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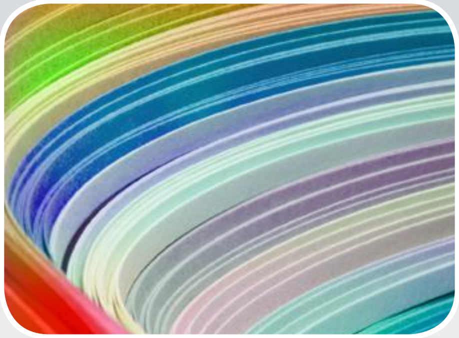
Using Biotechnology to Enhance Performance in Pulp and Paper Production Processes



This e-book examines the current and potential future use of biotechnology for enhancement of the various production and manufacturing processes involved in pulp and paper making, including the management of waste streams generated by the pulp and paper industries.

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Using Biotechnology to Enhance Performance in Pulp and Paper Production Processes

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Executive Summary

The Convention on Biological Diversity (1992) defines biotechnology as 'any technological application that uses biological systems, living organisms, or derivatives thereof, to make or to modify products or processes for specific use.' This broad definition ensures that virtually all applications that might impact biological diversity are covered by the Convention. It also allows a broad perspective on its present and future applications in the various production steps and manufacturing processes involved in pulp and papermaking, as this is essentially based on the production of woody and non-woody biomass-based fibres and their conversion into pulp and subsequently paper.

Since biotechnology can be applied in many different sectors and for many different purposes, it can be useful to differentiate between 'green' biotechnology for agriculture and forestry, 'white' biotechnology for industrial processes, waste management and soil remediation, 'blue' biotechnology for fishery and aquaculture and 'red' biotechnology for health-care applications. With respect to pulp and papermaking, a green biotechnologist's perspective allows him to examine the use of biotechnology in forestry and agriculture for the production of woody and non-woody biomass fibres, while the lenses of a white biotechnologist help to focus on the use of biotechnology in conversion of these biomass-derived fibres into pulp and paper, as well as in management of (toxic) waste streams.

In principle, green biotechnology provides novel opportunities for the breeding and growing of trees and crops that are more suitable for processing in food, feed, chemical, textile, pulp and paper and other industries. And white biotechnology offers new tools for this processing. Notably, environmental and energy concerns are often driving the use of white biotechnology across many industrial sectors, to not only remove pollutants from the environment but prevent pollution in the first place. Biocatalyst-based processes already play a major role in this context, as they generally operate at lower temperatures, and produce less toxic waste and fewer emissions and by-products compared to conventional (physical-) chemical processes. New biocatalysts with improved selectivity and enhanced performance for use in diverse manufacturing and waste degrading processes are steadily becoming available. Moreover, biotechnological production processes are inherently attractive because they use the basic renewable resources of sunlight, water and carbon dioxide to produce a wide range of molecules using low-energy processes.

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At almost every step in current pulp and papermaking processes, there are opportunities to apply biotechnology, starting with the production of woody and non-woody biomass feedstock for pulp and paper making, through fibre, pulp and (recycled) paper processing and papermaking.

Through biotechnology and improved silviculture, trees and other biomass-resources can be specifically tailored to match the properties required in cellulose fibres for different product applications. This can increase useful paper yield from trees, enhance product quality and decrease requirements for energy and chemicals used in papermaking. Producing optimal fibres for papermaking through genetic engineering of trees and certain plant species is one of the objectives. Significant advances have been made with genetic engineering of several tree species such as poplar, birch, larch, pine and spruce. Traits included herbicide-tolerance, insect-resistance and modified lignin and cellulose content. A second wave of traits being researched now includes secondary cell wall characteristics (improved pulpability, increased cellulose content, better stability).

Overall, hemp, flax, jute, sisal and abaca are among the most commonly used non-wood fibre sources used for manufacturing of high-quality pulps for specialty papers. Other non-wood plant species, like for example alfalfa in North America, hemp and flax in Europe and acacia in Southeast Asia, might also be promising as feedstock for papermaking. However, the processing procedures for these non-wood species have to be improved further, in particular the knowledge of lignin composition in non-wood fibres are important for optimizing the pulping and bleaching processes.

The use of engineered micro-organisms and enzymes for displacement of many of the environmentally adverse practices used in pulp processing and papermaking is another biotechnology objective. Over the last two decades, numerous applications have been investigated for fungal and enzymatic treatment of pulp. These include modification of pulp properties, such as improved fibre flexibility and fibrillation, decreased vessel picking from tropical hardwood pulps, improved drainage in recycled fibres, specific removal of xylan for dissolving pulp manufacture, facilitated bleaching of kraft pulp, enzymatic pulping of herbaceous fibres, enzymatic pitch removal, stickies control and facilitated contaminant removal from recycled fibres (de-inking).

The penetration of enzymatic processes in the pulp and paper industry is still modest, as is the empirical evidence from studies that compare recent enzymatic processes versus chemical processes. Based on available quantitative and qualitative data, a recent study suggested: 1) large relative environmental improvement potentials of enzyme use in bleaching and refining of pulp; 2) moderate relative improvement potentials in de-inking and control of pitch and stickies, and; 3) a considerable potential for the application of enzymes for peroxide removal, fibre modification, anionic trash control, starch removal, drainage improvement, starch preparation for paper coating and slime control.

In recent years, biopolymers have been the focus of much research because of the interest in their use as edible and biodegradable films and coating for food packaging. Biopolymers, like proteins, polysaccharides, lipids or combinations of those components, offer favorable environmental advantages of recyclability and reutilization compared to conventional, petroleum-based synthetic polymers. In addition, biopolymer-based films and coatings can act as efficient vehicles for incorporating various additives, including antimicrobials, antioxidants, colouring agents and nutrients.

The pulp and paper industry has suffered from persistent low profitability in North America and Europe for many consecutive years now. One strategy to combat this persistent lag has been to intensify Research & Development (R&D) efforts to identify new products and entire new businesses, such as biofuels. For the foreseeable future, the bulk of the industry's revenues will continue to be generated from traditional pulp, paper and board products. However, further advances of white biotechnology and the adoption of biocatalysts by the pulp and paper industry can help to enhance the economic and environmental performance of several processing steps as well as to develop new paper products. Moreover, the bio-refinery concept offers a promising outlook for the pulp and paper industry to make use of fibres from both woody and non-woody biomass and to produce not only paper products but also biofuels and 'green' chemicals.

TABLE 0.1 Biotechnology transition table, 2011 – 2021

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Introduction and Methodology

Objective and Scope

The objective of this report is to examine the current and potential future use of biotechnology for enhancement of the various production and manufacturing processes involved in pulp and paper making, including the management of waste streams generated by the pulp and paper industries.

Over the years, many definitions have been provided for modern biotechnology. In the broadest sense, biotechnology may be understood to include such traditional biology-based processes as conventional plant and animal breeding and fermentation for beer brewing, bread baking and cheese production. In the narrowest sense, biotechnology may be taken as a term describing molecular technologies applied for genetic modification of living organisms. The Convention on Biological Diversity (1992) defines biotechnology as 'any technological application that uses biological systems, living organisms, or derivatives thereof, to make or to modify products or processes for specific use.' This broad definition ensures that virtually all applications that might impact biological diversity are covered by the Convention.

A broad definition of biotechnology also allows a broad perspective on its present and potential future applications in the various production steps and manufacturing processes involved in pulp and papermaking, as this is essentially based on the production of woody and non-woody biomass-based fibres and their conversion into pulp and subsequently paper.

Since biotechnology can be applied in many sectors and for many purposes, it can be useful to differentiate between 'green' biotechnology for agriculture and forestry, 'white' biotechnology for industrial processes, waste management and soil remediation, 'blue' biotechnology for fishery and aquaculture and 'red' biotechnology for health-care applications. Yet, the boundaries between green, blue, white and red biotechnologies are not always clear or obvious. For instance, the production of 'red' (sub-unit) vaccines or 'white' molecules, such as enzymes or (monomers for) biopolymers, blur the boundaries between these green, red and white biotechnologies. With respect to pulp and paper making, a green biotechnologist's perspective allows him to examine the use of biotechnology in forestry and agriculture for the production of woody and non-woody biomass fibres, while the lenses of a white biotechnologist help to focus on the use of biotechnology in conversion of these biomass-derived fibres into pulp and paper, as well as in management of (toxic) waste streams.

In principle, green biotechnology provides novel opportunities for breeding and growing of trees and crops that are more suitable for processing in food, feed, chemical, textile, pulp and paper and other industries. And white biotechnology offers new tools for this processing. Notably, environmental and energy concerns are often driving the use of white biotechnology across many industrial sectors, to not only remove pollutants from the environment but prevent pollution in the first place. Biocatalyst-based processes already play a major role in this context, as they generally operate at lower temperatures, produce less toxic waste and fewer emissions and by-products compared to conventional physical-chemical processes. New biocatalysts with improved selectivity and

In principle, green biotechnology provides novel opportunities for breeding and growing of trees and crops that are more suitable for processing in food, feed, chemical, textile, pulp and paper and other industries.

Introduction and Methodology

enhanced performance for use in diverse manufacturing and waste degrading processes are steadily becoming available. Moreover, biological production processes are inherently attractive because they use the basic renewable resources of sunlight, water and carbon dioxide to produce a wide range of molecules using low-energy processes.

Most paper is manufactured from wood, a natural and renewable raw material, and pulp—the basic ingredient for the manufacture of paper and board—is produced from fresh wood, woodchips from sawmills, recovered paper, sometimes from textiles, agricultural by-products and industrial crops. While papermaking has been around for some 2,000 years, it is only since the middle of the last century that there have been significant technological developments in the processes, resulting in a complex industry. In essence, the current pulp and paper production process consist of the following steps: 1) Forestry —harvesting, waste materials 2) Debarking, chipping, recycling 3) Pulp preparation, mechanical or chemical 4) Washing, bleaching 5) Stock preparation, paper formation, and 6) Paper finishing. At almost every step in this pulp and paper making process, there are opportunities to apply biotechnology (tools), starting in the forests and plantations where the trees are harvested, through the chipping, pulping, bleaching and papermaking. Against the background of developments in green and white biotechnology, the scope of this report will therefore include the application of biotechnology to the following steps in pulp and papermaking production processes:

- Production of woody and non-woody biomass feedstock for pulp and paper making
- Fibre, pulp and paper processing: bio-pulping, enzyme-aided pulp and paper processing and paper recycling
- Bio-refining in pulp and paper mills
- Use of bio-based materials in paper and paperboard applications

Methodology

Extensive research was carried out into biotechnology developments related to tree breeding, forestry and pulping and paper making processes from scientific literature, trade publications and reports from national and international bodies.

Definitions

Biofuel is liquid or gaseous fuel for transport produced directly or indirectly from biomass.

Biomass is the biodegradable fraction of products, wastes and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste; biomass does not include material embedded in geological formations and transformed into fossils.

Black liquor is a liquid product from the chemical pulping step in the pulp and paper industry, which can be gasified or pyrolised as a biomass energy source.

Bleaching is the means by which pulp is whitened in preparation for making many kinds of paper.

Chemical papers are manufactured from chemical pulp. In chemical pulping, plant material is separated into its constituent fibres using chemicals and heat. Chemical papers are also referred to as wood-free or free-sheet papers.

Feedstock is any substance used as raw material in industrial production processes, including fermentation processes.

Fermentation is the decomposition of organic material to alcohol, methane, etc., by organisms such as yeast and bacteria, usually in the absence of oxygen.

Furnish means any ingredient such as wood fibre, fillers, starches, dyes and other materials blended and used in a paper machines to manufacture paper.

Mechanical papers are manufactured from mechanical pulp, in which the fibres in the raw material, e.g. logs or chips for wood-based papers, have been separated by mechanical means, such as grinding. Common mechanical papers such as newsprint may be manufactured through a process that includes heat as well as mechanical separation.

Printing and writing paper is an umbrella term for paper grades, including uncoated and coated mechanical papers, and uncoated and coated wood-free papers.

Pulp is an intermediate stage in the manufacturing process of paper. Plant materials such as wood are separated into their constituent fibres through chemical or mechanical means. The resulting pulp can be dried and shipped to an off-site paper mill or sent directly to a nearby paper machine.

Recycled paper is manufactured from fibres that have previously been used to make paper. The recyclable paper must be separated into its component fibres, and any ink left from previous usage must be removed. When ink is removed, the resulting material is called de-inked pulp (DIP).

Virgin fibre is fibre that has never been used for paper making purposes; sometimes it is referred to as fresh fibre.

Biotechnology Developments for Papermaking

Introduction

This section will first provide a general inventory of biotechnology as a platform of technologies and their use in primary production and industrial production. This will be followed by an overview of biotechnology applications specifically for the production of woody biomass and its processing into pulp and paper.

Overview of Biotechnology

Platform Biotechnologies The basic science underpinning biotechnology in primary production, industry and health care is similar, with all three applications fields sharing the same set of platform technologies or research tools (OECD 2009).

At present, the most important of these technologies relate to reorganize genetic information of living organisms through genetic modification (GM), which has been performed since the 1970s, usually to insert a gene with a desired trait. While in first instance this used to be a very laborious process, it is now commonplace and used in a wide variety of biotechnology applications.

Other important technologies concern the analysis of how genes function (genomics), how proteins function (proteomics) and how cells function (metabolomics). In this context, it should be noted that DNA sequencing—that is, determining the order of the nucleotides (the base sequence) in a DNA molecule—is key to discovering the structure and function of genes. The productivity of gene sequencing technologies, measured by the number of base pairs that can be sequenced by one operator per day, has increased 500-fold over the last decade, with costs declining by three orders of magnitude. An increasing range of sequencing technologies is available, from those that rely of PCR (polymerase chain reaction) to amplify genetic material before they can be used to those that require a single molecule to determine its sequence.

Once desired DNA (and RNA) sequences are known, they can be synthesized for use in research or in the production of a product. As with gene sequencing, gene synthesis technologies have improved significantly. Over the last decade, gene synthesis productivity increased 700-fold and the costs declined to a thirtieth of previous levels. Interestingly, gene synthesis companies are active all over the world and provide synthesized DNA by mail from specifications received over the Internet.

Bioinformatics covers the construction and analysis of databases with information on genes, proteins and other complex cell processes. Analysis of databases containing information on human, animal, plant and microbial genomes are likely to lead to a better understanding of gene functions. Given the large amounts of data obtained through the use of ‘omics’ technologies, bioinformatics has led to new hardware and software developments. As biotechnology evolves from a gene-based to a multidisciplinary science that takes into account their full cellular modules and their interaction with the external environment, bioinformatics will play an increasingly important role. This will include systems modeling and the construction of three-dimensional models of a variety of biological components.

Over the last decade, gene synthesis productivity increased 700-fold and the costs declined to a thirtieth of previous levels.

Moreover, molecular biology and genomics research assisted by bioinformatics have yielded a series of new tools to alter genes as well as the expression of genes. Besides 'classical' genetic modification/engineering, e.g. transgenesis, it is now possible to breed new varieties of crops and trees using techniques like RNA interference (RNAi), oligonucleotide-directed mutation, reverse breeding, agroinfiltration, zinc finger nucleases, cisgenesis and intragenesis. In particular RNAi has emerged a new platform technology to alter gene functioning in organisms. RNAi is based on the use of segments of double-stranded RNA molecules to turn on or off targeted genes.

Since a couple of years synthetic biology is emerging as a new field, based on an engineering approach that enables the design and construction of new biological parts, devices and systems, and the redesign of existing, natural biological systems for useful purposes. The purpose of 'synbio' is to increase biological efficiencies by designing a cell system for a specific function, thereby eliminating the production of unwanted products that waste a cell's energy. One technique within synbio involves altering a micro-organism's metabolic pathway, aiming at the production of a wanted product or the degradation of unwanted substances such as, for example, toxic pollutants.

