	Steam turbine (as pressure seal at high temp in both high pressure & low pressure). Compressor, blower & fans (air & gas sealing).	Dry/wet	50.8 m/s	—	350°C
	(air & gas sealing).	Dry/wet	50.8 m/s	—	350°C

Usually in dry operations the maximum permissible load depends on the wear rate that can be allowed. The maximum permissible speed is determined by local heating at the rubbing surface. Wet operation on the other hand (with water, petrol, liquid chemicals etc.) has the advantage that it reduces friction and mechanical wear, and at the same time dissipates the frictional heat. Carbon bearings runs satisfactorily under conditions which are so varied that it is impractical to give maximum load and speed figure, which can be applied universally; Accordingly an approximate guide has been evolved called PV-factor (product at unit pressure, kg/cm_2) based on projected area of bush i.e., total load divided by length times bush I.D and shaft peripheral speed (m/s) which experience has shown to be satisfactory with grades and operating conditions mentioned in above table.

Above company is also producing carbon brush holders in collaboration with MCL-Bown of UK. On the other hand, indigenous development in this direction includes setting up of private companies like Beni Ltd. (Patiala, Punjab) in 1956 with N.P.L, New Delhi know-how for making carbon brushes used mostly in railway carriage fans, and later metal graphite brushes supplied by Assam Carbon. Metal graphite brushes are now produced in small-scale sector at Varanashi and also elsewhere in the country. India is now self-sufficient with respect to metal-graphite brushes which constitute 25–30% of total brush consumed in this country. Rest 60–65% is electro-graphite grade brushes. Resin bonded and graphite grades are roughly 10–15% of the total market. The main reason for shortfall in the latter production is due to non-availability of raw materials which is mandatory from quality of finished product point of view and must adhere to strict regulations. Table 7.21 shows the raw material and processes adopted by carbon brush industry.

And finally, let us look at another variety of graphite used in sliding application for its mechanical property and no electrical requirement.

These materials are called “colloidal graphite” and indigenously developed by R.R.L., Hyderabad. Use of these graphites are mainly for lubrication of heavy machineries, but also finds certain other applications as well like, in electronic industry for coating TV –screen, cathode ray picture tube etc. In metal forging industry they are used to reduce frictional

Table 7.21 Raw material and processes for carbon brushes

Graphite	Natural, electro-graphite.
Coke	Petroleum, retort, calcined coal
Carbon-black	Lamp black, furnace black.
Metal	Copper, silver and others.
Processes	Grinding, mixing, sintering.
Binder	Tar, pitch, resin
Heat treatment	Kiln & by graphitization
Impregnation	Oil, resin, and others.

forces thus preventing cracks on the press mould and the moulded material. In glass industry, it finds application as dispersant for parting the formed glass article from the mould in hot condition and also as a lubricant for drawing tungsten and molybdenum wire. These products are made by dispersing finely ground graphite powder (about –300 BS mesh size) in mineral or lubricating oil. The choice of the dispersing medium depends on the specific use and thus products may have viscosities in the range 5–500 cps and flash point 50–250°C. Graphite content in the mix varies from 10 to 20% and specific gravity 1 to 1.25.

7.6 Resistor coke

For the production of graphite (Acheson process), carbon granules are used as packing material which act as conductors and provide electrical resistance for the generation of heat in the furnace. This carbon is called “resistor coke” and should satisfy certain norms like, it should not undergo rapid graphitization even at 3000°C and should retain sufficient mechanical strength. Carbon granules from CPC is often used as resistor-coke in graphitization furnace. But from electrical conductance point of view, it is inferior to metallurgical coke because graphitizability and hence conductivity of petroleum coke is considerably more than that of metallurgical coke. Even in case of metallurgical coke the electrical conductivity sharply increases with temperature of calcinations. Hence ordinary coke as such is not suitable for this purpose. It appears that coke prepared from carbonization of a proper blend of high and low rank coals, provides solution to this problem. In high rank coal cross-linking is much weaker, structure is more compact and crystallites are existing in nearly parallel orientation. In coals of lower rank, cross linking is strong and orientation of crystallites is random. Hence the later is non-graphitizing and less conducting. With increase in rank the number of fused rings increase from 3 to 7 to 8 and in anthracite it goes upto 30 or more; This along with the fact that cross- linking decreases, explains graphitizability with increase in rank. Benzene insoluble part of a solvent refined coal (non-fusible) gives non-graphitizing carbon. CFRI, Dhanbad (India) studies indicate that blending of high rank Jharia coal and low ash (2–3%) low rank Assam coal generates on carbonization a coke which is reasonably strong and at the same time non- graphitizable with less conductivity for its disordered structure. As time passed since the, low ash Assam coal is becoming scarcer and this necessitates modification of earlier blends. Extended work on the subject later showed that coke produced from the revised blend of beneficiated Jharia coal and much lower proportion of ROM-Assam coal (9–10% ash), has all the specification meeting standard resistor-coke. The new formulation is expected to reduce the cost of resistor

coke by the full utilization of Assam coal without resorting to the current practice of hand picking in order to reduce ash content at the production site.

7.7 Graphite refractories

This group of carbon refractory constitute multiphase materials made from flaky natural graphite along with refractory materials such as zirconia, alumina etc. These materials are designed to withstand molten salts/metals and slags. Flaky graphite is preferred for crucible and stopper-head manufacture which is bonded with high percentage of clay. N.M.L. Jamshedpur (India), has developed such materials and present aim is to manufacture larger sizes which are capable of taking more heat. The amorphous graphite sometime used to enhance slag resistivity of plastic clay refractory. Carbon-brick and block are used extensively as a refractory and may be made from foundry coke, petroleum coke, or anthracite coal, bonded with pitch or tar or low moisture material. Such refractory are being used increasingly for blast furnace where reducing atmosphere prevails within furnace. As graphite is readily oxidized at the temperatures required to process molten steel, also copper, aluminium alloys and furthermore soluble in iron, it is principally used in multiphase refractory. Graphite also markedly improves thermal shock resistance power which is paramount for refractory pieces which are often by many standards, massive weighing 25–50 kg. The SiC-bodies are used essentially for the melting of non-ferrous metals, usually in the form of crucibles. Typically induction frequencies in the range 1000–3000 Hz is used for such melting purpose, this calls for a known and controlled resistance in the crucible; accordingly the clay constituent in such crucible is very important (use of an organic binder leading finally to a coke bond generates a much lower resistance). These graphite bodies show typical behavior of dispersed resistor electrical characteristics (i.e., at low level of conductance, resistance is high and at high conduction level the resistance is low). However, bulk consumers of clay-bonded graphites are blast furnace operators. The alumina-graphite, zirconia graphites are used exclusively for refractory for controlling and protecting the flow of steel during continuous casting. Morphological difference between flaky graphite and the more regular refractory particles makes processing difficult.

