Chemical Recovery in Pulp and Papermaking

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Contents

List of tables

List of figures

Foreword

As a result of the increasing high cost of energy and chemicals, coupled with stringent environmental regulations that limit particulate and gas emissions, solid waste disposal and mill effluent discharge, the need for improved recovery of energy and chemicals from black liquor has become a critical economic factor in kraft pulp mill operation. It is essential for mills to maximise their steam and power production capacity, reduce recirculating chemical dead loads, and minimise chemical losses. The reliability and the efficiency of recovery boilers, evaporators, causticising plants and lime kilns have a direct impact on the quantity and quality of white liquor, and, ultimately, on the quantity and quality of pulp produced by kraft mills.

This report examines the scientific and technical advances that have been made in chemical recovery, including the very latest developments. It looks at general aspects of the chemical recovery process and its significance, black liquor evaporation, black liquor combustion, white liquor preparation and lime reburning. It also describes the technologies for chemical recovery of nonwood black liquor, as well as direct alkali regeneration systems in small pulp mills. In addition, it includes a discussion of alternative chemical recovery processes, i.e. alternative causticisation and gasification processes. Furthermore, it discusses the utilisation of new value streams (fuels and chemicals) from residuals and spent pulping liquor, and the environmental challenges.

Introduction

1

Scope of the report

This report examines in great depth the scientific and technical advances in chemical recovery. It looks at general aspects of the chemical recovery process and its significance, black liquor evaporation, black liquor combustion, white liquor preparation and lime reburning. It also describes the technologies for chemical recovery of nonwood black liquor and direct alkali regeneration systems in small pulp mills. In addition, it includes a discussion of alternative chemical recovery processes, i.e. alternative causticisation and gasification processes. Furthermore, it discusses the use of new value streams (fuels and chemicals) from residuals and spent pulping liquor, and the environmental challenges.

This report will be of interest to students, as well as researchers and managers in pulp and paper organisations and paper mill associations. The information given in the report is up to date.

Methodology

Information has been collected from scientific literature, reports from international and national agencies, websites, conference presentations, patent literature, university research groups, and technology and equipment suppliers.

Objectives

The report aims to explore the chemical recovery process and the scientific and technical advances, including the very latest developments, the technologies for chemical recovery of nonwood black liquor, direct alkali regeneration systems in small pulp mills, alternative chemical recovery processes, the use of new value streams, and the environmental challenges. This topic is currently extremely important, as the need for improved recovery of energy and chemicals from black liquor has become a critical economic factor in pulp mill operations.

Overview of the chemical recovery process

When producing paper from wood, the fibres have to be liberated from the wood matrix. This process is called pulping, and can be done mechanically or chemically. In chemical pulping, the fibres are released via a chemical reaction that dissolves the lignin that holds the fibres together.

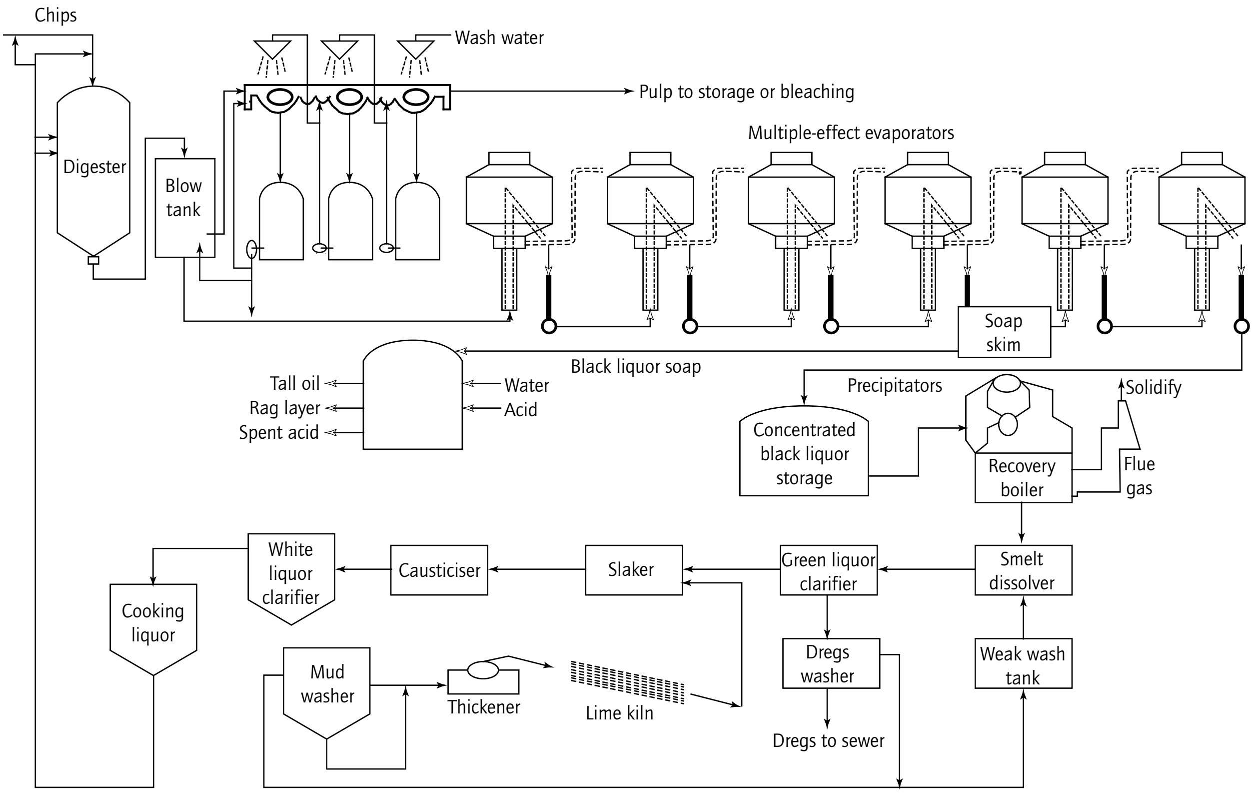
The major chemical pulping process is the kraft pulping process. Globally, about 130 million tonnes of kraft pulp is produced per year, accounting for two-thirds of the world's virgin pulp production, and for more than 90% of chemical pulp (Tran and Vakkilainen 2007). The high strength of kraft pulp, the ability of the process to handle almost all species of softwood and hardwood, and its favourable economics resulting from chemical recovery efficiency of about 97%, all give the kraft process an advantage over other pulping processes.

In the kraft process, the pulping liquor is called white liquor and contains sodium hydroxide and sodium sulphide. The active ions during the cook are HS^-, which is the primary delignifying agent, and OH^-, which keeps the fragments of lignin in solution. The wood chips are treated with the white liquor at elevated temperature and pressure and form the pulp, which is further processed to paper plus a solution called black liquor. The black liquor contains the spent pulping chemicals and dissolved organic material, which corresponds to about half of the wood material used for pulping.

The efficient recovery of both the pulping chemicals and the energy latent in the organic material is a requirement for the pulping process to be economically feasible. The commercial success of the kraft process relied, however, on the development of a suitable chemical recovery process in which sulphate, the main chemical constituent, could be cheaply reduced to sulphide. The development of practical chemical furnaces between 1928 and 1934 greatly lowered production costs and paved the way for the large increase in capacity of kraft pulping (Tomlinson and Richter 1969).

Figure 1.1 shows a simplified schematic diagram of the kraft pulping process and the corresponding chemical and energy recovery process.

FIGURE 1.1 The kraft pulping process and chemical and energy recovery cycle



Source: based on Smook 1992

The primary operations of the kraft recovery process are:

- concentration of black liquor by evaporation;
- combustion of the strong black liquor converts the recovered inorganic chemicals to smelt, which, along with sodium sulphide and sodium carbonate, is dissolved in water to give the green liquor;

- the sodium carbonate is causticised to sodium hydroxide using calcium hydroxide, which is recovered as calcium carbonate;
- recovery of by-products such as tall oil, energy, and turpentine;
- regeneration of calcium carbonate to calcium hydroxide in a lime kiln (Vakkilainen 2000a).

Washing separates the pulp from the black liquor, and the resultant weak black liquor contains 12–20% organic and inorganic solids. Burning this weak black liquor would require more heat than it would produce, and so the black liquor must be concentrated for efficient energy recovery. Evaporation produces a black liquor that is sufficiently highly concentrated with minimum chemical losses. The main steps in the evaporation of black liquor are:

- separation of the water from the black liquor to generate concentrated black liquor and condensate;
- processing the condensate to segregate clean and fouled condensate fractions;
- separation of soap from the black liquor.

To decrease black liquor viscosity, a liquor processing stage, such as a liquor heat treatment unit, can also be present. The liquor heat treatment (LHT) ensures a high level of dry solids even with high viscosity liquors. The LHT process treats the liquor at an elevated temperature for an extended period of time, during which high molecular weight polysaccharides and lignin are broken down and the viscosity is permanently reduced (Rauscher et al. 2006).

Another possible component is a black liquor oxidation stage. The potential advantages of black liquor oxidation include:

- improvement in multiple-effect evaporators through reduced scaling on heat transfer surfaces;
- reduced corrosion of metal evaporating surfaces;
- possible increases in tall oil yield;
- reduced chemical make-up requirements for sodium sulphate and calcium oxide;
- increases in yield from higher white liquor sulphidities in the digester;
- reduced total reduced sulphur (TRS) emissions.

In modern high solids evaporators, recovery boiler electrostatic precipitator ash is mixed with 30–45% dry solids black liquor. Non-condensable gases from evaporation require collection for processing. When using a direct contact evaporator stage, efficient oxidation of the black liquor is necessary to suppress release of odorous gases into the flue gas stream.

The evaporation of black liquor uses direct or indirect heating plus flashing of the black liquor. Most industrial evaporators are the multiple-effect, steam-heated type. Vapour recompression evaporation is often a component in the first stage of evaporation of weak black liquor as a capacity booster.

The properties of black liquor vary from mill to mill depending on many factors, including the mill location, digester conditions, pulp yield, wood species, white liquor properties, chemical-to-wood ratio, and brownstock washing efficiency. In general, hardwood pulping requires fewer chemicals, has a higher pulp yield and, consequently, generates fewer black liquor solids than does softwood pulping (Tran and Vakkilainen 2007). Hardwood black liquor generally contains fewer organics, tall oil and soap, and has a heating value that is about 5% lower than that of softwood black liquor.

In Brazil, Chile and other tropical countries, eucalyptus is the dominant wood species used in kraft pulping. Since the properties of eucalyptus black liquor are similar to those of other types of hardwood black liquor, the chemical recovery process in eucalyptus kraft mills is essentially the same as that in others.

When processing nonwood black liquors, small mills use direct contact evaporation. Hot flue gas from the recovery boiler heats a film or spray of black liquor. This technique can evaporate to a maximum of only 65% dry solid content because liquor viscosity increases sharply at higher dry solid contents.

Unoxidised black liquor releases organic sulphur compounds on contact with flue gases, which can be partly avoided by oxidation of the weak black liquor. The economics of the process favour the installation of indirect heating as unit size increases, so that all flue gas heat can then generate steam and electricity.

Concentrated black liquor contains dissolved wood residues (organic) and inorganic cooking chemicals. Combustion of the organic portion of the liquor produces heat. The organic compounds in black liquor serve as a fuel for the production of steam, which is used to generate electricity. The heat released as a result of black liquor combustion is recovered as high pressure/temperature superheated steam in the recovery boiler.

The efficiency of converting the fuel value in kraft black liquor (13,000–15,000 kJ/kg) to steam is typically lower than for fossil fuel combustion because of the heat used to evaporate the water entering with the black liquor, the heat of reaction consumed in producing sodium sulphide, and the heat taken away in the molten smelt. The amount of steam produced is typically about 3.5 kg per kilogram of black liquor solids, but can range from 2.5–3.8 kg steam per kilogram of black liquor solids, depending on the thermal efficiency of the recovery boiler (Tran and Vakkilainen 2007). The high pressure steam is passed through a steam turbine to generate electricity. Depending on the quality of the steam and the type of turbine, a 1,000 t/d kraft pulp mill can generate 25–35 MW of electricity by burning 1,500 t/d black liquor dry solids in its recovery boiler. The lower pressure steam exiting from the turbine is used in various processes in the mill.

Combustion in the recovery furnace needs careful control. A high concentration of sulphur requires optimum process conditions to avoid production of sulphur dioxide and reduced sulphur gas emissions. Besides environmentally clean combustion, efficient reduction of inorganic sulphur must occur in the char bed.

The process that takes place in the recovery boiler includes the following steps:

- combustion of organic material in black liquor to generate steam;
- reduction of inorganic sulphur compounds to sodium sulphide;

- production of molten inorganic flow consisting primarily of sodium carbonate and sodium sulphide;
- recovery of inorganic dust from flue gas;
- production of a sodium fume to capture combustion residues of the organic sulphur compounds released (Biermann 1996; Vakkilainen 2000a; Reeve 2002).

A lime kiln calcines lime mud to reactive lime (calcium oxide) by drying and subsequent heating. The calcination process can use a rotary furnace or a fluidised bed reactor (Adams 1992a; Venkatesh 1992; Biermann 1996).

The main processes that take place in the lime kiln are the drying of lime mud and the calcination of calcium carbonate. Some additional operations can also be present:

- the lime kiln combusts small amounts of odorous non-condensable gases;
- the lime kiln process produces dust that requires capture;
- for larger amounts of oxidised sulphur gases, flue gas scrubbers are necessary;
- the drying of lime mud and the calcination of calcium carbonate to calcium oxide require heat;
- this heat comes from burning oil or natural gas in the lime kiln, although other fuels, such as gasified biomass can also be used.

The causticising process converts the sodium carbonate in green liquor to sodium hydroxide. The operations involved in the causticising process include:

- dissolving the molten smelt to weak white liquor in order to produce green liquor;
- clarification or filtration of the green liquor;
- the mixing of green liquor and lime in a slaker to form sodium hydroxide and lime mud, with subsequent completion of the causticising reaction in reaction tanks;
- white liquor clarification and filtration for lime mud separation;
- lime mud washing (Biermann 1996; Arpalahti et al. 2000).

Molten smelt from the recovery boiler contains small amounts of unreacted carbon and non-process elements. The small undissolved particles in green liquor require separation for disposal, which can be achieved using settling or filtration. Washing the dregs minimises chemical losses.

Table 1.1 gives key energy and environmental facts for the kraft chemical recovery process.

TABLE 1.1 Kraft chemical recovery: energy and environmental facts

	Evaporation	Recovery boiler	Recausticising	Calcination
Energy use (MJ) per net tonne of pulp	2,163–5,645	1,192–4,220 Generates 4,220–21,101	475–1,197	992–2,648
Emissions	Non-condensables (TRS, VOCs, alcohols, terpenes, phenols)	Fine particulates, TRS, sulphur dioxide, carbon monooxide, nitrogen oxides	Particulates (sodium salts), sulphur dioxide, TRS	Fine and coarse particulates (sodium and calcium salts) TRS, sulphur dioxide, carbon monooxide, nitrogen oxides

TABLE 1.1 Kraft chemical recovery: energy and environmental facts (continued)

	Evaporation	Recovery boiler	Recausticising	Calcination
Effluents	Foul condensate (suspended solids) Black liquor storage tanks – spills	–	–	–
By-products/ hazardous wastes	–	–	Dregs	–

Note: TRS = total reduced sulphur emissions, including hydrogen sulphide, methylmercaptan, dimethyl sulphide and dimethyl disulphide; VOCs, volatile organic compounds
Source: based on Martin et al. (2000); US Department of Energy (2005)

Table 1.2 summarises the inputs and outputs of the main processes involved in chemical recovery.

TABLE 1.2 Inputs and outputs of the processes involved in chemical recovery

Process	Inputs	Outputs
Black liquor evaporation	Weak black liquor, primary steam	Strong black liquor, clean condensate, foul condensate, tall oil soap
Black liquor combustion	Strong black liquor, boiler feed water	Smelt, steam, flue gases
Recausticising	Smelt, lime mud wash water, dregs wash water, fresh make-up water	White liquor, grits, lime mud (calcium carbonate), dregs wash water, dregs, vent gases
Lime reburning/calcination	Lime mud (calcium carbonate), fuel (oil, natural gas), water	Reburned lime (calcium oxide), lime mud wash, water, flue gases

Source: based on US Department of Energy (2005)

Significance

The chemical recovery process is essential to the cost-effective operation of kraft pulp mills. The process recovers the kraft pulp digestion chemicals, minimising the amount of new chemicals required for pulp digestion, and reducing the effluent load that must be treated prior to discharge. As part of the recovery process, energy is generated from the spent cooling liquor for use in other plant processes.

The magnitude of the recovery process is often not fully appreciated. Globally per year, more than 1.3 billion tons of weak black liquor is processed, and about 200 million tons of black liquor dry solids are burned in recovery boilers to recover, as sodium oxide, 50 million tons of cooking chemicals and to produce 700 million tons of high pressure steam. This makes black liquor one of the most important fuels in the world, after coal, oil and natural gas (Reeve 2002). Since black liquor is derived from wood, it is the most important renewable biofuel.

Key drivers and current trends in chemical recovery

Developments in chemical recovery are being driven by a mixture of ecological concerns, competition leading to improved overall efficiency, high energy costs, and stringent environmental regulations. This has directed the recovery boiler technology towards co-generation, high steam temperature and pressure operation, and waste heat recovery. The trend in recent years has been to burn higher volumes of black-liquor solids (Table 1.3).

TABLE 1.3 Current trends in chemical recovery

▶ Further increase in black liquor solids towards 90% by concentrators using elevated steam pressure
▶ Significant increase in recovery boiler and evaporator capacities
▶ New, high-efficiency recovery boilers being built, geared to producing more electricity
▶ Higher design pressure and temperature because of the increasing demands of power generation
▶ Superheater materials of high-grade alloys
▶ Burning of biological effluent treatment sludge and bark press filtrate effluent
▶ Installations of burners with concentrated non-condensable gases (CNCG) burners (low volume high concentration [LVHC] gases)
▶ Dissolving tank vent gases returned to the boiler
▶ Chloride and potassium removal from fly ash when recovering bleaching filtrates
▶ Fourth air level for control of nitrogen oxides
▶ New recausticising system giving green liquor with fewer than 20 ppm of suspended solids

Source: based on Vakkilainen (2004, 2007a)

Several mills are using super combustion systems that allow more efficient burning of black liquor in the recovery boiler at up to 90% solids. Reduction efficiency is better, and sulphur dioxide emissions are significantly reduced. In some mills, biological sludge (from secondary effluent treatment) is burned in the recovery boiler with the black liquor at about 85–90% solids.

With the trend towards bigger pulp mills, recovery boiler and evaporator capacities have greatly increased during recent years. The new recovery installations are bigger, more efficient, and produce more electricity than before. Recovery boiler capacity has surpassed 5,000t of dry solids per day, and around six evaporators have been built to exceed 1,000t of water per hour.

The traditional five-effect evaporator has almost disappeared, and rising film designs have vanished from the market. Falling-film evaporators are the modern choice, and the most common evaporator type selected for black liquor. Use of Duplex steel materials for all surfaces exposed to black liquor above 70% dry solid content is now standard, and the majority of new evaporator projects use the principle of mixing the recovery boiler electrostatic precipitator (ESP) ash before the last evaporation stage (Vakkilainen 2007a). Recausticising is changing with the advent of disc filtration technology and larger lime kilns.

The latest recovery boilers run at steam pressures greater than 8,000 kPa at 480°C. In future they may reach 10,000 kPa and 505°C. With modern recovery boilers, most mills will make approximately 10% of their total revenue from sales of surplus electricity, bark, and wood residue. Most of the larger mills now produce as much power as some electricity generating stations, more than 100 MW.

New recovery boilers are commonly equipped with chloride and potassium removal systems for deposit accumulation control, quaternary air systems for control of nitrogen oxides, and high-temperature corrosion-resistant materials for waterwall and superheater tube protection. Recovery boilers in Japan often burn black liquor together with oil to meet the mill's energy and steam demands.

Many boilers are equipped with a sophisticated co-generation control system that enables the boilers to switch automatically to a power-generating mode to burn black liquor with an auxiliary fuel, based on the relative electricity price the mill can obtain from the local power station during the day. This 'swing' operation requires a greater degree of automation of black liquor firing. New recovery boilers are large in order to accommodate the co-firing of black liquor and auxiliary fuel.

Future trends for pulp mills include black liquor gasification, borate autocausticisation, and the use of alternative fuels for lime kilns.

Glossary

Black liquor
This is the mixture of cooking chemicals and dissolved wood material remaining after cooking. Black liquor is recovered during pulp washing, concentrated by evaporation and burned in the recovery boiler to recycle the cooking chemicals and generate energy.

Causticisation
This is a process by which green liquor, separated from the smelt produced in the recovery boiler, is converted to white liquor with the help of quicklime, thus allowing the cooking chemicals to be reused.

Chemical pulp
A generic term that describes the pulp produced by chemical (as opposed to mechanical) processes. These chemical processes include kraft (sulphate) and sulphite processes.

Chemical recovery
The process of burning concentrated black liquor in a recovery boiler to derive the usable chemicals and to extract the heat energy from the used liquor.

Dregs
The solids that settle out in the clarifiers in the causticising process.

Evaporation plant
This is the pulp mill department where spent cooking liquor is concentrated to make it suitable for burning and chemical recovery.

Flue gas
A mixture of gases resulting from combustion, emerging from chimney or stack.

Green liquor
This is produced by dissolving the cooking chemicals digested in the recovery boiler. It is turned into white liquor using quicklime. White liquor is a cooking solution of pulp.

Hardwood

Pulpwood from broad-leaved dicotyledonous deciduous trees.

Kraft process

Worldwide, this process is the leading chemical pulping process because of the strength of pulp it produces. The process involves cooking (digesting) wood chips in an alkaline solution, where the active cooking agent is a mixture of sodium hydroxide and sodium sulphide. The dissolved lignin is later removed, leaving behind the cellulose fibres. The term ‘kraft’ is interchangeable with ‘sulphate’ and is derived from the German word Kraft, which means ‘strength’ or ‘power’.

Kraft pulp

A chemical pulp produced by combining wood chips and chemicals in huge vats known as digesters. The effect of the heat and the chemicals dissolves the lignin that binds the cellulose fibres together without breaking the wood fibres, creating a strong pulp product.

Lime kiln

This is used to reburn lime sludge (calcium carbonate) to form calcium oxide, which can be reused in causticisation.

Lime sludge (calcium carbonate)

This is calcium carbonate in solid form. It is formed in the manufacture of white liquor and is extracted from white liquor by means of clarification and filtration.

Particulate

A small, discrete mass of solid or liquid matter that remains individually dispersed in gas or liquid emissions. Particulates take the form of aerosol, dust, fume, mist, smoke or spray. Each of these forms has different properties.

Particulate emissions

Fine liquid or solid particles discharged with exhaust gases. Usually measured as mg/m^3.

Recovery boiler

This is used to burn black liquor from sulphate pulping for recovery of inorganic chemicals as well as for energy production.

Salt cake

The chemical – generally sodium sulphate – added to black liquor to make up for soda loss.

Smelt

The molten ash that flows out of the recovery furnace as a white hot liquid.

Softwood

Wood obtained from evergreen cone-bearing species of trees, such as pines and spruces, which are characterised by having needles.

Tonne

The tonne is equivalent to 1,000 kg or approximately 2,204.6 lb.

Total reduced sulphur (TRS)

This parameter is a measure of the amount of odorous sulphur compounds.

White liquor

This consists of sodium hydroxide and sodium sulphide, and is used as cooking solution of sulphate pulp.

Black liquor evaporation

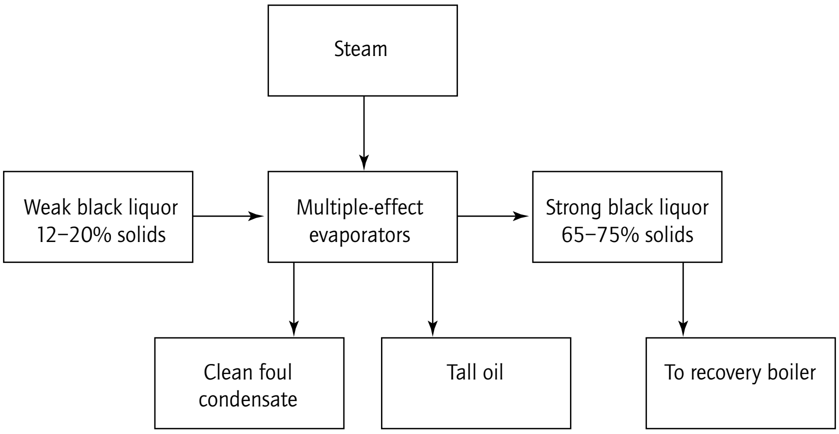
2

The black liquor is heated in order to increase the dry solids content by evaporating water until a concentration is reached that allows burning in the recovery boiler (Figure 2.1). This concentration is generally 65–75% dry solids, but many modern installations operate at a level that is greater than 80% solids.

The properties of black liquor vary widely according to the type of raw materials used in the pulping process. The main constituents are:

- water;
- organic pulping residues including lignin, polysaccharides, carboxylic acid and extractives;
- inorganic cooking chemicals (Vakkilainen 2000a; Adams 2001).

FIGURE 2.1 Evaporation of black liquor



Source: Pira International Ltd

Accurate analysis of black liquor is necessary to provide data about energy consumption, gas flows and production. Table 2.1 shows the temperature and solids content for one type of black liquor at various stages of evaporation and firing. Also listed are some important black liquor properties, several of which change dramatically through the liquor loop.

TABLE 2.1 Typical property values at various stages of black liquor evaporation and firing

	Solids (%)	Temperature (°C)	Boiling point rise (°C)	Liquor viscosity (mPa·s)	Heat capacity (J/kg/°C)	Density (kg/m^3)
Weak liquor	15	77	1.4	0.7	3,870	1,070
Liquor in evaporation	18	57	1.7	1.1	3,790	1,100
Liquor in evaporation	21	74	1.9	0.9	3,740	1,110
Liquor in evaporation	26	87	2.8	0.9	3,660	1,130
Liquor in evaporation	35	132	4.2	0.8	3,560	1,150
Liquor in evaporation	50	104	8.1	5.0	3,230	1,270
Strong liquor	65	104	13.9	63.0	2,960	1,360
Strong liquor, as-fired	65	118	13.9	34.0	2,960	1,350
High solids liquor	80	182	26.7	48.0	2,670	1,390

TABLE 2.1 Typical property values at various stages of black liquor evaporation and firing (continued)

	Solids (%)	Temperature (°C)	Boiling point rise (°C)	Liquor viscosity (mPa·s)	Heat capacity (J/kg/°C)	Density (kg/m^3)
High solids liquor, as-fired	80	146	26.7	253.0	2,660	1,440

Source: reproduced from Frederick (1997), with permission from TAPPI Press

Composition of black liquor

The composition of black liquor depends on the alkali charge, the pulp yield, and the wood species used (Boniface 1992; Grace 1992a; Vakkilainen 2000a). Significant differences exist between liquors from different raw materials. The typical composition of black liquor from different raw materials is shown in Tables 2.2 and 2.3.

TABLE 2.2 Typical composition of virgin black liquor from different raw materials

Chemical element (%)	Scandinavian wood				North American wood				Tropical wood			
	Softwood (pine)		Hardwood (birch)		Softwood (pine)		Hardwood		Hardwood		Mixed tropical wood	
	Typical	Range	Typical	Range	Typical	Range	Typical	Range	Typical	Range	Typical	Range
Carbon	35.0	32.0–37.0	32.5	31.0–35.0	35.0	32.0–37.5	34.0	31.0–36.5	34.8	33.0–37.0	35.2	34.0–37.0
Hydrogen	3.6	3.2–3.7	3.3	3.2–3.5	3.5	3.4–4.3	3.4	2.9–3.8	3.3	2.7–3.9	3.6	3.1–4.2
Nitrogen	0.1	0.06–0.12	0.2	0.14–0.20	0.1	0.06–0.12	0.2	0.14–0.20	0.2	0.1–0.6	0.3	0.1–0.9
Oxygen	33.9	33.0–36.0	35.5	33.0–37.0	35.4	32.0–38.0	35.0	33.0–39.0	35.5	33.0–39.0	35.5	33.0–39.0
Sodium	19.0	18.0–20.0	19.8	18.0–22.0	19.4	17.3–22.4	20.0	18.0–23.0	19.1	16.2–22.2	18.8	16.5–22.5
Potassium	2.2	1.5–2.5	2.0	1.5–2.5	1.6	0.3–3.7	2.0	1.0- 4.7	1.8	0.4–9.2	2.3	0.5–6.3
Sulphur	5.5	4.0–7.0	6.0	4.0–7.0	4.2	2.9–5.2	4.3	3.2–5.2	4.1	2.4–7.0	3.0	2.4–5.0
Chlorine	0.5	0.1–0.8	0.5	0.1–0.8	0.6	0.1–3.3	0.6	0.1–3.3	0.7	0.1–3.3	0.8	0.5–2.4
Inert	0.2	0.1–0.3	0.2	0.1–0.3	0.2	0.1–2.0	0.5	0.1–2.0	0.5	0.2–3.0	0.5	0.2–3.3
Total	**100.0**		**100.0**		**100.0**		**100.0**		**100.0**		**100.0**	

Source: based on data from Vakkilainen (2000a)

TABLE 2.3 Typical composition of virgin black liquor from miscellaneous pulping materials

Chemical element (%)	Bamboo typical	Bagasse typical	Straw typical
Carbon	34.5	36.9	36.5
Hydrogen	3.3	3.9	3.9
Nitrogen	0.4	0.3	0.7
Oxygen	34.1	36.3	33.9
Sodium	18.3	18.6	17.5
Potassium	4.0	0.6	2.1
Sulphur	3.3	2.5	2.8
Chlorine	1.6	0.4	2.1
Inert	0.5	0.5	0.5
Total	**100.0**	**100.0**	**100.0**

Source: reproduced from Vakkilainen (2000a), with permission from Fapet Oy, Finland

The proximate analysis of black liquor determines the main components necessary for the combustion calculations. Proximate analysis usually consists of:

- the higher heating value (HHV, a measure of the amount of heat released)
- the dry solids content of the black liquor
- the non-reactive material in the black liquor dry solids
- the inert material that is organic compared with inorganic
- the ratio of reactive to non-reactive portions that are organic compared with inorganic.

The advantage of proximate analysis is that it is simple to perform and no complicated equipment is necessary. Proximate analysis can estimate black liquor ultimate analysis and combustion properties.

The substances in black liquor derive from two sources: wood and cooking liquor (Grace 1992a). Black liquor contains:

- water
- organic residue from pulping
- inorganic cooking chemicals.

The primary organic compounds are:

- lignin
- hydroxy and low molecular weight organic acids
- extractives (fatty acids and resins)
- inorganic compounds (Vakkilainen 2000b).

The alkali lignin in black liquor is degraded from its state in wood. Part of the lignin (10–20%) is dissolved as comparatively small molecules, but the bulk is solubilised as large macromolecules. These are condensed, cross-linked macromolecules containing many aromatic groups of related structures such as phenols, catechols, and quinones.

As a first approximation, softwood lignin can be treated as polymerised phenylpropane units, with a methoxyl content of about 0.96 per monomeric unit. Hardwood lignin has about twice the methoxyl content, otherwise it is similar.

Some of the methoxyl groups are removed during pulping and replaced by hydroxyl groups. These reactions of the methoxyl groups help to solubilise the lignin and are responsible for the formation of volatiles such as methanol, mercaptans and other odorous gases.

Alkali lignin is stabilised and solubilised because of the presence of ionised hydrophilic groups, mainly phenolic and carboxylic groups. The ionised groups prevent the macromolecules from agglomerating and precipitating because of the electrical charge on the macromolecule. It has been estimated that, per monomeric unit, there is about 0.8–1.0 phenolic hydroxyl (R-OH) group and about 0.16 carboxyl group (R-COOH). The phenolic hydroxyl groups are the most prevalent. These groups have the greatest effect on solubility.

The state of ionisation of the solubilising groups is dependent on the pH. Lowering the pH can convert ionised groups into the un-ionised form. When the black liquor pH is in this range, lignin precipitation will occur. Because of the heterogeneous nature of alkali lignin, this effect comes on gradually, proceeding from a slow thickening at higher pH values to actual precipitation at lower values. Most of the reported effects of residual alkali on black liquor properties are due to this behaviour. Viscosity is especially sensitive: a residual active alkali content of 5% (as sodium oxide) on the black liquor solids is normally sufficient to avoid detrimental effects.

Practically all of the carbohydrates dissolved during kraft pulping are degraded to a complicated mixture of non-volatile hydroxy acids and simple mono- or dicarboxylic acids. Table 2.4 presents data on the composition of these mixtures for a hardwood and a softwood liquor. These substances are very soluble in water and show no apparent tendency to precipitate from concentrated liquor. They tie up a significant portion of the sodium in the black liquor. Because these substances are well oxygenated, they have relatively low heating values.

TABLE 2.4 Composition of carboxylic acid mixture in black liquors of pine and birch

Carboxylic acid	**Relative composition (%)**	
	Birch liquor	**Pine liquor**
Acetic	28.9	11.4
Formic	12.1	16.2
Lactic	10.6	10.7
Glycolic	4.1	3.2
2-Hydroxybutanoic	15.9	4.3
2,5-Dihydroxyvaleric	2.0	2.7
Xyloisosaccharinic	11.4	4.1
Glucoisosaccharinic	9.0	38.7
Miscellaneous acids	6.0	8.7
Total	**100.00**	**100.00**

Source: reproduced from Grace (1992a), with permission from PAPTAC

The extractives in the wood tend to pass through the pulping process unchanged. They are made up of three groups – resin acids, fatty acids and neutrals – and are present in the black liquor as soaps (Venkatesh and Nguyen 1992). Resin acids are aromatic in character and consist of various $C_{20}H_{30}O_2$ isomers. Fatty acids are long-chain hydrocarbons with an acid group (carboxyl group) on one end. They can be either saturated or unsaturated (may or may not contain double bonds). Neutrals or unsaponifiables are not organic acids. They are mainly high molecular weight alcohols such as sterols or terpene alcohols. The fatty and resin acids exist in the black liquor as sodium salts. They contain a polar hydrophilic end and a non-polar hydrophobic end, and associate to form a micellar colloid. The basic micelles are aggregates that have their polar end directed outwards and their non-polar end directed inwards.

The polar groups are ionised, and the resultant electric charge stabilises the micelles and prevents their agglomeration. The neutrals are solubilised with the hydrocarbon layer of the micelle. Increased concentration of counter ion (Na+) tends to neutralise the negative charge on the micelles and allows them to associate. This leads to a precipitated soap phase. Soap begins to precipitate from the black liquor as it is concentrated. For a typical black liquor, maximum insolubility of soap occurs in the range of 25–28% solids content. The inorganic fraction of the liquor is somewhat imprecise because some of the sodium is associated with inorganic anions and some of it with organic anions. One estimate of the organically bound sodium content is given in Table 2.5.

TABLE 2.5 Organically bound sodium

	Unit consumption of sodium (mol)	Sodium as a proportion of organic solids	Proportion of liquor solids (%)
Carbohydrate	1.6/hexose unit	0.2	6.0
Lignin	0.8/monomer	0.1	4.0
Acetate	mol/mol	0.4	2.0
Soap	mol/mol	0.1	0.3
Total			**12.3**

Source: reproduced from Grace (1992a), with permission from PAPTAC

There are also a number of simple inorganic salts present. These are sodium carbonate, sodium sulphate, sodium thiosulphate, sodium sulphide, sodium hydroxide and sodium chloride. The most important of these are sodium carbonate and sodium sulphate, sodium sulphide and caustic soda.

The inorganic salts come directly from the white liquor. The main white liquor components (sodium hydroxide and sodium sulphide) react with the wood and tend to be consumed during pulping. The remaining inorganic salts in white liquor (sodium carbonate, sodium sulphate, sodium thiosulphate and sodium chloride) pass through the pulping process unchanged. A small amount of additional sodium carbonate may be formed by reactions that liberate carbon dioxide from organic acids, but the influence of such reactions on the carbonate content of black liquor is minor.

Properties of black liquor

Viscosity

The viscosity of black liquor depends on:

- the wood species
- the cooking conditions
- the percentage of solids
- the residual alkali content
- the temperature
- the shear rate.

It can also be affected by recovery operations (Söderhjelm and Sågfors 1992; Söderhjelm et al. 1992; Ramamurthy et al. 1993; Frederick 1997). Table 2.6 shows the effect of pulping conditions on the viscosity of black liquor.

TABLE 2.6 The impact of pulping variables on the viscosity of black liquor

Pulping variable	Effect on viscosity	Reason why
Wood/kappa		
Softwood/>50	High viscosity	High content of high molecular weight lignin
Softwood/<30	Low viscosity	Low molecular weight of both lignin and polysaccharides
Hardwood	Viscosity decreases with decreasing kappa	Polysaccharides dominate viscosity behaviour
EA*/wood†	Viscosity may increase or decrease with increasing EA/wood	For shorter cooks, more lignin and polysaccharides are extracted, but higher alkali degrades them more rapidly
Sulphidity†	Viscosity decreases	Lower molecular weight lignin with increasing sulphidity

*Note: *EA = effective alkali; †effect of the variable indicated with kappa number held constant*
Source: reproduced from Frederick (1997), with permission from TAPPI Press

Viscosity can vary significantly from mill to mill. Viscosity increases with increased dry solids content, and an increase in temperature lowers the viscosity. The practical limit for handling the liquor is the pumping limit of 300–500 mPa·s. The viscosity must always be below this level, and is usually much lower in the evaporation plant. If the liquor at final concentration is stored at atmospheric pressure, the limit of the final concentration is 70–75% dry solids at the maximum temperature of 115°C. If the final product liquor is stored in a pressurised storage tank, the final concentration can be 75–85% dry solids, and even higher at a storage temperature of 125–150°C.

These extremely high concentrations might require using medium pressure steam in the evaporation plant. A heat treatment process can also reduce the viscosity. Certain flow additives are available (Gagnon et al. 1996; Llamas et al. 2007) to reduce the viscosity of the liquor in such a way that high solids firing is possible in the conventional recovery furnace. High solids firing is environmentally attractive as it reduces hydrogen sulphide and sulphur dioxide emissions as well as carry-over in the furnace. Several papers have been published on high solids firing (Jones and Anderson 1992; Ryham and Nikkanen 1993; Haaga and Putkonen 1997; Vakkilainen et al. 1998).

Studies have revealed that polysaccharides, especially xylan found in birch kraft cooking, influence the viscosity of strong black liquor at elevated temperature (Söderhjelm and Sågfors 1992). A sharp fall in viscosity was observed when xylan was removed from the liquor. The study demonstrated that the viscosity of strong black liquor did not change over several months' storage, while a weak liquor from laboratory birch cook altered considerably after a few days' of storage. This liquor formed a deposit that contained 94.7% polysaccharides, the main component being xylose.

Specific gravity

The density of black liquor is important in the calculation of flow characteristics. When solids content is high, the density depends on the organic and inorganic solids; when solids content is very low, the density is close to that of water at the same temperature (Vakkilainen 2000a).

The inherent density of most organic material in black liquor is close to that of water, while that for the inorganic components is nearly twice that of water. Because of this, the inorganic components will have the strongest effect on the density of the black liquor.

The apparent density of black liquor can also be affected by entrained air. This air enters the liquor during various stages of the processing, including black liquor oxidation. It is not an inherent constituent of the liquor, but can affect the apparent density, both in operation and in laboratory testing.

