

Marcelo Hamaguchi

ADDITIONAL REVENUE OPPORTUNITIES IN PULP MILLS AND THEIR IMPACTS ON THE KRAFT PROCESS

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium 1383 at Lappeenranta University of Technology, Lappeenranta, Finland on the 18th of December, 2013, at noon.

Acta Universitatis
Lappeenrantaensis 562

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ISBN 978-952-265-540-0
ISBN 978-952-265-541-7 (PDF)
ISSN-L 1456-4491
ISSN 1456-4491
Lappeenrannan teknillinen yliopisto
Yliopistopaino 2013

Abstract

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Lappeenranta 2013

69 pages

Acta Universitatis Lappeenrantaensis 562

Diss. Lappeenranta University of Technology

ISBN 978-952-265-540-0, ISBN 978-952-265-541-7 (PDF), ISSN-L 1456-4491, ISSN 1456-4491

Although the concept of multi-products biorefinery provides an opportunity to meet the future demands for biofuels, biomaterials or chemicals, it is not assured that its implementation would improve the profitability of kraft pulp mills. The attractiveness will depend on several factors such as mill age and location, government incentives, economy of scale, end user requirements, and how much value can be added to the new products. In addition, the effective integration of alternative technologies is not straightforward and has to be carefully studied. In this work, detailed balances were performed to evaluate possible impacts that lignin removal, hemicelluloses recovery prior to pulping, torrefaction and pyrolysis of wood residues cause on the conventional mill operation. The development of mill balances was based on theoretical fundamentals, practical experience, literature review, personal communication with technology suppliers and analysis of mill process data.

Hemicelluloses recovery through pre-hydrolysis of chips leads to impacts in several stages of the kraft process. Effects can be observed on the pulping process, wood consumption, black liquor properties and, inevitably, on the pulp quality. When lignin is removed from black liquor, it will affect mostly the chemical recovery operation and steam generation rate. Since mineral acid is used to precipitate the lignin, impacts on the mill chemical balance are also expected. A great advantage of processing the wood residues for additional income results from the fact that the pulping process, pulp quality and sales are not harmfully affected. For pulp mills interested in implementing the concept of multi-products biorefinery, this work has indicated possible impacts to be considered in a technical feasibility study.

Keywords: black liquor, chemical recovery, hemicellulose, lignin, wood residues

Acknowledgements

This work was carried out in the department of Sustainable Energy Systems at Lappeenranta University of Technology, Finland, between December 2008 and January 2013. First and foremost I want to thank my supervisor Prof. Esa Vakkilainen, who contributed immensely to my personal development. I appreciate all his ideas, opinions and advices that made my experience in LUT productive and motivating. These all made me feel more confident in facing the most difficult challenges in my professional life.

I thank my officemate, Kari, who helped to create a very pleasant work environment. I am also grateful to many friends, especially to Alex, Daniel, Ernesto & family, Henri, Iris, Jussi, Marcos, Mark, Sai, Teemu, Verr, Will and Zé, for all the enjoyable time we have shared.

I want to acknowledge the Energy Graduate School in Finland for providing funds to attend important courses and conferences between 2009 and 2011. I also thank those who immensely contributed to the published articles. Special thanks to Professor Marcelo Cardoso for his great advices and friendship.

I would like to thank my family for all their support. For my parents who raised me with love, and who taught me how to pursue my objectives in life with honesty and humility. And most of all for Piia, whose love, company and faithful support during this period of PhD is so appreciated. Thank you.

Marcelo Hamaguchi
November 2013
Lappeenranta, Finland

To my parents

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Abstract

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List of publications

This thesis is based on the following papers which are referred to in the text by the Roman numerals I–V.

- I. Hamaguchi, M. and Vakkilainen, E. (2010). Influence of Cl and K on operation and design of chemical recovery equipment. *Tappi Journal*, 10(1), pp. 33–39.
- II. Hamaguchi, M., Vakkilainen, E., and Ryder, P. (2011). The impact of lignin removal on the dimensioning of eucalyptus pulp mills. *Appita Journal*, 64(5), pp. 433–439.
- III. Hamaguchi, M., Kautto, J., and Vakkilainen, E. (2013). Effects of hemicellulose extraction on the kraft pulp mill operation and energy use: Review and case study with lignin removal. *Chemical Engineering Research & Design*, 91(7), pp.1284–1291
- IV. Hamaguchi, M., Cardoso, M., and Vakkilainen, E. (2012). Alternative technologies for biofuels production in the kraft pulp mills—potential and prospects. *Energies*, 5(7), pp. 2288–2309.
- V. Hamaguchi, M., Saari, J., and Vakkilainen, E. (2013). Bio-oil and biochar as additional revenue stream for South American kraft pulp mills. *Bioresources*, 9(3), pp. 3399–3413.

Author's contribution

The author is the principal investigator in papers I–V, with Prof. Vakkilainen participating actively as a technical advisor. In paper II, Mr. Ryder contributed with his great expertise in pulping process engineering. In paper III, experimental data from Mr. Kautto was used as a basis for evaluating the integration of hemicellulose extraction in pulp mills. Mr. Kautto contributed to the literature survey and final discussion. In paper IV, Prof. Cardoso supported the idea of writing a literature review of technologies that allow the production of alternative biofuels. He spent two months in Finland as part of LUT international mobility, and made important contributions to the paper. In paper V, Mr. Saari was responsible for conducting the simulation of the biomass drying and torrefaction processes using the IPSEpro software. He also helped with the economic analysis which is used to evaluate the feasibility of the thermo-chemical conversions in the study.

Relevant conference proceedings

Hamaguchi, M. and Vakkilainen, E. (2010) Influence of Cl and K on the operation and design of chemical recovery equipment. Proceedings of TAPPI/PAPTAC International Chemical Recovery Conf., 29 March 29–1 April 2010, Williamsburg, VA, USA.

Hamaguchi, M. and Vakkilainen, E. (2010) The influence of lignin removal on the energy balance of future pulp mills. Proceedings of 21st Tecnicalpa/6th Ciadicyp, 12–15 October 2010, Lisbon, Portugal.

Fiorentin, M., Hamaguchi, M., and Vakkilainen, E. (2011) Methodology for studies on increasing kraft recovery boiler capacity. Proceedings of 18th Latin American Congress of Recovery Boilers, 15–17 August 2011, Fray Bentos, Uruguay.

Hamaguchi, M., Kautto, J., Vakkilainen, E., and Lobosco, V. (2011) Effects of lignin removal and wood extraction on the kraft pulping process and energy use. Proceedings of 44th Pulp and Paper International Congress & Exhibition, 3–5 October 2011, São Paulo, Brazil.

Other Publications (not included in the thesis)

Hamaguchi, M. and Vakkilainen, E. (2010). Corrosion of superheater tubes in recovery boilers: a challenge. *O Papel*, 71(6), pp. 57–71.

Fracaro, G., Vakkilainen, E., Hamaguchi, M., and Souza, S.M.N (2012). Energy efficiency in the Brazilian pulp and paper industry. *Energies*, 5(9), pp. 3550–3572.

Nomenclature

Latin alphabet

c_p	specific heat capacity at constant pressure	J/(kg K)
C	annual cost	\$/a
C_{in}	investment cost	\$
h	differential head	m
H	heat requirement	kW
HV	total heating value	kJ/kg
hv	specific heating value	kJ/ADt
L	heat of vaporization	kJ/kg
m	specific mass	kg/ADt
MC	moisture content	kg/kg
P	power	kW
P_e	power generated	MW _e
q	liquor volumetric flow rate	m ³ /h
T	temperature	°C
t	time	s

Greek alphabet

ρ	liquor density	kg/m ³
η	efficiency	m

Subscripts

blw	black liquor fraction from white liquor oxidation
d	dried
DSt	steam for dryer
h	hydraulic
inorg	black liquor fraction from inorganics
in	inlet
ligP	lignin in pulp
ligR	lignin removed
ligW	lignin in wood
O&M	operating and maintenance
org	black liquor fraction from organics
out	outlet
prod	products for sale
red	reduction
s	shaft
ut	untreated

Abbreviations

AA	Active alkali
ADt	Air dry tons (pulp)
CE	Causticizing efficiency
Cl	Chloride
DME	Dimethyl ether
DS	Dry solids
EA	Effective alkali
FBC	Fluidized bed combustion
HHRR	Hearth heat release rate
HHV	High heating value
HR	Hemicelluloses recovery
IRR	Internal return rate
K	Potassium
LHV	Low heating value
LR	Lignin removal
NPE	Non process elements
NPV	Net present value
NTA	Non-titratable anions
PHL	Pre-hydrolyzate
RB	Recovery boiler
TAC	Total anion concentration
TTA	Total titratable alkali

1 Introduction

This section shortly describes the history and development of the kraft pulping and why the process has become so important for the global paper industry. The potential contribution of pulp mills to the bio-business sector is also introduced. Finally, the objective, methods applied and outlines of the thesis are presented.

1.1 Background

The use of sulphide as a means to accelerate the alkaline pulping had already been tested in England in the early 1800's (Grace and Malcom, 1989). In spite of this, it was not until 1884 that a patent was granted for the development of the so-called kraft pulping. In this process, a mixture of sodium sulphide and sodium hydroxide is utilized to pulp the wood, providing therefore conditions to produce paper with "kraft" characteristics. This term derives from the Swedish/German word for strength. According to Grace and Malcom (1989), the kraft process has had two significant periods of expansion. The first was in 1934–1942, when a demand for strong and inexpensive packaging material was created, e.g. in the USA, Finland and Sweden. Since the kraft pulp was found to be suitable for many wood species, it was considered as a great potential to meet such a demand.

The advent of a chemical recovery system was then crucial to make the technology advantageous and highly competitive. The first Tomlinson kraft recovery boilers, for example, were put into service in the 1930s (Vakkilainen, 2005) to help the mills to reduce costs with chemicals and become more self-sufficient in both thermal energy and electricity. The second expansion period is related not only to the resurgence of industry after the Second World War but also to the advance in bleaching techniques. This resulted in more striking expansion in many parts of North America and Nordic countries. All these factors made the kraft process a successful and dominant method for producing pulp, reaching over 130 million tons of bleached and unbleached kraft pulp in 2012 (FAOSTAT, 2012). Currently, a third expansion phase can be observed, attributed to the development of fast growing tree plantations and subsequent reduction in the costs of raw-material. It started with South-East Asia in the 1990s and has been now occurring in South American countries such as Brazil, Chile and Uruguay.

Although efforts to improve the operation of conventional equipment are still ongoing, they are not as extensive as some years ago. One reason is that good levels of development have already been achieved. Some examples, targeting improvements of the chemical recovery area, are indicated in Figure 1.1. Nevertheless, advances towards more sustainable processes have continuously been targeted with research activities. These include the increased closure of mill water circuits as well as the reduction of gaseous emissions. The decrease in the emission levels can be attributed not only to the advances in boiler technology but also to the increase in the concentration of black liquor dry solids and better efficiency of electrostatic precipitators. The disposal of solid

residues has been also decreasing due to high costs related to solid waste dumping. Technically, all these improvements mean that non-process elements such as potassium (K) and chlorine (Cl) tend to enrich in the liquor cycle. The importance of controlling these elements in the pulp mill is described in section 2.

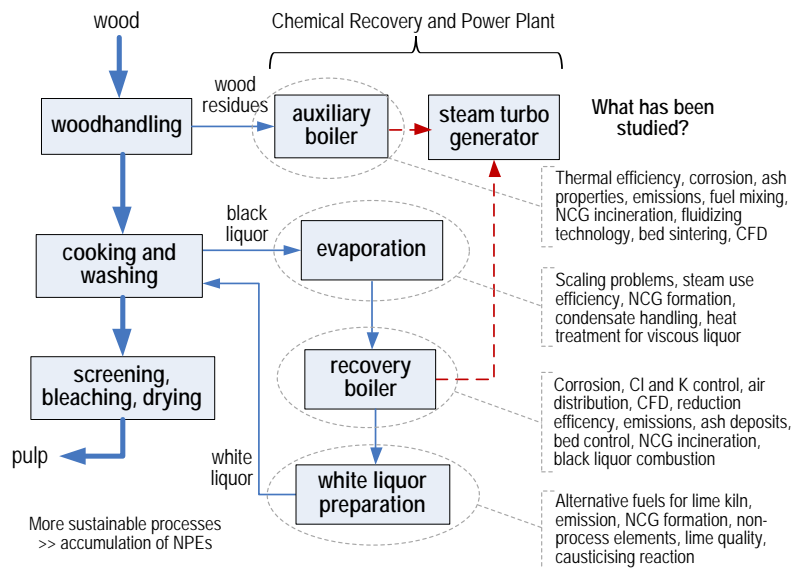


Figure 1.1: Conventional kraft pulp mill and examples of research topics.

Today, due to stricter environmental regulations, global competitiveness and new uncertainties surrounding the oil market, the mills are encouraged to go beyond the traditional production of pulp. Methods to improve the profitability range from replacing fossil with renewable fuels to the implementation of biorefineries, providing, therefore, an opportunity to mitigate climate change and meet the future demands for energy, fuel and chemicals. It is a fact that black liquor is seen today as an efficient source of bioenergy. The same way of thinking can be applied for example to the forest residues.

The effective use of biomass as an energy source has typically been influenced by the instabilities in the world oil market. In the eighties, as a consequence of the second oil crisis, biomass gasifiers were installed in several pulp mills with the purpose of replacing fossil fuels in the lime kilns (Palonen and Nieminen, 1999). Although a number of these mills ceased to produce the syngas after the oil price decreased, the experience had shown the vulnerability of the fossil based economy. Matching this concern, extensive efforts have been made to improve or develop renewable-based processes, especially during the eighties and nineties. Examples include pilot scale kiln trials using kraft lignin (Richardson *et al.*, 1990), black liquor gasification (Whitty,

2009) and production of pellets. Other potential alternatives for pulp mills include the generation of bio-oil through fast pyrolysis, torrefaction of biomass, and hemicelluloses extraction from wood for the production of bioethanol or biomaterials. Although the possibilities of implementing these non-conventional technologies have gained attention, their actual integration into the mills is not straightforward and has to be investigated.

1.2 Objective

The objective of the thesis is to contribute to the understanding of alternative processes that enables the creation of additional biomass-based revenue streams in kraft pulp mills. This is approached by answering the following research questions:

- 1) How do the changes occurring inside traditional pulp mills affect the chemical recovery cycle and energy balance?
- 2) What are the potential alternative technologies that can be possibly integrated to kraft pulp mills?
- 3) How would these integration alternatives affect the design and operation of conventional kraft mills?

1.3 Methods

The first question was posed to give a better understanding of the role of black liquor as a bioenergy source and also to identify operational trends and challenges in the chemical recovery cycle. The main idea was to form a scientific basis to start exploring alternative processes that can be integrated into conventional kraft pulp mills. During the initial stage of the doctoral work, a detailed balance was developed for designing pulp mills. A calculation spreadsheet was also elaborated with the objective of estimating flows rates and heating values of the main components of black liquor. This led to the possibility of studying how the NPE, especially Cl and K, would affect the chemical recovery system (Paper I).

Later on, alternative processes such as lignin removal (Paper II), hemicelluloses extraction (Paper III), and pyrolysis/torrefaction of biomass (Paper V) were integrated into the mill balance to evaluate the possible impacts on the mill operation. Although other routes are available for converting pulp mills into multi-products biorefineries (Paper IV), only these four were investigated in more detail. One reason is that the implementation of these technologies in large scale has widely been discussed among the academia and industry. Table 1.1 summarizes the main methods applied and the sources of information that were utilized.

Table 1.1: Summary of methods and references used

Question	Method	Paper	Reference	Discussion
1	Technical opinions, mill balance spreadsheet, analysis of operational data	I	literature data, practical experience, mills data	sections 2 and 4
2	Literature review	IV	literature data, personal communication	section 3
3	Mill balance spreadsheet, power plant simulator	II, III, V	literature data, personal communication	sections 3, 4 and 5

1.4 Outline of the thesis

Section 2 presents a brief description of the kraft pulping process and, in more detail, the most important sources of bioenergy in the mill: black liquor. The origin and characteristics of black liquor are discussed to help understanding how its properties can be affected with the implementation of alternative processes. The section also describes the factors affecting the mill energy balance and introduces the importance of controlling the Cl and K in the liquor cycle.

Section 3 describes alternative technologies that have been studied in this thesis. Firstly, two processes that possibly modify the black liquor properties are presented: hemicellulose extraction prior to cooking and lignin removal from black liquor. The section also presents two thermo-chemical conversion technologies of biomass: torrefaction for the production of biochar and pyrolysis for the production of bio-oil.

Section 4 presents the basic calculation guidelines that were utilized in papers I–III and V. It also discusses the key assumptions adopted to study each integration alternative. Since hundreds of calculations are involved, a tool for tracing the dependent variables became very important. This feature made Microsoft Excel particularly user friendly for all the balances.

Section 5 summarizes the main findings of the thesis. Although it was possible to achieve the research objectives, the attractiveness of the processes proposed will depend on many other factors. These challenges, in addition to some recommendations for future work, are also pointed out in this section. Finally, the conclusions are presented, followed by the list of references and five journal publications.

2 Bioenergy usage in the kraft pulp mills

An overview of the kraft pulping process is shown in Figure 1.1. The white liquor, an aqueous solution that contains NaOH and H₂S as main active components, is consumed during the cooking of wood chips. The result is the production of a pulp containing dissolved organic and soluble inorganic materials that can be mostly removed during a washing stage. The washed pulp is sent to be screened, and the separated liquid, known as diluted black liquor, is sent to the multi-effects evaporators. After being concentrated to 70–85% DS, the black liquor can be effectively burned in the recovery boiler for the regeneration of pulping chemicals and for the production of high pressure steam.

The black liquor is sprayed into the lower part of the boiler where it is burned in an oxygen deficient environment so that Na₂S is formed. The extent of sulphide formation is measured by the reduction efficiency, typically over 90%. The non-combusted fraction is recovered as a molten smelt consisting mostly of Na₂S and Na₂CO₃. The smelt is conducted from the bottom of the furnace to a tank where it is dissolved in water. Green liquor is then formed and subsequently pumped to the recausticizing plant, where it reacts with lime (CaO), to convert Na₂CO₃ to NaOH. The precipitated CaCO₃ from the causticizing reaction is washed and sent to a lime kiln where it is heated to a high temperature to regenerate CaO for reuse.

2.1 Black liquor

Studying the pulping process is an important step to understand the origin and characteristics of black liquor. The wood to be processed usually contains 40–50% cellulose, 23–32% hemicellulose, 15–30% lignin and 2–5% extractives on a dry basis (Alén, 2000). The primary goal of pulping is the wood delignification, which should be carried out while also preserving the cellulose and hemicelluloses to the possible extent. Such a step is accomplished by using a desired aqueous solution containing hydroxyl (OH⁻) and hydrosulphide (HS⁻) ions as active components at set temperature and time. However, because the hemicellulose polymers exist in amorphous form, they are often partly dissolved in both acid and alkaline conditions. Cellulose is more resistant, and only a minor amount is typically dissolved during cooking (Gullichsen, 2000). The resulting pulp, consisting mostly of cellulose, should have the desired strength and opacity and provide good sheet formation.

With a cooking yield of 50%, approximately 20% of the original wood is lost due to polysaccharides, primarily hemicelluloses (Grace and Malcolm, 1989). This leads to the fact that most of the hemicelluloses and almost all the lignin end up in the black liquor (Adams and Frederick, 1988). Table 2.1 shows a typical composition of black liquor obtained from the pulping of birch. The organic components consist of ligneous materials, degraded carbohydrates, carboxylic acids and extractives. The major inorganic constituents are the sodium compounds from the cooking chemicals, although small amounts of inorganic elements can enter the process with the wood.

Table 2.1: Composition of black liquor from birch (Soderhjelm, 1994)

Organic Compounds, % by weight	78
Degraded lignin, including Na and S	37.5
Saccharine acids, including Na (hemicelluloses)	22.6
Aliphatic acids, including Na (lignin, carbohydrates)	14.4
Fat and resinous acids, including Na (extractives)	0.5
Polysaccharides (cellulose and hemicelluloses)	3
Inorganic Compounds, % by weight	22
(Na+K)OH	2.4
(Na+K)HS	3.6
(Na+K) ₂ CO ₃	9.2
(Na+K) ₂ SO ₄	4.8
(Na+K) ₂ S ₂ O ₃ , (Na+K) ₂ SO ₃ and (Na+K) ₂ S _x	0.5
(Na+K)Cl	0.5
Others	0.2

The amount of black liquor dry solids produced per unit of pulp varies considerably. It ranges from 910 kg DS/ADt for a high yield semi chemical pulp used for the manufacturing of brown boxes to approximately 1590 kg DS/ADt for a high strength and low yield bleached grade (Grace, 1989). A modern eucalyptus pulp mill can achieve 1330 kg DS/ADt (Pöyry, 2006). Since the pulping conditions vary depending on the pulp grade, process conditions or wood species, different black liquor composition and heating values are expected between mills. Figure 2.1 shows the contents of sodium and carbon in black liquor for different raw materials.

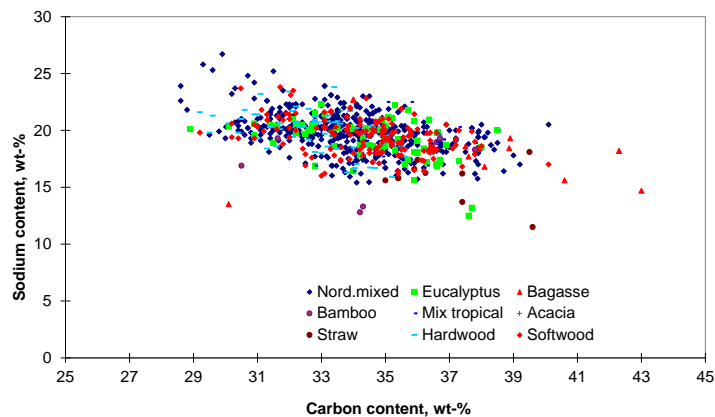


Figure 2.1: Sodium and carbon in various black liquors (after Vakkilainen, 2000)

Non-process elements present in black liquor can endanger and complicate the continuous operation of the chemical recovery cycle. Potassium (K) and chloride (Cl), for example, are very soluble in liquor, and they neither accumulate in the lime cycle nor have a negative impact on the recausticizing process itself. However, their presence in black liquor leads to corrosive impacts on the recovery boiler superheaters (Salmenoja, 1996). In addition, they can affect the operation of the chemical recovery equipment (Grace and Tran, 2009).

The main source of Cl and K are wood, mill freshwater, makeup chemicals and spent acid from chemical manufacturing. These inputs can vary depending, for example, on the wood species or whether the pulp is processed in coastal or inland mills. The typical net input for chloride in eucalyptus mills varies between 1–3 kg Cl/ADt and, for potassium, 2–5 kg K/ADt. For softwood mills, these values are respectively 0.3–1 kg Cl/ADt and 1–2 kg K/ADt (Jaakkola, 2009). Figure 2.2 shows how the contents of Cl and K in black liquor can vary between mills.

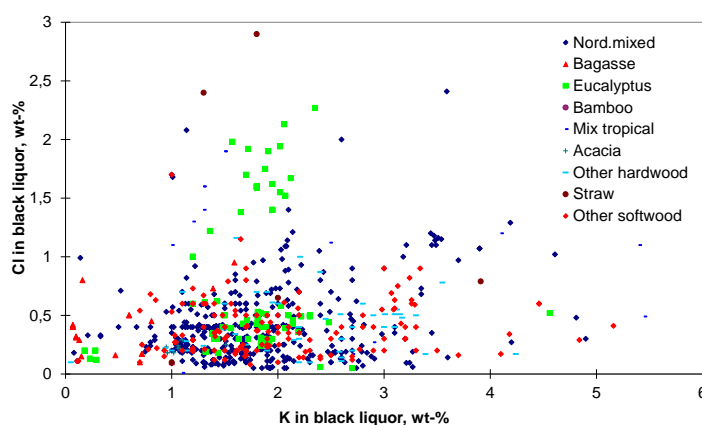


Figure 2.2: Cl and K in various black liquors (after Vakkilainen, 2000)

2.2 Factors affecting the mill energy balance

Some factors affecting the energy balance strategy of pulp mills are discussed in this section. The heat consumption and the amount of surplus electricity generated depend essentially on the size and geographic location of the mill. In standalone pulp production, modern recovery boilers are able to generate much more steam than what is required to run the mill. As a result, there is no actual need to incinerate the wood waste in a dedicated boiler.

The wood logs can be also debarked either at the forest or at the mill, with the decision depending essentially on the electricity and steam demand. This includes, for example, the existence or not of an integrated paper machine or a sodium chlorate unit for the

production of bleaching chemicals. Selling surplus electricity to the external grid can be an interesting option, although it often requires incentives to become attractive. Figure 2.3 shows a typical energy balance in modern kraft pulp mills.

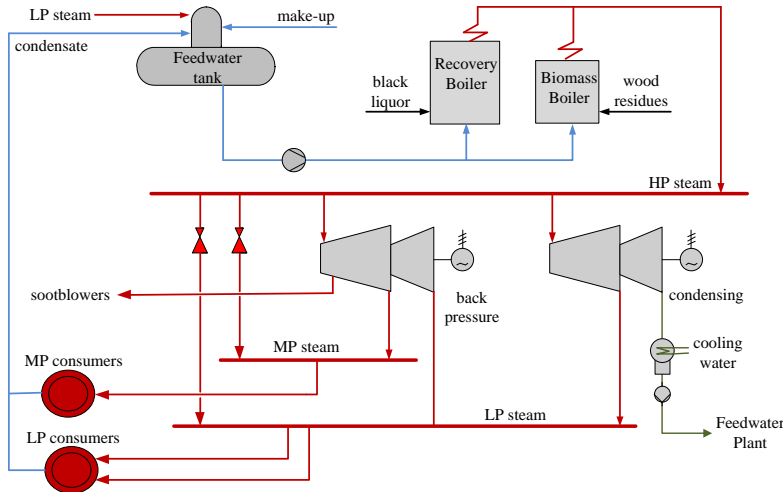


Figure 2.3: Schematic diagram of energy production in a kraft pulp mill

2.2.1 Wood species

Different wood species require different pulping conditions, resulting therefore in a varying amount of black liquor and wood residues generated per ton of pulp produced. Some examples are shown in Table 2.2. It can be observed that a higher pulp yield results in a lower load of organic material to the recovery process and a higher wood consumption per ton of pulp produced.

Table 2.2: Examples of specific load variations for fixed pulp production

		Scots pine	Silver birch	<i>Eucalyptus grandis</i>	<i>Eucalyptus globulus</i>
Cooking yield	%	46.0	50.0	52.0	53.0
Sulfidity ^a	%	40	35	32	28
EA ^b charge on dry wood	% NaOH	19	17	17	18
Chips consumption	kg(dry)/ADt	2090	1925	1833	1815
Wood waste ^c	kg(dry)/ADt	298	274	261	259
Black liquor yield	kgDS/ADt	1740	1450	1330	1320

^a value used to monitor the balance of NaOH and Na₂S in the liquor

^b effective alkali: value used to calculate the white liquor flow rate required in the cooking vessel

^c based on 1.5% screening loss, 10%-wt bark at delivery and 3% losses at debarking

2.2.2 High power features and ash treatment

Increasing the steam parameters is one way of achieving high efficiency power generation. However, in the Southern countries, the parameters are limited by the corrosive elements (Cl and K) present in the black liquor. Cardoso *et al.* (2009) have shown that some eucalyptus black liquor can contain 1.5–2.2 wt% K and 1.9–4.0 wt% Cl. For modern recovery boilers producing steam at 490°C, the contents in black liquor are typically limited to 0.5 wt% Cl and 2.0 wt% K (Pekkanen, 2010).