A key theme in synbio is the construction of a so-called 'artificial genome' or 'minimal cell,' either by inserting a fully synthetic genome into a cell whose original DNA has been removed, or by constructing a synthetic cell from predesigned biological parts. Ongoing research in this area is assisted by several public databases on metabolic pathways. The design of 'biological parts' is facilitated by an open-access library of several hundred standard parts (BioBricks) that can be assembled into various biological devices.

Biotechnology in Primary Production In primary production, biotechnology is used to develop new varieties of trees, plants and animals with improved traits, advanced propagation techniques, new diagnostic tools and therapeutics and vaccines for veterinary diseases.

One of the biotechnology tools for the development of a new crop or tree variety with commercially valuable genetic traits consists of genetic modification, based on the transfer of genetic information across species that cannot interbreed (transgenesis). Recently, similar techniques have been developed that use only genetic information from species that can interbreed (cisgenesis, intragenesis). Biotechnologies such as Marker Assisted Selection (MAS), which uses biological or chemical markers to identify traits, can also be used to improve accuracy and reduce the time required to develop new varieties based on conventional breeding techniques. Both GM and non-GM programs focus on one or more of the following traits: 1) Herbicide-tolerance 2) pest-resistance3) biotic stress-resistance, and 4) product quality characteristics. By 2015, approximately half of global production of the major food, feed and industrial feedstock crops is likely to come from varieties developed using modern biotechnology.

GM varieties of over a dozen of different plant species have received regulatory approval for cultivation somewhere in the world. However, the large majority of genetically modified (GM) plantings are for soybean, cotton, maize and rapeseed (canola). Uptake of GM crop varieties in many regions of the world has been rather rapid compared to the adoption of many other agricultural technologies in the past, except in Europe because of a perceived lack of consumer acceptance of GM food.

The adoption of GM for forestry has been relatively slow compared with GM crops. This is due to the genetic complexity of trees, the long breeding times required, and multi-gene modification requirements for most traits. Most GM programs for trees are still in the research phase, with the exception of insect-resistant GM poplar plantations in China. Besides traits as herbicide-tolerance and pest-resistance, genetic modification is used to develop trees with modified lignin that could reduce paper production costs, as well as faster-growing trees for timber, pulp and paper, and biofuels. Over the last couple of years, the pace of research on GM trees has increased significantly. While only 93 field trials were conducted from1987 to 2000, this number increased to 387 for field trials with GM trees conducted between 2000 and 2007. GM trees of faster-growing tree species could be ready for commercialization by 2012 and GM tree varieties with altered lignin could be available for use in pulp and paper or bioethanol production by 2015 (OECD 2009).

Biotechnology is also applied to the propagation of plants and trees, usually to propagate genetically superior varieties. Sometimes coupled with MAS, biotechnology-based propagation techniques can substantially speed up breeding programs.

It should be noted that the economics of tree plantations for wood, fibre and biofuel production favor tropical and semi-tropical regions, where annual biomass production is many times higher than in temperate zones. GM programs have therefore often focused on fast-growing, short-rotation trees such as pine and eucalyptus that are adapted to warm climates. According to FAO-BioDec (2010), 858 non-GM and 47 GM programs in developing countries are related to forestry. Due in part to a surplus of wood in Northern countries, interest in developing new tree varieties for temperate zones has been modest so far, with the exception of research on GM poplar species.

Biotechnology in Industrial Production White—or industrial—biotechnology is used in the production of bio-based chemicals and materials. There are many industrial applications based on enzymes either produced by GM micro-organisms or selected using other modern biotechnology tools. Research is also underway to combine a number of bio-based processes into a single bio-refinery.

Biotechnology can be used to produce a number of biofuels, bulk chemicals (including some organic acids), and specialty chemicals (including enzymes, vitamins, amino acids, organic acids, solvents, antibiotics and biopolymers). Bulk chemicals have high global production volumes and low prices and profit margins, whereas specialty chemicals are produced in low volumes and have high prices and profit margins. In many cases, biotechnology processes can compete with chemical synthesis, while they can have several advantages, such as more specific reactions, less demanding production conditions (lower temperatures, lower pressures and milder pH) and lower energy inputs, waste and impact on the environment. Despite these advantages, the uptake of biotechnology in chemical production is still rather limited, due to the high costs of enzymes or bio-reactors and the cost of building or modifying production facilities to use biotechnology. Ongoing research aims to make white biotechnology more cost-competitive through improved production methods such as process intensification and in situ recovery, as well as through the use of GM and metabolic pathway engineering to increase the output productivity of micro-organisms.

In addition to traditional bio-based materials like wood and cotton, bio-based chemicals can be used to create packaging and containers, fabrics and consumer durables (electronic casing or car components). While some niche applications exist, the most important bio-based material to date is bioplastic made from biopolymers. Some bioplastics are biodegradable, whereas others, like most petrochemical-based plastics, are not. Some bioplastics, including the most common starch-based polymers, can be produced without using modern biotechnology, but many others require advanced fermentation or designer micro-organisms for the production of polymers and monomers.

Enzymes are proteins that can repeatedly catalyze biochemical reactions without being affected by those reactions. In addition to their use in the production of chemicals, enzymes have numerous applications in food and feed, detergent, textile, biofuel and pulp and paper production. Enzymes can replace chemicals in some processes, and this may have significant environmental consequences, for instance, a reduction in greenhouse gas emissions attributable to lower energy use when processes are carried out at lower temperatures and pressures. While enzymes have been used in detergents since the 1930s, enzymes in the pulp and paper industry have only been used for the past two decades or so. The industry uses enzymes to modify starch for the production of coated papers and to break down lignin to reduce the use of chemicals in bleaching. Other applications include enzymes to reduce pitch (which can create holes in papers and interfere with machinery during production), and to facilitate recycling by removing residues and improving the de-inking process. Table 2.1 provides an overview of the most common types of enzymes and the reactions, in which they act as biocatalysts.

TABLE 2.1 Common enzymes, their reactions and applications

There are many enzymes on the market for application in these various areas. Most enzymes are produced using modern biotechnology, and research is ongoing to expand the range of useful enzymes. Biotechnology can also help to create new enzymes through MAS, protein engineering, genetic modification, directed evolution and advanced selection and high-throughput screening techniques. Currently there are about 117 enzyme producers worldwide, with the majority (80) located in Europe, 21 companies in the U.S., and the rest distributed in other regions. The most important companies in terms of production volume are Novozymes (Denmark), Danisco/Genencor (Denmark), DSM (The Netherlands), AB Enzymes (Finland), Chr. Hansen (Denmark) and DIREVO Biotech AG (Germany). Market share among these companies is not known, as each has strength in different types of enzymes, which compete in different markets (EC 2007).

Bio-remediation is another biotechnology that is based on the use of micro-organisms to monitor and treat waste streams from agriculture, industries and municipalities. Bio-remediation technologies have been used for many years and form the technological basis of most modern sewage treatment plants. Waste streams from industry, such as heavy metals; from agriculture, such as chemical fertilizers; and from nuclear plants are posing a challenge that might be addressed through genetic modification and metabolic pathway engineering of micro-organisms to neutralize these harmful substances.

A bio-refinery is a facility that integrates biomass conversion processes and equipment to produce fuels, powers and chemicals from biomass. The bio-refinery concept is analogous to a petroleum refinery that produces multiple fuels and products from petroleum. Many industries, including food and pulp and paper processing, already process biomass that yields a product with energy as by-product. For example, a pulp and paper mill can produce a variety of papers from wood (and recovered paper) using wastes and residues to generate electricity. Another example is the production of ethanol from sugar cane or sugar beet, which relies on conventional fermentation, while the by-product of sugar fermentation—molasses—is burned to generate power or heat. But these industries cannot be considered full-fledged bio-refineries, as the emerging bio-refinery anticipates a (disruptively) new configuration of processing facilities for the optimal use of different types of woody and non-woody biomass for the production for pulp/paper, green chemicals, biofuels, power and heat.

Bio-based Economy

In a bio-based economy, food, feed, fibres, fuels and chemicals are produced from biomass—that is, raw materials from algae, plants and animals, as well as organic wastes—and knowledge gleaned from green and white biotechnology is important in the production of such goods. In almost every part of the world, governments, businesses and researchers believe that this development will lead to a sustainable alternative for an economy based on fossil resources. For businesses, biotechnology-based production processes could be of interest, if, of course, they reduce the costs of energy, water and greenhouse gas emissions and thus lead to an economically more efficient production. For governments, there are still other reasons to promote the development of a bio-based economy, such as enhancement of industrial competitiveness, regional and rural redevelopment and decrease of reliance on imports of fossil oil from 'politically unstable' regions in the world.

Technological developments will expand the number of economically competitive applications of biotechnology, hastening the emergence of the bio-economy. More powerful and affordable platform technologies will continue to be used in all biotechnology applications, including bio-informatics, metabolic pathway engineering and synthetic biology. As a result, supply-chain linkages between agriculture, forestry and industry could become more robust, particularly if new feedstock trees and crops that are adapted to the needs of bio-refineries reduce the production costs of biofuels and bio-based chemicals. It can further be expected that white biotechnology will be able to produce many precursors of pharmaceuticals, while some bio-pharmaceuticals are likely to be produced in GM plants. Table 2.2 provides an overview of the research and development (R&D) expenditures by leading firms in green and white biotechnology in 2006.

TABLE 2.2 R&D expenditures by leading biotechnology firms, 2006 (US$ million)

Primary production		Industrial production	
Company	Biotech R&D	Company	Biotech R&D
Syngenta	510	Novozymes	95
Monsanto	470	BASF	55
Bayer CropScience	310	DuPont	45
DuPont – Pioneer	190	Akzo Nobel	40
BASF	170	Dow	40
Limagrain	85	DSM	15
KWS	65	Kyowa Hakko Kogyo	9
Dow Agrosciences	55	Ciba	6
		Wacker Chemie	6
		BHP Billiton	2

Source: OECD

Yet, many of the potential socioeconomic and environmental benefits will remain elusive, without any major technological breakthroughs. Likewise, R&D is also influenced by how markets and businesses are structured, how intellectual property and research are distributed, as well as how those working on such developments are educated and trained, and how products are distributed and sold.

Moreover, several industrial processes based on biotechnology could have disruptive effects on economies by replacing production systems based on fossil oil. Other processes might have radical effects, such as the use of micro-organisms or plants developed through metabolic pathway engineering. This could disrupt current methods of producing chemicals and require new infrastructure for large-scale chemical production or produce novel chemicals with possible disruptive effects on other economic sectors.

Biofuel production provides an example of the potential of biotechnology to bring about either disruptive or radical innovation, depending on the scale of production. Large-scale production through the use of biomass will, for instance, require investment in the development of new (GM) crop varieties to provide an adequate supply of biomass, technical solutions to reduce the costs of transporting biomass to bio-refineries, new biomass transportation infrastructure and specialised pipelines or tankers to distribute the biofuel to the market. In addition, if woody biomass is increasingly used for renewable energy generation, this will inevitably lead to complex changes in global and regional trading patterns of woody biomass, which will affect its prices as well, as it is not only used for renewable energy generation, but also for pulp and paper making and various other wood processing industries.

Overview of Biotechnology in Pulp and Papermaking

Through the lenses of a green and a white biotechnologist, the following biotechnology application areas can be distinguished specifically in relation to pulp and paper making:

Biotechnology Developments for Papermaking

Production of Woody Biomass Feedstock for Pulp and Papermaking Through biotechnology and improved silviculture, trees and other biomass resources can be specifically tailored to match the properties required in cellulose fibres for different product applications. This can increase useful paper yield from trees, enhance product quality and decrease requirements for energy and chemicals used in papermaking. Producing optimal fibres for papermaking through genetic engineering of trees and certain plant species is one of the objectives. Research has yielded GM (transgenic) tree lines that have much lower lignin content than unmodified counterparts, but the lignin they do produce is more easily pulped. It is also feasible to alter the genetic composition so the lignin produced by a softwood tree resembles the lignin of a hardwood tree, which is easier to remove during pulping. Other research aims at altering the degree of crystallinity of the cellulose in the wood, which could help to lower its resistance to enzymatic degradation during the production of cellulosic biofuels. Genetic engineering of trees can also be paired with clonal propagation, so that large plantations of GM trees with uniform (fibre) properties can be established. A specific issue that deserves serious attention is the potential unwanted spread of genetic material from GM trees to native related species and the implementation of appropriate physical and biological containment measures.

Moreover, especially during the last two decades, Eucalyptus species as sources for fibre for paper making has become one of the most sought-after types of pulp for various applications, including printing papers and tissues. Plantation technology has become well established, particularly in tropical and sub-tropical South America, which has become a ‘fibre basket.’ Acacia fibres, which are finer than Eucalyptus fibres, have gained considerable importance, because like eucalyptus, they, too, have high growth rates, relatively quick maturation cycles and highly uniform fibre properties.

Fibre, Pulp and Paper Processing The use of engineered micro-organisms and enzymes for displacement of many of the environmentally adverse practices used in pulp processing and paper making is another biotechnology objective.

For example, after felling, logs can be treated with fungi to improve debarking or to protect the (pulp) wood against blue staining and decay. Inoculation of softwood logs with the white-rot fungus Phlebiopsis gigantean, helps to loosen bark, reduce pitch and protect the wood against sap staining, while the fungus Ophiostoma piliferum can protect timber against blue staining. Moreover, bio-pulping is a solid-substrate fermentation process where lignocellulosic materials are treated with fungi prior to pulping to reduce energy during mechanical pulping or to reduce chemical consumption during chemical pulping. Research has also yielded promising approaches using fungal enzymes to improve the penetration of pulping liquor into wood chips. It is evident that different fungi are suited to different pulping processes, but these processes also need to be adapted to achieve the full potential of bio-pulping for the reduction of the usage of energy and chemicals.

In addition, bio-bleaching can replace current bleaching of (kraft) pulp through the use of enzymes, like xylanases, which are unable to degrade lignin but are able to cause just limited degradation of hemicelluose in kraft pulp to expose lignin to further breakdown by bleaching chemicals. A typical chemical saving associated with the use of xylanases is about 15% active chlorine. Another approach is based on the use of oxidative enzymes, like laccase and (manganese) peroxidase, to delignify pulp.

Another type of enzyme, namely cellulases, can be used for de-inking of recovered paper, such as old newsprint and office paper waste. The cellulases are able to hydrolyse fines to releases ink particles. The ink can then be removed by chemical or air flotation.

Notably, most of the applications of enzymes to enhance the papermaking characteristics of pulp are aimed at the improvement of secondary (recovered) fibre. Application of cellulases and hemicellulases to modify fibre can have the following benefits: Improved beating to save energy, higher freeness, enhanced drainage, improvement of certain strength properties, and decreased disintegration of time of recycled pulp. In other applications, enzymes are used to remove the non-fibrous fractions of secondary fibre that hamper drainage during paper making, such as residual starch that is especially abundant where old corrugated containers are used as raw materials. Amylases can be used to degrade remaining starch that would not contribute to the web characteristics of the paper, but, rather, would restrict its drainage.

Furthermore, biocides and enzymes can be used to control microbial fouling in pulp and paper mill water systems that cause biofilm build-up, odor and corrosion with consequences as increased web breakages, holes and spots in the paper as well as increased costs of maintenance. Biocides are commonly used to control microbial build-up, and deposits are removed during boiling with sodium hydroxide or dispersants. Inoculation of water systems with competing micro-organisms or bacteriophages has been researched, but the most feasible biotechnological approach seems to be to utilize enzymes, like proteases ands carbohydrases (cellulases), to prevent aggregation of biofilm-producing micro-organisms.

