OPPORTUNITIES FOR BIOREFINERIES IN THE PULPING INDUSTRY

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INTRODUCTION

Increased energy and raw material prices along with tougher competition and contracting markets for pulp products have highlighted the need for the pulp industry to enlarge their traditional product portfolio with new value-added products. There is also a strong growing interest from society to replace petroleum-based products with products from renewable sources. The spent cooking liquor, called black liquor, is today used for electricity and steam production, but it could partly be converted into other valuable products, making use of the chemical structures of complex organic compounds derived from the wood components. Moreover, the cellulose fraction which is currently used for paper products can be used for other purposes, such as production of biofuels or specialty cellulose products. In addition, there are new possibilities to make use of low quality biomass, for example forest residues.

The pulp mills have good prerequisites to become the future biorefineries. Firstly, the scale of the industry means both large volumes of biomass feedstock in large production sites permitting economies of scale. Secondly, some by-product streams, e.g. black liquor, are already partly processed in pulp production and can be more suitable for further refining than wood waste, agro fibres or other natural-fibre feedstock. Biomass is a more complex raw material than petroleum and utilizing partly processed streams permits a very efficient resource use. Thirdly, location of the new industries at the pulp mill means excellent process integration opportunities (access to heat sources and heat sinks, waste and effluent handling, water, general infrastructure and logistics).

The size of the global pulp production implies that only parts of the biomass-containing process streams could be used for production of chemicals and materials, unless the market for the products increases considerably. Nevertheless, the value of these products could be significant (Chapter 3). In contrast, there is one product category with virtually no demand limit. For electricity and biofuels, the market exceeds the possible production capacity, even if all the biomass currently processed in pulp mills would be used (Chapter 4, Figure 4.1).

All these factors contribute to a strong driving force to develop pulp mills into biorefineries that convert biomass into a wide range of products. However, how to best balance the selection of outputs and combine different processes is a very complex issue. This chapter, therefore, aims to present possible pulp mill biorefinery pathways and related processes, focusing on the kraft pulp industry, and discusses factors influencing the optimal design of a pulp mill biorefinery.

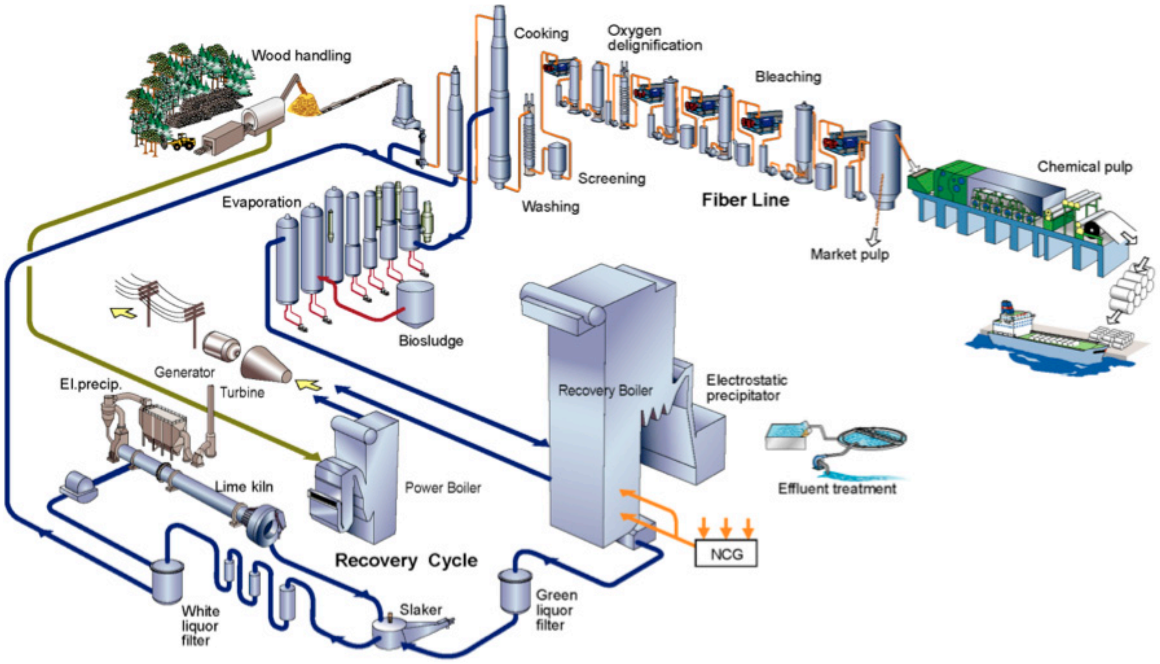

Figure 5.1 Overview of a conventional kraft pulp mill © 2008 Kvaerner Pulping

PULP PRODUCTION

There are two principle ways to produce pulp, by chemical or mechanical separation of the cellulose fibres. In Sweden, for example, about two thirds of the pulp is produced by chemical separation, with the kraft (sulphate) process as the predominant method. [1] This chapter will focus on chemical pulp production, in particular kraft mills, since the opportunities for these mills to be developed into biorefineries are larger than for mechanical mills. The remaining part of chemical pulp production is mainly done using the sulphite process, which has many similarities with the kraft process and therefore also similar opportunities. The production of chemical pulp is dominated by relatively few countries including USA, Canada, Japan, Sweden, Finland and Brazil.