Due to their highly volatile nature at high temperatures, NaCl and KCl vaporize from the recovery boiler furnace. As the flue gas temperature decreases, these compounds condense as fume and become enriched in the precipitator ash (Gonçalves *et al.*, 2008). Therefore, K and Cl can be removed by treating this ash.

Although it is possible to dump the ash directly for controlling the mill liquor sulfidity, this practice might not be enough for removing desired amounts of corrosive elements. In addition, since a large fraction of the ash consists of Na₂SO₄, the sodium loss would be high. One alternative is to install Cl and K removal systems to reduce the corrosion rate in the boiler, recover part of the sodium, and in some cases, increase the steam parameters to more energy efficient levels.

Additional features to enhance the power generation in the mill are: black liquor firing at higher dry solids content, increase of boiler feedwater temperature, turbines with controlled extraction, improvements in the sootblowing strategy, flue gas heat recovery and preheating of combustion air with steam from turbine bleed (Kankkonen, 2010).

2.2.3 Mill age and capacity

The specific heat and electricity consumption is influenced by the size and age of the mill. Old mills are typically smaller and operate with less energy-efficient equipment than the modern ones. This means that, in general, larger mills consume less heat per ton of product than smaller mills. The consumption figures are lowest at the design production rate, when the machines operate more efficiently. The size of the pulp mills has been increasing during the last years, mostly because of the reduced investment and manufacturing costs per ton of pulp produced. The large mills are being built especially in South America, where the climate and soil conditions are favorable for rapid growth of trees with good quality fiber.

The start-up of the most recent mill took place in Três Lagoas, Brazil, in 2012, with a design annual capacity of 1.5 million tons of fully bleached eucalyptus market pulp. This single mill has increased the total black liquor burning capacity in the country by 11%. Interestingly, the size of recovery boilers has also grown significantly during the past few decades. Twenty years ago the average capacity was around 1700 tDS/d. Today, one single boiler can achieve the capacity over 7000 tDS/d. Figure 2.4 shows that the total installed capacity of Brazilian recovery boilers reached approximately

70000 tDS/d of virgin black liquor in 2012. The figure also shows that the consumption of natural gas has increased and that of oil decreased. This is mostly attributed to the installation of large lime kilns and the preference of natural gas over oil.

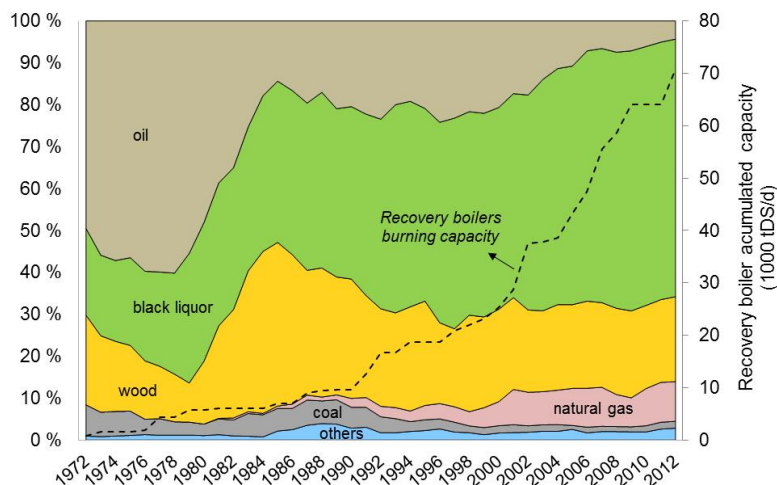


Figure 2.4: Energy sources (electricity excluded) in the Brazilian pulp and paper industry (BEN, 2013)

The implementation of large pulp mills in South America is also favoured by the reduced transportation cost between the forest and mill facility. One advantage of these modern mills is that the entire wood material supply comes from eucalyptus plantations usually within the maximum distance of 200 km from the mill. In addition, since the forest productivity (harvestable wood produced per year per hectare), is higher in South America than in typical Northern countries, larger mills can be built in South America. This is also supported by the fact that manufacturers have learned how to make larger recovery boilers and single cooking vessels.

2.2.4 Efficient incineration of wood residues

Major technological developments in biomass boilers have occurred in recent years. These include large steam generation capacities of over 500 t/h, high steam pressure and temperature, and burning of multitude of low grades residual fuels. The advances in fluidized bed combustion (FBC) have also provided the ability to burn various biomass fuels in the same unit in an efficient way. Large-scale boilers using the FBC technology are a common practice in countries such as Finland and Sweden. In Brazil and Chile, fluidized bed boilers have been installed in pulp mills with capacities ranging from 90 to 200 t/h of steam.

Some research topics related to the improvement of FBC process include: increasing limits of fuel flexibility, decreasing tube corrosion, preventing bed agglomeration and finding optimum mixing of secondary air. Hupa (2013) has shown how bed sintering, superheater fouling, and high-temperature corrosion are crucial factors to be taken into account when fuels are selected for FBC. According to the author, the sintering is caused by the change of the bed particle (e.g. quartz or silica sand) chemistry because of the interaction with ash-forming matter. Therefore, although the FBC provides the opportunity to mix different types of fuels, special attention is required when non-conventional fuels such as mill sludge (Charlson and Taylor, 1999) are used.

2.2.5 Energy policy

The use of biomass as a source of energy in Brazil is not only dependent on economic decisions but also on political-historical aspects. What drives the electricity market in the country is the pursuit of low generation costs to provide affordable tariffs for the mass population. Today, Brazil obtains most of its electric energy from hydro power and an additional from fossil based thermal sources. Bio-based sources still represents a small share in the electricity market. According to a Brazilian decennial plan for the expansion of the electricity sector (MME/EPE, 2011), a significant contribution from renewable resources is expected. This is however limited to the burning of sugar cane bagasse and establishment of wind mills.

As a basis for comparison, the Nordic countries have been setting ambitious and long-term goals for reducing greenhouse gas emissions (NETP, 2013). They are at the forefront of commercial applications for woody biomass, using an array of policy instruments to support the development of both the supply and demand for renewable energy. The result is a strong focus on energy technology research, development and demonstration of innovative processes. In Finland, CO₂ taxes, feed-in tariffs and tax subsidies on renewable energy are among the instruments used to increase the use of bioelectricity and district heat production. One reason is that the country has been, for many years, a net importer of electricity, purchasing from Russia.

The bioenergy sector in Finland has strong traditional competences mainly developed within the pulp and paper industry. This know-how has been gradually exported to South America, since Finland is also a major supplier of biomass procurement machinery. In Sweden, main policy instruments include oil taxation, green certificates for the production of bioelectricity and rural programmes to support the production of domestic bioenergy. Even in Norway, where the economic growth has been fuelled by the petroleum exploration, biofuel support schemes have become an important issue for the government.

2.3 Biorefining opportunities

Pulp mills have been identifying new pathways to go beyond the production of pulp and electricity. One widely discussed approach is the integration of multi-products biorefineries, providing, therefore, an opportunity to contribute to the future demands for energy, fuels and chemicals. The potential is vast, considering that the sector is already engaged with the development of tree seedlings, forest management and transportation of logs to the industrial facilities. In addition, pulp mills have the competence to process wood chips and residues in a very effective way. On the other hand, achieving profitable growth through the introduction of new sellable products might be challenging and has to be carefully evaluated. Section 3 describes the main routes explored in this work.

3 Analysis of alternative routes

There are different pathways to produce alternative fuels in the kraft pulp mills (Paper IV). The choice will depend on the process maturity, investment cost, and especially on the market development for the new revenue streams. The impacts on the conventional operation of kraft pulping are also important and have to be carefully studied. This thesis emphasizes four integration alternatives: lignin removal from black liquor, hemicelluloses extraction prior to wood pulping, torrefaction and fast pyrolysis of biomass.

3.1 Modified black liquor

The valuable chemical properties of lignin and hemicelluloses are not well utilized when black liquor is simply burned in the recovery boiler for energy recovery. Instead, these two components could be used as raw-materials for producing for example biofuels or speciality chemicals. Although there is the possibility of extracting lignin and hemicelluloses from black liquor, it is important to evaluate its effects on the conventional pulping process (Figure 3.1). Here, the term “modified” is attributed to the assumption that the black liquor composition and characteristics can be changed from the original structure when subjected to the following steps: i) precipitation of lignin from black liquor and ii) extraction of hemicelluloses from wood chips. When hemicelluloses extraction is applied, it is normally done through pre-hydrolysis technique prior to chip pulping. In this case, not only the black liquor properties can be affected but also the pulp yield and quality.

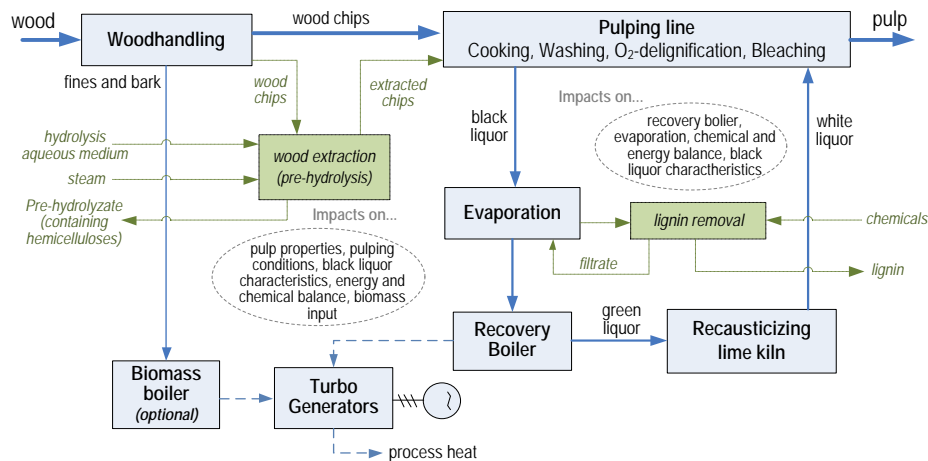


Figure 3.1: Lignin removal and pre-hydrolysis: main impacts on the kraft process

3.1.1 Lignin lean black liquor

Removing lignin from black liquor is interesting for three main reasons: Firstly, it can be used to decrease the heat load on the recovery boiler per ton of pulp produced (Vakkilainen and Välimäki, 2009). This means that if the recovery boiler is the mill bottleneck, more pulp can be produced. Secondly, the separated lignin might be used to replace fossil fuels in the mill (Wadsborn et al., 2007) as a means of achieving carbon neutral pulp mills or used as a sellable renewable fuel. Finally, the lignin after refining has the potential of being a raw material for new products such as carbon fibres, adhesives/binders, dispersants and metal chelating agents as well as vanillin and lignin-based polyurethanes (Borges da Silva *et al.*, 2009; Öhman et al., 2007; Stewart, 2008).

One method to separate lignin from black liquor is the acidic precipitation. The black liquor is pumped from the evaporators, at 30–40% dry solid content, to the precipitation vessel where the pH is altered. The acidification is carried out by using preferably CO₂ (carbonic acid is formed). The lignin precipitate is filtered and then washed. The remainder of the black liquor is returned to the evaporation plant. In the lignin washing operations, mineral acid (H₂SO₄) is used to minimize the sodium content in the final product (Tomani, 2010). The washing filtrate can be sent to the evaporators, which means that an increase in the evaporation load is to be expected. Special attention is required when a sulphur-containing compound is added to the liquor cycle. Since it can affect the liquor sulfidity of the mill, extra ash from the recovery boiler electrostatic precipitator has to be discharged, mostly in the form of Na₂SO₄. This means that additional NaOH might be needed to control the mill chemical balance.

The influence of lignin removal on the energy balance of eucalyptus pulp mills was the focus of Paper II. When lignin is removed, the organic content of black liquor decreases, but the inorganic portion remains essentially unchanged. This will directly affect the recovery boiler operation and steam generation rate. If the target is to keep the heat load into the boiler, more lignin lean black liquor needs to be fired. It is important to emphasize that the attractiveness of this technology is dependent on whether or not the mill can sell the lignin that has been taken out.

3.1.2 Hemicellulose lean black liquor

Hemicelluloses extracted from wood prior to cooking can be a valuable source of hexose and pentose sugars. They can be further converted into value-added products such as ethanol, xylitol or polymers. Different methods of extraction have been identified and are discussed in Paper III. However, the ethanol production followed by pulping faces a number of challenges to become an implemented technology (DeMartini *et al.*, 2008). Firstly, the volume of ethanol produced per ton of pre-extracted wood is relatively small. Secondly, there are limits to how much wood can be extracted before the pulp strength drops too low. Thirdly, the impacts on the operations of the pulp mill can be significantly high.

Therefore, the added value created by the new revenue stream is essential to make the hemicelluloses extraction prior to pulping economically attractive. Different methods have been proposed for the aqueous phase extraction of hemicelluloses in combination with pulp production. In acidic pre-hydrolysis processes, hemicelluloses (mostly xylan) are hydrolyzed to oligomeric and monomeric sugars and dissolved in the pre-hydrolyzate (PHL) either in a dilute solution of a mineral acid (e.g. H_2SO_4), which acts as a catalyst of hydrolysis (Frederick *et al.*, 2008; Parajó *et al.*, 1994; Al-Dajani *et al.*, 2009; Mendes *et al.*, 2009), or auto catalytically (auto-hydrolysis, AH or hydrothermal). In both processes, the hydrolysis is catalyzed by hydronium ions (H_3O^+).

In auto-hydrolysis, the acidic conditions are created through the cleavage of acetyl groups from xylan backbone and consequent release of acetic acid in hot water at a temperature of 130–175°C (Al-Dajani *et al.*, 2009; Mendes *et al.*, 2009; Casebier and Hamilton, 1969; Colodette *et al.*, 2011; Garrote and Parajó, 2002; Yoon *et al.*, 2008; Leschinsky *et al.*, 2009; Kautto *et al.*, 2010). In alkaline conditions, hemicelluloses extraction is carried out with green liquor in a so-called near-neutral process (Mao *et al.*, 2010), with strong alkaline solutions in low temperatures (Al-Dajani *et al.*, 2008), or with white liquor (Helmerius *et al.*, 2010).

3.2 Production of bio-oil and biochar from wood residues

The amount of wood residues generated varies from mill to mill. Even though debarked logs are brought from the forest to be processed in the pulp mill, residues are still generated in the wood handling area. In Brazil, they consist basically of fines from screening and residual bark, representing approximately 2% of the total wood required for cooking. Usually, auxiliary boilers are still installed to incinerate these residues and, thus, produce surplus heat. If the market becomes attractive, there is the possibility of converting them into sellable biofuels. For this purpose, two thermo-chemical pathways are evaluated: fast pyrolysis and torrefaction. Table 3.1 shows the main differences between these two pathways and the combustion of biomass in fluidized bed boilers.

Table 3.1: Alternatives processes compared with fluidized bed combustion

	Torrefaction ^a	Fast pyrolysis ^b	FBC ^c
Temperature	220-300°C	450-500°C	800 - 1000°C
Mean reaction time	0.5-1.5h	0.5-2s	5 – 20s [*]
Core product	biochar	bio-oil	heat
Main co-products	volatiles	volatiles, biochar	ash

^a Almeida *et al.*, 2010; Bergman *et al.*, 2005; Demirbas *et al.*, 2009; Prins *et al.*, 2006;

^b Demirbas *et al.*, 2009; Envergent, 2012; Kumar *et al.*, 2010; Pollex *et al.*, 2012; Wright *et al.*, 2010;

^c Basu, 2006. ^{*}char reaction time excluded

Although biomass can also be gasified and further converted to advanced liquid fuels, the gasification process has been considered more as a way of replacing fossil fuels in the lime kilns. The technology, therefore, is not explored in this thesis. Thus, the focus of Paper V is to evaluate the feasibility of torrefaction and fast pyrolysis as alternatives to combustion (Figure 3.2). The attractiveness of each process would depend very much on the market prices for electricity, bio-oil and biochar.

It is important to point out that the integration is not straightforward, since there will always be the challenge of using the co-products such as volatiles and char in an optimum manner (Oasmaa *et al.*, 2010). Moreover, in order to achieve good conversion rates, the biomass has to be dried before it enters the reactors. Water embedded in the feed consumes process heat and contributes to lower process yields. For drying, low pressure steam and hot water can be used as heat sources.

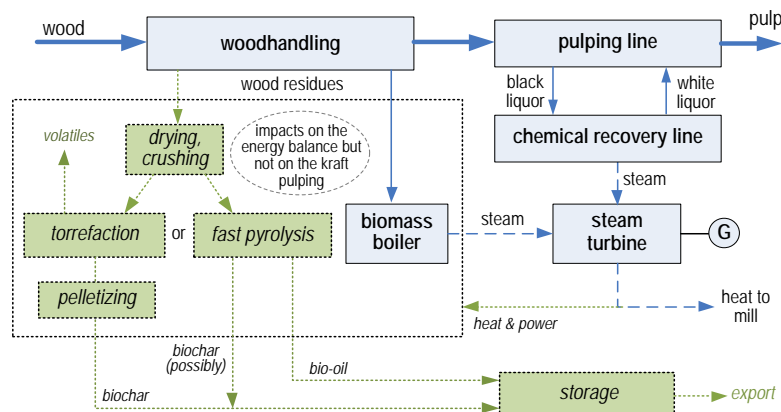


Figure 3.2: Alternative thermo-chemical conversion of woody biomass to biofuels

A great advantage of processing the wood residues for additional income comes from the fact that the pulping process, pulp quality and sales are not harmfully affected. Since wood residues are the main raw-material in the study, these alternatives are ideally applicable to standalone pulp mills operating without a biomass boiler. For existing mills, where residues are usually incinerated, additional logs or biomass residues should be brought from the forest.

3.2.1 Fast pyrolysis

There has been a considerable growth of activities over the last few years, either with innovation in pyrolysis (Bridgwater, 2012) reactors, or in attempts to find optimum process conditions. The chemical composition, moisture and particle size of the raw material, are key factors to be considered when studying the quality and production

potential of bio-oil. The main concern regarding the use of wood residues for pyrolysis is that they contain higher amount of extractives and alkali metal salts when compared to bark-free wood. Since mineral salts are known to catalyze pyrolysis reactions of biomass, their presence can result in significant impacts on the bio-oil yield (Oasmaa *et al.*, 2010).

Several types of reactors have been developed for fast pyrolysis tests (Hulet *et al.*, 2005; Brown, 2005). Currently, one of the most favoured options is to utilize hot sand as heat carrier, since high heat transfer rates can be achieved from the sand to biomass particles. The fluidized bed pyrolyzer types have, therefore, good technological strength and market attractiveness for large-scale units. They can be classified into bubbling fluidized bed, with the bed material remaining suspended in one reactor, or circulating fluidized bed. The latter, sometimes referred to as transport bed, has often a separate combustion reactor used to re-heat the sand, which is continuously recirculated. Gas exiting from the pyrolysis reactor contains entrained particles that are separated through cyclones. Examples of companies that commercialize fluidized bed technology are Envergent, Metso, and Dynamotive.

After the cleaned gases exit the cyclone unit, they must be cooled for the formation of bio-oil and separation of non-condensable pyrolysis gases to prevent further detrimental reactions from taking place. The non-condensable gases can be used as fluidizing agents, although other gases such as N₂ can also be applied for this purpose. In a typical continuous process, the oil can be cooled, recirculated, and sprayed to quench the gases through direct contact heat transfer.

Regarding yields of pyrolysis products, different results are usually observed in literature, which can be attributed to variations in biomass composition, process conditions, apparatus reliability and measurement errors. The average values for bio-oil yield, however, including commercial scale units, are in the range of 60–70% of the dry feedstock (Badger *et al.*, 2012; Dynamotive, 2013; Envergent, 2013; Kumar *et al.*, 2010; Oasmaa *et al.*, 2010), with lower yields expected for forest residues.

3.2.2 Torrefaction

Torrefaction occurs at significantly lower temperatures and requires longer reaction times than fast pyrolysis. The moisture is removed and hemicelluloses decomposed, causing the release of volatiles compounds. The resulting material becomes brittle and, typically, more hydrophobic, with intermediate characteristics between coal and untreated biomass.

The severity of the torrefaction process depends on the biomass type, residence time and temperature. The effect of temperature is significant, with mass and energy losses increasing fast above 250°C (Bergman *et al.* 2005). Severe torrefaction would result in increased brittleness of the product, which could bring problems for the integrity of the produced pellets.

At 250°C, most experiments have resulted in 90 to 95% of the energy and 80 to 90% of the mass of the untreated dry biomass retained in the product (Prins *et al.* 2006; Almeida *et al.* 2010; Arias *et al.* 2008; Chew and Doshi 2011; Oliveira and Rousset 2009). The higher loss of mass than heating value therefore leads to slightly increased LHV. One important issue is to determine the appropriate design for the heat integration. This means that the most economical source of heat for torrefaction and the heat exchanging method have to be defined (Bergman *et al.* 2005), and it has to be decided where the volatiles generated will be incinerated.

4 Pulp mill calculations

The calculations are performed using a mill spreadsheet that has been developed during the research period. It includes a detailed mass and energy balance, and it can be used to design pulp mills by equipment vendors and to evaluate new processes alternatives. The calculations were based on theoretical fundamentals, practical experience and analysis of operational data from existing mills. In the cases where non-conventional processes are integrated into pulp mills, a literature survey and personal communication with experts in the area were also considered. One of the essential steps was to develop an appropriate tool for studying changes in the characteristics of black liquor.

The first target was to evaluate the possible effects of Cl and K on the operation of kraft chemical recovery cycle (Paper I). The magnitude of changes was calculated by varying the content of both elements in black liquor. Since thousands of variables and calculations were involved, tools for tracing the dependent variables became important. This feature made Microsoft Excel particularly useful for the tasks. A project of a modern eucalyptus pulp mill in South America served as a base case model. The tool was later checked against operating data of a modern 600,000 ADt/a softwood pulp mill and 700,000 ADt/a integrated pulp and paper mill in Northern Europe.

4.1 Black liquor calculation tool

The composition of black liquor has a direct impact on its heating value and also on the flue gas properties, and therefore, is of great importance for recovery boiler designers. The heating value of black liquor is affected for example the relative proportion of lignin and degraded carbohydrates, degree of white liquor oxidation and amount of inorganic material. A database containing the analysis of different black liquors (after Vakkilainen, 2000) is also included in the balance. The black liquor total heating value can be represented by Equation 4.1:

$$HV_{BL} = \frac{H_{BL}}{M_{BL}} = \frac{(hv_{blw} + hv_{org} + hv_{inorg})}{(m_{blw} + m_{org} + m_{inorg})} \quad (4.1)$$

The organic fraction of black liquor accounts for approximately 90% of the total heating value ($h_{v_{org}}$). Most part of the heat released comes from the dissolved lignin and organic acids from carbohydrates. Minor contributions come from fatty acids and other organic compounds formed during pulping. The amount of reduced sulphur has also an influence on the HV_{BL} . Assuming that the black liquor contains 116 kg/ADt of Na_2S ($h_{v_{inorg}} = 116 \times \Delta H_{red} = 116 \times 12900$) in 1380 kgDS/ADt of total dry solids (M_{BL}), the heating value would be 1.09 MJ/kgDS. This means that the contributions from the inorganic fraction ($h_{v_{inorg}}$) should not be ignored.

The calculation guideline is essentially based on the Adams and Frederick (1988) method, which includes the correction for white liquor causticity and sulphur reduction efficiency. The tool was modified during the thesis to initially include eucalyptus as a

raw material and to take the effect of white liquor oxidation (h_{blw}) into account. Later on the changes required for lignin and hemicelluloses extraction were added.

4.2 Lignin removal

Studying the influence of lignin removal on the energy balance of modern eucalyptus pulp mills was the focus of Paper II. The lignin in black liquor can be calculated by subtracting the lignin in pulp (m_{ligP}) and the removed lignin (m_{ligR}) from the lignin content in wood (m_{ligW}). The contribution of the heating value of lignin to the total heating value of black liquor solids can be calculated by solving the following equation:

$$h_{lig} = (m_{ligW} - m_{ligP} - m_{ligR})HV_{lig} \quad (4.2)$$

The lignin in the pulp that goes to bleach plant depends on the desired brown pulp kappa number, which differs from project to project. The mass percentage and structure of lignin can also vary between wood species. As a consequence, the consumption of chemicals should be evaluated for each case (Tomani et al., 2012).

In order to evaluate how the lignin removal process affects the dimensioning of a kraft pulp mill, two study cases are considered: A) A study of the design of a pulp mill with lignin removal rate ranging from 0% to 30% and B) A study of the impacts on this pulp mill when up to 30% of lignin is removed and the heat load into the recovery boiler is fixed. In case B, it is assumed that the pulp production has to be increased. This means that the recovery department capacities are fairly constant, but the pulping line size changes. The derived balances are used to show the influence of the lignin removal on the design and operation parameters of new pulp mills.

4.3 Hemicelluloses extraction

The integration of pre-hydrolysis using hot water is presented in Paper III. The mill balance calculations were based on auto-hydrolysis experiments using pine chips prior to pulping (Kautto *et al.*, 2010). Essential data are needed for the mill balance, which include the PHL characterization, amount of extracted matter, changes in cooking yield, EA charge and sulfidity. Such variables affect, for example, the black liquor calculation and, consequently, the chemical recovery cycle operation.

After the pre-hydrolysis, the PHL liquid can be recovered (as hemicelluloses), but part is entrained in the extracted wood pores. As a consequence, the evaporation load will be affected. With the analysis data of PHL and original wood, the extracted wood composition can be estimated. The analysis of PHL provides the amount of organics removed as carbohydrates, lignin, formed acids and extractives at a defined liquor-to-wood ratio and hydrolysis temperature.

Because the heat load into the recovery boiler is increased with the implementation of hemicellulose extraction, the lignin removal is used as an alternative to reduce the organic fraction in the black liquor. It is then assumed that more extra load is added to the evaporators due to the return of lignin washing filtrate.

Since the actual end product manufactured from the PHL is not specified in this work, the analysis is limited to the hemicellulose extraction process. This means that heat, electricity and chemicals consumed in the processing of the PHL as well as the combustion of the additional residues are not considered in the mass and energy balances.

4.4 Biofuels from wood residues

The main focus of Paper V was to study the economic viability of torrefaction and fast pyrolysis technologies in a kraft pulp mill. For this purpose, four cases are considered: Incineration of the available wood residues in a biomass boiler, with generation of additional steam and electricity (BB); Torrefaction of wood residues, with biochar for sale (T); Fast pyrolysis of wood residues, with bio-oil and biochar for sale (FP); and fast pyrolysis of bark-free biomass and incineration of wood residues, with bio-oil for sale (FP2). The latter scenario is specifically applicable to existing mills already operating with a biomass boiler and is, therefore, treated as an isolated case.

For the case studies, it is assumed that one third of logs would be delivered with 10 wt% of bark, with the remaining logs (forest-debarked) carrying 2 wt% of the residual bark. It is important to remind that feedstock drying is crucial to improve the efficiency of both torrefaction and fast pyrolysis processes. The energy requirement of biomass dryers, H_{DSt} , can be obtained from equation 4.3.

$$H_{DSt} = \frac{\dot{m}_{ut}}{\eta_{dryer}} \{ [(1 - MC_{ut})c_{p,dry} + MC_{ut}c_{p,wL}] (T_{out} - T_{in}) + (MC_{ut} - MC_d)L \} \quad (4.3)$$

where c_p is the specific heat, MC the moisture content and L the heat of vaporization. Low pressure steam is utilized as a source for drying the biomass prior to torrefaction and fast pyrolysis. The moisture content is reduced from 45 to 10% and a dryer efficiency maximum of 60% is considered. A $c_{p,dry}$ value of 1.6 kJ/kg.K is assumed for the biomass.