Bio-based Materials Many fillers, pigments/ink, adhesives, etc., in paper and paperboard applications can be derived from natural resources using biotechnology. These organic fillers and pigments can be used as substitutes for inorganic fillers and pigments to improve the recyclability and other properties of paper products.

Wastewater Treatment Various biotechnologies are already playing a major role in the treatment of agricultural and municipal waste (bio-remediation), and this role is expected to expand considerably as methods are continuously developed and deployed for bio-remediation of all kinds of industrial effluents, including those from pulp and paper mills. Biotechnological processes are usually deployed in secondary or polishing treatments that follow sedimentation or other primary treatment. They include aerated stabilization basins, activated sludge, oxygen-activated sludge, trickling filters, rotating biological contactors, anaerobic filters and anaerobic fluidized beds. All these systems are based on complex microbial communities.

Bio-refining Global developments, such as increasing oil and energy prices, concerns about greenhouse gas emissions and decreasing prices for pulp and paper products have reinforced the urgency for traditional pulp and paper manufacturers, particularly those in temperate zones, to change their business concepts, not least because their competitors in tropical regions have started using advanced, large-scale facilities and have wood and labor-cost advantages. The new concept foresees the transformation of a chemical pulp mill into an integrated forest bio-refinery that in addition to pulp could also produce higher value-added commodity products, such as biofuels, biopolymers and green chemicals.

Conceptually, bio-refining is similar to fossil oil refining, except that that biomass, the feedstock for bio-refining, is in principle renewable and carbon-neutral. So far, the chemicals in wood that are dissolved during pulping are, with limited exceptions, only used for energy production. But dissolved lignins, hemicelluloses, sterols, prenols, flavonoids, tannins, stilbenes and many other substances can after further processing be developed into families of functional, 'green' chemicals. Although pulp and paper mills can be considered bio-refineries at a nascent stage, they are not yet true bio-refineries, as such categorization still requires substantial R&D efforts and relatively high capital investments. Eventually, it might even be possible to produce carbon dioxide-free paper. Figure 2.1 provides a schematic representation of an advanced forest bio-refinery.

FIGURE 2.1 Advanced forest bio-refinery

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Raw Materials and Production Processes

Introduction

This section will first examine developments in forest biotechnology for the production of wood as feedstock for the pulp and paper industry. This will be followed by a review of alternative, non-wood feedstock options that are currently being investigated for the pulp and paper industry. This section will close with a review of biotechnological alternatives to chemical pulping and bleaching.

Forest Biotechnology

Paper consists of a web of pulp fibres derived from wood or other plants from which lignin and other non-cellulosic components are separated by cooking them with chemicals at high temperatures. In the final stages of paper making, an aqueous slurry of fibre components and additives is deposited on a wire screen and water is removed by gravity, pressing, suction and evapouration. The fibre properties of the raw material affect the quality and use of the paper. For fine paper, both long and short fibres are needed. The long fibres from softwoods (coniferous trees) or from non-woody species such as flax, hemp and kenaf form a strong matrix in the paper sheet. The shorter hardwood fibre (deciduous trees) or grass fibres contribute to the properties of pulp blends, especially opacity, printability and stiffness.

Wood from forests has been a major feedstock of the pulp and paper industry, especially since the invention of the kraft chemical pulping process in the 1880s. But wood is also used for many other purposes, and it is vital to the world economy and human communities everywhere. But the pressure of human development and the growing demand for wood are contributing to the degradation of natural forests worldwide, creating serious dilemmas over future wood supplies.

Although wood is a highly prized commodity, the economics of its production have always been problematic (Fenning et al. 2002). Unlike conventional agriculture, it is usually cheaper to harvest trees from the wild than to plant and harvest, and this is often accomplished by clear cutting with little regard for the success of regeneration and other environmental consequences. Wood consumption is now exceeding the natural rate of regeneration in many areas. An alternative that has been pursued is plantation forestry, but this has not happened on the scale needed because of the long timeframes and heavy capital outlay involved. Large areas of land need to be dedicated to what would amount to a single crop, which only realizes its value once every few decades and can be lost to storms, diseases or fire at any time. To try and overcome these problems, governments have often undertaken planting schemes themselves, or encouraged others to do so with subsidies and tax breaks, but the scale of planting is still inadequate. Prospects of a bio-based economy might contribute to accelerate the scale of planting.

According to the FAO 2002 forest assessment, 43.6 million hectares of plantations existed throughout the world in 1990, while in 2000 this figure had increased to 187 million hectares. The FAO estimated the global annual rate of new planting at 4.5 million hectares to about 230-240 million hectares today, with Asia accounting for 70% of this growth, predominantly in China, Indonesia, Malaysia and Vietnam. In addition, an emerging trend

> ...the pressure of human development and the growing demand for wood are contributing to the degradation of natural forests worldwide, creating serious dilemmas over future wood supplies.

was observed that will advance the plantation system closer into what is often referred to as 'fast-wood forestry.' The biggest difference between fast-wood forestry and traditional plantations is how the trees are managed. Whereas in traditional plantation, a tree is planted and left to mature with only limited fertilization, weed control, thinning and pruning, fast-wood forestry requires intensive management throughout a rotation. This results in much higher per-hectare yields and much shorter periods between planting and harvesting. Fast-wood forestry plantations are usually harvested within 20 years of being planted, while traditional plantations have a 20- to 30-year rotation in tropical climates and a 40- to 80-year rotation in temperate zones. Figure 3.1 provides an overview of the trends in areas of productive forest plantations.

FIGURE 3.1 Trends in areas of productive forest plantations

Moreover, the potential for tree improvement has largely remained untapped so far, as most of the trees used even in plantations are still essentially wild, mostly coming from simple seed collections. The process of domesticating trees to human needs has only just started and similar improvements in yield of agricultural crops might well be possible. Nonetheless, the long generation times, self-incompatibility mechanisms and space requirements of trees make them more difficult to work with than other plants. In addition, there is a need to assess the wood quality and disease-resistance characteristics of mature trees. Only a handful of forest tree species are likely to be subject to further domestication and adaption to human needs, including Douglas fir (Pseudotsuga menziesii), Eucalyptus species, loblolly pine (Pinus taeda), Monterey pine (Pinus radiate), poplar species (Populus) and spruce species (Picea).

The two main objectives for domesticating forest trees are the need to understand the process of wood formation and the desire to shorten the juvenile phase. So far, progress has been made in breeding trees with for altered xylem-fibre lengths and lignin content, which is valuable to the pulp and paper industry. In turn, much less progress has been made in improving timber quality, precisely because wood formation is poorly understood. Advancements in the understanding of the genetics of flowering of trees have opened up the prospect of breeding trees in much less time than was previously needed, either directly by genetic engineering, or by some other treatment made possible by the knowledge gained.

Forest biotechnology is associated with a broad spectrum of modern methods applicable to agricultural and forest science and the technologies used can be grouped in five overlapping categories: propagation, molecular markers, marker-assisted selection and breeding (MAS/MAB), 'omics' (genomics, proteomics, metabolomics) and genetic modification (genetic engineering) (FAO 2010).

Propagation For centuries, plant cloning using grafts and cutting has been for the method for tree breeding and propagation. Some tree species are easier than others to propagate by cuttings—for instance, easy-to-root hardwood species like poplars (Populus spp.), willows (Salix spp.), some eucalypt (Eucalyptus) species, and conifer species like spruces (Larix spp.), redwood (Sequoia sempervirens) and some pines (Pinus spp.). These tree species are widely planted as cuttings in family or clonal plantations and, in the future, the use of vegetatively propagated trees for intensively managed high-yielding plantations is expected to increase in all regions of the world.

Micropropagation refers to the in vitro vegetative multiplication of selected tree genotypes, using organogenesis and/or somatic embryogenesis. About 34% of all biotechnologies activities reported in forestry over the past decade were related to these techniques, which are used to multiply desirable genotypes to create large numbers of genetically identically individuals of clones or varieties. Since vegetative propagation offers the opportunity to bypass the genetic mixing associated with sexual reproduction, micropropagation techniques have gained increased attention by foresters and tree breeders. Organogenesis methods, which involve in vitro culture of very small plant parts, tissues or cells—in particular, meristems—from germinating embryos or juvenile plant apices, have been developed for hardwoods such as poplars, willows and eucalypts and for conifers such as coast redwoods, radiata pine, loblolly pine and Douglas fir. Somatic embryogenesis methods, which involve in vitro culture of embryogenic tissue typically from immature seed, have been developed for hardwoods, spruces, larch, pines and Douglas fir. Although these techniques need to become more efficient, they nonetheless have the potential to produce unlimited quantities of embryos of desirable genotypes less expensively than current control-pollinated seeds.

Molecular Markers, MAS and 'Omics' The introduction of biochemical (terpenes, flavonoids) and Mendelian-inherited (allozymes) protein markers over the last thirty years has advanced evolutionary biology studies in forestry. In the last decade, the development of molecular markers based directly on DNA polymorphisms has largely replaced the use of biochemical and protein markers for most practical and scientific applications. This replacement was accelerated by the development of the polymerase chain reaction (PCR) that allows minute amounts of DNA molecules to multiply. Molecular markers have come in many forms and are now routinely used, mostly for estimating the genetic diversity in natural and artificial populations of tree species. It is estimated that about 25% of all forest biotechnology activities over the past decade were related to molecular marker applications, mainly focused on diversity. Other applications include the study of gene flow and mating systems, tracking clonal and seedling material in breeding programs, paternity studies, gene conservation and construction of genetic linkage maps.

Marker-assisted selection (MAS) and marker-assisted breeding (MAB) are methods in breeding that rely on the statistical association of molecular markers with desirable genetic variants. With the development of new and easily obtained molecular markers in the 1990s, the prospect for using MAS/MAB was bright; not so now, as more than two decades of research around the globe has slightly tempered this prospect.

Genomics is a rather recent field that encompasses a range of activities, including gene discovery, gene space and genome sequencing, gene function determination, comparative studies among species, genera and families, physical mapping and bioinformatics. The ultimate goal of genomics is to identify every gene and its related function in an organism. The completion of a whole-genome sequence for Populus trichocarpa in 2006 set the foundation for reaching this objective in poplar species. Such efforts have also been undertaken for eucalypt species and pine species, but progress has been slower due to their larger genome sizes.

Proteomics is the large-scale study of proteins expressed by the genes present in an organism—whether a microbe, a plant or an animal. Proteomics focuses primarily on understanding protein structure and function, which can also be of value to tree breeding. For example, a proteomic study with somatic embryogenesis in Picea glauca identified a series of differentially expressed proteins across different stages of embryogenesis. This knowledge might help researchers to better understand and manipulate the process of embryogenesis.

Metabolomics, the study of the unique biochemical fingerprints that specific cellular processes leave behind, can be used to understand variations that are induced by genetic or environmental factors. For instance, a metabolomics study with field-planted Douglas-fir found that environmental variation was greater than genetic variation. Metabolomics can also be a tool for determining the phenotype caused by genetic engineering, such as gene deletion or gene insertion.

Notably, 'omics' technologies require substantial investment and are usually done on a very large scale, primarily by commercial parties with highly trained laboratory staff, technology protection by intellectual property rights and vast bio-informatics and statistical capacity.

Genetic Engineering The use of genetic engineering for crop breeding has attracted great attention from both the scientific and lay communities. This is as true for forestry as it is for agriculture. In the public mind, genetic engineering is often considered synonymous with the term biotechnology. A major concern with genetic modification is the possible widespread gene transfer via escapes and hybridization with related native species, particularly in areas where inter-fertile species are present in the vicinity of a field with GM crops or a plantation with GM trees and when measures to prevent gene flow are not considered. Various approaches haven been researched to ensure molecular-biological containment, including genetically engineered sterility.

Compared with advances in genetic engineering of crops, forest genetic engineering is lagging behind, mainly due to much fewer resources, longer rotation times and significant hurdles to overcome with regard to efficient tissue culture and propagation techniques. Nonetheless, significant advances have been made with genetic engineering of several tree species such as poplar, birch, larch, pine and spruce. Traits included herbicide-tolerance, insect-resistance and modified lignin and cellulose content. A second wave of traits being researched now includes secondary cell wall characteristics (improved pulpability, increased cellulose content, better stability).

Forestry genetic engineering activities are taking place in at least 35 countries, 16 of which host some form of experimental field trials

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that are usually short of duration. In many countries, such trials must be destroyed before seed production occurs. In other countries, experimentation is restricted to laboratories or greenhouses. To date, only China has reported the establishment of approved, commercial plantations of GM insect-resistant poplar trees.

TABLE 3.1 Forest biotechnology transition, 2011 – 2021

Non-wood Feedstock for the Pulp and Paper Industry

The earliest information on the use of non-woody plant species for paper making dates back to 3,000 BC in Egypt, where pressed pith tissue of papyrus sedge (Cyperus papyrus L.) was the most widely used writing material (Saijonkari-Pahkala, 2001). Straw was used for the first time as raw material for paper around 1800. After the invention of new chemical pulping methods in the 1880s, paper could also be made from wood—and this quickly became the primary feedstock for papermaking. However, as in many countries wood is not available in sufficient quantities to meet the rising demand for pulp and paper, active research has been undertaken, particularly in Europe and North America, to find new, non-wood raw materials for paper production.

In China and India a large majority of the raw material used by the pulp industry comes from non-woody plants, mostly agricultural residues from monocotyledons, including cereal (rice) straw and bagasse from processed sugar cane. Bamboo, reeds and some grass plants are also grown or collected for the pulp industry. The main drawbacks that limit the use of non-woody fibres are certain difficulties in collection, transportation and storage.

TABLE 3.2 Annual dry matter (DM) and pulp yields of various fibre plants

Plant species	DM yield (tons/ hectare)	Pulp yield (tons/ hectare)
Wheat straw	2.5	1.1
Oats straw	1.6	0.7
Rye straw	2.2	1.1
Barley straw	2.1	1.9
Rice straw	3	1.2
Sugar cane waste (bagasse)	9	4.2
Bamboo	4	1.6
Elephant grass	12	5.7
Reed canary grass	6	3.0
Tall fescue	8	3.0
Common reed	9	4.3
Kenaf	15	6.5
Hemp	12	6.7
Temperate hardwood (birch)	3.4	1.7
Fast-growing hardwood (eucalypt)	15	7.4
Scandinavian softwood (conifers)	1.5	0.7

Source: Saijonkari-Pakhala (2001)

The most common plant species used for papermaking are coniferous trees and deciduous trees, while non-woody plants for paper production includes grasses and leaf fibre plants. Of several field crops studies, reed canary grass has been of the most promising species for fine paper production in Finland and Sweden, and cereal (wheat) straw and other grasses, like tall fescue and switchgrass, can also be used for that purpose. In central Europe, elephant grass has been studied as a raw material for paper and energy production. Table 3.2 compares the biomass productions capacity and pulp yields between non-woody species and woody species.

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Non-wood plant fibres can be divided into several groups depending on the location of the fibres in the plant: Grass fibres, bast fibres, leaf fibres and fruit fibres.

Grass Fibre Grass fibres currently used for papermaking are mainly obtained from cereal straw, sugarcane, reeds and bamboo. Wheat straw is used most in commercial pulping in North America and Europe, followed by rye straw and oats straw, whereas bagasse is the most used non-woody fibre source in Asia and South America. In the case of esparto grass (Stipa tenecissima L.), only leaves are used, whereas bamboo pulp is commonly made from the pruned stem and bagasse pulp from sugar cane waste. When grass species are pulped for paper making, the entire plant is usually used.