In addition, graphite presents predominantly a surface of very low energy which wets, if at all, with difficulty. Oxides such as – alumina, mullite, magnesia, and zirconia, typical of these used in conjunction with graphite are all readily wet by both aqueous and organically based binders. This difference in chemistry is reflected further in subsequent firing processes when although oxides will diffuse at temperature considered sensible by

refractory manufacturers. The natural graphite is relatively inert. Furthermore, should the temperature be raised to that at which mobility of carbon atoms might be achieved, chemical reactions would occur leading to the reduction of the oxides and the destruction of the graphite. As a consequence, the phases are normally cemented together by a third phase. This might be carbonaceous as typical of the bond in many carbon, graphite artefacts and derived from tars, pitches, resins or even sugars. It may also be a clay or similar oxide binder. In this case, the bond is essentially between the non-graphite phases in view of the non-wetting of the graphite by the oxide phases. Graphite offers thermal shock resistance by absorbing its own expansion (with temperature) within the void age of its structure. Considering electrical resistivity of graphite, the resistance/composition curves for such bodies are typical of dispersed resistors. Clay-bonded graphite crucibles are given shape in the same manner a earthen potter gives shape to his earthenware, but the silicon carbide crucibles are hydraulically pressed to generate desired shape. A good quality crucible thus, can sustain 50–60 heats in metallurgical industries.

7.8 Active carbon

These carbons are produced by partial gasification in steam and makes use of fluidized bed technology. Generally anthracite coal is used for this purpose although sometime it is also blended with other coals. Fluidized bed technology is adopted as it gives uniform burn-off to each granular particles. The activation process is based on the removal of carbon atoms as gaseous oxides by the reaction of carbon and steam, leaving behind a matrix of inter-connected internal pores. Carbon-steam reactions are the same as those used in coal gasification processes but the aim is to activate minimum for conversion to gas, consistent with adequate burn-off for the required pore structure. The plant operates batch wise and by varying the extent of carbon burn-off, the activity of the product can be controlled. The burn off also reduces VM as well as hydrogen content of the product. With progressive burn-off, the pore volume and mean pore size of the product increases, but at the expense of a reduced yield. The compromise is reached by limiting the operation between 750 and 1000°C. These products are mainly used as water clarifier and various effluent treatment plant. It is also used in filtering sugar to make it white and also as catalyst support. It is also used in pharmaceutical industry as the water and other material absorbents in the production of medicines. Semi-anthracitic coal available at Rajhara sub-basin of Daltonganj Coalfields (Bihar) has been found suitable for this purpose. A number of other materials like coconut and rice husk, coconut shell has also been used for manufacture of active carbon.

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8.1 Introduction

Generally there are two types of coal wastes – one generated at the mine head as fine coal powder and the other produced when coal is burnt for power generation. The later kind of waste commonly called coal ash and can not be disposed simply into river streams as it may contaminate surface water and choke the drainage system down stream. Coal combustion products (in short called CCP) are produced in various coal combustion and flue gas cleaning apparatus and includes fly ash, bottom ash, flue gas desulfurization discharges, boiler slag, FBC ash and cenospheres.

Ash is a porous media, a strong absorbent and thus can act as a great receptacle or container for many substance. It can make an ideal insulator. Large internal surface imparts strong adsorption-desorption properties. One of the ideal solution of fly ash disposal is its acceptability in agriculture as a soil conditioner. Ash can be made to act as a substance to fertilizer applicator. Work of a forestation and ash-biomass interaction need to be studied in detail. Another simpler ways of ash disposal in land reclamation or even stumping of mine excavation; since many Indian fly-ash are poorer in lime content, therefore have lower binding strength and thus they are considered more suitable for slope stabilization than brick making. Indian coals also contain considerable amount of halogen particularly chlorine and fluorine. With many transitional elements present in the ash matrix, which are known to be excellent catalysts for forming chlorofluorocarbon (CFC) during coal burning and cause damage to ozone layer (even for trace CFC production) and the present industrial production of CFC would be mere peanut in such case. Production of CFC in power plants need to be checked. As such many poly-aromatic hydrocarbons have already been detected in coal ash. Some ashes is likely to contain trace elements especially Indian coal ash needs to be checked for U and Th and possibly Se and Ge.

Volume wise among all the CCP's produced, fly ash constitute about 58%, bottom ash 26%, and boiler slag along with FBC ash collectively constitute 17%. Uptill now the most common beneficial use of CCP has

been as a replacement of original materials in concrete and cement production, structural fill and producing gypsum board. Thus typically out of total CCP generated 41% of fly ash, 43% of bottom ash, 87% of FGD collect, 97% of boiler slag, and 69% of FBC ash is utilized for above purpose. It may be mentioned here that places where high sulfur coal is used in FBC boiler for power generation, lime is injected into the combustor for arresting sulfur and fixing it into the bed as calcium sulphate. The FBC boiler ash after necessary treatment can be used for neutralizing acid mine water generated in the same region and thus protect valuable mining equipments from corrosion (Ref: Mazumder B, Indian Patent (filed by CSIR, New Delhi) No. 759/DEL/90, 1990).

Table 8.1 shows various beneficial use of CCP's based on their physical and chemical characteristics

Table 8.1 indicates the following:

- (a) concrete, wall board, structural fill, cement and waste stabilization comprises the highest volume beneficial use of CCP's.
- (b) the use of fly ash as a pozzolanic binder in concrete represents the largest single beneficial use application of a CCP material. Flyash can substitute for finished portland cement in concrete and can be a valuable additive to concrete mixtures that enhances the strength, durability and workability of the concrete product. Reaction between alkaline port- land cement with certain siliceous rocks and mineral, causes abnormal expansion which results in crack in the resultant concrete. Use of class-F fly ash reduces such expansion and thus beneficial in using this CCP to structural concrete making. It may be mentioned here that two classes of fly ash are defined in ASTM C618 – Class-F and Class-C. These classifications are related to amount of free lime (CaO) present in the ash and grade of coal. Both class-F and class-C fly ash have pozzolonaic properties. Class-F fly ash typically contains 2–6% CaO and requires additional lime to obtain self hardening properties. Class- C fly ash on the other hand typically contains 15–35% CaO and does not require additional lime for self hardening properties. The beneficial use of fly ash in concrete are – improved workability of concrete due to the nature and shape of the ash particle. The physical properties of coal fly ash specifically, unique spherical shape and particle size distri- bution make it a good mineral filler in hot mix asphalt applications as well. It improves the fluidity of the flowable fill and grout and reduces permeability of the concrete. Accordingly fly ash is used as a borrow material for highway embankment and as a flowable material in back- fills. Similarly for its unique property mentioned above fly ash is also used as a mineral filler in asphalt pavement making.