4.4.1 Torrefied biomass production

The biomass drying and torrefaction models were developed by using IPSEpro, which is an equation oriented steady-state software developed by SimTech for power plant simulation. It is a flexible tool for the modeling, analysis and design of components and processes in energy and process engineering. The software is used for this research to create the required models where needed. The steam and power balance of the reference pulp mill was reproduced with the objective of evaluating the possible

changes after integration. The torrefaction module was adjusted to produce a solid product, with mass and energy contents obtained experimentally from the torrefaction tests of *E. grandis* (Almeida *et al.*, 2010) for both wood and bark. The solid mass flow rates and LHV values are given on a dry ash-free basis.

In this work, the steam used for boiler sootblowers provides indirect heat to the torrefaction reactor. The integration also allows the released volatiles to be incinerated in the recovery boiler, Figure 4.1. For the torrefaction model, the gas exits at 250°C from the reactor. The module was adjusted to produce a solid product, with mass and energy contents obtained experimentally from the torrefaction tests of *E. grandis* (Almeida *et al.* 2010) for both wood and bark.

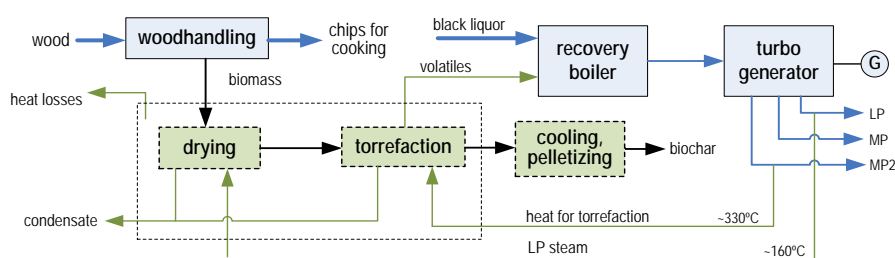


Figure 4.1: Torrefaction process integrated to a pulp mill

4.4.2 Bio-oil production

Mill balances were performed for two configurations: Co-production of biochar (FP) and co-production of steam (FP2). In FP case, the biochar is not fully mixed with the recirculating sand and can be alternatively recovered. As a result, biochar becomes a sellable high heating value by-product. The FP2 scenario is suitable to existing mills already operating with fluidized bed boilers. Therefore, a separate combustor for the pyrolysis by-products would not be necessary. The bio-oil production, however, would be limited to the boiler heat load and solids recirculation capacities. The schematic diagram of the overall balances is shown in Figure 4.2.

Since large scale units processing eucalyptus are not presently in operation, exact values for product yields, heat for conversion or equipment efficiencies are not yet available. For estimating the potential of bio-oil production, personal communication with technology suppliers and literature survey were required. It is assumed that the yields of crude pyrolysis oil of 60% (FP1) and 70% (FP2) can be achieved for extended periods of operation.

For FP2 case, it is assumed that the poor biomass (bark and debris) available is incinerated and that approximately 280 t(dry)/d of bark-free additional biomass, brought from the forest, enter the pyrolyzer unit. This results in an acceptable pyrolyzer-to-boiler

feed ratio according to one technology supplier. Higher ratios could lead to instabilities in the recirculation of bed material.

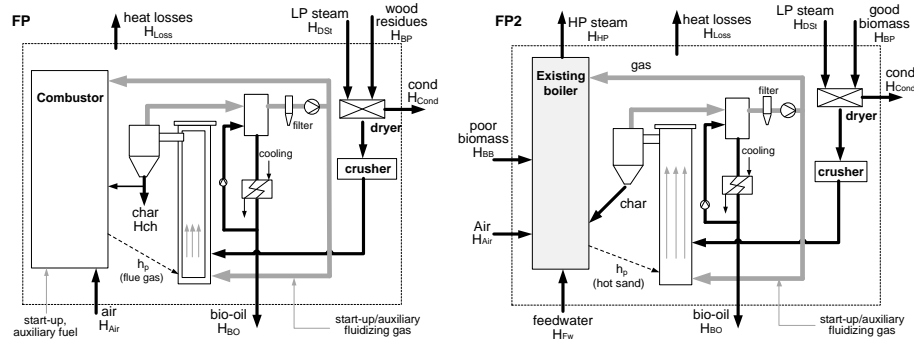


Figure 4.2: Fast pyrolysis process diagrams

4.4.3 Economic analysis

Investment and operational costs for fast pyrolysis or torrefaction are not easy to access. One reason is attributed to the lack of references for large-scale units. Predicting future renewable energy prices is also a subject to considerable uncertainty, since the market for the products is still developing and may vary between countries. The results of the economic analysis are then presented in the form of series of curves at different investment costs, showing internal rate return (IRR) as a function of energy price. The analysis was based on solving the interest rate by finding such present value factor a that yields a NPV of zero.

$$NPV = a(C_e + C_{prod} - C_{O\&M} \pm C_{wood}) - C_{inv} \quad (4.5)$$

The variable $C_e = \Delta P_e \cdot t \cdot c_e$ represents the difference in the annual value obtained from exported electricity in comparison with the reference mill. In the specific case of FP2, the C_e value is compared to the BB scenario. C_{prod} is the annual value of produced fuels for sale, $C_{O\&M}$ the annual operating and maintenance cost and C_{inv} the total investment cost. The parameter C_{wood} refers to the cost for disposing the residues or for the additional wood brought from the forest.

Fixed amortization period of 10 years, NPV zero at the end of payback time and annual operating time of 8400h/a, same as for the reference mill, are considered for all cases. When economical parameters were not treated as variables, the values presented in Table 4.1 were used. To evaluate the influence of the selling electricity prices on the IRR, two scenarios are considered for T and FP2.

Table 4.1: Basics for the economic analysis

		BB	T	FP	FP2
Investment cost C_{inv}	M US\$	50±15	40±15	75±20	45±15
Residues disposal	US\$/t	30	30	30	0
Electricity price, c_e	US\$/MWh	35–80	30/60	50	30/60
Additional wood	US\$/MWh	0	0	0	10
Biochar price	US\$/MWh	0	10–30	15/30	0
Bio-oil price	US\$/MWh	0	0	20-60	45–85

5 Main findings and discussion

It is important to have in mind that it is not possible to provide accurate answers to the research question number 3 until the demonstration plants have been put into operation. Some of the results obtained from this work are based on assumptions and experimental data. On the other hand, with the practical experience in the kraft pulping and bioenergy areas, in addition to valuable published references, a good approximation can be reported.

5.1 Operational changes to current pulp mills

In order to evaluate the influence of Cl and K on operational variables, calculations were performed using a detailed balance for a 1.25M ADt/a bleached eucalyptus pulp mill. Costs saving calculations were based on realistic conditions, where the Cl content ranges from 0.5 to 2.0% and the K content from 1.1 to 3.2% (wt in black liquor). They are identified as points B1 and C1. These points represent, for example, a coastal mill with the intention to invest in technologies for removing Cl and K. The base case model is represented by point B1. Graphical comparisons were done by varying the Cl content from 0.5 to 3.0% and the K content from 0.2 to 3.5% (wt in black liquor). These are identified as points B and C. Grace and Tran (2009) have stated that around 20% of the recovered inorganics that circulate through the cycle are as inactive species. Table 5.1 shows comparable values with several Cl and K levels.

Table 5.1: Mill balances with fixed AA content in white liquor (138.1gNaOH/l)

		B	B1	C1	C
Cl in black liquor	% wt	0.5	0.5	2.0	3.2
K in black liquor	% wt	0.2	1.1	3.2	3.5
White liquor TTA	gNaOH/l	156.6	156.6	157.8	158.8
White liquor TAC	gNaOH/l	160.5	160.5	170.1	177.6
Causticizing efficiency	%	83.61	83.60	82.71	81.98
White liquor flow rate	m ³ /h	456.8	456.6	456.0	455.9
Inorganics in black liquor	kg/ADt	415.1	419.8	473.5	508.8
Black liquor HHV	MJ/kg (dry)	14.32	14.28	13.76	13.43
Evaporation capacity	t _{H2O} /h	1103	1107	1149	1177
- Steam consumption	t/h	183.9	184.5	191.9	196.8
- Cooling water flow rate	m ³ /h	11647	11682	12127	12424
Power generation	MW	162.5	162.4	161.5	160.9

The assumption in Table 5.1 of fixed AA concentration is the basis for the graphical comparisons. Pulp mills operate normally causticizing plants to target the active or effective alkali concentration. It can be observed that parameters such as the

evaporation load, black liquor heating value and recovery boiler load might be affected. Increasing inert load, for example, can result in an increased black liquor dry solids flow rate and decreased black liquor heating value. Basically, the white liquor flow rate does not change, and hence, the causticizing capacity is not significantly affected. The white liquor causticizing efficiency is however affected.

5.1.1 Effects on black liquor properties

The organic content of black liquor remains basically the same, but as the contents of Cl and K increased, the inorganic content increased from 415.1 kg/ADt (point B) to 508.8 kg/ADt (point C). This corresponds to the change in dead loads in black liquor ranging from 107.5 kg/ADt to 205.2 kg/ADt. The magnitude is in accordance with the values referenced by Grace and Tran (2009), who have suggested the total dead loads ranging from 7% to 15% of the total black liquor solids.

5.1.2 Effects of Cl and K on evaporation load

If the amount of inorganics in the weak liquor to be removed from pulp increases, additional dilution is required. Consequently, the evaporation load increases along with low pressure steam and cooling water consumption. The balance shows both steam and cooling water consumption increasing by around 4% from point B1 to C1. The differences are equivalent to 7.4t/h of low pressure steam and 445 m³/h of cooling water.

5.1.3 Effects on recovery boiler operation

It is reasonable to assume that the reduction efficiency is not significantly affected by the presence of dead loads. Thus, a fixed reduction efficiency of 96% was taken as the basis for the balance calculations. Figure 5.1 shows the impacts on smelt flow rate. The change in the smelt flowing to dissolving tank will not significantly affect the mill energy balance. Smelt sensible heat represents approximately 21% of the total heat losses in the recovery boiler. The smelt heat losses are roughly proportional to the mass flow rate. Because the total smelt mass flow rate changes only by 5 %, the percentage remains roughly the same.

The energy balance results show that the steam generation is increased by 1% by increasing the potassium content from point B to point C. This can be also attributed to the heat absorbed during the reduction of K₂SO₄ to K₂S (9630 kJ/kg). Since the reduction heat for Na₂SO₄ to Na₂S is higher (13090 kJ/kg), the net heat for steam production becomes slightly higher. The heats absorbed during the Na₂S and K₂S reduction represents around 35% of the total heat losses. The remaining losses refer to the heat lost in hot flue gas, smelt sensible heat and some other minor streams. It is typical for flow rate instruments to state the accuracy as 1–2 % of the measured value.

Hence, the small change of 1% in the steam generation would not be noted in practical mill operation.

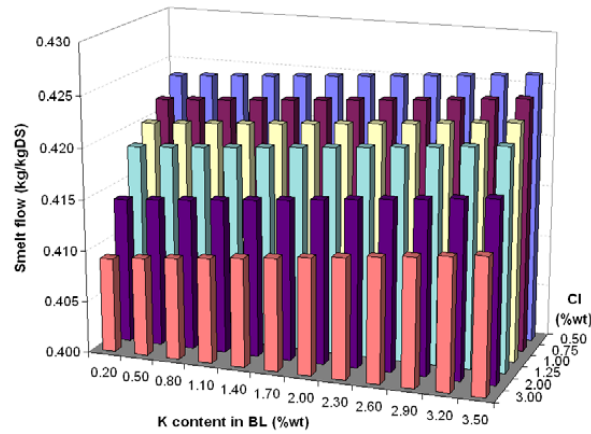


Figure 5.1 - Effect of Cl and K on smelt flow rate

5.1.4 Effects on causticizing efficiency

Dorris (1990) states that Goodwin’s curve (highest achievable causticizing degree) correlates not only with TTA but also with the non-titratable anions (NTA). The difference of 3.5% to Goodwin’s curve assumed in this work defines the causticizing efficiency (CE) for each alkali level. With the fixed AA concentration, the CE decreases with the increasing of Cl as shown in Figure 5.2. At the same time the total anion concentration (TAC) is increased by 11% from point B to C.

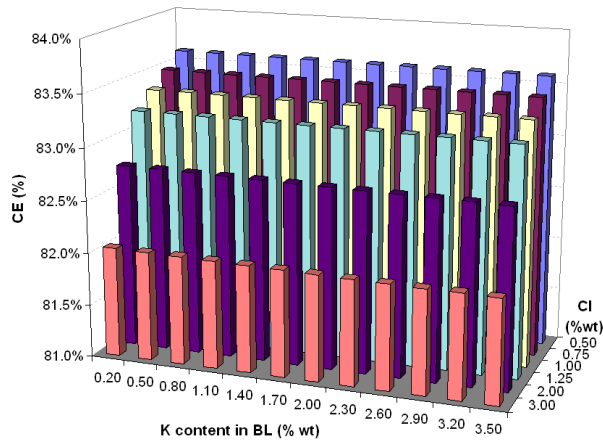


Figure 5.2 - Effect of Cl and K on CE for fixed AA concentration

When the TAC in white liquor increases, the amount of sodium carbonate will also increase with the decreasing CE. This may for example disturb the operation of the evaporation plant, especially if combined with a high content of sodium sulphate in black liquor (Arpalahti *et al.*, 2000). Table 5.1 shows that the CE decreases by 1.9% from point B to point C.

According to Saeidi *et al.* (2009), coastal mills are predicted to have a CE 1%–2% lower than that of inland mills. This is due to the Cl concentration in liquors of coastal mills being 2–4 times higher than those of inland mills. It is important to emphasize that they have considered, for this case, fixed values for the TTA. In practice, if constant TTA is required by the pulp mills, the CE will be inevitably lower.

5.1.5 Effects on pumping cost

One of the aspects studied was the magnitude of change in liquor pumping due to the increased K and Cl levels. Four pumping systems were considered in the evaluation: weak black liquor pumping from cooking to evaporation plant (P1), white liquor pumping from causticizing to cooking (P2), green liquor pumping from dissolving tank to causticizing (P3) and cooling water pumping from cooling towers to evaporation plant (P4). Realistic design data were used to better estimate the pumping costs which are shown in Table 5.2. The saving cost evaluation is done by using the range from point B1 to point C1. The hydraulic ($P_h = q \rho g h / 3.6 \cdot 10^6$) and shaft ($P_s = P_h / \eta$) power in kW for each pumping are defined as follows:

Table 5.2: Change in pumping cost for fixed AA from point B1 to C1

Description	unit	P1	P2	P3	P4
Head	m	60	35	40	40
Pump efficiency	%	78	78	78	78
Change in shaft power	kW	35.0	1.8	0.7	100
Change in pumping cost	€a	8800	453	166	50000
Pumping cost increase	%	11.8	3.0	1.0	11.9

An electricity price of 30 €/MWh was used as the basis for cost evaluation. It is assumed that pump efficiencies do not change according to their characteristic curves. Table 5.2 shows that the white liquor (P2) and green liquor pumping systems (P3) will present no significant changes. Even so, the difference in cost for all the pumps reaches 59,000 €/per year. In practice, these cost differences for P2 and P3 and even P1 are not representative for each pulp mill.

5.1.6 Effects on power generation

The modern bleached eucalyptus pulp mill equipped with a condensing tail turbine has a potential for generating 162 MW of electricity at design point B1. For a fixed AA, the energy balance shows that an increase from point B1 to C1 in steam consumption mainly by the evaporation process decreases electricity generation by 0.9 MW. From point B to C, the decrease reaches 1.6 MW. This is caused by the reduction of steam flow rate to the condensing tail part of the steam turbine. Since it is typical for pulp mills to sell the surplus electricity to the grid, it is interesting to estimate the cost involved. Thus, considering the most realistic range (from B1 to C1) and assuming 30 €/MWh in 350 operation days, the cost of 0.9 MW is equivalent to about 252,000 €/a.

5.2 Lignin removal in kraft pulp mills

The derived balances are used to show the influence of lignin removal on the design of a 1.5M ADt/a eucalyptus pulp mills in South America. In this study, the average cooking yield is assumed to be 53%. Although impacts are expected on the evaporation load, liquor viscosity, boiling point rise or mill Na/S balance, it is not possible to provide accurate results until real scale plants are put in operation. The main focus in this work is to evaluate the impacts on the recovery boiler loading and mill energy balance. A lignin heating value of 25 MJ/kg(dry) is considered for all the balances.

5.2.1 Decrease in power generation

Since the organic load is reduced but the inorganic load remains the same, more lignin removed black liquor dry solids needs to be fired in order to maintain the same steam load. The highest impact is on the recovery boiler process because of the changes in the fuel properties. This will significantly affect the power generation. If lignin is removed from black liquor, the size of the recovery boiler decreases but also the steam generation will be significantly lower, Table 5.3. The boiler HHRR decreases faster than the mass flow rate as the removed lignin has a higher heating value than the black liquor average. Therefore, the recovery boiler steam generation also drops faster than the firing rate indicates.

It is acknowledged that the removal of lignin from black liquor could affect the combustion properties. The devolatilization stage is dependent on specific liquor properties. The rate of combustion reactions, for example, is increased with higher swelling (Vakkilainen *et al.*, 1998). This can be explained by the larger available surface area for highly swelling black liquor. Studies (Noopila *et al.*, 1991) show that the swelling for both softwood and hardwood is proportional to the ratio of lignin to aliphatic acids in the liquor.

In addition, Alén (2000) stated that the lignin can affect not only the swelling but also the pyrolysis and char burning time of a black liquor droplet. This means that changes in boiler firing practices need to be done to accommodate differences in black liquor

burning characteristics. In a study by Vakkilainen et al. (1999), it was noted that in industry, very different black liquors can be successfully fired. Although the black liquor lignin concentration has an influence on the combustion process, the design capacity of the recovery boiler would not be affected.

Table 5.3: Calculated values for different rates of lignin removal

Variable	Unit	0%	10%	30%
Dry solids in BL after lignin removal	kg/ADt	1359	1312	1219
Lignin in black liquor	kg/ADt	469	422	328
Lignin/total dry solids in black liquor	wt-%	36.3	33.9	28.5
Black liquor HHV	MJ/kg(dry)	14.1	13.7	12.8
Heat load into recovery boiler	MW	948	889	772
Hearth heat release rate	kW/m ²	3445	3233	2809
Virgin black liquor flow rate	tDS/d	5825	5624	5223
Removed lignin	tDS/d	0	201	603
Air flow rate (wet), at 1.15 air ratio	Nm ³ /s	232.6	216.8	185.1
Recovery boiler flue gas flow rate (wet)	Nm ³ /s	288.9	270.8	234.6
Recovery boiler steam production	MW	890	825	696
Power generation	MW	192.9	174.9	137.5

In the case study, the power generation decreases by about 29% when 30% of lignin is removed from black liquor. Consequently, less surplus electricity is available for sale. In a modern eucalyptus pulp mill it is still possible to generate surplus electricity after removing 30% of lignin from the black liquor. However, a biomass boiler becomes indispensable to the achieving of this goal. The energy balances also show that, without the operation of such a boiler, the lignin removal rate is limited to approximately 20%. Any value higher than that would result in the process steam demand being higher than the steam generated by the recovery boiler.

The whole energy efficiency of the process also depends on the strategy defined by the pulp mill. The operational costs, for example, will vary according to the number of effects in the evaporation plant or configuration for the feedwater pre-heating system. This work considers an evaporation plant operating with 6-effects, which is a common practice for modern pulp mills in South America.

5.2.2 Fixing the heat load into the boiler

A study case (Välämäki *et al.*, 2010) showed that pulp mill capacity, if limited by the recovery boiler, can be increased by 25% when approximately 0.16t/ADt of lignin is recovered from black liquor. This can be done by keeping the heat load into the boiler constant, and subsequently, by increasing the capacity of other equipment. A mill

balance for 30% lignin removal (0.14t/ADt) was performed with a constant heat load into the recovery boiler. The pulp mill with lignin removal can be designed for higher pulp capacity without investing in a bigger recovery boiler. Although the boiler capacity is not currently the limiting factor, there are challenges to manufacture larger and larger boilers (Mäkelä, 2009). It is important to emphasize that the recovery boiler design is not limited by the dry solids flow rate (tDS/d) but by the flue gas flow rate. One can see from Table 5.4 that the flue gas flow rate has remained almost constant.

It can be observed that with 30 % of lignin removed the black liquor flow rate has to be about 10% higher to maintain the heat load, but at the same time, the steam production is about 4% lower. This occurs partly due to the higher heat losses caused by higher production of smelt. These losses include the sensible heat of smelt and the heat consumed during the reduction of sulphate to sulphide. On the other hand, 340,000 ADt/a more pulp can be produced, which represents an increase of 22.7%. In addition, 740 t(dry)/d of lignin can be recovered.

Table 5.4: Calculated pulp capacity with fixed heat load

Variable	unit	0%	30%
Pulp mill capacity	ADt/a	1500000	1840000
Recovery boiler steam production	t/h	917	884
Heat load into recovery boiler	MW	948	948
Heat loss due to reduction reactions	kJ/kgDS	1124	1268
Heat loss due to smelt	kJ/kgDS	643	701
Virgin black liquor flow rate to furnace	tDS/d	5825	6407
Power generation capacity	MW	193	179
Recovery boiler flue gas flow rate (wet)	Nm ³ /s	289	288
White liquor production	m ³ /h	13140	16120
Lime kiln required capacity	t/d	1180	1440

Trends show that the design of 1.8M ADt/a pulp mill for a single line is expected in the near future. The design capacity of a recausticizing plant would reach 17900 m³/d of white liquor. The evaporation plant would also be large, i.e. 1850 tH₂O/h. Since more pulp can be produced, the electricity usage is going to be about 21MW higher. At the same time, the power generation is going to decrease as a consequence of the lower steam production. The electricity usage per ton of pulp produced is going to be reduced by 2.4%. The study case seems favourable regarding the heat and electricity balances.

5.3 Recovery of hemicelluloses in pulp mills

Mill balances were performed to identify the possible effects of hemicelluloses extraction on the operation of a 600,000 ADt/a bleached softwood kraft pulp mill. In the

balance calculations, the amount of wood extracted prior to pulping was set to 14.1%. According to the test results by Kautto *et al.* (2010), this reduces the overall pulping yield by about 13.4% when compared to the reference. The pulp production was kept constant, and the main mass balance results are presented in Table 5.5. It can be observed that the extraction of hemicelluloses is reflected on the change in wood composition to the digester.

Table 5.5: Mass balance with hemicelluloses recovery and lignin removal

Variable	Unit	Pulp mill	Pulp mill +HR	Pulp mill +HR+LR
Wood demand (with bark)	BDt/d	4140	4780	4780
Wood composition, C:H:L:E ^a	wt-%	39:30:27:4	45:23:30:2	45:23:30:2
Overall pulping yield	%	46	40	40
Evaporation load ^b	t _{H2O} /h	639	725	740
Black liquor average flow rate	tDS/d	3030	3270	3090
Recovery boiler flue gas flow rate (wet)	Nm ³ /s	150	168	151
Recovery boiler steam production	t/h	445	505	446
Total organics in black liquor	wt-%	62.5	66.0	63.5

^a approximate values, calculated for chips entering the digester, cellulose:hemicellulose:lignin:extractives

^b washing filtrate return: 2m³/t lignin (Tomani, 2010)

Part of the extractives in wood is also removed during auto-hydrolysis, which indicates that the tall oil generation could be affected. Considering the fact that tall oil is an important raw material for various products, this could be a major drawback when assessing the feasibility of hemicelluloses extraction. The impacts of auto-hydrolysis on the tall oil yield were, however, not taken into consideration in this study. The chemical composition of the wood extractives includes lipophilic (fats, waxes, steroids, etc.) and hydrophilic constituents (Horvath, 2006). It is then expected that a large fraction of the extractives in the PHL (solubilised after auto-hydrolysis) originates from the hydrophilic (water soluble) constituents. Although this implies that the tall oil generation rate is not significantly affected, the actual impacts should be experimentally tested.

In the cooking tests of hydrolyzed chips, the overall pulping yield was decreased, but the actual digester yield was rather unchanged. Because the white liquor charge per dry wood was kept constant, an insignificant change was expected in the causticizing utilization capacity. The main impacts can be observed in the black liquor evaporators. Because a part of the PHL is carried over to the digester, the chips after the pre-extraction contain more water than the chips prior to pre-extraction.

The total additional load increased the required evaporation capacity by almost 16%, which contributed to the increase of the mill steam consumption. In spite of this, there was an increment of approximately 13MWe in the mill electricity production, Table 5.6.

The reason is that more steam is generated in the recovery boiler. The PHL present in the wood pores increased the organic solids in black liquor. This partly explains the increase in the heating value, which is also attributed to the lower ratio of organic acids to lignin in the black liquor. As a result, the net heat available for steam production in the recovery boiler was increased by about 13.5%.

Table 5.6: Energy balance for the pulp production with average values

Variable	Unit	Pulp mill	Pulp mill +HR	Pulp mill +HR+LR
Black liquor HHV	MJ/kg(dry)	14.2	14.7	13.9
Total heat load to the RB	MW	524	583	524
Heat loss in the RB ^a	MW	180	192	181
LP steam required (4 barg, 155°C)	MW _{th}	147	155	157
MP steam required (11 barg, 200°C)	MW _{th}	66	71	73
Electricity usage ^b	MW _e	49.2	51.0	52.6
Electricity production	MW _e	77.8	90.5	73.0

^a losses due to flue gas, radiation & convection, smelt sensible heat, reduction and unburned carbon

^b power demand of lignin removal estimated at 0.35 kWh/t of lignin (Tomani, 2010)

The removal of approximately 17% of lignin from the black liquor would put the flue gas side of the boiler back to the original required capacity, and in turn, prevent the turbo generators from overload instabilities. The decrease in the black liquor flow rate and heating value is proportional to the lignin removal rate. It can be observed that, although lignin is recovered, the integration of both the hemicelluloses extraction and lignin removal decreased the condensing power by 4.8 MWe compared to the reference, which is mainly attributed to the higher steam demand.

Investments in the evaporation plant for higher utilization capacity seem to be inevitable due to the additional load. This, however, can be reduced if the extracted wood is, for example, washed and dried before entering the digester. Consequently, more dissolved material could be recovered and the additional load to evaporation minimized. On the other hand, washing and drying of a considerable amount of chips can be costly for pulp mills. It would also have a negative effect on the heat integration between hemicelluloses extraction and cooking.

5.4 Production of biofuels from wood residues

The reference mill in the study is designed to produce 1.5M Adt/a of bleached eucalyptus pulp in Brazil, operating without a biomass boiler. The amount of residues generated is based on an average pulping yield of 52.5%, reminding that for BB, T and FP cases, part of the logs are delivered to the mill with barks. This represents approximately 125MW_{th} of fuel available. In addition, for FP2 scenario, approximately

3% more logs is brought from the forest for the production of bio-oil. Table 5.7 summarizes the main results from the integrated mill balances.

Table 5.7: Results of integrated mill balances

		BB	T	FP	FP2
Main inputs					
LP steam	MW _{th}	3.7	24.1	24.1	10.1
MP2 steam (torrefaction)	MW _{th}	-	4.9	-	-
Heat load to boiler/combustor	MW _{th}	124.7	-	13.2 ^a	120.3 ^a
Pyrolysis/torrefaction feed	MW _{th}	-	124.7	124.7	56.4
Main outputs					
Steam generation	MW _{th}	102.4	-	-	95.9
Volatiles	MW _{th}	-	4.1 ^b	-	-
Bio-oil	MW _{th}	-	-	69.3	35.4
Biochar for export	MW _{th}	-	121.1	37.7	-
Power balance					
Diff in power generation ^c	MW _e	+34.2	-4.3	-4.0	-4.1
Net power diff, ΔP_e ^c	MW _e	+32.2	-10.3	-9.0	-7.1
Sellable power ^d	MW _e	76.7	34.2	35.5	69.6

^a It includes the partial incineration of pyrolysis co-products.