Bast Fibres Bast fibres refer to all fibres obtained from the phloem of the vascular tissues of dicotyledons. Hemp, kenaf, ramie (Boechmeria nivea L.) and jute (Corchorus capsularis L.) fibres are derived from the secondary phloem located in the outer part of the cambium. In flax, fibres are mainly cortical fibres in the inner bark, on the outer periphery of the vascular cylinder of the stem. Bast fibres must be isolated from the stem by retting, a process whereby micro-organisms release enzymes (pectinases) that digest the pectic material surrounding the fibre bundles, thus freeing the fibres. Bast fibres are used for paper when strength, permanence and other special properties are needed. Examples include lightweight printing and writing papers, currency and cigarette papers.

Leaf Fibres Leaf fibres are obtained from leaves and leaf sheaths of several monocotyledons, including both tropical and sub-tropical species. Strong Manila hemp, or acaba, is derived from leaf sheaths of Musa textilis L., and is mainly used in cordage and for making strong but pliable papers. Sisal is produced from vascular bundles of several species in the genus Agave, especially A. sisalana Perrine (true sisal) and A. foucroydes Lemaire (henequen). Leaves of esparto grass are used to make soft writing papers.

Fruit Fibres Fruit fibres are obtained from unicellular seed or fruit hairs. The most important is cotton fibre that is formed by the elongation of individual epidermal hair cells in seeds of various Gossypium species. The longest fibres of cotton (lint) are used as raw material for the textile industry, whereas the shorter ones (linters), as well as textile cuttings and rags are used as raw material for high-quality writing and drawing papers. Kapok is a fibre produced from fruit and seed hairs of two members of the family Bombaceae: Eriodendron anfractuosum produces Java kapok and Bombax malabaricum produces Indian kapok. Kapok fibres originate from the inner wall of the seed capsule.

Overall, hemp, flax, jute, sisal and abaca are among the most commonly used non-wood fibre sources in the manufacturing of high-quality pulps for specialty papers. Other non-wood plant species, such as alfalfa in North America, hemp and flax in Europe and acacia in Southeast Asia, might also be promising as feedstock for paper making (Peterson Rock et al., 2009; González-Garcia et al., 2010). However, the processing procedures for these non-wood species need further improvement, particularly regarding lignin composition in non-wood fibres, which is important for optimizing the pulping and bleaching processes (del Rio, J.C. et al., 2006).

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While the chemical structure of softwood and hardwood lignins is much better known, studies on non-wood lignin structure are comparatively scarce. In addition, chemical properties and pulping quality of non-woody plant materials fluctuate more than do those of woody species, mainly due to differences in growing conditions (soil type, nutrient levels, climate) and the development stage of the plant at time of harvest. High dry mass (DM) yield, which is important for the economics of production, is acutely affected by management practices such as harvest timing, fertilizer application, age of the crop stand and choice of the variety. For instance, low mineral content is a desired quality for raw material for pulp and paper making, and is a main consideration of breeding programs for fibre crops.

In addition, freshwater algal biomass and peels from oranges and lemons have been researched for use as a supplement in softwood and hardwood pulps (Ververis et al., 2007). The cost of these materials is about 45% lower than that of tradition pulp, resulting in a 0.9-4.5% reduction in final paper prices upon their addition to the pulp.

TABLE 3.3 Non-wood feedstocks transition, 2011 – 2021

Enzymes in Pulping and Paper Making

Traditional Pulping Processes Pulping for papermaking is a process of delignification of non-wood feedstock, whereby lignin is chemically dissolved permitting the separation of fibres. Paper pulp is actually an aggregation of the cellulosic fibres that are liberated from the plant material. The fibres are separated by treatments with alkali, sulfite or organic solvents, which partly remove the lignin and other non-cellulose components from the matrix. Fibres can also be separated through mechanical or chemi-mechanical pulping processes. After the fibres have been separated from the aqueous suspension, they are washed and bleached. For the final paper-making process a water suspension of different fibre components and additives is pressed and dried on a fine screen running at high speeds, and formed into a thin paper sheet. This procedure bonds the fibres into a layered network. The inter-fibre bonding is pivotal in determining the strength of the paper.

The choice of pulp type depends on the quality desired in the end product. In fine paper, the amount of short fibre (fibre lengths 0.6-1.9 mm) is 20-100%. Long fibres from softwoods (conifers) or non-wood plants (flax, hemp, kenaf) are necessary to form a matrix of sufficient strength in the paper sheet. The shorter hardwood fibres (deciduous trees, grass fibres) contribute to the opacity, printability and stiffness of the paper. In high-quality papers such as writing and printing papers, chemical pulps are used, whereas chemi-mechanical pulps are raw materials for newspapers. Moreover, recycled fibres are not as strong as virgin fibres due to a loss of the ability to hydrate the fibre, swelling and fibre flexibility that occurs in the paper forming and drying.

In mechanical pulping, the fibres are separated from the wood mechanically. Many processes are used, the simplest of which, stone-ground wood (SGW), involves grinding logs against a stone wheel at atmospheric pressure. However, there can be variations in the temperature or pressure during grinding, pretreatments with steam, enzymes or chemicals, or combinations of these. Chemical pulping processes are more complex than mechanical pulping, as the pulping chemicals must be recovered and the lignin that was extracted from the wood must be dealt with. Chemical pulps are much stronger than mechanical pulps because the fibres have been damaged less and can collapse to form a large bonded area with other fibres, but overall they are more expensive than mechanical pulps. For most grades of paper, the goal is usually to minimize the amount of chemical pulp and maximize the amount of mechanical pulp.

The primary chemical pulping method used today is kraft pulping. After debarking and chipping, the chips are sent to the digester to remove a substantial part of the lignin that binds the fibres together as well as the fibrils within the fibre cell wall layers. The waste wood and bark are sent to a hog fuel boiler as fuel. In the digester, the wood chips are exposed to 'white liquor,' a solution of sodium sulphide and sodium hydroxide. The pulping chemicals permeate the chips and enter the lumens of the fibre, where they dissolve lignin and hemicellulose and advance through the fibre to the interlamellar region, where they dissolve the lignin, thus separating the fibres. A washing step separates the mostly cellulosic fibres for possible bleaching and subsequent paper making or to be sold as market pulp. The remaining solution of the original pulping chemicals, now containing lignin and hemicellulose, is referred to as 'black liquor.' About half of the energy contained in the wood is present therein, and to capture this energy content, the black liquor is concentrated by evapouration to a solids content of around 80% (from about 20%), and then burned in a Tomlinson recovery boiler. The organic components of the black liquor burn to produce steam, and the inorganic components leave as a molten smelt. The latter, comprised mostly of sodium sulphide and sodium carbonate is dissolved in water (green liquor) and sent to a causticiser; lime (calcium oxide; CaO) is added to convert the sodium carbonate back to sodium hydroxide, which is then converted back to calcium oxide the lime kiln. The lime kiln itself typically uses fossil fuel to generate the heat required. That could be changing with biofuels derived from biomass gasification. The entire kraft pulping and recovery process is complex and wood cooking, pulping chemical recovery and liquor evapouration account for about one third of the total energy consumed by an integrated pulp and paper mill. Figure 3.2 provides a schematic representation of kraft chemical pulping and recovery processes.

FIGURE 3.2 Kraft chemical pulping and recovery processes

Several of the pulping processes are resource intensive in terms of water and energy usage, and they produce emissions to air and water, as well as solid waste. The main pollutants are NOx, SO_2, CO and CO_2 and particulate matter, while wastewater contains absorbable organically bound halogens (AOX) and is characterized by high biological and chemical oxygen demand (BOD and COD). Notably, chlorine emissions have been drastically reduced over the past decades, as many pulp and paper mills now use elementary chlorine-free (ECF) or totally chlorine-free (TCF) processes (EC 2007). While ECF bleaching involves the use of chlorine dioxide (ClO_2 produced from $NaClO_3$), alkaline, peroxide (H_2O_2) and oxygen in defined sequence, TCF involves the use of oxygen, ozone or peracetic acid and peroxide alone or with alkali.

Biocatalysts for Pulping Over the last two decades numerous applications have been investigated for fungal and enzymatic treatment of pulp. These include modification of pulp properties, such as improved fibre flexibility and fibrillation, decreased vessel picking from tropical hardwood pulps, improved drainage in recycled fibres, specific removal of xylan for dissolving pulp manufacture, facilitated bleaching of kraft pulp, enzymatic pulping of herbaceous fibres, enzymatic pitch removal and facilitated contaminant removal from recycled fibres. Table 3.4 provides an overview of biocatalyst applications in pulp and paper making.

TABLE 3.4 Biocatalyst applications in the pulp and paper industry

Bio-pulping For woodchip pre-treatment with fungi and/or enzymes the term bio-pulping has come into use. Studies suggest that this technology can cut energy consumption in mechanical pulping by approximately 30%, although the real effect of this application is still uncertain, mainly because the technology does not yet seem to be commercially mature (EC, 2007). The pre-treatment consists of biotechnological modification of the raw material with white rot fungi, like Ceriopsis subvermispora or Phanaerochaete chrysosporium, which are present in natural wood-decay processes. These fungi help overcome some of the drawbacks of mechanical pulping, namely poorer fibre-strength properties, high electrical energy requirements and the few wood species suitable for pulping.

In first instance, the bio-pulping focused on the use of white-rot fungi, which have complex extracellular ligninolytic enzymes (lignin peroxidase, manganese peroxidase, laccase) that can selectively remove or alter lignin and allow cellulose fibres to be obtained for further processing. Treating the wood with steam and creating a ventilation system provides a good environment for fungi to thrive in. Since the wood is softened through this bio-pulping when it goes to the final steps to be made into paper, the remaining steps of the process require less energy and less chemicals.

Enzymatic pre-treatment using cellullases, hemicellulases and pectinases have also been shown to enhance kraft pulping (Kenealy et al. 2003), as the process allows for better delignification of the pulp and reduction of bleaching chemicals without altering paper strength. Cellulases have been tested on mechanical pulps as well, showing an increased brightness and decreased energy consumption. Other enzymes, such as laccases and proteases, have been reported to reduce energy requirements as well, while laccase treatment has the additional benefit of increasing fibre bonding, which enhances the strength of the paper.

The use of enzymes in the refining of virgin fibres has been ongoing for decades. Kraft pulp has been treated with cellulases and xylanases, and both enzymes can help to reduce the energy required for further refining. Xylanase treatments are generally more effective on unbleached pulps than they are on bleached kraft pulps.

The yield of thermomechanical pulping can also be increased by the use of enzymes, Using an acetyl esterase was shown to precipitate the galactoglucomannan of Norway spruces onto the fibre and increase the yield from the process.

Dissolving pulps are derived from pulps that contain a high level of cellulose. Traditionally, these pulps are treated to form soluble reactive carbohydrate chains that are then extruded into fibres of films. The use of endoglucanase can decrease the viscosity and chain length and increase the reactivity of pulps made from eucalyptus and acacia.

Finally, microbial or enzymatic retting can pulp herbaceous fibres. Microbial retting is an ancient process that dates back to the beginning of human civilization and uses mixed microbial population with crude inocula. Fibres that are retted include flax and jute. Nowadays, selected microbial strains and/or purified enzymes, like cellulases, hemicellulases, pectinases and other polysaccharidases (endo-polygalacturonase), are used in retting. Enzymatic retting is faster and produces fewer odors, but it may not always be economically competitive with traditional methods.

Pitch Control Bio-pulping processes have also been shown to reduce the amount of pitch caused by substances, like wood resin, in the pulp (Gutiérrez et al., 2009). Generally, wood resin includes a complex mixture of chemical compounds, among which are alkanes, fatty alcohols, fatty acids, resin acids, sterols, terpenoids, triglycerides and waxes. These so-called lipophilic extractives cause pitch deposits along the pulp and paper-making processes. Pitch deposition is a serious problem since it is responsible for reduced production levels, higher equipment maintenance costs, higher operating costs and an increased incidence of defects in the finished papers, which reduces quality and benefits. Furthermore, process effluents containing wood extractives may be toxic and harmful to the environment.

Traditional methods to control pitch problems in the pulping and paper-making processes include deliberate storage of logs and woods in the mill before pulping (natural 'seasoning') and adsorption or dispersion of the pitch particles with chemicals, like alum, talc, ionic or nonionic dispersants, cationic polymers and other types of additives. During wood storage, the content of the lipophilic extractives is decreased because some of them are degraded by plant enzymes as well as by wood-colonizing micro-organisms. However, prolonged storage causes a decrease in pulp brightness and yield due to the uncontrolled action of the wood-colonizing microorganisms (fungi). The current industrial practice does, therefore, not include overlong log or wood storage times.

As an alternative, the use of selected fungi to accelerate and control the seasoning of wood as well as the use of enzymes to treat the pulp have been researched and developed. It is, however, far from easy to implement fungal and enzymatic technologies on an industrial scale, as there are significant differences in resin content and composition among tree/plant species and even among various parts of the tree/plant due to the growing conditions, age and other genetic and environmental factors. Thus far, particularly the resin content and composition of softwoods commonly used for pulping and paper making, such as Scots pine and Norway spruce, have been extensively studied. Whereas triglycerides, resin acids and fatty acids represent a high percentage of lipophilic extractives from Scots pine, Norway spruce lipophilic extractives contain triglycerides, resin acids and steroids. Extractives from hardwoods, like silver birch and trembling aspen, contain significantly higher proportions of sterols and other lipids than softwoods, and extractives from eucalypt contain mainly sterols and fatty acids. The chemical composition of lipophilic extractives from non-woody species used by the pulp and paper industry has as yet not been studied to the same extent as that of woody species, although knowledge has been increased over the last few years. For example, alkanes, fatty alcohols and aldehydes, sterols and waxes are the major pitch-causing compounds that have been identified in flax, hemp, kenaf, sisal and abaca. In summary, the nature and severity of pitch problems depend not only on the raw materials used, but also on the specific pulping and papermaking processes at the mill.

Fungal removal of lipophilic extractives from wood prior to pulping has been researched and developed to control pitch problems. Two different species of fungi have received the most attention so far: Sapstain fungi and white-rot fungi.

Sapstain, also called blue stain, is caused by pioneer wood-colonizing fungi, such as Ophiostoma, Ceratocystis, Leptographium or Sphaeropsis species, which utilize fatty acids, triglycerides, simple carbohydrates and other components of the sapwood. Biotechnological research for pitch control has so far focused mainly on Ophiostoma pileferum strains. This has, for example, led to the commercialization of an albino strain, Cartapip™, which was originally marketed by Sandoz Chemicals/Clariant Corporation and has been used for the past 15 years. The effectiveness of this and other strains to degrade both triglycerides and free fatty acids has been demonstrated on both softwood and hardwood species. On the other hand, Cartapip™ and other sapstain fungi seem unable to efficiently remove free sterols from hardwoods and resin acids from softwoods.

In addition to pitch reduction, albino strains of Ophiostoma pileferum and related species exert a bio-control effect, preventing sapstaining and other wood-rotting fungi from growing on logs and wood chips, because of their ability as an early wood colonizer, excluding late colonizers, like white-rot fungi, and other sapstaining species that cannot grow when albino strains are already present. When Cartapip™ is used as bio-control agent, it has the trade name Sylvanex™ .

Furthermore, the degradation of most of lipophilic wood extractives by white-rot fungi, such as Funalia trogii and Bjerkandera species, has been studied and demonstrated in Scots pine. In addition, the use of fungal species, like Phlebia radiata, Ceriporiopsis subvermispora, and Pleurotus pulmonarius, for pitch control from eucalypt species has shown additional benefits. Since these fungi not only remove resin but also lignin in eucalypt wood, their use results in energy savings in mechanical and chemical pulping.