Table 8.1 Use of CCP in making various industrial products

Types of CCP	Beneficial use
Fly ash	<p>Concrete: constants of a mixture of approximately 25 % fine aggregate (sand), 45 % gravel, 15 % Portland cement, and 15 % water. Class C and class F fly ash can replace a percentage of the Portland cement component of concrete. Fly ash to enhanced concrete strength and durability, and is typically less expensive than Portland cement.</p> <p>Cement clinker: Clinker is an intermediary product of the portland cement manufacturing process. Clinker is formed when a raw mix consisting of limestone, clay, bauxite, iron and quartz are heated in a kiln at higher temperature. Fly ash can be blended with limestone or shale and fed into the cement kiln to make clinker, which is then ground into Portland cement.</p> <p>Structural fill: Structural fill is an engineered material used to raise or change the surface contour of an area and to provide ground support beneath building foundations. It can also be used to form embankments. Depending on the soil type, flyash can replace a percentage (generally 50 %) of virgin rock, dirt, sand or grave in structural fill.</p> <p>Waste stabilization: fly ash can be used in place of Portland cement kiln dust, or time to solidify and harden wet or liquid waste before it is land filled. Class C fly ash hardens by itself in contact with moisture, but class F fly ash must be mixed with another hardening agent, such as Portland cement, in order to be used in waste stabilization.</p> <p>Wallboard: Gypsum wallboard (or drywall) is used as interior finish in the construction of homes and building. Wall board is comprised of a layer of gypsum stucco sandwiched between two sheets of heavy paper. FGD gypsum can replace 100 % of virgin gypsum in wallboard after the excess moisture</p>
FGD Gypsum:	<p>Agricultural soil amendment: FGD gypsum can be used to replace liming agents as an agricultural soil amendment soil and crop types.</p> <p>Cement additive: In the production of portland cement, clinker is blending with a small amount of gypsum prior to grinding into finishing Portland cement. FDG gypsum can be used to offset virgin gypsum in cement manufacture.</p> <p>Structural fill: Structural fill is an engineering material used to raise or change the surface contour of an area and to provide ground support beneath building foundations. It can be used to form embankments. Bottom ash can be used to offset virgin sand and gravel in structural fill.</p>
Bottom ash:	<p>Road base: A road base is a foundation layer underlying a pavement and overlying a subgrade of natural soil or embankment fill material. It protects the underlying soil from the detrimental effects of weather conditions and from the stresses and strains induced by traffic loads. Bottom ash can be used to offset virgin sand or gravel in road base.</p> <p>Concrete: Bottom ash can be used as a coarse aggregate for concrete blocks, with its porous nature often qualifying the product for lightweight classification.</p> <p>Blasting Grit: Blasting grit is an industrial abrasive used to shape, cut, sharpen, or finish a variety of other surfaces and materials. Boiler slag can be used as a replacement for other slags or virgin sand as blasting grit.</p> <p>Boiler Slag:</p> <p>Structural fill: is an engineered material used to raise or change the surface contour of an area and to pro be used to form embankments. Boiler slag is occasionally used to offset virgin sand and gravel in structural fill.</p>

- (c) FGD gypsum serves as a substitute for virgin gypsum in wall board construction. This high value represent the second largest use of CCPs by volume, and second highest utilization rate at 77%.
- (d) although one of the smaller material streams, boiler slag beneficially used as blasting grit, structural fill and waste stabilization, as the highest percentage of all CCPs used. Boiler slag possess two key properties that make it ideal for beneficial use: the highly uniform quality of boiler slag increases its acceptance among potential end users and boiler slags unique abrasive properties make an excellent material for blasting grit and asphalt shingles.

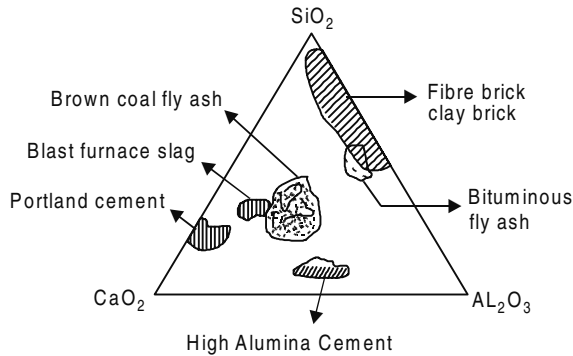
Since most of the CCPs goes towards replacement of virgin material, it is important to make a comparison in price between the virgin material and the CCP replacing it. An example of such comparison has been provided by American Coal Ash Association and shown in Table 8.2.

8.2 Powder coal and coal briquetting

Good amount of coal fines are generated in all mine heads which because of its under size do not find any market and consequently rejected leading to environmental pollution. Additionally, North-Eastern coals because of their inherent friable nature generates as much as 40% coal fines with each ton of coal mined or at the stockpiling head. One of the best method of using them is to form them into briquettes (after adding necessary binders) which can find ready market both in domestic and industrial sector. Hot stage briquetting of Indian Coals have been studied extensively by

Table 8.2 Sample CCP and virgin material prices for CCP application

Virgin material	2005AVG price (per ton, free on board)	CCP substitute	2005 AVG price (per ton, free on board)
Portland cement	80 \$	concrete quality fly ash	0 to 45 \$
Virginal aggregate for fill	3 \$	flyash for flowable fill	not available
Virginal aggregare for road base	5 \$	bottom ash or fly ash for road base	4 to 8 \$
Lime for soil stabilization (hydrated lime)	83 \$	fly ash for soil stabilization	10 to 20 \$
Lime for waste stabilization (Quicklime)	66 \$	fly ash for waste stabilization	15 to 25 \$
Virginal aggregate for snow and ice control	5 \$	bottom ash for snow and ice control	3 to 6 \$
Gypsum for wallboard interior	4.50-12.0 \$	FGD Gypsum	0- 8.00 \$



8.1 Composition of various coal ashes and composition of cements shown by triaxial diagram.

CFRI, Dhanbad and a method evolved for briquetting Indian coals, lignites at 100–400°C temperature and 1–2 ton/sq. in. pressure.