^b torrefaction gases as additional heat load to recovery boiler.

^c in comparison with reference case for BB, T or FP, and with BB case for FP2

^d power consumption: 300 kWh per ton of pellets (T) and 210 kWh per ton of dry input biomass (FP)

For BB and FP2 cases, additional steam is generated. These differences result in varying amounts of exportable electricity that will affect the economic calculations. The attractiveness of the processes in study will strongly depend on how the selling price of the new products sets itself in the market. Therefore, the purpose of the economic analysis is not to define the option with the highest revenue, but rather to show the main variables affecting the viability of each option.

The heat required for biomass drying is high due to the low dryer efficiency assumed in this work. Dryer technology has been improving, and, in practice, pulp mills can use also hot water available as heat source. The consumption of live steam could be then reduced and the mill energy efficiency enhanced.

As expected, the ΔP_e values are negative for T and FP, and positive for BB and FP2 scenarios. If incentives are offered for selling bioelectricity, the surplus amount can be increased almost 72% by installing a biomass boiler. When the residues are fully torrefied or pyrolyzed, the surplus amount of electricity is decreased by 23 or 20%, respectively. Nevertheless, approximately 35 MWe can still be sold to the grid.

5.4.1 Results from economic evaluation

It is important to emphasize that when a mill (e.g. the reference mill) is designed to operate without an auxiliary boiler, 100% of the logs should be debarked at the forest to avoid the accumulation of bark. Even so, a minimum amount of residues is still generated consisting of fines from screening and residual bark. These residues have to be preferably disposed if not processed. With the integration of BB, T or FP cases, it is assumed that the cost with disposal would be saved. On the other hand, values of C_{inv} should include the additional investments required for processing the logs with bark and, in the case of FP2, the extra logs. Figure 5.3 shows satisfactory prospects for new investments, reminding that FP2 is not comparable to any other but to the BB case. A rate of 5% for the $C_{O\&M}/C_{inv}$ is considered for all cases.

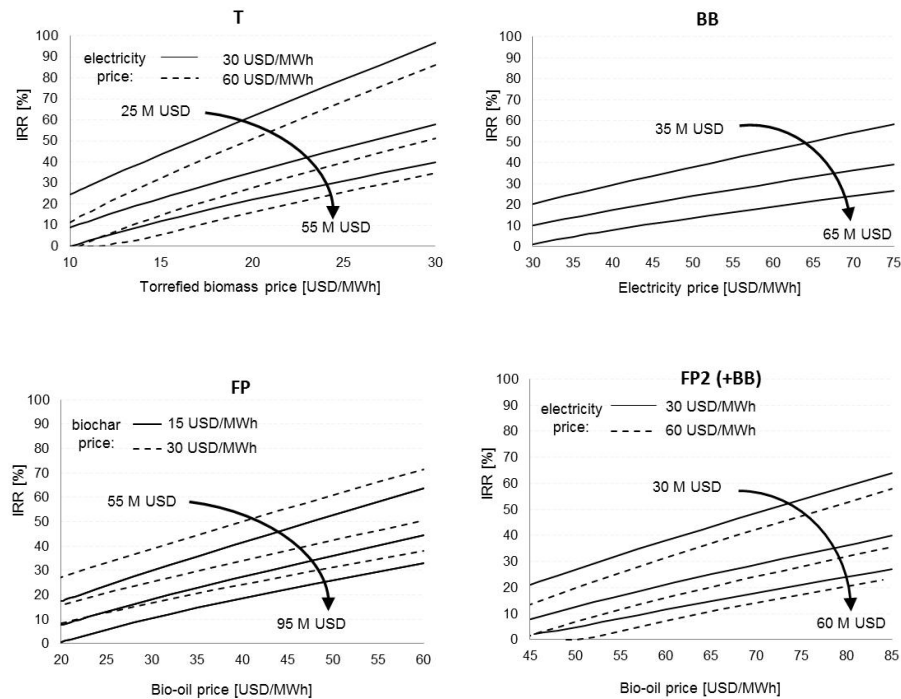


Figure 5.3 Internal return rate for the different cases

It can be observed that with a torrefied pellet price of over 17 USD/MWh, an IRR of higher than 10% can be achieved for the estimated range of investment costs. The figure also shows that torrefaction becomes more viable when electricity prices are not attractive for sale. The same concept is valid for the FP scenario, where there is also a challenge to assess the market values for two sellable products. In order to achieve an

IRR of over 10% with biochar at 15 USD/MWh, the price of bio-oil would range from 20 to 30 USD/MWh.

The new stream revenue has to then compensate for the decrease in exportable electricity and for the extra wood. In addition, the cost of disposal is not accounted for. When the price of FP2 bio-oil is 48 USD/MWh or higher for the electricity price of 30 USD/MWh, or 54 USD/MWh or higher for the electricity price of 60 USD/MWh, the IRR of over 10% is achieved for the estimated investment cost. For the upper bound of the investment cost, a bio-oil price of 58–64 USD/MWh is required to achieve an IRR of over 10%. On the other hand, bark-free wood is used as feedstock, and a better quality for the bio-oil is expected. It is important to mention that the revenue from pulp sales has no effects on the IRR calculation.

5.5 Discussion

The integrated production of bio-based technologies might make economic sense, especially when lignocellulosic residues can be used as raw material. However, the attractiveness will depend on critical factors such as possibility to invest, required internal rate of return, maturity of the process and especially the market development for the new products. One should also have in mind that there is interdependence between bio-based products and bioelectricity which influence the degree and timing of introduction of new revenue streams into the market.

5.5.1 Is it worth creating new lignocellulosic revenue streams?

Incinerating black liquor in chemical recovery boilers has become a standard procedure for kraft pulp mills. Hemicelluloses and lignin are therefore important sources of heat and bioelectricity. This shows that the value created by the new outflows is essential to make the integration of the alternative processes economically attractive. At minimum, it should compensate for the increased wood demand, other extra inflows and also for the additional capital and operational expenses. In spite of the great potential, recovering these components might not make economic sense until the market for new products is established or impacts on the pulp mill operations minimized.

Removing lignin from black liquor is an attractive way of debottlenecking recovery boilers to further increase the pulp production. However, it is difficult for mills to assume the risk until the questions related to the usability of lignin are properly answered, or until the first large scale plant demonstrates that high availabilities can be achieved. Regarding kraft lignin being used as a raw-material for chemicals and biomaterials, one of the challenges is to find one efficient and not expensive method of lignin purification. Afterwards, more valuable products such as carbon fibres, vanillin or phenols could be manufactured.

Different from lignin removal, the attractiveness of wood pre-hydrolysis would be mostly driven by the demand of hemicelluloses based products in the market. Some

post-treatment pathways for the PHL include the production of xylitol or furfural. Although there is also the possibility of producing ethanol, the processing of C5 sugars for this purpose still faces some challenges. In addition, its productivity would be rather low (Colodette *et al.*, 2011) to justify the required investment. Taking the example of Brazil into account, the alternative would hardly compete with the second generation ethanol from sugar cane bagasse. One should also consider that the possible effects on the kraft process and pulp quality would create several disagreements among pulp producers.

5.5.2 Increasing power generation versus producing biofuels

Although the answer depends on the factors mentioned in section 2.2, a very debatable question is raised. In order to get involved with this discussion, it is important to bear in mind that biofuels are not only limited to liquid transportation fuels such as bioethanol or biodiesel. They are actually all fuels derived from biomass conversion which can be used as energy sources in power plants, furnaces or vehicles. They can be supplied in the form of liquid (e.g. bio-oil and ethanol), gaseous (e.g. biogas and bio-SNG), or solid (e.g. pellets and biochar). Firewood is one example of natural biofuel that does not require a conversion process and that can be directly burned to produce heat.

The current lack of process maturity is discouraging investments in technologies to produce transportation biofuel from wood residues. Although there is the possibility of gasifying biomass for further synthesis via Fischer-Tropsch (Kumar *et al.*, 2009) to produce for example DME or methanol, pulp mills would rather burn the bio-SNG to replace fossil fuels. The same way of thinking is applicable to bio-oil, which can be eventually upgraded to transportation fuels but requires full de-oxygenation followed by conventional refining. Therefore, at mid-short term, bio-oil would be used as a direct substitute to fossil fuels in power plants.

Producing torrefied pellets comes basically as an alternative for replacing mineral coal in power plants. The solid biofuel can be exported at reduced costs, since the energy density of biomass is slightly increased. However, the prices to be charged for torrefied pellets have to be competitive to prices being paid for thermal coal. This is a key factor to make the production to scale up over the next years. As the market for biofuels develops, becoming more mature, not only the forest residues can be used as raw-material but also fast growing trees that can be planted specifically for this purpose.

5.5.3 Market challenges and R&D efforts

Bringing a new technology or product to market can be very challenging. Petrochemical producers, for example, have the benefit of fully amortized refineries, economies of scale, reliable supply chains and longstanding customer relationships (Milken Institute, 2013). On the other hand, the biorefinery players still have to prove their technologies, establish large scale factories and convince customers that the new products are cheaper or better than the current ones.

Although efforts have been made to develop alternative technologies, many bio-based products are still needed to bridge the gap between laboratory tests and commercial viability. In addition, it is still far from obvious how pulp mills could diversify their product portfolio, without taking risks, in the short or mid-term. On the other hand, this can be speeded up through e.g. committed cooperation between forest, energy and chemical companies. Finland is one example where major companies are showing the way to bio-economy era (Karlsson, 2012). These companies also demonstrate how continuous investments in R&D are indispensable to push the concept of biorefineries forward.

In general, however, policy uncertainty still poses a challenge to the biorefining industry. Today, a single product can be subject to regulations at more than one agency, making compliance with the law very complex and expensive. Such bureaucracy differs between countries and can represent an inevitable barrier for the effective implementation of bio-based technologies at short-term. In other words, putting a new revenue streams into the market depends on a number of legal acts and public policies. Therefore, the biorefinery players need to work together also to create an innovative vision for the future and then persuade policy makers to support this vision.

6 Conclusions

Decreasing Cl and K content is not only beneficial to minimize the impacts on recovery boilers corrosion and fouling rates. As this work showed, their presence in liquor might affect also the operation costs and department sizing of pulp mills. Studying these effects helped to form a scientific basis to start exploring alternative processes that can be integrated into kraft pulp mills. The chosen technologies included lignin removal from black liquor, hemicelluloses recovery prior to cooking and pyrolysis or torrefaction of biomass. The effective integration will depend on several factors such as wood species, process maturity, policy instruments, market development for the new products, and end-user requirements. Impacts on the conventional kraft process are also expected and were investigated in this work using detail mill balances.

The recovery boiler is one of the most affected departments when dimensioning a kraft pulp mill with a lignin removal system. For a fixed pulp production, the results showed that for a 30% removal rate, the steam production will decrease about 22%, which will cause a reduction in power generation. Another alternative is to consider the lignin removal rate to increase the pulp mill capacity but with a smaller recovery boiler. In comparison to a 1.5M ADt/d, the pulp production could be about 23% higher but without increasing the recovery boiler size. Lignin removal is then an attractive alternative that can be used not only to debottleneck an existing recovery boiler but also to design a Greenfield pulp mill with a smaller boiler. On the other hand, the implementation has to be carefully studied if one considers that impacts on the mill Na/S balance and also on the evaporation process are expected. These impacts are proportional to the lignin removal rate. For a large pulp mill, removing e.g. 5% of lignin from black liquor might not be significant. Furthermore, approximately 100 t/d of dry lignin could be produced in a 1.5M ADt/d mill. When removal rates go to high, major modifications would be required in many parts of the mill.

Regarding the recovery of hemicelluloses in a 600,000 ADt/a softwood pulp mill, the balance showed that when wood is extracted prior to the pulping of pine chips through auto-hydrolysis, the steam generation in the recovery boiler is increased. In order to minimize this effect, lignin was removed from black liquor to avoid extensive modifications in the boiler. This simultaneous integration of lignin removal and hemicelluloses extraction would however reduce the excess power produced. Also the recovery of crude soap would be affected. Moreover, impacts on evaporation load and wood handling area seems to be inevitable. These led to the conclusion that even though additional outflows are available to increase the mill revenue, they have to compensate for the increase in the operating and capital costs as well as for possible revenue losses. In addition to economic factors, the attractiveness would strongly depend on the hydrolysis conditions, effective treatment of the pre-hydrolyzate, and how the quality of pulp is affected.

Evaluating the future market value of the new products is challenging but indispensable to assess the feasibility of the technologies in study. In the case of torrefaction and

pyrolysis of wood residues, the investment cost and electricity price are important factors affecting the attractiveness. In a 1.5M ADt/a eucalyptus pulp mill, approximately 121 MW_{th} of torrefied pellets or 107 MW_{th} of bio-oil and biochar could be produced using the wood residues. On the other hand, considering that the mill operates without a biomass boiler, the amount of electricity for sale would be reduced. This is attributed to the fact that additional steam and power are required to operate new equipment. Incinerating the wood residues in a boiler becomes an attractive option depending on the selling price of electricity. In case a pyrolysis unit is attached to an existing biomass boiler, additional wood should be brought from the forest to be pyrolyzed. However, the use of bark-free biomass would result in bio-oil with higher quality.

It is important to bear in mind that more accurate answers are not possible to access until real scale plants are put into operation. Tests should be also performed to adequate the process conditions to different biomass species. The results obtained from hemicelluloses extraction study, for example, are only valid for pre-treatment using auto-hydrolysis of Northern European pine. Similarly, the study involving the lignin removal was based on lignin content in Brazilian eucalyptus. Nevertheless, for companies interested in implementing the concept of multi-products biorefinery, this work has pointed out the main impacts to be considered in a technical feasibility study.

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Publication I

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Influence of Cl and K on operation and design of chemical recovery equipment

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Tappi Journal

Vol. 10, pp. 33–39, 2010

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Influence of chlorine and potassium on operation and design of chemical recovery equipment

MARCELO HAMAGUCHI AND ESA K. VAKKILAINEN

ABSTRACT: The main objective of this study is to evaluate the effect of chlorine (Cl) and potassium (K) on the operation and design of equipment in the chemical recovery cycle. Due to stricter environmental regulations, mill closure tends to increase, causing the accumulation of undesirable elements such as Cl and K in the kraft liquor cycle. Total inorganic solids in pulping liquors increase in the presence of Cl and K, which affects the operation of chemical recovery equipment. The objective here is to show the magnitude of these impacts and estimate operational cost differences by using different Cl and K contents in liquors. Pulp mill material and energy balances for each case are used for this purpose, and a modern Brazilian pulp mill served as a base case model. The results show that for one specific range, the solids content in black liquor can be 6.6% higher by increasing the mass percentage of Cl and K in black liquor. This difference reduces the black liquor higher heating value by 6.2% and increases the amount of dry solids to burn in the recovery boiler, also by 6.6%. The evaporation load increases along with steam consumption. This lowers total electricity output by up to 1.6 MW due to reduced flow to the condensing stage of the steam turbine. The balances also demonstrate that some pumping costs can be 12% higher when operating from a low to high concentration of Cl and K in black liquor.

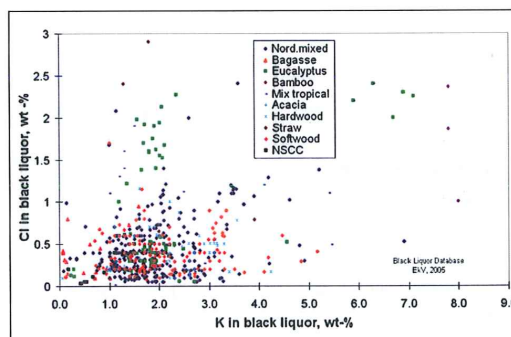
Application: Showing the influence of the Cl and K dead loads on the recovery system could help some pulp mills understand the additional cost acquired and the equipment capacity reduction.

Elements such as chlorine (Cl) and potassium (K) accumulate in the pulp mill liquor cycle. Research on the role of Cl and K in pulp mills is mostly concentrated on their impact to the recovery boiler corrosion and fouling rates, caused by the enrichment of these elements in ash [1]. Cl ions form in pulping liquors dead loads of potassium chloride (KCl) and sodium chloride (NaCl). Potassium acts similarly as sodium, so active (potassium hydroxide [KOH] and potassium sulfide [K₂S]) and non-active (potassium carbonate [K₂CO₃], potassium sulfate [K₂SO₄], etc.) compounds are formed. The influence of white liquor concentration on pulp mill energy consumption was studied by Kojo decades ago [2]. The relevance of K and Cl on the whole pulp mill operation has been raised recently. Two such examples analyzing the effects of dead loads on the recovery system have been studied by Grace and Tran [3] and Saiedi et al. [4].

Cl and K in the liquor cycle

Cl and K inputs to the kraft pulping process include wood, mill freshwater, makeup chemicals, and spent acid from chemical manufacturing. These inputs can vary a lot depending on, for example, whether pulp is processed in coastal or inland mills. The typical net input for chloride in eucalyptus mills varies between 1–3 kg Cl/a.d. metric ton and, for potassium, 2–5 kg K/a.d. metric ton. For softwood mills, these values are, respectively, 0.3–1 kg Cl/a.d. metric ton and 1–2 kg K/a.d. metric ton [5].

Cardoso et al. demonstrated that black liquor in Brazilian eucalyptus mills can contain 1.5–2.2 wt% K and 1.9–4.5 wt% Cl [6]. The range probably refers to a coastal forest region due to the high concentration of chlorine found in coastal regions. For the base case, lower values were considered, i.e., about 1.1 wt% for K and 0.5 wt% for Cl. It is important to note that an ash treatment system must then be installed to achieve these lower levels of Cl and K in liquor. **Figure 1** shows a summary of the various types of black liquor found worldwide [7]. Although values up to 8 wt% for potassium can be found in exceptional cases, the maximum amount that is considered in this work is 3.5 wt% K.



1. Chloride (Cl) and potassium (K) content in black liquor [7].

CHEMICAL RECOVERY

TARGET MILL

The target mill was a new eucalyptus mill in South America, with a production capacity of 1250000 a.d. metric tons/year [8]. The cooking operation and yields were assumed to remain constant. This implies no significant changes in the bleaching and wood preparation operations. The operating systems that were evaluated included: evaporation, recovery boiler, and causticizing. The cost impacts of liquor and cooling water pumping are also accounted for in this study.

Evaporation

To achieve the efficient removal of metals, dilution water is needed during the pulp washing process. If the amount of inorganics in the weak liquor to be removed from pulp increases, additional dilution is required. Thus, the effective capacity of the evaporator becomes limited as the water carrying extra chemical loads increases. Simply, the total water entering the evaporator is increased [3]. The boiling point rise (BPR) of black liquor is also affected by increased dead load level. The change in the BPR impacts the equipment design and process conditions. However, it is difficult to estimate the magnitude of the BPR change, since black liquor is a complex solution of various organic and inorganic compounds and few rigorous methods exist for predicting the BPR [9]. Taking these difficulties into account, this present work does not evaluate the impacts of dead loads on the boiling point rise. The dry solids flow of black liquor, which is the focus of this section, is not affected by the change in BPR.

Recovery Boiler

The recovery boiler burns black liquor and provides appropriate conditions for the reduction of sulfate ions. In such an environment, the desirable anions, such as S^{2-} , can be reactivat-

ed. The reduction efficiency in the recovery furnace determines the amount and content of sodium and potassium sulfate dead loads circulating with the various liquor flows. The increased dead load reduces the black liquor high heating value and, subsequently, reduces the lower furnace temperature. This makes operation more problematic, causing, for example, lower reduction with higher sulfur emission [10]. It is also expected that if the dry solids in black liquor increase, the flow of the virgin black liquor to the recovery boiler furnace will increase in the same proportion. The increase in the flow of dry solids and decrease in the black liquor heating value can leave the heat load (GJ/a.d. ton) to the recovery boiler furnace relatively unchanged.

Causticizing

A white liquor of good quality is essential for the proper operation of the pulping process. Good quality in this case means a high concentration of active ions (OH^- and S^{2-}) and a low concentration of inert ions such as CO_3^{2-} , SO_4^{2-} or Cl^- . Thus, a high causticizing efficiency (CE) is desired to reduce the dead load of sodium carbonate in the liquor cycle. It is known that Goodwin's curve describes the highest achievable causticizing degree. In order to avoid adverse consequences of over-liming, many mills operate below the equilibrium value. They typically try to achieve values about 3% below the theoretical, resulting in causticizing efficiencies between 82%-84% [11]. Mills without an appropriate control system can develop unstable operation with a CE below 80%. Some authors [12,13,14] have researched the influence of inorganic salts on causticizing equilibrium.

Traditional use of total titratable alkalis (TTA) to determine causticizing degree is misleading, as according to Dor-

Variables	Unit	A	B	B1	C1	C
Cl in black liquor	% wt	0.0	0.5	0.5	2.0	3.2
K in black liquor	% wt	0.0	0.2	1.1	3.2	3.5
Dry solids in black liquor	kg/a.d. metric ton	1338.7	1351.1	1355.2	1406.4	1440.6
White liquor AA	gNaOH/l	138.1	138.1	138.1	138.1	138.1
White liquor TTA	gNaOH/l	156.3	156.6	156.6	157.8	158.8
White liquor TAC	gNaOH/l	157.8	160.5	160.5	170.1	177.6
Causticizing efficiency	%	83.85	83.61	83.60	82.71	81.98
White liquor flow	m ³ /h	456.9	456.8	456.6	456.0	455.9
Inorganics in black liquor	kg/a.d. metric ton	402.3	415.1	419.8	473.5	508.8
Total dead loads in white liquor	kg/a.d. metric ton	94.6	107.5	113.3	169.6	205.2
Black liquor HHV	MJ/kg	14.45	14.32	14.28	13.76	13.43
Weak black liquor flow	m ³ /h	1235.3	1246.7	1250.5	1297.7	1329.3
Virgin black liquor flow to furnace	tDS/day	4939	4985	5000	5189	5315
Evaporation capacity	t _{H2O} /h	1093	1103	1107	1149	1177
- Steam consumption	t/h	182.2	183.9	184.5	191.9	196.8
- Cooling water flow	m ³ /h	11539	11647	11682	12127	12424
Power generation	MW	162.7	162.5	162.4	161.5	160.9

I. Mill balances with fixed active alkali (AA) content in white liquor. All tonnage references are metric.

CHEMICAL RECOVERY

Variables	Unit	A	B	B1	C1	C
Cl in black liquor	% wt	0.0	0.5	0.5	2.0	3.0
K in black liquor	% wt	0.0	0.2	1.1	3.2	3.5
Dry solids in black liquor	kg/a.d. metric ton	1340.9	1351.1	1355.2	1398.5	1426.3
White liquor active alkali (AA)	gNaOH/l	140.0	138.1	138.1	132.0	127.4
White liquor TTA	gNaOH/l	159.0	156.6	156.6	148.8	143.3
White liquor TAC	gNaOH/l	160.5	160.5	160.5	160.5	160.5
Causticizing efficiency	%	83.44	83.60	83.60	84.15	84.54
White liquor flow	m ³ /h	450.6	456.8	456.6	477.6	494.3
Inorganics in black liquor	kg/a.d. metric ton	404.4	415.1	419.8	465.9	494.7
Total dead loads in white liquor	kg/a.d. metric ton	96.7	107.5	113.3	161.8	191.1
Black liquor HHV	MJ/kg	14.43	14.32	14.28	13.83	13.56
Weak black liquor flow	m ³ /h	1229	1239	1242	1282	1308
Virgin black liquor flow to furnace	tDS/day	4939	4985	5000	5160	5262
Evaporation capacity	t _{H₂O} /h	1087	1095	1100	1134	1157
- Steam consumption	t/h	181.2	182.6	183.2	189.4	193.4
- Cooling water flow	m ³ /h	11474	11562	11597	11971	12210
Power generation	MW	162.8	162.6	162.5	161.7	161.2

II. Mill balances with fixed total anion concentration (TAC) in white liquor. All tonnage references are metric.

ris [15], for example, the causticizing reaction equilibrium constant is a function of the total anion concentration (TAC), i.e., the sum of non-titratable anions (NTA) and TTA. The effect of a larger concentration of Cl in liquor, for example, is to lower the equilibrium constant of the causticizing reaction, thereby reducing the equilibrium causticity and the effective alkali for a fixed TTA. The presence of these undesirable ions, such as NaCl, has an adverse effect on the conversion of Na₂CO₃ to NaOH.

Saeidi et al. have recently observed the influence of some alkali salts on the causticizing equilibrium [4]. They use a thermodynamic model based on experimental data to calculate the phase equilibrium in aqueous solutions of ionic salts. Their results show that the causticizing efficiency (CE) decreases with an increasing amount of chlorine in the liquor. Potassium and sulfate ions caused only a slight impact on the CE. Saeidi et al. have evaluated this change by fixing the TTA for different levels of Cl and K.

MILL BALANCE AND RESULTS

In order to evaluate the influence of Cl and K on certain operational variables, calculations were performed using a detailed pulp mill balance developed in Microsoft Excel format. Since thousands of variables and calculations are involved, tools for tracing the dependent variables become important. This feature makes Excel particularly user friendly for the task. A modern Brazilian pulp mill served as the base case model and different inputs for Cl and K in the dry black liquor were tested.

The cost saving calculations are based on more realistic conditions, where the Cl content ranges from 0.5% to 2.0% and K from 1.1% to 3.2% (wt in black liquor). They are identified as point B1 and point C1. These points represent, for ex-

ample, a coastal mill with the intention to invest in available technologies for removing Cl and K. The hypothetical case when both Cl and K equal zero is also calculated and is identified as point A. The base case model is represented by point B1. **Table 1** shows some variables at these specific points. Graphical comparisons were done by varying Cl content from 0.5% to 3.0% and K from 0.2% to 3.5% (wt in black liquor). These are identified as point B and point C.

Grace and Tran stated that around 20% of the recovered inorganics that circulate through the cycle are as inactive species [3]. Table 1 shows comparable values with several Cl and K levels. The balance is calculated with regard to the following major assumptions:

- Active alkali (AA) fixed as 138.1 gNaOH/l
- Difference of CE to Goodwin's curve: 3.5%
- Fixed values for sulfidity (32%) and reduction (96%)
- Formation rate of thiosulphate and sulfite compounds are fixed
- Weak black liquor concentration fixed at 15.2%
- No ash treatment for Cl and K removal
- Operation hours: 350 days or 8400 h
- Problems regarding fouling and corrosion are not considered

The assumption in Table 1 of fixed AA is the basis for all the graphical comparisons. Pulp mills normally operate the causticizing plant to target the active or effective alkali. Later, as in **Table 2**, an alternative is evaluated by assuming fixed TAC in white liquor.

Table 1 shows that, with constant AA but different Cl and K content in liquor, the mill operating parameters do change, such as evaporation capacity, black liquor heating value, and

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recovery boiler load. Increasing inert load can be seen as the black liquor dry solids flow increases and black liquor heating value decreases. The white liquor flow basically does not change and hence the causticizing capacity is not significantly affected. The white liquor causticizing efficiency is, however, affected.

Effects of Cl and K on black liquor properties

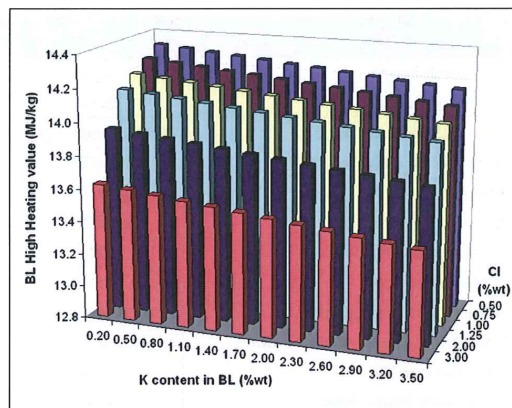
The dry solids in black liquor consist of both organic and inorganic fractions. The organic content remains basically the same but as we increase the Cl and K content, the inorganic content increased from 415.1 kg/a.d. metric ton (point B) to 508.8 kg/a.d. metric ton (point C). This change corresponds to change in dead loads in black liquor ranging from 107.5 kg/a.d. metric ton to 205.2 kg/a.d. metric ton. The total black liquor dry solids formed for the same points ranged from 1351.1 kg/a.d. metric ton to 1440.6 kg/a.d. metric ton (Table 1). The magnitude is in accordance with values referenced by Grace and Tran [3], who have suggested total dead loads ranging from 7% to 15% of the total black liquor solids.