Surface tension

The practical implication of surface tension in an evaporation plant is that low surface tension will increase the tendency to foam. Surface tension increases as the concentration of dry solids increases, and decreases with an increase in temperature (Frederick 1997). Foaming is a problem mainly in evaporator elements operating at low concentration. To overcome this, the feed liquor concentration is often increased by recirculating a portion of the concentrated liquor. Crude tall oil and soap will decrease the surface tension. They therefore need to be separated from the liquor if the contents are high, especially when softwood is the raw material for the pulp.

Specific heat

The specific heat capacity of black liquor depends on the heat capacities of its constituents. Any increase in dry solids will decrease the specific heat capacity, and an increase in temperature will decrease it.

Thermal conductivity

Thermal conductivity is an important property that is used to estimate the rate of heat transfer in black liquor evaporators and to dry droplets in the furnace (Ramamurthy et al. 1993). The thermal conductivity of the black liquor depends on the temperature and dry solids content. A temperature increase will increase the thermal conductivity, and an increase in the dry solids content will decrease the thermal conductivity.

Water vapour pressure

The water vapour pressure of black liquor is an important parameter in evaporator operation since it determines pressure–temperature relationships (Holmlund and Parviainen 2000). This property is usually expressed in terms of the boiling point rise (BPR) of the black liquor. The BPR is defined as the difference between the boiling temperature of black liquor and that of pure water at the same pressure. The BPR is a strong function of liquor solids content, and only a very weak function of pressure (and hence temperature). BPR is normally measured at 1 atm and then assumed to apply at all pressure levels encountered in an evaporator.

Heating value

The heating value of fuel signifies the amount of heat that fuel can produce upon incineration. The heating value of the black liquor used in North America is the HHV. Typical values for the HHV of kraft black liquor lie between 13,400 kJ/kg and 15,500 kJ/kg of black liquor solids (Frederick 1996). Both the organic component and the reduced sulphur in the black liquor contribute to the HHV. Other inorganic components act as diluents, lowering the heating value of black liquor.

Measurements of HHV are made in an oxygen bomb calorimeter using oxygen substantially in excess of the stoichiometric requirement. The final combustion products from a bomb calorimeter and boiler are somewhat different, resulting in an overestimation of the actual heating value. The net heating (net calorific) value (NHV) calculated from the measured HHV more nearly reflects the actual energy released.

Knowing the heating value of the black liquor is important in the design and operation of a recovery boiler. The heating value of black liquor has a large impact on the steam generation rate and on the maximum pulp production rate that a boiler can support. Typical heating values for different raw materials are shown in Table 2.7.

TABLE 2.7 Typical HHVs for different raw materials

Raw material	Typical (mJ/kg)	Range (mJ/kg)
Nordic softwood	14.2	13.3–14.8
Nordic hardwood	13.5	13.0–14.3
North American softwood	14.2	13.3–15.0
North American hardwood	13.9	13.0–14.8
Tropical hardwood	14.1	13.4–14.8
Bagasse	14.8	–
Bamboo	14.1	–
Straw	14.7	–

Source: reproduced from Vakkilainen (2000a), with permission from Fapet Oy, Finland

Analysis of black liquor

Various laboratory methods are used for the analysis of black liquor, and the results often vary as a consequence because they are based on different principles or standards (Torniainen 2007). Most methods for determining the residual and active alkali of black liquor are potentiometric. If the sample is titrated to a lower pH value than 11, there is a risk that the results will be too high.

An elementary analysis provides the main elements in black liquor, which normally include carbon, hydrogen, sodium, potassium, sulphur and chlorine. Black liquor also contains many varieties of minor inorganic components, or inerts. The main problems with the methods used to measure the nitrogen content of black liquor are that their determination limits are too high, or not all nitrogen compounds are included in their results. These problems have been resolved in the Kjeldahl method.

The most common/recent principles for metals determination are based on atomic absorption spectroscopy and plasma emission spectroscopy. Ultraviolet (UV) spectrophotometric methods are typically used for the measurement of lignin in black liquor samples, but there are also newer methods based on gas chromatographic analysis.

Several methods have been used to measure the dry solids content of black liquor (Grace 1992a; Frederick 1997), including oven drying, azeotropic distillation, moisture balances, refractometers, and microwave oven drying. Each method offers some advantages and has some disadvantages, and each results in a slightly different value for dry solids content.

The current TAPPI standard for the determination of black liquor solids is method T650 pm-84. Black liquor is dried at 105°C for a minimum period of 6h with an inert surface extender (sand) and a controlled flow of dried air to increase the drying rate and eliminate moisture entrapment. Strong black liquors are diluted to allow volumetric handling and to reduce scum formation. Sand is the only material found to be inert in this procedure. Diatomaceous earth and aluminium have been found to react with residual carbonate and caustic in black liquor, leading to incorrectly low solids results. This method is satisfactory but it takes a long time, so quicker methods are often used for calibration purposes, but they should be calibrated against T650.

Where continuous measurement of solids content is required, it is necessary to measure some property that is dependent on the solids content. These indirect techniques are subject to error from other variables, such as composition, that also affect the property being measured. All these methods require frequent calibration by appropriate reference methods to be sure that the indication of solids content is precise.

An azeotropic distillation method was used by Söderhjelm et al. (1994) in comparison with oven-drying to measure black liquor solids content. There was an increase in mass originating from oxidation of the sulphide during oven-drying. The results could be corrected provided that a calculation of the sulphide content in the liquor was known. The oven-drying results, after correction, were lower than those obtained by distillation. Distillation is a realistic alternative to oven-drying.

The density of low solids black liquor can be measured by several methods, such as buoyancy force, bubble tubes, hydrometer, etc. (Grace 1992a). The angle of the density/solids line is dependent on the liquor composition. In general, the density at a given solids level increases as the inorganic content increases.

Density measurements are subject to error from aeration of the liquor, as black liquor has a great capacity to aerate and foam, which can lead to false readings. On-line measurement of the solids content of heavy black liquor can be made with a refractometer.

The refractive index is a solution property that varies with concentration in a linear manner. It is also temperature-sensitive. Because of the opacity of black liquor, refractometers for use in it employ the critical angle principle.

The main inorganic compounds in black liquor are sodium sulphide, sodium carbonate, sodium sulphate, sodium hydroxide, sodium thiosulphate and sodium chloride (Grace et al. 1977). Methods for the analysis of black liquors are given in TAPPI method T625 hm-85. The development of ion chromatography shows promise for determining the inorganic constituents in black liquor as well as some of the low molecular weight organic acid anions such as formate, acetate, lactate and oxalate. Concentrations of sodium hydroxide, sodium sulphide and sodium carbonate in white and green liquors are often determined by the so-called ABC test, a series of acid titrations.

Elemental analysis of the liquor solids is needed for accurate combustion calculations. This consists of the weight percentages of the elements sodium, sulphur, carbon, hydrogen, oxygen, potassium and chlorine. Standard procedures for elemental analysis of black liquor have not been defined. Various procedures are available for determining individual elements (Grace et al. 1977). It is recommended that determinations be made for each element (including oxygen), and that none be determined by difference. The degree that the individual values sum to 100% can then be used to judge the reliability of the data.

The only organic analyses normally done on black liquor are for tall oil or soap. The potential tall oil in black liquor can be determined by extraction with petroleum ether. Procedures for analysis of tall oil soap skimmings are given in T635 om-82.

Black liquor evaporation

The first step in chemical recovery is concentration of black liquor by evaporation. The black liquor collected from the pulp washing system is referred to as weak black liquor and contains 13–17% solids. For firing in the recovery boiler, this must be concentrated to about 65% solids (Holmlund and Parviainen 2000).

In systems in which liquor is concentrated to about 50% solids in multiple-effect evaporators and then raised to 65% solids in a direct contact evaporator, the 50% solids liquor is usually called strong black liquor while the liquor fired into the furnace is called heavy black liquor.

In systems where the liquor is brought up to firing strength in multiple-effect evaporators, the terms strong black liquor and heavy black liquor are sometimes used interchangeably.

The relationship between the amount of water evaporated and the change in liquor solids content is highly non-linear. Much more water is evaporated at the low solids end.

Evaporation equipment

There has been considerable evolution in evaporator systems over the years (Wei and Huang 1993; Meng and Hsieh 1995; Frederick 1996; Koh and Lindberg 1999). The climbing-film, long-tube-vertical (LTV) evaporator came into use for black liquor during the 1920s and 1930s. It rapidly became the standard system for concentrating black liquor, and is still the most widely used type of evaporator.

Prior to the 1970s, the almost universal practice in North America was to concentrate the liquor to about 50% solids in a five- to seven-effect LTV evaporator, and complete the concentration in a direct-contact evaporator using the recovery boiler flue gas as the heat source. Since then, more and more operations have used indirect, steam-heated evaporator systems to accomplish all the concentration required.

Recently, new types of evaporators have been developed. These include falling-film evaporators (both plate and tube types), preheat-falling-rising types (PFRs), forced circulation units, and crystallising evaporators. Other variations include vapour-compression evaporators (VCEs) and waste-heat evaporators, and sophisticated condensate treatment systems (e.g. integral steam-stripping).

Evaporators are simple in their essentials. The two major requirements are to provide the necessary heat transfer and to separate the vapour from the concentrated liquor. In addition, provisions must be made for feeding and removing process streams. In many types of evaporators, the heat transfer component and the vapour/liquid separation component are physically separate sections of the evaporator. In other types they are integral. Black liquor evaporators are categorised according to the characteristics of the liquor movement or heating section design (Table 2.8).

TABLE 2.8 Summary of evaporator types

Film evaporators	▶ Rising-film type ▶ Long-tube-vertical type ▶ Falling-film type ▶ Long-tube-vertical type ▶ Plate-type ▶ Horizontal-tube – spray-film ▶ Combination type ▶ Rising-/falling-film ▶ PFR* type (P = preheat, F = falling film, R = rising film)
Natural circulation evaporators	▶ Short-tube-vertical type
Special evaporators using forced circulation	▶ LTV with recirculation ▶ Forced-circulation type ▶ Integrally mounted vertical-tube section in single pass ▶ Externally mounted tube section in single pass or two passes: ▶ Horizontal tube ▶ Inclined tube ▶ Vertical tube ▶ Evaporator/crystalliser

*Note: *PFR is a registered trademark of the Unitech Division, Ecodyne Corp.*
Source: reproduced from Venkatesh and Nguyen (1992), with permission from TAPPI Press

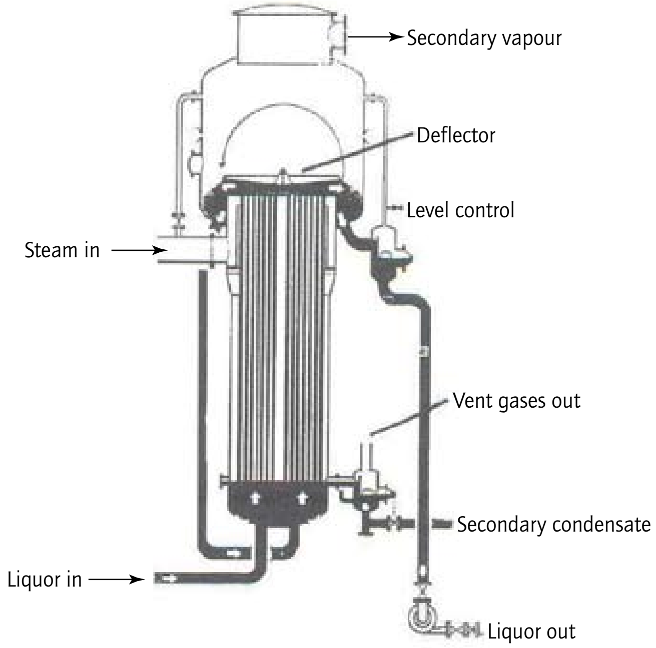
Long-tube-vertical evaporators

Long-tube-vertical evaporators, also called rising-film (RF) evaporators (Grace 1992a), were widely used for black liquor evaporation in the pulp industry until the mid 1980s. New installations now tend to prefer the falling-film type. Figure 2.2 shows the principle of the RF evaporator.

The heating element is a single pass, shell-and-tube heat exchanger mounted vertically with the liquor flow inside the tubes. The tube is typically 8.5 m in length, with a nominal diameter of 50 mm and a wall thickness of 1.5 mm. The tubes are expanded or rolled into the holes of the tube sheets. Liquor is fed into the bottom liquor box where it is distributed to the tubes. Steam or vapour is fed into the shell side of the heating element, and the heat is transferred through the tube walls into the liquor.

The liquor rises inside the tubes where it first undergoes preheating and then gradually begins to boil. The vapour released at the boiling has a high specific volume,

FIGURE 2.2 Rising-film evaporator



Source: reproduced from Holmlund and Parviainen (2000), with permission from Fapet Oy, Finland

which increases the velocity of the mixture of liquor and vapour, and the heat transfer rate in the heat exchanger. At low evaporation rates, the boiling is unstable. The average heat transfer rate is low, and scaling and foaming problems are common because of local hot spots. Above a partial load of 50%, the flow conditions normally stabilise, as the vapour velocity inside the tubes is sufficiently high. This behaviour means that RF evaporators cannot be used at a low partial load.

Vapour and liquor are separated first by a deflector plate placed above the upper tube sheet. The vapour flows through the vapour head, also called the vapour body or separator. It is cleaned by an impingement-type drop separator before exhausting to the succeeding evaporator-effect heating element. The RF unit, especially in the last effects, often has a baffling plate in the shell side. Its purpose is to separate the condensate into two fractions so that cleaner vapour condenses in front of the baffle. More contaminated vapour containing volatile organic sulphur compounds and methanol condenses behind the baffling plate in the after-condensing section. The term for this is condensate segregation. A disadvantage of the RF-type is that a plugged tube cannot be cleaned by washing. It requires manual cleaning by mechanical means or by hydroblasting.

Falling-film evaporators

Falling-film evaporators are used in several countries to produce black liquor slurry with up to 80% solids content for firing in the recovery boiler (Meng and Hsieh 1995; Vakkilainen and Holm 2000). Falling-film evaporators are used much like conventional evaporators except that the mechanism of evaporation in each stage is different. In each stage, steam, or sometimes hot water in the first stage, is used as the heat source and flows between stainless steel plates spaced about 30 mm apart. Large banks of these plates are aligned radially outwards in each effect. Dimples in the metal plates keep the plates a fixed distance apart and increase the strength of the metal plates.

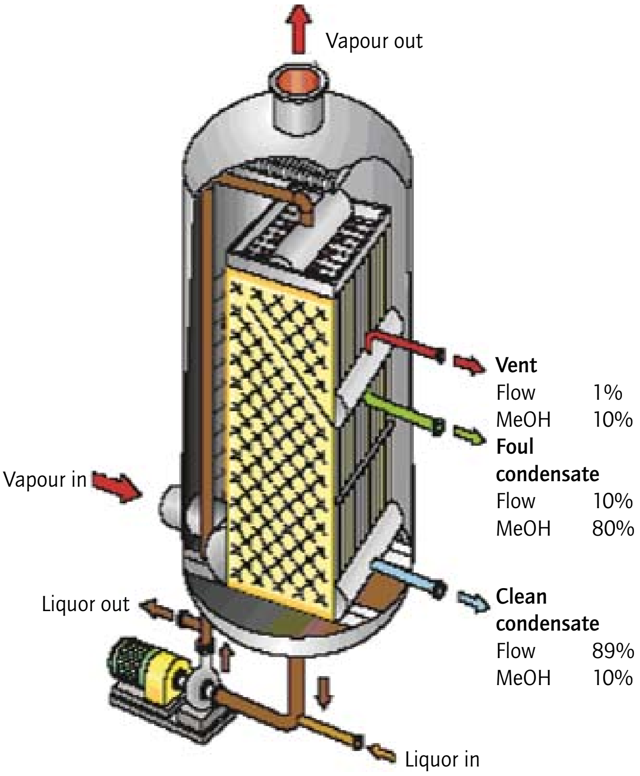
Falling-film plate evaporators are less subject to fouling than LTVs and require boil-outs much less often. They also operate at a lower overall vacuum than conventional evaporators, with the last stage operating at 660 mmHg. Black liquor must be recirculated within each stage. Falling-film evaporators can be used in conjunction with blow heat recovery at mills using batch digesters, as lower temperature gradients are required. The steam discharged during blowing is used to heat large quantities of water, which is then used in liquor evaporation until the next digester blow reheats it. This provides a levelling effect for the intermittent heat generation of blowing with batch digesters.

In this evaporator type, the liquor is fed to the bottom of the evaporator body where a fixed level is maintained. It is then raised to the top of the heating element by a circulating pump, and flows down on to the heating surface by gravity. The concentration within the effect is practically constant at the concentration of the out-feed liquor. The circulation rate is also constant. These features make the falling-film evaporator insensitive to variations in the evaporation load, which means that they can therefore operate with a load of 30–100% of the rated capacity, depending mostly on the precision of the control elements. These advantages have resulted in the selection of falling-film evaporators for most new installations in recent years.

Plate-type falling-film and tubular-type falling-film evaporators are similar in design and usage.

In plate-type falling-film evaporators, black liquor is fed into the bottom of the unit, from where a circulation pump lifts the liquor up to the top. A liquor distribution system (usually a box with a perforated plate bottom) spreads the liquor evenly on the external surfaces of the heating elements. The liquor flows down and begins to boil. The vapour is separated immediately after generation from the black liquor and flows to the surrounding space. A drop separator at the top of the evaporator ensures the purity of the secondary vapour. The heating medium (steam or vapour) is inside the lamella heat transfer surfaces. In effects where segregation of the condensate is desirable, the vapour is fed to the bottom of the heating element. In other cases, a top feed is preferable. Figure 2.3a shows a plate-type of falling-film evaporator.

FIGURE 2.3a Plate-type falling-film evaporator



Source: reproduced from Holmlund and Parviainen (2000), with permission from Fapet Oy, Finland

Condensate segregation occurs by dividing the heating surface into pre- and post-condensing sections. Cleaner vapour condenses in the pre-condensation section and volatile, odorous, organic sulphur compounds and methanol are carried into the post-condensing section with a small part of the vapour. The vapour feed to the bottom of the heating element increases the efficiency of the segregation through an internal counterflow stripping of the cleaner condensate fraction as it flows down the heating surfaces.

In tubular-type falling-film evaporators, liquor flows both inside and outside the vertical tubes. In the first case, the evaporator has a heating element and a vapour body. The heating element is very similar to that of an LTV evaporator, consisting of a vertically mounted shell and tube heat exchanger. Liquor is pumped to the liquor distributor, which is either a tray with a perforated bottom, or a spray-nozzle type. The liquor and vapour mixture leaving the tubes pass through the vapour body in the bottom of the evaporator where vapour separates from the liquor. A drop separator cleans the vapour before it exits. Separation of the condensate into clean and foul streams is achieved by dividing the shell side into pre- and post-condensing sections using the baffle plate. For cleaning plugged tubes, the same comments apply as for the RF. Washing cannot clean them. Figure 2.3b shows a tube-type falling-film evaporator where liquor flows outside the tubes.

FIGURE 2.3b Tube-type falling-film evaporator where liquor flows outside the tubes

Source: reproduced from Holmlund and Parviainen (2000), with permission from Fapet Oy, Finland

The evaporator construction is more similar to a lamella-type evaporator than to the tubular evaporator with liquor flowing inside the tubes. The tubes are connected to headers that allow an even liquor distribution for the outside of the vertical tubes and the vapour inside the tubes. With current designs, one disadvantage is that the vapour side cross-section area is limited. This type cannot be used in the last effects due to insufficient room for the vapour to pass through. Both lamella and tube falling-film designs with liquor outside the tubes are currently available for medium pressure steam applications.

Andritz Inc. has developed a state-of-the-art evaporation system (Rauscher et al. 2006). Features include the supply of 80–85% firing liquor to the recovery boiler, increasing power and production. The crystallisation technology minimises boil-out frequency. Small electrostatic precipitator (ESP) ash particles are mixed in the liquor and act as nuclei for further crystal growth, enabling supersaturation to be naturally controlled to a low value and the potential for deposition on the heating surfaces to be minimised. Properly selected construction materials offer high dry solids operation. The liquor heat treatment (LHT) ensures high dry solids even with high viscosity liquors. Falling-film technology offers effective heat transfer even at high concentrations and a wide turn-down ratio.

Andritz falling-film evaporators employ dimpled-plate heating surfaces for high dry solids concentrations, using a special heating surface designed for high density liquor. There are low emissions due to optimised condensate segregation and handling and proven process concepts, with quick start-up and easy operation. Crystallisation technology has been also used by Japanese researchers for evaporating black liquor to high dry solids (Jaakola and Hatano 2007).

Forced-circulation evaporators

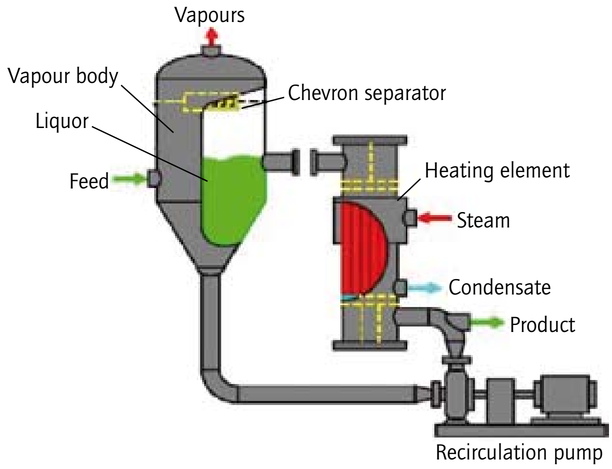
The viscous properties and fouling nature of heavy liquors have led to adaptations of film evaporation technology that was historically used at lower solids, or application of forced circulation crystalliser technology. Falling-film or forced-circulation equipment is typically applied for evaporation to high solids. It is available with liquor film inside or outside the tubes or on plates, usually with provisions for on-line washing and scale removal. Forced circulation equipment is characterised by liquor flow inside the tubes of submerged heat exchangers designed with sufficient back pressure to suppress boiling within the tubes. Forced-circulation units do not typically require frequent washing to maintain a clean heat-transfer surface (Craig and van Dyke 2004).

The enhanced forced-circulation design is an evolution of the conventional forced-circulation technology that has been used for decades for crystallisation of liquor above critical solids. The forced-circulation design is very robust, and there is generally no need for washing or dilution. Above critical solids (typically near 50% total solids), sodium salts begin to precipitate from black liquor. To avoid scaling difficulties, evaporation equipment at this point must be designed to be crystallisers to allow these salts to form in the bulk liquor and not on heat transfer surfaces.

As with any crystalliser, the forced-circulation unit is designed with sufficient retention volume for crystal growth. However, the supersaturation developed in the tube of a forced-circulation unit is lower than that in a falling-film system because boiling within the forced-circulation tube is suppressed. In addition, the temperature rise through the heater is carefully selected to minimise any adverse temperature effects (sodium carbonate and burkeite salts exhibit an inverse solubility). The high tube velocity typically required for the forced-circulation design also counters the effects of high viscosity via shear thinning and increased turbulence.

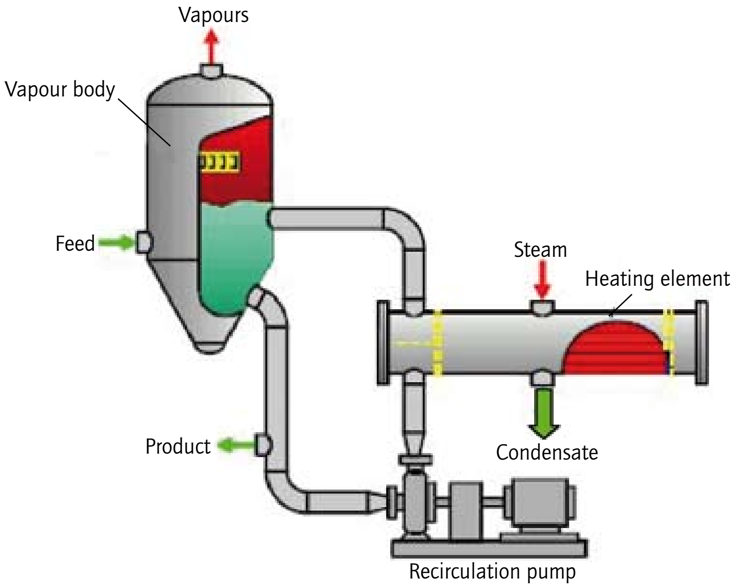
The forced-circulation crystalliser can be supplied with a vertical or horizontal heater. Figures 2.4a and 2.4b illustrate the vertical and horizontal configurations of forced-circulation crystalliser units.

FIGURE 2.4a Forced-circulation crystalliser (vertical heat exchanger)



Source: based on Holmlund and Parviainen (2000); Craig and van Dyke (2004)

FIGURE 2.4b Forced-circulation crystalliser (horizontal heat exchanger)



Source: based on Holmlund and Parviainen (2000); Craig and van Dyke (2004)

A patent was given to Ahlstrom Machinery in 1998 for forced-circulation crystallisers that, they claim, prevent harmful fouling of heat transfer surfaces by controlling crystallisation during the treatment of black liquor. The black liquor is concentrated to a high dry solids content (of at least about 70%, i.e. about 75–90%) in a falling-film crystallising apparatus (e.g. falling-film evaporator). Part of the liquor flowing from the heat transfer surfaces and collected in a retention vessel (e.g. an interior volume of the evaporator) is recirculated to the heat exchange surfaces, and part of the liquor is discharged for further treatment (e.g. combustion in a recovery boiler). Part of the black liquor in the recirculation system is returned directly to the retention vessel in order to facilitate mixing and thus to bring about, in the retention vessel, crystallisation of inorganic salts of the black liquor that is as complete as possible. Some of the discharged black liquor may also be returned, and a mixer and/or baffles disposed in the retention tank in order to enhance the mixing still further (Agren 1998).

In 1990, pilot testing was initiated to study the possibility of applying enhanced heat transfer technology to the high solids crystalliser design. The requirements of the enhanced unit were to increase heat transfer efficiency, decrease power consumption, minimise the possibility of fouling, and still allow for full access to the tubes in case boil-out or mechanical cleaning became necessary because of a severe upset leading to pluggage. A proprietary spiral rib-type design was developed and tested. The design has allowed for an increase of 50–75% in the heat transfer coefficient, and a reduction of 50% in power when compared with the conventional forced-circulation design (Rieke 2002).

In the US, Weyerhaeuser fires up to 80% solids liquor in the recovery boilers at several of its mills. As such, reliable and economical evaporation technology is required to meet the concentration and throughput demands for black liquor consistently. The evaporation systems at Bennettsville and Hawesville have been expanded several times in recent years to meet changing mill needs arising from expansion or upgrades. A great deal of operating experience with different technologies and strategies has been gained as Willamette overcame many problems associated with producing 80% solids on very difficult liquors (rapid-displacement heating, hardwood, neutral sulphite semi-chemical). The introduction of enhanced forced-circulation crystalliser systems in the autumn of 1998 finally allowed high solids liquor production at the rate and reliability required by both mills (Clark et al. 1999; Rieke et al. 2000).

Multiple-effect evaporation

Most black liquor is concentrated in multiple-effect evaporators. These evaporators contain several units (effects), which are connected in series by vapour piping. The water vapour boiled off from the liquor in one effect acts as heating steam in the steam chest of the following effect (Grace 1992a; Bremford and Müller-Steinhagen 1994; Konopa 1997; Holmlund and Parviainen 2000). The principle behind multiple-effect operation is to save the heat in the vapour by causing it to be condensed in another effect operating at a lower pressure and temperature, thereby raising the concentration of black liquor solids in stages. The major performance factors in evaporator plants are:

- steam economy (the amount of water evaporated per unit of live steam used)
- evaporator capacity (the heat transfer rating)
- scaling of the evaporator tubes (scaling causes a loss in evaporator productivity).

Increasing the number of stages increases steam economy, which is also affected by factors such as:

- the type of evaporator
- the characteristics of the feed/discharged liquors, steam and condensate
- the liquor/vapour flow sequence
- condensate flashing.

The temperature of the feed liquor considerably affects steam economy, improving it as the feed liquor temperature increases. The operating steam pressure in the first evaporator effect also affects steam economy, with high steam pressures decreasing the economy. This is caused partly by the higher temperature levels in the evaporator, and partly by the lower latent heat of the steam at high pressures. Steam economy is reduced when an evaporator becomes scaled and the steam pressure is increased to maintain evaporator capacity.

Steam economy is affected by the total solids concentration of the evaporator feed and the discharged liquors. It decreases if the feed solids concentration is increased and the discharged liquor concentration is reduced. This is due to the fact that more liquor is pumped through the evaporator in relation to the evaporation rate. The additional liquor should be heated to the boiling point in the evaporator effects, meaning that less heat is available to cause evaporation.

Most black liquor evaporators are provided with liquor and condensate flash systems (Holmlund and Parviainen 2000). Steam economy is affected by the number of stages of liquor and condensate flash and the temperatures of the discharged liquor and condensate. The steam condensate should not be flashed as this requires additional boiler feed water heating.

The liquor flow sequence within the evaporator system can significantly affect steam economy. Generally, the feed liquor is introduced into the high vacuum effects and the liquor is pumped in a straight backwards flow to the first or steam effect. The feed liquor is ideally introduced into the effect nearest the liquor temperature to reduce liquor preheating or flashing, as a result of which many LTV evaporators use variations of the backward flow to increase steam economy. Many liquor flow sequences are possible in LTV trains that feature integral liquor preheaters or after-heaters.

The vapour flow sequence could have a direct influence on steam economy. Falling-film multiple effect evaporators with a lower required temperature differential and specific liquor loading may allow designs with a larger number of effects than rising-film LTV units. Steam economy generally improves as the number of effects increases.

To determine the evaporator capacity, the heating surface area, available temperature drop, and the overall heat transfer coefficients are used. To evaluate the capacities of evaporators with a different number of effects, the average heating surface per effect should be taken into consideration. A six-effect evaporator with the same amount of total heating surface as a five-effect evaporator would have a lower evaporation capacity because the capacity of a multiple-effect evaporator is also directly proportional to the total temperature difference, or the sum of the temperature drops for the various effects. Because of the boiling point rise of the liquor being concentrated, the total effective temperature difference is decreased as more effects are added. A five-effect evaporator operating under the same process conditions will have more capacity than the six-effect system.

The temperature distribution in a multiple-effect evaporator depends mainly on the individual heat transfer coefficients in the various effects (Smook 1992). The heat transferred in each effect is equal or almost equal, and so the temperature drop for each effect is inversely proportional to the heat transfer coefficient for that effect.

Evaporator scaling and scale formation is dealt with on page 36.

Production of black liquor of high solids

Black liquor is concentrated to at least 60% solids before it is fired into the recovery furnace. Multiple-effect LTV evaporators are not able to produce firing strength liquor. They are usually limited to about 48–52% solids because they are prone to severe fouling beyond about 50% solids and are sensitive to high liquor viscosity. The following approaches are used to produce firing strength liquor:

- Liquor is concentrated to about 50% solids in a multiple-effect evaporator train and then brought to firing strength in a concentrator.
- Liquor is concentrated to 65% solids in a multiple-effect train using evaporators that are not as sensitive to viscosity and fouling problems. These are usually falling-film units.
- Liquor is concentrated to 50% solids in a multiple-effect train and then brought to firing strength in a direct contact evaporator.

Several problems are created when black liquor is concentrated to high solids:

- high liquor viscosities
- increased chance of scale formation
- significantly increased BPR
- a strong tendency for local overconcentration.

As solids are increased beyond 60%, the viscosity of black liquor increases rapidly. A typical 65% solids black liquor will have a viscosity of about 200 mPa·s at 93.3°C. Viscosities of about 200 mPa·s for softwood liquors with 70% solids content at 110°C have been reported (Co et al. 1982; Sandquist 1983). This is a practical limit for the use of centrifugal pumps, and sets the minimum liquor temperature at about 93.3–110°C, depending on product solids levels.

High viscosity also affects the heat transfer coefficient. From this point of view, it would be advantageous to operate at the highest temperature possible, but there are other reasons for avoiding high temperatures in the high solids stage. Heat transfer coefficients are generally lower in concentrators because of the high viscosity.

For almost all black liquors in the range of 48–53% solids, the solubility limit for sodium sulphate and sodium carbonate in black liquor is exceeded. Liquors concentrated to firing strength are beyond the carbonate–sulphate solubility limit. These inorganic salts will precipitate as the liquor is concentrated and can foul the heat transfer surface. Carbonate–sulphate precipitation is a concentration-driven process, and the bulk of the material will come out at the point where the concentration occurs.

At high surface temperatures, scaling becomes a big problem (Grace 1992a). It has been reported that scaling problems can be reduced by keeping the condensing steam temperature below 135–143°C. This sets the upper temperature limit for the operation. Steam should be saturated. Desuperheating is not important when the tube surface is clean since the good heat transfer will condense the steam and it will self-desuperheat. When scale builds up, it acts as an insulating blanket and allows the surface temperature to approach the superheated steam temperature. This bakes the deposit on, making it hard to remove.

The BPR of the liquor rises rapidly above 50% solids. It may approach 13.9°C or more at 65% solids. Since the sum of all boiling point rises is deducted from the total temperature difference in determining working ΔT, this can be strictly restrictive, especially if the concentrator is introduced directly in the multiple-effect sequence. To avoid this problem, the concentrator usually operates separately from the balance of the evaporator. Liquors at high solids are very sensitive to local overconcentration because a small amount of vaporisation causes a relatively large increase in solids concentration. This sensitivity, coupled with the strong tendency for viscosity to increase as solids increase, can lead to regions of very high solids content that then become baked-on deposits.

Concentrators are simply steam-heated evaporators. These are designed to produce liquor suitable for firing directly and not to involve contact between the black liquor and the flue gas. Successful concentrator designs deal effectively with the problems mentioned above.

Not much can be done to reduce the viscosity of the liquor at high solids contents, but steps such as avoiding oxidation and maintaining adequate residual alkali can be taken to avoid very high viscosities. The concentrator design handles the higher viscosity liquor by providing for additional heat transfer surface to accommodate the lower heat transfer coefficients. Higher flow velocities may also be used.

The concentrator design must allow for the precipitation of sodium sulphate and sodium carbonate that will occur. There are two main approaches:

- the design can allow frequent washing with low-solids liquor, which will dissolve the deposits that are soluble in weak liquor;
- the design can provide for crystallisation of the carbonate and sulphate in the bulk liquor rather than on the heat transfer surface.

BPR is an important factor in concentrator performance, and must be used in the design of the system. Since BPR causes a loss in potential working temperature drop, it can be handled by increasing the amount of heat transfer surface, by using a small number of effects and by using evaporator types that work with low ΔTs. Problems due to local overconcentration can be overcome by eliminating stagnant or low flow areas in the heating section. High recirculation rates are helpful, as are measures that provide positive flow distribution over the heating surface.

Different types of concentrators have been used. The original systems were modified LTVs, the most successful of which was the preheat-falling-rising evaporator. For optimum concentrator operation, proper selection of the area ratios for the preheat, falling and rising film sections and the circulation pump capacity is essential. Problems with flow distribution and plugging in the upper part of the falling zone have been encountered. In new installations, plate-type falling-film evaporators and crystalliser/evaporators are mostly used. Falling-film evaporators are being used to produce liquors at solids contents of more than 65%. Plate-type falling-film units are operated to final solids of 67–70%, and operation to 75% or higher has been reported (Rosenblad 1976; Fosberg and Claussen 1982).

Falling-film evaporators are capable of operating with low ΔTs, and falling-film concentrators are generally incorporated at the lead end of the multiple-effect train. Plate-type units are in the majority. Fouling problems are easy to control because the scale is readily accessible to the wash liquor, and the relatively flat surface of the heating elements increases scale cracking and thus makes it easy to remove subsequently. Automatic switching of liquor between heating sections can allow periodic washing with weaker liquor without shutting down the evaporator. The key to successful high solids operations is the proper evaporation rate per unit area and the liquor recirculation rate.

As already discussed, crystalliser-type concentrators employing the forced-circulation concept are also extensively used for concentrating black liquor to 67–73%, with concentration beyond 75% possible. These are mostly used in new installations.

Metso pioneered superconcentration and high dry solids firing in the mid 1980s. Since then, it has installed most of the concentrators in the world that produce liquor in the 80–85% concentration range. Increasing dry solids concentration improves recovery boiler capacity and performance, and increases steam production. Concentration to 80% solids in a commercial operation has been reported by Hyoty and Ojala (1988). The superconcentrator system is placed between the salt cake mix tank and the furnace. The main components are a tube-type falling-film evaporator and a flash tank. The steam supply to the evaporator is at 10 bar. The liquor side of the falling-film evaporator and the flash tank are kept under sufficient pressure to sustain a liquor temperature at which viscosities are 200 mPa·s or lower. There is provision for circulation of liquor back to the mix tank. Liquor storage is at the relatively low concentration (65%) that exists in the mix tank. The flash tank can be used for temporary storage of high solids liquor while the falling-film evaporator is being washed. The availability of the system was as high as 93% during the first 18 months of operation.

The three-dimensional model was used by Karvinen et al. (1991) to investigate the effects of increasing the dry solids content of black liquor on its combustion in a recovery boiler. It was found that increasing the solids content to more than 75% produced advantages over conventional firing. The temperature in the lower part of the furnace of a conventional boiler increased with a higher dry solids content. This in turn caused higher reduction rates, reduced fouling and lower sulphur emissions. At the same time, fuming and the amount of fly ash increased, but corrosion of colder parts decreased.

Vakkilainen and Holm (2000) studied firing of very high solids black liquor in recovery boilers. Liquor sheets formed from firing 90% black liquor were visually similar to those from 75% black liquor. No significant problems were observed with the spraying or burning of 90% dry solids black liquor.

Direct-contact evaporators are also used for producing black liquor of high solids. In direct-contact evaporators, liquor is concentrated by bringing it into direct contact with hot flue gases from the recovery boiler. Direct-contact evaporators utilise the low level heat available in the flue gas, which can be expensive to recover by other means. These evaporators are relatively free of the problems associated with solids precipitation and high liquor viscosities. The drawbacks of these evaporators are a relatively low heat economy and a problem of release of odorous gases.

Two types of direct contact evaporators are in use: the cascade evaporator and the cyclone evaporator. The odour problem can be solved by oxidising the black liquor before it enters the direct contact evaporator, which is subject to problems with plugging and fires. Direct contact evaporators are nowadays outdated, although many remain in operation.

Other methods of concentration

Other methods of concentration include vapour-compression evaporation (VCE), blow-heat evaporation, and flash-steam evaporation (Venkatesh and Nguyen 1992; Holmlund and Parviainen 2000).

Vapour-compression evaporation

It is possible to obtain very high energy efficiency with this method by eliminating the latent heat losses. The vapour produced by the boiling liquor is passed through a compressor to increase its pressure and temperature before it is returned to the heating element as the steam supply. Compression is required to increase the saturation temperature of the vapour in order to establish a heat transfer driving force. The increase in saturation temperature needed equals the BPR plus the heat transfer driving force.

In the VCE system, condensate leaving the unit is used to preheat the feed and improve the overall economy. A small amount of make-up steam is used to supply the vent losses and to start the system up. VCEs can operate with very high equivalent steam economies. The energy required for VCE is mechanical or electrical energy, while the multiple-effect system uses steam. VCE is suitable for areas where electricity is cheaper than steam.

Multistage compressors can be used to increase the differential pressure and temperature, but the resulting increase in capital and power costs has to be assessed. The use of low temperature differences across the boiling surface of a VCE involves designing evaporators with high heat transfer coefficients and minimal fouling tendencies. Falling-film evaporators are used in the design of new installations. Good entrainment separation characteristics of the evaporator body and a short, well-insulated vapour line are used to minimise droplet carry-over, which is damaging to the compressor blades. Some degree of superheat at the vapour inlet is maintained by returning a small part of the discharge vapour to the suction inlet. Since this is wasteful of compressor horsepower, superheat should be kept to a minimum. The superheat protects the impeller from any entrained droplets.