Binderless briquetting which essentially uses high temperature and pressure method was also developed by above institute. National Coal Board, UK. reported a process for binderless briquetting by compaction of coal powder under pressure and shear strain. The briquettes thus produced have more strength than those produced by simple pressing. High rank coal with volatile-matter of about 17.5% when briquetted by this process, burns more freely in open grate than the parent coal and thus a suitable fuel for smoke-controlled areas. The carbonization of low rank coal in a fluid-bed can be followed by binderless char briquette to form a premium smokeless domestic fuel. Coal India Ltd., N.E. Coalfields, Margharitta (Assam) made attempts to briquette high volatile N-E coals. Special problem with these coals fines is that besides its high sulfur content, high volatile matter (30–40%) makes the briquettes liable to disintegration while heating due to excess gas formation within the briquettes and its passage through the briquette breaks it. The basic process developed by this organization involves coal preparation (fines), mixing with binder, followed by briquetting and carbonization of the briquettes under controlled condition. Fine coal (-3 mm size) is mixed with clay binder in the 95:5 ratio and pressed into briquettes which is dried in a horizontal drying tunnel at 150–200°C. Carbonization is done in a vertical furnace with sloping floor for continuous operation at 800–900°C. Production of briquettes, however, in this region has received a set-back for the simple economic reason that C.V. of the briquettes do not equal to the long distance transportation cost from this region necessary, specially for this area to find a wider market. Moreover availability of gas in the region competes with the economy of such process in industrial sector as well. CFRI, Dhanbad also developed a pellet coke process for domestic fuel production

(patent No. 127909, Indian Patent). The process involves fine milling of the raw material, mixing the fine with additive, palletizing the mixture in pan or disc type pelletizer in presence of water sprays, without application of mechanical pressure, drying the green pellets and finally carbonizing the dried pellets. The uniqueness of the process is that it does not require any steam or additional fuel like oil, gas, etc., (the heat required for processing is supplied by the raw material itself). The raw material is coking coal or a composite mixture having caking-index above 10 (BS). Ingredients other than caking coal, such as non-caking coal, char/coke-breeze, limestone, dolomite, iron ore, etc., can be added in the raw mix as and when necessary. The product burns nicely on conventional domestic "chullah."

8.3 Coal wastes as adsorbent

CFRI, Dhanbad has found another alternate approach towards utilization of coal fines (-3 mm size) and coke breeze (-3 mm size) as solid adsorbents. Char produces less cumulative fines than its parent coal indicating better size stability under identical condition of exposure. Char prepared from high volatile coal at 650–700°C possess well developed pores while distorted and squeezed pore openings characterize char from low volatile coal and anthracite. Fly-ash on heat treatment affects the mineral matter and generates extremely fine pores, around 130°C, with variation from 50 to 350°C. With bed porosity ranging from 0.47 to 0.65 char/fly ash can be used for different throughout rates in fixed-bed clarification or decolourization. Char can remove mild acidity from water. Char/coke breeze thus produced can also be used as adsorbents in process industry for removing undesired small constituents from fluid. Char can effectively remove clay suspension in water and thus works as a clarifier. Odours from liquids can also be removed with longer residence time. Thus chars, Coke-breeze, and coal-fines possess properties that qualify them to be used either as good filters-aids, Activation of these material by physical and chemical methods further enhance their adsorbent property. Raniganj coal chars found suitable for gas adsorption in industrial pollution air.

8.4 Utilization of fly-ash

Finely divided ash, collected by precipitators from the flue of pulverized Coal-fired thermal power station (dry bottom) is commonly called fly-ash or pulverized fuel ash. Fly ash has 15–20% fine particles as collected as bottom ash (60–70% below 76 micron) and the rest coarser part contains spongy or heavy material. Mineralogically in general fly-ash contains 20–40% crystalline material mainly quartz, tridymite, mullite, magnetite, and rest being glassy mass. The amount of glassy material in fly-ash

Table 8.3 Chemical composition of some fly ashes (%)

Chemical Composition	Bokaro DVC	Durgapur DVC	Korba MPEB	Indraprastha	Neyveli NLC	Fluidized Bed Combustion
Loss on ignition	0.02	11.33	3.3	4.9	2-Jan	-
SiO ₂	50.4	50.03	58.3	60.1	45-59	59
Al ₂ O ₃	30.7	18.2	24.6	18.6	23-33	25.7
Fe ₂ O ₃	3.3	10.2	4.4	6.4	0.6-4.0	7.4
CaO	3	6.4	5.4	6.3	16-May	2
MgO	0.9	3.2	3.9	3.6	1.5-5.0	2
TiO ₂	0.9	-	-	-	0.5-1.5	1.5
Mn ₂ O ₃	0.3	-	-	-	-	-
P ₂ O ₅	0.3	-	-	-	-	1.2
SO ₃	1.7	-	-	-	Traces to 2.5	0.45
Alkalies	3.1	-	-	-	-	0.83
Specific surface cm/g		2759	1325	2084	4016	2800-3250

determines its pozzolanic (i.e., susceptible to reaction with lime to form calcium-silicate hydrate) activity. Fly-ash is used in France, Netherland and UK for making roads, as fillers and for manufacture of cellular concrete blocks. In India it is used as soil stabilizing agent, production of light aggregates, production of block, bricks with clay as binder, and for making non-sintered chemically bonded bricks. The last is the most promising and developed by Mazumdar et al of CFRI, Dhanbad (Patent No. 128684, Indian Patent) and involves mixing fly-ash with requisite quantity of lime and sand (sand provides coarse phase which allows moisture movement within the body. Sometime crushed bottom-ash is also added), and a small amount of accelerator. The mixture is shaped as brick under a pressure of 100–200 kg/cm² in a hydraulic or mechanical press. The brick is then kept in shed at ambient temperature for about 48 hs for primary reactions between lime accelerated by the additive. Then steam curing is done at 95–105°C for 4 h or 120–125°C for 2 h, or at 150°C for ½ to 1 h. The bricks further gain strength storage or during use. These bricks have density 1550 kg/m³, crushing strength 70–200 kg/cm² and free-lime less than 0.2%. West-Bengal Housing Board (with fly-ash of Durgapur Power plant) and M/s Jagadhatri Brick Work, Barrackpore (W.B.) with fly-ash from Titagarh Thermal plant, have set-up commercial units for production of flyash bricks.

8.5 Use of fluid-bed boiler ash

Table 8.4 below shows the general composition of various coal ashes vis-à-vis that of common cement. Earlier attempts to convert coal ash to cement involved shifting the composition to necessary phase composition by addition of limestone and other ingredients. Fluid-bed boilers using high sulfur coal, where lime is added to arrest sulfur in-situ, still provides another

Table 8.4 Composition of Bituminous and Brown coal ashes of cement

Component	Bituminous coal ash (%)	Brown coal ash (%)	Cement composition
SiO ₂	45-55	20-70	23%
Al ₂ O ₃	20-30	3-15	4.5
Fe ₂ O ₃	10-20	2-25	3.11
CaO	2-5	10-45	64.1
MgO	1-3	0.5-10	0.79
SO ₃	0.5-3	2-15	—
K ₂ O	1-5	1-3	0.64
Na ₂ O	0.5-2	—	0.54

type of ash which has very low percentage of unburnt carbon but saturated lime with CaSO₄. Present author has used N.E coals (high sulfur) in FBC-boiler ash of which after microscopic examination showed an impervious thin layer of CaSO₄ in each lime particle and having a core of 90% unconverted lime. A patent filed by the author utilized these spent ash after crushing to bring out unreacted part, and after necessary adjustment in composition used in cement making by vertical shaft kiln technology. These resulting cements were found to meet all statutory ISI- specification for pozzolonaic cement.