Figure 5.1 shows an overview of a conventional kraft pulp mill. After the pulp wood has been debarked and cut into wood chips, it is added to the digester where it is mixed with cooking liquor, known as white liquor, containing the cooking chemicals (NaOH and Na_2S) and water. Cellulose fibres in the wood chips are then separated from lignin (which acts as a glue between the fibres) because lignin reacts with the chemicals in the white liquor. The chemicals and lignin form so called black liquor. The black liquor also contains other substances, mainly hemicellulose (a part of the hemicellulose remains in the pulp however) but also extractives (fat and resinous acids), aliphatic acids and inorganics like Na_2CO_3 and Na_2SO_4. The fibres are separated from the black liquor in a washing step and are then screened and possibly bleached before pulp is obtained. The pulp is either dried and transported to a paper mill (this is called a market pulp mill), or processed further to paper at the mill (called an integrated pulp and paper mill).

The black liquor, which contains large amounts of water, is evaporated before it is burned in a special boiler, called a recovery boiler. In the recovery boiler, combustion of the organic compounds releases heat that is used for production of steam. The remainder of the liquor can be found at the bottom of the boiler in the form of a smelt. The smelt is dissolved to form green liquor, which is sent to the chemical preparation where white liquor for the digester is produced. Thus, the recovery boiler functions both as an energy and chemical recovery unit. In the lime kiln, which is part of the white liquor preparation, fuel oil and natural gas are the most commonly used fuels today.

1 Swedish Forest Industries, 2009. Skogsindustriernas miljödatabas: Bruk 2009.

The steam produced in the recovery boiler is used in a back-pressure steam turbine for electricity generation. The steam is then used to satisfy the heating requirements in the pulping process, such as in the digestion, evaporation and drying stages. In cases where the steam from the recovery boiler is not sufficient to satisfy the mill steam demand, an additional boiler is used to produce steam for the back-pressure turbine. The fuel in this boiler is often bark from the debarking of the logs, possibly supplemented by purchased forest residues, fuel oil or natural gas. A surplus of steam can also occur, that is, more steam is produced by the recovery boiler than is needed at the mill. This steam could for example be used to produce additional electricity in a condensing steam turbine. A surplus of electricity from the mill could be exported to the grid. If located within reasonable distance from a district heating network, excess steam or heat from the mill could also be used to supply district heating demand (see Chapter 8). Several mills also produce tall oil, which is derived from extractives in the black liquor and can be separated into different fractions that can be used as fuel or be further processed to other products.

BIOREFINERY TECHNOLOGIES IN THE PULPING INDUSTRY

In a sense, biorefineries already exist. From the description in the previous section it is apparent that conventional kraft pulp mills can be regarded as biorefineries, since, apart from the pulp, electricity and possibly district heating and chemicals from tall oil are produced. In addition, implementing non-conventional alternative biorefinery concepts in pulp mills is not a new subject. Already in the 1940s attempts were made to produce pure lignin from pulp mills.[2]

In Sweden, Domsjö Fabriker in Örnsköldsvik, owned by Aditya Birla Group, is an example of a mill that has taken steps towards a more complex biorefinery. It has a sulphite-based process and produces specialty cellulose (used e.g. as textile), ethanol, lignin, carbonic acid and biogas. Another example of an existing biorefinery is Borregards facility in Sarpsborg in Norway. It has also a sulphite-based process and produces specialty cellulose used e.g. in celluloses ethers. It is also a leading global supplier of lignin-based binding and dispersing agents. Other products from Borregard are vanillin and fine chemicals for the pharmaceutical industry.

Figure 5.2 gives an overview with examples of possible kraft pulp mill biorefinery concepts and end-products. Pulping biorefineries can be categorised in different ways, for example with respect to end-product, i.e. energy, materials or chemicals, or with respect to processes, where one mainly can see two pathways; thermochemical processes and processes for separation and refining. Another important distinction is between processes that are based on process streams from the kraft process, e.g. extraction of hemicelluloses from the wood, lignin from the black liquor and gasification of black liquor, and processes that could be integrated to a pulp mill, for example gasification of solid biomass or other types of biomass upgrading such as torrefaction and pyrolysis, using forest residues or falling bark from the mill (see also Chapter 2). In the following sections we will take a closer look at some of these options.

In addition to processes and products included in Figure 5.2, there are other examples of biorefinery concepts that could be implemented at pulp mills, such as separation and refining of extractives from wood and bark for production of tailored polymers, coating agents, antioxidants, etc. Another interesting future opportunity for pulp and paper mills is CO_2 capture and storage. It could potentially contribute to large reductions of CO_2 emissions as well as high profits for large mills at future high costs for CO_2 emissions.[3]

2 Tomlinson G.H. and Tomlinson G.H. Jr. (1946): Method for treating lignocellulosic material. US Patent, US 2406867.

3 Hektor E. (2008). Post-combustion CO_2 capture in kraft pulp and paper mills – Technical, economic and systems aspects. Chalmers University of Technology, Göteborg, Sweden. Jönsson J and Berntsson T. (2010). Analysing the Potential for CCS within the European Pulp and Paper Industry. In Proceedings of 23rd International ECOS Conference, Lausanne, Switzerland, June 14-17, 2010;676-683. Pettersson, K. (2011). Black Liquor Gasification-Based Biorefineries – Determining Factors for Economic Performance and CO_2 Emission Balances. PhD Thesis. Göteborg: Chalmers University of Technology.