The use of centrifugal compressors has allowed larger system capacity and lower capital cost. Rosenblad (1976, 1979, 1981) suggested a VCE system with two single-stage compressors to concentrate black liquor from 15–65% solids. The evaporator is split into multiple sections, which operate in parallel on the steam side and in series on the liquor side so that only a small portion of the evaporator is exposed to the most concentrated liquor with its low heat transfer coefficients and high BPR. Steam for this section of the evaporator has two-stage compression, which provides sufficient temperature differential for good performance. The specific power consumption is estimated at 29kWh/tonne of evaporation.

In comparison with conventional evaporators, the capital investment is higher in VCE systems because of the added compressor costs and the lower available temperature difference, which dictates greater heating surface areas. In certain cases, this added cost may be recovered in savings on operating expenses.

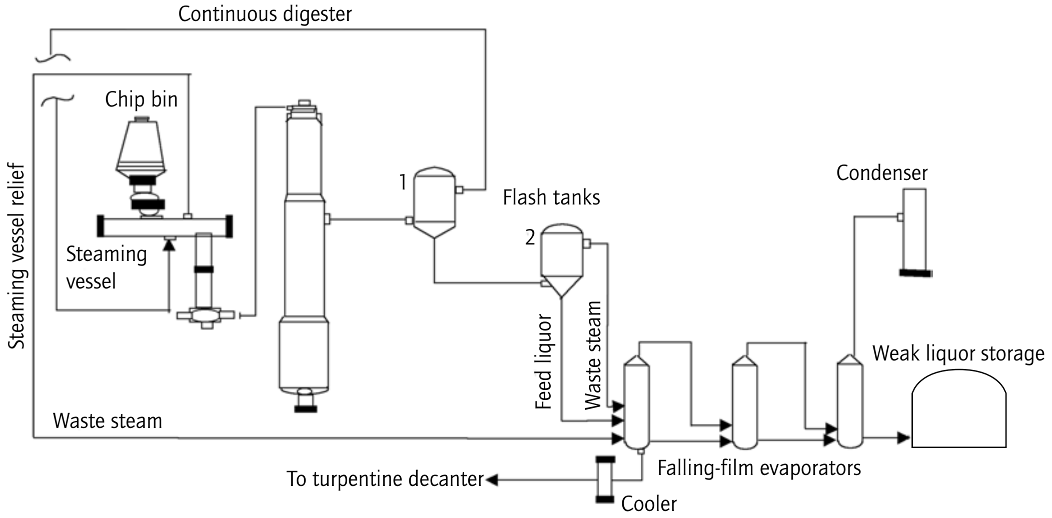
Blow-heat evaporation

The blow-heat evaporator was developed and patented by Jacoby in the early 1960s, and has been refined since then. Batch digesters are usually blown into an atmospheric pressure blow tank. The steam released is usually condensed in a barometric condenser mounted above a large hot water accumulator. The condensate produced is at a temperature of about 96.1–98.8°C, and can be used as a heating medium for a two- or three-effect evaporator used as a preconcentrator. Three-effect systems are also in use (Rosenblad 1976).

Flash-steam evaporation

Evaporation systems have been developed that employ flash steam from continuous cooking systems, utilising the higher heat content of the extraction stage black liquor. This liquor, usually at about 160°C, is flashed in two stages. In the first flash stage, steam is used for pre-steaming wood chips, and in the second steam is used to produce hot water. Kamyr's two- or three-effect falling-film evaporator system and the Lockman multiflash evaporator both use flash steam to concentrate weak liquor in a pre-evaporation step prior to multiple-effect evaporation. Figure 2.5 shows a three-effect evaporator operating on flash steam from a continuous digester. Steam from the second flash tank and pre-steaming vessel exhaust are used as the steam supply to a three-effect falling-film evaporator. This system is capable of reducing steam consumption in the subsequent evaporation step by 20–30%.

FIGURE 2.5 Three-effect flash-steam evaporator



Source: reproduced from Venkatesh and Nguyen (1992), with permission from TAPPI Press

The Lockman multiflash evaporator has been used for kraft liquor pre-evaporation up to 18% solids. In this system, the extraction liquor from the digester is flashed down to 100–120°C in two consecutive flash tanks. The vapour from the first flash tank is used in the pre-steaming vessel, and the vapour from the second flash tank is combined with the relief steam from the pre-steaming vessel in the primary heat exchangers of the evaporator column. Alternatively, vapours from both flash tanks can be used in the primary heat exchangers.

Modern evaporation

The capacity of the evaporator has increased, and there are now around six evaporators operating at or more than 1,000 tonnes of water per hour. The number of effects is commonly seven or more. The traditional five-effect evaporator has almost disappeared because of increased attention to energy efficiency and operating costs (Vakkilainen 2007a).

As evaporator technology has evolved, the final black liquor dry solids content has increased. Greenfield mills have been designed to use 80–85% dry solids, with 80% dry solids in use in Asia and South America (hardwood liquors), and 85% in use in Finland (softwood liquors).

Falling-film evaporators are the modern choice, and the most common evaporator type selected for black liquor. Biosludge is often evaporated to be burned with black liquor in the recovery boiler. New evaporators achieve better secondary condensate purity (i.e. better overall methanol removal), so more efficient reuse of condensates can be made at the mill. All new plants have efficient foul condensate stripping and a methanol liquefaction system integrated with the evaporator train. The use of Duplex steel materials for all surfaces exposed to black liquor above 70% dry solids content has become standard.

High solids units seem to require much more heat surface per ton of evaporation than the rest of the evaporation. The principle of the LHT system, as either a stand-alone unit or as extended time at high temperature in an evaporator body, is applied to lower the liquor viscosity at high dry solids content.

Almost all new evaporator projects utilise the principle of mixing the recovery boiler ESP ash before the last evaporation stage, which improves the evaporator operation. New evaporators tend to store the firing liquor under pressure in order to maintain a high enough temperature to manage viscosity at high dry solids content. Much more emphasis is now being placed on total integration of evaporators into the mill secondary heat balance. Examples are:

- higher weak liquor temperatures to evaporation;
- the production of hot water with steam from evaporator low solids effects and surface condensers;
- integration of pre-evaporation of effluents (chemi-thermomechanical, bleach plant effluents) into the main evaporator train.

Scaling and scale control

Scale is solid matter that originates from materials that are insoluble or have low solubility in the weak or strong black liquor. Severe scaling may be a serious bottleneck to pulp production, especially if the evaporators are undersized or if the mill is dependent on a single train of evaporators and weak liquor storage capacity is limited (Westervelt et al. 1982; Grace 1985, 1992a; Holmlund and Parviainen 2000).

Evaporator scaling indicates that something is wrong in the pulp mill. When black liquor is concentrated, the scaling or fouling of heating surfaces will appear at the concentration typical for each type of scale deposit. When scaling starts in the evaporator, malfunctions are possible in the following departments of the pulp mill:

- recovery boiler;
- causticising plant;
- de-barking plant;
- cooking and washing;
- evaporation plant;
- excessive amount of spent acid from the chlorine dioxide or tall oil plant is introduced to the evaporators.

Black liquor from the pulping of nonwoody raw materials contains a very high amount of silica and aluminium, both of which contribute to hard, glossy scaling that is very difficult to remove. Normally, a heavy liquor concentration with a maximum of 50% dry solids can be reached in multiple evaporation, and the final concentration is made in a cascade- or cyclone-type direct contact evaporator.

Table 2.9 shows the scale material present in black liquor. Insoluble materials such as dirt, fibre, or pipe linings can also plug the tubes or restrict flow. Other materials – such as tall oil soap, lignin, calcium carbonate, or sodium salts – generally coat the tube surface.

TABLE 2.9 Insoluble materials in black liquor

Material insoluble in weak (15% solids) liquor:

- Fibre
- Sand, dirt, etc.
- Miscellaneous (pieces of pipe, gasket material, etc.)

Material insoluble in stronger black liquor:

- Tall oil soap (at 25–30% solids)
- Lignin (at pH below 11)
- Calcium carbonate scale:
  - water insoluble
  - forms at higher temperatures from calcium-organic complexes
- Sodium carbonate–sodium sulphate
  - Double salt forms when critical solubility limit is reached (usually about 50% solids)
- Silica and aluminium-silica scales
  - Difficult to remove

Source: reproduced from Venkatesh and Nguyen (1992), with permission from TAPPI Press

There are two major types of scale caused by the inorganic salts present in black liquor: water-soluble scale, and water insoluble calcium scale. Water-soluble scale is sodium sulphate–sodium carbonate double salt, which generally precipitates at higher black liquor solids (above 50%). Water insoluble calcium scale is calcium carbonate precipitate that occurs at all solids levels and at temperatures above 120°C.

Calcium carbonate scaling is the main cause of evaporator scaling and reduced evaporator capacity, and results from the high calcium content in the weak black liquor. Water-soluble (sodium sulphate–sodium carbonate) scale, while prevalent, is less of a problem with respect to sustaining evaporator capacity as it is relatively easy to remove. Insoluble calcium carbonate scale can also form as rapidly as the soluble sodium sulphate–carbonate scales, and thus affect short- and long-term evaporator performance.

The wood supply is the main source of calcium. Calcium scaling is greater in mills that use hardwoods. The rate of calcium carbonate scaling depends strongly on the temperature, but does not appear to be strongly dependent on the solids content of the liquor. Scale distributions have been found to be reasonably uniform in the boiling region.

Both soluble and insoluble scale depositions are complicated by the presence of organics in the black liquor. Organic components such as lignin or hydroxy acids, which contain adjacent hydroxyl groups, may form a chelate with calcium that greatly increases its solubility in black liquor. These organic components are divided into two groups with respect to their impact on calcium carbonate scaling.

The first group includes organics whose ability to form complex salts with calcium depends on pH in the normal range for black liquor, and whose stability constant decreases with increasing temperature. This group will contribute to calcium carbonate scaling by releasing ionic calcium as the temperature increases.

The second group consists of compounds whose ability to interconnect with calcium does not change significantly with the pH, and whose stability constants are temperature-independent or increase with temperature. This second group does not contribute to calcium carbonate scaling. Consequently, as long as the first group of compounds and sufficient calcium are present, calcium carbonate scaling will form. Because of the relationship between the pH and the release of complexed calcium ion, caustic is sometimes added to weak black liquor to control calcium carbonate scaling.

Interest has been renewed in the thermal deactivation of free calcium bound to the organics by precipitation. The calcium is precipitated out, and the liquor is considered deactivated since it has lost its tendency for calcium scaling. A study conducted by Siren (2007) to clarify the mechanisms involved in calcium carbonate scaling in black liquor evaporation and to discover a basis for countermeasures, found that burkeite plays a significant role in the formation of calcium carbonate scale. When the solubility limit of burkeite is exceeded, hard calcium carbonate scale ceases to occur. The species of wood also has an effect. Consideration of scaling countermeasures has revealed that there is no universal solution to the problem. Countermeasures may be aimed at lowering the level of dissolved calcium, improving the complexing ability of the liquor, or shifting the burkeite solubility limit downwards. The level of dissolved calcium may be lowered by deactivation and changing liquor concentrations in the cooking department.

With the shift to falling-film evaporators, scaling problems are much less of an issue. Falling-film units are subject to significantly less scaling than the LTV evaporators because no bulk boiling takes place inside the tubes or on the plates, and consequently no dry spot formation exists where scaling can start. Falling-film evaporators are run at lower steam pressures than the LTV systems, which minimises the scaling caused by reverse solubility compounds such as sodium sulphate or temperature-sensitive calcium complexes. Tube pluggage in the higher solids effects (53% or more concentration) of some tube-type units has been observed, caused either by poor liquor distribution or high heat flux due to abnormally high working temperature differences. Scaling can be reduced by designing falling-film units operating in the 50–60% solids range with a lower temperature differential and heat flux. In plate-type systems, pluggage cannot occur. Typically, falling-film units may require washing twice a year during regular mill shut-downs.

Tables 2.10 and 2.11 suggest strategies for the prevention and control of water-soluble and insoluble calcium scale in LTV evaporators.

TABLE 2.10 Prevention and control of calcium scale

Operation	▶ Low stream temperatures to minimise scaling rate ▶ Efficient soap separation ▶ Liquor recirculation pumps to prevent tube pluggage ▶ Isolate hardwood liquor ▶ Calcium deactivation
Cleaning	▶ Steam shock during water boil-out ▶ Periodically dump flow boxes to remove calcium flakes ▶ Periodically wash high-temperature effects with acid solution ▶ Hydroblast as necessary to clean plugged tubes
Don'ts	▶ Weak liquor oxidation ▶ Chemical additives ▶ Add alkali above 1% soda liquor solids

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TABLE 2.11 Prevention and control of water-soluble scale

Liquor composition:

- Improve reduction efficiency to lower sulphate content
- Improve causticising efficiency to lower carbonate content
- Add sidestreams – such as brine, chlorine dioxide spent acid and neutral sulphite semi-chemical liquor – to heavy liquor
- Do not add caustic to liquor since this lowers critical solids
- Keep fibre to a minimum

Evaporator operation:

- Run product solids below the critical solids
- Recirculate liquor around first effect
- Weak liquor boil-out to remove scale, not water boil-out
- Stable operation – prevent localised overconcentration

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Water and weak liquor boil-out are also routinely practised to keep fouling at tolerable levels. When scaling is severe, chemical cleaning with inhibited hydrochloric or sulphamic acid is recommended as a longer-term solution. As a last resort, hydroblasting can be used when tubes are plugged, or acid cleaning when short-term and regular boil-outs cease to be effective because of severe calcium carbonate (and in some cases silica) scaling on the liquor side and inside the tubes.

Black liquor also gets baked on to the tube surfaces with the inorganic calcium. These deposits are best removed by treatment with a 5% inhibited hydrochloric acid solution, or with sulphamic acid.

Sodium aluminium silicate scale is mainly comprised of aluminosilicate with a small amount of sodium carbonate and sodium sulphate, producing a hard glassy deposit. Sodium aluminium silicate scale forms a persistent layer that grows very slowly on the heating surfaces. Even a thin layer reduces the heat transfer markedly. The deposits normally form on the heating surfaces of the first effect and the final concentrators, although the other effects can also become fouled. The aluminium concentration determines the scaling rate. An aluminium content of 0.02% dry solids is the limit above which one can expect problems with aluminium and silica scaling.

In North American and Scandinavian mills, silicate scaling is not a common problem because its input into the recovery cycle is small. Silicate scaling does, however, plague evaporators for bamboo, bagasse and various straw liquors in these mills. Silicate can be controlled by purging lime mud or lime kiln ash. Silicate removal systems for black liquor operate in soda pulping mills. Silicate removal from green liquor in a soda-based pulp mill may be achieved by lowering the pH of the liquor with carbon dioxide-containing flue gases from the lime kiln or other sources. In-plant measures for scaling abatement include a silicate removal system for liquor from soda-based pulping only. Other possibilities are thermal shocks or cleaning. The second option uses an acid wash or a chemical treatment. The acid wash uses an inhibitor that reduces the corrosion on the metal surfaces of the evaporator.

Under certain circumstances, other types of deposits may also occur. Lignin precipitation is a potential problem if the liquor alkali level drops too low, although this usually shows up as a viscosity problem rather than a scaling problem. Tube wall temperatures in excess of 150°C can initiate thermal decomposition of liquor organics and result in baked-on deposits.

Evaporator troubleshooting

The main problems that can be encountered with multiple-effect evaporators are:

- low capacity
- low steam economy
- contaminated condensate
- instability (Venkatesh and Nguyen 1992).

The indications of low capacity are clear when sufficient liquor cannot be fed to the evaporator to maintain levels in the weak liquor tanks and at the same time produce acceptable solids in the recovery boiler. This problem is related to the working temperature drop and heat transfer coefficient of the evaporator system, and scaling, discussed above, is the main cause of reduced heat transfer coefficient. The condenser vacuum can have a direct effect on capacity (Marr 1996; Marr and Adams 2000). The ejector system does not create the vacuum; it is designed to remove the non-condensable gases. The vacuum will decrease if there is too much non-condensable gas in the feed liquor or air infiltration. Operators will increase steam temperature to compensate in an effort to maintain capacity, which can increase scaling problems.

The likely causes of low steam economy are:

- excessive venting, especially from the first, second and third effects;
- vapour blowing or liquor flowing into downstream effects and product flash tanks and fouling after-heaters so that liquor from a colder effect is not properly reheated before entering a hotter effect.

Exclusion of after-heaters can require high preheat duties on the upstream effects. If malfunctioning of after-heaters is suspected, approach temperatures can be determined and compared with those of clean heaters.

Contaminated condensates are generally produced by non-functioning entrainment separators or by evaporator tube leakage.

Instability in multiple-effect evaporators is often characterised by fluctuations in steam flow and product solids concentration. During normal operation, steam flow and product solids should be stable. Evaporator instability is usually due to unsteady liquor flow.

Instrumentation and process control

Instrumentation has enabled mills to troubleshoot, improve evaporator performance, schedule boil-outs, and institute preventive maintenance programmes. For good evaporator operation, effective process control systems are necessary. The objectives for process control of black liquor evaporators are:

- stabilise evaporator operation and maintain uniform product concentration
- maximise black liquor solids throughput
- improve overall evaporator efficiency in terms of steam economy
- respond to swings in production rate.

Control of product liquor concentration in a steam-limited situation is achieved by adjusting the weak black liquor flow. If the steam supply is not limited, the steam pressure is the primary control variable. The main requirements of an evaporator control system are:

- to damp oscillations in product solids quickly
- adjust steam flow
- compensate for upstream changes in header pressure
- correct feed liquor solids concentration.

Distributed control systems are replacing the conventional instrumentation panel in newer installations. Several vendor-packaged systems are currently available in which the vendor supplies the necessary hardware, software and support programs. Computer simulation models describing the dynamics and control of multiple-effect evaporators have been published (Rosenblad 1981; Grace 1992a). The control strategies proposed have relied on classical feedback/feedforward algorithms.

Auxiliary operations

In addition to the concentration of black liquor, other operations can take place in the evaporator area under the control of the evaporator operators. These include fibre removal from weak liquor, soap recovery, black liquor oxidation and condensate treatment.

Black liquor combustion

3

The recovery boiler is an extremely important area in chemical recovery, acting both as a chemical reactor and a steam generator (Perecin 2006). The invention of the recovery boiler by GH Tomlinson in the early 1930s, was a milestone in the advancement of the kraft process. The kraft recovery boiler has three basic functions:

- it burns the organic material in the black liquor to generate high pressure steam;
- it recovers the inorganic chemicals from black liquor;
- it minimises discharges from several waste streams in an environment-friendly way (Adams 1992b; Smook, 1992; Vakkilainen 2000a, 2000c, 2005).

To maximise the recovery of the inorganic chemicals, the furnace's smelting area must be in an oxygen-deficient reducing atmosphere. Conversely, an oxygen-rich oxidising zone must be maintained to combust the organic material efficiently. A further complication is introduced by the very nature of the black liquor fuel. As-fired (to the furnace) black liquor contains approximately 30% water by weight, which must be evaporated within the lower furnace before pyrolysis and combustion reactions can begin.

Development of recovery boiler design

Interest in kraft recovery boilers spread fast as chemical recovery gave kraft pulping an economic advantage over sulphite pulping (Boniface 1992). The first recovery boilers had a horizontal evaporator surface followed by superheaters and more evaporation. These boilers resembled the state-of-the-art boilers of some 30 years earlier.

The first recovery boilers had severe problems with fouling (Deeley and Kirkby 1967). The tube-spacing of a coal-fired boiler had to be widened to become suitable for recovery boilers, which gave satisfactory performance for 5.5 days before water washing was necessary. Mechanical sootblowers were quickly adopted, as were electrostatic precipitators in order to control chemical losses. There is thus more than 50 years' experience of reduction of dust-loss in flue gases.

The number of air levels in recovery boilers soon became standardised at two. One primary at the char bed level, and a secondary one above the liquor guns. Initially, the furnace lining was of refractory brick. The flow of smelt on the walls required frequent replacement, however, and soon designs were developed that eliminated the use of brick. The standard then became the tangent furnace wall, with membrane wall use becoming widespread in the 1960s.

Significant changes in kraft pulping have occurred in recent years (Ryham 1992; Lindberg and Ryham 1994; Vakkilainen 1994). The combined use of extended cooking, hot alkali extraction and oxygen delignification make it possible to reach kappa numbers as low as 10 before bleaching, which has increased the degree of organic residue recovery. Black liquor properties have reflected these changes (Table 3.1).

TABLE 3.1 Development of black liquor properties

Property	1982	1992	2002
Liquor dry solids (kg dry solids per tonne pulp)	1,700	1,680	1,760
Sulphidity: Na2S/(Na2S + NaOH)	42	45	41
Black liquor higher heating value (mJ/kg dry solids)	15.0	13.9	13.0
Liquor dry solids (%)	64	72	80
Elemental analysis (% weight)			
C	36.4	34	31.6
H	3.75	3.50	3.40
N	0.1	0.1	0.1
Na	18	18.4	19.8
S	5.4	5.9	6
Cl	0.2	0.4	0.8
K	0.75	1.0	1.8
Cl/(Na + K) (mol %)	0.70	1.37	2.49
K/(Na + K) (mol %)	2.39	3.10	5.07
Net heat to furnace (kW/kg dry solids)	13,600	12,250	11,200
Combustion air* required (m^3N/kg dry solids)	4.1	3.7	3.4
Flue gas* produced (m^3N/kg dry solids)	4.9	4.3	3.9

*Note: Na2S, sodium sulphide; NaOH, sodium hydroxide; C, carbon; H, hydrogen; N, nitrogen; Na, sodium; S, sulphur; Cl, chlorine; K, potassium; *at air ratio 1.2*

Source: reproduced from Vakkilainen (2000c), with permission from Fapet Oy, Finland

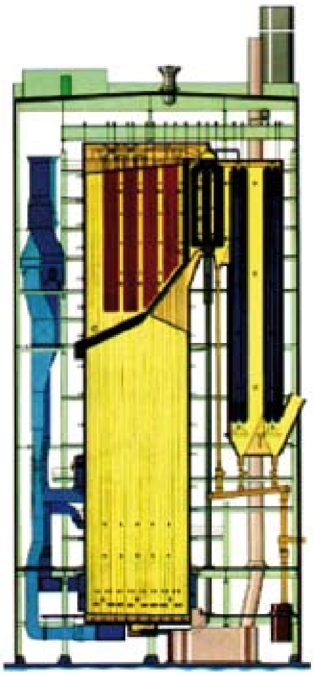
Steam generation increases as black liquor dry solids content increases. For a rise in dry solids content from 65% to 80%, the main steam flow increases by about 7%. The increase is more than 2% for each 5% increase in dry solids. Steam generation efficiency improves slightly more than steam generation itself, mainly because the drier black liquor requires less preheating.

There are recovery boilers that burn liquor with solids concentrations that are higher than 80%. However, unreliable liquor handling, the need for pressurised storage and high pressure steam demand in the concentrator have frequently prevented sustained operation at very high solids. The main reason for the handling problems is the high viscosity of black liquor associated with high solids contents. Black liquor heat treatment can be used to reduce viscosity at high solids (Kiiskilä et al. 1993).

Two-drum recovery boiler

Most of the recovery boilers operating in 2008 are of the two-drum design (Figure 3.1). Their main steam pressure is typically about 85 bar (absolute), with a temperature of 480°C (Vakkilainen 2000c). The maximum design solids handling capacity of the two-drum recovery boiler is about 1,700 tonnes of dry solids per day. Three-level air and stationary firing are employed.

FIGURE 3.1 The two-drum recovery boiler

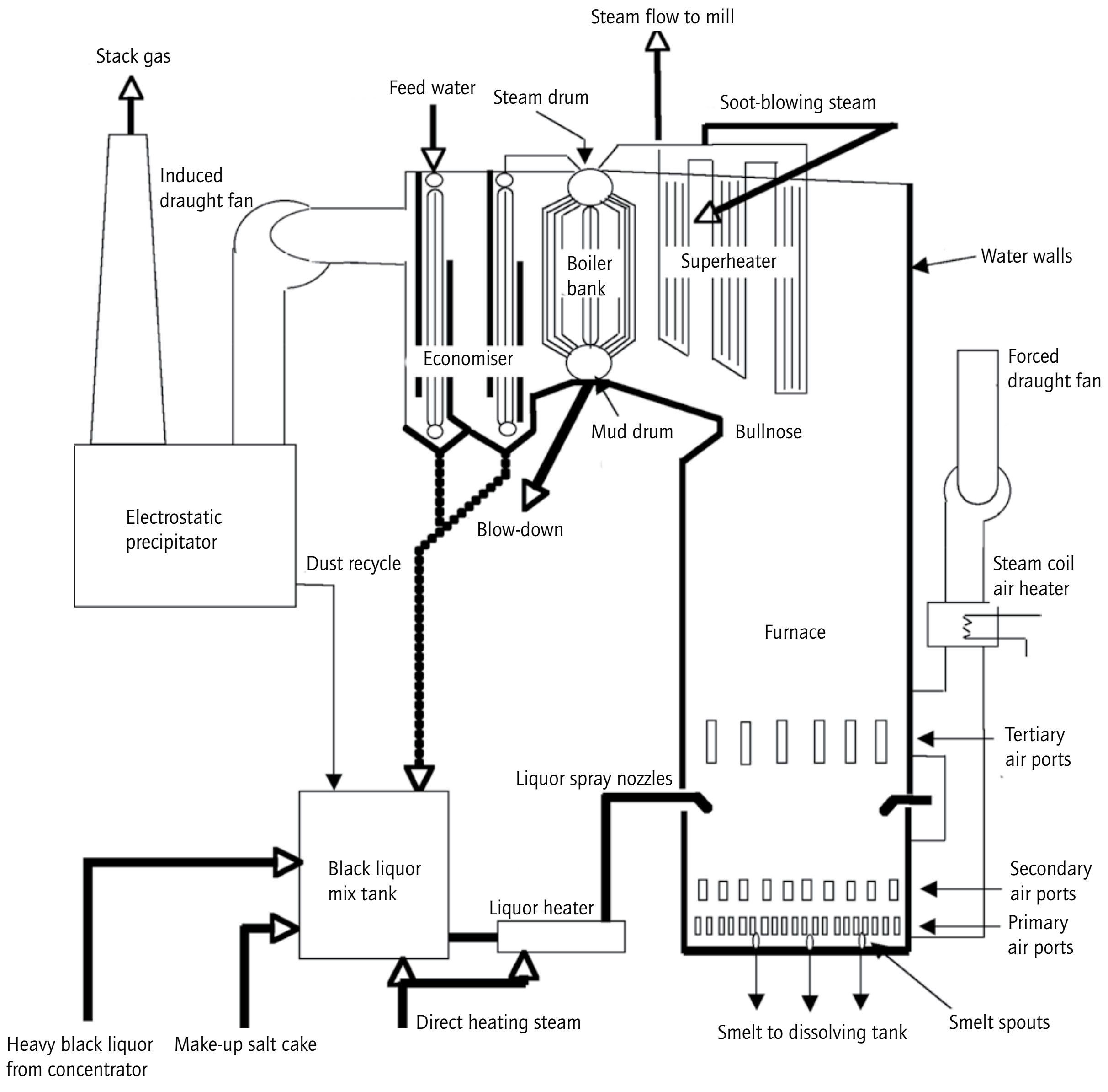


Source: reproduced from Vakkilainen (2000b), with permission from Fapet Oy, Finland

The two-drum boiler represents one successful stage in a long evolutionary path, and it signified a design in which the sulphur emissions could be successfully minimised. The main steam temperature was increased to 480°C using this design. Two-drum recovery boilers are constructed with a water screen to protect superheaters from direct furnace radiation, to lower flue gas temperatures, and to decrease combustible material carry-over to superheaters.

The two-drum boiler was the first type to use vertical-flow economisers, which replaced horizontal economisers because of their improved resistance to fouling (Figure 3.2) (Adams 1992b, 1997).

FIGURE 3.2 Schematic diagram of a kraft recovery boiler system with a two-drum boiler



Source: reproduced from Adams (1992b), with permission from PAPTAC

Modern recovery boiler

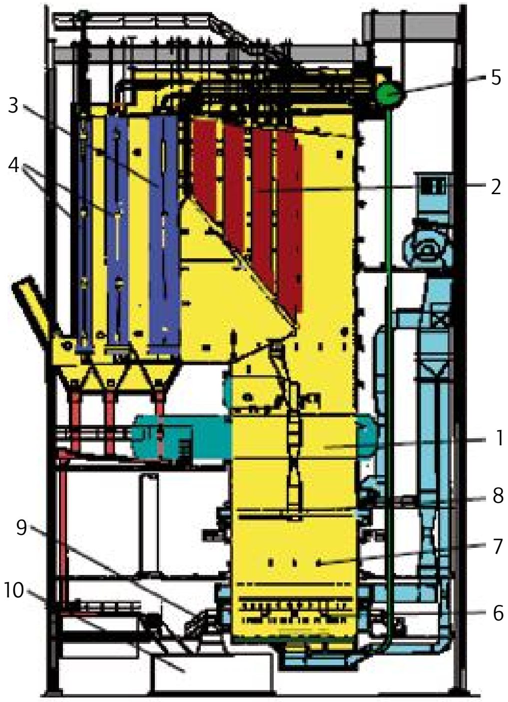
The modern recovery boiler is a single-drum design, with a vertical steam-generating bank and widely spaced superheaters. The most marked change has been the adoption of single-drum construction, which has been partly facilitated by more reliable water quality control. Single-drum boilers offer better safety and availability than bi-drum boilers, and can be built with higher operating pressures and bigger capacities. Savings can be achieved with decreased construction time. There are fewer tube joints in the single-drum construction, allowing drums with improved start-up curves to be built.

The construction of the vertical steam-generating bank is similar to that of the vertical economiser. The vertical boiler bank is easy to keep clean (Tran et al. 1988), and the spacing between the superheater panels has increased – all superheaters are now widely spaced to minimise fouling. This arrangement, in combination with sweet water attemperators, ensures maximum protection against corrosion. In addition, there have been several improvements in recovery boiler materials to limit corrosion (Nikkanen et al. 1989; Klarin 1993; Hänninen 1994).

The modern recovery boiler has heat transfer surfaces made of steel tubing. The example shown in Figure 3.3 has the following components:

- furnace
- superheaters
- boiler generating bank
- economisers.

FIGURE 3.3 Modern recovery boiler



Note: 1) superheaters; 2) boiler-generating bank; 3) economisers; 4) steam drum; 5) design is the single-drum-type; 6) primary and secondary air ports; 7) liquor guns; 8) tertiary air ports; 9) smelt spouts; 10) dissolving tank
Source: reproduced from Vakkilainen (2000b), with permission from Fapet Oy, Finland

The steam drum design is the single-drum-type. The air and black liquor enter through the primary and secondary air ports, the liquor guns, and the tertiary air ports. The combustion residue and smelt exit through smelt spouts to the dissolving tank.

The nominal furnace loading has increased and will continue to increase (McCann 1991). Changes in air design have increased furnace temperatures (MacCallum and Blackwell 1985; Lankinen et al. 1991; MacCallum 1992; Adams 1994), which has enabled a significant increase in hearth solids loading (HSL), with only a modest design increase in hearth heat release rate (HHRR).

The average flue gas flow decreases as water vapour is reduced, so the vertical flue gas velocities can be reduced, even with increasing temperatures in the lower furnace. The vertical flue gas flow path improves the cleanability with high dust loading (Vakkilainen and Niemitalo 1994). To minimise the risk of plugging and maximise the efficiency of cleaning, both the generating bank and the economisers are arranged with generous side-spacing. Two-drum boiler-bank pluggage is often caused by the tubes being too tightly arranged. The spacing between all superheater panels has therefore increased to minimise fouling.

With the increased number of superheaters, the difference in the heat transfer between a clean and fouled surface is less. This facilitates control of the superheater outlet steam temperature, especially during start-ups. Plugging of the superheaters becomes less likely, the deposit cleaning is easier, and the sootblowing steam consumption is low. The lower loops of the hottest superheaters can be made of material that offers better corrosion-resistance. The steam velocity in the hottest superheater tubes is high, decreasing the tube surface temperature. Low tube surface temperatures are essential to prevent superheater corrosion. A high steam-side pressure loss over the hot superheaters ensures uniform steam flow in the tube elements.

Current recovery boiler

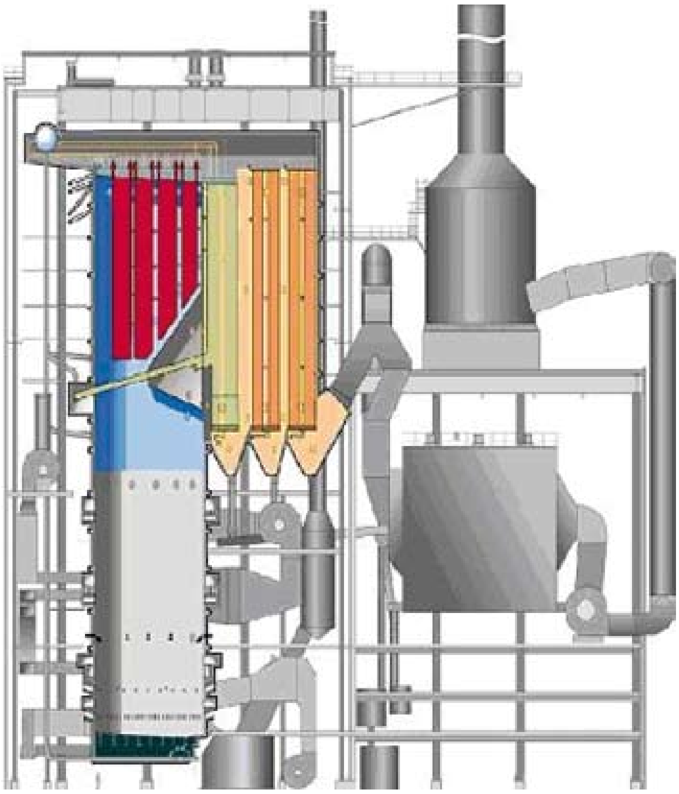
The recovery boiler is continuing to evolve. The desire to maximise the generation of electricity is driving increases in main steam pressures and temperatures. If the main steam pressure is increased to 104 bar and the temperature to 520°C, then the electricity generation from recovery boiler plant increases by about 7%. For design dry solids load of 4,000 tds/d, this means an additional 7 MW of electricity (Raukola et al. 2002).

Current recovery boilers can be much larger than previously (Figure 3.4), with some having bottom areas of more than 200 m^2. The largest recovery boilers are challenging circulating fluidised boilers for the title of largest biofuel fired boiler.

The superheater arrangement is designed for optimum heat transfer with extra protection to furnace radiation. Mill closure and decreased emissions mean higher chloride and potassium contents in the black liquor. Almost all superheaters are placed behind the bullnose to minimise the direct radiative heat transfer from the furnace. An increase in the demand for superheating and pressure decreases the need for boiler bank and water screen arrangements.

The higher main steam outlet temperature requires more heat to be added in the superheating section, and the furnace outlet gas temperature has therefore increased. The alternative is to increase the superheating surface significantly, and decrease the boiler bank inlet flue gas. If the boiler bank inlet gas temperature is reduced, the average

FIGURE 3.4 One of the most modern boilers



Source: reproduced from Vakkilainen (2004), with permission

temperature difference between the flue gas and steam is also decreased. This reduces heat transfer, and substantially more superheating surface is needed. This approach has been abandoned because of increased costs.

With increasing dry solids content, the furnace exit temperature can safely increase without fear of corrosion caused by carry-over. Increasing the recovery boiler main steam temperature affects the corrosion of the superheaters. Designing for higher recovery boiler main steam pressure increases the design pressure for all boiler parts. The temperature of the lower furnace walls in the recovery boiler increases with higher operating pressure, while the air flow per unit of black liquor burned in the recovery boiler furnace decreases. The number of air ports must therefore also be decreased.

The features of a state-of-the-art recovery boiler are shown in Table 3.2. The customer often gives the boiler vendor a list of the main parameters required for the recovery boiler to be purchased, as it is so important to choose the features carefully.

TABLE 3.2 The main features of a state-of-the-art recovery boiler

- One-drum boiler with three-part superheater and water screen (optional)
- Steam design data: 9.2mPa/490°C
- Design for more than 80% dry solids with pressurised heavy liquor storage tank
- Liquor temperature control with flash tank, indirect liquor heaters eliminated
- High-volume low-concentration (HVLC) gases are introduced to the boiler
- Low emissions of total reduced sulphur (TRS), sulphur dioxide and particulates
- Flue gas cleaning with electrostatic precipitator (ESP) ash (no scrubbers)
- Upper level distributed control system (DCS) applied

Source: based on Vakkilainen (2004)

Higher black liquor dry solids generates more steam, and the main steam parameters (pressure and temperature) can usually be increased from traditional values, allowing significantly more power generation to be achieved. The trend in recent years has definitely been in favour of increased temperatures and pressures. The newest Scandinavian lines have chosen main steam values in excess of 80 bar and 480°C (Vakkilainen and Holm 2000; Wallén et al. 2002). Only a marginal increase in power production is attained by changing the steam temperature from 480°C to 500°C if steam pressure is kept constant. The largest recovery boilers can now process more than 5,000 t/d (dry solids basis) of black liquor, 25% higher than five years ago and double the capacity of a decade earlier (Macleod 2007).

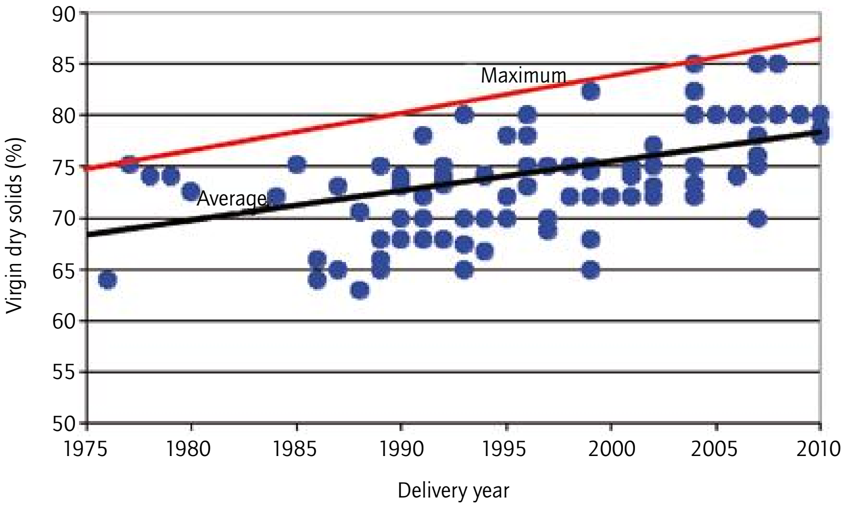
The maximum steam data can be limited by the ash properties. The first melting curve at the superheater front should be taken into account. Increasing mill closure with high chlorine and potassium decreases melting temperatures. The overall mill heat balance should be used to optimise the feed water and flue gas temperatures (Suutela and Fogelholm 2000). The average steam temperature increases with size because small boilers tend to have low pressure to reduce specific cost. There are many boilers with main steam parameters higher than 500°C, and they are mostly in Japan. An increase in the main steam temperature is usually accompanied by an increase in the main steam pressure. Increasing either steam pressure or temperature has only a small effect on back-pressure electricity generation.

As-fired black liquor is a mixture of organics, inorganics and water. Typically the amount of water is expressed as a mass ratio of dried black liquor to a unit of black liquor before drying. This is called the black liquor dry solids ratio. If the black liquor dry solids ratio is below 20%, or the water content in black liquor is above 80%, the net heating value of black liquor is negative. This means that all the heat from combustion of the organics in the black liquor is spent evaporating the water it contains. The higher the dry solids, the less water the black liquor contains and the higher the adiabatic combustion temperature.