Yet in another trial (Mazumder patent No. 759/DEL/90, CSIR) after bringing out the unreacted part of the spent lime ash, it was found suitable for neutralizing acid mine water in North-Eastern coalfields. Application rate of the ash depends on the acidity of the mine water.

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Pollution generation by coal and its abatement

9.1 Introduction

Pollution due to coal starts from the mine head itself. Here the fine coal dust generated due to mining pollutes both the water and atmosphere. Since it is not being carried away further, it is best contained by utilization of gas mask which is commercially available in the market and meant mainly for mine workers. The other pollution problems due to coal can be classified into three categories – solid, liquid and gaseous pollutants. We discuss in detail containment procedures for all these pollutions, but before that let us see the actual statutory government norms for gaseous pollutants.

9.2 Environment pollution standards

Maximum allowed toxic gases in environment varies from country to country and even from place to place within a country. Besides, one time concentration limit and inhalation time is also important in determining hazard from a particular pollutant. Along with toxic gases, particulate materials and noise level also poses a great risk to our health.

According to “British Gas Engineers Handbook,” maximum allowed gas concentration of H_2S , CO and CO_2 is as follows:

Carbon-dioxide	= 5000 ppm = 9000 mg/m ³
Carbon-monoxide	= 100 ppm = 110 mg/m ³
Hydrogen sulphide	= 20 ppm = 30 mg/m ³
	= 4 ppm (for pipeline gas)
	= 0.01 ppm (for industries)

It may be noted from above that, in industries H_2S limit is lower as in processes it may cause catalyst poisoning. In combustion 1% sulfur content in coal gives about 700 ppm of SO_2 and 4% sulfur content in coal gives about 0.35% SO_2 concentration in the flue. Health limit of these later gases are:

CO	= 10 mg/m ³ (9 ppm) for 8 h inhalation
	= 40 mg/m ³ (35 ppm) for 1 h inhalation

$$\begin{aligned} \text{NO}_x &= 100 \text{ mg/m}^3 = 0.05 \text{ ppm} \\ \text{SO}_2 &= 13 \text{ mg/m}^3 \end{aligned}$$

Environmental standards in Japan are still different because of its high population density: These standards are as follows:

$$\begin{aligned} \text{SO}_x &= 85 \text{ ppm (0.16 lb/10}^6 \text{ Btu fuel)} \\ \text{NO}_x &= 60 \text{ ppm (0.13 lb/10}^6 \text{ Btu of fuel)} \\ \text{Dust} &= 20 \text{ mg/m}^3 \text{ (0.014 lb/10}^6 \text{ Btu fuel)} \end{aligned}$$

In USA Environment Pollution Agency' (EPA) has put forward following limits for harmful gases:

$$\begin{aligned} \text{SO}_x \text{ (lb/10}^6 \text{ Btu)} &= 1.20 \text{ (or SO}_2 = 4.3 \text{ kg/10}^6 \text{ kcal)} \\ \text{NO}_x \text{ lb/10}^6 \text{ Btu)} &= 0.70 \\ \text{Dust} &= 0.10 \text{ lb/10}^6 \text{ Btu.} \end{aligned}$$

In India, a flexible attitude has been adopted towards fixing these norms. These can be seen from followings as set forth by State Pollution Board, Bombay:

$$\begin{aligned} \text{SO}_x \text{ from sulfuric acid plant} &= 600 \text{ ppm} \\ \text{NO}_x \text{ from nitric acid plant} &= 300 \text{ ppm} \\ \text{Dust from fertilizer plant} &= 60 \text{ mg/m}^3 \end{aligned}$$

This last item dust or particulate matter again has been differentiated based on population at various places:

$$\begin{aligned} \text{Particulate} &= 150 \text{ mg/m}^3 \text{ for large cities.} \\ &= 250 \text{ mg/m}^3 \text{ for medium size cities.} \\ &= 500 \text{ mg/m}^3 \text{ for small cities.} \end{aligned}$$

With respect to thermal power plants, a altogether different set of standards have been set by "Stack Emission Regulation" norms:

- (a) Particulate emission standards for thermal power plants (Ref: Thermal power emission regulation, Part-I; Comprehensive Industry Documentation. COINDS/17/83-84, CBPCWP, New Delhi 1984):

Boiler size	Allowed in protected	Other areas (old before '79)	Now (April '79)
Less than 200 MW	150 mg/m ³	600	350 mg/m ³
200 MW and above	150 mg/m ³	300	150 mg/m ³

- (b) SO
- ₂
- emission standards for power plants (Ref: above):

Boiler size	Stack height
Less than 200 MW	$H = 14.K^{0.3}$ (K=SO ₂ emission in kg/h H = stack-height in m)
200 to 499 MW	200 m
500 MW and above	275 m

- (c) Revised particulate emission regulations and appropriate control device (Ref: Boiler emission regulation. Part-IV; Comprehensive Industry Document, New Delhi, 1987)

Capacity of boiler	Control device	coal consumption	Particulate emission
Less than 2 ton/h	Cyclones	8.5 MT/day	1600 mg/m ³
2–15 ton/h	Multiclones	8.5–64 MT/day	1200 mg/m ³

Steam generation cap.	Coal consumed (ton/day)	Stack height
Less than 2	8.5	2.5 times neighbouring highest building
2–5	8.5–21	12 m
5–10	21–42	15
10–15	42–64	18
15–20	64–104	21
20–25	104–105	24
25–30	05–126	27
More than 30	More than 126	30

9.2.1 Pollution monitoring equipments

In earlier times pollution analysis was done through tedious methods like wet-chemical analysis or batch analysis using a gas-chromatograph. But in the past one decade or so, a number of continuous and direct on line assessing devices have appeared in the market, which makes all previous methods obsolete.

All currently available pollution monitoring devices, can be classified under two categories – one stationary (as is used for continuous on line monitor of flue gas composition at a high chimney) and the other portable/mobile unit for monitoring time to time at different locations. Both the instruments use more or less same type of analysis procedure: CO₂ is

monitored by thermal/fuel-cell detector, CO by infra-red detector, SO₂, H₂S by ultra-violet detector, and NO_x by the chemi-luminiscense principle. Gases are received by a special probe which sucks the gas by an incoming air jet, filtered and sent to a sample conditioner where it is being diluted by a carrier gas to a definite ratio and then goes into the detector. Chemiluminiscense detector has a ozone generator built into it. Oxygen is being detected by a Zirconia fuel-cell system. These detectors are fast, accurate and gives programmable time-average results.