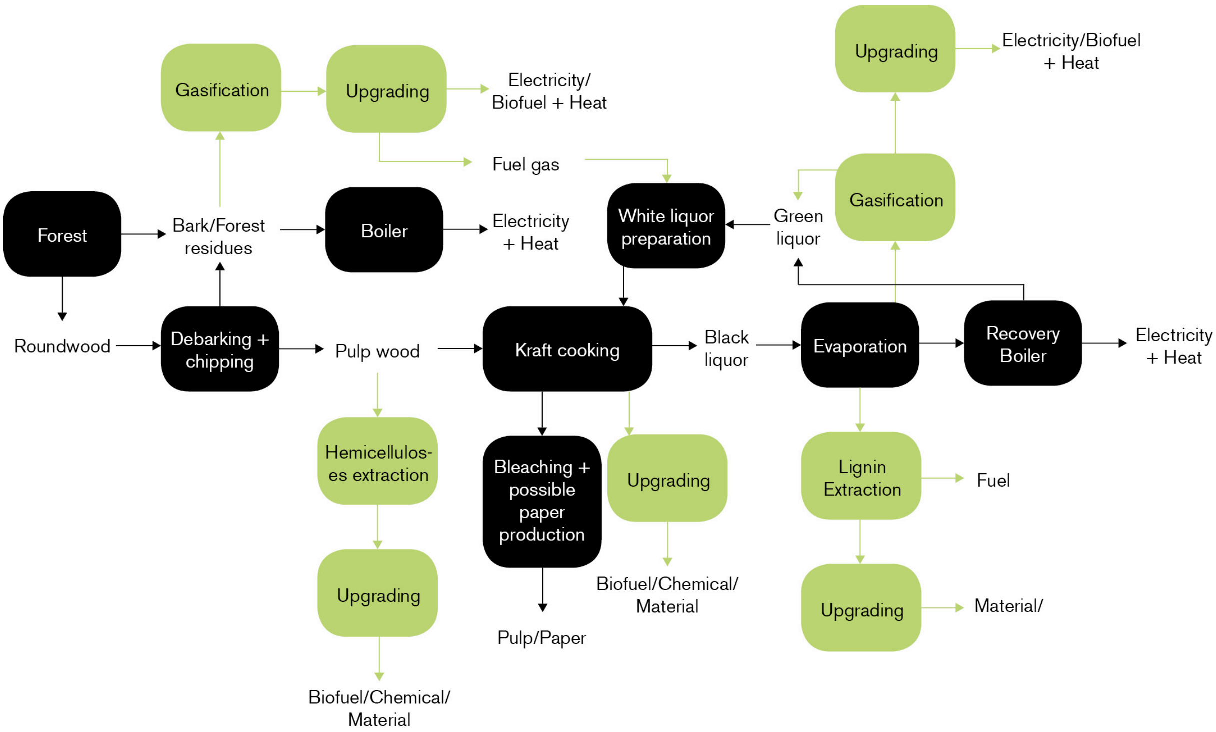

Figure 5.2 Example of biorefinery concepts and products (green process units) that could be implemented at a kraft pulp mill (conventional process units are black)

HEMICELLULOSES EXTRACTION

Hemicelluloses consist mainly of macro-molecular sugars with different characteristics, such as glucuronxylans and galactoglucomannans oligomers, from which a wide range of value-added products can be produced, e.g. ethanol, butanol, xylitol, lactic acid, fiber additives and hydrogels.

In a conventional kraft mill, most of the hemicelluloses end up in the black liquor. Hemicelluloses can be extracted from black liquor via different methods such as heat treatment, ultrafiltration and a combination of ultrafiltration and nano-filtration. Extraction of hemicellulose from black liquor has caught the interest in particular when lignin extraction from black liquor is targeted, because a lower content of hemicelluloses in the black liquor would facilitate the extraction of lignin as well as increase the purity of final lignin product, e.g. less ash content in separated lignin.[4,5]

The hemicelluloses could also partially be extracted prior to pulping (Figure 5.2). In dissolving pulp processes, hemicelluloses should be removed prior to pulping since a pure cellulose-based product is to be produced (these processes will be discussed in a coming section).[6] There has also been an interest in extracting hemicellulose prior to pulp production in kraft pulp mills and thermomechanical pulp mills.[7] Several hemicelluloses pre-extraction methods can be found in the literature e.g. dilute acid hydrolysis, steam explosion, hot-water extraction, pre-extraction using organic solvents, alkaline extraction and near-neutral extraction using green liquor as extracting solvent. These methods differ in extraction yield, chemicals used and steam demand and in to what extent they affect the quality and quantity of the pulp.