One of the first enzymatic methods to control pitch in pulping and paper making was treatment of pulp by using a hydrolytic enzyme, namely lipase (Gutiérrez et al., 2009). A lipase commercialized by Novozymes under the trade name Resinase® A2X was successfully applied at mill scale for enzymatic pitch control in softwood mechanical pulping in Japan in the early 1990s. In Europe and China, pilot-scale trials for enzymatic pitch control in softwood sulfite pulping and groundwood thermomechanical pulping, respectively, also provided good results. More recently, Novozymes, through directed evolution, developed a Resinase variant that is more temperature-stable than the wild-type enzyme. Currently, Resinase® A2X and Resinase® HT are used in mills from North America, China, Japan and other countries.

While lipase treatments have been shown to reduce pulp triglycerides successfully, other pitch-causing compounds, like free and esterified sterols, resin acids, fatty alcohols, alkanes, etc., are also responsible for pitch problems. Several other lipases and sterol esterases have been suggested for pitch control. However, hydrolysis of sterol esters would increase the amount of free sterols, which have been shown to increase the viscosity and deposition tendency of wood resin. Therefore, enzymes acting from a broader range of substrates are being investigated.

Oxidoreductases constitute a class of enzymes that has been subject to research their application in pulping and papermaking, laccases in particular. However, their action is limited to the phenolic compounds in lignin that only represent a small fraction in lignin. After discovering the effect of some synthetic mediator compounds, including 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) and 1-hydroxybenzotriazole (HBT) that expanded the action of laccases to non-phenolic compounds, research efforts were stepped up because of this increased potential in the degradation of lignin. Recently, it was reported that for the first time the high efficiency of the laccase-mediator system for the removal of lipophilic extractives present in pulps from different origins regardless of the pulping process. In these studies, the laccase from the fungus Pycnoporus cinnabrinus in the presence of the mediator HBT was very efficient in removing free and conjugated sterols from eucalypt kraft pulp; triglycerides, resin acids and sterols from spruce thermomechanical pulp; and fatty alcohols from flax soda pulp. However, the use of HBT and related synthetic mediators is costly and has possible toxicity issues. Research for natural compounds has therefore become an objective, and some fungal mediators have already been suggested.

Recently, another class of enzymes consisting of lipoxygenases, which catalyze the oxygenation of unsaturated fatty acids and their esters, has been suggested for pitch control in softwood thermomechanical pulp. It was, however, found that some of the extractives, like resin acids, and lignin products may have inhibitory effects on these enzymes. Additional studies on lipoxygenases for pitch control are now underway.

Bio-bleaching A very common application of enzymes in pulping is to enhance bleaching, due in large part because of the extreme economic importance of kraft pulping worldwide and the environmental effects of chlorine bleaching. While the effectiveness of the use of xylanase as a pre-bleaching agent for pulp was demonstrated in 1986 and has been one of the success stories of enzymes in the pulp and paper industry, laccases and manganese peroxidases—either alone or in combination with low molecular weight mediators—have been made subject to research more recently (Kenealy et al., 2003).

Bleached kraft pulp is the largest component of paper manufacturing worldwide. Kraft pulping removes lignin, dissolves and degrades hemicellulose without damaging cellulose, and results in pulp fibres that are flexible, readily hydrated and the pulp matrix is accessible to enzymes used in further paper making. However, degradation products generated during kraft pulping become trapped in the pulp matrix and impart a brown colour to kraft pulp. Cooking consumes chemicals and residual xylan along with covalently linked degradation products (chromophores) precipitates on the surfaces of the cellulosic fibres. They are hard to extract because they become covalently bound to carbohydrate structures in the pulp matrix. Elemental chlorine (Cl_2) and chlorine dioxide (ClO_2) are used to bleach the chromophores. Chlorine bleaching can, however, cause environmental problems, as this leads to toxic and recalcitrant chlorinated aromatic hydrocarbons, including a minute amount of dioxins. Pulp manufacturers must, therefore, use special processes to remove them from effluent streams.

As an alternative, enzymatic treatment of pulp can reduce chemical demand in subsequent bleaching. For instance, xylanases are effective on both hardwoods and softwoods, but they have their greatest effect on hardwood kraft pulps. The degradation of hemicellulose appears to partially loosen the pulp structure, thereby enhancing lignin extraction, reducing chemical consumption and attaining higher brightness. For these enzymatic treatments, the purity of the xylanases is of high importance; cellulases should not be present, as they decrease pulp viscosity because of the removal of lower weight xylans. If pure xylanases are used, the mechanical strength of the cellulose fibres is not impaired, although they could weaken inter-fibre bonding. However, more research is needed to arrive at effective xylanases. First, they should be stable on kraft pulps. Some xylanases non-specifically absorb to pulp fibres and are inactivated by degradation products from kraft pulping. Second, they should have a neutral to alkaline pH optimum and good thermal stability. The pulp is hot (75 degrees Celsius) when it first comes out of the stock washers, and residual alkali leaks out of the pulp during enzyme treatment. The pH of even well-washed pulp stocks can shift dramatically. Third, factors affecting the interaction of the enzymes with the pulp are important. These include the effective molecular weight, net ionic properties and specific action pattern. Although xylanase pre-bleaching is used at various kraft mills worldwide, the working mechanisms are not yet completely understood. Nonetheless, research efforts are ongoing (Gallardo et al., 2010). The typical reduction in chemicals associated with the use of xylanases is about 15% active chlorine, but there is a limit of about 20% in chemical savings, which cannot be exceeded. Enhanced bleaching by xylanases as well as mannases has meanwhile become commercially worthwhile.

In general, the effect of xylanases of the final pulp brightness is considered indirect, as it removes reactants with the bleaching agent or obstacles to the bleaching action. Although there are some reports of direct brightening due to xylanase treatments, most of the direct bleaching with enzymes is done using oxidative enzymes that directly degrade the colour-producing compounds in the lignin, such as laccases and manganese peroxidases. These oxidative enzymes can also be used in pre-bleaching, which helps to reduce the use of chemicals in bleaching (Piscitelli, A. et al., 2010). The most important obstacles to commercial application remain the lack of sufficient enzyme stocks and the high cost of (synthetic) mediators.

Control of Microbial Fouling

Micro-organisms in pulp and paper mill water systems cause a buildup of biofilm slime, odor and corrosion (Kenealy et al. 2003). When micro-organisms approach inert surfaces, they first bind by weak forces involving their external structures such as flagella, fimbriae or capsular components. As they remain attached to the surface for some time, they excrete sticky extracellular polymeric substances (EPS), forming a biofilm matrix that embeds several layers of micro-organisms once the biofilms mature. EPS are composed of a wide variety of materials, including polysaccharides, proteins, nucleic acid, uronic acid and other substances (Molobela et al. 2010). The consequences of this microbial fouling are increased web breakages, holes and spots in paper as well as increased maintenance costs. Oxidizing and non-oxidizing biocides are generally used to control microbial buildup, and any deposits are traditionally removed by sodium hydroxide or dispersants. Inoculation of water systems with competing microorganisms or bacteriophages has been proposed, but the most feasible biotechnological approach appears to utilize enzymes to prevent aggregation of biofilm-producing microorganisms and degrade the extra-cellular polysaccharides they excrete. These enzymes include proteases and carbohydrases (amylases, glucanases, cellulases) and combinations of these enzymes are often applied. Due to the variety of the EPS produced by microorganisms, it is important that the structural components are known before the application of enzymes.

One approach for removal of slime from equipment is to produce sufficient slime from organisms isolated from the source, set up enrichments and select micro-organisms that will grow on it. This approach can provide a source of new enzymes to be used for cleaning such deposits.

TABLE 3.5 Enzyme technology transition, 2011 – 2021

Enzymes	Factors in 2011	Drivers and trends	Features in 2021	Impact
Bio-pulping Bio-bleaching Pitch control Microbial fouling control	Only a few enzyme-based technologies are commercially mature	Need to decrease inputs of energy and chemicals Need to reduce costs of machine maintenance and repair	Increased supply of commercially mature enzyme-based technologies	Reduction of the use of energy, chemicals and greenhouse gas emissions

Source: Pira International Ltd

4

Biotechnology Applications in Papermaking

Introduction

This section will first address the use of enzymes in fibre recycling, fibre modification, de-inking and stickies control. This will be followed by a review of the deployment biopolymers for coating of paper products. This section will close with a review of demand drivers that influence the use of biotechnology in paper making.

Enzymes in Fibre Recycling

The primary objectives in recycling paper are to remove ink and other contaminants while retaining optical and strength properties of the fibres. Enzymes can be used to enhance dewatering (drainage) rates, facilitate contaminant removal, and increase bond strength in recycled fibres. Drainage resistance of fibres has a negative impact on sheet formation, slows operation of the paper machine and increases drying energy. Likewise, de-inking and removal of contaminants can benefit from enzyme treatments that facilitate separation of fibres in the washing and flotation process.

Refining and Drainage Recycled fibres tend to have much lower drainage rates than virgin fibres, which slows the paper-making process. Treatment of recycled fibres with cellulases and xylanases can improve the drainage rate of recycled fibres, although their efficacy is highly dependent on the fibre type. Since mechanical fibres are much more resistant than chemical fibres to enzymatic activity, such treatments are most effective with kraft fibre, while they can increase handsheet density and reduce coarseness with minimal effects on strength (Kenealy et al., 2003).

Moreover, starches used in sizings can accumulate in the treatment water of fibre recycling mills and interfere with drainage. In such instances, alpha-amylase can improve drainage properties. Amylase treatments have been shown to increase the drainage of recycled paper pulp, allowing the paper machines to run faster.

It has further been reported that mixes of cellulases and hemicellulases can help to improve drainage of pulps from old corrugated containers and liner boards and to allow a lower amount of polymeric additives to be used to strengthen the paper. The use of these enzymes can be a problem with anionic surfactants that are often used during recycling, whereas the use of cationic or nonionic surfactants enhances their activity.

A commercial cellulase enzyme preparation (Pergalase A-40) based on Trichoderma has been used in several mills to improve drainage. These types of enzymes are applied after the refining and beating of the pulp, mainly to improve the dewatering (Pramod, B.K., 2011). Recently, a cellulase enzyme with endoglucanase activity (FibreCare® D), developed by Novozymes, has been reported to substantially increase the runnability of recycled furnishes and reduce the amount of steam used in drying paper or treating the pulp with enzyme after refining.

De-inking Of the wide variety of fibres and contaminants that are present in the recovered paper, like mixed office waste (MOW) paper, it is the toners and other non-contact polymeric inks from laser-printing processes that are the most difficult to deal with. Toner and laser printing ink are synthetic polymers with embedded carbon black that do not readily disperse during conventional pulping

The primary objectives in recycling paper are to remove ink and other contaminants while retaining optical and strength properties of the fibres.

processes and alkaline de-inking processes. Moreover, they are not readily removed during flotation or washing either. Because of these problems, recovered papers contaminated with non-contact inks have a relatively low market value. Moreover, conventional de-inking uses surfactants to float toners away from fibres. It further uses high temperatures to make toner surfactants form aggregates as well as high-intensity dispersion for size reduction. Most of the de-inking chemicals and high-energy dispersion steps are relatively expensive.

As an alternative, the use of hydrolytic enzymes, like cellulases, hemicellulases, pectinases, amylases and lipases, can enhance de-inking of recycled fibres (Pala et al., 2003). Also laccase, an oxidative enzyme, is being tested for de-inking purposes (Nyman et al., 2011). According to their specificity, these enzymes can either act directly on the fibres or on the ink film. However, a thorough enzyme selection and the optimization of the process are generally needed in order to achieve a good quality final product. Different pulps may react differently to similar de-inking protocols, either chemical or enzymatic, although the enzymatic process depends more critically on the furnish characteristics than the chemical ones. Considering the wide variability on the industrial wastepaper supplies, this is probably the most important disadvantage of enzymatic de-inking. Nonetheless, enzymatic de-inking can be as effective as chemical de-inking, although the results depend on the types of enzymes used (Pala et al., 2006). The hydrolytic activity is frequently associated to a reduction on the paper mechanical properties. On the other hand, the drainability of enzymatic-treated pulp is better. Balancing these effects, enzymatic de-inking is an alternative to the use of chemicals for de-inking because of its lower environmental impacts.

Stickies Control Recovered paper is recycled from various sources, including mixed office waste (MOW) paper, old newspaper (ONP) and old corrugated containers (OCC). The adhesives, glues, coatings and binders present in recycled paper can cause the accumulation of stickies in the pulp slurries. When stickies accumulate to larger particles, they cause problems in paper making and need to be removed from the paper machines.

An interesting enzyme application for stickies control has been developed by Buckman Labs. The enzyme is an esterase that targets polyvinyl acetate (a component of stickies), hydrolyzing the PVA to the less-sticky polyvinyl alcohol. As shown in Table 4.1, a coated paperboard mill using Buckman's Optimyze® technology experienced a US$1.33 million annual return by eliminating stickies.

TABLE 4.1 Estimated annual savings through stickies reduction using Optimyze®

Problem caused by stickies	Benefits of control	Annual saving ($US)
Reduced life of forming fabrics	Reduced four fabrics per year	100,000
Downtime for cleaning fabrics	Increase production	170,000
Chemicals used for cleaning	Replace chemicals	160,000
Paper machine downtime	Eliminate 45 breaks of 2 hrs per year	900,000

Note: Estimates made for a 400 tonne per day coated paperboard mill
Source: Patrick, 2004

Buckman's Optimyze® stickies control product was introduced to the paper industry in 2002 and won the Presidential Green Chemistry Challenge Award in 2004. The enzyme is now in use at many mills around the world (Patrick, 2004). There are no typical points in a mill's process to apply the enzyme treatments; this has to be determined on a case-by-case basis.

Fibre Modification

When properly applied, several classes of enzymes can enhance or restore fibre strength, reduce beating time and increase inter-fibre bonding through fibrillation. It is thereby important to achieve these objectives while increasing drainage rates and avoiding cellulose depolymerisation. Beating and refining are mechanical processes to improve paper strength by enhancing fibrillation and inter-fibre bonding. Pulp fibrillation by cellulases from the fungus Aspergillus niger was discovered as a means to enhance strength properties as early as 1959, and it was principally applied to cotton linters and other non-wood pulps. The main challenge in using enzymes to restore fibre bonding properties is to enhance fibrillation without reducing pulp viscosity, for example, by using 'cellulase-free' xylanase from mutants of the fungi Sporotricum pulverulentum and Sporotricum dimorphosphorum to defibreize pulp.

In the nearly 50 years since the pioneering studies describing the interaction of cellulases and cellulose fibres, there have been some limited successes in the application of cellulases to cellulose fibres. The more successful use of commercial cellulases has been in the textiles area, where cellulases have been adopted as a part of the garment wet-processing industry to provide special effects in finished garments, such as stone-washing of blue jeans. This application has taken advantage of the very aggressive nature of the cellulases produced by Trichoderma sp. fungal systems.

Meanwhile, research has led to a better understanding of the several types of cellulases and showed that multicomponent cellulases are probably best suited for cellulose hydrolysis of lignocellulose materials, while monocomponent cellulases are better suited for fibre modification (Esteghlalian et al., 2002). In some instances, these enzymes can be used to improve paper properties in specific ways. For example, tropical hardwoods contain large vessels that render a rough paper surface. During printing, these vessels prevent complete contact of the ink with the paper surface and lead to an imperfect image, which is of increasing significance as Brazilian eucalyptus pulps are being used in larger amounts. Cellulases can reduce this vessel picking.