The method used for calculating the black liquor higher heating value [16] takes into account the dead load content. Its correlation with Cl and K can be observed in **Figure 2**. The trends show that an increase in potassium causes a lesser decrease on the black liquor heating values than increasing chlorine content. For a fixed percentage of Cl, the heating value decreases by around 1.2% when K in black liquor increases from 0.2% to 3.5%wt. For a fixed percentage of K, the heating value decreases by around 4.5% when Cl in black liquor increases from 0.5% to 3.0%wt. Because the amount of organics in black liquor remained constant, the heat load to furnace did not change from about 19.4 GJ/a.d. metric ton.

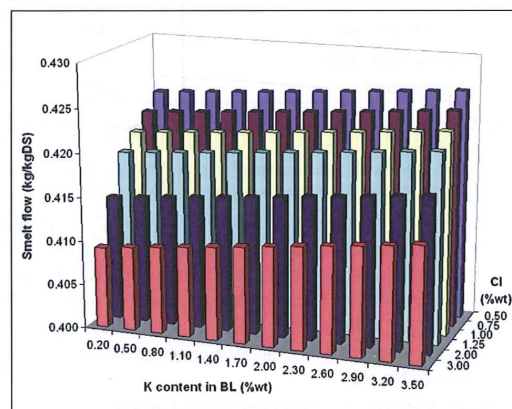
Effects of Cl and K on recovery boiler operation

It is reasonable to assume that the reduction efficiency is not significantly affected by the presence of dead loads. Thus, a fixed reduction efficiency of 96% can be taken as the basis for the balance calculations. **Figure 3** shows the impacts on smelt flow. The change in the smelt flowing to dissolving tank will not significantly affect the mill energy balance. Smelt sensible heat represents around 21% of total heat losses from black liquor combustion. The smelt heat losses are roughly proportional to the mass flow. Because the total smelt mass flow changes only by 5%, the percentage remains roughly the same.

The energy balance results also shows that the steam generation is increased 1% by increasing the potassium content from point B to point C. This can be attributed to the heat absorbed during the reduction of K_2SO_4 to K_2S (9630 kJ/kg). Since reduction heat for Na_2SO_4 to Na_2S is higher (13090 kJ/kg), the net heat for steam production becomes slightly higher. The heats absorbed during Na_2S and K_2S reduction represents around 35% of the total heat losses. The remaining losses refer to heat lost in hot flue gas, smelt sensible heat, and some other minor streams. It is typical for flow instruments to state the accuracy as 1%-2% of the measured



2. Effect of Cl and K on the black liquor heating value.



3. Effect of Cl and K on smelt flow.

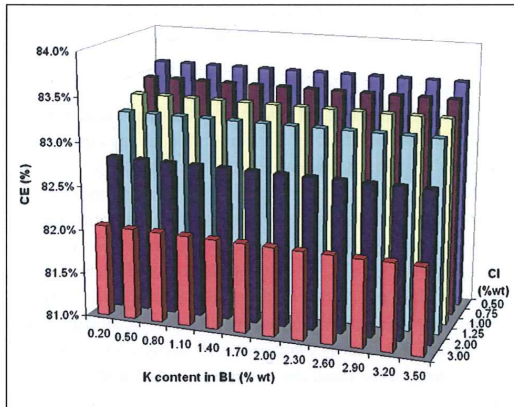
value. Hence the small change of 1% in the steam generation would not be noted in practical mill operation.

Effects of Cl and K on causticizing efficiency

Dorris states that Goodwin's curve correlates not only TTA, but also with NTA [15]. The difference of 3.5% to Goodwin's curve assumed in this work defines the causticizing efficiency for each alkali level. With fixed AA, the causticizing efficiency decreases with the increasing of Cl, as **Figure 4** shows. At the same time, the total anion concentration (TAC) is increased by 11% from point B to C. When the TAC in white liquor increases, the amount of sodium carbonate will also increase with decreasing CE. This may disturb, for example, the operation of the evaporation plant, especially if combined with a high content of sodium sulphate in black liquor [17]. Table 1 shows that the causticizing efficiency decreases by 1.9% from point B to point C.

According to Saecidi et al., coastal mills are predicted to have a CE 1%-2% lower than that of inland mills [4]. This is due to the Cl concentration in liquors of coastal mills being

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4. Effect of Cl and K on causticizing efficiency for fixed AA.

2–4 times higher than those of inland mills. It is important to emphasize that they have considered, for this case, fixed values for the TTA. In practice, if constant TTA is required by pulp mills, the causticizing efficiency will be inevitably lower.

Effects of Cl and K on evaporation load

If the amount of inorganics in the weak liquor to be removed from pulp increases, additional dilution is required. Consequently, the evaporation load increases, along with low pressure steam and cooling water consumption. The balance shows both steam and cooling water consumption increasing by around 4% from point B1 to C1. The differences are equivalent to 7.4 metric tons/h of low pressure steam and 445 m³/h of cooling water.

Mill balances for fixed TAC

The second set of comparisons is made by performing balances with fixed TAC. These have a fixed amount of alkali (constant TAC) in white liquor. Table 2 thus illustrates how the mill balance would change for the same amount of circulating alkali if the K and Cl would change. The alternative has been evaluated in this work, especially for the causticizing process, because some authors have published valuable data using TTA as variable [4,15]. The change in recovery capacity for evaporation and the recovery boiler is smaller, but the

white liquor flow changes. It is clear that to achieve same cooking yield, mills should dramatically change the cooking time. So, in practice, mills operate according to Table 1.

Table 2 shows that potassium causes no visible changes in the CE which, surprisingly, may increase by 0.9% in the presence of chlorine from point B to point C because of the decrease in the TTA content of white liquor.

Effects of Cl and K on pumping cost

One of the aspects studied was the magnitude of change in liquor pumping because of increased K and Cl levels. Four pumping systems are considered in the evaluation: weak black liquor pumping from cooking to evaporation plant (P1), white liquor pumping from causticizing to cooking (P2), green liquor pumping from dissolving tank to causticizing (P3), and cooling water pumping from cooling towers to evaporation plant (P4). Realistic design data were used to better estimate pumping costs and are shown in Table 3. The cost saving evaluation is done by using a range from point B1 to point C1. The hydraulic (P_h) and shaft (P_s) power in kW for each pumping are defined as follows:

$$P_h = q \rho g h / 3.6 \cdot 10^6$$

$$P_s = P_h / \eta$$

q: liquor volumetric flow [m³/h]
 ρ : liquor density [kg/m³]
h: differential head [m]
 η : pump efficiency

An electricity price of 30 Euros/MWh was used as the basis for cost evaluation. It is assumed that pump efficiencies do not change according to their characteristic curves. Table 3 shows that, from point B1 to C1, the pumping cost increased by 54000 Euros/year for fixed TAC. If AA is fixed, the white liquor (P2) and green liquor pumping systems (P3) will present no significant changes. Even so, the difference in cost for all the pumps reaches 59000 Euros/year. When TAC is fixed, the costs for P2 and P3 become higher, because the AA charge for cooking does not change since the chip flow to the digester remains the same. Thus, the white liquor flow has to increase in order to compensate for its reduced AA. In practice, these cost differences for P2 and P3 and even P1 are not representative for each pulp mill.

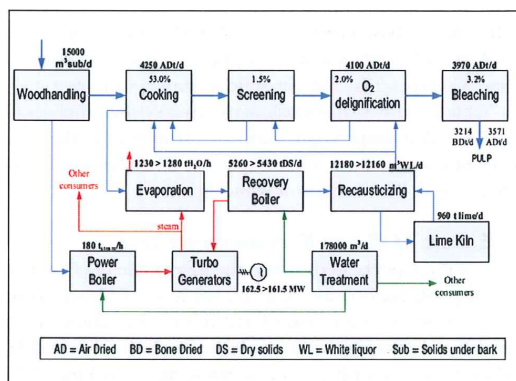
Effects of Cl and K on power generation

A modern 1250000 a.d. metric ton/year pulp mill equipped

Description	Unit	WBL, P1	WL, P2	GL, P3	CW, P4
Head	M	60	35	40	40
Pump efficiency	%	78	78	78	78
Change in shaft power AA (TAC)	kW	35.0 (29.0)	1.8 (10.5)	0.7 (9.8)	100.0 (165.3)
Change in pumping cost AA (TAC)	Euros/year	8800 (7700)	453 (2649)	166 (2470)	50000 (41660)
Pumping cost increase AA (TAC)	%	11.8 (9.9)	3.0 (15.9)	1.0 (14.7)	11.9 (10.0)

III. Change in pumping cost for fixed AA and fixed TAC (in parentheses) from point B1 to C1.

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5. Schematic diagram of 1.25 million a.d. metric tons/year pulp mill, with design capacities indicated above each block.

with a condensing tail turbine has a potential for generating 162.4 MW of electricity at design point B1. For a fixed AA, the energy balance shows that an increase from point B1 to C1 in steam consumption, mainly by the evaporation process, decreases electricity generation by 0.9 MW. From point B to C, the decrease reaches 1.6 MW. This is caused by the reduction of steam flow to the condensing tail part of the steam turbine. The power change is equivalent, for example, to one modern wind turbine. Since it is typical for pulp mills to sell surplus electricity to the grid, it is interesting to estimate the cost involved. Thus, considering the most realistic range (from B1 to C1) and assuming 30 Euros/MWh in 350 operation days, the cost of 0.9MW is equivalent to about 252000 Euros/year. For a fixed TAC, the cost would reach about 215000 Euros/year.

Pulp mill design

The stream flows and equipment capacities in pulp processing are calculated by assuming cooking yield (53%) and fixed shrinkage percentages. The changes can be seen in **Figure 5** for a fixed AA. Both the fixed TAC and fixed AA cases are also presented in **Table 4**. All inputs are based on actual data typically used for dimensioning pulp mills. References for some values can be consulted online [18].

As Table 4 shows, an increase of K and CI can significantly increase the required design capacities of recovery depart-

ments. Therefore, the predicted level of K and CI in the pulp mill to be considered is of utmost importance.

CONCLUSIONS

The results of this study show that NPEs like CI and K affect the operation and capacity of chemical recovery equipment. The detailed pulp mill balance from our Microsoft Excel format deals with complex processes and contains hundreds of inputs and interrelated parameters that are not mentioned in this paper. Although the results do not represent actual measured process values, they show that pulp mills having high concentrations of CI deserve attention with regard to chemical recovery equipment operation. It is clear from the results that K and CI do affect departmental sizing and operations costs at pulp mills; thus, decreasing K and CI will be beneficial. **TJ**

ACKNOWLEDGMENTS

We would like to thank the personnel involved in the Brazilian mill project for their help in gathering the required data that was used to check the reference case for balance calculations.

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System	Unit	Fixed TAC				Fixed AA			
		B	B1	C1	C	B	B1	C1	C
Recovery boiler	tDS/day	5250	5260	5430	5540	5250	5260	5460	5590
Causticizing	m³WL/d	12180	12180	12740	13180	12180	12180	12160	12160
Evaporation	t H₂O/h	1220	1220	1260	1290	1230	1230	1280	1310

IV. Selected design for studied cases. All tonnage references are metric.

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ABOUT THE AUTHORS

It is well known that dead loads (poor reduction and causticizing degree) cause negative impacts on pulp mill operations. While there was ample research on the impacts of elevated potassium (K) and chlorine (Cl) on corrosion, there were few studies about their role as additional dead load. We realized that it was possible to evaluate the magnitude of these impacts by using real process data in an advanced pulp mill balance that we developed.

The effects of K and Cl on individual pulp mill department operations have previously been studied. Our research expands the previous whole mill operation studies by considering new variables related to potassium and chlorine. Our most difficult challenge in this study was to accurately correlate the non tritable anions with the causticizing efficiency. This was addressed by conducting a literature survey and by consulting companies with practical expertise.

One interesting finding from this study was that the increased content of Cl and K in black liquor can significantly increase the amount of dry solids to be burned in the recovery boiler.

The results from this study show the importance of removing non process elements (NPEs), such as Cl

and K, from the liquor cycle. Not only do corrosion costs increase with elevated levels of Cl and K, but significantly higher pulp mill operations costs result as well.

Using our research, pulp mills can better estimate the magnitude of impacts from Cl and K on their recovery processes and determine the best levels for these NPEs in their operations.

One of the next interesting areas of study for us will be the influence of NPE on the chemical recovery process when certain amounts of lignin are removed from the black liquor.

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Publication II

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The impact of lignin removal on the dimensioning of eucalyptus pulp mills

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Appita Journal

Vol. 64, pp. 433–439, 2011

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The impact of lignin removal on the dimensioning of eucalyptus pulp mills

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SUMMARY

Lignin removal decreases the quantity of organics in pulp mill black liquor, while the inorganics remain essentially unchanged. Balances have been performed to show how lignin removal affects the sizing of different pulp mill departments and the operation of equipment. A modern South American eucalyptus pulp mill served as the base case model. This work shows that the energy balance and the recovery boiler operation are important factors that limit the removal rate of lignin. At 30% lignin removal, steam generation from the recovery boiler decreases 22%, the black liquor heating value decreases about 9% and the required recovery boiler capacity (in terms of dry solids flow, tDS/d) decreases by about 10%. A key calculation result shows that if the heat load into the recovery furnace is fixed, an increase of 23% in pulp production can be achieved if 30% of lignin is removed. The simulation results show that removing lignin should be considered as one alternative for new pulp mill projects.

KEYWORDS

black liquor, lignin removal, recovery boiler, power generation, process engineering

INTRODUCTION

Pulpwood usually contains 40-50% cellulose, 23-32% hemicellulose, 15-30% lignin and 2-5% extractives on a b.d. basis. After pulping, most of the soluble organics – most importantly the lignins – and the residual pulping chemicals are washed from the pulp and the resulting black liquor is directed, via the evaporation plant to the recovery boiler, for steam production. Separation and removal of

lignin from black liquor is considered for several reasons.

Firstly, the flue gas capacity of the recovery boiler is often a bottleneck that limits pulp production. In principle, removing part of the lignin from the black liquor decreases the heat load on the recovery boiler per tonne of pulp produced (1-3). Secondly, the separated lignin might be used to replace fuel oil or natural gas in the lime kiln used for regenerating lime from the residual pulping chemicals (4). (Burning lignin in the lime kiln would make kraft pulp mill virtually fossil fuel free except for start-up and shut-down.) Thirdly, modern pulp mills already have an energy surplus that is exported as either electricity or biofuels, e.g. bark sales, and Lignin separation adds another option in the form of saleable renewable biofuel. Finally, separated lignin after refining has the potential of being a raw material for several new products such as carbon fibres/materials, phenols, adhesives/binders, dispersants and metal chelating agents (5).

There are currently two interesting methods being used to separate lignin from black liquor: ultrafiltration in the digester (6) and acidic precipitation in the evaporation plant (5,7,8). The acidic precipitation method is commercially known as Lignoboost (Fig. 1). Black liquor is pumped from the evaporators, at 30-40% dry solid content, to the precipitation vessel where pH is altered. The required pH change can be carried out by for example,

sulphuric acid or CO₂. Sulphuric acid is easy to handle in the mixing stage but the sulphur balance in the mill will be affected. The use of CO₂ avoids this balance problem but the mixing stage is more complicated. The lignin precipitate is first filtered and then washed to purify the product. The remainder of the black liquor is returned to the evaporators.

Recovery boiler operation can be negatively affected if the lignin removal rate is too high. Some balance calculations have been used to evaluate the influence of lignin removal on recovery boiler operation (1,3) and on the energy savings in pulp mills (9). The removal of lignin reduces the heat available in the furnace (less actual combustibles but same amount of inorganics). The portion of the heat in black liquor needed for reduction increases. Predictions for lower furnace temperature and ash generation indicate that at lignin removal rates of about 50%, the furnace behaviour starts deviating significantly from those conditions that normally occur in recovery boilers (1).

Lignin removal has been carried out in some large pulp mills in Sweden for several years but not at 30% level. At low removal rates, long term operation has resulted in no significant deviation from 'normal operation' (10). There is no operational data from mills where 30% of lignin is removed from the black liquor and the aim of this work was to simulate the effect of higher lignin removal rates, quantifying trends rather than providing absolute values.

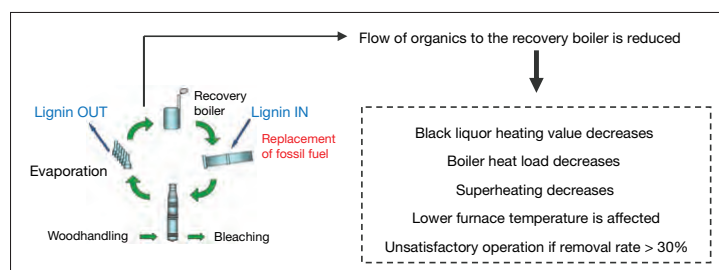


Fig. 1 Lignin removal and its implications regarding recovery boiler performance (3)

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MILL BALANCES

Millflow Software

The dimensioning of pulp mills is essentially based on standard engineering methods. They are modified along with practical experience and advances in equipment technologies. The target of pulp mill design is a reference report which gives detailed results of mass and energy balances. Pulp mill design calculations in this study were performed using the *MillFlow* program, a mill spreadsheet that has been progressively developed at LUT Energy (1,3). The software includes a detailed mass and energy balance and it has previously been used to design pulp mills by equipment vendors (the Gunns project (11) is an example of how the *Millflow* can be used) and also for some preliminary studies of lignin removal (2,3). The main reason for integrating lignin removal into the mill balance was to study the changes in black liquor composition and, subsequently, the impacts on the chemical recovery operation and energy usage. A modern eucalyptus pulp mill project in South America served as the base case model for the conventional (without removing lignin) kraft process. In order to find out how the lignin removal process affects the dimensioning of a kraft pulp mill, two studies based on a 1.5 million AD t/a pulp mill (typical of new Eucalyptus pulp mills being considered in Oceania and Asia) were considered in this work:

A. A study with lignin removal rate ranging from 0% to 30%, where the fibre-line remains unchanged while the

recovery equipment size is varied.

B. A study of the impacts on this pulp mill if up to 30% of lignin is removed but the heat load into the recovery boiler is fixed. In this study the recovery department capacities are fairly constant while the fibre-line size increases.

It is important to point out that the composition of black liquor changes when lignin is removed. Some calculations are based on correlations given by a black liquor database (12), which is included as a constituent part of the *MillFlow* program.

Calculation guidelines

Full balances consist of hundreds of calculations, which make the detailed description of the design procedure difficult. The basis of the developed calculation model is shown in a schematic (Fig. 2) where the numbers represent the main input and output variables of the mass and energy balance. The variables are detailed in Table 1.

After defining the desired capacity of the pulp mill (18), the dimensioning of the pulping line (41) is initiated, by a back calculation from the drying machine to the wood handling area (51). The wood demand per ton of unbleached pulp (6 and 7) can be calculated based on the cooking yield (15) and pulping losses before bleaching (16). Details about these equipment losses, e.g., during washing and screening of pulp, are well described in literature (13). The inorganic flow, i.e., pulping chemicals, can be calculated from a digester balance (14).

Three important inputs for the recovery boiler module are calculated in the black liquor tool module: the total dry solids flow (11), its composition (14) and heating value (13). Grace's method for calculating the black liquor heating value without lignin removal is described in the literature (15). In this work, the balance calculations in the *Millflow* program were improved by taking into account the lignin removal (13). The lignin in black liquor can be found by subtracting from the lignin content in wood (2), the lignin in pulp (8) and the removed lignin (9). The lignin in the pulp to the bleach plant depends on the desired kappa number, which differs from project to project.

The inorganics in white liquor (10) is an input because it also contributes to the black liquor composition and heating value. The pulp washing efficiency (5) is mainly used to estimate the amount of inorganic losses (13) that end up in black liquor. The total heating value of black liquor (variables 1, 3 and 4) can then be calculated. For the elemental composition, shown in Table 2, estimation from proximate analysis of black liquor (11) is used.

Other important inputs and outputs of the recovery boiler module are indicated in Figure 2. The hearth heat release rate (49), for example, can be calculated if the furnace area (48) is known. In this study, such area is based on recent projects in South America. A detailed mass and energy balance for the recovery boiler can be found has been reported (16).

After the steam production from both power boiler (27) and recovery boiler (50) are calculated, the turbo generator (TG) balances are performed in detail. For this purpose, standard turbine efficiencies are used. It is important to emphasize that the steam balance (33) of the mill will directly affect the power generation (26). For the mill energy balance, the electricity and heat usage (53) for each department has to be used. These values can be found in the literature (17).

Another improvement to *Millflow* in this work is the calculation of the inorganic compounds in white liquor, which consist of active (OH^- and S^{2-}) and inactive ($\text{S}_2\text{O}_3^{2-}$, CO_3^{2-} , SO_3^{2-} , SO_4^{2-} , Cl^-) fractions. Some basic inputs such as alkali charge, sulfidity, reduction, and the content of Cl and K in liquor (20, 21, 22 and 35) are then needed. The formation rate of thiosulfate and sulphite (12) are assumed to be constant. The calculation of the causticiz-

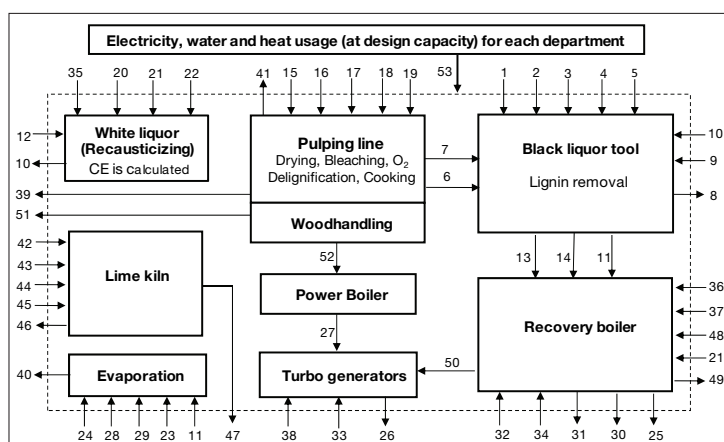


Fig. 2 Schematic diagram showing the basic inputs and outputs for mass and energy balance

Table 1
Description of inputs and outputs indicated in Figure 2

ID	Description	ID	Description
1	Lignin heating value (~25 MJ/kg)	27	High pressure steam flow, power boiler, t/h
2	Wood composition, wt-%	28	Strong liquor virgin concentration (80%)
3	Heating values of inorganics, (Na ₂ S, K ₂ S)	29	Steam economy (420 kJ/kgH ₂ O)
4	Organic heating values (acids, resins, etc)	30	Flue gas generation, Nm ³ /h
5	Washing efficiency of pulp (98-99%)	31	Air ratio, excess air (15%)
6	Dry wood demand, t/h	32	Blowdown (1.5 kg/s) and sootblowing (11.4 kg/s)
7	Dry unbleached pulp, t/d	33	All steam requirements (flow, T and P)
8	Lignin in pulp, kg/ADt	34	HP steam parameters (486 °C and 85 bar)
9	Lignin removal rate, %	35	Cl and K content in liquor, wt-%
10	Inorganic compounds in white liquor, kg/BDt	36	Combustion air temperatures (30-120 °C)
11	Dry solids generation, tDS/d	37	Recycled ash (~10% of variable 11)
12	Formation rate of S ₂ O ₃ ²⁻ (30%) and SO ₃ ²⁻ (8%)	38	Condensate return from the departments, t/h
13	Black liquor heating value, MJ/kg	39	Recausticizing required capacity, m ³ WL/d
14	Black liquor composition, wt-%	40	Evaporation required capacity, t/h
15	Cooking yield (53%)	41	Pulping line required capacity, ADt/d
16	Equipment losses, %	42	Availability of burnt lime (85%)
17	Effective alkali charge, as NaOH (18.5%)	43	Availability of make-up lime (89%)
18	Desired bleached pulp capacity, ADt/a	44	Residual lime (1%) and CaCO ₃ (3%) in lime mud
19	Dilution water in pulp washing (~2800 kg/ADt)	45	Kiln heat requirement (5.MJ/kg)
20	Sulfidity (32%)	46	Amount of lignin to be burned, t/d
21	Reduction (95%)	47	Kiln required capacity, t lime/d
22	Active alkali charge (138 gNaOH/l)	48	Recovery boiler furnace area (275m ²)
23	Medium pressure steam /total steam usage (4%)	49	HHRR and heat load, kW/m ² and MW
24	Additional load to be evaporated (~19 t/h)	50	High pressure steam flow, recovery boiler, t/h
25	Smelt production, kg/s	51	Wood handling required capacity, m ³ sub/d
26	Power generation, MW	52	Bark to burning, BDt/d

ing efficiency takes into consideration not only the active but also the inactive compounds (18). The calculation of the required recausticizing capacity (39) is based on the white liquor requirements for the cooking and O₂ delignification (17), not on the smelt production (25).

The total kiln product (47) depends on many factors. It is important to define, for example, the make-up (43) material to be used. It is a common practice to use fresh lime (CaO) in Brazil. The use of limestone (CaCO₃) is another alternative. The percentage of residual lime and CaCO₃ in lime mud (44), as well as the availability of burnt lime (42), will directly affect the kiln required production. To estimate the amount of lignin to be burned (46), the heat required in the lime kiln (45) is needed. A guaranteed value used by equipment suppliers is about 5900 MJ/t of burnt lime for modern projects. If the effective heating value of the lignin is known, a simple calculation can define the total lignin to be burned.

The evaporation (40) dimensioning does not require the balance of each evaporation effect, which can be checked in details in the literature (19) where information about steam economy (29) is found. This value, together with the steam requirement (23), can be used to calculate the heat consumption. For dimensioning

purpose it is important to find the total weak black liquor flow going to the evaporation plant. This can be calculated by defining all the water going with the black liquor dry solids (11). The dilution water in the pulp washing (19), the water contained in wood and the water in white liquor are the biggest contributors. This will result in a watery solution with a dry solids content of about 15%. An additional load can be evaporated (24). This refers, for example, to biosludge (optional), spills and chemical plant by-products. The evaporation load is finally calculated by subtracting from the total liquor flow (watery solution + 24), the total as fired liquor that is pumped to the recovery boiler (11/28 + 37).