LIGNIN EXTRACTION

Extracted lignin from the black liquor can be used either within the mill, e.g. by replacing fossil fuel

4 Wallmo H. et al. (2009). "The influence of hemicelluloses during the precipitation of lignin in kraft black liquor", Nordic Pulp & Paper Res. J., 24(2): 165-171.
5 Lundqvist F. et al (2009). "Separation of lignin and hemicelluloses from alkaline process liquors" in Proceeding, NWBC, Helsinki.
6 Liu Z. et al. (2011). "Application of hemicelluloses precipitated via ethanol treatment of pre-hydrolysis liquor in high-yield pulp" Bioresource Technology, 102 (20): 9613-9618.
7 Bilek E.M. et al (2011). P., "Evaluation of a value prior to pulping - thermomechanical pulp business concept, part 2", TAPPI Journal, May 2011: 31- 38.

oil in the lime kiln, or externally e.g. in CHP plants. Lignin can also be used as a raw material for the production of chemicals and materials, e.g. carbon fibers, activated carbon or phenols.

When lignin is extracted, the steam production in the recovery boiler decreases due to reduction of organic content in the black liquor. In many pulp mills the recovery boilers are the bottleneck when an increase in the production capacity is planned. Lignin extraction can therefore remove the need for increased recovery boiler capacity (so called 'debottlenecking'). This can also be accomplished by extraction of hemicelluloses (see previous section), however not to the same extent, because lignin is the main organic component in the black liquor and it has a higher heating value. However, there is a limit to how much lignin that can be extracted without affecting the combustion properties in the recovery boiler.

A commercially available technology for lignin extraction is LignoBoost, developed by Chalmers University of Technology and Innventia AB and today owned by Metso. The technology is based on addition of CO_2 to a black liquor side stream that is diverted from the evaporation plant, which results in lignin precipitation. The precipitated lignin is then filtered and washed.[8]

GASIFICATION OF BLACK LIQUOR

Black liquor gasification (BLG) is currently being developed as an alternative technology for energy and chemical recovery. In the gasification process the main fraction of the organic content in the black liquor is converted to a synthesis gas (syngas) and the pulping chemicals are recovered and returned to the pulping process, similar to the recovery boiler process. The syngas can be used as a feedstock for production of biofuels such as DME (dimethyl ether), methanol, FT (Fisher-Tropsch) fuels or hydrogen, or as a fuel for electricity generation in a combined cycle cogeneration unit. Several BLG technologies have been under development during the past 30 years. Today, the major developer of BLG technology is the Swedish company Chemrec. Their technology is based on pressurized, high-temperature (950-1000°C), oxygen-blown, entrained-flow gasification.[9] (See Chapter 9 for a discussion on prerequisites for a future development of this and other gasification technologies in Europe.)

Replacing the recovery boiler with a BLG plant will change the mill's energy balance. Excess heat at suitable temperature levels from the BLG plant can be used to generate steam. Some steam is used internally at the BLG plant, but there is a significant surplus that can be used in the mill processes. However, it should be noted that less steam is produced compared to the conventional recovery boiler powerhouse configuration, since either motor fuels or more electricity are produced in the case of BLG. Even highly energy-efficient market pulp mills will have a significant need for external wood fuel if black liquor gasification with motor fuel production is to be implemented.[10]

ALTERNATIVE PRODUCTS FROM CELLULOSE

Changed consumers' habits, resulting in lowered consumption of paper, along with a growing market for other high-value products from the cellulose, makes it interesting for kraft pulp mills to partly, or fully, convert their production to e.g. dissolving pulp. As it has been mentioned, in dissolving pulp production hemicelluloses are removed prior to cooking. There are two chemical processes for production of dissolving pulp, the modified sulfite process and the pre-hydrolysis kraft process. The dissolving pulp is currently used either for specialty products, e.g. rayon yarn for industrial products such as tire cord or for viscose staple fibers, e.g. rayon for textile and disposable wipes.

Converting an existing pulp mill or one of the fibre lines, to an ethanol production plant is another alternative for utilizing cellulose. The ethanol

8 FRAM (2005). FRAM Final report Application area: Model mills and system analysis, FRAM Report No 70. STFI-Packforsk, Stockholm, Sweden.

9 See e.g. Chemrec (2011). and Ekbom T et al (2005). Black Liquor Gasification with Motor Fuel Production – BLGMF II. Nykomb Synergetics, Stockholm, Sweden.
10 Pettersson, K. (2011). PhD Thesis, Chalmers University of Technology, Göteborg.