Cellulases can be classified into two broad groups according to the specific function they perform. Endo-cellulases break internal bonds to disrupt the crystalline structure of cellulose to expose individual polysaccharide chains. Exo-cellulases, on the other hand, cleave two to four units from the ends of the cellulose chains, which results in much smaller tetra- or disaccharide molecules. The enzymes used in paper making are principally of the endo-cellulase type. A number of running applications in the paper industry are already using these fibre modification enzyme (FME) products, and the number of applications is growing (Hoekstra et al., 2008). When used to treat paper-making pulps, FMEs deliver a number of beneficial effects on the manufacturing process and paper properties. The main process-related benefits include a reduction in refining energy, substitution of expensive pulps by more cost-effective ones, an increase in dewatering, lowering of drying energy, and reduction in starch use. In some cases, increases in machine speeds and, therefore, productivity have been realised. Effects on paper quality include an increase in tensile strength, higher bulk, porosity and tissue softness. Successful applications result in delivering substantial return on investment for the paper makers.

The mechanism by which endo-cellulose can increase the strength of paper made from refined bleached pulps is thought to involve the random cleaving of internal bonds in the cellulose molecule, resulting in the disruption of the crystalline structure. This weakens the fibre surface in these regions, allowing a greater degree of fibrillation to occur when the fibre is refined. It may also be that the type of fibre fibrillation is subtly changed when compared to untreated refined fibre. Higher degree of fibrillation increases the sheet strength and allows the refining energy to be considerably reduced until sheet strength returns to desired levels. The enzyme is carried with the fibre stream and some may end up in the sheet where it is denatured by the heat applied during drying. Hence, no residual enzyme activity remains in the paper product. FMEs are typically applied at the pulping stage of the paper-making process. Fibre type, process temperature, pH, pulp consistency, contact time between the fibre and enzyme, and key process and paper quality parameters are taken into consideration before and during the treatment. As yet, FMEs are found to be most effective on chemically bleached fibre; few applications have been successful on other raw materials. This will undoubtedly change as other types of cellulases are produced. Currently, the focus has been on tissue manufacture, but the use of FMEs is spreading to other types of paper grades.

Since its emergence as a new technology and its first commercial use in Europe in 2007, the number of applications for FMEs in paper mills has grown significantly. Although the majority of applications are in mills using bleached pulps—and, with some exceptions in recovered paper—work is currently underway to identify enzymes that will also perform in mechanical pulps and recovered fibre.

FibreZyme G200 is an example of a high-performance enzyme custom designed to significantly improve the economics of pulp and paper production (Dyadic, 2011). It is a specially designed liquid cellulase preparation that is selectively active on wood cellulose to improve subsequent pulp refining and fibre-to-fibre bonding. For tissue operations, it allows mills to extract more value from wood fibres by improving softness while reducing the costs of production. FibreZyme G200 can reportedly be utilized to: enhance and restore fibre strength and increase inter-fibre bonding through fibrillation; increase paper machine production rates and efficiencies; allow for lower-cost fibre substitution and rationalization; reduce pulp refining energy requirements by 10% to 50%; improve softness in tissue production; restore fibre strength in dried market pulps that are hornified from the pulp drying process; enhance pulp drainage rates and reduce paper drying demand; decrease paper drying steam demand, and reduce petroleum-derived chemical usages.

Biotechnology Applications in Papermaking

Enzyme applications were also applied to black spruce thermomechanical pulping (TMP) to selectively enhance the physical properties of the resulting pulp (Sabourin et al., 2010). Previous studies revealed some application difficulties between pulp and enzymes. However, a recent study showed a new method of enzyme application, which involves fibreising the wood chips; the fibreised material is cooled prior to enzyme application to maximize its surface for enzyme reaction and to obtain optimal enzyme reaction temperatures. Fibreised chips are those that have been destructured in a converging screw chip press followed by low energy refining to produce extremely coarse fibre pulp. Adding a monocomponent pectinase enzyme was found to significantly improve various physical properties and increase the specific surface area of the resulting pulp. Interestingly, a multicomponent, more aggressive pectinase enzyme evaluated was less effective at enhancing physical properties. The new fibreising application method employed prior to enzyme application was found to reduce the specific refining energy requirements by 7%. When evaluated at a constant freeness, the enzyme treatment in conjunction with the new application method was found to reduce specific refining energy by about 9%. The enzyme application had only minimal impact on energy requirements. The enzyme application did significantly enhance the tensile and tear index of the resulting pulp. Dramatic increases in the amount of fibrillation and fibre surface disruption were also found to result from specific enzyme action upon the fibre. The resulting fibre wall thickness was reduced as a result of the enzyme action as well.

A recent study using two commercial enzyme preparations, Celluclast 1.5 L® (cellulases mixture) and Viscozyme L® (carbohydrases mixture), showed that eucalypt kraft pulp drainability can be improved by up to 80% at the same level of refining energy (Gil et al., 2009). Pulp degradation was evaluated by the pulp viscosity determination, which was in agreement with the fibre length determination that showed a slight reduction with the enzymatic treatment. The strength properties of the pulp were not affected by enzyme treatment; in fact, an increase was observed in paper internal bonding.

There is also growing interest in the use of laccases and peroxidases to polymerize or co-polymerize material with wood-based fibres (Kenealy et al., 2003). Attachment of guaiacol sulfonate using laccase made lignin more water soluble. Pulps were modified with 4-hydroxyphenylacetate in the presence of laccase, which increased water retention, tensile strength and burst strength of the resulting paper. Laccase has also been used for enhancement of the bonding in fibreboard made from Norway spruce and beech fibres, as well as for grafting of acrylamide onto lignin. The addition of methyl syringate (MS) in the presence of laccase significantly improved wet strength of pulp (Liu et al., 2009).

Moreover, a recent study demonstrated the potential of laccase-facilitated grafting of amino acids to high-lignin content pulps to improve the physical properties in paper products (Witayakran et al., 2009). Several amino acids were tested and histidine provided the best yield of acid groups on pulp fibre. Pulp treated with laccase-histidine showed an increase in strength properties of the resulting paper.

Biotechnology Applications in Papermaking

Brightness in totally chlorine-free (TCF) pulp is more unstable than it is in elemental chlorine-free (ECF) pulp, apparently by effect of the former containing greater amounts of oxidizable structures such as hexenuronic acids (HexA). Brightness reversion can be alleviated by using an effective biotechnological method involving an enzyme–mediator treatment (Cadena et al., 2010). The joint use of laccase from Trametes villosa and the mediator hydroxybenzotrialoze (HBT) in TCF pulp removes hexenuronic acids by 23% and reduces brightness reversion by 8.4%. Additional tests conducted to assess the effect of HexA on pulp refining revealed that these oxidizable structures introduce hydrophilicity in the pulp. Removing hexenuronic acids from TCF pulp alters its refining outcome in terms of drainability and water retention capacity, and results in paper with comparable strength-related properties that requires no additional refining energy.

Further, the use of manganese peroxidase in aqueous organic solvents allows the polymerization of guaiacol and other phenolic compounds and aromatic amines. The ability to function in organic solvents and modify polymeric compounds in the fibres, offers wider opportunities, but the bond formation in the polymerization process is difficult to control and direct (Kenealy et al., 2003).

Biopolymer Coatings

Paper is often associated with other materials, such as plastics and aluminium, for their good barrier properties that can be advantageously combined with paper stiffness. Paper products, like packaging materials, can be coated with ethyl vinyl alcohol (EVOH), a polymer with good oxygen-barrier properties. However, because of the polar groups of EVOH, which act hydrophilic, an additional polymer layer based on polyolefins is used to prevent water sorption. Polyolefins are generally chosen as paper-coating materials that overcome porosity and hygroscopicity of paper. Other paper coating materials are based on polyethylene, rubber latex and fluorocarbon.

In recent years, natural and renewable biopolymers have been the focus of much research because of the interest in their use as edible and biodegradable films and coating for food packaging (Kwaldia et al., 2010). Biopolymers, like proteins, polysaccharides, lipids or combinations of those components offer favorable environmental advantages of recyclability and reutilization compared to conventional, petroleum-based synthetic polymers. Polycaprolactone, polylactic acid (PLA) and cellulose derivatives have also been the focus of research (Andersson et al., 2009). Biopolymer-based films and coatings can act as efficient vehicles for incorporating various additives, including antimicrobials, antioxidants, colouring agents and nutrients. Biopolymers can be applied to paper or paperboard via various coating techniques, such as surface sizing, compression molding and curtain coating, depending on the appropriate coating material and type of paper used.

Protein-based Coatings Proteins can be successfully formed into films and/or coating and are suitable for coating fruits and vegetables, meats, eggs, nuts, other dry foods and paper packaging. Protein coatings on paper include milk proteins, wheat gluten, gelatin, corn zein and soy protein isolate (SPI). Protein-based coatings generally show an excellent oxygen barrier property at low to intermediate relative humidity as well as fairly good mechanical properties, but their barrier against water vapour is poor due to their hydrophilic nature.

Milk proteins, like casein and sodium caseinate (NaCAS), have several key characteristics in edible films and coatings, such as solubility in water and the ability to act as emulsifiers; they possess good mechanical properties as well. These properties make caseinate an attractive polymer for the coating of cellulose-based material for food packaging purposes.

Whey protein, a by-product of the cheese industry, is known as an excellent barrier to oxygen, aroma and oil and can be used as a coating material for improving the oxygen barrier property of food packaging. Compared to currently used sizing agents and pigment adhesives, whey protein may have some advantages. It forms an intact water-insoluble film out of aqueous solution, due to the formation of disulfide bonds after heat denaturation, resulting in a cross-linked structure of the whey protein. Studies have shown that whey-protein-coated paper improves packaging material performance by increasing oil resistance and reducing water vapour permeability. It has further been demonstrated that whey protein isolate (WPI) and whey protein concentrate (WPC) enhance the strength and toughness of the paper. WPI may replace commercial paperboard coatings, such as polyvinyl alcohol and fluorocarbon as grease and oxygen barriers while maintaining desirable colour and gloss.

Soy protein films generally have inadequate mechanical properties and are poor moisture barriers because of the hydrophilic character of soy protein. Nonetheless, paper coated with SPI (soy-protein-isolate) can function as a gas and oil barrier as well as exhibit adequate mechanical properties for extending the shelf life of food products. In addition, SPI coatings can be cross-linked by formaldehyde post-treatment or composited with organically modified montmorillonite to enhance mechanical and water vapour barrier properties of biodegradable films and coatings for food-packaging application. The more commonly used covalent cross-linking agents are glutaraldehyde, glyceraldehyde, formaldehyde, gossypol and tannic and lactic acids. However, using films treated with such cross-linking agents on food is highly questionable because of possible toxicity. Further research is needed to analyse the amount of chemical residue remaining in the film and the extent to which such residue could migrate to foods.

Wheat gluten has functional properties, like selective gas barrier properties, insolubility in water, adhesive/cohesive properties, viscoelastic behaviour and film-forming properties, and has been exploited in the development of edible coatings. Techniques have been developed for the production of paper-coating dispersions, in which wheat gluten is used as a binder. These suspensions show good film-forming properties, and the resulting coating has a strong adhesion to various substrates.

Corn zein protein coatings are used as oxygen, moisture and grease barriers for nuts, candies and other foods. Corn zein films and coatings have relative insolubility in water, and they form strong, glossy films resistant to grease and oxygen permeation. Corn zein coatings do not interfere with paper recycling, do not require separating protein and paper layers and have been suggested as an alternative to polyolefin materials.

Polysaccharide-based Coatings Polysaccharides are non-toxic and widely available. They are also excellent gas, aroma and lipid barriers. They form strong films, but because of their hydrophilic nature, they exhibit poor water vapour barrier properties. The polysaccharides used most often for paper coating include chitosan, alginates and starch.

Chitosan is derived by deacetylation of chitin, the second most abundant occurring biopolymer after cellulose. Chitosan films are tough, long-lasting and very difficult to tear. Most of their mechanical properties are comparable to many medium-strength commercial (synthetic) polymers. It has been reported that chitosan films can be used to increase the storage life of fresh produce and foodstuffs with higher water activity values. Chitosan exhibits good oxygen barrier properties due to its high crystallinity and the hydrogen bonds between the molecular chains and is a good barrier against grease as well.

Alginates, which are extracted from brown seaweeds, are the salts of alginic acid. They are resistant to solvents, oil and grease and exhibit interesting film-forming properties. Moreover, alginates can also act as a penetration controller when associated with pure starch. Alginates are generally used in sizing and/or coating paper to produce surface uniformity. Alginate combined with chitosan has been shown to increase the fat barrier of coated papers and, at the same time, reduce the treatment costs.

Starch is one of the most commonly used agricultural raw materials since it is inexpensive and widely available. Starch films have poor physical properties, but these can be improved by blending starch with cellulose derivates and proteins. Dispersion of starch granules is usually applied to function as a paper-coating agent with the main objective to smooth the surface of the paper without changing its barrier properties. The surface sizing treatment used native starch and modified starches to improve paper properties, like physical strength, oil/grease resistance and optical properties. The acetylation reaction, which allows the attainment of thermoplastic and hygroscopic materials to starch, can be used to decrease the hygroscopicity of starch-coated papers. There are also opportunities to coat paperboard with starch at a size press so that lamination is more effective, with better adhesion to the board, fewer defects and possibilities to decrease the weight of the laminate or advanced coating layer. Another strategy to overcome problems with defects such as pinholes, rips and deletions in barrier coating is to design self-healing features into the barrier layer (Andersson et al., 2009)

Lipid and Composite Coatings Lipid compounds, like long-chain fatty acids and waxes, can be incorporated in the film or coating matrix because of their hydrorepellency. Waxes are the most efficient substances to reduce moisture permeability. Their high hydrophobicity results from esters which contain a high content of long-chain fatty alcohols and acids as well as long-chain alkanes. Paper and paperboard, which are the most widely used materials in food and drink packaging, are frequently wax coated to improve their water resistance and increase the shelf life of packaged products. Lipid coatings provide a good moisture barrier, but they have certain disadvantages, such as brittleness, lack of homogeneity and presence of pinholes and cracks in the surface of the coating. Composite coatings or multilayer coatings, applied either in the form of an emulsion or in successive layers have been prepared to combine the good structural and gas barrier properties of hydrocolloid coatings with the good moisture barrier properties of lipids. The method of application affects the barrier properties of the coatings obtained.

Using a combination of corn zein and paraffin wax can lead to a bi-layer coating, in which the corn zein layer contributes grease barrier properties and the paraffin wax layer water resistance. It has further been found that adding a wax layer on paper already coated with NaCAS substantially increases water vapour barrier properties.

Biotechnology Demand Drivers Sustainable papers are one of the few categories of paper showing consistent growth trends in virtually every market around the world (Allen, 2010). Sustainability, as it relates to the paper industry, is, however, a relatively new concept and one that is still not familiar to many paper producers, consumers and others in the supply chain.

Historically, paper mills, their customers and the entire paper supply chain evolved primarily to get appropriate fibres out of the forest, to the mill, and the resulting product into the right hands in an economical fashion. The fact that harvesting vast numbers of trees has the potential to affect adversely the global environment and the forested area itself was not even imagined when many of today's paper mills were first built. Most mills have now been retrofitted with systems to reduce air and water pollution, among other changes, but the industry grew up over many decades with no awareness of the impact on the global climate of such emissions or the energy consumed in making paper. Pollution, energy consumption and the landfill implications associated with the transport of paper, printing or converting it, distributing the printed product and then disposing of it after its use, were previously only considered when there were immediate economic implications, e.g. when a paper mill installed a different power system to reduce exposure to a higher cost fuel.

Over the last decade, political and public concerns about environmental degradation, biodiversity loss and global warming have increased, resulting in a sense of urgency among many parties, including pulp and paper manufacturers, to address these problems. Allen (2010) noted that parties throughout the paper supply chain are committed to the concept of sustainability. Companies continue to implement policies related to sustainability, and those without such policies are beginning to add them.