RESULTS AND DISCUSSION

Design conditions

All the balances in this work consider that the lignin which is removed from the liquor cycle is burnt in the lime kiln. In a modern eucalyptus pulp mill 100 % of the lime kiln oil or natural gas used could be replaced by about 13% of lignin removal. This enables significant replacement of fossil fuel now used in the pulp mills. The studied pulp mill has the following design conditions:

- Pulp cooking yield: 53%; active alkali concentration: 138.1 gNaOH/l

- Cooking liquor charge, as NaOH on BD wood: 18.5%
 - Wood composition: Cellulose 46.3%, hemicellulose 24%, lignin 27%, extractives 2.7%
 - For the black liquor elemental analyses, see table 1
 - Cl and K content in black liquor: 0.4 wt-% and 1.2 wt-%
 - Sulfidity: 32%; Reduction: 95%; Causticizing efficiency: 83%.
 - Weak and strong black liquor concentration: 15.0% and 80.0%
 - Lignin heating value for hardwood: 25.1 MJ/kg (dry)
 - Operating hours: 350 days or 8400 h/a
- The content of Cl and K in black liquor varies depending on the pulp mill location and the type of wood used. The design conditions adopted in this work are in the range of normal black liquor analysis of eucalyptus woods (20). For the electricity output calculation, the following design conditions were considered:
- LP steam: 3.3 bar(g) and 155 °C
 - MPI steam: 11 bar(g) and 200 °C
 - MPII steam: 28 bar(g) and 330 °C (Sootblowing)
 - HP steam from boilers: 84 bar(g) and 486 °C
 - Power boiler thermal efficiency: 86.7%
 - Biomass burned for : 68% of total wood waste (almost no debarking in the forest)
 - One back-pressure turbine (extraction of MPI, MPII and LP steam)
 - One steam condensing turbine (extraction of LP steam)
 - Changes in the steam production affect primarily the condensing turbine size

CASE STUDY A: DESIGN OF 1.5 M ADT/A PULP MILL – LIGNIN REMOVAL WITH CONSTANT FIBRE-LINE AND REDUCED RECOVERY

Since the organic load is reduced but the inorganic load remains the same, more lignin removed black liquor dry solids needs to be fired in order to maintain the same steam load. On the other hand, if the reduction of steam production is taken as an alternative, some parameters of chemical recovery process are affected. The highest impact is on the recovery boiler process because of changes in the fuel properties. This will significantly affect the power generation. We now discuss various aspects of the calculation results.

Effects on black liquor properties

With the removal of lignin there is a reduction in black liquor flow and a change in black liquor composition. Table 2 shows that changes in black liquor composition have a high impact on the fuel heating value. The black liquor loses about 9% of its original heating value if 30% of lignin is removed. The H/C ratio is not expected to change much with the changed lignin concentration they generally show a fairly constant value over a wide range of different wood black liquors with varying C content (Fig 3).

The physical properties of eucalyptus black liquor were studied by Cardoso *et al.* (20). According to them, the concentration, molar mass and molecular conformation of lignin and polysaccharide in black liquor affect the rheological behaviour. Liquors with low lignin and polysaccharide concentrations tend to have lower viscosity, since these compounds can agglomerate in a more compact and spherical molecular structure. Hence extracting lignin from black liquor may be an opportunity for decreasing the viscosity of black liquor. The effect of lignin removal on black liquor viscosity has been studied by Moosavifar *et al.* (21) who showed that there was some decrease in viscosity for softwood pulping.

Effects on evaporation load

Black liquor viscosity increases with increased dry solids content particularly after a certain point (19). For evaporators this poses a flow limit at some dry solids content. An increase in temperature will lower the viscosity. The practical limit for handling the liquor is the pumping limit of 300 – 500 mPa.s. The viscosity at every evaporator effect must always be below

Table 2
Calculated changes in black liquor composition at varying lignin removal rates

Variable	Percentage of lignin removal			
	0%	10%	20%	30%
Black liquor HHV, MJ/kg	14.1	13.7	13.2	12.8
Carbon (C), %-wt	34.4	33.6	32.6	31.6
Hydrogen (H), %-wt	3.37	3.29	3.20	3.10
Nitrogen (N), %-wt	0.10	0.10	0.10	0.10
Sulphur (S), %-wt	4.10	4.25	4.41	4.58
Sodium (Na), %-wt	20.8	21.4	21.9	22.5
Potassium (K), %-wt	1.20	1.24	1.27	1.31
Chloride (Cl), %-wt	0.40	0.41	0.42	0.44
Oxygen by difference, %-wt	35.6	35.8	36.1	36.4

Table 3
Calculated values for different rates of lignin removal

Variable	Percentage of lignin removal			
	0%	10%	20%	30%
Dry solids in BL after lignin removal, kg/ADt	1359	1312	1265	1219
Lignin in black liquor, kg/ADt	469	422	375	328
Lignin removed, t/ADt	0	0.05	0.09	0.14
Lignin/total dry solids in black liquor, wt-%	36.3	33.9	31.3	28.5
Heat load into recovery boiler, MW	948	889	831	772
Hearth Heat Release Rate (HHRR), kW/m ²	3445	3233	3021	2809
Virgin black liquor flow to furnace, tDS/d	5825	5624	5424	5223
Lignin needed in the lime kiln, tDS/d	251	251	251	251
Removed lignin, tDS/d	0	201	402	603
Smelt flow, kg/kgDS	0.43	0.44	0.45	0.47
Air flow (wet), at 1.15 air ratio, Nm ³ /s	232.6	216.8	200.9	185.1
Recovery boiler flue gas flow (wet), Nm ³ /s	288.9	270.8	252.7	234.6

this level, and is usually much lower in the low dry solids effects of an evaporation plant. In addition, the changes in viscosity may affect the global heat transfer coefficient and, consequently, the technical specification of evaporators or the steam economy. As mentioned before, the removal of lignin will decrease the black liquor viscosity, however, for dimensioning purposes in this study, it has been assumed that the final concentration and the evaporation capacity are not affected because of lignin removal.

Changes to black liquor boiling point rise (BPR) could decrease the evaporation especially in high concentration effects. Removal of lignin can lower the boiling point rise (BPR) of black liquor, but this reduction is not significant (21). In this study, it has been assumed that the final concentration and the evaporation capacity are not affected because of effects of lignin removal on boiling point rise.

In calculating the initial concentration of weak black liquor, it has been assumed that the amount of dilution water in the pulp washing process is fixed. With lignin removal, because water is needed to wash the precipitated lignin, the evaporation load might be slightly higher if the filtrate is returned to the evaporators. It is still difficult to know the exact amount of water required for washing in Lignoboost until data from real operating lines are available. Approximate values can be found in literature. Tomani (10), for example, shows that the wash filtrate that returns to evaporators is about 2 m³/t lignin. Olsson *et al.* (27) stated that evaporation plants with lignin removal have 3-11% higher steam demand than an equivalent plant without lignin removal. Such demand varies with the added washing

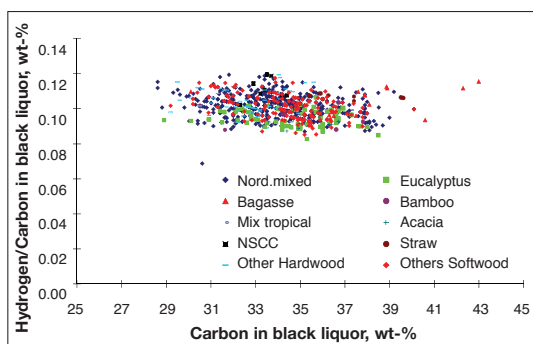


Fig. 3 General trend in black liquors for hydrogen to carbon ratio (11)

water, which depend on the amount of lignin removed. Their calculations are based on removal rates that vary from 0.15 to 0.23t/ADt. The maximum calculated value using Millflow is about 0.14t/ADt (Table 3). Therefore, because the evaporation dimensioning is normally based on design ratio of 90%, it is reasonable to assume that the nominal capacity of the evaporation plant remains unchanged.

Effects on recovery boiler

The recovery boiler is the most costly equipment in the pulp mill. Designing for a lower capacity boiler can represent major savings. If lignin is removed from black liquor, the size of the recovery boiler required decreases but also the steam generation would be significantly lower (Table 3).

The hearth heat release rate (HHRR) decreases faster than the mass flow as the removed lignin has higher heating value than the black liquor average. Therefore the recovery boiler steam generation also drops faster than the firing rate indicates (Table 3).

The virgin black liquor elemental compositions were used to calculate recovery boiler air flows and flue gas flows. With increased lignin removal the air requirement at air ratio of 1.15 per mass unit of black liquor decreases. The specific smelt flow per dry solids is expected to increase, by about 9%.

It is acknowledged that removal of lignin from black liquor could affect the combustion properties. The devolatilization stage is dependent on specific liquor properties. The rate of combustion reactions, for example, is increased with higher swelling (23). This can be explained by the larger available surface area for highly swelling black liquor. Studies (24) show that the swelling for both softwood and hardwood is proportional to the ratio of lignin to aliphatic acids in the liquor. Alén (25) states that the lignin can affect not only the swelling, but also the pyrolysis and char burning time of a black liquor droplet and thus boiler firing practices may need to be altered. Vakkilainen *et al.* (26), noted however, that across the pulp sector very different black liquors can be successfully fired and thus we have assumed that although black liquor lignin concentration may affect the combustion process, the design capacity of the recovery boiler would remain unchanged.

Effects on power generation

The power generation decreases by about 29% if 30% of lignin is removed from black liquor. However, the calculated values in Table 4 show that it is still possible to generate surplus electricity even after removing 30% of lignin from the black liquor. However, the power boiler is essential as the energy balances also show that, without it, the lignin removal rate is limited to about 20%. Any value higher would result in the process steam demand being higher than the steam generated by the recovery boiler.

The overall energy efficiency of the process depends on the strategy adopted. The investment and operational costs, for example, will vary according to the number of effects in the evaporation plant or on the strategy adopted for the feedwater pre-heating system. This study assumes an evaporation plant operating with 6-effects, which is a common practice for modern pulp mills in South America. Although the investment cost is lower, the steam consumption is higher than for a 7-effect evaporation plant.

These results provide interesting data for those mills that may prefer to sell lignin rather than electricity. In order to minimize the surplus electricity, the balance should consider only the steam consumption required at the mill and a minimum flow to the condensing tail of the turbine. The 30% removal rate is close to this operational condition.

Burning lignin in the lime kiln

One can observe that a minimum amount of lignin should be removed from black liquor in order to replace the fossil fuel in the lime kiln (Table 3). The balance showed that at least 13% removal rate is needed.

Lime kilns use mainly natural gas and heavy fuel oil to dry, heat and calcinate the lime mud. Lime kiln operation

depends on the fuel used. Firing biogas produces lower firing end temperatures. Because the capacity of the lime kiln is determined by the heat exchange from flue gas to solids, to maintain the same capacity requires higher firing rates for biogas and results in higher drying end temperatures. Practical experience with lime kiln burning different fuels was reported by Wadsborn *et al.* (4). A negative point is that emissions of SO₂ are expected to increase (27).

Lignin as a lime kiln fuel can be placed somewhere between biogas and natural gas. There is more flue gas production per unit of heat. Therefore the kiln production is lowered by 5 to 10 % (1), and since the flue gas losses increase (back end temperature increases), the fuel consumption (as heat) will be negatively affected. Wadsborn *et al.* (4) stated that the assumptions regarding flame length have great influence on the maximum temperature and thereby also on the degree of sintering of the reburned lime. They concluded that lignin shows a temperature profile similar to fuel oil. Although the replacement of fossil fuels by lignin might affect slightly the kiln dimensions, the nominal capacity of the lime kiln remains the same.

The main operational problems in lime kilns is the formation of hard deposits called rings that have to be removed manually. Lime kiln rings are connected to variability of fuel heating value or mass flow, free sodium and free sulphur in fuel. If the washing of lignin is properly done, lignin burning should not be a problem. In trials to be conducted the stability of lignin heating value needs to be tested, but it can be assumed that this is not a major problem.

Dimensioning the pulp mill

Pulp mills have some requirement to be

Table 4
Power and steam variables calculated for different rates of lignin removal

Variable	Percentage of lignin removal			
	0%	10%	20%	30%
Power boiler steam production, t/h	204	204	204	204
Recovery boiler steam production, t/h	890	825	760	696
Flow to turbine condensing tail, t/h	238	166	95	23
Power generation, MW	192.9	174.9	156.4	137.5
Electricity usage ^(a) , MW	108.1	107.8	107.4	107.0
Surplus electricity ^(b) , MW	84.8	67.1	49.0	30.5

^(a) Electricity usage for the lignoboost process is not considered

^(b) According to design values

flexible. One aspect of this could be achieved by designing the mill to run at zero lignin removal (typical dimensioning (12)), and then, depending on the fluctuations of lignin or electricity prices, the pulp mill can decide at what capacity they want to run the lignin removal system.

It is important to remember that recovery boiler disturbances can become an important issue if the lignin removal rate is too high. Figure 4 shows the design operation figures for a eucalyptus pulp mill based on a lignin removal rate of 30%, with the design capacity of the chemical recovery system for a conventional mill (without lignin removal) is indicated in parentheses.

The figures shown in the design (Fig.4) are based on pulping losses as shown (1.5% at the screening stage, 2.0% at the delignification, and 3.1% at the bleaching stage). The pulp mill is designed to achieve an average production of 4290ADt/d (air dry ton). (The wood handling capacity is based on a design ratio of 75 %.)

As mentioned before, the main impacts are observed in the recovery boiler and turbo generators. The boiler capacity (in terms of dry solids flow, tDS/d) will be about 10% smaller when compared to one in a conventional kraft pulp mill. For this reason and because the black liquor heating values decreases, the power generator capacity can be about 28% lower. Since kraft pulp mills produce surplus electricity, such reduction will not limit the mill operation. The changes in evaporation load are not significant, and thus the design of the evaporation plant can be considered unchanged. The nominal capacities of the lime kiln and recausticizing plant are not affected for a fixed pulp production, i.e., 14600 m³WL/d (volumetric white liquor flow) and 1180 t lime/d respectively.

The operation of power boiler enables significant production of surplus electricity. It is used especially to burn the residues from the wood handling area. The decision to debark the wood in the forest will also define the power boiler capacity.

The pulp mill would be able to produce about 600 t/d of lignin, from which ~40% could be used in the lime kiln as alternative fuel. Further economic analysis involving electricity, wood and lignin prices as well as the capital required for the lignin removal, to assess if this option can provide an attractive return (22).

CASE STUDY B: FIXING THE HEAT LOAD INTO THE BOILER WHILE INCREASING FIBRELINE

Although recovery boiler capacity is not currently a limiting factor for new pulp mills, there are challenges to manufacturing larger and larger boilers (28). On the other hand, existing mills with output limited by recovery boiler capacity, might achieve increased fibre line capacity using lignin removal to overcome the recovery limit. A previous case study (2) showed that pulp mill capacity, if limited by the recovery boiler, can be increased by about 25% when about 0.16 t lignin/ADt is recovered from black liquor.

For the present study a mill balance at 30% of lignin removal (0.14 t/ADt) with the heat load into the recovery boiler constant and power output close to 947 MW was carried out using Millflow. (Table 5) A higher dry solids flow is required to

compensate for the reduction in the heating value of black liquor. It is important to emphasize that the recovery boiler design is not limited by the dry solids flow (tDS/d) but by the flue gas flow. One can see from Table 5 that the flue gas flow has been kept almost constant.

It can be observed that with 30% lignin removed the black liquor flow has to be about 10% higher in order to maintain the heat load, but at the same time the steam production is about 4% lower. This is partly due to the higher heat losses caused by higher production of smelt. These losses include the sensible heat of smelt and the heat consumed during the reduction of sulphate to sulphide (Table 5). On the other hand, 340,000 ADt/a (22.7% increase) more pulp can be produced and 740 t/d of lignin can be recovered. The amount of lignin needed to replace the fossil fuel in the lime kiln would be about 307 t/d.

Table 5
Calculated pulp capacity with fixed heat load

Variable	Unit	Lignin Removal	
		0%	30%
Pulp mill capacity	ADt/a	1500000	1840000
Recovery boiler steam production	t/h	917	884
Hearth Heat Release Rate (HHRR)	kW/m ²	3445	3445
Heat load into the furnace	MW	947	947
Virgin black liquor flow	tDS/d	5825	6407
Recovery boiler flue gas flow (wet)	Nm ³ /s	289	288
Heat loss due to smelt	kJ/tDS	643	701
Heat loss due to reduction reactions	kJ/kgDS	1124	1268
Power generation capacity	MW	193	179
Electricity usage ^(a)	MW	108	129
Surplus electricity ^(b)	MW	85	50
White liquor production	m ³ /h	13140	16117
Lime kiln design	t/d	1180	1440

^(a) Electricity usage for the lignoboost process is not considered

^(b) According to design values

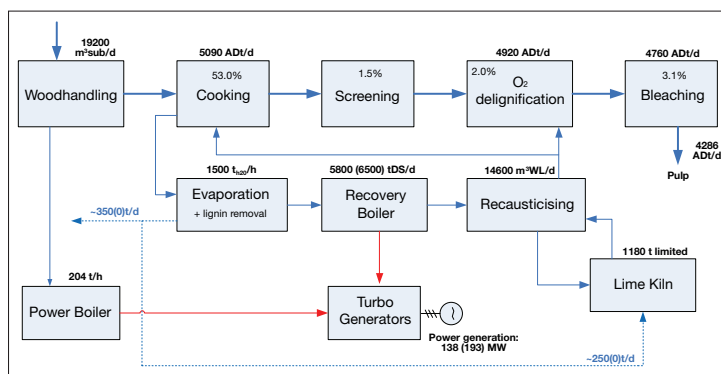


Fig. 4 Design of 1.5M Adt/a pulp mill with 30% of lignin removal at fixed pulp production

The fibreline design for the 1.84M ADT/a pulp is still challenging, but trends show that such capacity for a single line is expected in the near future. The design capacity of recausticizing plant would reach 17900 m³/d of white liquor. The evaporation plant would also be large - about 1850 t_{H₂O}/h. Since more pulp can be produced, the electricity usage is going to be about 21MW higher. At the same time, the power generation is going to decrease as a consequence of the lower steam production. The electricity usage per ton of pulp produced is going to be reduced by 2.4%. The case study results are overall quite encouraging regarding heat and electricity balances.

CONCLUSION

This work shows that recovery boiler capacity is the most sensitive design variable when dimensioning a kraft pulp mill with a lignin removal system. The *Millflow* program was used to analyse the changes in the black liquor heating value and in the pulp mill balance. With a fixed pulp production rate, the results showed that at 30% lignin removal rate, steam production will decrease about 22%, which will cause a reduction of 29% in power generation.

The study was extended to consider the alternative of using lignin removal to increase pulp mill capacity with a fixed recovery boiler. Based on a 1.5M ADT/d conventional pulp mill, and 30% lignin removal, pulp production could be about 23% higher without increasing the recovery boiler size. Lignin removal is then seen as an alternative that can be used not only to debottleneck an existing recovery boiler but also to design a Greenfield pulp mill with smaller recovery boiler.

ACKNOWLEDGEMENTS

We would like to thank the personnel from Pöyry Melbourne and Sao Paulo offices for their help in gathering the required data.

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Original manuscript received 7 January 2011,
revision accepted 7 July 2011.

Publication III

Hamaguchi, M., Kautto, J. and Vakkilainen, E.,
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Chemical Engineering Research and Design
Vol. 91, pp.1284–1291, 2013
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Chemical Engineering Research and Design

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Effects of hemicellulose extraction on the kraft pulp mill operation and energy use: Review and case study with lignin removal

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ABSTRACT

The implementation of wood extraction prior to pulping (pre-hydrolysis), with subsequent recovery of hemicellulose, is expected to affect the operation of a conventional kraft pulp mill. The magnitude of impacts will depend especially on the extraction conditions. In this specific work, the consequences of integrating the auto-hydrolysis process are studied using a detailed mill balance. A softwood pulp mill in Finland was used as a reference. With 14.1% of wood extracted, the wood demand increased by 15.5% and the steam generation in the recovery boiler by 13.5%. The removal of approximately 17% of lignin from black liquor would put the flue gas side of the boiler back to the original required capacity. In turn, this would enable the simultaneous recovery of lignin and hemicellulose. To make this process economically feasible, the extra revenue from the sales of lignin and hemicellulose products would need to compensate for the additional operating costs in the pulp mill.

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Keywords: Black liquor; Hemicellulose extraction; Energy balance; Lignin removal; Pulp mill

1. Introduction

The wood to be pulped normally consists of (in bone dry basis): cellulose 40–50%, hemicellulose 23–32%, lignin 15–30% and extractives 2–5% (Vakkilainen, 2000). In the kraft pulping process, the lignin and most of the hemicelluloses end up in the spent pulping liquor for combustion. If valuable chemicals, materials or biofuels were produced from the lignin or hemicelluloses, the pulp mill could be converted to a multiproduct biorefinery. Taking this issue into account, two technologies are being considered: lignin removal from black liquor and hemicellulose extraction prior to pulping. Fig. 1 shows the operation of a conventional kraft pulp mill and the alternative technologies in discussion. Removing lignin from black liquor is interesting for three main reasons: Firstly, it can be used to decrease the heat load on the recovery boiler per tonne of pulp produced (Vakkilainen and Välimäki, 2009). Secondly, the separated lignin might be used to replace fossil fuels in the mill (Wadsborn et al., 2007) or used as a saleable renewable fuel. Finally, the lignin after refining has the potential of being a

raw material for new products such as carbon fibres/materials, adhesives/binders, dispersants and metal chelating agents (Öhman et al., 2007) as well as vanillin and lignin-based polyurethanes (Silva et al., 2009).

One method to separate lignin from black liquor is the acidic precipitation. The black liquor is pumped from the evaporators, at 30–40% dry solid content, to the precipitation vessel where the pH is altered. The required pH change can be carried out for example by using H₂SO₄ and CO₂. The lignin precipitate is first filtered and then washed to purify the product. Mineral acid can be used in the washing operations to minimize the sodium content in the final lignin product (Tomani, 2010). The remainder of the black liquor is then returned to the evaporators. As a consequence, the lignin removal will affect mostly the chemical recovery operation and the mill energy balance. Special attention is however required when sulphur-containing compounds are added to the liquor cycle. Since they can affect the mill chemical balance, additional ash have to be discharged from the recovery boiler electrostatic precipitator, mostly in the form of Na₂SO₄. This means that NaOH might be needed to control the Na/S balance.

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Received 14 April 2012; Received in revised form 30 December 2012; Accepted 5 February 2013

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<http://dx.doi.org/10.1016/j.cherd.2013.02.006>

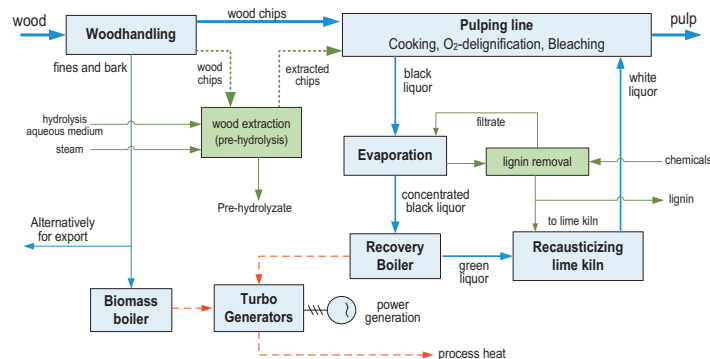


Fig. 1 – Example of lignin removal and hemicellulose extraction integrated into a kraft pulp mill.

In hemicellulose extraction, a fraction of the lignocellulosic material (mostly hemicelluloses) is hydrolyzed and recovered from wood chips prior to pulping. As a steam-phase pre-hydrolysis process (pre-hydrolysis-kraft, PHK), hemicellulose extraction is conventionally applied in the production of dissolving pulp (high-purity cellulose) to remove hemicelluloses of the wood prior to kraft cooking (Sixta, 2006a). However, this current practice followed by a neutralization step prevents the recovery of valuable hydrolysis products. The removed matter is then typically incinerated for energy production. For the recovery of hemicelluloses, the extraction would need to be carried out in aqueous phase at a liquor-to-wood ratio that would allow the separation of sufficient amount of extracted matter (pre-hydrolyzate or PHL).

The hemicellulose extraction has gained interest due to its capacity of producing fermentable sugars from lignocellulosic feedstock (Girio et al., 2010; Frederick et al., 2008) and because the heating value of hemicelluloses is rather low. In this respect, their partial extraction before pulping and subsequent conversion to ethanol, chemicals or biomaterials, with higher added values, might make economic sense. The attractiveness of these processes will however depend on many factors such as energy policies (e.g. oil taxation or incentives for the use of biomass), market development for the new products, process efficiency, wood availability and impacts that the integration would cause on the existing kraft mill. The main objective in this work is to evaluate the impacts of hemicellulose extraction on the existing mills, the magnitude of which is strongly dependent on the method of hydrolysis. First a general literature review will be presented, followed by detailed mill balances to assess the effects of hemicellulose extraction on the pulp mill operation and energy use. Removal of lignin from black liquor could be used to offset the impacts caused by hemicellulose extraction on the chemical recovery. Therefore, a case where the heat load to the recovery boiler is kept constant by lignin removal will be also presented.

2. Hemicellulose extraction in kraft pulp mills

Different methods have been proposed for the aqueous phase extraction of hemicelluloses in combination with pulp production. In acidic pre-hydrolysis processes, hemicelluloses are hydrolyzed to oligomeric and monomeric sugars and dissolved in the hydrolyzate either in a dilute solution of a mineral acid (e.g. H_2SO_4), which acts as a catalyst of hydrolysis

(Frederick et al., 2008; Parajó et al., 1994; Al-Dajani et al., 2009; Mendes et al., 2009), or auto catalytically (auto-hydrolysis, AH or hydrothermal). In both processes, the hydrolysis is catalyzed by hydronium ions (H_3O^+). In auto-hydrolysis, the acidic conditions are created through the cleavage of acetyl groups from xylan backbone and consequent release of acetic acid in hot water at a temperature of 130–175 °C (Al-Dajani et al., 2009; Mendes et al., 2009; Casebier and Hamilton, 1969; Colodette et al., 2011; Garrote and Parajó, 2002; Yoon et al., 2008; Leschinsky et al., 2009; Kautto et al., 2010a). In alkaline conditions, hemicellulose extraction is carried out with green liquor in a so-called near-neutral process (Mao et al., 2010), with strong alkaline solutions in low temperatures (Al-Dajani et al., 2008), or with white liquor (Helmerius et al., 2010).

Table 1 shows the experimental results from different pre-hydrolysis conditions with subsequent pulping of hydrolyzed chips. It can be observed that the auto-hydrolysis (AH) has been frequently tested. This process was already studied in the 50s (Richter, 1956), but with more emphasis on the pulp quality improvement. Currently, the process is being considered more as an option to fractionate and valorise lignocellulosic components more thoroughly. The use of hot water can be favourable for many reasons: the PHL contains a reasonable amount of hemicellulose dissolved, the core fraction (cellulose) is only slightly degraded, expenses with extra chemicals can be reduced and the use of water as aqueous phase is less harmful to the environment. In spite of these advantages, impacts on the mill operation are expected and have to be investigated.

In addition to the impacts on the mill operation, the auto-hydrolysis kraft pulping has other drawbacks such as the formation of sticky precipitates (Sixta and Schield, 2009) in the pre-hydrolyzate. The formation of these precipitates is attributed to the condensation products created by the fragments of lignin dissolved in the PHL. Their content is determined by the auto-hydrolysis duration. This change in the lignin reactivity during the hydrolysis can make the processing of PHL very difficult, affecting also the efficiency of subsequent cooking operations (Leschinsky et al., 2008). Taking this issue into account, the hydrolysis time becomes an important factor. Other potential drawbacks of auto-hydrolysis kraft pulping include the reduced pulp yield on wood after cooking and the impacts on pulp properties (Kautto et al., 2010a).

The temperature has also a great influence on the hydrolysis process. As an example, for the same extraction yield, the

Table 1 – Impacts of different methods of pre-hydrolysis on the experimental cooking process.