Black liquor dry solids have always been limited by the ability of the evaporation technology available to handle highly viscous liquor (Holmlund and Parviainen, 2000). As technology has evolved, so has the final black liquor dry solids. Figure 3.5 shows the virgin black liquor dry solids of recovery boilers as a function of the purchase year of that boiler.

It can be observed that, on average, dry solids have increased. This is especially true for the latest very large recovery boilers. Design dry solids for greenfield mills has been either 80% or 85%; 80% (or before that 75%) dry solids has been in use in Asia and South America; 85% (or before that 80%) has been in use in Scandinavia and Europe.

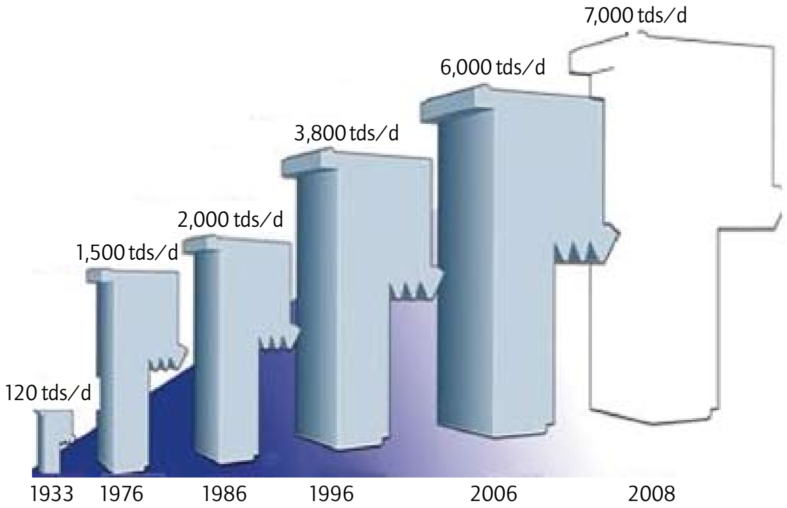
FIGURE 3.5 Virgin black liquor dry solids as a function of the purchase year of the recovery boiler



Source: reproduced from Vakkilainen (2004), with permission

Recovery boiler size keeps increasing, doubling about every 20 years (Vakkilainen et al. 2008). Boilers with bottom areas in excess of 200 m^2 are typical for the largest new greenfield mills. Figure 3.6 shows that the capacity of recovery boilers continues to grow as mills get bigger.

FIGURE 3.6 The capacity of recovery boilers continues to grow as mills get bigger



Note: tds/d, tonnes of dry solids per day

Source: Metso Paper (2008), reproduced with permission

Recovery boiler selection criteria

The design of a chemical recovery boiler starts with selection of the furnace. The important design variables in selecting the furnace are:

- dry solids flow to the unit
- higher heating value (HHV) of the dry solids.

On the basis of this information, the width, depth and height of the furnace are selected (Lefebvre and Santyr 1992). The plan area of the furnace is selected to give an optimum HHRR. This is an important variable as it affects the temperature in the lower part of the furnace. It can be used to optimise the unit's reduction efficiency, sulphur dioxide and TRS emissions, turn-down stability, and operating flexibility. The design values for HHRRs range from 0.91 to 1.02 MJ/h/cm^2. It should be stated during the design stage itself whether a range of HHVs is expected due to changing process conditions, or if the unit is expected to operate at different dry solids capacities. This will allow the designer to select the furnace plan area to optimise the performance of the unit over the specified range.

Once the required plan area of the furnace is ascertained, the furnace width and depth are selected to provide an approximate square shape. Another variable to be selected is the furnace height. It sets the black liquor combustion volume that establishes the furnace residence time, the furnace exit gas temperature, and the degree of combustion and smelting occurring in the upper furnace regions. There is a minimum furnace height required to optimise upper furnace performance. The furnace height should provide a furnace exit gas temperature in the range of 885–954°C.

After selection of the dimensions of the furnace, the heating surface upstream of the generating section is selected (McCann 1991). This surface consists either of water-cooled screens plus a superheater, or a superheater alone. The selection is based upon controlling the gas temperature entering the generating section and maintaining the required superheated steam temperature over the desired operating range. The gas temperature entering the generating section is critical because this is typically the first area of closely spaced convective surface, and is the most sensitive to ash characteristics. The steam temperature and control range are also important because the steam generated by the recovery boiler is used for either power generation or process steam (Adams 1992b). With the furnace size selected, the flue gas temperature leaving the furnace is fixed. The air requirement for combustion and the resultant flue gas weight and composition is determined by elemental analysis of black liquor dry solids.

Increasing the height of the furnace is not a sensible means of controlling the gas temperature going into the generating section because little effective surface is added for every metre of furnace height. Oversizing the superheater is not favoured as a means of controlling the gas temperature entering the generating section. As an alternative to oversizing the superheater, multiple stages of desuperheater can be used to keep the peak metal temperatures below those requiring austenitic steels. The combination of increasing the furnace height and oversizing the superheater is often the favoured means of controlling the gas temperature entering the generating section (Marr 1996).

The convective surface in a recovery boiler consists of a generating section and an economiser (Biermann 1996). The generating section is the first area of closely spaced tubes in the recovery boiler and so is prone to gas-side fouling, depending on the ash characteristics. Consequently, the first critical design parameter for either style of generating section is the gas temperature entering this section. This temperature should be below the ash sticky temperature. Another important parameter is the gas velocity across the face of the tubes. Higher gas velocities increase the plugging potential. Design gas velocities are typically 4.6–7.6 m/s to minimise this potential problem.

The economiser is selected to reduce the gas temperature to the specified value to optimise the unit's overall thermal efficiency while minimising the potential for cold-end corrosion.

The potential for plugging is increasing in modern recovery boilers. The recycling of waste streams has resulted in increased concentrations of trace elements. One way to reduce the plugging potential is to limit the amount of particulate present in the gas stream. The particle size of black liquor spray should be coarse and uniform. Fine liquor particles will tend to be entrained with the gas stream and carry over into the upper furnace. Similarly, a non-uniform liquor stream leaving the nozzle will result in a smaller fraction being carried over. The splash plate nozzle and the flat spray nozzle have been designed to achieve this goal, producing a more consistently coarse black liquor spray. Maintaining these nozzles in a fixed position and spraying horizontally or on a slight downward tilt will also reduce the potential for carry-over. Operators need to adjust the gun position and fine-tune the black liquor firing temperatures and pressures to obtain the benefits of reduced spray particle entrainment and carry-over (Adams 2000a).

The height of the furnace does not have a direct effect on black liquor carry-over, but it may affect the performance of the upper furnace (Adams 2000a). Sufficient residence time is required to complete the combustion within the furnace cavity and reduce the gas temperature entering the radiant heat recovery surface to below approximately 927°C. If this furnace volume is not available, combustion and smelting can occur in the superheater, and gas temperatures entering the generating bank and economiser will increase above the first melting point of the ash. Sticky ash deposits will adhere to the closely spaced generating bank and economiser tubes, eventually plugging the unit.

Another area to be addressed to reduce the potential for plugging is the gas temperature distribution and the heat recovery surface layout. The first melting point of boiler deposits is extremely low (538–760°C) compared with deposits from other fuels. It is not possible to reduce the gas temperature to below these levels upstream of any heat recovery surface. Instead, special design features are used for the heat recovery surface located in this critical zone in the furnace. The screens and superheater are typically located in this region. To reduce the potential for plugging, these surfaces are designed to be spaced on wide centres of 30cm or greater, sootblowers are spaced on close centres to provide good coverage, and, in many cases, tangent tube superheaters and screens are used to eliminate the ash's potential to encircle the tubes and become anchored to the panels.

For trouble-free operation, the gas temperature must be kept below the sticky point of the ash. The generating bank tube layout usually consists of tubes with an outside diameter of 6.4cm laid side to side with spacing of 11.4–22.9 cm. The tubes are usually not tangential to each other in the direction of gas flow as this makes the generating bank susceptible to sticky deposits encircling the tubes and building up to the point where they restrict the gas flow if gas temperatures are not controlled below the ash sticky temperature.

Another main parameter is the gas velocity perpendicular to the tubes. The impact velocity affects the deposit accumulation. Higher velocities increase the rate of deposit build-up on the face of the tube. To reduce this effect, design velocities of 4.6–7.6 m/s are typical for generating banks.

The economiser is also a closely spaced section, with a typical layout consisting of tubes with an outside diameter of 5.1–6.4 cm laid side to side and spaced at 10.2–15.2 cm. The gas temperature entering this section is almost always below the ash sticky temperature. Plugging in this area is usually due to high gas velocities and localised restricted gas flow paths. If the operation of the unit is not optimised and sulphur dioxide concentrations increase significantly, the ash may become sticky in this region. In newer units with optimised air systems, this is not typically a problem.

Most new boilers are designed with some form of corrosion protection in the lower furnace (Tran 1997; Adams 2000a, 2000b). Several methods of lower furnace protection are available, including close-spaced pin studs, flame- or plasma-sprayed coatings, weld overlay, composite tubes, or chromised tubes. The corrosion potential of superheaters has also increased. The move to power generation in pulp mills has driven up the final steam temperature. The move to minimise effluents by increasing recycle streams has changed the chemistry of the liquor and ash. The melting temperature of ash has been lowered to the point where it is difficult for the ash to freeze on the surface of the superheater; instead, accelerated corrosion occurs. The trend to eliminate water-cooled screens in front of the superheater exposes the superheater to direct radiation. This increases the metal temperature and the potential for corrosion. New recovery boilers are designed with fully or partially parallel flow superheaters (Adams 2000a).

Recent trends have led to progressively lower exit gas temperatures, which in turn increases the potential for economiser corrosion. The most effective method of eliminating this is to control the water temperature to prevent condensation of flue gas on the tubes.

Black liquor droplet combustion

The amount and the composition of the black liquor depend on the type of wood species and the pulping method used. Black liquor contains several organic and inorganic compounds. The organics are burned in the recovery boiler furnace and the inorganic portion is recovered as smelt. Because of its large inorganic content, black liquor has the lowest heating value for an industrial fuel. Combustion of black liquor is difficult because of its high water content, huge ash content, and low heating value.

Black liquor combustion occurs as a droplet sprayed by the furnace gun or in the char bed at the bottom of the recovery boiler furnace (Hupa et al. 1987, 1994; Frederick 1990; Frederick et al. 1991a, 1991b; Frederick and Hupa 1993a, 1993b, 1997; Vakkilainen 2000c, 2005). Black liquor is sprayed into the furnace through many liquor guns. In many combustion applications, the objective is to produce very small droplets in order to maximise the combustion rates and temperature, but black liquor is not finely atomised as it enters the furnace, being sprayed as very coarse droplets (with an average diameter of about 2–3 mm). The objective is to produce sufficiently large droplets so that unburned material can reach the char bed.

The typical stages in black liquor droplet combustion are shown in Table 3.3 and Figure 3.7. Black liquor swells during combustion because of high volatile yields and suitable surface properties.

TABLE 3.3 Stages in black liquor combustion

Stage	Characterised by	Time in furnace for a 2mm droplet (s)
Drying	▶ Water evaporation ▶ Constant diameter after initial swelling	0.1–0.2
Devolatilisation	▶ Appearance of flame, ignition ▶ Swelling of the droplet ▶ Release of volatiles	0.2–0.3
Char burning	▶ Disappearance of flame ▶ Decreasing diameter ▶ Reduction reactions	0.5–1.0
Smelt	▶ Constant or increasing diameter ▶ Reoxidation	Long

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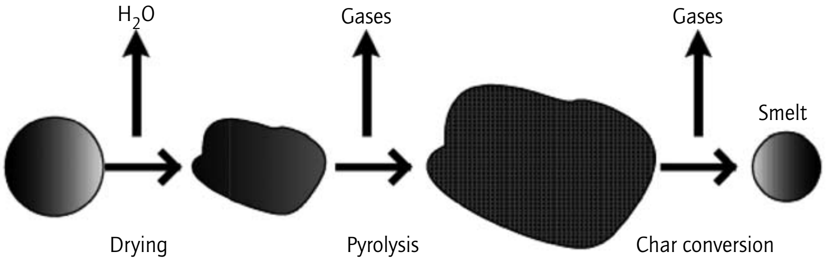
FIGURE 3.7 Typical stages in black liquor droplet combustion



Note: H2O, water

Source: based on Vakkilainen (2000b)

Drying involves the transfer of heat to the droplet to provide the latent heat of vaporisation (Adams 1992b; Frederick and Hupa 1997). The drying of black liquor proceeds as fast as the heat transfers to the droplet. Even in the furnace, the heat flux to the droplet limits drying. The black liquor diameter increases by 1.3–1.6 times the original diameter during the first couple of milliseconds after insertion into the furnace. As water evaporates, the density decreases, but the diameter stays constant. Swelling begins again with the onset of volatile release. The black liquor droplet is not completely dry at the beginning of volatile release, with about 5% moisture remaining typically. As the black liquor dries and the temperature increases, reactions with the lowest activation energies start to take place. For organic fuels, the release of low molecular weight component gases starts. Devolatilisation is typically the start of the increase in the volume of the black liquor droplets, the release of volatile gases from the black liquor droplet, and the appearance of the visible flame. The last condition is the most typical criterion for determining the length of devolatilisation time in experimental droplet combustion studies.

The black liquor droplets swell significantly during devolatilisation (Frederick and Hupa 1997). The swelling is continuous from the start of ignition until devolatilisation is complete. The conditions required for the char particle to swell are that gas generation must occur, and the droplet must have plastic surface properties. Swollen, devolatilised particles have a porous, foam-like structure. Swelling for softwood and hardwood liquors is proportional to the ratio of lignin to aliphatic acids. A longer cooking time generally increases swelling. The maximum swollen volume for industrial black liquors can change from less than 10 cm^3/g to 50 cm^3/g. Droplets that are well swollen show extensive macroporosity and often have a hollow central core. The addition of sodium sulphate or sodium carbonate decreases swelling. Many reactions occur during devolatilisation. The main form of sulphur release is dimethyl sulphide and methylmercaptan. Hydrogen sulphide forms rapidly during decomposition reactions after gases are released from the droplet. Water evolution ends at the beginning of char oxidation, which means that substantially all of the hydrogen reacts during pyrolysis.

The solid material remaining after the black liquor has completely pyrolysed is referred to as char. During the final stage of combustion, the organic carbon in the char is gasified to carbon monoxide and carbon dioxide, while the inorganic material is converted to smelt containing mostly sodium carbonate and sodium sulphide.

Char combustion starts as the volatile release comes to an end, although in practice char combustion and devolatilisation overlap significantly. The term 'organic combustion time', i.e. the sum of devolatilisation and char combustion times, is often used to describe combustion.

After the devolatilisation stage, the combustion residue is large but the structure is porous. Almost all the inorganic matter remains with the carbon char. Half the carbon typically remains in the char. Table 3.4 shows the typical composition of kraft char. Approximately two-thirds of original carbon and less than one-third of hydrogen is present, but no organic oxygen remains. The reduction rate is about 50%. Char continues to burn, with the droplet temperature increasing from outside to inside. The inorganic residue remains in the droplet as liquid smelt.

TABLE 3.4 Typical composition of kraft char

	Symbol	Mol/mol sodium	Weight (%)
Sodium sulphide	Na_2S	1/6	9.0
Sodium sulphate	Na_2SO_4	1/6	16.4
Sodium carbonate	Na_2CO_3	2/3	49.0
Carbon	C	3	24.9
Hydrogen	H	1	0.7

Source: reproduced from Vakkilainen (2000c), with permission from Fapet Oy, Finland

Reduction reactions occur during char combustion (Adams 1992b). Carbon has a major role in the reduction reaction. Sodium sulphate reacts with carbon to form sodium sulphide. While the carbon in the char bed burns, it causes the reduction of sodium. The rate of the reduction reactions depends on the carbon content of the char and on the temperature, and high reduction efficiencies are obtained in modern kraft recovery boilers. The final reduction process is slow and requires significant residence time to complete to a high degree. If sufficient oxygen reaches the char surface, the carbon in the char reacts with the oxygen. If there is insufficient oxygen, the char gasifies with the carbon dioxide and water vapour to form carbon monoxide, which further oxidises to carbon dioxide when it contacts oxygen.

The rate of combustion increases with higher swelling because of the larger surface area available for highly swelled black liquors. The inorganic residue remains at the end of char combustion. The black liquor droplet first enlarges and then shrinks to a liquid droplet (Vakkilainen 2005). If oxygen contacts the smelt, the smelt particles reoxidise to sodium carbonate and sodium sulphate in the recovery boiler, so it is necessary to have sufficient reacting material on top of the smelt to avoid this.

The lower part of the recovery furnace has three air levels: primary, secondary, and tertiary. A char bed covers the furnace bottom. The black liquor sprays from black liquor guns. Combustion of black liquor in the furnace is computer-controlled.

Vakkilainen (2007b) has published an excellent paper on recovery boiler liquor spraying practices.

Recovery boiler operation

The operation of recovery boilers consists of a number of distinct systems, including:

- the black liquor firing system
- the air supply system
- the flue gas removal system
- the auxiliary fuel system
- the smelt dissolving tank (Lefebvre and Santyr 1992; Andrews 1994).

Although each system has its own control functions and equipment, the systems interact with one another.

During recovery boiler operation, several factors must be properly controlled: the proper timing of sootblowing and the minimisation of potassium and chloride enrichment to dust. Spent pulping liquors contain inorganic salts. During combustion and reduction reactions, temperatures increase to levels such that significant amounts of chemicals vaporise. Small char fragments and liquor particles may entrain to flue gas flow. This ash collects on all heat transfer surfaces, fouling them.

Fouling and fouling-related phenomena have long been a concern in recovery boiler design and operation (Vakkilainen 2002; Vakkilainen and Pekkanen 2002), and fouling is a limiting factor to some degree for load increase in all recovery boilers. However, modern computer-based control has made it possible to recognise changes in the fouling of individual heat transfer surfaces so that sootblowing can be directed to the heat transfer surfaces where it is most needed.

Sootblowers are usually located in pairs on the left and right sides of the boiler. The sootblowing sequence typically uses continuous operation of a single sootblower, which keeps the furnace pressure stable.

Although computer control allows various methods of sootblowing to be used, a large decrease in sootblowing steam consumption has not materialised (Vakkilainen 2000c), often because of a lack of understanding of the best possible control strategy. The methods for predicting fouling of the heat transfer surfaces are visual observation of them by experienced operators and prediction of fouling derived from operating parameters such as temperature and pressure measurements, with the latter being the most common method in modern sootblowing control systems. The main fouling indicators are pressure loss measurements, flue gas temperature measurements, and steam and water temperature measurements.

The heat flow in a heat transfer surface is a function of the heat transfer area and the temperature difference between the flue gas and the steam and water (Vakkilainen 2005). The heat flow decreases as the heat transfer surface becomes fouled. A reduction in performance is due to the increased heat transfer resistance of deposits. As the heat transfer surface becomes fouled, the accumulation of deposits decreases the gas flow area, which leads to an increase in flue gas flow velocity. The pressure loss in a heat transfer surface increases as flue gas velocity increases, and this is a more important parameter than the decreasing heat flow. The flue gas-side pressure loss usually limits the maximum capacity of the recovery boiler. Fouling can increase until the flue gas fan cannot supply sufficient pressure and flow, at which point the recovery boiler load must decrease or the boiler water must be washed. Positioning a gas-side pressure measurement element before and after the heat transfer surface provides pressure difference information to help predict fouling. The pressure decreases of the economisers and the boiler bank are significant. The pressure decreases of the superheater section are always lower than 10 Pa.

Pressure losses increase during the first hours after start-up because of load increase. This rise decreases after a few days. Flue gas flow also influences measured pressure loss. The flue gas flow can be assumed to be directly proportional to the boiler load. The most reliable boiler load measurement is main steam flow. To compensate for the changes in boiler load, the measured pressure differences can be scaled with the square of the steam flow. With modern instrumentation, pressure loss measurements can predict the fouling of boiler banks and economisers.

The temperature of flue gas is measured at several locations. Measurements include char bed temperatures, furnace temperatures from different heights, boiler bank inlet temperature, and the flue gas exit temperature (Andrews 1994). The furnace temperature measurements are mainly for operating purposes and are not normally used to predict fouling. Temperature measurements at the superheaters, boiler bank, and economisers can predict fouling. An increase in operating temperatures may be due to increased fouling at the preceding heat transfer surfaces.

The main problem with predicting fouling with flue gas-side temperature measurements is the limited number of measuring points. Accurate prediction of fouling at individual superheaters needs far more gas-side temperature measurements than are usually available. Using the steam-side temperature increases of the superheaters can predict fouling. These temperatures are reliable and easily measured. At constant steam flow, the temperature increase in a superheater is directly proportional to the heat flow to that surface. When the superheating decreases, the fouling in the superheater has increased.

Another good index of total superheater fouling is the attemperating flow (Adams 2000b). Since the heat flow to superheaters decreases, less attemperating is necessary. The attemperating water flow describes how much the superheated steam requires pooling to keep the main steam flow temperature constant. A clean heat transfer surface conducts heat better, and the superheating is thus more effective. Direct measurements are not usually made of attemperating flows as they can be measured as the temperature decrease between the superheaters. The best fouling indicators are degradation of thermal performance and visual observations.

Recovery boiler dust contains mainly sodium sulphate and sodium carbonate, with small amounts of chlorides and potassium, and is a mixture of deposited fume and carry-over particles. The coarser carry-over particles contain a high percentage of sodium carbonate, and the small fume particles consist mainly of sodium sulphate plus chloride and potassium salts. The amount of chlorides is highest in the electrostatic precipitator dust, and lower in the hottest surfaces at the boiler bank and economiser. This is in accordance with the theory that sodium chloride in fume is formed by the reaction of hydrochloric acid vapour with sodium salts.

The amount of chloride in electrostatic precipitator dust does not seem to be sensitive to changes in the level of chloride in the black liquor. The amount of potassium in the black liquor does not influence the amount of potassium in the dust. There is a clear difference between the dust from hot surfaces and that from cool surfaces, and in the enrichment of hot surface dusts and that from cool surfaces.

The ratio of carry-over to fume in dust decreases as it progresses down the flue gas passage. Many boilers show an increase in the chloride content of electrostatic precipitator dust with higher black liquor dry solids. The sulphur content in black liquor affects the chloride enrichment, with high sulphidity in liquors decreasing the chloride level in the electrostatic precipitator dust.

Issues caused by non-process elements in the recovery cycle

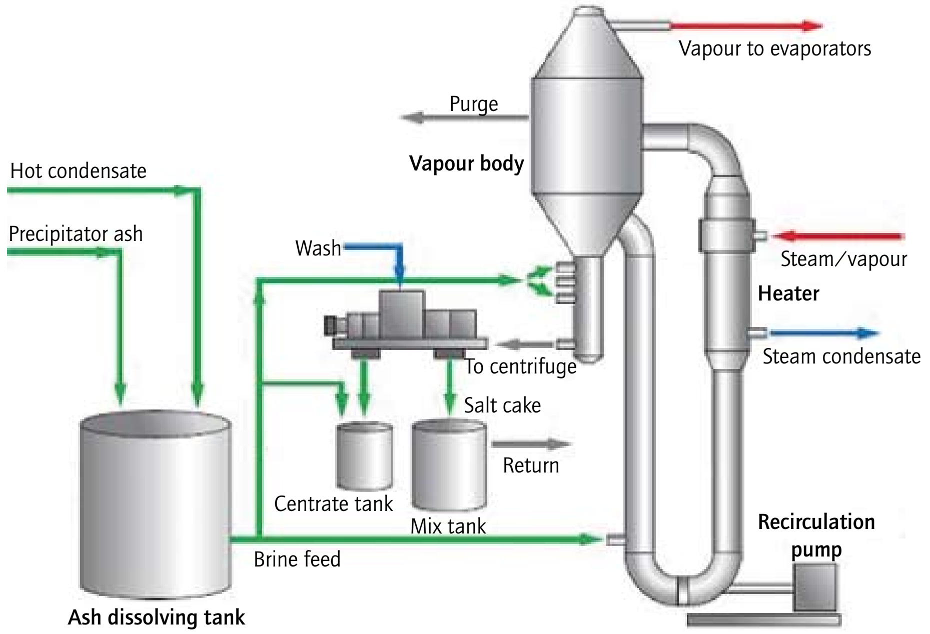
As pulp mills continue to improve the efficiency of spill collection and pulp washing, the removal of non-process elements from the recovery cycle becomes a critical issue. Non-process elements, including chloride and potassium from the wood and chemical make-up, accumulate in the recovery cycle and have an adverse impact on the operation of the boiler. Problems caused by this accumulation include:

- plugging of the superheater
- corrosion of the recovery boiler
- increased steam demand.

The installation of an integrated chloride removal process (CRP) system (Figure 3.8) allows the recovery of precipitator ash while purging contaminants from the process. In addition, the mill benefits from a reduction in the overall costs of chemical make-up, and from improvements in the operation of the recovery boiler. The CRP system is a more efficient solution:

- chloride removal 99%
- potassium removal 99%
- sodium recovery 85–93%.

FIGURE 3.8 Flow diagram of a chloride removal process system



Source: HPD (2008), reproduced with permission

The CRP system takes advantage of the fact that chloride and potassium are enriched in the recovery boiler fume. As a result, the best way to manage chloride and potassium is to treat the subsequent precipitator ash. The CRP system dissolves precipitator ash in condensate and feeds it to an evaporative crystalliser. As the water evaporates, sodium sulphate and, depending on the ash composition, sodium carbonate crystals are precipitated. The resulting slurry is transferred to the centrifuge where the crystals are de-watered, washed and returned to the black liquor for chemical recovery. The liquor, with the concentrated chloride and potassium, recirculates back to the crystalliser, and is partially purged to remove these components from the liquor cycle. The CRP system increases mill efficiency by:

- reducing chemical make-up costs
- increasing the stability of mill operation, with less frequent stoppages for washing
- reducing corrosion in the recovery boiler
- increasing recovery boiler steam production
- creating steam savings from reduced sootblows
- allowing a higher superheater temperature for increased power generation.

Safety aspects

One of the main hazards in the operation of recovery boilers is a smelt-water explosion (Grace 1994, 1997). This can happen if even a small amount of water is mixed with the solids at high temperature. A smelt-water explosion is purely a physical phenomenon, and the liquid–liquid type of explosion has been established as one of the main causes of recovery boiler explosions. In a smelt-water explosion, even a few litres of water can violently turn to steam in a few tenths of a second when mixed with molten smelt. Char bed and water can co-exist because steam blanketing reduces heat transfer, but if some trigger event destroys the balance, then water is evaporated quickly through direct contact with smelt, and this sudden evaporation causes an increase in volume and a pressure wave of some 10,000–100,000 Pa. The force is usually sufficient to cause all furnace walls to bend out of shape. For the safety of personnel and equipment, the recovery boiler must be immediately shut down if there is the possibility that water has entered the furnace. All recovery boilers have to be equipped with a special automatic shut-down sequence.

The other type of explosion that is possible is of the combustible gases. For this to happen, the fuel and the air have to be mixed before the ignition. Typical conditions are either a black-out (loss of flame) without purge of the furnace, or continuous operation in a substoichiometric state. Flame-monitoring devices are therefore installed to detect a black-out and institute a subsequent interlocked purge and start-up process.

Combustible gas explosions are connected with oil/gas firing in the boiler. As there is continuous monitoring of oxygen in almost every boiler, non-combustible gas explosions have become very rare.

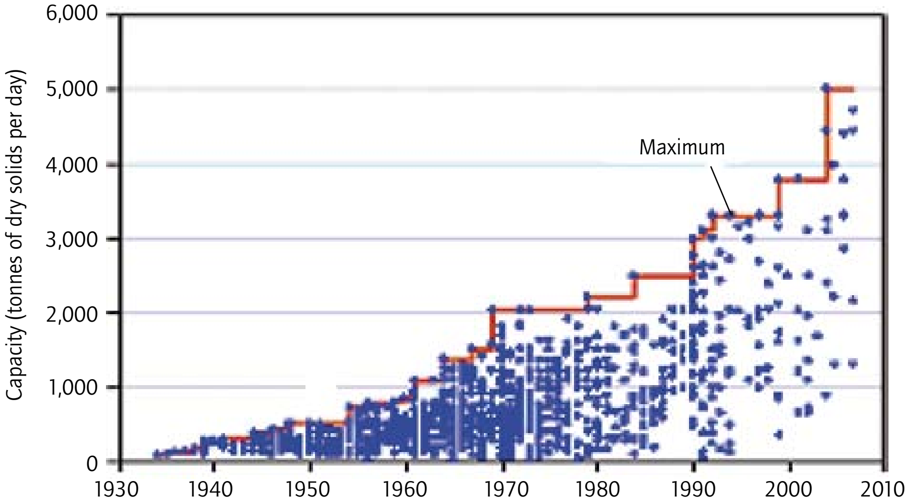
Modern recovery practices

An important development in recovery boiler operation is high-solids firing, a term that refers to burning black liquor at solids content greater than 75% (Vakkilainen and Holm 2000; Tran and Vakkilainen 2007; Vakkilainen 2007a). The practice significantly increases steam generation and improves combustion stability, resulting in lower TRS and sulphur dioxide emissions, and less boiler fouling and plugging. It also provides for more capacity in existing units.

The amount of power a recovery boiler can generate from black liquor combustion depends on the pressure and temperature of the steam that the boiler produces. Traditionally, recovery boilers have operated at moderate steam pressures (90 bar) and temperatures (<480°C) because of concerns about superheater corrosion and the high cost of material construction. The current trend, however, is towards higher pressures and temperatures, with Japan and Finland taking the lead in this area. A number of recovery boilers now operate at 110 bar and 510°C. Steam generation rates can be as high as 3.8 kg of steam per kilogram of black liquor solids, and power generation can reach 0.6 kWh/kg base-load of dry solids.

Figure 3.9 shows the firing capacity of more than 1,000 recovery boilers and their start-up date (Vakkilainen 2005). While fewer units have been built since 2000 than in previous decades, they are larger on average, with the maximum black liquor firing capacity being double that of those built in the early 1980s.

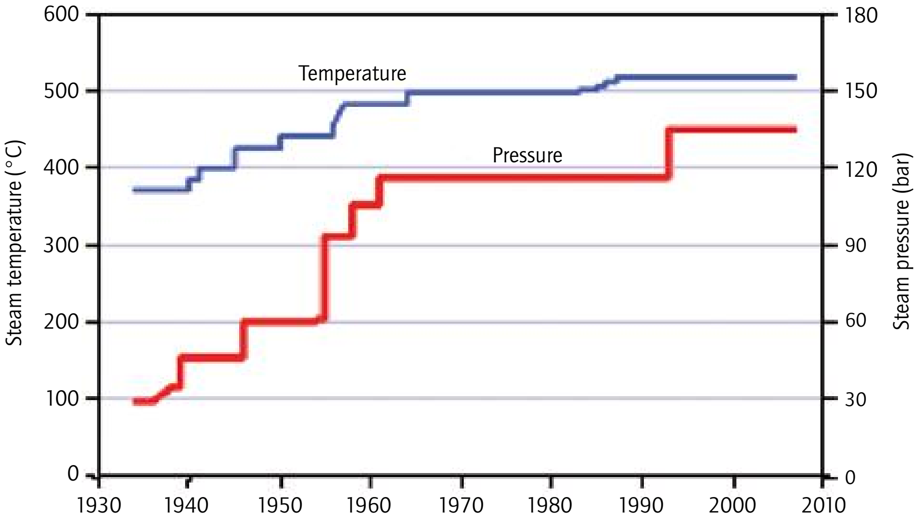
FIGURE 3.9 Black liquor firing capacity of recovery boilers compared with their year of start-up



Source: reproduced from Tran and Vakkilainen (2007), with permission

The boiler steam temperature and pressure are also higher (Figure 3.10) in order to allow for maximum power generation.

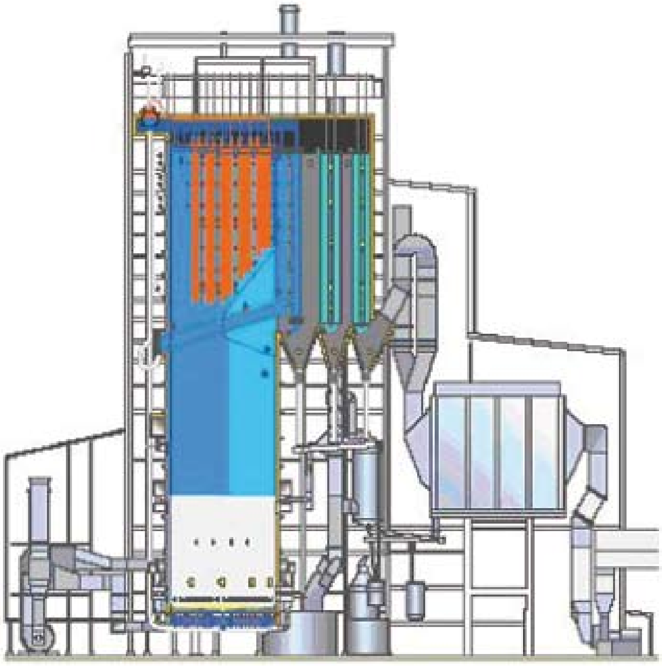
FIGURE 3.10 Maximum steam temperature and pressure of recovery boilers compared with their year of start-up



Source: reproduced from Tran and Vakkilainen (2007), with permission

The largest recovery boiler in the world in 2008 is the Kvaerner unit started up in November 2004 at the Hainan Jinhai Pulp & Paper Industry Co. Ltd on Hainan Island, south China (Figure 3.11). The unit is sized at 16.4 m × 16.4 m × 65 m (H). It has a nominal firing capacity of 5,000 t/d dry solids, with a maximum of 6,000 t/d dry solids. It produces 734,400 kg/h of steam rated at 84 bar and 480°C (Hagga and Laitinen 2006).

FIGURE 3.11 The world's largest recovery boiler at Hainan Jinhai Pulp & Paper Co. Ltd, Hainan Island, China

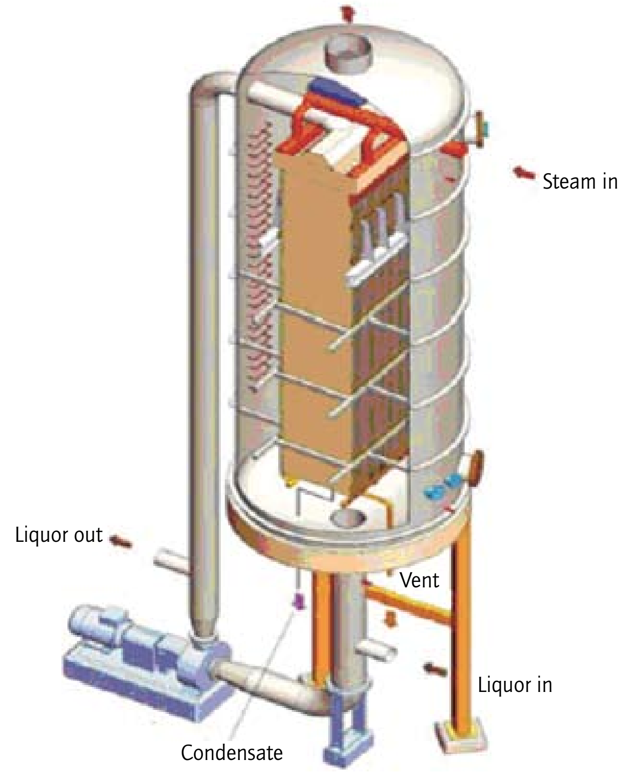


Source: reproduced from Tran and Vakkilainen (2007), with permission

There are plans to build recovery boilers that are able to handle more than 7,000 t/d of dry solids for Asia Pacific Resources International Holdings Ltd, one of the world's leading producers of fibre, pulp and paper (Maheshwari 2008).

A state-of-the-art mill might have high-solids evaporators/concentrators to bring the liquor to 80–85% solids for firing in the recovery boiler. Figure 3.12 shows a high dry solids evaporator by Andritz.

FIGURE 3.12 A high dry solids evaporator

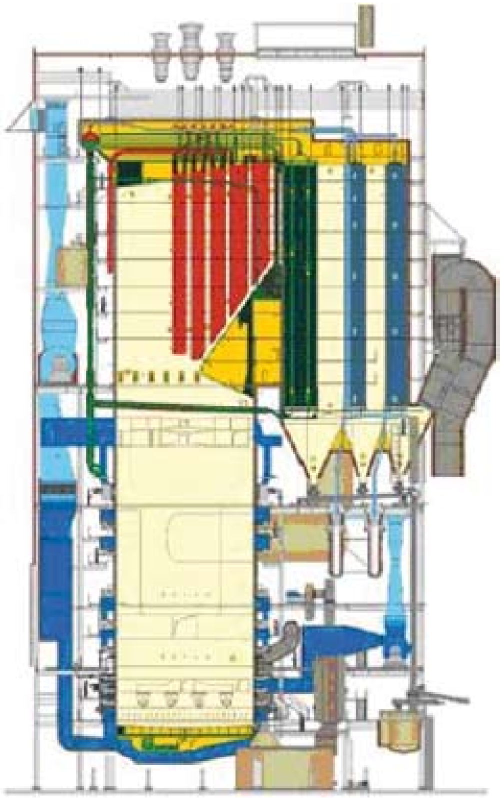


Source: reproduced from Tran and Vakkilainen (2007), with permission

The evaporator has much greater heat surface than conventional evaporators. Because of the high viscosity of the black liquor at high solids contents, a liquor heat treatment (LHT) system is used to lower the liquor viscosity and make it easy to process.

The recovery boiler design is that of a single drum high solids firing unit with multiple levels of air supplied by separate fans (Figure 3.13).

FIGURE 3.13 State-of-the-art recovery boiler



Source: reproduced from Tran and Vakkilainen (2007), with permission

The boiler has a greater superheater surface area, and is equipped with feed water preheaters and/or combustion air preheaters in order to produce high pressure/temperature steam. It is also equipped with a back-pressure turbine combined with a condensing turbine to maximise power generation. The sootblowers, which are used to control deposit accumulation on tube surfaces in recovery boilers, are equipped with fully expanded nozzles, variable lance speeds and intelligent blowing systems to maximise deposit removal efficiency while minimising sootblowing steam usage.

New recovery boilers use low pressure steam (10–15 bar) after the steam turbine for sootblowing instead of the conventional high pressure steam (20–24 bar).

The causticisation plant incorporates slakers with cyclones and scrubbers to minimise dusting, and pressurised disc filters instead of gravity settlers for liquid/solids separation (Anon 2005). The calcination system incorporates effective lime mud de-watering, a flash mud dryer, and product coolers to improve the thermal efficiency of the kiln.

Tightly controlled kraft mills use some method for deliberate chloride and potassium removal. This might take the form of simply disposing of a substantial proportion of the precipitator ash, or the use of elaborate ash treatment systems for selectively removing chloride and potassium (Tran and Earl 2004).

Complex systems for the collection and incineration of non-condensable gases (NCG) are universally used. These handle not only the concentrated NCG streams, but also various dilute NCG streams that contribute to mill odour, and eliminate malodorous gases collected from contaminated condensates. There are increased pressures to use the recovery boiler to process at least a proportion of the NCG load.

In bleached kraft mills, increasingly some of the process streams from the bleach plant are incorporated into the recovery cycle. Oxygen delignification liquor is disposed of in the recovery cycle, and there are increasing incentives for bringing alkaline stage effluents back into the pulping cycle through counter-current washing.

Japanese recovery boilers operate at the highest steam temperatures and pressures of any in the world (Arakawa and Tran 2003).