Paper made from traditional sources, with no consideration given to its environmental attributes, might perform perfectly well for end users and in many cases could probably cost less than the price of equivalent 'sustainable' paper. Yet, buyers go to the trouble of sourcing papers based specifically on their environmental attributes. Two of the main demand drivers include pressure from environmental and nature conservation groups and increased sustainability reporting by corporations.

Biotechnology Applications in Papermaking

Since the early 1960s, pressure from environmental and nature conservation groups and other civil society organizations (CSOs) have made significant impacts on paper markets. They began then with campaigns against air and water pollution, and these CSOs implemented other initiatives from the 1970s until now, including the protection of natural habitats, the preservation of the world's forests, the mitigation of climate change and the use of certain biotechnologies, in particular, genetic engineering techniques in agriculture and forestry. These campaigns have awakened many businesses to the need to align their own processes with many of the CSOs' priorities. In addition, the insistence of some companies to do business in an environmentally responsible way may require their vendors to do the same.

In addition, increased sustainability reporting by corporations has raised the profile of these environmental issues. The U.S. Securities and Exchange Commission (SEC) has said it believes that companies 'should warn investors of any serious risks that global warming might pose to their businesses,' and private groups, such as the Global Reporting Initiative (GRI) and others, have been working on guidelines for sustainability reporting by corporations. Such oversight raises the incentive for companies to communicate their positive environmental actions through steps such as purchasing recycled paper or paper produced from certified sustainable forestry practices, as well as reducing their own greenhouse gas emissions or saving energy and/or water.

For these reasons, companies that buy and use wood fibre are paying much more attention to the environmental attributes of the paper they produce and sell, while their customers are much more attentive to the attributes of the paper they buy and use. In this context, biotechnology offers several promising tools to enhance the sustainability performance of pulp and papermaking processes by reducing the need for the use of energy, water and chemicals. Though, for the near future it can be expected that some biotechnology applications, particularly genetic engineering of trees and plants, will remain the subject of public and political controversies. As a consequence, it will be difficult in the to include GM non-woody biomass in commonly agreed standards and certification schemes for sustainable paper.

Allen (2010) further noted that the weak economic conditions since 2008 are likely to slow growth in sustainable paper usage in at least five ways:

1. Feeling that the effort of certification is not justified by an increased volume or pricing, some owners of woodland have postponed or slowed down efforts to get certified in the interest of reducing expenses;
2. The combination of volatile wastepaper prices and depressed end-product demand has forced some 100% recycled paper mills out of business, and led other mills that make recycled/virgin blends to reduce the proportion of recycled fibres in these blends;
3. Faced with revenue and cost pressures during the economic downturn and now, in many printing paper markets, with rising paper prices across the board, some paper buyers are probably reluctant to buy a significant quantity of paper at a price premium;

4. Now that economic conditions have improved at least a little from the recent downturn, some paper mills may be reluctant to sell paper products with value-added or specialized properties—and possible added costs—without recouping some price premium;
5. In some cases, small companies such as book and magazine publishers find the administrative effort and delays in getting individual titles certified to be daunting; some have postponed specifying certified paper in order to consider staff cuts and other ways to streamline operations.

5

Future Trends

Introduction

This section will examine the outlook for biotechnology in papermaking applications over the next five to ten years. It will first review the use of biotechnology for improving process efficiency and reducing energy and chemicals consumption, followed by a discussion of pulp and paper mills as emerging bio-refineries and the use of non-woody fibres for pulp and papermaking. This section will close with an outlook on the future of biotechnology in the pulp and paper industry.

Pulp and Paper Mills and the Environment

In 2007, the pulp and paper industry was the fourth largest industrial consumer of energy, consuming about 6% of total annual industrial energy use. However, unlike most other industrial sectors, the pulp and paper industry also produces energy as a by-product and already generates approximately 50% of its own energy needs from biomass residues. The main energy-consuming processes in the pulp and paper industry are: 1) chemical and thermochemical pulping; 2) mechanical pulping; 3) paper recycling, and; 4) paper production. Mechanical pulping uses large amounts of electricity, whereas chemical pulping yields black liquor as a by-product, which is then incinerated in a recovery boiler to produce heat and electricity. Depending on its recovery energy and its configuration, a chemical pulping mill can be a net energy producer.

As energy use can represent up to 35% of the production costs, there has always been an incentive for the pulp and paper industry to improve its energy efficiency. This has, for instance, led to the widespread adoption of combined heat and power (CHP) technologies that have allowed energy savings of more than 30% compared with conventional boilers. Furthermore, the pulp and paper industry is one of the largest producers and users of biomass fuels derived from residual woods, bark, black liquor and sludge. Overall, about 30% to more than 50% of the global energy use of the pulp and paper industry is derived from such biomass. Since fossil fuel and electricity prices and governmental policy efforts to reduce greenhouse gas emissions are expected to remain very important to the profitability of pulp and papermaking, most pulp and paper mills have created programs to improve the energy efficiency of their operations.

Almost half of all paper is produced from wastepaper, with recycling usually occurring where the wastepaper is generated. Recycling plants tend to be smaller and more dispersed than primary production plants, and their energy needs for making paper are higher. On the other hand, the energy that would go into pulping is saved. This saving by far exceeds the additional energy used. In many developed countries, paper recycling actually exceeds paper production from primary biomass.

Europe is the leader in paper recycling, while North America is the largest exporter of recovered paper, and Asia—especially China—is the main importer of recovered paper. The supply of recovered paper is heavily influenced by government policies on waste disposal and renewable energy. Tighter policies on waste disposal can lead to higher recycling rates, and policies promoting the use of renewable energy can cause competition for wood and fibre and thus affect the supply of wood pulp. There is mounting concern in the pulp

> As energy use can represent up to 35% of the production costs, there has always been an incentive for the pulp and paper industry to improve its energy efficiency.

and paper industry that the current push by governments toward increased use of renewable energy will encourage the use of wood as an energy source when new rather than at the end of its lifecycle.

Apart from wood (virgin fibres) and recycled fibres, other inputs for production include water and chemicals for various pulping, bleaching and paper-making processes, depending on the paper type produced. Table 5.1 provides an overview of chemical inputs in typical kraft pulp mill. Note that the figures are averages, as the mill-specific figures can vary greatly. In addition, in relation to bleaching, much depends on whether Elemental Chlorine Free (ECF) or Totally Chlorine Free (TCF) bleaching is used. Using ECF bleaching involves the use of chlorine dioxide (ClO_2 produced from $NaClO_3$), alkaline, peroxide (H_2O_2) and oxygen in defined sequence, whereas TCF bleaching used oxygen, ozone (or peracetic acid) and hydrogen peroxide alone or with alkaline. Moreover, regarding the use of recycled paper, there is additional chemical input of hydrogen peroxide and sodium peroxide.

TABLE 5.1 Chemical inputs in a typical kraft pulp mill

Chemical	Kilograms per ton pulp
NaOH	25 – 50
O_2	5 – 25
$NaClO_3$	20 – 50
EDTA	0 – 4
SO_2	2 – 10
H_2O_2	2 – 30
O_3	0 – 5
$MgSO_4$	0 – 3
CaO	5 – 10

Source: EC, 2007

Besides substantial inputs of water, energy and chemicals for production, pulp and paper mills produce discharges to water and air, in addition to solid waste. The main emissions to air are well known pollutants like NO_x, SO_2, CO, CO_2 and particulate matters, while some chlorine compound emissions are still reported (EC, 2007). Wastewater from pulp and paper mills is typically characterized by high biological and chemical oxygen demand (BOD and COD) and contains chlorinated organics (AOX), nitrogen and phosphor. The amounts of emitted substances are highly dependent on the choice of techniques and processes for delignification and bleaching. The use of chlorine has decreased significantly in the past years due to public concern, resulting in a decrease of the associated emissions. Most production today is based on ECF or TCF bleaching processes, while the use of elemental chlorine (Cl_2) has been practically abandoned.

As previous sections suggested, biotechnology tools can enhance the performance of several processing steps in the pulp and paper-making industry by reducing the use of energy and/or chemicals, in particular the application of enzymes. Although there are already many commercially available enzymes, their present application by pulp and paper manufacturers is still rather limited.

The most mature enzyme technologies are probably the cellulose-aided and xylanase-aided processes in terms of low running costs, low investment needs and high productivity. Based on available data, estimates were made for three archetypical pulp and paper mills in Europe in terms of economic and environment effects of the deployment of xylanases in chemical ECF pulping, mechanical

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pulping and the fibre production from recycled paper (EC, 2007). Table 5.2 summarizes the estimated economic and environmental effects of the use of xylanases in pulp and paper mills.

TABLE 5.2 Estimated economic and environmental effects of xylanases in pulp and paper processing (€)

Notably, in bleaching of chemical pulping, the economic cost-effectiveness of completely substituting chemicals with xylanases is actually positive, even before the inclusion of the environmental effects. It represents an example of an application of enzymes, where factors other than average production costs stand in the way of fulfillment of the potential (EC, 2007). Furthermore, in mechanical pulping, the saved energy expense is not sufficient to tip the scale in favor of cellulases. The price gap is rather big and a price subsidy on cellulases in this use must have the magnitude of 70% to make it as cheap as the chemical alternative. On the other hand, there might be associated social welfare gains for reducing carbon dioxide emissions, but it was not possible not assess them. Moreover, enzymatic de-inking was assessed to hold neither economic advantages nor disadvantages in comparison to the chemical alternative.

It should be noted that this limited assessment was based on studies and observations dating to the end of the 1990s. Further research and development of enzymes for the pulp and paper industry and their commercialization may well have improved the performance of enzyme usage in various processing steps over the last years. Yet, the number of reports with empirical evidence from studies that compare more recent enzymatic processes versus chemical processes is limited. The picture of the quantitative environmental characteristics of enzyme processes in industry presented in the literature is actually pieced together by relatively few enzyme applications.

A recent study by Skals et al. (2008) addressed this unsatisfactory situation with a systematic study of the environmental opportunities of enzymatic processing in the pulp and paper industry by quantitative means where data are available and by qualitative means where data are absent or incomplete. The results of this study should be seen as quite rough indications (particularly for refining) because the impacts of pulp and paper productions and the effects of using enzymes depend on the raw material basis, mill setup, etc., and are subject to variation as well. The study results suggested large relative environmental improvement potentials of enzyme use in bleaching and refining of pulp and moderate relative improvement potentials in de-inking and control of pitch and stickies. The study results further suggested a considerable potential for the application of enzymes for peroxide removal, fibre modification, anionic trash control, starch removal, drainage improvement, starch preparation and slime control.

Table 5.3 provides an overview of the potential avoidance of greenhouse gas emissions for various enzymatic processes for which quantitative data were available, whereas Table 5.4 provides an overview of the enzyme applications that were subject to qualitative environmental assessments.

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TABLE 5.3 Reduction in greenhouse gas emissions using enzymes in pulp and paper processing

TABLE 5.4 Benefits of using enzymes in pulp and paper processing

According to Skals et al. (2008), the penetration of enzymatic processes in the pulp and paper industry is still modest. The main drivers for acceptance usually include problems complying with governmental regulations and downtime for pulp and paper machines that cannot be resolved with conventional methods. The main barriers for their acceptance are that too few are playing a role in the promotion of new technology, with service providers being the most important. To achieve greater penetration of enzymatic solutions, awareness of the potential of enzyme technology in the pulp and paper industry should be amplified. One way to heighten awareness is to integrate enzymatic production methods in the relevant Best Available Technology (BAT) notes within the framework of the European Directive on Integrated Pollution Prevention and Control (IPPC) as experience of full-scale production increases.

Pulp and Paper Mills as Bio-refineries

For some years, the global pulp and paper industry supported by governments and public research institutions has been working at taking better advantage of its own forest and processes wastes. The bio-refining of biological wastes, including both mill waste and those from other sources, offers a way of generating new products, including heat, electricity and synthetic gas for chemicals and liquid fuels. While not a new concept to industry in general—or the pulp and paper industry in particular— bio-refining has now assumed much greater urgency than before because of the rapid increase in the price of fossil fuels and because of pressures from markets and governmental policies and regulations to reduce greenhouse gas emissions (Schenkelaars, 2007; Baum, 2008).

Conceptually, bio-refining is similar to fossil oil refining, except that biomass—the raw material for bio-refining—is, in principle, renewable while carbon neutral and fossil oil are not. Although pulp and paper mills can be regarded as bio-refineries at a nascent stage, turning them into full-fledged bio-refineries (see Figure 2.1) still requires substantial research and development activities, as well as huge capital investment. Compared to Black Liquor Gasification (BLG) technologies, where the simplest application is to replace the recovery boiler with a gasifier, implementation of the concept of integrated forest bio-refinery, including BLG, highly likely requires the design and building of new mills (Schenkelaars 2007). However, in the end it might even be possible to produce 'carbon dioxide-free' paper (Farahani 2004).

While most pulp and paper manufacturing facilities (in the USA) today do not export electricity and none export transportation biofuels, their established infrastructure for collecting and processing biomass resources provides a strong foundation for gasification-based bio-refineries. If the biomass resources from which energy carriers are produced in such bio-refineries are sustainably grown and harvested, there would be few net lifecycle emission of carbon dioxide associated with bio-refineries and their products. To the extent that the bio-refinery products replace fossil fuels and fossil fuel-based chemicals, there would be net reductions in carbon dioxide emissions from the energy system as a whole. The reductions would be even more significant if by-product carbon dioxide generated at bio-refineries were to be captured for long-term underground storage. Table 5.5 provides an overview of some bio-refining for the pulp and paper industry.

TABLE 5.5 Bio-refining opportunities for the pulp and paper industry

Bio-based feedstock	Bio-refining processes	Bio-based products
Forest residues	Aerobic digestion, composting	Fuel gas
Debarking waste	Anaerobic digestion	Acetic acid
Waste wood chips	Biomass gasification	Propanediol
Black liquor	Black liquor gasification	Butanol
Paper mill residues	Combustion	Ethanol
Sawdust	Fast pyrolysis	Lactic acid
Mill wastewater	Fermentation of lignocellulose	Succinic acid
Wood chips	Lipid extraction	Hyroxyproprionic acid
Tall oils	Thermochemical liquefaction	Polyhydroxyalkanoate
Turpentine	Vitrification, fibre composite	Pyrolytic bio-oil; composite materials, specialty chemicals (sterols, suberin, prenols, flavenoids, tannins, stilbenes, lignans and other aromatic compounds)

Source: Pira International Ltd.

Non-woody Biomass as Feedstock

Within an emerging bio-based economy, current concern in the pulp and paper industry might bolster the push by governments toward increased reliance on renewable energy, such as the use of wood when it's new rather than at the end of its lifecycle. Moreover, there is a rising demand for pulp and paper. As a consequence, pulp and paper manufacturers in North America, Europe and other regions have initiated research to find non-woody raw materials for paper making.

In 2004 the worldwide production of paper and paperboard amounted to about 310 million tonnes, with 30% produced in North America, 30% in Europe, 30% in Asia, 5% in Latin America and 5% in other countries (Blanco et al., 2004). Although total production has slowed slightly since 2000, the annual increase since 1994 has been about 3%. Almost 50% of the raw materials involved in paper making in North America and Europe were recovered fibres from recycled paper; the rest is mainly virgin wood fibres and non-woody fibres (< 2%). In particular, China and India are leaders in the utilization of non-woods for paper making in terms of volume. In North America, Latin America, Europe, the Russian republics and Africa, the use of non-wood fibre sources has been relatively limited. In 2004, non-woody fibres represented about 6.5%-11% of the world's virgin fibre production. But in developing countries or countries with few forestry resources, non-woody fibres made up 33% of total pulp production.