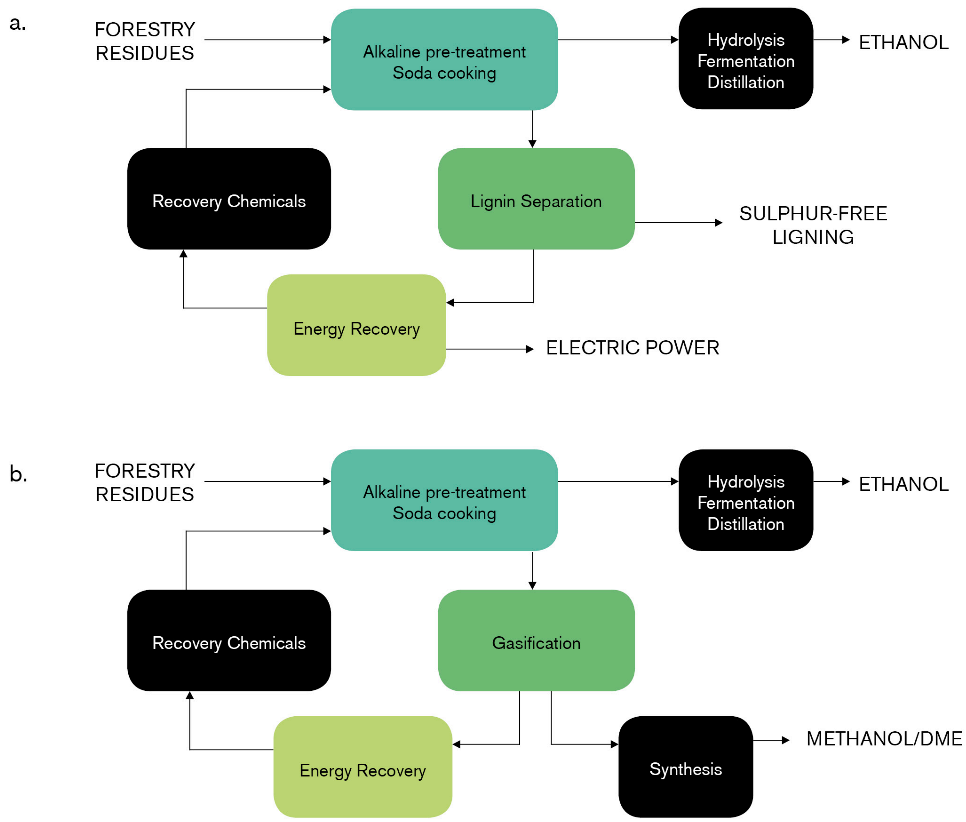

Figure 5.3 Conceptual designs of a pulp mill converted to an ethanol production plant. (a) – Option with lignin separation and (b) – Option with methanol/DME production. The black liquor could of course also go directly to the recovery boiler. Source: Olm L. et al (2007). Ethanol from Swedish wood raw material by simplified alkline cooking process. STFI-Packforsk report no. 291, August 2007.

production plant may have a potential of enabling largescale production of ethanol with relatively low investment costs as many of the process units required for ethanol production already exist in a kraft pulp mill.[11] A process suitable for integration in a pulp mill is alkaline and sulphur-free pretreatment of lignocellulosic material.[12] The process starts with rather pure cellulose in the hydrolysis stage, which makes it unique from other processes that aim to produce ethanol from lignocellulose. Figure 5.3 suggests two conceptual designs for a pulp mill converted to an ethanol production plant.

ENERGY COMBINES

Another type of biorefinery, not directly utilizing the process streams from the kraft process, can be created when a mill and another consumer, or producer, of heat are integrated to achieve synergistic effects such as heat cascading. This has been called an “energy combine”. In this concept, mills with a heat surplus can be integrated with processes such as lignocellulosic ethanol production[13] or different types of biomass upgrading, for example drying, torrefaction or pyroloysis that require heat (see Chapter 2). For mills with a heat deficit, integration with for example solid biomass gasification with production of motor fuels and/or

11 Jansson, M. et al. (2010), Cellulose Chem. Technol., 44(1-3): 47-52.

12 von Schenck A. et al (2011). Ethanol from Nordic wood raw material by alkaline simplified sodacooking pretreatment, Proceedings of the ISAF conference in Verona, Italy.

13 As described in the previous section, where one of the pulp lines can be converted for ethanol production using the existing process equipment, but also exchanging heat with the remaining pulp lines, or integration of other types of lignocellulosic ethanol production that only exchanges heat with the pulp mill processes.

electricity, which in total has a heat surplus, could be an option.

Since there is a substantial heat surplus from gasification processes, integration with other industrial processes or district heating systems can improve both the economic performance and the CO_2 emission balances of the process (see Chapter 8). There are a limited number of heat sinks that are large enough and that are able to accept excess heat all year round. In countries like Sweden and Finland, the pulp and paper industry constitutes a significant integration potential for solid biomass gasification concepts (see also Chapter 9 for a discussion on the potential for integration in the Nordic countries in relation to the size of the European fuel markets).

FACTORS INFLUENCING THE OPTIMAL DESIGN OF A PULPING BIOREFINERY

What is the optimal design of a biorefinery in the pulping industry? The optimal design of a pulp mill biorefinery is dependent on a number of characteristics of the mill such as type of mill, steam (heat) balance, size, need for investments, available investment capital, and geographical location. It also depends on a range of external factors such as prices of energy carriers, chemicals and materials and the presence of policy instruments. In order to discuss the different process options presented in this chapter in relation to these factors, the presented processes are summarized, structured and commented further in Table 5.1. Table 5.1 also includes the level of investment and operating and maintenance costs for the different processes, as well as examples of possible contributions of the processes in a Swedish perspective. Ethanol is used as an example of a potential alternative product derived from the cellulose fraction instead of pulp. Since energy combines do not refer to a specific process, they are not included in Table 5.1.

The *type of mill* is the main factor influencing its *steam balance*, which determines the applicability and performance of different biorefinery concepts. For example, as discussed, implementation of solid biomass gasification is suitable at mills with a steam deficit, while torrefaction is suitable to implement at mills with a steam surplus.