The basic requirements of recovery boiler technology – maximum recovery of chemicals, high efficiency, high utilisation of black liquor calorific value, and safe operation – have remained unchanged during 50 years of use.

Major recent changes in recovery boilers are the adoption of single-drum construction and wider spacing between the superheater panels. New materials have been adopted to accommodate the higher operating temperatures and pressures. Recently, operating temperatures have increased to 500°C, operating pressures to 100 bar, and black liquor dry solids content to an average of 75% and a maximum of 90%. Current models have a bottom area of 200 m^2.

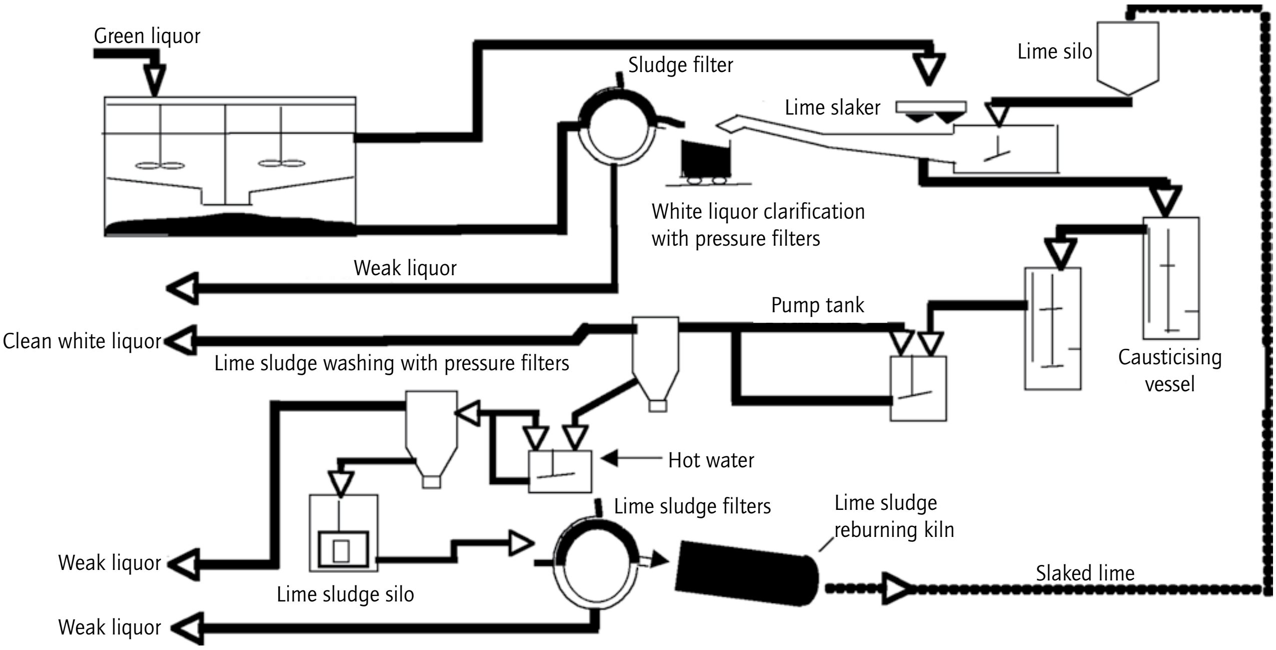
Modern mill designs have succeeded in reducing heat consumption, while recovery boiler designs have increased power generation, resulting in an ability to provide a net power surplus (Vakkilainen 2004).

4

White liquor preparation

The recausticisng process (also called causticising), is an essential element of the chemical recovery process in pulp manufacturing facilities (Arpalahti et al. 2000). The process includes mixing clarified green liquor with lime, causing a chemical reaction to produce sodium hydroxide, sodium sulphide and calcium carbonate. The calcium carbonate, an insoluble mud, is filtered out, washed, filtered again and then calcined in the lime kiln, where it is converted back into lime suitable for slaking more green liquor. The sodium hydroxide and sodium sulphide, or white liquor, is then introduced into the digester, along with wood chips. This procedure is known as the lime cycle (Figure 4.1).

FIGURE 4.1 White liquor preparation via the lime cycle



Source: based on Smook (1992); Arpalahti et al. (2000)

The following operations are required to recover the sodium hydroxide (Cornell 1992; Grace 1992b; Biermann 1996):

- treatment of the green liquor to remove solid impurities (dregs) that would otherwise enter the lime loop;
- treatment of the green liquor with lime to form sodium hydroxide (caustic) and solid calcium carbonate (lime mud); this is the slaking/causticising reaction;
- separation of the white liquor from the lime mud;
- treatment of the lime with aqueous sodium carbonate to form solid calcium carbonate (lime mud);
- separation of the solid lime mud from the aqueous caustic white liquor;
- calcination of the lime mud to reform lime (calcium oxide).

The lime reburning system is a closed recovery system where fresh chemicals are used only to replace process losses and for the purge of lime that is necessary to correct the contamination of chemical cycles. The alkali that is needed in oxygen delignification is also causticised before sulphide oxidation.

Characteristics of green and white liquors

The major compounds in green and white liquors are sodium hydroxide, sodium sulphide, sodium carbonate and sodium sulphate (Grace 1992b). The composition and properties of green liquor are shown in Tables 4.1 and 4.2.

TABLE 4.1 Typical composition of green liquor

Component	Concentration (g sodium oxide/l)
Sodium carbonate	80–100
Sodium sulphide	40–50
Sodium sulphate	3–6
Sodium hydroxide	5–20
Other dissolved matter	5–10
Suspended solids	0.6–1.5

Source: reproduced from Arpalahti et al. (2000), with permission from Fapet Oy, Finland

TABLE 4.2 Physical properties of green liquor

Temperature (°C)	80–100
Density (kg/l)	1.12–1.20
Viscosity (mPa·s at 90°C)	0.9
Heat capacity (kJ/kg/°K)	3.3–3.8

Source: reproduced from Arpalahti et al. (2000), with permission from Fapet Oy, Finland

The density of green liquor can be used as a measure of total titratable alkali (TTA), which describes the chemical content or total alkali content of the liquor. The dregs content gives the amount of solid impurities in the liquor. These consist primarily of carbon and lime mud particles, but non-process impurities such as metal hydroxides and sulphides are also present. These impurities are separated from the green liquor by sedimentation or filtration before the recausticising process. If they are not removed, they could disturb the filtration properties of lime mud and become enriched in the recirculated lime. The important properties of the dregs separated from the green liquor are the alkali content and moisture. The alkali content of dregs depends strongly on the moisture content and describes the alkali loss caused by purging dregs from the process.

Table 4.3 shows the composition and Table 4.4 the characteristics of white liquor.

TABLE 4.3 Composition of white liquor

Compound	Concentration (g sodium hydroxide/l)	Concentration (g sodium oxide/l)	As compound (g/l)
Sodium hydroxide	95.0	73.6	95.0
Sodium sulphide	40.0	31.8	39.0
Sodium carbonate	23.0	17.8	30.5
Sodium sulphate	4.0	3.1	7.1
Sodium thiosulphate	2.0	1.6	4.0
Anhydrous sodium sulphite	0.5	0.4	0.8
Other compounds	–	–	3.0
Effective alkali	135.0	105.4	–
Active alkali	115.0	89.5	–
Total alkali	**164.5**	**128.3**	**179.4**

Source: reproduced from Arpalahti et al. (2000), with permission from Fapet Oy, Finland

Sulphidity is also influenced by the efficiency of causticising according to the definition by Cornell (1992). If causticising efficiency drops for some reason, the sulphidity rises even if the sulphur:sodium ratio in the system remains constant. The sulphidity is therefore not a direct measure of the balance between sodium and sulphur in a mill.

TABLE 4.4 Characteristics of white liquor

Sulphidity (%)	29.6
Sulphur:sodium equivalent ratio	0.58
Causticising degree (%)	80.5
Reduction degree (% based on total sulphur)	82.2
Reduction degree (% based on sulphate)	90.9

Source: reproduced from Arpalahti et al. (2000), with permission from Fapet Oy, Finland

The total suspended solids in white liquor are mostly lime mud particles that have passed through the white liquor filtration or sedimentation stage. The purity of the white liquor does not therefore relate to the purity of green liquor. The terms used to characterise the cooking liquor are given in Table 4.5. All values are based on equivalent sodium oxide.

TABLE 4.5 The terms used to characterise the cooking liquor

Active alkali (AA)	Active alkali is the active ingredients in the pulping process: $AA = NaOH + Na_2S$
Effective alkali (EA)	Effective alkali are the ingredients that will actually produce alkali under pulping conditions: $EA = NaOH + ½ Na_2S$
Sulphidity (% active alkali basis)	Sulphidity is the ratio of Na_2S to the active alkali, usually expressed as a percentage: Sulphidity = $Na_2S/NaOH + Na_2S$ (as Na_2O)
Total chemical or total alkali (TA)	TA is the sum of all sodium salts in liquors (as Na_2O) that contribute to AA, i.e. $NaOH + Na_2S$, or are capable of being converted to AA in the kraft cycle: $TA = NaOH + Na_2S + Na_2CO_3 + Na_2SO_3$ (as Na_2O)

TABLE 4.5 The terms used to characterise the cooking liquor (continued)

Total titratable alkali (TTA)	TTA is the sum of all of the bases in the white liquor that can be titrated with strong acid: TTA = $NaOH + Na_2S + Na_2CO_3 + ½Na_2SO_3$ (as Na_2O)
Causticity	Causticity is the ratio of NaOH to active alkali Causticity = $NaOH/NaOH + Na_2S$ (as Na_2O)
Causticising efficiency	The causticising efficiency is the ratio of NaOH to NaOH plus Na_2CO_3 (as Na_2O); it is used as a measurement of how efficient the causticising process is
Reduction efficiency	The reduction efficiency is the ratio of Na_2S to Na_2S plus sodium sulphate in green liquor; it is a measurement of the efficiency of reduction of sulphur species in the recovery boiler
Deadload	In the kraft pulping process, liquor chemicals other than the active cooking chemicals are considered to be deadload. The active cooking chemicals in kraft pulping are NaOH and Na_2S. While reusing the pulping chemicals from the recovery process, several inactive chemicals or deadloads (Na_2SO_4, Na_2CO_3, $Na_2S_2O_3$)are formed.

Note: NaOH, sodium hydroxide; Na_2S, sodium sulphide; Na_2O, sodium oxide; Na_2CO_3, sodium carbonate; Na_2SO_3, sodium sulphite; Na_2SO_4, sodium sulphate; $Na_2S_2O_3$, sodium thiosulphate
Source: Pira International Ltd

Green liquor and white liquor contain minor amounts of other sodium compounds such as anhydrous sodium sulphite, sodium thiosulphate, sodium sulphide and sodium chloride. These compounds require consideration when calculating the total alkali amount using sodium analysis in the liquor. The liquors also contain a variable amount of potassium that requires consideration in cation/anion comparisons.

The properties usually measured from lime mud for process control purposes are consistency in various process stages (percentage of dry solids), final dryness (percentage of dry solids), and residual water-soluble alkali content after lime mud washing (percentage of sodium oxide on dry mud basis). These properties influence lime reburning and lime kiln operation. For design purposes, knowing the porosity or the free surface of the lime mud and its filterability are also useful.

The residual carbonate content and lime availability usually describe the quality of the burned lime. The residual carbonate shows how well the calcination has succeeded. The available lime is a measure of the alkaline content of the reburned lime that reacts with acid. Availability is affected by the contamination of the lime. Low availability usually means that phosphorous, silicon, magnesium, aluminium or iron have enriched the lime cycle, requiring replacement of some of the lime with fresh make-up lime.

Instead of lime availability, the causticising power of lime is often measured. The causticising power is a measure of how efficient the lime is; it represents the percentage of calcium oxide and calcium hydroxide in lime that reacts with sodium carbonate. The causticising power also correlates with the reactivity of lime. It depends on its porosity, free surface area and purity.

Near infrared (NIR) spectroscopy can be used to measure:

- the EA, AA, TTA, total dissolved solids (TDS) and total dissolved deadload (TDD) in white liquor;
- the EA, AA, TTA, TDS, TDD and reduction efficiency in green liquor;
- the residual effective alkali (REA), residual active alkali (RAA), lignin and TDS in black liquor (Hodges et al. 2006).

NIR-based process analysers offer very low maintenance, multicomponent analysis, simple architecture, integrated turnkey design, and simple and low cost installation, with minimal training of mill personnel together with standard technology.

Recently Trung et al. (2007) investigated the use of Fourier-transform NIR (FT-NIR) for on-line determination of green-liquor reduction efficiency and total titratable alkali, carbonate, sulphide, sulphate and thiosulphate as well as EA and AA in green liquor.

Slaking/causticising chemistry

During recausticisation, two consecutive reactions – slaking and causticising – occur (Arpalahti et al. 2000) in the solid phase of the heterogeneous mixture of lime and green liquor. When green liquor is mixed with calcium oxide, it slakes with water and forms calcium hydroxide. This continues to react with sodium carbonate in the green liquor to produce sodium hydroxide and calcium carbonate.

The slaking of lime is a strongly exothermic reaction. Slaking occurs rapidly at elevated temperatures of green liquor and lime. The subsequent causticising reaction begins simultaneously with slaking. The slaking reaction takes about 10–30 min to complete, depending on the quality of lime. The temperature of the solution still has a major influence on the reaction rate. Below 70°C, the reaction rate is significantly slower than at the normal operating temperature, which is close to 100°C. In practice, all the lime that is capable of slaking will react with water. The causticising reaction is an equilibrium reaction, and does not have any significant heat effect. Calcium hydroxide and calcium carbonate are insoluble and participate in the reaction as solids. The equilibrium in the causticising reaction is reached with some reactants still present in the mixture. The total liquor strength will determine the equilibrium composition. An increase in the concentration of the liquor will shift the equilibrium to the reactant.

The causticising reaction occurs between solid and dissolved species, and depends on the rate of diffusion of the species. It is a slow reaction that takes about 1–1.5 h to complete to an adequate extent for white liquor separation. A continuous reaction that occurs in mixing tanks in series will require approximately 2–2.5 h average residence time. If the residence time is shorter, excessive unreacted calcium hydroxide will remain in the lime mud and will deteriorate the filterability or de-watering properties and blind the filter media with precipitated calcium carbonate.

Chemical equilibrium determines the ratio of sodium hydroxide and sodium carbonate expressed as the causticising efficiency (Cornell 1992; Biermann 1996). The causticity, and therefore also sodium hydroxide content, in white liquor can only vary in the recausticising plant within the limits set by the composition of the green liquor. The sodium to sulphur balance in the mill liquor inventory and the reduction in the recovery boiler determine the amount of sulphide in proportion to the total alkali in the liquor. The ratio of sodium sulphide and sodium hydroxide usually expressed as sulphidity can therefore vary countercurrently with the causticising efficiency.

Reactions in lime reburning

Lime mud converts to lime by heating or reburning (Smook 1992; Venkatesh 1992). The dissociation of calcium carbonate to calcium oxide and carbon dioxide begins when the temperature goes beyond 820°C. An increase in temperature greatly speeds up the reaction. To obtain a sufficient reaction rate, reburning uses a temperature of approximately 1,100°C. Lime mud also contains some unreacted lime as calcium oxide, water, a small amount of alkali, and impurities, in addition to the main component, calcium carbonate. The amount of impurities in lime mud dry solids is typically about 7–10%, depending on the amount of impurities introduced into the process with green liquor and make-up lime.

Green liquor treatment

The green liquor clarifier is the only spot in the recovery cycle where dregs can be removed. Dregs must be removed here, or they will continue through the recovery cycle and become a deadload in the system. Clarifying the green liquor can improve causticising efficiency, white liquor clarification, mud settling, mud washing, and soda removal on the lime kiln precoat filter (Shrinath and Buettner 2000; Vargara and Jimenez 2003).

Green liquor consists of several inorganic chemicals, such as sodium carbonate, sodium sulphide and sodium sulphate, originating from kraft recovery boiler smelt. Sodium hydroxide, which usually occurs in green liquor, originates from weak white liquor returned from recausticising to smelt dissolving (see Table 4.1). The concentration of green liquor depends on sulphidity, white liquor active alkali, and the efficiency of white liquor separation. The strength of green liquor as a TTA is typically 110–140 g of sodium oxide per litre. The clarifying process used in the treatment of the green liquor can be limited by the liquor's strength because increased liquor density or strength makes sedimentation of dregs difficult, particularly when the TTA is 135–140 g of sodium oxide per litre or higher. The physical properties of green liquor were shown in Table 4.2.

The volumetric flow of green liquor depends primarily on the amount of white liquor that must be produced. It is also influenced by the recausticising process and equipment selection. Some white liquor separation processes recirculate more alkali in weak white liquor to the dissolving tank than others. The volumetric ratio between green liquor and white liquor from one process to another can be 1.05–1.25 m^3 of green liquor per cubic metre of white liquor.

Various studies indicate that the pretreatment of wood chips with industrial green liquor prior to kraft pulping can lead to faster delignification, a decrease in the overall consumption of pulping chemicals, and better pulp strength properties. Green liquor is a rich and recyclable source of hydrosulphide (Svedman and Tikka 1998; Hultholm and

Lonnberg 2000; Singh et al. 2002; Filpponen et al. 2006). New cooking methods that use green liquor as an impregnation liquor are available. This use may represent 10–20% of the entire green liquor volume. Various methods for the production of sulphide-rich impregnation liquor have also been proposed.

Separation of dregs

The basic purpose of green liquor treatment is to make the green liquor coming from the smelt dissolver into a proper feed for recausticising (Arpalahti et al. 2000). This treatment consists of removing solid impurities (dregs) from the liquor, adjusting the temperature, and stabilising the system flow and concentration fluctuations.

Dregs reduce the causticising efficiency by limiting the reaction of slaked lime and sodium carbonate. Calcium carbonate particles have an affinity for dregs. They surround and attach themselves to the dregs particles and produce less dense, and therefore slower settling, particles in the white liquor clarifier. This results in calcium carry-over in the white liquor, which contributes to digester and evaporator scale problems.

Slower settling also reduces mud washing efficiency, and means that more soda and water must be sent to the kiln, which can lead to an increase in balls and rings, total reduced sulphur (TRS) emissions, and fuel consumption. Dregs stay with the lime and are recycled through the system.

The composition of dregs varies, but includes carbon and various amounts of iron, calcium, alumina, silica, magnesium, and some sulphides. An analysis of dregs from two different mills is given in Table 4.6.

TABLE 4.6 Chemical analysis of green liquor dregs from two mills

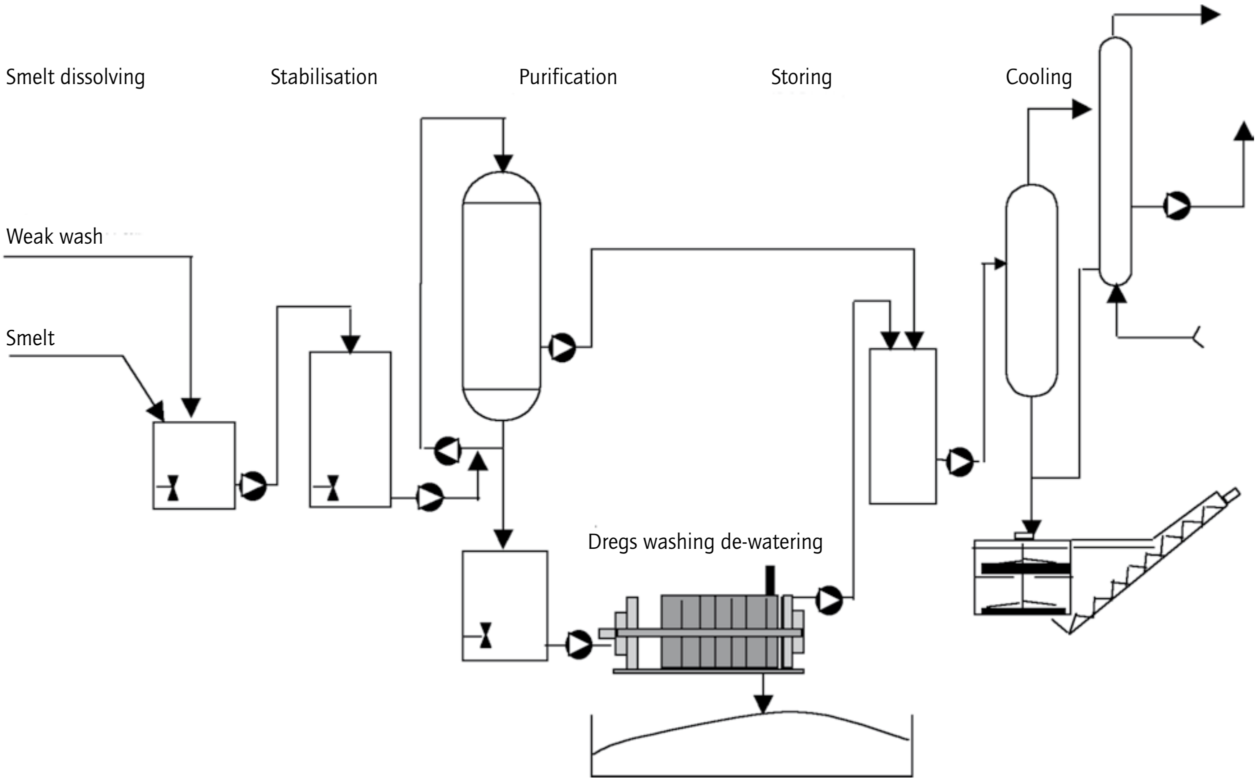
Analysis	**Mill A (% by weight)**	**Mill B (% by weight)**
Ignition loss	56.0	76.0
Calcium oxide	16.5	9.0
Miscellaneous oxides (R2O3 group)	4.7	–
Iron	2.2	1.0
Sodium oxide	2.2	1.0
Total sulphur	3.0	3.0
Acid insolubles	0.3	1.0

Source: reproduced from Cornell (1992), with permission from TAPPI Press

Figure 4.2 shows a basic flow diagram for the handling of green liquor. The treatment process includes the following stages:

- separation of solid impurities and dregs from the green liquor
- cooling of the green liquor for recausticising
- treating the dregs for proper disposal.

FIGURE 4.2 Basic flow diagram for the handling of green liquor



Source: reproduced from Arpalahti et al. (2000), with permission from Fapet Oy, Finland

To protect the lime cycle from contamination, suspended solids must be removed from the green liquor. Although they can be separated effectively, dissolved impurities will remain in the green liquor, and could contaminate the lime cycle if they form sparingly soluble compounds with reburned lime. The use of precipitating agents can reduce the solubility of the impurities somewhat (Ulmgren 1987).

The separation of the solids normally uses sedimentation or filtration methods (Lownertz and Ingelman 1998; Lownertz et al. 1999). Green liquor purification is achieved by clarification (sedimentation, sludge blanket clarification) or filtration (cake filtration with or without precoat).

A conventional method of green liquor purification is sedimentation of the dregs in a clarifier without any settling aids. When the clarifier load increases with mill production, there might be a need for various flocculants to increase the sedimentation rate. The use of so-called blanket clarifiers has achieved the highest loads. Clarifiers represent a simple, proven technology, and their energy consumption is low. Recovery boiler and dissolving tank outputs often fluctuate unpredictably. A clarifier dampens these fluctuations, but this may result in a variation in overflow quality. Variations in liquor strength, temperature, and carbon content can have a negative effect on clarifier performance. Improper use of the stabilisation tank and inadequate control of dregs removal can sometimes cause disturbances in the clarifier. Although clarifiers can adjust themselves to variations in flow and do not usually limit production, the liquor purity cannot be guaranteed with a high volume load.

Clarifying by sedimentation uses the density difference between the solid material and the liquid in green liquor. A clarifier is normally an open-top, cylindrical tank. The solid material that is heavier than the liquid settles to the bottom of the clarifier to form sludge. The clear liquor in the upper part of the clarifier is subsequently decanted.

Liden (1995) has reported that magnesium may cause problems in green liquor clarification because it is present as magnesium hydroxide in alkaline conditions. It forms very fine particles that are difficult to settle without using flocculation aids.

The operation of a sludge blanket clarifier involves bringing the feed beneath a flocculated sludge layer so that this layer acts as a filtering medium through which the liquor must pass. The use of a high dose of flocculating agents is normally necessary. Considerably high surface loads are possible with this method. The surface area of a sludge blanket clarifier is often only 10–20% of the area of a conventional clarifier. This method depends completely on flocculants. A mistake in flocculant dosing may cause the sludge blanket to mix into the system, causing very high suspended solids in the overflow. If a green liquor storage tank is necessary, it is usually built separately instead of on top of the clarifier. Some Japanese mills use sludge blanket clarification for green liquor.

Significant efforts have been made to find a more effective green liquor purification method to replace clarification (Grace 1992b), and several green liquor filtration concepts have been suggested. Maintaining a pressure difference through a filter medium forces green liquor into the filtration. The medium can be a filter cloth, a lime mud cake, a dregs cake, or a mixture of lime mud and dregs. In cake filtration, the dregs that are separated from green liquor are collected in the cake. In crossflow filtration, the dregs are collected in circulating liquor sludge outside the filter cloth. Compared with clarification of green liquor, filtration ensures better liquor clarity because the incoming liquor properties do not have any substantial effect on the filtrate quality.

The liquor quality and variations can influence the filtration capacity. Plugging and wearing of filter cloths is impossible to avoid as they age, and occasionally they will require washing by acid or complete replacement. These operations often require dividing the green liquor storage volume into two separate tanks. One tank is for storage for 6h before the filter, and the other (of the same size) is for the filtrate.

Cooling of green liquor

The temperature of green liquor entering the slaker in recausticising is controlled to prevent boiling in the slaker (Grace 1992b). Boiling can occur because of the exothermic slaking reaction. Cooling the weak white liquor fed to the dissolving tank usually indirectly controls the temperature of the green liquor. The cooling of green liquor is almost impossible with indirect heat exchangers because of rapid scaling and plugging, and even weak white liquor coolers require regular cleaning. The temperature of weak white liquor is typically about 50–60°C, which requires large amounts of cooling water.

Another concept for green liquor cooling involves flashing hot liquid under vacuum. Liquor is normally stored at high temperatures and cooled immediately before feeding to the slaker. In flash cooling, green liquor is fed to a vacuum vessel where the pressure corresponds to the desired temperature. Water vapour formed during flashing condenses by indirect cooling so that the cooling water is at 75–80°C at the outlet. A vacuum pump removes the non-condensable gases. With this type of cooler, it is easier to adjust the green liquor temperature to 80–90°C by controlling the vacuum in the expansion vessel. Since no direct contact exists between green liquor and the surface of the heat exchanger, no plugging problems can occur.

Treating the dregs for proper disposal

The volume of dregs in green liquor is often 600–2,000 mg/l (Arpalahti et al. 2000), although this can vary considerably from one mill to another. The chemical composition of the dregs also varies depending on factors such as the raw materials, the pulping process and mill closure. Green liquor handling can have different goals. If recovering only the major alkali loss is important and dregs discharge concentration is not important, a washing clarifier will be suitable. One-stage or two-stage clarifier washing will work if it is followed by dregs removal at a consistency that is suitable for pumping. The de-watering of dregs is necessary before they are discarded in a solid form to landfill.

Lime mud is a common filtering aid, either mixed with dregs or as a precoat on a precoat filter, since filtering green liquor dregs as such is difficult. Dregs slurry is most commonly filtered with a vacuum precoat drum filter. With this type of filter, the cake becomes relatively dry. The process can be automatic, and the filter requires very little maintenance. Typical lime mud consumption with precoat filtration is about 1.2 times the volume of the separated dregs. The cake dryness is 30–50%, depending on the quality of the dregs. Alkali loss is usually 4–5% as sodium oxide in the discharged cake.

Dregs washing and final de-watering can occur simultaneously with green liquor purification when using a pressure precoat disc filter for green liquor purification. In practice, the use of precoat filtration means that lime mud acting as a filter aid more than doubles the total amount of discharge for dumping. This mud can partially match the amount of mud produced by fresh make-up lime. The cost of landfill and certain environmental quality issues have initiated a search for alternative methods. Dregs should be washed better than with the existing methods and de-watered effectively without any lime mud.

Two different types of filtering presses are now commercially available for green liquor dregs filtration (Leichliter and Beer 2001). One has the filtering chambers stacked horizontally, and the filtering medium is a movable cloth, the other has a stationary cloth around vertically stacked chambers. The filtration procedure itself is very similar for both filters. A new pulp mill in Brazil is installing a two-stage centrifuge system for dregs removal (Beer et al. 2006).

The X-filter falling-film concept of crossflow filtration for green liquor has been described by Keskinen et al. (1995). The X-filter has the potential to produce green liquor that consistently contains less than 20 mg/l of dregs. The filterability of the lime mud is improved, and it is possible to produce 5% more white liquor through the tubular and pressurised disc filters.

Recausticising

Process

The recausticising process converts the sodium carbonate in green liquor to sodium hydroxide (Grace 1992b; Sata 1997). The reaction products separate from each other as lime mud in the precipitate and white liquor in the solution. The major components of white liquor are sodium hydroxide and sodium sulphide, which are active chemicals in the cooking process. White liquor also contains some inert compounds such as sodium sulphate and sodium carbonate, which form during the recovery process. Some non-process elements may also enrich the white liquor.

The maximum concentration of green liquor occurs in the smelt dissolving tank. The liquor then becomes weaker by dilution during the recausticising process. There have been many advances in the field of causticisation (Muniz 2004). The basic recausticising process consists of three main steps:

▶ slaking and causticisation
▶ white liquor separation and clarification
▶ lime mud washing and de-watering.

Slaking and causticising

The slaking and causticising reactions proceed simultaneously, and about 80–95% of the causticising reaction can be completed in the agitator section of the slaker. The causticisers then provide residence time for the remaining 5–20% of the conversion. During the slaking process, the violent, exothermic hydration of the lime disintegrates the lumps or pebbles, producing more surface area for reaction, and freeing the inerts for removal. The causticised slurry passes through a mechanical classifier, integral to the slaker, before overflowing to the first causticiser. This removes the overburned and/or unburned lime, sand, and other clinkerous materials down to about 65 mesh. These rejects, called grits, are usually 0.5–2% of the lime feed. It is very important to control the proportions of lime and alkali to be converted, and this occurs at the slaker. Excess lime causes poor lime mud separation, and under-liming gives poor conversion of carbonate to caustic.

The causticising reaction must proceed to completion to decrease the deadload (carbonate content) in white liquor and to avoid any unreacted calcium hydroxide in lime mud. Unreacted lime could make separation of white liquor difficult, especially when using filtration, which is more sensitive to unreacted lime than settling because calcium carbonate will begin to form within the filter medium (cloth), eventually blinding the cloth.

Empie et al. (2006) and Branham et al. (2006) have examined a new causticising process involving the use of barium hydroxide and barium sulphide to react with the soluble deadload sodium chemicals to produce sodium hydroxide, sodium sulphide, barium carbonate and barium sulphate. The reactions of barium hydroxide with sodium carbonate and sodium sulphide to form barium carbonate and barium sulphate approached full conversion after a 5–10 s reaction at room temperature with 0.1 mol/l feed solutions. Kinetic data for these reactions showed them to be very fast and essentially reversible. These fast causticising kinetics would enable a commercial process to replace the present stirred-tank causticisers with a low capital cost pipeline-flow reactor.

The slaked lime slurry must remain in the causticisers for sufficient time, and the liquor must have proper contact with the lime mud particles at all times. The necessary residence time depends on the method selected for white liquor separation. If the white liquor separates by settling, an approximate residence time of 1.5–2 h is enough because reactions can continue in the clarifiers. If filtration is applied, the residence time in the causticisers is usually about 2.5 h.

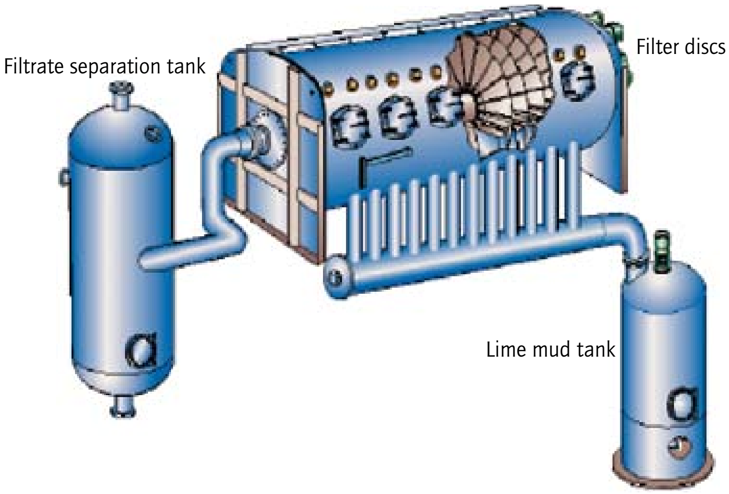
The distribution of residence time in causticisers is of primary importance because the amount of lime that has passed quickly through the causticisers without reaction must be as small as possible. To minimise the effect of this short-cutting, the causticiser tanks must have independent operating chambers. Most causticiser trains have nine chambers. Earlier causticisers were constructed as separate tanks. Today, every causticiser tank usually has three chambers on top of each other, and a causticiser train typically has three such tanks in series. The agitators in the causticisers are of the propeller or turbine type.

White liquor separation

The reaction products of recausticisation, i.e. lime mud and white liquor, are separated from each other. The objective of separation is to produce clear white liquor without any residual lime mud. Efficient separation means a reduced deadload of recirculated alkali in the recausticising plant. The product should also be at high temperature and concentration. Cooling or dilution is undesirable.

White liquor separation can be carried out using settling or filtration. Pressurised candle filters or pressurised disc filters are used nowadays for filtration. Figure 4.3 shows Kvaerner's (currently Metso Paper) pressurised disc filters, and Figure 4.4 shows Andritz's CD filter.

FIGURE 4.3 Pressurised disc filters for white liquor preparation



Source: reproduced from Arpalahti et al. (2000), with permission from Fapet Oy, Finland

FIGURE 4.4 Andritz CD filter

Source: Andritz, reproduced with permission

Sanchez (2001) has reported high yield recausticising through the use of white liquor pressure disc filters and high-yield drum filters (Anon 2006; Lownertz 2006).

White liquor clarification

Settling is commonly used for white liquor clarification (Cornell 1992). Lime mud settles to the bottom of a tank, and the clarified white liquor overflows to storage. Lime mud is collected from the bottom, using a rake mechanism in the middle of the clarifier, and is pumped from there at 35–40% suspended solids concentration to the lime mud washing stage.

Mud washing is usually carried out by first diluting and then settling the slurry in a similar type of clarifier. The upper part of the clarifier can be used as storage to eliminate the need for a separate storage tank. The operation of the clarifier is stable and reliable, and it always reaches the required capacity with low energy consumption. If some disturbances occur, the suspended solids content in white liquor may increase. The separation efficiency of clarification is low. This results in a substantial need for washing and a high alkali circulation in the recausticisation, approximately 20% of the white liquor production. The clarifiers are large and require considerable space.

Vacuum filtration with a belt filter ensures good separation efficiency and lime mud washing with the same piece of equipment. Because of the vacuum applied during the operation of the filter, the liquor cools by approximately 15°C. This disadvantage is one of the main reasons why many mills replace belt-type filters with pressurised filters.

The use of candle filters for white liquor separation became more common during the energy crisis in the 1970s. This method avoided the cooling of liquor and ensured continuous good quality of white liquor (suspended solids content of less than 20 mg/l). In the candle filter, lime milk is pumped into a pressure vessel in which liquor will pass through tube-like filter elements while lime mud remains on the surface of the filter cloth. Once the thickness of the cake on the surface of the filter cloth is sufficient (approximately 3 min), the liquor is back-flushed though the filter elements for 1–2 s to release the lime mud cake from the cloth. After a short delay of about 30 s, lime mud starts to settle towards the bottom of the filter, and a new filtration sequence can begin.

Lime mud is continuously withdrawn from the bottom of the filter to be washed. The washing stage generally uses dilution washing. Lime mud is separated with the same kind of filter. Lime mud slurry is mixed with washing waters in a mixing tank before the lime mud wash filter. From the wash filter, lime mud slurry with 30–35% suspended solids is pumped to the lime mud storage tank. Lime mud can also be separated by sedimentation or a belt-type filter after dilution for washing. The candle filter produces white liquor with no major heat losses and a low suspended solids content. Occasional operational disturbances in the recausticising plant can influence capacity. Such disturbances can lead to blinding problems in the filter media. The separation efficiency of the candle filter is the same as that of the clarifier, which means that the need for lime mud washing and the alkali circulation in the recausticising are similar, and that the lime mud washing stage is unavoidable. The filter cloths require maintenance so that they can maintain sufficient throughput. The cloths must be washed with dilute acid at one- to three-monthly intervals, and changed after one year of use.

The requirements for closure of the mill water balance have placed new demands on lime mud washing (Venkatesh 1992): it should use less water and be more efficient. These requirements, plus the need for heat economy, have led to the use of pressurised disc filtration for white liquor separation and lime mud washing.

The pressurised disc filter consists of disc-shaped filter elements attached to a central shaft that rotates in a horizontally placed pressurised vessel. A part of each disc passes through the lime milk in the bottom of the vessel. The pressure difference across the filter surface is maintained by withdrawing gas from the internal parts of the filter elements, compressing it, and returning it to the vessel outside the discs. Lime mud remains on the filter cloth surface, while white liquor passes through the cloth and inside the discs. The liquor goes from the discs via channels in the filter shaft to a pressurised vessel in which the filtrate and gas separate from each other. White liquor is pumped to storage, and gas is compressed back to the filter inside the pressure shell. The lime mud cake formed on the cloth rises above the lime milk level when the discs rotate. The pressure difference across the cake and cloth drives the filtrate through, resulting in about 60% dry solids content in the cake. The cake is further washed with water showers and then de-watered. The top layer of the lime mud cake is removed with a scraper before the discs again rotate partly under the lime milk surface. The remaining cake acts as a precoat during the next filtration cycle. Lime mud passes through chutes to a pressurised mixing vessel where it is suspended in water and pumped to the lime mud storage.

The disadvantages of the pressurised disc filter are:

- it is more complex and demanding than a clarifier, both technically and operationally;
- the need for maintenance is greater than in most filtration methods
- the power consumption is higher than for clarifiers.

Developments in process automation allow the programming of complex operating sequences with a distributed control system (DCS) to reduce operator work-load. In addition, pressurised disc filtration does offer many significant benefits, including:

- white liquor that has a low suspended solids content (less than 20mg/l);
- high separation efficiency for white liquor and lime mud separation;
- the ability to perform lime mud washing with the same piece of equipment (Anon 2006).

The washing water dilutes the white liquor and decreases TTA by approximately 2–5 g/l. Because of the high separation efficiency, white liquor plants with disc filters have only minor alkali circulation of about 5%, whereas alkali circulation can be 20% in mills with clarifiers.

Lime mud de-watering

Lime mud is stored between recausticising and the lime kiln to ensure stable and continuous operation of the kiln as a slurry at approximately 35–40% suspended solids (Biermann 1996). Keeping the lime mud suspended and ready for pumping requires continuous agitation in the lime mud tank with compressed air or a mechanical agitator. The target in lime mud de-watering is to complete lime mud washing and increase the dry solids so that lime mud can be fed to the lime kiln. The moisture in lime mud has a significant effect on the energy consumption of the kiln. The trend has therefore been to increase the dryness of lime mud after the filter. Dry solids contents of 80–90% are often possible nowadays. Water-soluble alkali in the lime mud after the filter remains under 0.1% as sodium oxide on dry mud. To obtain such a high dry solids content, lime mud requires proper washing before lime mud de-watering. Non-process elements should not contaminate the lime circulation. The specific load for lime mud filters is approximately 5–7 t/m^2/day. Lime mud de-watering is carried out using vacuum drum filters in the main, although other techniques including a belt filter have also been tried.