In developed countries, non-woody fibres are primarily used for the production of specialty papers, such as tea bags, filter papers, bank notes, etc. On the other hand, there is a growing need, particularly in North America and Europe, to consider alternative strategies that move an agricultural industry purely focused on food production to one that supplies the needs of other industrial sectors, like paper and textiles. Non-woody fibres could therefore gain importance as raw materials in this transformation to a bio-based economy (Ververis et al., 2003; NCASI, 2009; Marques et al., 2010).

The main sources of non-woody raw materials are agricultural residues from monocotyledons, including cereal straw and bagasse, or plants grown specifically for the fibre, such as bamboo, reeds and some other grass plants, like flax, hemp, kenaf, jute, sisal or abaca. Conditions in most developing countries are more economically favorable for non-wood fibre use than they are in more advanced countries. For the near future, it is likely that Asia and the Pacific region will remain the largest user of non-wood fibre sources. Native non-wood species suitable for fibre production exist in this region, and the technology to utilize them for fibre already exists. India and China are likely to remain the two countries that rely most on non-woods. Non-woods also have the potential to increase in importance in Latin America and in Africa, where technology is being introduced and choices for capital investment are being made. These regions have the necessary climate and long growing seasons necessary to make non-woods an attractive alternative to pulpwood forest plantations. The North American and European regions are unlikely to use non-woods extensively because of the climate in these regions and the presence of existing, highly developed wood production and processing technologies.

The Outlook for Biotechnology in Pulp and Paper

The pulp and paper industry has suffered from persistent low profitability in North America and Europe for many consecutive years (Uronen, 2010). Companies have been forced to close down excess capacity, reduce costs and divest non-core assets, and the whole industry is considered to be in crisis and in need of transformation in the developed countries. Industry transformation and strategy renewal are thus needed in order for the industry to return to healthy profitability. Reduction in costs and overcapacity will need to be continued, certainly, but companies need to develop entirely new products or reengineer their business models to reduce costs enough to avoid further commoditization of their products and services.

Research and development efforts have been intensified to find new products and entire new businesses, such as biofuels. In the near future, the bulk of the industry's revenues will continue to be generated from the traditional pulp, paper and board products. However, further advances of white biotechnology and the adoption of biocatalysts by the pulp and paper industry could enhance the economic and environmental performance of several processing steps as well as develop new paper products. Moreover, the bio-refinery concept offers a promising outlook for the pulp and paper industry to make use of fibres from both woody and non-woody biomass and to produce not only paper products but also biofuels and 'green' chemicals.

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TABLE 0.1 Biotechnology transition table, 2011 – 2021

Technology	Factors in 2011	Drivers and trends	Features in 2021	Impact
Forest biotech: Micropropagation Marker Assisted Selection (MAS) and Marker Assisted Breeding (MAB) Genetic engineering	Need to increase efficiency and productivity of wood production in plantations Domesticating trees has only just started Poor understanding wood formation processes Desire to shorten juvenile phase and to increase resistances to (a)biotic stresses Using MAS/MAB technologies is not controversial in contrast to genetic engineering	Wood consumption is now exceeding the natural rate of regeneration Demand for wood will increase not only because of increased demand for pulp and paper and timber but also because of increased demand for bio-energy, including cellulosic-bioethanol	Wood production is shifted to Latin America (and Africa) GM trees are not only grown commercially in China but also in Latin America	Availability of faster growing trees with characteristics like improved pulpability and increased cellulose content helps to increase efficiency of pulp and papermaking
Non-wood feedstock: Straw from wheat, oats, barley, rice Bagasse from sugar cane and sugar beet Reeds and grasses Hemp and kenaf	Insufficient availability of wood for pulp and papermaking in North America and Europe Pulp and papermaking in China and India traditionally largely based on non-wood feedstocks	Difficulties with collection, transportation and storage of non-wood feedstocks involve profound organizational and logistical issues Increased understanding of lignin composition of non-wood feedstocks helps to improve pulping and bleaching	Increased usage of non-wood feedstocks by pulp and paper industries not only in China and India but also in North America and Europe	With a view to high demands for wood from various industries, non-wood feedstocks offer alternative input options for pulp and papermaking
Enzymes: Bio-pulping Bio-bleaching Pitch control Microbial fouling control	Only a few enzyme-based technologies are commercially mature	Need to decrease inputs of energy and chemicals Need to reduce costs of machine maintenance and repair	Increased supply of commercially mature enzyme-based technologies	Reduction of the use of energy, chemicals and greenhouse gas emissions

Source: Pira International Ltd.

TABLE 2.1 Common enzymes, their reactions and applications

Type of enzyme	Substrate	Reaction catalyzed by the enzyme	Industrial applications
Proteases	Protein	Proteins are degraded into shorter fragments, peptides and eventually amino acids	Detergents, food, pharmaceuticals, chemical synthesis
Carbohydrases (cellulases)	Carbohydrates	Conversion of carbohydrates into sugar	Food, feed, pulp and paper, textiles, detergents
Lipases	Fats	Hydrolysis of fats into fatty acids and glycerol	Food, effluent treatment, detergents
Pectinases	Pectins	Clarification of fruit juices	Food, beverage
Cellulase	Cellulose	Hydrolysis of cellulose	Pulp, textiles, feed, detergents
Amylases	Starch	Hydrolysis of starch into smaller carbohydrates, like glucose and maltose	Food

Source: Pira International Ltd.

TABLE 3.1 Forest biotechnology transition, 2011 – 2021

Forest biotech	Factors in 2011	Drivers and trends	Features in 2021	Impact
Micropropagation Marker Assisted Selection (MAS) and Marker Assisted Breeding (MAB) Genetic engineering	Need to increase efficiency and productivity of wood production in plantations Domesticating trees has only just started Poor understanding wood formation processes Desire to shorten juvenile phase and to increase resistances to (a)biotic stresses Using MAS/MAB technologies is not controversial in contrast to genetic engineering	Wood consumption is now exceeding the natural rate of regeneration Demand for wood will increase not only because of increased demand for pulp and paper and timber but also because of increased demand for bio-energy, including cellulosic-bioethanol	Wood production is shifted to Latin America (and Africa) GM trees are not only grown commercially in China but also in Latin America	Availability of faster growing trees with characteristics like improved pulpability and increased cellulose content helps to increase efficiency of pulp and papermaking

Source: Pira International Ltd.

TABLE 3.3 Non-wood feedstocks transition, 2011 – 2021

Non-wood feedstock	Factors in 2011	Drivers and trends	Features in 2021	Impact
Straw from wheat, oats, barley, rice Bagasse from sugar cane and sugar beet Reeds and grasses Hemp and kenaf	Insufficient availability of wood for pulp and papermaking in North America and Europe Pulp and paper making in China and India traditionally largely based on non-wood feedstocks	Difficulties with collection, transportation and storage of non-wood feedstocks involve profound organizational and logistical issues	Increased understanding of lignin composition of non-wood feedstocks helps to improve pulping and bleaching Increased usage of non-wood feedstocks by pulp and paper industries not only in China and India but also in North America and Europe	With a view to high demands for wood from various industries, non-wood feedstocks offer alternative input options for pulp and papermaking

Source: Pira International Ltd.

TABLE 3.4 Biocatalyst applications in the pulp and paper industry

Process stage	Biocatalyst	Benefits
Raw material pre-treatment:		
Debarking	Pectinases	Energy and raw material savings
Wood preservation	Fungi	Environmentally benign methods
Mechanical pulping:		
Pre-treatment	Fungi	Pitch removal, energy savings
Refining	Cellulases, lipases	Energy savings, improved quality
Chemical pulping:		
Bleaching	Xylanases Laccases	Improved brightness, chemical savings, increased capacity, reduced AOX formation
Papermaking:		
Drainage	Cellulases	Chemical savings, improved quality
De-inking	Hemicellulases	Chemical savings
Wet end chemistry management	Various enzymes	Improved runnability, slime control, improved quality, chemical savings

Source: EC, 2007

TABLE 5.2 Estimated economic and environmental effects of xylanases in pulp and paper processing (€)

Costs to treat 1,000 tonnes of raw material input	Chemical pulping	Mechanical pulping - reject refining	Recycled paper - de-inking
	Substitution of bleaching chemicals with xylanases	Energy conservation through the use of cellulases	Substitution of hydrogen peroxide and sodium hydroxide with cellulases
Economic effects			
Chemical savings	2,000		2,200
Enzyme costs	675	2,200	2,200
Energy savings		600	
Total economic costs	1,325	- 1,600	0
Environmental effects			
AOX high / medium / low	135 / 73 / 28		
CO2 reduction		++	
Total environmental costs	135 / 73 / 28	0	0
Socio-economic value	1,460 / 1,398 / 1,353	- 1,600	0

Source: EC, 2007

TABLE 5.3 Reduction in greenhouse gas emissions using enzymes in pulp and paper processing

Process	Enzyme	Function	Reduction in greenhouse gas emissions	Relative improvement potential (%)
Bleach boosting of kraft pulp	Xylanase	Saves bleaching chemicals by degrading xylans and enhancing lignin extraction	37 kg CO_2-eq.ton pulp	7
Refining of TMP	Cellulase	Saves energy by softening cellulose fibres	145 kg CO_2-eq.ton pulp	22
Pitch control of TMP	Lipase	Saves downtime and cleaning pitch by hydrolysing pitch	8.7 kg CO_2-eq.ton pulp	0.7
De-inking	Cellulase	Saves conventional de-inking chemicals and releases ink	6.4 kg CO_2-eq.ton pulp	0.4
Stickies control	Esterase	Saves chemicals and energy during downtime by hydrolysing PVAc	13 kg CO_2-eq.ton pulp	0.8

Note: TMP = Thermomechanical pulp. Reduction in GHG emissions as compared with chemicals used in typical chemical processing steps.

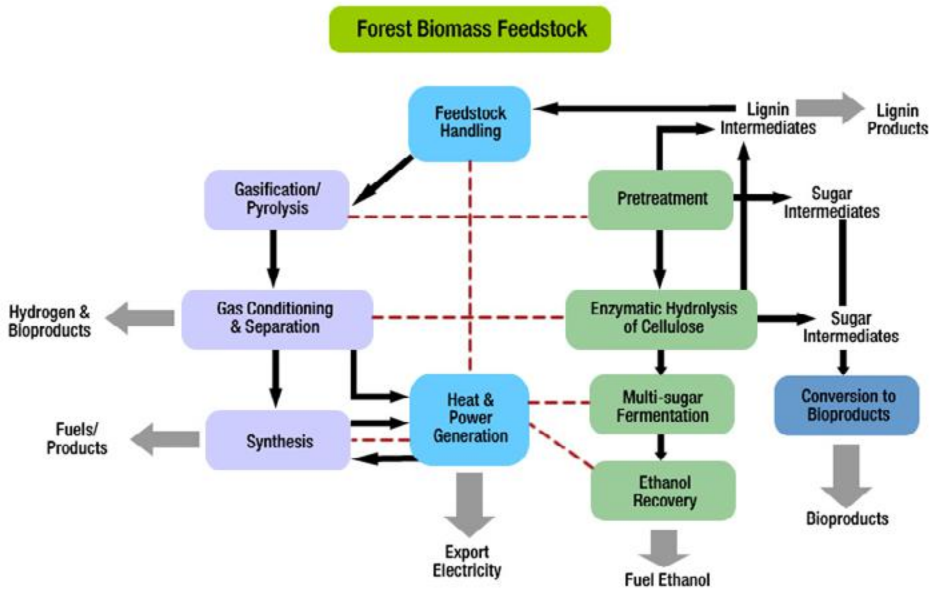
Source: Skals et al., 2008

TABLE 5.4 Benefits of using enzymes in pulp and paper processing

Process	Enzyme	Function
Peroxide removal	Catalase	Increases lifetime of equipment by preventing corrosion
Fibre modification	Laccase, cellulase	Increases paper strength
Anionic trash control	Pectinase	Saves retention aids & energy for drainage by degrading pectin
Starch removal	Amylase	Saves de-inking chemicals by improving de-inking efficiency
Drainage improvement	Cellulase, hemicellulase	Saves energy for drainage by improvement of secondary fibres' fibril structure
Starch preparation	Amylase	Preparation of starch for paper coating
Slime control	Protease	Reduces biocides input by degrading slime

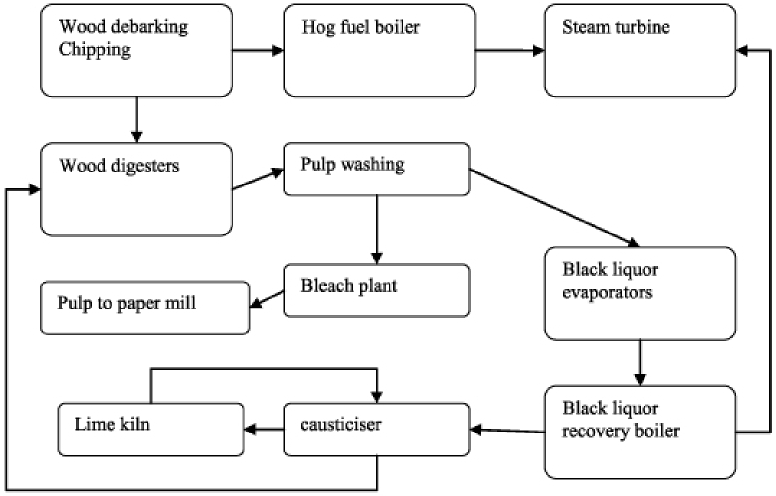
Source: Skals et al. 2008

FIGURE 2.1 Advanced forest bio-refinery



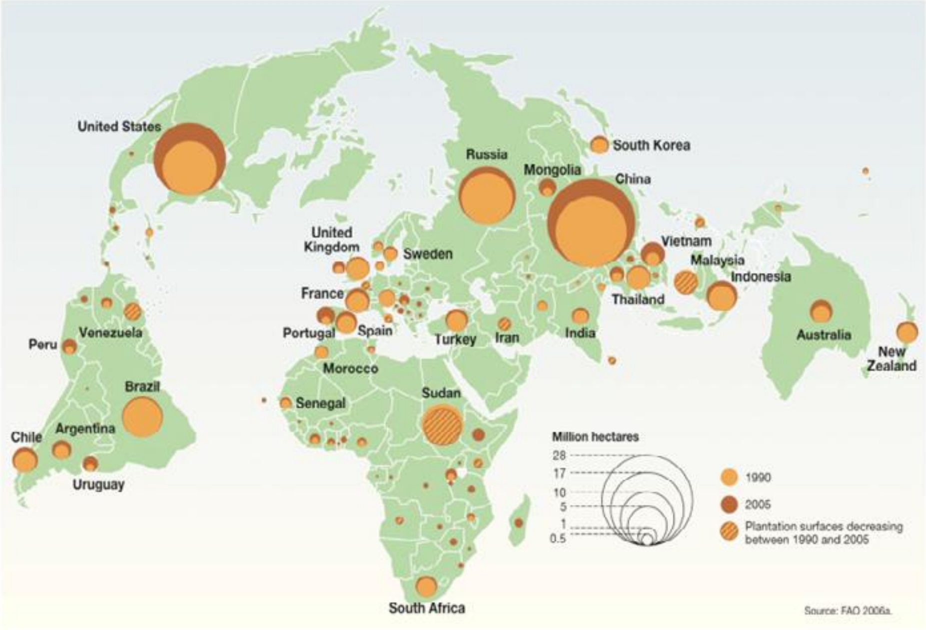
Source: Federal Laboratory Consortium Midwest Region

FIGURE 3.2 Kraft chemical pulping and recovery processes



Source: Pira International Ltd.

FIGURE 3.1 Trends in areas of productive forest plantations



Source: Global Forest Assessment 2002

List of Tables and Figures