The energy efficiency of pulp mills is increasing and already today many market pulp mills have a steam surplus. In the future, the steam surplus is expected to increase further, making it possible to e.g. extract large amounts of lignin or hemicelluloses without creating a steam deficit and making the plant dependent on external fuel. However, at integrated pulp and paper mills the steam surplus will be small or non-existent, even at future mills with higher energy efficiency. Thus, implementation of biorefinery concepts that partly utilize the organic content in the black liquor will create a steam deficit, or increase the existing steam deficit, and thus increase the need for external fuel, e.g. wood fuel, at the mill.

Consequently the profitability of an investment in e.g. lignin extraction in market pulp mills and in integrated pulp and paper mills depends on the development on two different energy markets (compare the discussion on reference systems in Chapter 7). At the market mills the electricity price is influencing the profitability (assuming that the alternative use of existing steam surplus is electricity production) while at integrated mills the wood fuel price is influencing the profitability (assuming that the steam deficit is covered by a conventional biomass CHP plant).[14]

Previous studies show that the economic performance, as well as the potential to reduce global CO_2 emissions, is generally better for biorefinery processes such as lignin extraction and black liquor gasification at mills with a significant steam, or heat, surplus.[15] This emphasizes the importance of considering different steam saving measures such as increased heat integration and investments in new energy-efficient equipment at a pulp mill. The lower steam demand a mill has, the greater the part of the organic content in the black liquor that can be used for production

14 In the latter case the electricity production is practically unaffected, since the decreased electricity production in the recovery boiler's steam turbine is compensated by the electricity production in the biomass CHP.
15 See e.g. Pettersson, K. (2011), PhD Thesis, Chalmers University of Technology, Göteborg.

of more valuable products instead of steam (assuming constant usage of external wood fuel). For example, lowering the steam demand at a market pulp mill enables the mill to extract more lignin or hemicelluloses without making the mill dependent on external wood fuel. Several studies have shown that these types of energy efficiency measures generally are both profitable and lead to decreased global CO_2 emissions.[16]

The influence on the steam balance of producing other products than pulp from the cellulose is dependent on the type of product produced. Ethanol production, for example, leads to slightly lower steam usage, as indicated in Table 5.1. Another important factor influencing the steam balance, not just for the cellulose-based processes but also for the other biorefinery concepts described here, is how much of the refining that takes place at the mill. Extracted lignin, for example, could be sold directly to replace oil as a feedstock in an industrial process located elsewhere or be refined to products such as carbon fibers or phenols at the mill. As mentioned above, the mill could provide excellent integration opportunities regarding for example heat exchanging and general infrastructure and logistics.

Generally, most processes benefit, to some extent, from economies of scale. Therefore, the size of the mills and its streams such as raw material, black liquor and steam surplus or deficit influence the specific investment cost of biorefinery concepts. For example, the minimum capacity of gasification plants in order to be competitive is about 200 MW of fuel input (corresponding to 6 PJ, or 2 TWh, per year).[17] Thus, the steam deficit of a mill has to be of a certain size if integration with solid biomass gasification is to be considered. Studies indicate that the size of a possible ethanol production plant using extracted hemicelluloses as feedstock is too small to be economically feasible at a normally sized mill.[18] However, the upgrading of the hemicelluloses to specific chemicals and materials with higher market value can make an operation economically feasible also at lower volumes. There is also a possibility to refine a stream to intermediate products at the mill, which are sent to a larger plant elsewhere. One example could be to produce FT liquor from gasified black liquor at the mill and then sent it to an oil refinery for final upgrading to diesel and gasoline.

The mill's need for investments is also an important factor. For example, the recovery boiler has to have reached the end of its technical lifetime before it makes economic sense to consider implementation of full-scale BLG plants. As has been discussed, investment in lignin extraction, or to some extent hemicelluloses extraction, is a way to 'debottleneck' the recovery boiler when increasing the production capacity at a mill. A smaller BLG plant could also be an option for this. Previous studies show that both investment in lignin extraction or a small BLG plant are more cost-efficient ways to achieve a capacity increase than rebuilding the existing recovery boiler.[19]

The extent to which a biorefinery process is a part of the actual pulping process is also a factor that will determine the desirability of implementation, i.e. if an interruption of a novel process will interrupt the pulp production? Black liquor gasification is maybe the technology with the highest level of integration with the pulping process. It needs to continuously process pulping chemicals to provide the mill with green liquor. This makes heavy demands on the technology when it comes to achieving stable and continues operation, which is currently the greatest challenge for BLG technology development.

In principal, several different biorefinery concepts could be combined. For example, a mill can extract hemicelluloses from the wood and lignin from the black liquor, gasify the black liquor and at the same time also gasify solid biomass in

16 See e.g. Jönsson J and Algehed J (2010). Pathways to a sustainable European kraft pulp industry: Trade-offs between economy and CO_2 emissions for different technologies and system solutions. Applied Thermal Engineering 2010;30(16):2315-2325.