Water pollution, on the other hand, is largely determined by wet analysis or by spectrophotometric means. With increase in contamination, additional metal ions are being detected and every year norms of health hazard due to new metals is being revised. One such contaminants is detergent; Earlier non-biodegradable detergents mix with underground potable water and accordingly statutory regulations are being imposed to replace them by biodegradable types.

9.3 Solid pollutants and its abatement

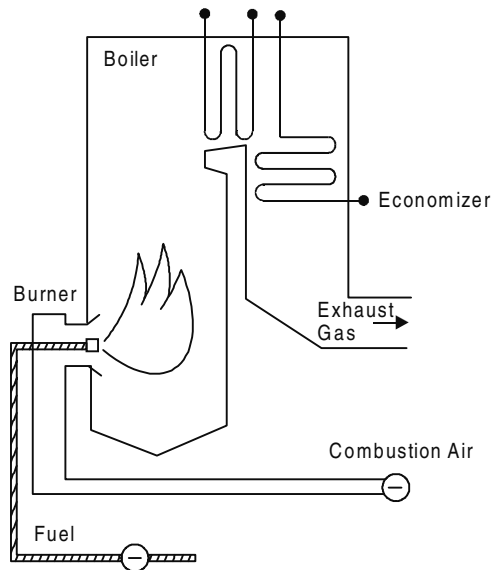
Solid pollutants are particulate materials emanated by thermal power stations through their chimneys. Limit of such pollution is mentioned in above section. Larger particles can be easily separated by use of proper cyclone. Present author has used cyclone separator-cum-water-scrubber with fluid-bed boiler using highly friable coal and obtained excellent results in this direction. It may be noted here that particles having sizes below 100 micron is different to trap by dry cyclones. They are trapped by electrostatic precipitators or bag-house filters.

9.4 Liquid pollutants and its abatement

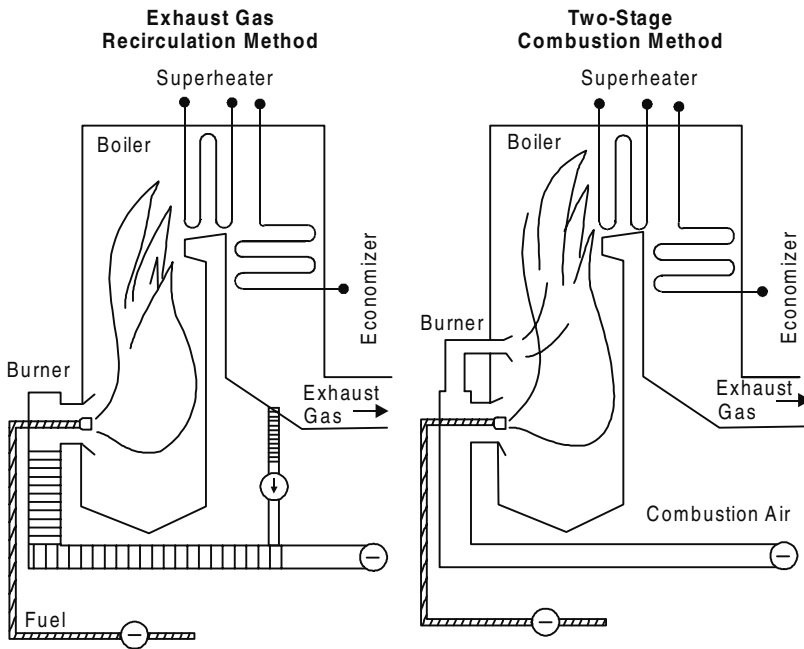
These are the pollutants discharged in large volume by coal washeries mainly. Central Mining Research Station, Barwa Rd, Dhanbad (Bihar), made a survey in June 1986 (under sponsorship of Dept of coal, Ministry of Energy, Govt. of India) and their findings as well as suggested methods of containments are as follows:

Down stream washery effluents is found not only to contaminate potable water, they also affect aquatic lives by polluting the rivers. Washery effluents contain suspended fine coal particles as well as various coal tar chemicals. The simplest way of treating these effluents is to sediment them in open pond and then recover the coal fines. In one method, the effluent is pumped to abandoned section of mines and the solids are allowed to settle there. Another method uses filters for the effluents and settling ponds for the filterates. The effluent may also be pumped to some properly prepared lagoons in the top of existing spoil heaps made from solid refuses

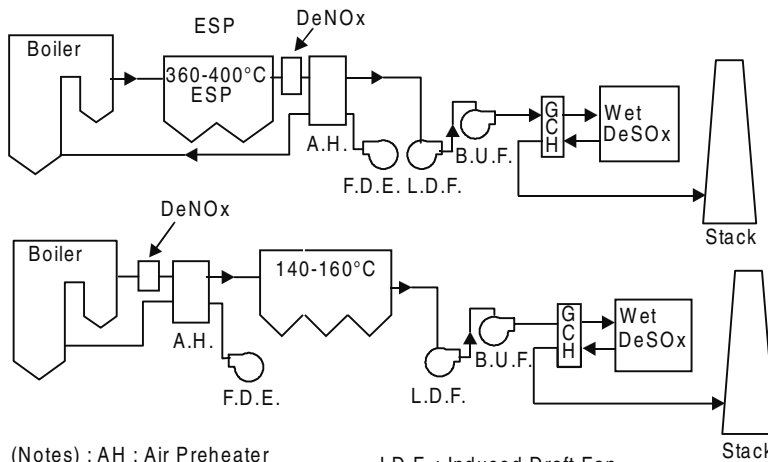
of the plant. This method is effective in removing suspended solids from the effluent but seepage might be undesirable due to leaching of various salts from the re-use bed (Smith, 1968). Hummer (1965) has recommended pumping the effluent to storage pond or dams of sufficient capacities and to allow the water to evaporate. Noone (1963) suggested a method for concentrating the froth-floatation tailings in thickeners, filtering the thickened sludge, disposing it off and recirculating the thickener overflow and the filtrate. An American patent (Shubert, 1974) suggested the clarification of washery effluent in two stages. Coal particles in the effluent are recovered in first step by agglomeration with heavy hydrocarbon-pil and filtering the agglomerates as cake while in the second step the filtered water is freed from mineral matter by settling. Gieseke (1963) prefers floatation of coal fines and suggests coagulation of floating tailings with synthetic coagulants for recovery of refuse water. Addition of coagulants is recommended by many authorities and appears to be in wide use in treatment of coal washery effluent (Bulovtskii and Pilyasov, Chattopadhyay et al, Kotkins and Rozhnova, Harpar, Rozgaj). This effluents from coal washeries are normally treated by plain sedimentation in settling ponds. The effluent is allowed to pass through two or three ponds in series and the overflow of the last pond flows out of washery. But in most cases, discharges from these washeries contain sufficient amount of coal fines which are again recovered by private parties by settling the fines in ditches. The overflows of these ditches go to river as the final effluent of the