Wood (Ref.)	Pre-hydrolysis conditions time, T, L:W, washing ^a	Extraction yield %	Pulping MaxT, sulfidity, EA ^d , L:W	Overall pulping yield without (with) extraction, %	Extracted matter analysis wt% or g/L
<i>E. globulus</i> (Mendes et al., 2009)	AH (hot water) 3 h, 150 °C, 4:1, yes	12.5	160 °C, 28%, 17.4%, 4:1	54.7 (45.1)	1–4 g/L as ethanol conc.
	Acid (0.4 H ₂ SO ₄) ^b 2 h, 140 °C, 4:1, yes	13.1	160 °C, 28%, 17.4%, 4:1	54.7 (39.7)	6.8–9.6 g/L as ethanol conc.
<i>E. urograndis</i> (Colodette et al., 2011)	AH (hot water) 0.5 h, 165 °C, 3.5:1, no	10.8	155 °C, 37%, 15.8%, 3.5:1	53.9 (41.9)	~40% of dry PHL as xylan
Birch (Helmerius et al., 2010)	AH (hot water) 1.5 h, 150 °C, 3:1, no	8.0	160 °C, 36%, 21%, 3.5:1	51.7 (43.2)	11.75 g/L as xylan
	Alkali (white liquor) ^c 1 h, 160 °C, 3:1, no	9.0	160 °C, 36%, 18%, 3.5:1	51.7 (46.0)	3.62 g/L as xylan
North. hardw (Mao et al., 2010)	Alkali (green liquor) 1.8 h, 160 °C, 4:1, no	9.0	160 °C, 30%, 14%, 4:1	48.0 (46.0)	40% as fermentable sugars
Aspen (Al-Dajani et al., 2008, 2009)	AH (hot water) 4.5 h, 150 °C, 4:1, no	19.0	160 °C, 25%, 21%, 4:1	53.3 (39.7)	46% as xylan
	Alkali (1.67 M NaOH) 4 h, 90 °C, 4:1, no	19.3	170 °C, 39.8%, 12%, 4:1	52.7 (53.3)	27.3% as xylan
Pine (Frederick et al., 2008; Kautto et al., 2010b)	Acid (0.5 H ₂ SO ₄) ^b 1 h, 150 °C, 5:1, yes	14.0	165 °C, 30%, 16%, 4:1	46.6 (36.5)	~70% carbohydrates (~50% hemicel.)
	AH (hot water) 1.7 h, 150 °C, 4:1, no	14.1	160 °C, 40%, 19.4%, 4:1	46.2 (40.0)	48% carbohydrates

^a Washing post hydrolysis, which may affect the cooking process due to PHL entrained in the pores.
^b wt% on dry wood.
^c EA 3%.
^d As NaOH.

auto-hydrolysis time can be significantly reduced by increasing the water temperature. Drawing from Table 1, however, one can conclude that a preferable condition for hemicellulose extraction is still not clear. Although it shows that the overall pulping yield is less affected with alkaline pre-hydrolysis, the amount of recovered xylan can be significantly lower when compared to dilute acid or auto hydrolysis. In the case of dilute acid, the cellulose can be highly degraded depending on the hydrolysis conditions (Frederick et al., 2008), which leads to a poorer quality of pulp. According to Girio et al. (2010), as also cellulose can be hydrolyzed in dilute acid, the process has been primarily considered as a pre-treatment step prior to the enzymatic hydrolysis. In this process, the hydrolysis of hemicelluloses renders the cellulose fraction more amenable for a further enzymatic treatment and fermentation. The process would be then more suitable for the standalone production of bioethanol than for the co-production of ethanol and pulp. Although the auto-hydrolysis can reduce the impacts on pulp quality, it requires a post-hydrolysis step to increase the concentration of fermentable sugars for ethanol production (Mendes et al., 2009).

The optimum point should therefore consider at least the hemicellulose recovery efficiency, operational costs, processing time, impacts on digester yield and the influence on pulp quality. Enhancing the quality and yield of the final pulp is the most important target of a pulp mill. Although the concept of biorefinery can be implemented, the negative effects on the core product properties and yield would discourage any investments in hemicellulose extraction. These effects are proportional to the conditions of the hydrolysis and therefore of primary importance.

The type of wood has also some influence on the hydrolysis process. In general, especially xylan (dominant hemicellulose in hardwoods) is dissolved under acidic conditions. On the other hand, the alkaline peeling reaction degrades glucomannan (dominant hemicellulose in softwoods) rapidly under alkaline conditions, while de-acetylated, solubilized oligomeric xylan is more stable due to the 4-O-methyl glucuronic acid side chains (Helmerius et al., 2010). Because xylan is more stable in cooking, different impacts on the pulping yield are expected for softwoods and hardwoods.

2.1. Impacts on the fiberline

The hemicellulose extraction has generally been reported to decrease required cooking times significantly. Kautto et al. (2010a) showed that the *H*-factor can decrease from 1600 (reference pulp) to 1000 (auto-hydrolysed pulp), with cooking time decreasing about 39% to obtain similar Kappa numbers. Yoon and van Heiningen (2008) reported 40–60% higher delignification rate constants for water pre-hydrolyzed chips. This has been attributed to the improved penetration of the cooking liquor caused by the increased pore volume and permeability of the cell wall as well as hydrolytic cleavage of lignin structures and covalent bonds of lignin–carbohydrate complexes (LCC) during pre-extraction (Sixta, 2006a). The alkaline extraction methods have been also reported to decrease the cooking times (Al-Dajani et al., 2008).

Because part of the PHL is entrained in wood pores after hemicellulose extraction, the neutralisation of water or dilute acid hydrolyzate can be assumed to consume alkali in the digester. On the other hand, because there are less hemicelluloses consuming alkali, the alkali charge (% on dry wood) is relatively unchanged (Colodette et al., 2011; Yoon and van Heiningen, 2008). In the case of alkaline extraction, the effective alkali in the digester is expected to be lower for hydrolyzed chips (Al-Dajani et al., 2008; Helmerius et al., 2010).

Dilute acid and water pre-hydrolysis processes have been reported to decrease the overall pulping yield (mass of brown stock pulp/mass of wood chips prior to extraction), while alkaline conditions have provided similar or slightly reduced yields (see Table 1). Since especially xylan is hydrolyzed in acidic conditions and xylan is relatively stable in cooking, it can be assumed that part of the reduced yield derives from reduced xylan yield. This can be seen in the increased cellulose/hemicellulose ratio of pre-hydrolyzed pulps (Al-Dajani et al., 2009; Kautto et al., 2010a). In addition to a decrease in overall pulping yield, some authors have reported a decrease in digester yield (mass of brown stock pulp/mass of chips to digester). This has been attributed to increased susceptibility of hemicelluloses and cellulose of pre-extracted chips to be dissolved during cooking (Frederick et al., 2008).

In oxygen delignification, hemicellulose content can affect both the degree of delignification and selectivity (Δ viscosity/ Δ kappa). With lower hemicellulose content, the degree of delignification of pre-hydrolyzed chips seems to be higher than that of unhydrolyzed chips under constant conditions (Kautto et al., 2010a; Sixta, 2006b). In line with this, other authors (Colodette et al., 2011; Zou et al., 2002) have reported reduced delignification in the O_2 -stage with increasing xylan-content of brown stock pulp. Hemicelluloses could therefore be assumed to affect the accessibility of the chemical reagents in the O_2 -stage. Selectivity has been reported to improve with the increasing hemicellulose content. This has been attributed especially to the protection of cellulose from radical attack of free hydroxyl radicals by hemicelluloses (Zou, 2002; van Heiningen and Violette, 2001), increasing viscosity. With a constant degree of delignification in O_2 -stage, hemi-poor hydrolyzed chips could exhibit poorer selectivity than unhydrolyzed chips.

Kautto et al. (2010a) have studied the bleachability of water pre-hydrolyzed pine wood chips. To obtain comparable final brightnesses after bleaching, they found the chemical consumptions in DED-bleaching, calculated as total active chlorine, to be lower for pre-hydrolyzed chips. The improved

bleachability could be partly explained by a lower *H*-factor in cooking and lower content of hexenuronic acids (especially with hardwoods) and metals of hydrolyzed pulps. After tests with hydrolyzed eucalyptus chips, Colodette et al. (2011) also concluded that pulp bleachability can be substantially improved.

2.2. Impacts on the pulp properties

The main effects of hemicellulose extraction on pulp properties can be seen in beating response and strength properties. Hemicelluloses contribute significantly to the swelling tendency of fibers. With decreased swelling of hemicellulose-extracted pulps, the interfiber contact during beating decreases, deteriorating external fibrillation and hence beating response. Compared to unhydrolyzed pulps, the required number of revolutions in a PFI-mill increased more than fivefold to obtain a given tensile index (Kautto et al., 2010a). Yoon and van Heiningen (2008) report considerably increased PFI revolutions for hydrolyzed pulps to obtain a given freeness.

Regarding strength properties, the main effect of low hemicellulose content can be seen in tensile and tear indexes. With a reduction of hemicellulose content in pulp, tensile index has been reported to decrease and tear index to increase (Colodette et al., 2011; Molin and Teder, 2002). Some authors suggest that the main effects of pre-hydrolysis on pulp strength properties would derive from reduced interfiber bonding (Yoon and van Heiningen, 2008). Other properties such as Zero-span wet tensile strength, Z-directional strength and Scott bond energy seem to be unaffected by the hemicellulose content in the pulps. Light-scattering coefficient (LSC) and opacity, as well as air permeability have been reported to increase with the hemicellulose extraction. Kautto et al. (2010a) suggested that the dimensions of pre-hydrolyzed fibers had been changed, enabling the formation of more opaque, porous and light-scattering sheets.

2.3. Impacts on the chemical recovery

The integration of water and dilute acid hydrolysis can decrease the overall cooking yield quite significantly. If wood consumption is fixed, less organics would dissolve in black liquor, thus potentially off-loading the chemical recovery. If pulp production is fixed, the wood demand can be significantly higher. Consequently, the flow of black liquor solids would increase, affecting mostly the recovery boiler operation and the electricity generation per ton of pulp produced. Assuming a constant pulp production, Frederick et al. (2008) discussed the effects of dilute acid extraction on the capacity utilization of different equipment. With 14% of extracted matter, the loads for evaporators, recovery boiler, recausticizing and lime kiln increased by about 23%, 19%, 10% and 10%, respectively. A higher increase in evaporation load can be attributed to an increased water content of pre-hydrolyzed chips.

In alkaline hydrolysis, the overall pulping yields have been rather close to those of the reference cooking. With a constant pulp production, this would limit or eliminate the increase in wood consumption, thus potentially reducing the amount of organic material dissolved in the black liquor. The use of alkaline chemicals in the extraction might, however, affect the recovery cycle. Mao et al. (2010) discussed the extraction of hemicelluloses from hardwood chips using green liquor

as the extracting agent. Under these conditions, there was a decrease in the required effective alkali level to obtain a given kappa number after cooking, which would decrease the load on the lime kiln. Marinova et al. (2009) described the effects of a near-neutral hemicellulose extraction process on the steam generation and utilization of a pulp mill. Due to the extraction of organic matter, the steam generation was reduced slightly and the processing of the extracted material to ethanol increases the steam demand of the mill. They further described ways to optimize the energy usage of this pulp and ethanol producing biorefinery.

The increased steam demand and ways to minimize the increase were also discussed by Lundberg et al. (2012). They also described the anticipated effects of near-neutral hemicellulose extraction on the Na/S balance of a pulp mill. With the utilization of green liquor in extraction, part of it is carried over to the hemicellulose stream, leading to a deficit of sodium and possibly also sulfur. Ghezzaz et al. (2012) presented near-neutral extraction as a way to reduce the load on the boiler in a mill producing semichemical pulp. Using strong alkali solutions with low temperatures, Huang et al. (2010) reported slightly higher yields on wood after cooking compared to reference kraft cooking. This would possibly reduce the amount of organics in the black liquor, but the strong alkali solution would need to be recycled back to the extraction process to avoid extensive loss of alkali.

3. Pulp mill balances

Mass and energy balances in this work were performed using the MillFlow spreadsheet. This program can be used to design pulp mills by equipment vendors and was previously used for preliminary studies of lignin removal (Vakkilainen and Välimäki, 2009). In this present task, the hemicellulose extraction prior to pulping was integrated into the mill balance. The main target was to analyze the effects on the kraft pulping process and energy usage. A softwood pulp mill in Finland was used as a reference. The tentative balance over hemicellulose extraction and cooking is based on laboratory data by Kautto et al. (2010b), who developed a simulation model for the co-production of ethanol and pulp in a pine based pulp mill.

Various data are needed for the mill balance, including the PHL characterization, amount of extracted matter, changes in cooking yield, EA charge and sulfidity. Such variables affect for example the black liquor properties and, consequently, the chemical recovery cycle operation. With the analysis data of PHL and original wood, the composition of the extracted wood can be estimated. White liquor, water in chips and black liquor are used to adjust the required liquor-to-wood ratio of 4:1. The white liquor charge is calculated based on dry wood demand, alkali charge and alkali concentration. The calculation of the black liquor heating value is based on the method by Adams and Frederick (1988), which was modified to comply with changes in the conventional process.

Regarding lignin removal, the effects are essentially based on material and energy balance. In the balance, a fraction of lignin (heating value of 25 MJ/kg) is subtracted from the spent liquor. This will affect the black liquor heating value and solid flow and, consequently, the heat load to the recovery boiler. A calculation guideline for lignin removal, as well as the possible impacts of its integration on a kraft pulp mill, was presented in a previous work (Hamaguchi et al., 2011).

Table 2 – Mill reference data, fixed for all balances.

Parameter	Unit	Value
Pulp production	ADt/d	1715
Alkali concentration	g NaOH/L	115
Causticity	%	81
Sulfidity	%	40
Reduction	%	94
EA charge on dry wood	% as Na ₂ O	18.8
Annual operating hours	h/a	8400

3.1. The reference mill

The pulp mill produces about 600,000 ADt/a of bleached softwood kraft pulp (BSKP). The recovery boiler is the only source of high pressure steam, which is sufficient to supply the required heat/power and still produce about 30 MW_e of surplus electricity. Barks and fines generated in the wood handling area (about 580 t(dry)/d) are sold to external power plants and, therefore, no auxiliary boiler is currently needed in the mill. One back-pressure and one steam condensing turbine generate the required heat. Each turbine is coupled to one generator and the changes in the steam and power production affect primarily the condensing turbo generator. The specific heat (MJ/unit), electricity (kWh/unit) and utilities usages in each department are in accordance with the reference mill design data. These specific values and those presented in Table 2 are considered fixed.

3.2. Key assumptions

It is assumed that the laboratory results (batch) are valid for the continuous operation of the mill. In the conventional mill, the chips are pre-heated to about 90–95 °C using flash steam from the pulping stage. With the integration, the hydrolysis water temperature of 150 °C is reached by using additional heat exchangers, flash condensers and MP steam. Consequently, the temperature of the extracted chips after draining is expected to be higher, with a fraction of hot PHL liquid being entrained in the wood pores. Because the chips are not washed before entering the digester, possibly less heat is required for the pulping of hydrolyzed chips. Considering that part of the heat lost during the draining of the hydrolysis vessel is recovered as secondary heat, it is assumed that the total steam demand in the digester and hydrolysis is unchanged compared to the reference digester.

Since the actual end product manufactured from the PHL is not specified in this work, the analysis is limited to the hemicellulose extraction process. This means that heat, electricity, and chemicals consumed in the processing of the PHL as well as the combustion of the additional residues are not considered in the mill balances. The balances of a fully integrated biorefinery, where mass and energy streams from the processing of the PHL are included, would therefore be slightly different from the values presented in this work. The balance of soap as crude tall oil (CTO) for a Finnish kraft pulp mill can be found in the literature (Laxén and Tikka, 2008). The crude soap content in wood is estimated from the amount of extractives and a soap recovery efficiency of 87% is assumed.

With the liquor-to-wood ratio of 4:1 in the extraction vessel, 60% of the PHL is recovered (draining) and 40% entrained in the extracted wood pores. These values are in accordance with those considered in literature (Al-Dajani et al., 2008; Kautto et al., 2010b; Mendes et al., 2009). Because part of the PHL is

Table 3 – Mass balance with hemicellulose extraction (HE) and lignin removal (LR).

Variable	Unit	Pulp mill	Pulp mill + HE	Pulp mill + HE + LR
Wood demand (with bark)	BDt/d	4140	4780	4780
Wood composition, C:H:L:E ^a	wt%	39:30:27:4	45:23:30:2	45:23:30:2
Overall pulping yield	%	46	40	40
Soap recovery	kg/ADt	75	37	37
White liquor to cooking plant	m ³ /d	7530	7470	7470
Additional load to evaporation	kg/ADt	0	720	930
Total evaporation load	t _{H₂O} /h	639	725	740
Black liquor average flow (virgin)	tDS/d	3030	3270	3090
RB flue gas flow (wet)	Nm ³ /s	150	168	151
RB steam production	t/h	445	505	446
Lignin/total dry solids in black liquor	wt%	31.3	32.7	28.7
Total organics in black liquor	wt%	62.5	66.0	63.5

^a Approximate values, calculated for chips entering the digester, cellulose:hemicellulose:lignin:extractives.

carried over to the digester, the chips after pre-extraction contain more water than chips prior to pre-extraction. This will impact the liquor-to-wood ratio and also the capacity utilization of evaporators. The entrained PHL solids are assumed to be dissolved in the black liquor after pulp washing and will affect the heating value calculation. Although the hydrolyzed pulp may affect the oxygen delignification stage, its influence on the black liquor composition is not taken into consideration.

Because the heat load into the recovery boiler (RB) is increased with the implementation of hemicellulose extraction, the lignin removal is used as an alternative to reduce the organic fraction in the black liquor. It is then assumed that more extra load is added to the evaporators due to the return of lignin washing filtrate. This extra load is estimated at 2 m³/t lignin and the power demand at 0.35 kWh/t of lignin (Tomani, 2010). Since the lignin is removed under acidic conditions, the mill chemical balance can be slightly affected. The consumption of chemicals has been reported for different black liquors (Tomani et al., 2012) and is assumed as 250 kg CO₂ and 200 kg H₂SO₄ per ton of precipitated softwood lignin. An alkaline solution is then needed to maintain the sodium sulphur balance.

4. Results and discussion

In the balance calculations, the amount of wood extracted prior to pulping was set to 14.1% which, according to test results by Kautto et al. (2010b), reduced the overall pulping yield by about 13.4% when compared to the reference. This will result in an increased demand of wood per ton of pulp produced. The main mass balance results are presented in Table 3. It can be observed that the extraction of hemicellulose is reflected on the change in wood composition to the digester. Because a great part of the extractives is dissolved during the

pre-hydrolysis process, the tall oil generation could decrease significantly.

Regarding the effect of hemicellulose extraction on tall oil generation, the results are here estimated as recovered crude soap after skimming. It should be kept in mind that there is not only tall oil but also residual black liquor, fibres, lignin and other impurities in the composition of crude soap (Laxén and Tikka, 2008). For the recovery of tall oil, other steps such as acidulation, purification and drying are still required. The effects of auto-hydrolysis on the tall oil yield have to be experimentally tested and were not taken into consideration in this study. The reduced amount of recovered crude soap would, however, indicate that the tall oil generation would be decreased. Considering the fact that tall oil is an important raw material for various products, this could be a major drawback when assessing the feasibility of hemicellulose extraction.

In the cooking tests of auto-hydrolyzed chips, the overall pulping yield was decreased but the actual digester yield was rather unchanged. Because the white liquor charge per dry wood is kept constant, an insignificant change is expected in the causticizing utilization capacity. Bigger impacts however are observed in the evaporators and recovery boiler. Because chips after extraction contains more water than chips prior to extraction, the total additional load increased the required evaporation capacity by almost 16%, which contributed to the increase of the mill steam consumption, Table 4. In spite of this, there was an increment of approximately 13 MW_e in the mill electricity production. The reason is that more steam is generated in the recovery boiler. The PHL present in the wood pores increased the organic solids in black liquor by 8%. This partly explains the increase in the heating value which is also attributed to the lower ratio of organic acids to lignin in the black liquor. As a result, the steam production in the recovery boiler is increased by about 13.5%.

Table 4 – Energy balance for the pulp production with average values.

Variable	Unit	Pulp mill	Pulp mill + HE	Pulp mill + HE + LR
Black liquor HHV	MJ/kg	14.2	14.7	13.9
Total heat load to the RB	MW	524	583	524
Heat loss in the RB ^a	MW	180	192	181
LP steam required (4 barg, 155 °C)	MW _{th}	147	155	157
MP steam required (11 barg, 200 °C)	MW _{th}	66	71	73
Electricity production	MW _e	77.8	90.5	73.0
Surplus electricity	MW _e	28.6	39.5	20.4

^a Losses due to flue gas, radiation and convection, smelt sensible heat and reduction.

Please cite this article in press as: Hamaguchi, M., et al., Effects of hemicellulose extraction on the kraft pulp mill operation and energy use: Review and case study with lignin removal. Chem. Eng. Res. Des. (2013), <http://dx.doi.org/10.1016/j.cherd.2013.02.006>

Table 5 – Estimated values for some additional mill streams.

Additional stream	Unit	Pulp mill + HE + LR
Inflows		
Pre-hydrolysis hot water	m ³ /h	547
Additional wood (with bark)	t(dry)/d	640
H ₂ SO ₄ /CO ₂ for lignin removal	t/d	36/45
Outflows		
Additional wood waste ^a	t(dry)/d	90
Pre-hydrolyzate (PHL) ^b	t(dry)/d	349
Lignin from black liquor	t(dry)/d	180

^a Bark average content of 10%, fines removal of 2%, debarking losses of 3%.
^b Crude PHL stream, based on 14.1% extraction; amount of oligomers and monomers estimated in 170 t(dry)/d.

The removal of approximately 17% of lignin from the black liquor would put the flue gas side of the boiler back to the original required capacity (Table 3), and in turn, prevent the turbo generators from overload instabilities. The decrease in the black liquor flow and heating value is proportional to the lignin removal rate. It can be observed that, although lignin is recovered, the integration of both hemicellulose extraction and lignin removal decreased the condensing power by 4.8 MW_e compared to the reference, which is mainly attributed to the higher steam demand.

Investments in the evaporation plant for higher utilization capacity seem to be inevitable due to the 930 kg/ADt of additional load. This however can be reduced if the extracted wood is, for example, washed and dried before entering the digester. Consequently, more dissolved material could be recovered and the additional load to evaporation minimized. On the other hand, washing and drying of a considerable amount of chips can be costly for pulp mills. It would also have a negative effect on the heat integration between hemicellulose extraction and cooking. In spite of this, adapting the existing digester to new cooking conditions is also required.

4.1. The value of additional streams

The value created by the new outflows is essential to make the integration of the alternative processes economically attractive. At minimum, it should compensate for the increased wood demand and for other extra inflows as well as the additional capital expenses. Table 5 shows the main additional streams considered in this work. The recovered lignin and hemicellulose are the major outflows that can possibly increase the mill revenue. The amount of lignin recovered would be sufficient to replace the fossil fuel in the lime kiln (estimated at 115 t/d) and also be exported. The chemicals and electricity required to remove the lignin however represent additional operational costs. The hemicellulose could be used to produce, e.g. biofuels or chemicals such as xylitol and furfural. Therefore, the attractiveness of the integration will also depend on the market development for these additional outflows. Economic analysis of the integration of hemicellulose extraction and lignin removal to a pulp mill is, however, beyond the scope of this study.

The purification and downstream processing of the drained PHL would depend on the intended end product produced from the hemicellulosic components of the PHL. The additional wood waste and possible residues generated in the

downstream processing of the PHL have calorific values and can be exported as a biofuel to external power plants. Another alternative would be to install an additional power plant, since the integration of hemicellulose extraction and lignin removal would decrease the power sold to the grid by 8.2 MW_e. The economic justification of an additional power plant would need to be assessed in a separate feasibility study.

5. Conclusion

This work shows that with 14.1% of wood extracted prior to pulping, the steam generation in the recovery boiler increased by 13.5% and the power generation by 16.3%. In order to minimize these effects, approximately 180 t/d of lignin was removed from black liquor to decrease the heat load and avoid extensive investments in the boiler. The integration of lignin removal and hemicellulose extraction would reduce the excess power produced by 8.2 MW_e. Also the recovery of crude soap would be reduced. The increase of evaporation load (16%) and wood handling area (15.5%) seems to be also inevitable. These led to the conclusion that even though additional outflows are available to increase the mill revenue, they have to compensate for the increase in the operating and capital costs and possible revenue losses. These impacts would require thorough consideration when studying the feasibility of hemicellulose extraction. In addition to economic factors, the attractiveness would strongly depend on the hydrolysis conditions, effective treatment of the pre-hydrolyzate, and how the quality of pulp is affected.

Acknowledgements

The authors would like to thank the Energy Graduate School in Finland, the Walter Ahlström Foundation and the Finnish Cultural Foundation.

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Publication IV

Hamaguchi, M., Cardoso, M., and Vakkilainen, E.

Alternative technologies for biofuels production in the kraft pulp mills - potential and prospects

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Energies

Vol. 5, pp. 2288–2309, 2012

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Review

Alternative Technologies for Biofuels Production in Kraft Pulp Mills—Potential and Prospects

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Received: 22 May 2012; in revised form: 21 June 2012 / Accepted: 2 July 2012 /

Published: 6 July 2012

Abstract: The current global conditions provide the pulp mill new opportunities beyond the traditional production of cellulose. Due to stricter environmental regulations, volatility of oil price, energy policies and also the global competitiveness, the challenges for the pulp industry are many. They range from replacing fossil fuels with renewable energy sources to the export of biofuels, chemicals and biomaterials through the implementation of biorefineries. In spite of the enhanced maturity of various bio and thermo-chemical conversion processes, the economic viability becomes an impediment when considering the effective implementation on an industrial scale. In the case of kraft pulp mills, favorable conditions for biofuels production can be created due to the availability of wood residues and generation of black liquor. The objective of this article is to give an overview of the technologies related to the production of alternative biofuels in the kraft pulp mills and discuss their potential and prospects in the present and future scenario.

Keywords: biofuels; black liquor; kraft pulp mill; wood residues

1. Introduction

The need to turn away from the fossil fuel era has opened new opportunities for the use of products from renewable resources such as biomass. Being a non-fossil fuel, and a renewable organic material,

biomass should be used to produce energy. The sources include terrestrial or aquatic vegetation, agricultural or forestry residues and industrial or municipal waste. It is believed that the use of biomass for energy and fuel production will be limited by maximum production rates and supply of biomass rather than the demand for energy and fuel [1]. In this scenario, the pulp mills have a large energy potential because they process a massive amount of lignocellulosic material, which represent the most significant percentage of vegetable biomass and the largest source of organic compounds in the biosphere. They contain varying amounts of cellulose, hemicellulose, lignin and a minor amount of extractives.

Cellulose is the main constituent of wood. It is a glucose polymer consisting of linear chains with an average molecular weight of approximately 100,000 grams per mole [2]. Since it is the main product of pulp mills, all the operating variables of the kraft process will be focused on obtaining maximum production of cellulose. Hemicellulose is a heterogeneous polymer composed of five-carbon and six-carbon monomeric sugars, with an average molecular weight of <30,000. Hardwoods are rich in five-carbon sugars while softwoods contain mostly six-carbon sugars. Hemicelluloses have the lowest average heating value among the components, Table 1. Removing the hemicelluloses from wood chips prior to pulping will provide kraft pulp mills with the opportunity to produce value-added products [3].

Lignin can be regarded as a group of amorphous, high molecular-weight, chemically related compounds. The building blocks of lignin are believed to be a three carbon chain attached to rings of six carbon atoms, called phenyl-propanes. Lignin has a higher heating value when compared to hemicellulose and is typically used as a fuel. Its structure suggests that it could also play an essential role as a chemical feedstock, particularly in the formation of supramolecular materials and aromatic chemicals [4].

Table 1 shows that there is variation in reported literature regarding the heating values of wood components [5–7]. They vary according to, for example, region and wood species. In most wood species, almost 40% to 45% of the dry substance is cellulose which is located primarily in the secondary cell wall. The amount of hemicelluloses and lignin in dry wood varies from 20% to 30% and from 20% to 40% respectively. However, there are variations in this percentage depending on the age, type and section of the wood. For example, there is approximately 28% lignin in stem wood, 36% in bark and 37% in branches, on a dry weight basis [8].

Table 1. Heating values of lignocellulosic components.