17 McKeough P and Kurkela E (2008). Process evaluations and designs in the UCG project 2004-2007. VTT, Espoo, Finland.

18 Frederick et al. (2008). Biomass and Bioenergy, 32: 1293-1302.

19 See e.g. Pettersson, K. (2011), PhD Thesis, Chalmers University of Technology, Göteborg.

order to maintain the steam balance. However, one can question whether it is realistic for a mill to implement several new processes, at least in a short-term perspective. In addition, the steam deficit and thus also the need for additional wood fuel could become very large. One also has to consider economies of scale, where for example the black liquor gasification plant would have a much smaller size if hemicelluloses and lignin are extracted and thus also a higher specific investment cost. However, there are processes that can benefit from being combined. For example, as mentioned earlier, studies indicate that extraction of hemicelluloses makes it easier to extract lignin. The amount of available investment capital is often also limited, and mills cannot make all desired, i.e. profitable, investments; they have to prioritize. The level of the investment costs for the different biorefinery concepts are indicated in Table 5.1. The level varies from relatively low to very high. (See also Chapter 9 for a discussion on technical and market risks associated with such investments.)

The *geographical location* of the mill is an important factor affecting the possibilities for implementation of different biorefinery concepts as it influences access to forest biomass, availability of infrastructures and distance to markets of final and intermediate goods.

The development of *prices* of different energy carriers (wood fuel, electricity, heat, motor fuels, etc.), chemicals and materials, and the presence of different policy instruments promoting production of renewable alternatives or policy instruments that put a price on CO_2 emissions, will to a large extent determine the future economic performance, and indirectly, the CO_2 emission balances of different biorefineries.

To give an idea of what impact the different biorefinery configurations may have on the energy system, their potential contributions in Sweden are given in Table 5.1. For example, the possible contribution from black liquor gasification is large compared to the potential of hemicellulose and lignin extraction. However, this is related to how much raw material (black liquor) the technology uses, and thus also to how much less steam that is produced.

In Table 5.1 it has been assumed that extracted hemicelluloses and lignin, as well as the cellulose, are used for energy purposes. This has been done in order to facilitate a comparison with biofuels produced via black liquor gasification. In addition, data concerning possible upgrading of hemicelluloses and lignin to different chemicals or materials are very scarce. Some chemicals and materials could have a much higher market value but also a much smaller market size (e.g. lignin-based carbon fibres), than energy commodities (Chapter 3). In some cases implementation of a technology in one mill might be enough to satisfy the entire world market. This could lead to a situation where different mills specialize on different products, in contrast to today's situation where most kraft pulp mills are quite similar.

There are large uncertainties regarding future prices of energy carriers and policy instruments promoting production of renewable energy commodities such as electricity and motor fuels. Therefore, it is difficult to estimate the future profitability of, for example, black liquor gasification (see Chapter 9 and Figure 9.3). When it comes to estimation of the future profitability of extraction and further upgrading of lignin or hemicelluloses to chemicals or materials, the uncertainties are even higher. This is both due to the uncertainty regarding which products could be produced and the markets for them, but also the uncertainty regarding if there will be any policy instruments promoting production of biomass-based chemicals or materials. Today, only policy instruments for biomass-based energy products, not biomass-based chemicals and materials, exist. Since there are such large uncertainties regarding future prices and policy instruments, it is critical that technology assessments that compare different biorefinery concepts show the economic performance under different future conditions that include different levels of prices and policy instruments (see also Chapter 1 for a discussion on changing system contexts).