The same lime mud that is being de-watered is used as a precoat in lime mud filtration. At the beginning of the filtration, a precoat of lime mud of approximately 10–15mm in thickness forms on the filter drum. The scraper removes the outermost layer of lime mud cake to the belt conveyor. Lime mud is conveyed to the feeding screw and fed to the kiln. Many methods can be used to apply the high pressure precoat renewal technique. The water nozzle can be under the scraper, or at the back of the filter drum below the wash sprays. In both cases, using a nozzle carriage that travels the whole length of the drum is possible. Other options are to manage part of the drum length using a nozzle tube that has several nozzles and oscillates.

The operation of the recausticising plant has a strong influence on the formation of carbonate scale, on carbonate deadload, and on evaporation demand. It is desirable to have a high degree of carbonate conversion, a high total concentration of active chemicals, and low amounts of non-reactive species (carbonate, thiosulphate and sulphate ions) and of non-process elements (aluminate, silicate and chloride ions) in the white liquor. Researchers at STFI-Packforsk have reported that lime dosage and lime quality have the greatest effect on the recausticising process (Ulmgren 1990).

The recausticising system can be considerably improved by relatively minor changes (Theliander 2004). Improvement of the green liquor quality can be made by investigating the mixing conditions in the smelt dissolver and, if necessary, modifying the mixers. Computational fluid dynamics (CFD) programs are excellent tools for evaluating different mixing alternatives. To improve control of the strength of the green liquor, the density meter should be replaced by a more precise instrument, such as a combination of a spectroscopic method or conductivity meter and a titration robot. To improve the quality of the reburned lime mud, the most important measure is to stabilise the flow of lime mud into the lime kiln by changing the control strategy of the lime mud wash filter from a feedforward to a feedback system. This requires measurement of the lime mud flow with a high degree of precision and results in a more uniform quality to the reburned lime mud produced.

Using pressurised gasification and pressurised recausticising systems would make it possible to produce white liquor with a temperature close to that in the digester, resulting in a major increase in energy efficiency of the kraft pulp process.

Lenko and Blackwell (1991) report that minor pulping changes are required to improve recausticising system performance by recycling lime mud to the slaker from the underflow of the white liquor clarifier. The deadload of inorganic compounds in the liquor cycle can thus be decreased by achieving a higher target for causticity, leading to a small increase in the productive capacity of the recovery boiler.

The most important variables affecting causticising plant operation are presented in Table 4.7 (Campbell 1985; Lindberg and Ulmgren 1986; Dorris and Allen 1987).

TABLE 4.7 Variables affecting causticising plant operation

Green liquor	▶ Dregs carry-over ▶ Strength (density) uniformity ▶ Activity and sulphidity ▶ Temperature flow rate
Lime	▶ Availability (% calcium oxide) ▶ Reactivity (causticising power) ▶ Addition rate ▶ Method of calcination
Operating factors	▶ Method of agitation ▶ Retention time for causticising reaction

Source: reproduced from Smook (1992), with permission from Angus Wilde

Metso Paper offers a complete range of proprietary recausticising products marketed under the brand name Caustec. These products, singly and in combination, are capable of performing all operations in the recausticising process, including the lime kiln, through cooperation with FFE Minerals.

Modification of white liquor

White liquor produced in the recausticising plant is normally used for cooking in a kraft pulp mill. Modifications of the cooking process can require liquors that vary in strength or composition. White liquor can also be oxidised and used as an alkali source in the oxygen delignification stage of a bleaching plant. A new white liquor oxidation technology has been developed by Air Liquide (Epiney et al. 2006). The white liquor oxidation system installed at Metsä-Botnia's Kaskinen mill, Finland, has been in operation since 2005.

Modern recausticisation

Modern causticising plants incorporate rather traditional-looking slakers and causticising tanks. However, green liquor dregs separation and white liquor purification are evolving (Tran and Vakkilainen 2007).

Pressurised disc filters have replaced settling by gravity for liquid/solids separation (see Figure 4.3). The main advantage of filtration is the improved removal of non-process elements from green and white liquors. Disc filtration seems to be the preferred method for lime mud filtering in the new, most modern installations. Disc filtration increases the lime mud dry solids to the lime kiln (Jantti 2005). Similarly disc filters are now used for green liquor filtration. Dregs and grits can now be de-watered with a centrifuge, which decreases the waste flow to landfill (Beer et al. 2006). Modern calcination systems incorporate effective lime mud de-watering, a flash mud dryer, and efficient product coolers, to improve kiln thermal efficiency. Several lime kilns are operating well with shell diameters of 4.5–5 m, but kiln size has become one of the main worries in new mills as the space requires more than 800 tonnes of calcium oxide per day.

Automation and process control

Recausticising is a very slow process and only slight automation has been possible thus far. However, the situation has recently changed for several reasons. Nowadays, the number of personnel in the mills has been reduced, requiring an increased level of automation in all processes. At the same time, the main process equipment at the recausticising plant has become more sophisticated, which also requires additional automation. The equipment has several fully automated sequences for operation, which has increased the number of instrumentation loops, especially the use of automated on/off valves.

In automation, operational sequence engineering has become increasingly important. An operational test of the DCS configuration before start-up is a requirement nowadays. In this factory acceptance test, the DCS vendor, process equipment vendor, and customer operators witness the complete simulation of the operation of the sequences and interlockings programmed into the DCS.

Proper material and equipment model selections are essential for recausticising field instrumentation to avoid erosion, blinding by sedimentation, and scaling. The standard measurement requirements and common practices are still valid in recausticising instrumentation installations. The main problem in using conductivity measurement with recausticising process liquids is the frequent need for sensor cleaning. Some vendors have developed automatic signal compensation to allow continued measurement with dirty sensors. This compensation can help the situation only to a certain level, and sensor cleaning with acid is still necessary on a regular basis. All density measurement of process liquids uses nuclear density transmitters.

In green liquor services, scaling is the main problem. Polytetrafluoroethylene-lined spools and special cleaning can correct the problem. Temperature compensation connected directly to the density transmitter is also widely used. In vessels such as candle filters, pressure difference transmitters with capillaries, water purging, or both, are used for density measurements.

Due to the nature of the process liquids, a magnetic flow meter is the main instrument used. Polytetrafluoroethylene is the most common material for the lining of magnetic flow tubes. Steam and air measurement uses standard orifice plates or vortex-type meters.

Sedimentation is the major problem with level measurement of recausticising process liquids. Using water purging to clean the transmitter face can avoid this problem. Process liquid temperature is often near 1,000°C, which sometimes leads to the use of capillary connections.

Most main process equipment consists of pressurised vessels causing a need for minus-leg compensation in the level measurements. Both dry and wet legs are used. In areas where vessels are outside and freezing can be a problem, a capillary tube is a good choice for minus-leg compensation. Standard pressure measurement devices with direct connection or capillaries are used. Temperatures in the recausticising area are near 100°C. Pt100 resistance thermo-elements can therefore handle all temperature measurements.

Erosion and scaling are the main problems for proper control and on/off valve selection. Ceramic valves can solve the erosion problem, but they are expensive and are appropriate only in places where erosion is severe, such as for lime mud flow control. Ball, segmented ball, and butterfly valves essentially cover all recausticising control valve needs. To avoid leakage caused by scaling, ball valves with scraper type seals are widely used in green liquor services.

The control of the recausticising department is still manual in many mills. Operators follow the process using laboratory analysis. The determination of total, active, and effective alkali per titration is the most common laboratory test method. Process delay between lime feeding to the slaker and the final product in the third causticiser vessel is approximately 2–3h. Because of this long process delay, manual control is very difficult and can cause overliming, which results in filter cloth plugging and requires more frequent filter acid and water washing.

Automatic control and optimisation packages for the recausticising process area have recently become popular. The automatic control systems commercially available today are:

- special four-electrode conductivity sensors with automatic compensation for scaling and contamination;
- automatic process titrator and control;
- temperature difference control;
- fuzzy control.

Tolonen et al. (2002) have used the Kajaani Alkali Analyzer (a fully automatic, on-line sampling and titration analyser) to optimise the whole causticising process. Practical implementation of this control at a Finnish pulp mill demonstrated more than 50% improvement in white liquor quality, more than 50% faster process start-ups after shut-down, and less frequent acid washings of the white liquor filter. Several benefits are expected with online alkali strength measurement and slaker control. Fully automatic, online sampling and titration of green liquor, causticised liquor and white liquor helps to stabilise the TTA of green liquor and to automate slaker control, enabling optimisation of the causticising process, which results in lower emissions, fewer process bottlenecks, higher production capacity and reduced operating expenses, both in the causticising plant and in the rest of the pulp mill.

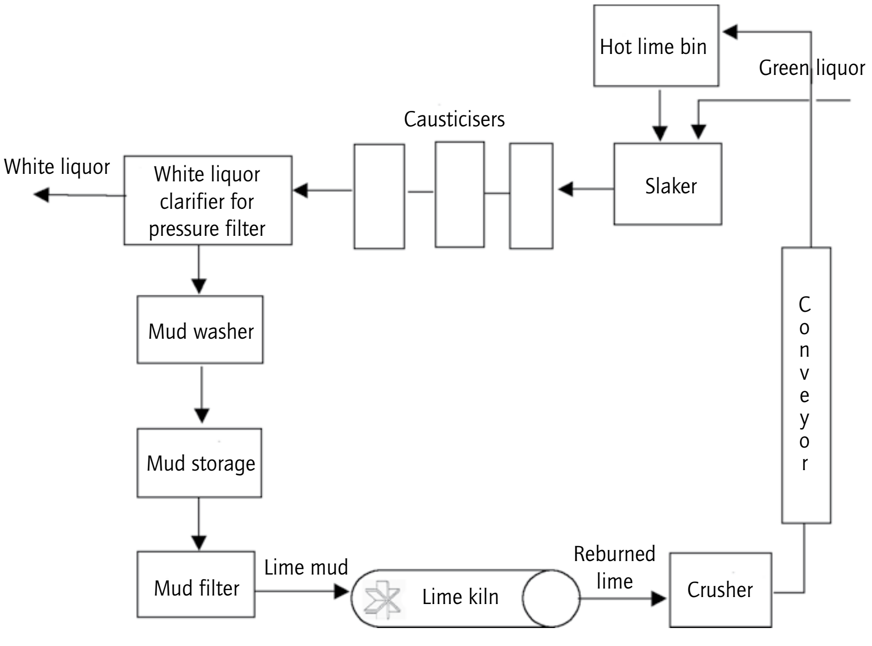
Lime reburning

5

Overview of the lime reburning process

Lime reburning is the process of converting the lime mud sludge (essentially calcium carbonate) generated in the causticising plant to reburned lime (calcium oxide). This reaction, called calcination, takes place at high temperatures (815.5°C and higher) in a rotary lime kiln, which is both a chemical reactor and a heat transfer device. Lime mud sludge is washed to remove the residual cooking liquor, and then de-watered on a precoat type vacuum filter to a solids content of 68% or more. The de-watered mud cake is fed to the lime kiln, where calcination occurs. The kiln product – reburned lime – is sent to a green liquor slaker (Adams 1992a; Venkatesh 1992; Arpalahti 2000). Figure 5.1 illustrates the lime process loop. Improved lime sludge reburning can be obtained if the dry content of the lime sludge is high. Researchers at Chalmers University of Technology have proposed improvements in the process with present day technology without excessive investment (Theliander 2004).

FIGURE 5.1 Lime reburning process flow loop



Source: reproduced from Venkatesh (1992), with permission from TAPPI Press

The causticising and lime reburning processes are extremely interdependent. Quality variations in the reburned lime product can cause problems during green liquor slaking and causticising . Ideally, reburned lime should be soft pebbles of about 2 cm in diameter. Reburned lime quality is judged in terms of availability, residual calcium carbonate, and reactivity.

The traditional lime kiln remains by far the most popular method of calcination, and this section concentrates on lime kiln operation. However, a few mills are using fluidised-bed systems, and a flash calcination system is being promoted as another alternative.

Three phases are involved in a typical calcination operation:

- drying the lime mud;
- raising the temperature of the lime mud to the level required for the calcination reaction (about 800°C);
- maintaining a high temperature for enough time to complete the endothermic reaction; the desired reaction is the chemical breakdown of calcium carbonate into quicklime and carbon dioxide.

A well-controlled calcination will yield a product that is 90–94% calcium oxide and reacts rapidly with the green liquor. Excessive temperature, along with chemical impurities, can promote the formation of non-reactive glass-like particles that are likely to be discharged as 'grits' from the slaker. The heat requirement for a modern calcination operation is detailed in Table 5.1. Many existing plants require much higher inputs of energy because of design or operating limitations. These limitations are manifested by a higher exit gas temperature, higher lime product temperature, and greater radiation losses.

TABLE 5.1 Heat requirement for lime calcination

Conditions	▶ 35% water in lime mud feed	
	▶ 350°C product temperature	
	▶ 90% calcium oxide product	
	▶ 10% excess air	
	▶ 230°C exit gas temperature	
Energy requirement	▶ Heat in exit gases:	1 Megajoule/tonne of product
	▶ sensible/latent heat of water	2,541
	▶ combustion gases	1,307
	▶ carbon dioxide gas from breakdown of calcium carbonate	148
	▶ Heat of dissociation	2,636
	▶ Radiation loss	1,054
	▶ Heat in lime product	316
Total		**7,590**

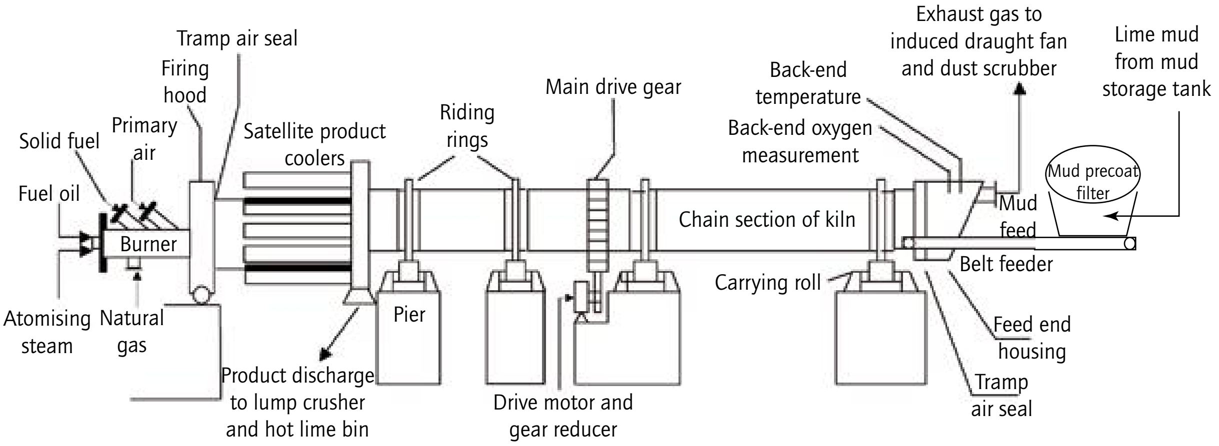
Source: reproduced from Smook (1992), with permission from Angus Wilde

Lime kiln

A typical lime kiln is shown in Figure 5.2. Wet lime mud is fed into the high end of the kiln, and the solid phase moves counter-current to the flow of hot gases as the kiln rotates. The transfer of heat into the mud at the cold end is optimised by providing an extended surface area, usually by means of steel chains attached to the kiln shell and hanging in the hot gases. In the hotter zones of the kiln, the metal shell is lined with refractory brick.

As its temperature is raised, the lime mud material becomes plasticised and forms into pellets, aided by the rolling and lifting action of the kiln (Adams 1996). Normally, the size of the aggregates ranges up to about 3 cm in diameter. Occasionally, the pellets keep on growing to form large balls, or adhere to the brick to form rings. The soda content of the lime mud has a significant effect on its aggregating properties during the reburning operation, and is typically controlled to less than 1% sodium oxide.

FIGURE 5.2 Schematic diagram of a rotary lime reburning kiln



Source: based on Adams (1992a); Smook (1992); Venkatesh (1992)

The hot end of the kiln is typically maintained at 1,150–1,250°C by firing oil or gas. Without reclaiming heat from the kiln product, the reburned lime would be discharged at a temperature of about 950°C. Most modern kilns are equipped with integral tube coolers to recover the major portion of this heat in direct contact with part of the entering air. These coolers are attached to the discharge end of the kiln in such a way that the calcined lime falls into one of the coolers; it then reverses direction and flows counter-current to the air to the opposite end of the cooler, where it is discharged at a temperature of about 350°C. Air is supplied to the kiln by a forced draught fan, but the major work is done by the induced draught fan, which pulls the combustion gases through the kiln.

The gases leaving the kiln are laden with lime mud dust, and must be cleaned up before discharge. In most cases, the dust is removed in a suitably designed scrubber, most commonly a Venturi-type. The electrostatic precipitators have become the equipment of choice for this service, especially for the largest-sized kilns (Adam 1992; Venkatesh 1992).

The feasibility of using fabric filters for efficient dust removal has also been demonstrated, but has not proved popular with the industry. Generally, to achieve the best time/temperature balance and obtain optimum thermal efficiency, a large kiln with a length-to-diameter ratio of more than 30 is required.

The retention time is controlled by the slope and rotational speed of the kiln. The slope is usually designed to be between 0.6 cm and 1.3 cm per 30 cm of length. The speed varies from 0.5–1.5 rpm. Retention time should fall into the range of 2–3 h.

The factors affecting productivity and fuel economy and steps for upgrading have been reviewed. Many of the older kilns still in operation are handicapped by having a low length:diameter ratio, and are often severely overloaded as well. It is now possible to lengthen an existing kiln by moving the evaporation zone outside the shell and using the entire length of the kiln for calcination. Both a flash dryer and cage mill are employed in a typical system where the kiln exit gases are used to dry the lime sludge before it enters the kiln.

The calcium carbonate content of mud fed to the kiln typically ranges from 94–95%. Table 5.2 shows the chemical composition of an acceptable lime mud. It is very important that the feed mud cake be well washed in the precoat filter, although the impurities do help with the formation of nodules to some degree: if the lime mud feed to a kiln were 100% calcium carbonate, no nodules would form and the kiln would be extremely dusty.

TABLE 5.2 Chemical composition of lime mud feed

Component	Composition (%)
Calcium carbonate	>95.00
Sodium oxide	<0.20
Silica	<0.20
Alumina	<0.50
Iron oxide	<0.50
Sodium sulphide	<0.01
Calcium oxide	<0.50

Source: reproduced from Venkatesh (1992), with permission from TAPPI Press

Soda is the major impurity in lime mud. The target for modern precoat filters is a mud soda content of 0.2% or less. A poorly washed mud will have a tendency to build rings or form large balls within the kiln. Rings or balls restrict production and kiln efficiency by requiring the kiln to be shut down for cleaning. Björk (2005) has suggested an approach for reducing ringing problems.

Lime mud containing minimum amounts of reduced sulphur compounds (sodium sulphide) is required to meet stringent kiln odour emission standards. Washing to a soluble soda content of 0.2% or less has recently been accepted as a means of ensuring low sulphide content. Many lime kilns incinerate sulphur-bearing non-condensable gases (NCGs), which has contributed to severe problems with rings. Fuel oils with high sulphur contents are another sulphur source. Alumina, silica and iron oxide enter the lime loop as impurities in the make-up lime, from dregs carry-over, and from the kiln refractory. Their impact is to reduce lime availability.

Impurities are also associated with the common calcination problems of balling and ringing. Ball formation typically occurs just past the chain section or just ahead of the kiln burning zone, and is associated with high soda, free lime, and moisture content in the incoming mud. Soda and sulphur compounds have lower melting points and consequently tend to coat the lime pellets and large balls that form and roll down the kiln. The mud balls can be 0.6–1.0 m or so in diameter, and have a white surface with a green or yellow core. Their composition is that of unburned mud.

Balling problems can be reduced by minimising mud feed flow or moisture content variations. A mud feed solids of 70% and low soda content can also greatly minimise the formation of balls.

In many modern mills, a more persistent problem is the accumulation of hard ring deposits on the refractory lining. Ring formation has been attributed to high levels of sulphur and/or sodium in the mud feed. In extreme cases, rings can severely constrict the flow of reburned lime and exhaust gases inside the kiln and reduce the lime throughput. Three types of rings have been identified in lime kilns:

- mud rings
- mud-kiln rings
- front-end rings (Barham and Tran 1991).

The three have a similar chemical composition but are thought to be formed by different mechanisms. These mechanisms are not fully understood, but it is thought that a high sodium content in the lime mud, high sulphur content in the fuel, high mud moisture content, unstable operation and poor flame characteristics are the main causes of ring appearance and growth.

Mid-kiln rings pose the main problem in modern kilns (Notidis and Tran, 1992; Tran et al. 1992). This problem is more persistent in kilns that burn NCGs, and many mills now scrub their NCGs with white liquor to remove sulphur before the gas enters the kiln. The presence of free lime, which can recarbonate in the heating-up zone, is also known to promote ring formation. Thus high dust recycle could be a factor.

Modern kilns are equipped with oversized precoat-type mud filters, which deliver lime mud cake in the range of 70–80% solids (20–30% moisture content). The kiln fuel requirements are related to the solids content: the greater the mud cake solids content, the lower the fuel requirements. A heat consumption of about 2.813 MJ can be assigned for each kilogram of water entering with the mud. The installation of oversized lime mud filters has been a major factor in the industry-wide improvement in lime kiln fuel economy from the 9,500–10,500 MJ per tonne of kiln product to below 7,500 MJ per tonne of kiln product.

Merely increasing the feed cake solids, however, does not automatically raise kiln fuel efficiency. Kilns are provided with a chain system at the feed end to assist in the evaporation of water and to act as a dust curtain. Chain section length and the quantity of chains are related to the feed mud moisture content. A smaller chain section is required as mud cake dryness increases without compromising the role of the chains as a dust curtain. Table 5.3 shows comparative fuel usages at different dryness levels.

TABLE 5.3 Comparative kiln fuel usage at different mud dryness levels

Lime mud dryness (%)	70	75	80
Exit gas temperature (°C)*	157	163	177
MJ/tonne of product (natural gas fuel)	6,594	6,204	5,919

*Note: *exit gas temperatures rise as dryness in feed increases*
Source: reproduced from Venkatesh (1992), with permission from TAPPI Press

The ideal operating requirements for the lime kiln involve meeting the recausticising needs while minimising energy consumption and total reduced sulphur (TRS) emissions.

Osmond et al. (1994) described the development of two control strategies for lime kilns operating close to their maximum capacities. The first uses the fuel flow rate to control the cold-end gas temperature, and the combustion air flow rate to control the hot-end bed temperature. The second strategy uses the combustion air flow rate to control the cold-end gas temperature, and the fuel flow rate to control the hot-end bed temperature. The first strategy would maintain better product quality if increased production requirements led to periodic fuel actuator saturation.

The lime kiln environment is very demanding for automation hardware and software. High-level optimisation control systems have been developed for this process area (Hagemoen 1993).

Jacket is an advanced monitoring system for rotary kilns (Koukkari et al. 2004). The temperature scanning system uses infra-red line scanners to provide kiln shell temperature measurements. The plant distributed control system (DCS) software receives thermal images, temperature histograms and temperature distribution data from around the lime kiln mantle in the form of a graphical output. A multiphase KilnSimu model for lime and alkaline chemistry reveals reaction zone profiles along with calculated temperature distributions of bed and gas streams. The thermodynamic model can calculate volumes of flow, enthalpies, heat capacities, heat fluxes, local temperatures and concentrations. The temperatures of the inner and outer mantle are also recorded. Recorded Jacket data can also be compared against calculated reference profiles for different process conditions. The system has application in revealing exact local information about hot spot temperatures, and enables fuel and combustion optimisation as well as shorter start-up times and trouble-free kiln operations.

Optimisation control systems have been implemented in a number of kraft pulp mills and have achieved lime kiln process stability and the even lime quality required for a more steady causticising process.

Metso's DNAlime optimisation control systems are designed to supervise the coordination of the basic lime mud washing, fuel combustion, lime burning, and kiln operation controls (Imelainen et al. 2005). The systems are able to provide lime kiln process stability by striking a balance between input and output conditions and the internal kiln temperature profile through the use of process running models adapted from operating experiences, and fuzzy logic controls. The steadiness of lime kiln operation achieved by the optimisation controls helps to improve causticising plant operations and minimise bottlenecks, increasing production levels. The controls, which include a specific energy monitoring feature, also help to reduce the process energy consumption of kraft pulp mills, which translates into significant energy savings and a reduction in the gaseous effluents produced. Improved plant results at Stora Enso's Veitsiluoto Mill (now Smurfit Nettingsdorfer kraft pulp mill) in Kemi, Finland, and in Austria attest to the stabilising effects of lime kiln optimising controls.

Jahn (2000) has reported that vertical shaft kilns are more thermally efficient than rotary kilns. The use of vertical kilns is likely to increase because of rising fuel costs, the need to reduce greenhouses gases, and taxes on carbon dioxide emissions. Comparison is made between different styles of lime kiln. Kilns need also to offer flexibility in terms of:

- their use of alternative fuels
- varying kiln production
- burning a maximum grain size range
- use of soft and decrepitating limestone
- burning limestone of varying chemical composition.

The parallel flow regenerative lime kiln is likely to become a valuable alternative to other types of kiln.

Lime kiln capacity constraints

There is no fixed upper limit to the capacity of the lime kiln itself. The production is limited by constraints on the peripheral equipment. There are nine major constraints on the production rate of a lime sludge kiln (Venkatesh 1992; Adams 1996):

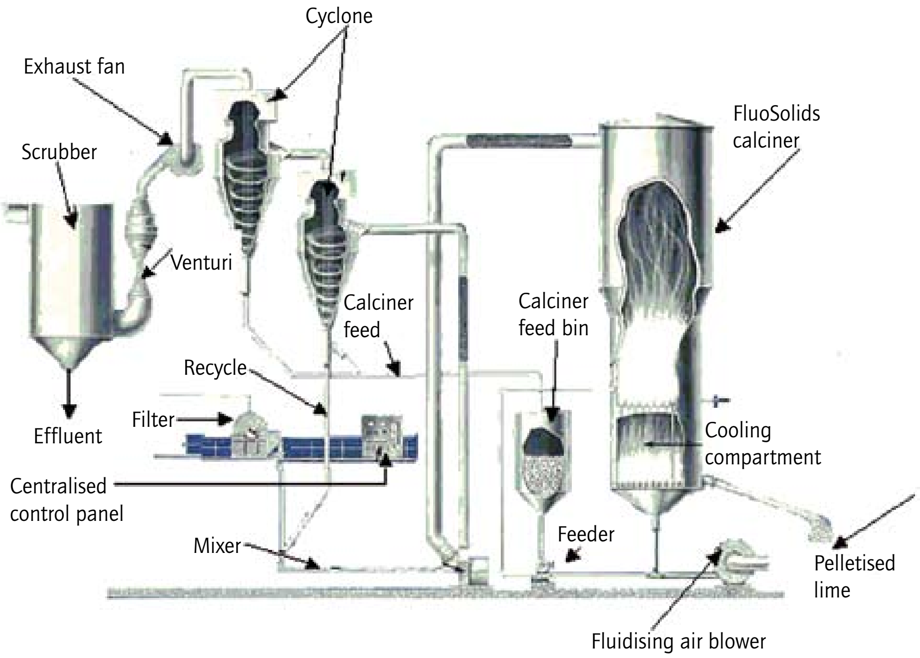
- mud flow into the kiln – mud filter, conveyors and feed screws;
- product flow out of the kiln – lump crusher, drag conveyors, bucket elevator and kiln drive;
- gas flow out of the kiln – induced draught fan;
- fuel flow into the kiln – fuel valve train, primary air fan and burner;
- air flow into the kiln – firing hood and coolers;
- materials temperature limits – metal shell, refractory surface, chains, induced draught fan and precipitator;
- environmental emissions – particulates, nitrogen oxides and TRS;
- structural design – kiln shell, trunnions, tyres and foundations;
- operational problems – mud balls, poor nodulisation and ring formation.

Ultimately, the material temperature limits and operation problems play the most significant roles in determining the maximum capacity for most kilns.

Fluid bed calciner

A fluid bed reburning system is illustrated in Figure 5.3. The exhaust gases from the fluid bed are used to dry the lime mud, which is then collected in two cyclones and discharged into a surge bin. The dry lime mud is blown into the calcination bed where the fuel is being burned, and is almost immediately transformed into lime pellets. The heavy pellets fall into the cooling compartment, while the lighter dust is recycled with the air for drying the mud. The system is compact, requiring much less space than a kiln of comparable capacity, and is capable of producing high-quality lime of uniform size. Other advantages claimed are good thermal efficiency and ease of start-up. These systems have been available for more than 30 years, but there are few such installations within the pulp and paper industry (Smook 1992). The economics of the fluid bed system may be more favourable for smaller-sized plants.

FIGURE 5.3 Technip FluoSolids calcination technology



Source: reproduced with permission from Technip USA, Inc.

Flash calcination

A few manufacturers are promoting flash calcination as another alternative for pulp mill lime reburning. The heart of the system is a swirl-type furnace in which the combustion of the fuel is in intimate contact with the material being calcined. The turbulent swirling mixture produces a uniform temperature profile, and conventional flame temperatures are never encountered because the material absorbs the excess heat instantaneously.

Technologies for the chemical recovery of nonwood black liquor

6

Soda or kraft pulping processes are generally used for the pulping of nonwood raw materials. The active pulping chemicals are sodium hydroxide in the soda pulping process, and sodium sulphide and sodium hydroxide in the kraft pulping process. During the pulping process, cellulose and hemicelluloses are separated, and lignin, along with some other chemicals such as silica and extractives, get solubilised in the cooking liquor, which is separated from the pulp and termed black liquor. To make the pulping process economical and environment-friendly, these cooking chemicals are recovered from the black liquor for reuse in the system.

In this recovery process, black liquor is first concentrated in evaporators and burned under reductive conditions in a recovery boiler. The sodium and sulphur present in the black liquor are converted to sodium carbonate and sodium sulphide. An aqueous solution of these chemicals is called green liquor. This is further causticised with calcium oxide to regenerate the pulping chemicals. The calcium carbonate formed during causticising may be recovered as calcium oxide after re-burning it in the kiln.

Nonwood plants contain a higher amount of silica than does wood. The maximum amount of silica gets dissolved during the pulping process and remains in the black liquor. The greater amount of silica in the black liquor from nonwood plants creates special operating problems during the chemical recovery process. Because of the open structure of nonwood plants, they require more cooking liquor. Silica also reacts with alkali during pulping, which further enhances the alkali requirement and increases the inorganic chemical load in the recovery process. This means lower organic/inorganic ratios, lower heating values, and more inorganic chemical to be reclaimed and reconverted (Grace 1987).

The higher silica content in the nonwood black liquor creates several problems during the evaporation and burning of the black liquor in the recovery boiler. A high concentration of silica in the lime sludge generated by causticising also creates problems during reburning in the kiln for lime recovery (Bist et al. 1981). Evaporators are very prone to scaling, and the concentrated alkali–silica solution decomposes at the hot surfaces to form siliceous scales, which do not respond to boil-out or to chemical treatment and must be mechanically removed. The alkali–silica solution also increases the viscosity of the liquor, which ultimately lowers heat transfer rates.

Combustion of high-silica liquors results in the formation of high viscosity silicate glass. This causes formation of 'honeycombs' on the boiler wall, plugging of convective boiler passages, difficulties in smelt drainage, and impaired combustion. Frequent shut-downs for cleaning are therefore required. In some cases where problems are especially severe, steam generation from liquor burning is not attempted. Direct contact evaporators in which the hot gases are used to concentrate liquor may provide the only heat recovery.

Silicates in green liquor will react with lime and precipitate as calcium silicate. This interferes with lime mud settling so that mud washing and filtration are more difficult and soda losses are increased. Silica forms glassy silicates in the kiln leading to sticky rings and low efficiency. These problems are usually so severe that lime reburning is not attempted when pulping siliceous fibre sources. Disposal of the lime mud then becomes a problem as residual sodium in the mud acts to prevent its use as a soil conditioner, even in lime deficient regions (Grace 1987).

Several techniques are available for removing silica from chemical recovery systems. The best point for silica removal is from weak black liquor, although desilication can also be carried out on green liquor. This avoids interfering with the organic compounds in the black liquor, but it does not prevent problems in the evaporators or combustion stage. Precipitating agents that have been considered include lime, alumina and ferric oxide. Carbonation is the only process used for desilication by acidification.

Desilication of black liquor

The ideal point to remove silica is from weak black liquor immediately after fibre separation, although it may be desirable partially to concentrate the liquor first in order to reduce the volume of liquor treated and improve the degree of desilication.

There are essentially two methods for the removal of silica:

- precipitation by a multivalent cationic material
- acidification.

Precipitating agents that have been considered include lime, alumina and ferric oxide. Carbonation is the only process used for desilication by acidification.

Lime desilication has received a lot of attention because lime is cheap and calcium silicate is quite insoluble, but no industrially viable process has emerged. Lime dosages have to be about six times the stoichiometric amount needed to form calcium silicate, and the filtration properties of the resulting lime mud are unfavourable. Many of these difficulties are lessened with green liquor desilication, but this does not alleviate evaporator or recovery furnace problems.

Alumina has not been found to be effective for removing silica from black liquor. However, when alumina is allowed to react with smelt in the recovery furnace, the aluminium silicate formed is insoluble in green liquor, and so can be removed with the green liquor dregs. This technique has apparently been used successfully at a mill in South Africa.

Carbon dioxide is the only practical reagent for silica precipitation by partial acidification because of the need to realkalise the liquor to regain lignin stability. Under proper conditions, it is possible to precipitate silica without precipitating lignin. The critical pH limit must be established for each liquor. As the pH drops, sodium bicarbonate is formed and silica precipitates according to Reaction 6.1:

$$Na_2SiO_3 + H_2O + 2CO_2 = 2NaHCO_3 + SiO_2 \qquad \text{[Reaction 6.1]}$$

In practice, carbonation is carried out at higher temperatures, despite the fact that silica solubility increases with increasing temperature, in order to conserve the heat in the black liquor. It is critically important to obtain the silica in a flocculated, easily filterable form, but this is not necessarily straightforward. The efficiency of silica removal by the acidification method depends on pH and temperature. At lower temperature, it is possible to precipitate silica at a higher pH range, whereas at high temperature, lower pH ranges are required (Kulkarni et al. 1984). Silica removal efficiency is higher at higher temperature and lower pH (Table 6.1).

TABLE 6.1 Desilication of black liquor at different temperatures*

Temperature (°C)	pH	Silica as SiO_2 (g/l)	Silica removed (%)
21	10.90	2.60	50.0
	10.65	1.10	78.8
	10.40	0.50	90.4
	10.30	0.50	90.4
52	10.10	4.10	21.2
	9.90	3.00	42.3
	9.75	2.65	49.0
	9.65	1.45	72.1
64	9.80	4.60	11.5
	9.60	0.90	82.7
	9.50	0.55	89.4
75	9.60	3.30	36.5
	9.40	0.55	89.4
	9.30	0.10	98.1

*Note: *initial pH of black liquor = 11.9, concentration of silica = 5.2g/l*
Source: Based on Kulkarni et al. (1984)

In India, Central Pulp & Paper Research Institute, with the technical support of Enmas, has demonstrated a few pilot/commercial-scale studies for the removal of silica from black liquor by acidification with carbon dioxide, obtaining silica removal of up to 85–98% (Table 6.2) (Nair et al. 1999).

TABLE 6.2 Desilication of black liquor from various raw materials

	Bamboo/reed-based mill	Bamboo-based mill	Rice straw -based mill	Straw/sarkanda-based mill
Status	Commercial	Commercial	Semi-pilot	Semi-pilot
Initial silica in black liquor (g/l)	3.7	3.7	12.3	3.7
Final silica in black liquor (g/l)	0.6	0.5	0.28	0.17
Desilication (%)	85	87	98	95

Source: Based on Nair (1999)

Desilication of green liquor

In the chemical recovery section of a pulp and paper mill, the smelt from the furnace is dissolved in water, and this green-coloured solution is called green liquor. The green liquor obtained from paper mills using nonwood raw material contains a higher amount of silica, which interferes in causticisation as well as in lime recovery. The lime sludge obtained from the causticisation of silica-rich green liquor is not suitable for recalcination and is generally discarded because the higher silica present in the lime mud prevents the conversion of calcium carbonate to calcium oxide. This may be due to the formation of trisodium silicate. It also induces uneven burning of the lime and increases furnace oil consumption.

For a proper recovery operation, the silica present in the green liquor needs to be removed before causticisation. The methods recommended for removing silica from green liquor are based on acidification using flue gas, or treatment with lime (Veeramani 1977).

When green liquor is carbonated with flue gas, silica is precipitated by the reaction of silicate with carbonic acid. Laboratory-scale results indicate that carbonation at 80°C to pH9.5 is able to remove up to 85% of silica (Idrees and Veeramani 1977). This method is not much used on a commercial scale.

Desilication of green liquor with sulphuric acid is also able to remove up to 90% of the silica, but the plant applications show some limitations (Ikram and Ali 2006). A green liquor from which 97% of the silica had been removed was compared with an untreated green liquor in the operations of clarification, washing and the filtering of lime mud. Removing the silica led to an increase in the solids content of the lime mud (Wang et al. 2003).

Several mills have recently started to desilicate green liquor with lime. The advantages of lime addition are:

- low cost
- reduced lime requirements
- less lime sludge generation
- reduced loss of organics
- loss of sulphate ions is reduced as side-reactions are suppressed.

A two-stage causticising method for the desilication of kraft green liquor is easily adoptable by mills, since the quantity of desilicated sludge to be handled is small and has a rapid settling rate (Rao et al. 1988). In the two-stage causticising process, lime is used in the first stage to remove the bulk of the silica and partly for causticising, while in the second stage it is used for causticising efficiency up to 80%.

When lime is added to green liquor, it preferentially reacts with sodium silicate and forms calcium silicate. Afterwards, lime reacts with sodium carbonate and forms calcium carbonate. This advantage is now being used to precipitate the silicates in the first stage. Approximately 60–65% of the lime mud generated with green liquor can be burned in the

TABLE 6.3 Effect of two-stage causticisation of green liquor

	Set 1	Set 2	Set 3
Initial silica in green liquor (g/l)	3.6	3.6	3.7
Lime used (g/l)	16.3	19.6	20.5
Final silica in green liquor (g/l)	1.3	2.0	1.8
Desilication (%)	63.9	44.4	51.4

Source: based on Kashikar et al. (2007)

kiln by adopting the two-stage causticisation process (Kashikar et al. 2007) (Table 6.3).

Soda recovery in the form of sodium hydroxide/sodium carbonate without heat recovery

Saroha et al. (2003) conducted laboratory-scale experiments to evaluate the feasibility of recovering soda from industrial nonwood spent pulping liquor by converting the lignin-bound sodium into free sodium, with subsequent causticisation to produce sodium hydroxide. After direct causticisation, soda recovery in the form of sodium hydroxide was found to be 79%. Recovery was further enhanced by converting lignin-bound sodium into free sodium using an oxidising agent. Potassium permanganate was found to be the optimum oxidising agent, producing 93% of the total sodium recovered in the form of sodium hydroxide under the study conditions.

Seppa and Venter (1998) have reported that sodium hydroxide from bagasse or soda-anthraquinone hardwood spent liquor can be directly recovered using calcium oxide. The sodium bound in the lignin molecule is exchanged for calcium, the sodium hydroxide goes into solution, and the calcium lignate precipitates. The degree of removal of the organic material depends on the amount of calcium oxide and coagulant added. Yields of up to 98% have been obtained. The method leads to a closed loop for sodium. The recovery efficiency depends on pulp washing efficiency. The concentration of the sodium hydroxide filtrate depends on the water input into the cycle.