9.1 Exhaust gas recirculation method and two-stage combustion method.



9.2 Variation in gas composition with coal grade.



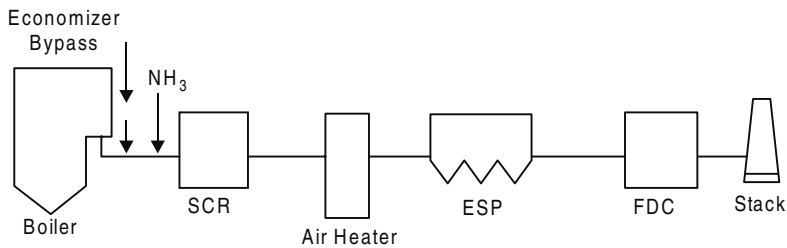
(Notes) : AH : Air Preheater
 F.D.F. : Forced Draft Fan
 I.D.F. : Induced Draft Fan
 B.U.F. : Boost Up Fan

9.3 Electrostatic precipitator systems (hot or cold ESP application).

washery. Overflow of the ditches going to river as the final effluent still contain significant amount of suspended solids and continues to seriously pollute the river water. Specifications for limit of pollutants, specially or washery effluent still does not exist, and these specified industrial effluents for inland surface waters have been accepted for this purpose. IS:2490

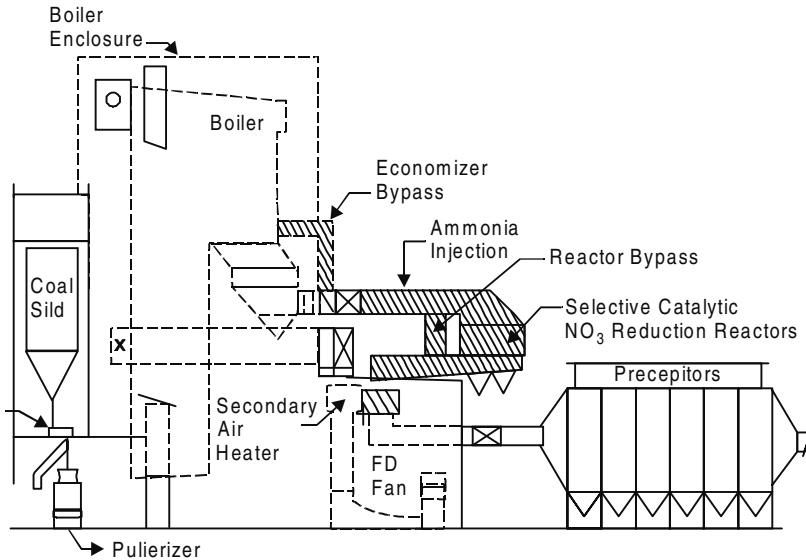


9.4 Hot electrostatic precipitator of Matsushima coal field power station (EPDC).



9.5 SCR System placement in flue gas stream.

(Part-I) specifies suspended solid limit as 100 mg per litre (1974) for industrial effluents. Commercially “Truefloc” a synthetic coagulant found to be effective for settling fine solid particles from washery. It is advised in normal cases to use two sets of settling ponds for better control of effluent treatment. Deposited solids should be timely excavated so that a set of empty ponds is available as soon as this is required to receive the effluent. Treated effluent water should be recirculated to the washery. Effluent water should also be tested for presence of possible coal chemicals and its recovery. Still research is going on for evolving synthetic materials for settling the sludges from washery effluents and render is advised to consult corrent literature for the same.



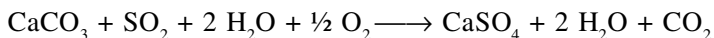
9.6 General arrangement of selective catalytic reduction (SCR).

9.5 Gaseous pollutants and its abatement

Free burning of coal in air goes out through following harmful gases like CO_2 , CO , NO_x and SO_2 (if sulfur is present in the coal). Out of these four gases, CO_2 do not causes any direct damage to our health but contributes to the global warming (greenhouse effect) CO on the other hand, is highly toxic and its limit set by pollution control board has been mentioned earlier. CO can be controlled by ensuring complete combustion of the coal. Proper fuel to air ratio should bring down CO level to acceptable limit. NO_x is responsible for acid rain and is formed when combustion temperature of coal exceeds 1200°C . One remedy to such problem is switching over to fluidbed combustion which operates much below 1200°C and gives higher combustion efficiency. Arresting particulate matters in the flue also becomes easier by resorting to such process. The fourth polluting gas, SO_2 , is a real problem with high sulfur coals and we discuss its abatement in detail in following section.

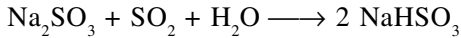
Sulfur, as mentioned earlier, occurs in coal both as inorganic form (like pyrites) or in organic form (like thiophenes, thiols, disulfides, etc). If it is present in the coal as pyrites, it is easier to separate them mechanical-means such as by magnetic or gravity separation. But if it is in organic form no mechanical means can separate them and it comes out as H_2S in reducing coal conversion process (e.g., coal gasification) or as SO_2 in combustion processes. Elemental sulfur can be formed when it is in H_2S form employing Claus Recovery unit, where H_2S is first burnt to form

SO₂ and then this SO₂ is made to react with rest of H₂S first in a combustion furnace and then in a catalytic converter. Since the reaction is equilibrium limiting, the processes modified further (like Sulfreeen or SNPA-Lurgi process) the reaction is carried out at low temperature where the sulfur formed is adsorbed on catalyst (alumina) and is regenerated by hot gas. The clauspol-15000 (IFP) accomplishes the Claus reaction in liquid phase using a high boiling point solvent, like poly-ethylene glycol, with continuous removal of molten sulfur. The CBA process developed by AMOCO (USA) is similar to that of sulfur process in the adsorption step, but the regeneration of the catalyst linked with the Claus unit operation is quite different. Another method known as Scott Process, an H₂S method, where all sulfur compounds are first converted to H₂S by Co/Mo on alumina catalyst at 300°C. The cooled gas is then counter-currently scrubbed with a di-isopropyl amine solution which selectively removes H₂S (and 10–40% CO₂). After stripping the rich solution, the top gas is recycled to the feed unit. It has already found widespread use in Japan, USA, and some European countries. The Beavon process is similar to Scot Process (first conversion of all H₂S) but in the second step, H₂S is converted to sulfur by wet method (Stretford process). Similarly, there is also SO₂ process where all sulfur compounds are first converted to SO₂ by air-oxidation and then it is absorbed with aqueous solution or a bulk catalyst. The end product can be sulfur (IFF-Clauspol 150) or SO₂ (Aquaclause Citrate Process, Shell Process) which is recycled or converted into sulfur, H₂SO₄ or gypsum (Chiyoda Process). All the processes of sulfur recovery mentioned above are economically feasible as long as the flue gas contains reasonably high amount of sulfurous gases. But if the S content in the gas is low, it is advisable to desulfurise the gas without recovery of sulfur from it. Such desulfurization of flue gas has been attempted by various techniques, but here we discuss only those methods which have successfully come up to commercial level. These methods are generally classified as once-through or regenerable type. In the once-through process (Bischoft process developed in Germany), limestone slurry is used to absorb the sulfurous gases and the absorber then discarded. The reactions involved in such processes are:

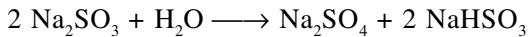
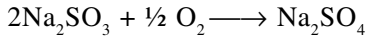


Generally such reactions have the problem that CaSO₄-hemihydrate is difficult to dewater and causes major sludge handling problem. The Bischoft process oxidizes the sludge at the bottom of the scrubber to

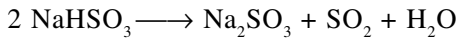
gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The effluent sludge is free settling and thus easy to handle. As per EPRI report (1982) total process capital cost for such a flue gas desulfurization process (FGD in short), is \$106/kW. The regenerable method known as "Wellman-Lord Process" involves the following reaction:



With the side reactions:



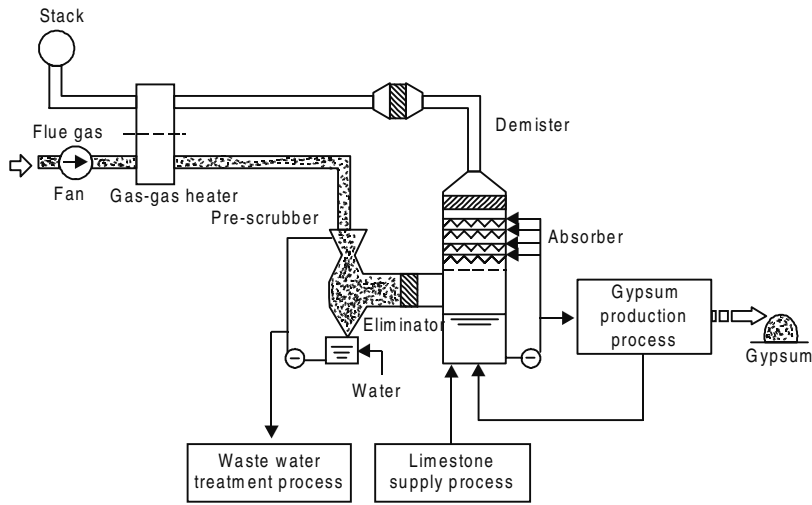
The side reactions necessitates a salt cake purge which is sometime difficult to effect. Salt cake is also difficult to dispose because of its solubility. The Na_2SO_3 can be regenerated by heating bisulphate crystals after evaporating the spent liquor from the absorber; the reactions involved are –



The SO_2 evolved is converted to elemental sulfur by Claus process using natural gas as reductant. The Wellman-Lord process requires a capital of about 1.5 times that of the Bischoff process.

Besides these wet method cum dry scrubbing technique (known as Mitsui-Desox system) has been tried in Japan. The process uses activated coke as an adsorbent in a moving bed system. The adsorption stage is effective only over a narrow temperature range (120–150°C) outside which the performance deteriorates sharply. The coke is regenerated by heating at 400°C producing SO_3 which is reduced to SO_2 and which once again converted to elemental sulfur by Claus process. Projected cost of Mitsui-Desox system is about 1.25 times that of Bischoff process. The dry process on the other hand, requires significantly less power to operate (only 16 MW compared to a 25 MW equivalent capacity wet system) but still has to dispose of 65 t/h of attrited coke. All the systems described above are sensitive to coal quality (capacity and hence capital cost requirement determined accordingly for a particular plant). Reduction in the feed sulfur content in coal from 4 to 1% will approximately half the operating cost. Significant reduction in feed ash would proportionately reduce the volume and hence the cost of solid waste disposal system.

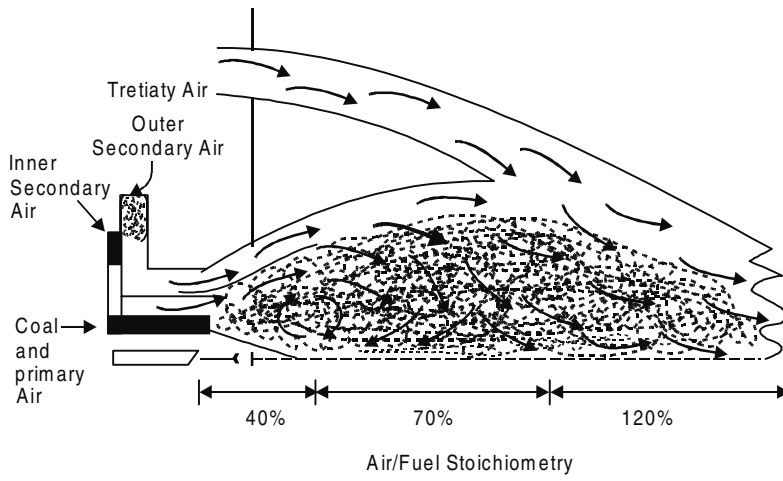
At present the major wet-type flue-gas desulfurization system used in Japan is the limestone process. Other processes being applied include the dual-alkali process and Wellman-Lord process. In the former, a water slurry of Na_2SO_3 is used as the absorbent for SO_2 ; limestone is added to the



9.7 Wet-type gas desulfurization process.

solution, Na_2SO_3 is regenerated and the solution is air oxidized to produce gypsum.

Since NO_x formation increase with rising temperature and the abundance of oxygen, with improved combustion methods such as exhaust gas recirculation and two stage combustion (both lowers combustion temperature) have been adopted. Some plants also has installed low NO_x burner for this purpose (Fig. 9.8). The “exhaust gas recirculation method” controls NO_x formation by reducing combustion temp. and diluting the oxygen concentration in the boiler. This is accomplished by recirculating a portion of the exhaust gas prior to emission from the stack and mixing it with the boiler air supply. In the “two-stage combustion method” complete combustion is restricted to 90–95% in first stage by controlling the supply of air. This reduces the combustion temperature and NO_x production. The air required for complete combustion is supplied in the second stage from a port situated at the upper part of the burner. In the new “Low- NO_x burner” the densifying burner is located centrally to the rarefying burner. Conventional burners mix air and fuel evenly which results in rapid and complete combustion which in-turn generates high temperature and high NO_x . These new low- NO_x burners have centrally located fuel rich output and low fuel concentration output at the top and bottom. In stack gas NO_x control system, ammonia is injected into the exhaust gas which then passes through a catalyst where NO_x is converted to harmless N_2 and water.



9.8 Concept of low NO_x burner.

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