Table 5.1 Characteristics of different pulping biorefinery technologies

Pulping biorefinery technology	Examples of products	Main influences on existing process[1]	Example of potential energy contribution in Sweden[2]	Economic aspects	Technology development status and challenges	Additional comments
Hemicelluloses extraction	Ethanol, buthanol, acetic acid, xylitol, fiber additives, hydrogels	-Decreased electricity and steam production in the recovery boiler	-Ca 7 PJ (2 TWh) ethanol/ year[3,4] -Represents ca 2 % of the Swedish motor fuel use -Will result in lower electricity production and increased use of wood fuel	-Low investment cost for the extraction process -Low/medium operating and maintenance costs for the extraction process -The total investment and operating and maintenance costs depends on the downstream processing of the extracted hemicelluloses	-Extraction prior to dissolving pulp production is commercialized and implemented -Extraction prior to kraft pulping is under development - The main challenge is to minimize the impact on the quality and quantity of the pulp -Several processes for upgrading the extracted hemicelluloses are under development	- Releasing capacity in the recovery boiler, thus enabling a mill capacity increase -Studies indicate that the scale of a possible ethanol production plant will be too small to be economically competitive (assuming Scandinavian sized mills) -Extraction of hemicelluloses makes it easier to extract a more pure lignin product
Lignin extraction	Fuel, carbon fibres, activated carbon, phenols	-Decreased electricity and steam production in the recovery boiler	-Ca 30 PJ (8 TWh) lignin/year -Represents ca 30 % of the Swedish fuel oil use -Will result in lower electricity production and increased use of wood fuel[5]	-Low/medium investment cost for the extraction process -Medium operating and maintenance costs for the extraction process -The total investment and operating and maintenance costs depend on the downstream processing of the extracted lignin	-There is a commercial technology available for lignin extraction -Several processes for upgrading the extracted lignin are under development -A demonstration plant exists for the LignoBoost technology and the EU has approved a 90 MSEK R&D grant awarded by the Swedish Energy Agency towards the industrial scale demonstration plant	- Releasing capacity in the recovery boiler, thus enabling a mill capacity increase -Some lignin extraction processes require CO_2, and they could therefore be interesting to combine with separation of CO_2 from flue gases or from the lime kiln
Black liquor gasification	Methanol, DME, FTD, hydrogen, electricity	-Replaces existing system for energy and chemical recovery -Biofuels: decreased electricity and steam production -Electricity: increased electricity and decreased steam production -Increased lime kiln load, thus increased need for lime kiln fuel	-Ca 70 PJ (20 TWh) methanol/ year -Represents ca 25 % of the Swedish motor fuel use - Will result in lower electricity production and increased use of wood fuel	*Biofuels:* -Very high investment cost -Medium operating and maintenance costs *Electricity:* -High investment cost -Medium operating and maintenance costs	-The technology is under development -Production of fuels from syngas are commercial processes, however not for biomass based syngas -The main challenge is to show that the technology can achieve stable and continuously operation -A development plant exists for the Chemrec technology and the EU has approved a 500 MSEK R&D grant awarded by the Swedish Energy Agency towards the industrial scale demonstration plant	-Enables increased pulp yield -The recovery boiler has to be in the end of its technical lifetime in order for a full-scale BLG plant to be implemented -BLG is a part the existing process to a larger extent than extraction of lignin and hemicelluloses, required to continuously process pulping chemicals and provide the mill with green liquor -When producing biofuels from the syngas, CO_2 is separated as part of the process -Investment in a smaller BLG unit (working in parallel with the recovery boiler) enables a mill capacity increase
Ethanol production	Ethanol	-Ethanol production instead of pulp production (partly or fully converted mill) -Usage of raw material of lower quality and a lower price than wood for the pulp process -Decreased steam use	-Ca 55 PJ (15 TWh) ethanol/ year[6] -Represents ca 15 % of the Swedish motor fuel use -Will be produced on the expense kraft pulp[7]	-Low/medium investment cost -Medium operating and maintenance costs	-Already established technology from the soda pulping process and the first generation ethanol production -Low theoretical yield of ethanol from lignocellulosic biomass so the lignin must give a valuable contribution as a by product	-Possible to extract sulphur-free lignin -A stream of almost pure CO_2 is produced in the ethanol fermentation step, that could e.g. be used if lignin is extracted

1 The influences for the hemicelluloses extraction and the lignin extraction are the influences resulting from only the extraction processes, not from possible following upgrading of the extracted material.
2 Assuming full implementation at all Swedish kraft pulp mills (market kraft pulp mills and integrated kraft pulp and paper mills). .
3 Acetic acid is produced in almost the same quantities as ethanol, and also with a higher market value.
4 If the kraft pulp mills are converted for production of dissolving pulp, about three times more hemicelluloses can potentially be extracted.
5 If lignin is assumed to be used as a fuel, it makes no sense to extract lignin from a mill without a steam surplus, since this has to be compensated by increased use of wood fuel, excepted to have the same price as the extracted lignin.
6 Can also contribute to increased extraction of lignin or increased electricity production, since the steam use decrease when the pulp production is changed to ethanol production.
7 It is of course not realistic that all kraft pulp mills should be converted to ethanol production plants, this is however just to give an idea about the possible contribution of the biorefinery technology.

Finally it should be emphasized that neither production of biofuels via black liquor gasification, nor production of materials and chemicals from extracted lignin or hemicelluloses are yet fully developed and commercial processes. Technical uncertainties still make it unclear when different biorefinery alternatives could be realized on a commercial scale.

CONCLUDING REMARKS

With increasing energy and raw material prices, tougher competition and contracting markets for pulp products, development of biorefineries is a possible way for companies in the pulp and paper industry to remain competitive. There are several biorefinery pathways enabling production of value-added products such as biofuels, electricity, chemicals and materials in addition to pulp. These biomass-based products could replace products produced from fossil fuels. This chapter has presented pulp mill biorefinery processes, with a focus on the kraft pulp industry, and discussed factors influencing the optimal design of a pulp mill biorefinery.

Examples of pulp mill biorefinery options to utilize process streams from the kraft process are extraction of hemicelluloses from wood or lignin from the black liquor, and gasification of black liquor. In addition, there are processes that could be beneficially integrated with a pulp mill, for example gasification or other types of biomass upgrading such as torrefaction and pyrolysis, using forest residues or bark from the mill. Finally, the cellulose fraction which is currently used for paper products can be used for other purposes, such as textile or ethanol production.

The optimal design of a pulp mill biorefinery is dependent on a number of characteristics of the mill such as type of mill, steam balance, size, need for investments, available investment capital, and geographical location. It also depends on a range of external factors such as prices of energy carriers, chemicals and materials and the presence of policy instruments. Thus, even for a given mill with known characteristics there are large uncertainties regarding both the absolute and relative future performance of the different biorefinery concepts. Furthermore, due to, limited, but yet attractive markets for many chemicals and materials, it is possible that future kraft pulp mills will need to specialize on different products, and hence display a greater variety as compared to the more homogenous industry of today.