The above processes have not yet been commercialised. Soda recovery from nonwood pulping liquors by means of wet air oxidation has been reported by Ellis (1982).

Direct alkali recovery system in small pulp mills

7

The direct alkali recovery system (DARS) is one of the first alternative recovery concepts based on the addition of an in situ causticising agent to spent pulping liquor prior to combustion (Tadashi et al. 1976; Covey and Ostergren 1985; Kulkarni et al. 1987; Rao and Kumar 1987; Venkoba Rao 1987).

In the basic process, patented by the Toyo Pulp Company in 1976, iron oxide combines with sodium carbonate to form sodium ferrite, which expels carbon dioxide to the flue gases (Reaction 7.1). When the sodium ferrite is dissolved in water, the salt decomposes to form sodium hydroxide plus insoluble iron oxide (Reaction 7.2), which can be removed from the caustic liquor and recycled to the fired black liquor (Tadashi et al. 1976) thus:

$$Na_2CO_3 + Fe_2O_3 = Na_2Fe_2O_4 + CO_2 \qquad \text{[Reaction 7.1]}$$

$$Na_2Fe_2O_4 + H_2O = 2NaOH + Fe_2O_3 \qquad \text{[Reaction 7.2]}$$

Coarse particles (1–3 mm in diameter) are maintained to allow more efficient de-watering of the ferric oxide after leaching. The fluid bed is a ‘bubbling bed’ type combustor to minimise particle size reduction, which would occur with a circulating bed (Grace 1987). The obvious advantage of this process is elimination of the lime-based causticising process, which requires fossil fuel for driving the lime mud calcination reaction. The DARS process is limited in application to non-sulphur pulping because iron reacts with the reduced sulphur to form undesirable compounds that cannot be recovered in useable forms for reuse in pulping.

The commercial realisation of the DARS process combined this process chemistry concept with a Copland-like fluidised bed combustor and associated solids-handling equipment. The concept was licensed from Toyo and successfully demonstrated by what is now Australian Paper in the early 1980s using an integrated pilot plant including a batch digester, spent liquor evaporator, and a 76cm diameter fluidised bed combustor.

In 1986, a full DARS plant was constructed by Associated Pulp & Paper Mills (APPM) to replace rotary incinerators at its Burnie, Tasmania soda process pulp mill. The fluidised bed combustion zone operated at approximately 1,000°C. Because there was no sulphur in the process, it was not necessary to operate in a reducing mode. The sodium ferrite bed solids were continuously removed from the combustor and leached by water in a counter-current contactor. The equilibrium concentration of sodium hydroxide from sodium ferrite hydrolysis could reach levels two to three times as high as with conventional lime-based causticisation. The solids were separated from the caustic liquor, mixed with make-up iron oxide, and returned to the fluidised bed. An expected challenge to operating this process was managing the fine dust generated from attrition of the porous leached bed solids. Accordingly, a baghouse filter was used to remove the dust from the flue gas, and this material was agglomerated by mixing it with a small amount of black liquor prior to recycling it to the fluidised bed combustor.

Difficulties were faced during the first five years of operation, especially in maintaining fluidisation and managing the large quantities of sodium ferrite dust. The system was able to operate for an extended period only after three major equipment rebuilds. By 1995, the Burnie mill had been acquired by Australian Paper, and the DARS plant was processing about 150 t of dry solids per day and supporting two-thirds of the mill production. By the late 1990s, the process was running well enough that a second DARS plant and expansion of the mill was under evaluation, but a decision was reached that, even with a capacity increase, the pulp mill was too small to be economically viable and so the entire operation was shut down.

Several companies have evaluated DARS for use in nonwood pulping operations, and at least two additional pilot plants have been built, but a second commercial unit has not yet been commissioned.

The DARS process shows promise for providing a simpler recovery technology suitable for smaller scale mills. The economic analysis indicates that the system offers a substantial reduction in both the capital investment and operating costs compared with conventional recovery systems (Table 7.1).

TABLE 7.1 Cost comparison of conventional and ferrite recovery processes

	Conventional recovery system			**Ferrite recovery system**		
Pulp mill capacity (tpd)	30	40	50	30	40	50
Capital investment (€ million)	0.24	0.28	0.33	0.16	0.19	0.22
Cost of sodium hydroxide production (€/tonne)	112.2	106.0	102.0	80.2	75.6	72.6
Reduction in capital investments (%)	–	–	–	32.6	31.5	30.7
Reduction in operating costs (%)	–	–	–	28.5	28.7	28.8
Depreciation (€/year)	16,833	19,667	23,333	11,333	13,333	15,500
Savings (€/year)	8,833	28,167	48,500	43,166	70,833	99,500
Payback period (years)	9.4	5.9	4.5	3.0	2.3	1.9

Source: based on data from Rao and Kumar (1987)

One drawback of the process is that it is not applicable to kraft recovery because the iron oxide is reduced under the conditions needed to form sulphide (Rao and Kumar 1987).

Silica is an undesirable element in all the spent liquors from the pulping of agricultural residues. Extensive studies on the effect of the presence of silica impurity in the recovery loop have revealed that during the ferrite autocausticisation process only a minor proportion of silica passes into white liquor (Table 7.2). This is an advantage of the process, and unlike conventional recovery it may not be necessary to have an additional stage of desilication of spent liquor prior to the recovery operation (Kulkarni et al. 1987).

TABLE 7.2 Solubility of silica in regenerated alkali

Serial no.	Concentration of regenerated alkali as sodium hydroxide (g/l)	Causticity (%)	Silica in white liquor (ppm)	Silica passed to white liquor (%)
1	36	83.7	Nil	Nil
2	132	93.9	433	0.83
3	218	92.1	1,634	1.47

Source: based on data from Kulkarni et al. 1987

Leaching is a key step of the ferrite process, and the conditions should be maintained to allow maximum causticity and soda recovery. It is necessary to ensure that the sodium ferrite is completely hydrolysed and that maximum extraction of sodium hydroxide in the form of concentrated solution is achieved. The most efficient leaching configuration will be pure counter-current contacting. Results show that a minimum of four stages of extraction would be required for sodium recovery of more than 90% (Kulkarni et al. 1987).

A substantial quantity of natural haematite ore as a source of iron oxide for autocausticising has been used in the ferrite process. There is a likelihood of the presence of some soluble iron compounds in the ore, which are subsequently carried into the white liquor regenerated during the ferrite process. Studies on the solubility of iron reveal that when high purity haematite ore is used, the solubility of iron is negligible and does not have any adverse effect.

Benefits

The DARS process offers the following benefits:

- operational flexibility – it is compact and simple in operation and requires less space than conventional systems;
- fuel economy – it minimises the quantity of high cost fuel needed;
- does not require a high degree of process automation;
- unlike the smelt in conventional recovery processes, the combustion product is solid, so the process is safe;
- the capital cost is low.

Constraints

From the activity of regenerated iron oxide, it is felt that ore should not be recycled more than six times. The reduced activity of silica rich ore is attributed to brittleness.

Alternative chemical recovery processes

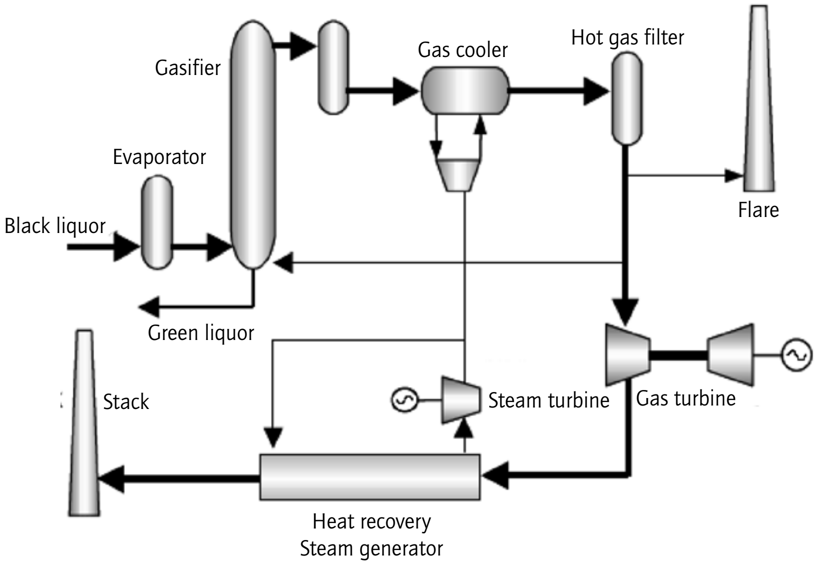
8

Over the years, several different alternative black liquor recovery processes have been developed. They can roughly be divided into processes for the chemical recovery (i.e. alternative causticisation processes), and the energy recovery (i.e. gasification processes) of black liquor. In addition, the alternative causticisation and gasification processes can be combined. The drawbacks of the conventional recovery process listed earlier have been the drivers for development of these new concepts.

Black liquor gasification

The gasification of black liquor and woody biomass residual materials is being intensively developed as an alternative to the current technologies. Gasification could become part of an integrated gasification and combined cycle (IGCC) operation, or lead to pulp mills becoming biorefineries (Larson et al. 2003). Figure 8.1 shows a simplified schematic for a black liquor IGCC.

FIGURE 8.1 Integrated gasification and combined cycle operation



Source: based on Sricharoenchaikul (2001)

In the gasifier, the organic matter in the black liquor is partially oxidised with an oxidising agent to form synthesis gas (syngas), while leaving behind a condensed phase. The syngas is cleaned to remove particulates and tars and to absorb inorganic species (i.e. alkali vapour species, sulphur dioxide, and hydrogen sulphide), in order to prevent damage to the gas turbine and to reduce pollutant emissions. The clean syngas is burned in gas turbines coupled with generators to produce electricity. Gas turbines are inherently more efficient than the steam turbines of recovery boilers because of their high overall air:fuel ratios (Nilsson et al. 1995). The hot exhaust gas is then passed through a heat exchanger (typically a waste-heat boiler) to produce high-pressure steam for a steam turbine and/

or process steam. The condensed phase (smelt) continuously leaves the bottom of the gasifier and must be processed further in the lime cycle to recover pulping chemicals.

In recovery boilers, essentially all of the alkali species and sulphur species leave in the smelt (mostly as sodium sulphide and sodium carbonate), but in gasifiers, there is a natural partitioning of sulphur to the gas phase (primarily hydrogen sulphide), and alkali species to the condensed phase, after the black liquor is gasified. Because of this inherent separation, it is possible to implement alternative pulping chemistries that could yield higher amounts of pulp per unit of wood consumed (Larson et al. 1998, 2003).

Gasification at low temperatures thermodynamically favours a higher sodium/sulphur split than gasification at high temperatures. This results in higher amounts of sulphur gases at low temperatures. Because a large amount of the black liquor sulphur species leaves the low-temperature process as hydrogen sulphide, this latter can be recovered via absorption to facilitate alternative pulping chemistries. Industry has numerous patented processes for accomplishing the absorption, including using green or white liquor as an absorbing solvent (Larson et al. 1998, 2003; Martin et al. 2000).

The partitioning of sodium and sulphur in black liquor gasification requires a higher capacity for the lime cycle than does the current technology. The sodium/sulphur split results in a higher amount of sodium carbonate in the green liquor because less sulphur is available in the smelt to form sodium sulphide. For each mole of sulphur that goes into the gas phase, one more mole of sodium carbonate is formed in the condensed phase (Larson et al. 2003). The increase in sodium carbonate results in higher causticisation loads, an increase in lime kiln capacity, and an increase in fossil fuel consumption to run the lime kiln. This leads to higher raw material and operating costs, which must be reduced in order to make the gasification process economically favourable.

Black liquor gasification can be performed at either low or high temperatures, based on whether the process is conducted above or below the melting temperature range (650–800°C) of the spent pulping chemicals (Sricharoenchaikul 2001). In low temperature gasification, the alkali salts in the condensed phase remain as solid products, while molten salts are produced in high temperature gasification. Low temperature gasification is advantageous over high temperature gasification because gasification at low temperatures yields improved sodium and sulphur separation. Additionally, low temperature gasification requires fewer constraints for the materials of construction because of the solid product. However, the syngas of low temperature gasification may contain larger amounts of tars, which can contaminate gas clean-up operations in addition to contaminating gas turbines upstream of the gasifier. These contamination problems can result in a loss of fuel product from the gasifier (Sricharoenchaikul 2001).

Gasification processes

The different gasification processes for kraft black liquor recovery can be roughly categorised into low and high temperature processes. Low temperature processes work below 715°C and the inorganic salts are removed as dry solids. High temperature processes operate above 900°C and an inorganic salt smelt is obtained. Trials to develop a commercially feasible process for black liquor gasification have been performed by several companies, and the history of black liquor gasification development is well described by Whitty and Baxter (2001) and Whitty and Verrill (2004). However, in 2008 only two technologies are being commercially pursued:

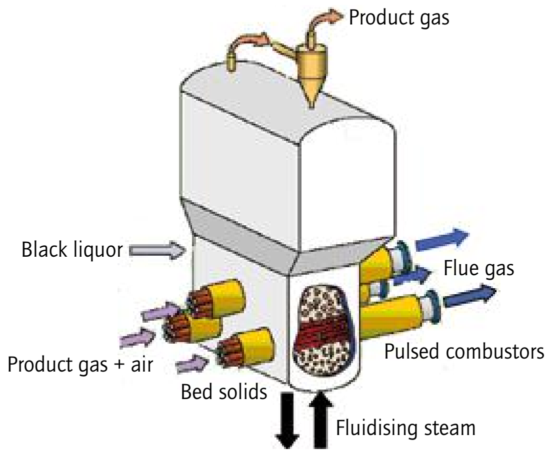
- the low temperature system developed by Manufacturing and Technology Conversion International, Inc. (MTCI) in Baltimore, MD;
- the high temperature system developed by Chemrec in Sweden.

The MTCI technology

The MTCI technology uses low-temperature gasification with a bubbling fluidised bed steam reformer (Durai-Swamy et al. 1991; Mansour et al. 1992, 1993, 1997; Rockvam 2001; Whitty and Verrill 2004) operating at 580–620°C. The bed is indirectly heated by several bundles of pulsed combustion tubes, which burn some of the gas produced. Black liquor is sprayed into the fluidised bed, where it coats the solids and is quickly dried and pyrolysed. The remaining char reacts with steam to produce a hydrogen-rich fuel gas (Rockvam 2001). Part of the bed material is continuously removed, dissolved in water and cleaned of unburned carbon to obtain green liquor.

The resultant gas is passed through a cyclone to separate the solids and then goes to a heat recovery steam generator. Part of the steam generated is used in the gasifier as both reactant and fluidising medium. The gas continues through a venturi scrubber, and a gas cooler, before removal of the hydrogen sulphide in a scrubber using some of the green liquor. The cleaned gas contains about 73% hydrogen, 14% carbon dioxide, 5% methane and 5% carbon monoxide (Rockvam 2001). The heating value of the gas is high at ~13 mJ/Nm^3. It can be burned in an auxiliary boiler, used in a fuel cell to generate electricity, or, if pressurised, it can be fired in a gas turbine. Figure 8.2 shows an MTCI steam reformer.

FIGURE 8.2 An MTCI steam reformer



Source: based on Whitty and Baxter (2001)

MTCI currently has two projects, both in mills with a sodium carbonate semi-chemical cooking process. The first project is for Georgia-Pacific Corp.'s Big Island mill in Virginia. This system is a full-scale gasifier designed to process 200 t of dry solids per day, and is fully integrated with the mill (Arosenius 2007). The second project is for the Norampac Trenton mill, Ontario, Canada, which had no chemical recovery before the steam reformer commission began in 2003 (Newport et al. 2004; Middleton 2006; Vakkilainen et al. 2008). This gasifier has a processing rate of 115 t of dry solids per day.

The Chemrec technology

Chemrec is working on both an atmospheric and a pressurised version of a high temperature downflow entrained flow reactor (Kignell 1989; Stigsson 1998; Brown and Landälv 2001; Whitty and Nilsson 2001; Whitty and Verrill 2004). The atmospheric version is mainly intended as a booster to give additional black liquor processing capacity, while the pressurised version is more advanced and could replace a recovery boiler or function as a booster.

In the atmospheric system, black liquor is fed as droplets through a burner at the top of the reactor. The droplets are partially combusted with air or oxygen at 950–1,000°C and atmospheric pressure. The heat generated sustains the gasification reactions. The salt smelt is separated from the gas, falls into a sump and dissolves to form green liquor. The gas produced passes through a cooling and scrubbing system to condense water vapour and remove hydrogen sulphide. The gas has a low heating value (~2.8 mJ/Nm^3) and is suitable for firing in an auxiliary boiler. It consists of 15–17% carbon dioxide, 10–15% hydrogen, 8–12% carbon monoxide, 0.2–1% methane and 55–65% nitrogen (Lindblom 2003). The thermal efficiency is quite low.

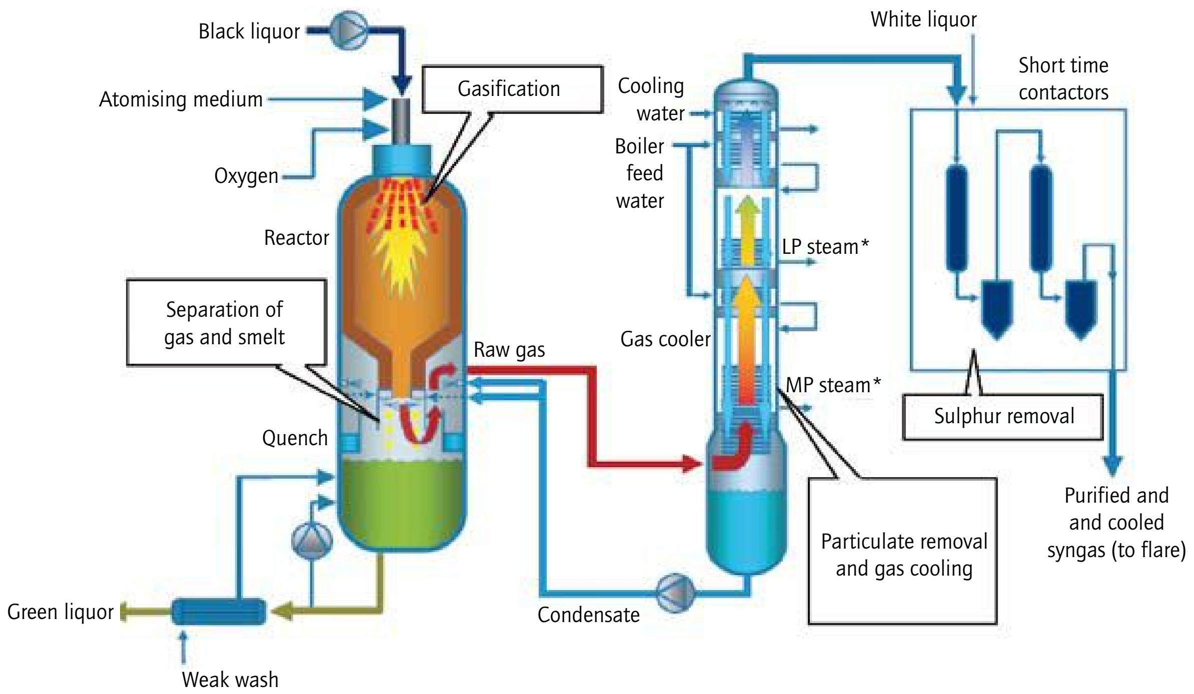
An atmospheric Chemrec Recovery Booster system with a firing rate of 270 t of dry solids per day has been in use at Weyerhaeuser's New Bern mill since 1997, although it was shut down between 2001 and 2003 because of extensive cracking in the reactor shell. During this period, the gasifier was rebuilt with a new reactor vessel as well as a modified refractory lining design, and has operated well since then (Brown et al. 2004)

The pressurised system is similar, but operates at a pressure of 30 atm. The salt smelt is separated from the gas in a quench device. The gas clean-up system is more advanced, cleaning the gas of fine particles and condensed hydrocarbons. The sulphur-rich gas stream, separated in an absorber/stripper system, can be used to prepare advanced pulping solutions. The gas produced has a higher heating value (~7.5 mJ/Nm^3) and can be, for example, fired in a gas turbine to produce electricity or used to produce biofuels such as methanol or dimethyl ether (DME). The exhaust from the turbine is passed through a heat recovery steam generator. The thermal efficiency is above 80%.

A pressurised system has been built under the Swedish national black liquor gasification programme (2004–06) in Piteå, Sweden. It is a development plant built for 20 t dry solids per day. The system includes the processes of gasification and quenching, gas cooling and gas cleaning. The gas produced contains about 41% hydrogen, 31%

carbon dioxide, 25% carbon monoxide, 2% methane and 1.4% hydrogen sulphide (Lindblom 2006). The aim of the programme is a verified process that will be ready for scale-up (by 15 times) as well as an optimised integration of the process with the pulping cycle. Figure 8.3 shows the Chemrec DP-1 plant.

FIGURE 8.3 The Chemrec DP-1 plant



Note: LP, low-pressure; MP, medium-pressure

Source: Chemrec, reproduced with permission (see www.chemrec.se/admin/UploadFile.aspx?path=/UserUploadFiles/2005%20DP-1%20brochure.pdf)

The Chemrec system for black liquor gasification with an integrated combined cycle (BLGCC system) has several advantages over recovery boilers, the most significant being a dramatically improved electricity yield. The Chemrec black liquor gasification methanol/dimethyl ether (DME) fuel (BLGMF) system combines black liquor gasification with a chemical synthesis plant for production of green automotive fuels.

The new combined pulp and chemicals production facility requires additional energy to compensate the pulp mill for the withdrawal of the new green automotive fuels. The efficiency of the Chemrec BLGMF system is very high, and the cost of these fuels from a full scale unit is competitive with petroleum-based alternatives.

The Chemrec BLGH2 system utilises the syngas from the black liquor gasifier as feedstock for novel green hydrogen production.

The cost of a full-scale pressurised black liquor gasification unit is estimated to be slightly higher than that for a new conventional recovery boiler (Warnqvist et al. 2000), although a BLGCC system does have the potential to double the amount of net electrical energy for a kraft pulp mill compared with a modern recovery boiler with a steam turbine (Axegård 1999). For a more closed system with less need of steam, this increase in electrical energy will be even higher.

Another advantage of the pressurised black liquor gasification process is the increased control of the fate of sulphur and sodium, which can be used to improve the pulp yield and quality for the mill. This control is very important for the quality of green liquor, and is quite limited with a conventional recovery boiler.

One disadvantage of gasification is that it increases the causticisation load, although black liquor gasification has a lower requirement for make-up salt cake than do recovery boilers.

Even though the pressurised black liquor gasification process does have a lot of advantages over the recovery boiler, there are still a number of uncertainties for this technology. Black liquor gasification is still a developing technology, and only small commercial atmospheric units, processing around 100–350 t of dry solids per day, have been built. Similar-sized pressurised demonstration units do not yet exist, and it will be some time before reliable large units are available. Black liquor gasification can produce more electricity (Vakkilainen et al. 2008), but current commercial atmospheric processes are not as energy efficient as the kraft recovery boiler process (Grace and Timmer 1995; McKeough 2003). The black liquor gasifier needs to operate under pressure to have an electricity advantage.

Many issues with the technology remain unresolved (Tucker 2002; Katofsky et al. 2003):

- finding materials that survive in a gasifier
- mitigating the increased causticisation load
- how to start up and shut down
- tar destruction
- alkali removal
- achieving high reliability.

The full impact of black liquor gasification on recovery cycle chemistry needs to be carefully studied with commercial units. The first large demonstration units will cost two to three times as nuch as a conventional recovery boiler, and although this will improve with time, the price will hinder the progress of black liquor gasification. A small black liquor gasifier with a commercial gas turbine of 70 MWe requires a mill size of more than 500,000 t of air-dried pulp per annum. Commercial gasifiers probably need to be more than 250 MWe in size. It is therefore expected that full sized black liquor gasifiers will be built in new greenfield mills rather than as replacement units for old recovery boilers.

Environmental impact

Whether it is conducted at high or low temperatures, black liquor gasification is still superior to the current recovery boiler combustion technology. The thermal efficiency of gasifiers is estimated to be 74%, compared with 64% in modern recovery boilers, and the IGCC power plant could potentially generate twice the electricity output of recovery boiler power plants given the same amount of fuel (Farmer and Sinquefield 2003). While the electrical production ratio of conventional recovery boiler power plants is 0.025–0.10 MWe/MWt, the IGCC power plant can produce an estimated 0.20–0.22 MWe/MWt (Sricharoenchaikul 2001; Farmer and Sinquefield 2003). This increase in electrical efficiency is significant enough to make pulp and paper mills potential exporters of renewable electric power. Alternatively, pulp mills could become manufacturers of biobased products by becoming biorefineries.

In addition, the new technology could potentially save more than 105,506 trillion joules of energy consumption annually, and within 25 years of implementation, up to 379,820 trillion joules/year of fossil fuel energy could be being saved (Larson et al. 2003).

The new technology also offers the benefits of improved pulp yields if alternative pulping chemistries are included, and reductions in solid waste discharges. Furthermore, the process is inherently safer because the gasifier does not contain a bed of char smelt (as do recovery boilers), which reduces the risk of deadly smelt-water explosions (Sricharoenchaikul 2001).

IGCC power plants will reduce waste water discharges at pulp and paper mills, even though they are unlikely to impact significantly on water quality (Larson et al. 2003). Also, IGCC power plants will reduce cooling water and make-up water discharges locally at the mill, and because the efficient gasifiers will cause grid power reductions, substantial reductions in cooling water requirements at central station power plants will also occur (Larson et al. 2003). Central station power plants have large water requirements for cooling towers in providing grid power to customers. Overall, the implementation of IGCC power plants will generate net savings in cooling water requirements and net reductions in waste water discharges.

The most significant environmental impact caused by black liquor gasification will occur in air emissions. Compared with the current recovery technology, the IGCC system could produce low emissions of many pollutants – such as sulphur dioxide, nitrogen oxide, carbon monoxide, volatile organic compounds (VOCs), particulates and total reduced sulphur (TRS) gases – and overall reductions in carbon dioxide emissions. Even with improved add-on pollution control features, the recovery boiler system still causes higher overall emissions than does the IGCC system (Larson et al. 1998, 2000, 2003).

Table 8.1 shows different emissions and their qualitative environmental impact, along with relative emission rates for both recovery boilers and gasifiers.

TABLE 8.1 Relative emission rates of different technologies

Pollutant	Relative environmental impact	Relative emission rates with controls on recovery boilers	Relative emission rates with gasification technology
Sulphur dioxide	High	Low	Very low
Nitrogen oxides	High	Medium	Very low

TABLE 8.1 Relative emission rates of different technologies (continued)

Pollutant	Relative environmental impact	Relative emission rates with controls on recovery boilers	Relative emission rates with gasification technology
Carbon monoxide	Low	Medium	Very low
VOCs	High	Low	Very low
Particulates	High	Low–medium	Very low
Methane	Low–medium	Low	Very low
Hazardous air pollutants	Medium–high	Low	Very low
TRS	Low	Low	Very low
Waste water	Medium–high	Low	Very low–low
Solids	Very low	Low	Low

Source: based on Larson (2003)

Because the biomass sources at pulp and paper mills are sustainably grown, a black liquor gasification based IGCC plant or biorefinery would transfer smaller amounts of carbon dioxide to the atmosphere than would using fossil fuels. The vast majority of the carbon dioxide emitted would be captured from the atmosphere for photosynthesis and used for replacement biomass growth, producing oxygen (Larson et al. 2003). According to Larson, if the pulp and paper industry converts the 1.6 quads of total biomass energy to electricity, 130 billion kWh/year of electricity could be generated. This electricity generation in a black liquor gasification-based IGCC plant could displace net carbon dioxide emissions by 35 million tons of carbon per year within 25 years of implementation. Within the same time-span, the IGCC plant could displace 160,000 net tons of sulphur dioxide, since most of the sulphur dioxide produced in the process would be absorbed during hydrogen sulphide recovery. Moreover, the overall reduction of TRS gases (i.e. hydrogen sulphide) using gasification technology will also reduce odour, which will improve public acceptance of pulp and paper mills, particularly in populated areas.

Clearly, black liquor gasification technology offers tremendous potential to make an impact on the environment. However, before it can totally replace the current recovery boiler technology, some work must be done to make it more economically attractive. One major area that requires attention is the causticisation process. Gasification technology can cause significant increases in capacity for the lime cycle, requiring significant increases in fossil fuel consumption, and to improve economic viability, alternative causticisation technologies must be considered.

Non-conventional causticisation technologies

The main idea in non-conventional causticisation processes is to add an amphoteric metal oxide or salt to convert molten sodium carbonate directly to $Na_2Me_xO_{y+1}$ and carbon dioxide in the furnace. The resulting smelt will yield the caustic directly by dissolving it in water (Nohlgren 2004).

The non-conventional causticisation technologies can be categorised by the solubility of the reaction product. In direct causticising, the reaction product is insoluble in caustic solution and is separated from the liquor. Titanate is considered to be the most promising agent for direct causticisation in kraft pulping (Nohlgren 2002; Nohlgren et al. 2003a, 2003b; Nohlgren and Sinquefield 2004).

In autocausticisation, the reaction product is soluble. Hence, the decarbonising agent follows the entire pulping and recovery cycle and changes the characteristics of the white liquor. Higher ion strength may be a disadvantage in both digestion and washing of pulp. Also, the deadload decreases the overall energy efficiency (Richards et al. 2002). Therefore, only partial autocausticisation is interesting, which is when an autocausticisation system is added to the conventional process. This could be attractive when the need for causticisation exceeds the capacity of the lime furnace, which may happen, for example, when a recovery boiler is replaced by a gasifier. Proposed oxides for autocausticisation in the literature are phosphorous oxide, silicon dioxide, aluminium oxide and boric oxide. Borates are the most promising ones for kraft pulping (Nohlgren 2004).

Partial borate autocausticisation

A phase diagram of the sodium oxide–boric oxide system shows that sodium oxide and boric oxide form 12 different sodium compounds with different sodium:boron ratios (Milman and Bouaziz 1968). This implies a high affinity of borates to sodium compounds. Sodium borates relevant to autocausticisation are listed in Table 8.2.

TABLE 8.2 Sodium borates relevant to borate autocausticisation

Compound	Na:B molar ratio
$Na_2B_4O_7$ (or $Na_2O.2B_2O_3$)	1:2
$NaBO_2$ (or $Na_2O.B_2O_3$)	1:1
$Na_6B_4O_9$ (or $3Na_2O.2B_2O_3$)	3:2
$Na_4B_2O_5$ (or $2Na_2O.B_2O_3$)	2:1
$Na_{10}B_4O_{11}$ (or $5Na_2O.2B_2O_3$)	5:2
Na_3BO_3 (or $3Na_2O.B_2O_3$)	3:1

Source: based on data from Nohlgren (2004) and Tran et al. (1999)

Janson was the first to suggest the use of sodium borates for causticisation in the late 1970s (Janson 1977, 1979a, 1979b), proposing that sodium metaborate reacts with sodium carbonate in the smelt to form disodium borate. In a second reaction step, the disodium borate can be hydrolysed in water to regenerate sodium metaborate and form sodium hydroxide in water solution (Reactions 8.1 and 8.2).

$$2NaBO_2 + Na_2CO_3 \rightarrow Na_4B_2O_5 + CO_2 \text{ (furnace)} \qquad \text{[Reaction 8.1]}$$

$$Na_4B_2O_5 + H_2O \rightarrow 2NaOH + 2NaBO_2 \text{ (dissolving tank)} \qquad \text{[Reaction 8.2]}$$

It can be seen that two moles of sodium metaborate are needed for every one of sodium carbonate to be causticised. Janson found that Reaction 8.1 is severely hindered if the molar ratio of the reactants is higher than 1.5:1, and will not occur at molar ratios higher than 3:1. Partial autocausticisation is likely to have a much higher ratio than that (Tran et al. 1999). Janson stated that sodium sulphide did not affect the autocausticisation reactions and that the presence of borates in molten carbonate reduces loss of sodium from smelt as well as lowering the melting point of the smelt.

Tran et al. (1999) determined that the smelt reaction could go one step further (temperature >900°C) (Reaction 8.3). The same conclusion was made at the Institute of Paper Chemistry in Appleton, WI, in 1987.

$NaBO_2$ (l) + Na_2CO_3 (l) $\leftrightarrow$ Na_3BO_3 (l) + CO_2 (g) [Reaction 8.3]

Tran et al. (1999) also found that the reaction could take place at any sodium:boron ratio, although it depends on the temperature and the pressure of carbon dioxide. The contradiction in Janson's conclusions is, according to Tran et al., caused by Janson's larger sample size and lack of purge to remove formed carbon dioxide, which hinders Reaction 8.3. Also Janson adjusted the sodium:boron molar ratio using an aqueous solution of sodium hydroxide, which is not realistic because there is little or no sodium hydroxide in smelt.

In water, the sodium orthoborate hydrolyses into sodium hydroxide and sodium metaborate (temperature <100°C) (Reaction 8.4):

Na_3BO_3 (s) + H_2O (l) $\rightarrow$ 2NaOH (aq) + $NaBO_2$ (aq) [Reaction 8.4]

According to the theory of Tran et al. (1999), borate autocausticisation is possible since the reaction occurs at the ratio of sodium:boron in the smelt (much higher than 3). In addition, only one mole of sodium metaborate is needed for every mole of sodium carbonate to be converted. Therefore, only half the amount of borate is needed compared with the reaction proposed by Janson (Reaction 8.2). This implies half as much sodium metaborate and a reduction of the deadload effects caused by the borate addition in the cooking liquors.

Multiphase chemical equilibrium calculations of the furnace process by Hupa et al. (2002) also show that the addition of boron to the liquor will change the smelt bed composition significantly under equilibrium conditions and result in formation of sodium orthoborate, which will be completely dissolved in the molten bed at furnace temperatures.

The effect of the presence of carbon dioxide on Reaction 8.3 is not a problem in a recovery boiler since the carbon dioxide pressure is very low in the smelt. Solid carbon is present in the smelt at high temperatures, and it consumes the carbon dioxide, forming carbon monoxide (Reaction 8.5):

C (s) + CO_2 (g) $\leftrightarrow$ 2CO (g) [Reaction 8.5]

Borax can be added to the system instead of sodium metaborate. The borax reacts with sodium carbonate to form sodium metaborate (Reaction 8.6), which then can react further to sodium orthoborate as described above (Tran et al. 2001). Borax is cheaper than sodium perborate (Na_2BO_3) and is therefore the make-up chemical most likely to be used in a commercial system (Tran et al. 1999):

$$Na_2B_4O_7 + Na_2CO_3 \leftrightarrow 4NaBO_2 + CO_2 \qquad \text{[Reaction 8.6]}$$

Sodium orthoborate can then be hydrolysed in water to sodium metaborate, which is still the main sodium borate compound in the solution (Tran et al. 1999).

The black liquor evaporator efficiency is affected by the boiling point rise of added sodium metaborate (aq). Therefore, Bujanovic and Cameron (2001) have studied the effect of sodium metaborate on the boiling point rise of black liquor. They found the effect to be low. At 120% autocausticisation to a 60% solids liquor, the boiling point rise was about 5K, and at lower degrees of autocausticisation the boiling point rise would also be smaller. At 30% autocausticisation, the boiling point rise was about 0.7 K.

Sodium borates can retard cellulose peeling reactions (Timelln 1965), and results from laboratory studies suggest that there can be an increase in pulp yield of 1–2% when sodium metaborate is added to the cooking liquor (Genco et al. 2002; Bujanovic et al. 2003). Furthermore, work by Econotech Services, Delta, Canada, suggests that the use of borate may give better pulp quality and less shrinking during bleaching (Tran et al. 1999).

Numerous mill trials with partial borate autocausticisation have been conducted and the problems encountered have been resolved. The technology is now being used at several mills in Sweden, Brazil, Indonesia and the US.

For a greenfield kraft pulp mill, with proper equipment design and operation, the technology has the potential to eliminate completely the causticisation plant and lime kiln, making the kraft process much simpler (Hoddenbagh et al. 2001; Kochesfahani and Bair 2002). Six mill trials are described by Kochesfahani and Bair (2002), who carried out short-term trials to evaluate the effect of the technology on specific parts of the mill, and long-term trials to demonstrate the overall effects of the technology on the mill operations. At autocausticisation levels up to 25%, no undesired effects could be observed on digesters, pulp quality, brownstock washing, black liquor evaporation, lime recausticisation or kiln operations.

The most apparent effect of autocausticisation on the liquor cycle is the increase in total inorganic salts in the system. This leads to an increase in the throughput of solids for evaporators, concentrators and recovery boilers. Because of the endothermic nature of the autocausticisation reaction, the black liquor heating value decreases. The evaporation load is not affected, however, and so the temperature may decrease in the recovery boiler. Even though Kochesfahani and Bair (2002) report the conversion of autocausticisation to be sensitive to operation conditions, especially temperature, they claim that the overall impacts on the recovery boiler are manageable.

One mill trial with partial borate autocausticisation was carried out in Sweden. It started in 2002 and lasted for 15 months. The autocausticisation level was typically 9–11%. The technology proved successful, with little effect on mill operations and without any negative effects on pulp quality or properties. The pulp yield was enhanced during the trial, which might be because of the borate addition, but this is not yet verified. No evidence was observed of corrosion or cracking in any equipment (Björk et al. 2004).

Another mill trial in North America also showed that the technology of partial autocausticisation worked well, with few operational problems, even though fouling in the evaporators was detected (Hoddenbagh et al. 2001). This was explained by an increase in pH in the evaporator feed. Borates are naturally occurring minerals in soil (10–20 ppm of boron), rocks (5–100 ppm of boron) and, at low concentrations, in inland freshwater (typically <1 ppm). The Swedish limit for boron in effluent to water recipient is 10 ppm (Timelln 1965). Kochesfahani and Bair (2002) and Björk et al. (2004) all reported the effluent of boron (from the treatment plant) to be below this value.

Borate autocausticisation is expected to have no negative effect on pulp properties, equipment corrosion, digester operations, pulp washing, black liquor evaporation, lime recausticisation, and lime kiln operations (Kochesfahani et al. 2006). The major impact is a higher inorganic solids load throughout the liquor cycle and a potential decrease in black liquor heating values. Some adjustments in the recovery boiler operating conditions may also be required.

The major benefit of partial borate autocausticisation results from a decrease in lime usage per ton of pulp, which leads to:

- increased throughput
- savings in lime purchase or lime kiln energy consumption
- improved lime mud separation and washing efficiency
- reduced mud disposal.

Borate autocausticisation with black liquor gasification

Research has been undertaken, on a conceptual level, into the potential synergy between black liquor gasification and borate autocausticisation (Leduc et al. 2004; Nohlgren and Sinquefield 2007). Experimental and theoretical results were used to establish a model for the combined gasification-autocausticisation process, with focus on a Chemrec-type booster gasifier with partial autocausticisation. Investigation was carried out into the chemical recovery aspects and energy consequences. According to this, it seems that autocausticisation does occur in an atmospheric gasifier.

The results were obtained with a thermodynamic equilibrium calculation where reaction restraints, i.e. reaction kinetics, were not considered. In a gasifier, there is no char bed where the solid carbon reacts with the present carbon dioxide, keeping the carbon dioxide pressure low. The gas phase characteristics are therefore important for the equilibrium of the autocausticisation reactions. Reaction 8.6 is highly reversible (Yusuf and Cameron 2001; Lindberg et al. 2005), and consequently, especially in a pressurised gasifier, the high partial pressure of carbon dioxide may hinder the borate autocausticisation. This is, however, still to be investigated.

Recently, research was carried out by Sinquefield et al. (2007) in which three in situ causticisation processes (titanate, manganate and borate) were evaluated for both the high and low temperature gasification of black liquor. Both the borate and titanate options were found to be effective auto- and direct causticisation agents. The two cases were evaluated for integration into a gasification-based recovery island using the Larson black liquor gasification cost-benefit study (Larson et al. 2003) as a reference case for economic forecasting. Although using the titanate direct causticisation process yielded a net present value of €19.5 million, using the existing lime cycle plus borate autocausticisation for extra capacity yielded a net present value of €12.48 million.

9

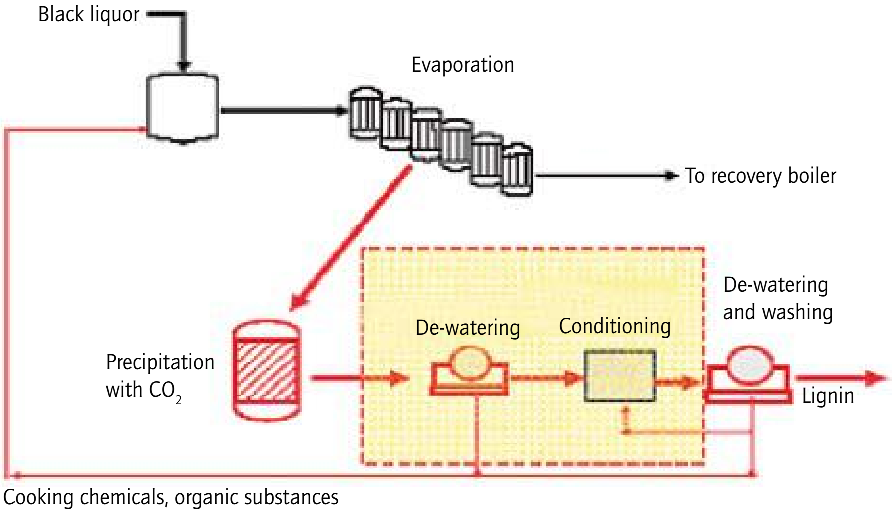
New value streams (fuels and chemicals) from residuals and spent pulping liquors

Removal of lignin from black liquor

Extensive research is under way to find new areas of usage for by-products from kraft pulping. The term pulp mill biorefinery is widely used in the US, Sweden and elsewhere. The pulp mill biorefinery can help pulp and paper mills use by-products and residual products of the pulp and papermaking process to create additional high value revenue streams. STFI-Packforsk has been active in this area since 1996. Activities include separation and purification of lignin and xylan from black liquor, xylan and glucomannan from wood chips/forestry residuals, and extractives from bark (Axegård 2006a, 2006b, 2007a, 2007b).

A new and cost-efficient process for extracting high quality lignin from kraft black liquor has been developed. This process is named LignoBoost (Axegård 2006a, 2007a, 2007b; Wallmo and Theliander 2007; Frisell 2008). Lignin is precipitated with carbon dioxide, de-watered in one stage and de-watered/washed in a second washing stage (Figure 9.1).

FIGURE 9.1 LignoBoost, a two-stage washing/de-watering process for lignin precipitated from black liquor



Source: reproduced with permission from Axegård (2007b)

Washing is done counter-currently. This eliminates the risk of lignin dissolution, which is the main drawback in the conventional one-stage process. Compared with that process, water use is lower, the lignin is cleaner with respect to ash and sodium, and the capacity is significantly higher. The lignin has very good properties, including 65–70% dry solids content, ash content of 0.1–0.5%, sodium content of 0.01–0.4%, and a heating value of 26 GJ/t. It can be used as biofuel, replacing coal and oil in, for example, the generation of power by pulp mills or in lime kilns.

LignoBoost gives customers the opportunity to increase the capacity of a pulp mill and turns pulp mills into significant energy suppliers. At the same time, the extracted lignin is also of interest to other process industries as a raw material for plastics, coal fibres and chemicals (Axegård 2007a, 2007b; Neumann 2008).

The four key operations in the LignoBoost process are:

- precipitation
- de-watering
- resuspension
- final washing.

In precipitation, the black liquor is acidified by absorption of black liquor and solid lignin precipitates. During the de-watering operation, the solid lignin is filtered off and de-watered by gas displacement. The resuspending phase involves the resuspension of the solid lignin and the reduction of the pH. In the final washing, the solid lignin is filtered off, washed by means of displacement washing, and finally de-watered by gas displacement.

The LignoBoost process enables the fast production of high quality lignin at low cost. Low filtration resistances can be maintained throughout the process, and an even lignin filter cake that is easy to wash and finally de-water is formed in the second filtration/washing stage. Using the novel process, the specific filtration resistance is one to two orders of magnitude lower than when separation and washing are done in a single filtration step. The separation of the pH, and the ion strength reduction into two different steps results in the lignin becoming much more stable in all process stages, with only a small amount of lignin dissolved during the final displacement washing.

The LignoBoost technology has proven its technical maturity over several years of research and laboratory testing, as well as during operation in an industrial-sized demonstration plant integrated into the pulping process at the unbleached kraft pulp mill of Nordic Paper Bäckhammar, Kristinehamn, Sweden, a subsidiary of STFI-Packforsk, which, along with Fortum Värme, Södra, Stora Enso and the Swedish Energy Agency have formed a subsidiary company called Demo AB to back the project (Anon 2007; Lennholm 2007).

The demonstration plant, which will afterwards remain in the possession of STFI-Packforsk, is expected to achieve an annual lignin production of about 4,000 t. Nearly all the lignin produced will be used in different incinerators, such as lime kilns, bark boilers, and Fortum Värme's heat and power plant in Stockholm. For the production of lignin, acid precipitation was selected as the most promising route, whereas for the production of xylan, membrane fractionation was preferred. These two methods can be successfully combined.

Lignins are used as binders, dispersants, emulsifiers and sequestrants. It has been proposed to isolate phenols from lignin and to produce carbon fibres. The LignoBoost technology also offers new opportunities for further use of a kraft pulp mill as a biorefinery, such as in xylan removal from black liquor, biomass gasification, and ethanol fermentation (Axegård 2007a, 2007b; Rodden 2007)

On 27 May 2008, Metso and STFI-Packforsk AB signed a purchase agreement regarding the shares of LignoBoost AB, the Swedish research company behind the LignoBoost technology. The transaction included all the intellectual property rights, as well as the LignoBoost brand and its related knowledge base. In addition, Metso and STFI-Packforsk signed a research and development agreement related to the LignoBoost technology. Both agreements came into force with immediate effect. The acquired company will become part of Metso Power, itself a subsidiary of Metso Paper's business area. The acquisition supports Metso's profitable growth strategy, and opens up an interesting biofuel business opportunity within the pulping processes. Metso Power sees great value in getting a process with such high future expectations.

Recently, Södra and STFI-Packforsk have demonstrated the use of lignin for up to 100% replacement of fossil fuel in the lime kiln of the pulp mill.

Future possibilities

Lignin removal with the LignoBoost process offers new opportunities for further conversion of kraft pulp mills to biorefineries. Examples are:

- removal of hemicellulose from black liquor
- ethanol fermentation
- biomass gasification (Axegård 2007a, 2007b; Axegård et al. 2007).

Hemicellulose can be separated from black liquor by membrane separation. It can be converted to xylose and other sugars, depending on the composition of the hemicelluloses in the biomass, and further converted to furfural, xylitol, sorbitol and bifunctional organic molecules. A mill trial was carried out in the future resource-adapted pulp mill (FRAM), a research programme in Sweden in 2003–04 that brought together partners from government, the universities and industry, co-ordinated by STFI-Packforsk, using a ceramic membrane in the black liquor in a continuous two-vessel digester system (Öhman 2006). The lignin separation was performed at a temperature of 145–155°C at full digester pressure without adjustment of the pH. Ceramic membranes with cut-offs at 5–15 kDa were used. The retentate is a mixture of lignin and xylan and further fractionation is needed.

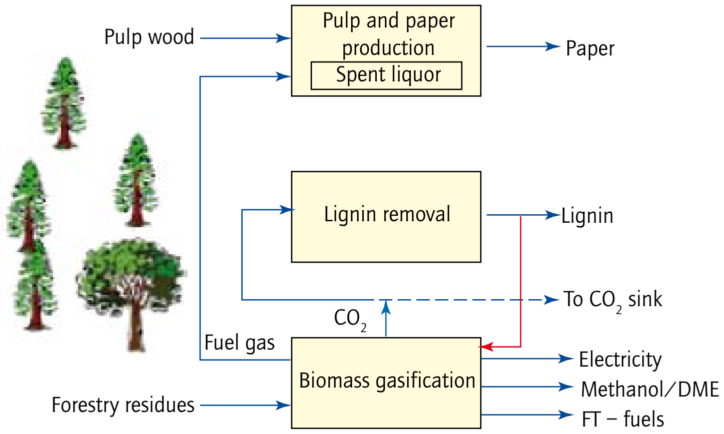
Another option is to apply membrane separation immediately before or after the LignoBoost process. In the former case, the performance of LingoBoost will be improved and the lignin will be purer. In the latter, the retentate will be relatively pure xylan as the high molecular weight lignin is precipitated in LignoBoost.

Precipitation of lignin requires carbon dioxide, and the bulk of the variable cost is due to carbon dioxide if the commercial product is used. It may be possible to use carbon dioxide from the lime kiln, but gas cleaning is a challenge. Carbon dioxide from ethanol fermentation yields about 1 t of pure carbon dioxide per tonne of ethanol produced. The current size of ethanol plants is too small to justify recovery of the carbon dioxide produced, but by combining lignin production with ethanol production, the carbon dioxide can be efficiently utilised and the economic performance significantly improved.

The amount of lignin (and xylan) that can be removed from black liquor depends mainly on the status of the recovery boiler. At a certain value of heat in the fired black liquor, performance deteriorates. In many mills, this critical level is when 10–30% of the lignin has been removed. One interesting way to handle this, is to add fuel gas from gasified biomass to compensate for the lost heat value (Figure 9.2).

The carbon dioxide produced can also be used for lignin precipitation (Axegård 2006b). The ultimate development would be removal of all the valuable organic components such as lignin, xylan and sugar acids from the black liquor, and instead to obtain all the fuel needed from gasified biomass, such as forestry residuals. Such an approach would make possible the complete removal of organic components in black liquor.

FIGURE 9.2 Integration opportunities between LignoBoost and gasification of forestry residues proposed by STFI-Packforsk and VTT



Note: DME, dimethyl ether fuel; FT, Fischer–Tropsch

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The traditional recovery boiler might also be replaced with less capital-demanding and less complicated techniques. STFI-Packforsk, VTT and selected partners have currently submitted proposals based on these ideas to a large collaborative EU-financed research and technological development project under the umbrella of the Seventh Research Framework Programme.

Other products

Extractives such as rosin and fatty acids are sometimes removed from the spent pulping liquor and processed into crude tall oil (CTO). In Canada, most of this is currently incinerated as fuel in the lime kilns of pulp mills, in place of fossil fuel. In the south-eastern US, where the extractive content of the wood is much higher, tall oil plants fractionate the CTO into value-added components.

There have also been processes proposed to convert both the fatty and rosin acid components of the CTO into green diesel fuel. Fatty acids can be directly esterified by alcohols into diesel fuel, while the rosin acids can be converted by the Supercetane hydrogenation process developed by the Canmet Energy Technology Centre, Natural Resources Canada. Turpentine recovered from process condensates in Canadian mills is generally incinerated as fuel in one of the on-site boilers. Processing it into consumer-grade products is possible but, in many cases, it is more valuable as a fuel.

The average 1,000 t/d softwood kraft mill has approximately 7 t/d of methanol in its foul condensate streams. Most mills use steam strippers to concentrate the methanol to about half its volume before incineration. Some mills use air strippers, which do not remove methanol effectively, or simply send foul condensates to effluent treatment where the methanol is consumed by biological activity. It is possible to purify this methanol for alternative uses, either on-site or by a purchaser. One pilot project has used the catalytic conversion process for converting the methanol to formaldehyde.

The waste organics sent to effluent treatment from pulp and paper mills are very different from municipal organic wastes, which have a very high carbon:nitrogen ratio. Certain bacteria in activated sludge treatment systems under normal operating conditions accumulate 3-hydroxybutyric acid, a potential building block for biopolymers. Extraction of 3-hydroxybutyric acid remains the significant hurdle to this process. Pulp and paper waste treatment sludge is typically buried in landfill, incinerated, or spread on land as a nutrient enhancer. Research is ongoing into how to improve the performance of microbes at converting the nutrients in effluents to 3-hydroxybutyric acid and other fermentation products.

In an optimised forest biorefinery, part of the hemicellulose that is now burned would be used to create new, more valuable products. A portion of hemicellulose can be extracted from wood chips prior to pulping using hot water extraction in low-pressure digesters (Thorp and Raymond 2004). Some acetic acid is formed during the extraction process, and this must be separated from the sugar solution. The sugars can then be fermented to ethanol or other high-value chemicals, creating an additional product stream. Removing part of the hemicellulose prior to the digester will increase the throughput potential of the pulping process. However, utilising some of the hemicellulose as a sugar feedstock reduces the energy content of the pulping by-product black liquor, which is an important renewable energy source for kraft pulp mills.

To optimise fully the forest biorefinery, the economic and energy implications of diverting a proportion of hemicellulose to other products will need to be balanced. The loss of this energy source can be offset by improved energy efficiency in the pulp and paper manufacturing process. Ultimately, forest biorefineries could potentially use a combination of new technologies that result in more complete, energy efficient and cost-effective use of the wood feedstock.

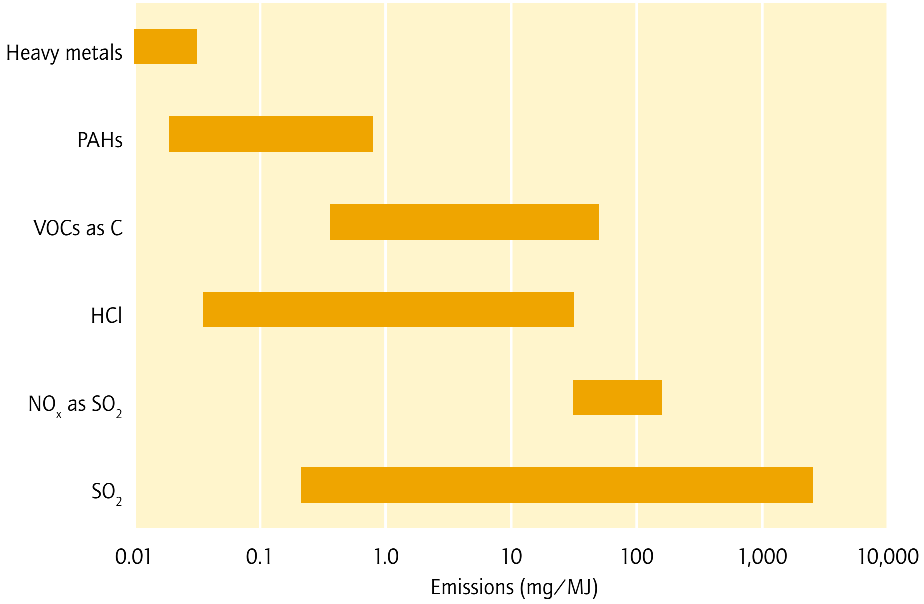
Environmental challenges

10

Air emissions

Black liquor contains a larger amount of sulphur and alkali metal salts than do more conventional fuels, but the amount of nitrogen and heavy metals is less. Traditionally, the emission problems associated with kraft recovery boilers have been total reduced sulphur gases (TRS) and particulate emissions, but with the implementation of more stringent air emissions regulations, other species must now be controlled as well. These include sulphur dioxide, nitrogen oxides, hydrochloric acid, volatile organic compounds (VOCs), heavy metals, and polycyclic aromatic hydrocarbons (PAHs). Typical emission levels of these substances are shown in Figure 10.1.

FIGURE 10.1 Typical emissions for recovery boilers



Note: C, carbon; HCl, hydrochloric acid; NO_x, nitrogen oxides, encompassing nitric oxide and nitrogen dioxide; SO_2, sulphur dioxide

Source: reproduced from Lisa (1997), with permission from TAPPI Press

Particulate emissions are mostly from the recovery boiler, the smelt dissolving tank and the lime kiln (NCASI 1993a, 1993b; Lisa 1997). Modern recovery boilers are equipped with sectionalised, dry-bottomed electrostatic precipitators that operate at high efficiencies (>99.5%). Smelt dissolving tank vent stacks are equipped with high efficiency wet scrubbers to control particulate emissions. Lime kilns are equipped with either wet scrubbers or precipitators to control lime dust and sodium fume emissions. Although wet scrubbers have the ability to control sulphur dioxide emissions, almost all new lime kilns have electrostatic precipitators to meet stringent particulate control requirements.

TRS are the main cause of kraft odour and have long been subject to control measures. TRS emissions from modern recovery boilers are kept well below 5 ppm. Another main source of TRS emissions are non-condensable gas (NCG) streams from the digesters and evaporators. They are normally collected and incinerated, either in bark boilers, dedicated incinerators, lime kilns, or recovery boilers.

Artificial neural network modelling was used to lower TRS emissions and other sulphur losses from a mill (Smith et al. 2000). The model was developed to optimise the boiler operating parameters so as to reduce TRS and sulphur dioxide emissions from the stack without compromising overall boiler productivity. The procedure for the mathematical modelling of TRS gaseous emissions from a reactive recovery boiler in a kraft pulp mill was developed by Quintana Moreira (2004).

There has been an increased trend towards burning NCGs in recovery boilers (Villarroel 1998), which is sufficient from both process and capacity standpoints and has the advantage of a built-in means for capturing the sulphur.

Sulphur dioxide emissions also come from many sources. Recovery boiler sulphur dioxide emissions depend strongly on boiler operating conditions. The sulphur dioxide concentration in the flue gas can approach zero if the temperature in the lower furnace is sufficiently high. Sulphur dioxide emissions from the lime kiln are dependent on the sulphur content of the fuel being burned, and on whether or not the calciner is being used for NCG incineration. If wet scrubbers are used for capturing lime dust, some sulphur dioxide recovery will also occur there.

The emission of sulphur dioxide from bark and power boilers depends on the sulphur content of the fuel used and on the efficiency of any wet scrubbers that might be employed. Sulphur dioxide emissions from NCG incinerators depend on scrubber efficiency.

Nitrogen oxide emissions from recovery boilers are relatively low, typically 50–100 ppm. Most of these nitrogen oxides come from the small amount of nitrogen compounds in the black liquor solids burned in the boiler (DeMartini et al. 2004; Saviharju and Aho 2006). It is not obvious if nitrogen oxide emissions can be controlled through changes in boiler operating practices. Nitrogen oxide emissions from lime kilns have recently attracted attention, particularly those from kilns that burn NCGs. Combustion control in modern recovery boilers is quite good, and carbon monoxide concentrations during normal operation are typically only a few hundred parts per million. However, carbon monoxide concentrations can be significantly higher during upset operation.

If sulphur dioxide concentrations are high and there is sufficient chloride in the black liquor, hydrochloric acid is emitted from the recovery boiler as a result of sulphation of alkali chlorides (sodium chloride and potassium chloride). Reductions in hydrochloric acid emissions can be obtained by operating the recovery boiler with high bed temperatures to minimise sulphur dioxide concentrations in the flue gas, and by purging chloride from the system.

Small amounts of ammonia and ammonium salts have been found in the dissolving tank vent (Tarpey et al. 1996). This comes from organic nitrogen in the wood that is dissolved during pulping, and ends up in the smelt stream leaving the recovery boiler. The nature of this problem and how to minimise it is now beginning to be understood

(Saviharju and Aho 2006). VOCs are formed during pulping and are present in contaminated condensates. They are stripped out using condensate strippers, and dealt with as a part of NCG and stripper-off gas incineration. They can also be incinerated as liquids. These substances also form during black liquor oxidation in older recovery boilers and can be stripped from the black liquor in direct-contact evaporators. The need to control these emissions may finally result in the total elimination of the use of direct-contact evaporators.

Mill closure

As the trend towards minimising the environmental impact of industries continues, pulp and paper mills are looking at ways of further reducing their effluent by developing closed cycles and chemical recovery (Ryham and Linderberg 1994). Numerous significant technologies have been developed and implemented in the progress towards pulp mill process closure (Reeve et al. 1983; Ricketts 1994; Wiseman and Ogden 1996; Bajpai and Bajpai 1999; Hamm and Gottsching 2002; Stratton et al. 2003; Aukia 2005; Hamm and Schabel 2006). Much of this new technology has focused on lowering chlorinated organic matter levels in bleached kraft mill effluents. Process closure methods have included:

- dry de-barking
- effective liquor spill control
- closed screening and washing
- condensate stripping.

Several new mills have been built that incorporate state-of-the-art process designs and equipment. Bleach plants have replaced chlorine with chlorine dioxide, oxygen, peroxide, ozone and other agents, and a few mills have totally chlorine-free bleach plants. A renewed interest in closed cycle bleaching has seen several mills implementing recovery of alkaline filtrates using post-oxygen or brownstock washers. A few have recovered acidic bleaching filtrates, while two linerboard mills have small bleach plants from which all of the filtrates are recycled. Many companies have reconsidered the role of process closure in minimising effluent impacts, and for many the optimum solution has been a high degree of closure with external biological treatment of the remaining process effluent (Bajpai and Bajpai 1999). Zero effluent bleached chemi-thermomechanical pulp mills have also been built.

Mill closure is aimed at reducing the overall use of water and the requirement for chemical make-up. Instead of fresh water, steam condensate is used where possible. However, condensates need to be cleaned in order to make them suitable for reuse. The organic substances present in contaminated condensates will go to parts of the system where they were not previously present, which can have unfavourable effects on the process.

The reduction in chemical make-up requirement does not necessarily result in an economic benefit, as it might force a change from inexpensive chemicals to more expensive ones. Kraft mills dispose of spent chemicals from chlorine dioxide generators by introducing them into the recovery system as make-up chemicals. A trend towards a reduced need for sulphur make-up has forced changes in chlorine dioxide generation technology to produce an effluent with less sulphur. This can also affect on-site acidulation of tall oil soap, since sulphuric acid is normally used for this purpose, but this is not a problem for hardwood mills where production of tall oil soap is minimal.

Non-process elements are present in the process cycle, entering with the wood, chemical make-up, process water from the bleach plant, and any waste streams that are disposed of within the process. These elements are of the following types:

- highly soluble in alkali, can build up without limit (potassium and chloride);
- partially soluble in alkali, can build up to significant levels before being naturally purged by precipitation (aluminium, silica, phosphorous);
- highly insoluble in alkali, are removed with green liquor dregs and therefore do not build up (calcium, magnesium, barium, iron).

The alkali insoluble non-process elements such as calcium and magnesium cause scaling problems in digesters and evaporators upstream of the green liquor dregs separator, but they do not accumulate in the cycle. Potassium and chlorine lower the melting points of the ash formed in the recovery boiler, and so can have a large effect on the recovery operation. Potassium is an active alkali, like sodium, and potassium hydroxide and potassium sulphide are effective pulping chemicals. In tightly closed mills, potassium can accumulate to more than 10% of the total alkali, particularly when hardwood is pulped.

A high level of potassium in the liquor intensifies superheater corrosion and increases fouling in the recovery boiler, particularly when it is also accompanied by a high chlorine or chloride level (Tran 1997). Chloride can have a major impact on recovery boiler fouling and plugging, and has been implicated in some corrosion problems around the system. As mill closures increase, deliberate purges of chlorine and potassium from the recovery cycle may be required.

Aluminium and silica form scales in the evaporators that are glassy and difficult to remove. To control this problem, aluminium inputs to the cycle should be minimised. Aluminium can also be removed from the cycle with the green liquor dregs, by co-precipitating it with magnesium. High levels of silica cause evaporator scaling and lime mud filtering problems. Phosphorous has a tendency to build up in the lime cycle and results in poor quality lime and operational problems in the lime kiln.

In recent years, there have been efforts to use the recovery system for disposal of biological sludge from the waste treatment system (La Fond 1998). There is some concern about this practice as it increases the load on process equipment, and is also a potential source of non-process elements. Sludges that contain significant levels of aluminium are especially troublesome.

Chemical recovery in papermaking

11

There is very little scope for chemical recovery in papermaking and converting sections, but some progress is being made in the recovery of filler, coating colour and pigments.

Ahlstrom, which is now a part of Metso, has developed a technology called FilRec for pigment recovery, in which the pigments of the hydrocyclone system reject are recovered for use as a raw material in paper production. The ash content of this reject can be as high as 80–85%. The reject of the hydrocyclone system includes a combination of fibres, fillers, pigments, latex and other additives originating from coating that cannot be reused directly, mainly because of their particle shape and size (Koepenick 1997).

This process has four stages. The feed flow of FilRec is typically the reject of the final stage of the short circulation hydrocyclone. First, the fractionation splits the feed flow into coarse and fine fractions with a screen, which has a slot size of 200 µm. The coarse fraction consists of stiff fibres and coarse solids, while the fine fractions contain mainly pigment flakes, filler and water. Secondly, the filler recovery stage classifies the solids according to particle size with an Ahlcleaner RB 77 Eliminator. The accept includes fine filler, as the particle size is mainly below 10 µm, which is returned to the paper production as recovered filler.

Pigment flakes and coarse filler are concentrated to 20–50% solid content and directed to the mineral dispersion stage, during which they are subject to turbulent shear forces. These forces, together with a crushing effect, break down the coarse particles. The pigment flakes and coarse filler particles are circulated in the dispersion loop an average of three to six times, until they are small enough to be accepted as fillers. However, a small outlet flow from the dispersion loop is taken with the coarse fraction from the screen to be classified in the reject stage of the Ahlcleaner RB 77, from where reusable fibres and fine fillers are returned to the paper production. Recovery of filler by FilRec is said not to have any effect on paper machine runnability or paper quality (Koepenick 1997).

Caledonian Paper, in Irvine, UK, started using the recovery of pigments system in the effluent treatment process in 1995 (Frette 1995) in its mill producing 200,000 t/a of low-weight coated paper. The recovery process separates paper clay from latex. The paper clay is returned to the coated broke line, and the latex is sent to the fluidised bed boiler, where it is burned with bark and fibrous material from the final stage of effluent treatment and thus produces steam for the mill. The boiler consumes the solid waste of the mill and decreases the need for solids disposal in a landfill; only ash is removed from the mill.

Some 10,000 m^3/d of liquid effluent is generated, containing 13–15 t/d of suspended solids. About half of the total effluent has a low suspended solids content (e.g. the clear filtrate from the paper machine), and this is sent directly to the local sewage pumping station for disposal at sea. The solids-bearing effluent is processed in the new effluent treatment plant, where first the mixture of water, china clay and latex is piped to a series of settling tanks for chemical pretreatment, and then it goes on to a lamella clarifier. Here it is mechanically separated, and the clay is precipitated out of the solution on to a series of sloping metal plates before being recovered from the bottom of the lamella.

The advantages of the recovery process for Caledonian Paper are the savings in the consumption of china clay (approximately 1,800 t/a), and the costs of transferring solid waste to the landfill (Frette 1995).

Metso Paper has developed an innovative filler recovery concept to help producers of coated paper and board solve the problem of solid waste disposal (Metso Paper 2008). The new technology eliminates the need to dispose of coating and filler pigments in landfills after being used only once. OptiThick GapWasher, a new technology developed for the twin-wire forming sections of paper machines, is a key component in Metso's new filler recovery plant concept, which will allow paper mills to cut the flow of solid waste to landfill sites and increase their reuse of filler pigments, offering the potential for considerable savings.

The concept was developed for paper machines equipped with several coating stations and producing a heavily coated end-product. These machines have high levels of pigment in their stock preparation and water management systems, resulting in a high solid waste load. The accepts in the OptiThick GapWasher system comprise only a few per cent by weight of particles larger than 45 µm in diameter as measured by wet-sieving. In some cases, pigment particles smaller than 45 µm in diameter (e.g. in centricleaner rejects), are acceptable for replacing new filler. Studies have shown, however, that more than 90% of the acceptable fraction of the latter rejects consists of particles smaller than 32 µm. Further cleaning of the accept flow is still needed for particles larger than 45 µm before it is returned to the paper machine approach system.

After separation in the GapWasher, the rejects fraction, which now comprises mostly low quality fibre, other wood-originated particles, and coarse pigment fraction, is in concentrated form. Its lower ash content and the lack of any viable reuse method mean that this fraction is dried and used as a fuel.

In typical GapWasher applications, the concentrated web is the accept and the filtrate is the reject, but in pigment recovery this is reversed. Since the feed pulp consists mainly of fine and coarse pigment particles, low quality fibres, and some impurities, the aim is to separate the fine pigment particles and water into the filtrate and leave the coarse pigment, low quality fibres and impurities between the wires. After separation, the pigment in the filtrate can be reused as filler.

Full-scale GapWasher use has produced excellent rejects cleaning efficiency to date. Feeding 50–100 t/d (on a dry basis) of rejects into an OptiThick GapWasher system has yielded a recovery rate of around 80%. Feed consistency has been 4–8%, and ash content around 70–85%. The recovered 80% portion of the pulp comprises some 80–90% ash. Measurements typically show that more than 95% of the sample mass consists of particles smaller than 45 µm in diameter.

The Wiggins Teape Group Ltd, Aberdeen, UK, has patented a fibre and filler recovery system (US patent no. 5478441 1995), in which the material recovered from the effluent is reused in paper production. The first step is the screening and/or cleaning of the paper mill waste sludge from the mechanical primary clarifier to remove large, dense contaminants. This is done at relatively low dry solids content within the range of 2–6% by weight using a high-density cyclone cleaner, followed by the further treatment of the accept by means of a high consistency rotating screen to remove lightweight contaminants. The rejects from both the cyclone cleaner and the rotating screen are then further treated by means of a pressurised vibrating tailing screen. Accepts from this are recycled back to an earlier process, while the rejects are discharged to landfill.

The second step is the thickening and heating of the resulting sludge. Thickening of the sludge is accomplished using a series of screw thickeners followed by one or more screw presses, effectively raising the consistency from around 4% to 30% by weight. The thickened sludge is then passed through a plug screw to produce a seal and thereby a closed system. From the plug screw, the fibre/sludge is fed to a fluffer, which transforms the compressed fibre sludge into crumbs before it passes into the heating chamber. Heating is conveniently done by the injection of superheated steam to a temperature of 125°C. The bleach addition is made at the point between the thickeners and the plug screw.

Once the fibre/sludge mixture has emerged from the disperser and been diluted, typically with white water, it is suitable for use in a conventional papermaking stock, normally when combined with additional papermaking fibre, which can be fresh virgin pulp or a different broke. Additional filler may be added if necessary, although filler is present in the sludge and in various types of broke. This additional papermaking fibre can be mixed with the sludge prior to the screening and/or cleaning step, or before a dispersion step, and/or the sludge can be treated on its own before being mixed with the additional papermaking fibre.

Stora Enso, headquartered in Sweden and Finland, is using Trenntechnik, its own filler recovery system for effluent treatment in its mill in Uetersen, Germany (Templer 1993; Pelikan et al. 1997). The effluent of two paper machines and one coating machine is collected for recovering the filler and reusing it in the paper machine. This is also the pretreatment method for the effluent before it goes to the municipal waste water treatment plant.

The first phase of the process is to separate the large particles, such as pieces of paper and bigger coating particles, from the waste water with a drum screen. After that there is a sand trap before the waste water is routed to the Fourdrinier wire, with which the pigments are separated from the filtrate. The pigment-containing filtrate is then channelled to the sedimentation and flotation phase, from where the sludge is pumped to the vibration screens. The last separation phase of the pigment recovery process is done with centrifugal cleaners. The excess of the sedimentation and flotation phase is pumped through the condensing tower to the municipal waste water treatment plant. The rejects of the process are utilised in cement/brickwork. The fibres of the reject can be used in the mill's own paper production or for other purposes.

ECC International, St Austell, UK, has applied the technique of forced evaporation to the recovery of diluted coating colours, which has been studied using laboratory and pilot scale tests. The research system included a screening system, a stirred storage tank, a heat exchanger and a forced circulation design evaporator unit. In a typical experiment, the waste colour was screened, and then it was placed in the stirred tank and recirculated through the evaporator via the heat exchanger. The evaporator was operated at 5–10 kPa and 50–70°C. The apparatus ran continually until the desired solids were achieved. The recovered colours could then be blended with fresh colour and used for their original purpose with no significant decrease in performance (Skuse et al. 1999).

The capital cost of the mill-scale equipment is said to be relatively low, and since only very low grade heat is needed, a lot of the energy requirement for the process could be readily available in the paper mill. The process produces very clean water as a by-product, leaves no wastes requiring treatment, and can raise the solids level of the split colour to above 60%. In addition, the majority of the soluble components of the colour, such as thickeners, optical brightening agents and dispersants are also recovered (Phipps et al. 1998).

In the laboratory and pilot-scale test at the ECC International Technicentre, Lixhe, Belgium, the coating performance of the recovered colours was the same as that of the fresh material. The evaporation process had no effect on the efficiency of the optical brightening agents used. Some changes in the viscosity of the recovered colours were observed, but once they were blended with fresh colour for the coating work no significant differences in viscosity or runnability were encountered (Phipps et al. 1998). This method was not considered further in this study partly because it has not been tested on a mill scale, and partly because there is no compelling need to raise the solid content of the recovered material when it is used as a filler in this case.

Ultrafiltration has become one of the main methods for the recycling of pigment and chemicals while retaining their functional value (Nygård et al. 1998; Singh et al. 1999; Siivonen and Genduso 2003; Tizon et al. 2005; Mahmood 2006; Roitto 2007). The Process Automation Activité Cellier division of ABB France, Aix-les-Bains, France, in cooperation will Pall Corp., East Hills NY, has developed an ultrafiltration system based on crossflow filtration technology with ceramic membranes for liquid/solid separation. Created especially for the paper industry, it is designed for the treatment of effluents (mainly rinsing water) resulting from the coating process (coating colour kitchen and associated equipment) (Tempesta 2007).

The system uses Membralox ceramic elements, which are asymmetric multichannel membranes consisting of a porous alumina support and a filtering layer (alumina or zirconia). The ceramic membranes are fitted with a 316 l stainless steel housing (module). They are resistant to chemical attacks and extreme pH and temperature values, and are compatible with organic solvents. The standard ultrafiltration range is 20–100 nm.

ABB ultrafiltration systems are composed of several Membralox modules in series and/or in parallel according to the required filtration area. Each system can be extended by adding new modules. The feeding is continuous and the working tank operates at a constant level. The feed stream moves parallel to the membrane filtration surface, and purified liquid passes through the membrane. The separation is driven by the pressure difference from one side of the membrane to the other – referred to as transmembrane pressure.

Crossflow filtration streams are divided into three parts:

- feed that enters the filtration channels
- permeate, a solution that passes through the membrane pores (clear water)
- retentate (or concentrate), the solution retained by the membrane (raw materials).

With the turbulence created by the crossflow velocity, particles are continually swept away, thus avoiding the clogging up of the membrane surface. The retentate is the result of the concentration of the original feed stream. It flows through the channel and is recycled back into the feed stream.

The ultrafiltration stage enables the rinsing water to be recycled by decreasing the chemical oxygen demand (COD) value and lowering the load on the waste water treatment plant as well as reducing the related operating and energy costs. The ultrafiltration unit also helps to minimise the perturbations in the waste water treatment plant, such as highly variable effluent flow and concentration rates, and COD peaks resulting from, for example, a paper break. Recovered permeate or clear water can be used as rinsing or process water in the paper mill. Depending on the application, solid matter contained in the concentrate slurry can be added as a component to the coating colour or precoat directly at the mixing stage. The system has been implemented at:

- Cascades Blendecques SA, France
- Cartiera di Sarego (Burgo Group SpA), Italy
- Thai Paper Co. Ltd, Thailand
- Advance Agro Public Co. Ltd, Thailand
- Susano de Papel e Celulose SA, Brazil.

Metso Papers has also developed an ultrafiltration process. Called OptiCycle C, the process is designed for the collection and screening of coating colour effluent and the recovery of coating colour solids. The core of the process is the OptiFilter CR, which consists of flat polymer membranes in a cell construction. Feed flow is kept turbulent by the use of rotors between the cells, which maintains high filtering capacity and promotes longer membrane operating life.

The system consists of one or several OptiFilter CR filters, piping, tanks and dosing systems for the concentrate and permeate, as well as the membrane detergent system. The dry solids content of the concentrate, and the pressure difference over the membranes, are measured and automatically controlled to maintain optimal performance in continuous operation. The concentrate is recycled in the fresh coating colour. The permeate can be reused in, for example, coating preparation as washing water, or as dilution water for starch.

The concentration process can be divided into two stages if required. In the first stage, ultrafilter concentrate is pumped to the second stage filter via an intermediate tank, and the final concentrate of high solids is collected in a storage tank. This process connection results in a considerably higher dry solid content in the concentrate. The second stage filter can be used alongside the first stage filter if needed. Metso's two-stage ultrafiltration plant allows pigments and chemicals to be recovered from coating effluent with solid contents of up to 50% (Roitto 2005).

Tullis Russell, Markinch, UK, was the first to implement the OptiCycle C process in the UK, installing it in its Glenrothes paper mill (Anon 2003) to improve the economics of coating by eliminating the loss of coating colour and the subsequent disposal costs. The system also reduces mill water consumption and its effluent load.

Other mills employing OptiCycle C are Stora Enso in Oulu, Finland, supplied by Valmet-Raisio (Kraatari and Ryyppö 1999), and M-real Husum, Sweden (Ryyppö 2006).

Summary and conclusions

12

The kraft chemical recovery process is a mature, effective technology that provides for recycling the pulping chemicals, efficient generation of steam and electrical power from the fuel value of the black liquor, and effective disposal of dissolved wood substances. Advanced energy integration and mill-wide control can improve the efficiency of energy and chemical recovery from black liquor and the overall performance of kraft pulp mills. The kraft chemical recovery process may achieve significant energy benefits through the use of new technologies in addressing issues related to effluent discharge, air emissions, and the need for better energy recovery and use. Steam and power production capacity should be maximised, chemical losses should be minimised, and recirculating chemical deadloads should be reduced. These are essential for kraft mills since the quantity and quality of white liquor and the pulp produced, and the profitability of pulp mills, are directly affected by the efficiency and reliability of recovery boilers, causticisation plants, evaporators, and lime kilns.

Future trends for pulp mills include black liquor gasification, borate autocausticising, and the use of alternative fuels for lime kilns. Gasifier technology has the potential to achieve greater power generation but with lower efficiency than recovery boilers. The driving force for these alternative recovery technology developments has been the potential for much greater electricity production. New high-efficiency recovery boilers have considerably reduced this gap. However, as many materials and gas clean-up issues remain to be resolved, in 2008 the first large-scale gasification plant still appears to be years away.

Attention is now shifting to the use of black liquor gasification to produce synthesis gas as a raw material for making higher-value chemicals for sale. This is sometimes referred to as the biorefinery concept. It is more probable that plants using direct biomass gasification will reach commercialisation first. Integration of these plants to pulp mills will provide new challenges and opportunities.

The recovery boiler as a producer of green energy requires new materials and attention to feed water quality. The role of chlorine and potassium removal in preventing superheater corrosion must be established. The recovery rating should be changed to tonnes of as-fired black liquor, because virgin black liquor is a non-measurable quantity in modern installations (due to complex recycling arrangements). The lime kiln is by far the largest producer of fossil carbon dioxide in a pulp mill. Finding new solutions that minimise kiln length and utilise biofuels will become important.

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