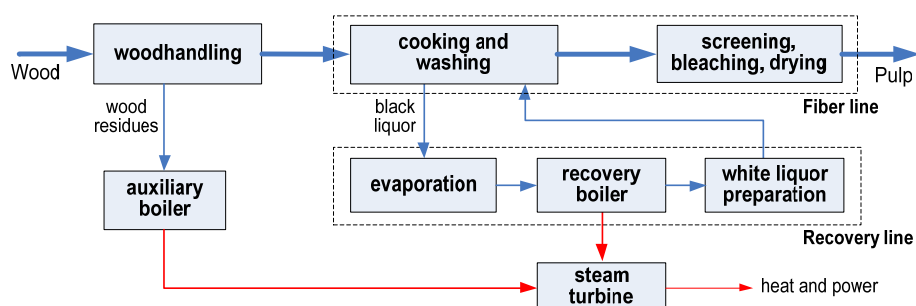
	Minimum (MJ/kg)	Maximum (MJ/kg)	Average (MJ/kg)
Cellulose	16.1	19.0	17.6
Hemicellulose	14.7	18.2	16.5
Lignin	22.3	26.6	23.7
Char	25.4	37.2	31.3

2. Conventional Kraft Pulp Mills

The primary goal of pulping is wood delignification. This process should be carried out while also preserving the cellulose and hemicelluloses to the possible extent and desirable amount. Such steps can be accomplished by using an aqueous solution containing hydroxyl (OH⁻) and hydrosulphide (HS⁻) ions as active components. This solution, widely known as white liquor, is consumed during the cooking of wood chips in pressurized vessels at approximately 160–170 °C [9]. The result is the

production of wood pulp containing dissolved organic and soluble inorganic materials. A washing stage is then needed to remove the majority of these materials. The washed pulp is sent to be screened and the separated liquid (black liquor), with a dry solids content of about 13%–16%, is sent to the recovery line, Figure 1.

Figure 1. Overview of a kraft pulping process.



A chemical recovery cycle is necessary to make the pulping process economically feasible. After being concentrated to 65%–85% at the evaporation plant, it can be effectively burned in the recovery boiler for the regeneration of pulping chemicals. In turn, the boiler generates high pressure steam and reduces some waste streams in an environmentally friendly way. The non-combusted fraction becomes a hot molten inorganic flow, consisting mostly of sodium carbonate and sodium sulphide. This molten smelt is dissolved and subsequently pumped to the recausticizing plant for white liquor preparation.

Typically pulp mills also have to eliminate the wood residues generated in the wood handling area, which consist basically of barks, sawdust or fines from screening. They are normally burned in auxiliary boilers. The high pressure steam from both recovery and auxiliary boilers is sent to the turbo generators to produce power and heat for the mill.

3. The Relevance of Wood Species for Biofuels Production

The chemical composition and wood density of the species used, combined with the applied process conditions (e.g., target kappa numbers or if the pulp is bleached or unbleached), are important factors to be considered when studying the potential of biofuel production. They have a great influence on the specific consumptions of wood, chemical charge, black liquor characterization as well as effluent to treatment and emissions rate. One important difference that has a direct impact on the kraft pulping process can be found between softwoods (SW) and hardwood (HW), specifically with respect to the species composition, Table 2.

Table 2. Examples of typical gross composition (%) of wood species for pulping [10–12].

Wood Species	Cellulose	Glucos-Mannan ¹	Glucuronoxylan ²	Lignin	Extractives	Other Carbo-Hydrates
Softwood						
<i>Pinus radiata</i> (Monterey pine)	37.4	20.4	8.5	27.2	1.8	4.3
<i>Pinus sylvestris</i> (Scots pine)	40.0	16.0	8.9	27.7	3.5	3.6
<i>Picea abies</i> (Norway spruce)	41.7	16.3	8.6	27.4	1.7	3.4
<i>Picea glauca</i> (White spruce)	39.5	16.0	8.9	27.5	2.1	3.0
<i>Larix sibirica</i> (Siberian larch)	41.4	14.1	6.8	26.8	1.8	8.7
Hardwood						
<i>Betula verrucosa</i> (Silver birch)	41.0	2.3	27.5	22.0	3.2	2.6
<i>Betula papyrifera</i> (Paper birch)	39.4	1.4	29.7	21.4	2.6	3.4
<i>Acer rubrum</i> (Red maple)	42.0	3.1	22.1	25.4	3.2	3.7
<i>Eucalyptus globulus</i> (Blue gum)	51.3	1.4	19.9	21.9	1.3	3.9
<i>Eucalyptus urophylla</i> *	51.0	1.5	14.9	26.1	2.5	4.0
<i>Eucalyptus urograndis</i> *	49.5	1.4	15.0	27.8	2.0	4.3
<i>Eucalyptus grandis</i> *	48.7	1.5	16.2	26.1	1.8	5.7
<i>Populus tremuloides</i> (Aspen) ³	44.5	1.7	21.4	23.3	2.1	7.0

¹ including galactose and acetyl in softwood; ² including arabinose in softwood and acetyl group in hardwood;

* composition based on analysis of Brazilian chips [11]; ³ cellulose as glucon and glucomannan as mannan [12].

One example is the pulp yield (mass of brown stock pulp/mass of wood chips), which is strongly influenced by the wood species processed in the mill. One reason is that glucuronoxylan (main hemicellulose in HW) is more stable than glucomannan (main hemicellulose in SW) in the cooking process. In addition, the hardwood lignin shows a lower recondensation tendency than softwood lignins [9]. The result is a better selectivity and higher pulp yield for hardwoods.

Average yield values for bleached market pulp from softwood, birch and eucalyptus are in the range of 44%–48%, 49%–52% and 50%–54% respectively [13]. The higher yield for eucalyptus pulping can be expected given the high percentage of cellulose and differences in lignin reactivity. Santos *et al.* [14] reported higher delignification rates for hardwoods when compared to pine, with the highest value achieved with *Eucalyptus globulus*. Although a minor amount can be also dissolved during the kraft pulping, the cellulose is less susceptible to alkali or acid attack than hemicelluloses [9]. According to Grace and Malcolm [15], for a 50% yield, about 20% of the original wood is lost due to polysaccharides, primarily hemicelluloses (amorphous structure). This leads to the fact that most of the hemicelluloses and almost all the lignin end up in the black liquor.

Another factor is related to the naturally occurring regional variability within species as well as the age of trees, which can lead to variations on pulp yield between mills using essentially the same raw material. In order to exemplify some of these effects, Table 3 attempts to illustrate some key factors related to the potential of alternative fuels in the pulp mills. The calculations are performed using a mill balance spreadsheet [16]. It can be observed that a higher pulp yield results in a lower load of organic material to the recovery process and a higher wood consumption per ton of pulp produced. The wood composition will also influence the process of hemicellulose extraction as well the production of tall oil from fatty acids and resins.

Table 3. Examples of specific load variations in bleached pulp mills.

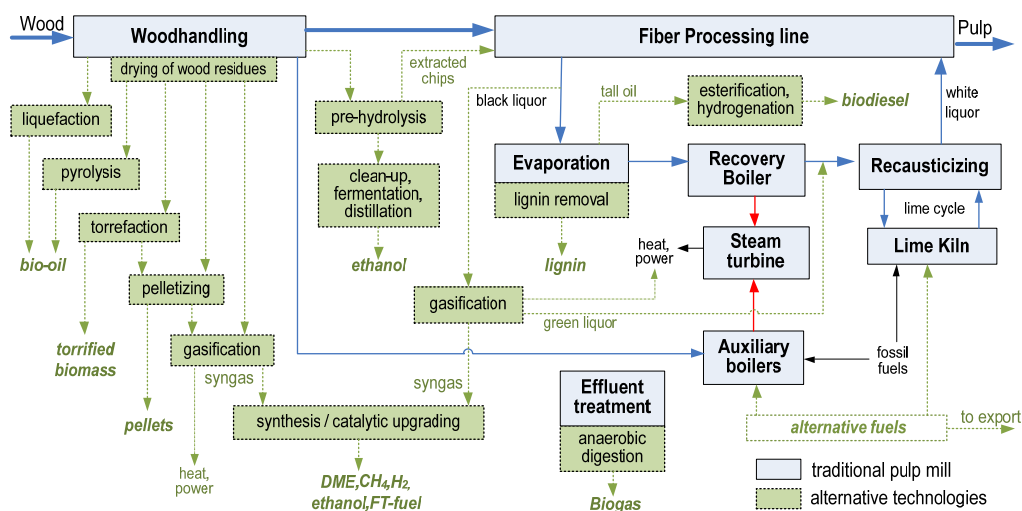
		Scots Pine	Silver Birch	<i>Eucalyptus Grandis</i>	<i>Eucalyptus Globulus</i>
Average Process Data					
Pulp yield	%	46.0	50.0	52.0	53.0
Sulfidity	%	40	35	32	28
EA charge on dry wood	% NaOH	19	17	17	18
Calculated Values					
Chips consumption	kg(dry)/ADt	2090	1925	1833	1815
Wood waste ¹	kg(dry)/ADt	298	274	261	259
Lignin in black liquor	kg/ADt	540	399	452	375
Black liquor yield	kgDS/ADt	1740	1450	1328	1320

¹ Based on 1.5% screening loss, 10 wt % bark at delivery and 3% losses at debarking.

4. Production of Alternative Biofuels in the Pulp Mills

Figure 2 shows an overview of a pulp mill in which alternative technologies have been integrated for biofuel production. A kraft pulp mill with these technologies can present a number of opportunities to make bio-products at several points in the process. They are classified in this article as wood based and black liquor based technologies. Although it is possible to generate bioenergy through processes targeting the pulp mill waste streams e.g., biogas by anaerobic digestion of sludge [17], these processes will not be explored in this article.

Figure 2. The kraft pulp mill and the alternative technologies for biofuels production.

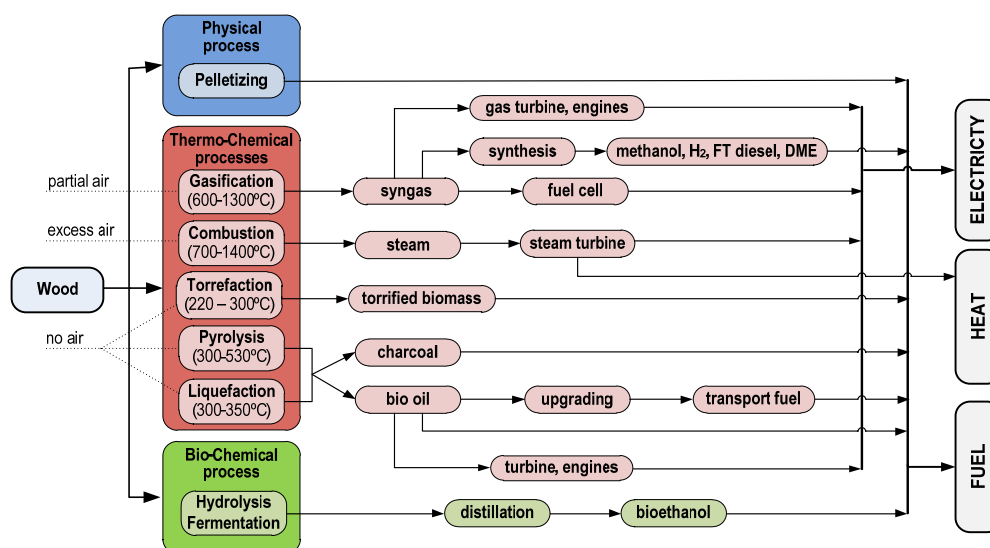


4.1. Wood-Based Technologies

Wood residues are considered attractive for being cheap and suitable as feedstock. Direct combustion is the traditional way of processing them in pulp mills. Alternative processes can be

divided into physical, thermo-chemical and biochemical processes, Figure 3. If economically feasible, not only can generated wood waste be used as raw material but additional wood and bark brought from the forest can also be processed. One drawback is the high water content of biomass, which can range from 35% to 60% [18]. The value depends on the weather conditions and storage period after cutting the tree. For the optimum use in the pelletizing, torrefaction, gasification or pyrolysis processes, the moisture content has to be reduced to 10%–15%, which is typically not required with direct combustion in efficient boilers. A drying pre-stage is then needed to fulfill the requirements. For such achievement, drying technologies using waste heat are available as reported by Johansson *et al.* [19]. Some dryers allow the use of, for example, hot water at 65–90 °C as a heat source.

Figure 3. Alternative technologies for biomass conversion to biofuels.



4.1.1. Pelletizing of Wood Residues

The pelletizing process is not necessarily only a physical process. There is usually the drying stage of biomass, which is a separate process that involves heat and mass transfer. However, almost no conversion of biomass occurs either by thermo-chemical or biochemical processes. In this article, the classification of a physical process is considered as being the occurrence of a significant change in biomass bulk density [20]. The bulk density of sawdust, for example, can be increased from 150 kg/m³ to 600 kg/m³ by pelletizing [18]. Advantages of this include improved handling, reduced transport costs and ability for stable storing. The pellets can be used as an environmentally friendly substitute to fossil fuels such as coal and petroleum products. End users also include the residential market and commercial power generation facilities, especially in central Europe.

Most pellets sold today are produced from sawmill by-products. They can also be produced from torrefied biomass, bark and residues streams such as tree tops and branches. A large part of the production cost of pellets is connected to the drying process. Anderson *et al.* [21] presented and

evaluated different energy efficient options for integrating drying and pelletizing with a modern energy efficient pulp mill process. The results of the study indicated that the most attractive integrated drying technology option is the flue gas dryer, using flue gases from the black liquor recovery boiler. Because modern recovery boilers typically operate with high efficiency using the flue gas to produce hot pressurized water, the modern biomass dryers can use low pressure steam or other sources of waste heat.

4.1.2. Torrefaction

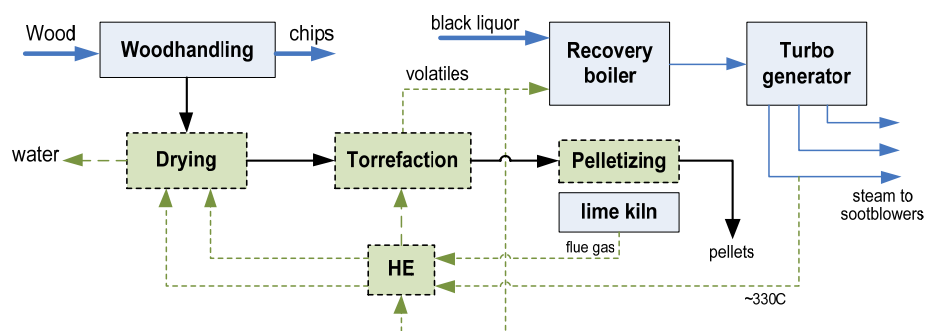
The objective of torrefaction is to create a solid biofuel with high energy density. The process occurs between 220 and 300 °C in the absence of oxygen, although some authors recommend not exceeding the limit of 280 °C to retain reasonable energy efficiency [22]. Under these conditions the moisture is removed and hemicellulose degraded, causing the release of acetic acid, fractions of phenol and other compounds of low heating value [23]. Lignin also suffers a slight polymerization. The resulting material is more brittle and has intermediate characteristics between coal and biomass.

The process causes a reduction in the energy content of the biomass because of partial devolatilization, but given the much higher reduction in mass, the energy density of the biomass increases. The average is a loss of 10% to 17% energy for 30% to 38% of original mass. A good review on biomass upgrading by torrefaction was recently published by van der Stelt *et al.* [24]. They emphasize that different reaction conditions (temperature, inert gas, reaction time) and wood type lead to different solid, liquid and gaseous products. As temperature and time increase, for example, the solid yield decreases and heating value (kJ/kg) increases. Another feature of torrefaction is that it reduces the hygroscopic property of biomass. As a consequence, torrefied product absorbs less moisture when stored. The fuel quality makes torrefied biomass very attractive for combustion and gasification applications in general [25,26]. Prins *et al.* [25] show that the thermodynamic losses are reduced if the biomass is torrefied prior to gasification.

There are different types of reactors that could be applied for the torrefaction process: rotary drum, screw conveyor, compact moving bed, microwave or belt conveyor. Although the heat integration for torrefaction can be designed in different ways, the developers typically apply the same basic concept in which the torrefaction gases are combusted in an afterburner [27]. The flue gas then provides, directly or indirectly, the heat necessary for the drying and torrefaction processes.

According to Table 3, one eucalyptus pulp mill producing 1.5M Adt/a of bleached pulp, for example, could generate approximately 390,000 t/a of dry wood waste that could be possibly torrefied. The biomass could be then converted to pellets for export. Determining the appropriate design for the heat integration in the mill is very important. Figure 4 suggests the direct heating of the biomass by using reheated volatiles gases. One disadvantage is that the concentration of organic acids and cyclic organic components will increase during the torrefaction process [27]. In addition, the energy content of the gases has to be sufficient to thermally balance the torrefaction process. Two options could be the use of flue gas from lime kiln or medium pressure steam. The optimized product and process can also depend on the customer requirements.

Figure 4. Optional process for integrated torrefaction in a pulp mill.



4.1.3. Pyrolysis

Pyrolysis is a thermal decomposition that takes place in the absence of oxygen, except in the case where partial combustion is allowed to provide thermal energy needed for this process. Large hydrocarbon molecules of biomass are broken down into smaller molecules. The pyrolysis can be broadly classified into slow and fast depending on the heating rate [28]. By also varying the residence time in the reaction zone and the final temperature, it is possible to change the relative yields of the solid, liquid and gaseous products of pyrolysis, Table 4.

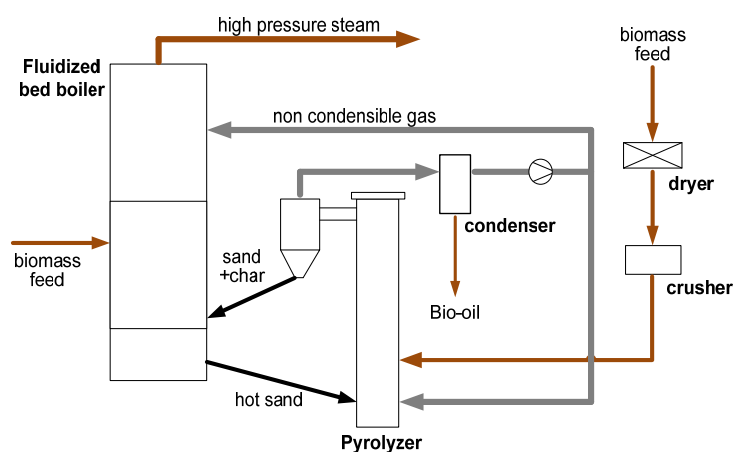
Table 4. Examples of variation in the product yield of pyrolysis [29].

Process	Temperature (°C)	Residence Time	Product Yield (wt %, solid, liquid, gas)
Slow pyrolysis	316	200 s	32–38, 28–32, 25–29
	510	30 s	22–28, 23–29, 40–48
Fast pyrolysis	343	5 s	29–34, 46–53, 11–15
	510	1 s	9–13, 64–71, 17–24
Mild pyrolysis (Torrefaction)	243	1800 s	85–91, 7–12, 2–5
Carbonation	357	days	mostly charcoal
Gasification	677	1800 s	7–11, 4–7, 82–89

The liquid fraction is known as bio-oil or pyrolysis oil. Maximizing its production is an attractive way of converting biomass into liquid, which can be done through fast pyrolysis, Table 4. The heating value of crude bio-oil is in the range of 16 and 19 MJ/kg [30] and the operation at atmospheric pressure can lead to bio-oil yields higher than 70 wt %. It is important to point out however that a reasonable fraction (15–30 wt %) of the crude bio-oil consists of water from both the original moisture and reaction product. In addition, the biomass composition has a great influence on the preferred feedstock, since each lignocellulosic component decomposes with different kinetics. Moreover, pyrolysis reactions are catalyzed by alkali metal salts present in the biomass, which can result in a decrease in the bio-oil yield. Currently there are several types of pyrolysis reactors that could be used: bubbling or circulating fluidized bed, fixing or moving bed, ultra-rapid, rotating cone or ablative. Each of these categories includes different proprietary technologies. According to Basu [28], in most cases it is necessary to burn the solid and gas fractions generated during the pyrolysis to provide the heat

required for the process. One example is the integrated combustion and pyrolysis process [31], where the unit utilizes the hot sand of the fluidized bed boiler as a heat source, Figure 5. The technology can be possibly implemented in existing pulp mills that already incinerate the wood residues in fluidized bed boilers.

Figure 5. Example of integrated combustion and pyrolysis.



Another example of commercial technology for fast pyrolysis is the Rapid Thermal Processing (RTP™) by Evergent [32]. It is a fast thermal process in which biomass is rapidly heated to approximately 500 °C in the absence of oxygen. A circulating transported fluidized bed reactor system is at the heart of the process. Contact with hot sand vaporizes the biomass, which is then rapidly quenched, typically yielding 55 wt % to 80 wt % of bio-oil depending on the process conditions and wood species, Table 5.

Table 5. Examples of bio-oil yields [33].

Species	Bio-oil yield %	Gross calorific value MJ/kg
Hardwood	70–75	17.2–19.1
Softwood	70–80	17.0–18.6
Hardwood bark	60–65	16.7–20.2
Softwood bark	55–65	16.7–19.8

The phase-separation and polymerization of the liquids, as well as the corrosion trends in containers make storage of these liquids challenging [34]. Aging, which leads to an increase in viscosity with time, can be reduced or controlled by the addition of alcohols such as ethanol or methanol [35]. The bio-oil can be used for electricity generation in stationary diesel engines, boilers or turbines [30]. One alternative for pulp mills is to consume the oil produced in the lime kilns to reduce the fossil fuel consumption. For this purpose, some improvements are still required. Due to the higher density and lower heating value of bio-oil compared to light fuel oil, the fuel feeding system should be re-designed. The adaptation of equipment material is also important to avoid high levels of erosion/corrosion, which

can be attributed to the bio-oil acidity and the presence of alkali and ash. Treatment includes filtration of bio-oil and upgrading through emulsification [36].

Another interesting and promising option is the upgrading of bio-oil to conventional transport fuel such as diesel, gasoline, kerosene, methane, jet fuels or LPG. This however requires full deoxygenation that can be accomplished, for example, by hydrotreating or integrated catalytic pyrolysis, followed by conventional refining. One implication of hydro-treatment is that the process requires high-pressure hydrogen, which is still not economically attractive. Regarding the integration of catalysis and pyrolysis, Bridgwater [35] suggests that sophisticated catalytic systems are needed, since the process requires operation at a single temperature and sufficiently robust catalyst to withstand the temperature and mechanical environment. The upgrading of bio-oil therefore has been constantly improved to become more competitive.

4.1.4. Biomass Gasification

The gasification involves conversion of carbonaceous materials, such as biomass, into useful gases and chemicals. It requires a medium for reaction and an operation temperature of 600 to 1300 °C. The resulting gas mixture is called syngas (synthetic gas). The gasification medium can be supercritical water or gaseous (air, steam, O₂) and has a great influence on the syngas composition and heating value. The advantage of gasification is that the burning of the syngas is more efficient than the direct combustion of the fuel. It also gives more flexibility to the process. It can be burned directly in gas engines or used to produce, for example, hydrogen or DME [37,38]. Via the Fisher-Tropsch process, the syngas can be converted into fuel such as diesel and gasoline. Based on the gas-solid contacting mode, gasifiers are classified into three principal types: fixed or moving bed; fluidized bed and entrained flow. Each is further subdivided into specific types.

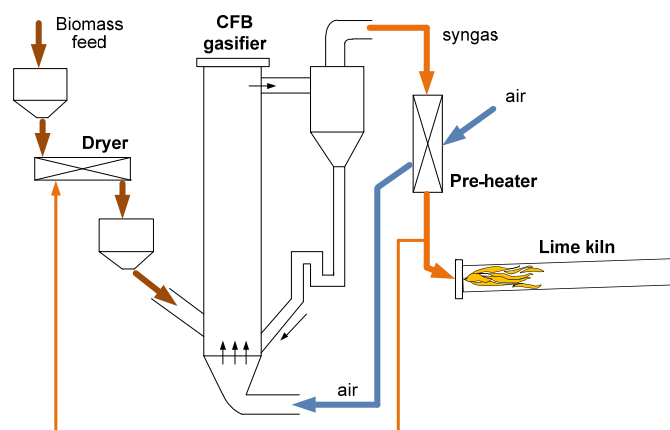
A gasification system consists of four main stages: feeding, gasifier reactor, gas cleaning, and utilization of combustible gas. These stages are in continuous development and differ according to their application. The cleaning is the most crucial challenge in the development of advanced gasification based processes. There are always high amounts of impurities in the syngas such as particulates, heavy metals, tars and nitrogen compounds. The tar is an unavoidable by-product that condenses in the low temperature zones of the pyrolysis or gasification reactors. Two consequences include plugging of equipment downstream and formation of tar aerosols [27]. The situation has improved but tar removal remains an important part of the development of biomass gasifiers.

There are three main types of commercially used biomass gasifiers [28]: fixed bed (especially for small scales); bubbling fluidized bed (BFB) and circulating fluidized bed (CFB). The latter is suitable for biomass gasification in scale over 60 MW [39]. Typically it comprises of a riser, a cyclone, and a solid recycle device. When entering the riser, which serves as a reactor, the biofuel particles start to dry in the hot gas flows at temperatures of 850–950 °C. The release of combustible gas occurs after the remaining particles, which contain fixed carbon, are slowly gasified. The syngas contains all the formed volatiles. The gas passes by the cyclone to separate the solid particles from syngas. These particles are continuously returned to the riser's bottom. The recycle rate of the solids and the fluidization velocity are high enough to maintain the riser in a special fluidization condition. Typically,

the syngas has heating values of about 5.0–6.0 MJ/Nm³ on dry basis using air as the oxidant. If oxygen is used as an oxidant, the syngas has heating values can reach 13.0–14.0 MJ/Nm³ on a dry basis [40].

Fixed bed and circulating fluidized bed gasifier technology has been applied in pulp and paper industry producing lime kiln fuel from biomass. Most practical experience exists from using circulating fluidized bed gasification [39]. In the eighties during the oil crises, circulating fluidized bed gasifiers were installed to produce fuel for lime kilns. The first commercial Foster Wheeler CFB gasifier (Former Ahlstrom Pyroflow CFB gasifiers) was supplied in 1983 to replace fuel oil in the lime kiln at Wisaforest mill in Finland, utilizing part of the generated gas for biomass drying [41]. Figure 6 shows an overview of the use of syngas in lime kilns.

Figure 6. Example of syngas as lime kiln fuel.



Since then, similar plants have been installed also in Sweden and Portugal. A biomass gasifier by Metso (former Götaverken) has been in function since 1987 in Södra Cell Värö pulp mill in Sweden [42]. In a more recent case, a Finnish pulp mill in Joutseno plans to replace 100% of the natural gas in the lime kiln by implementing a gasification unit supplied by Carbona/Andritz [43]. The wood residues are dried before gasification using waste heat available from mill. According to the project concept, the lime quality and burning efficiency will not be harmfully affected.

Two case studies involving biomass gasification integrated in the Billerud Karlsborg mill, Sweden, are analyzed by Wetterlund *et al.* [44]: BIGDME (Biomass Integrated Gasification Dimethyl Ether production) and BIGCC (Biomass Integrated Gasification Combined Cycle). They used some scenarios for 2030, with different prices of fossil fuels and different levels of CO₂ in the atmosphere. The annual cost of energy was then calculated for each concept and scenario. The results show that gasification of biomass for the production of electricity is more economically viable than the production of biofuels. It is important to point out that the conditions can differ from country to country due to differences in renewable energy policies or electricity market infrastructure. Currently there are, for example, large pulp mills being built in remote areas of Brazil. Selling substantial amount of electricity is sometimes not a good option since the connection to the local grid is limited. Guidelines could be then designed to stimulate the production and consumption of alternative biofuels.

4.1.5. Direct Liquefaction

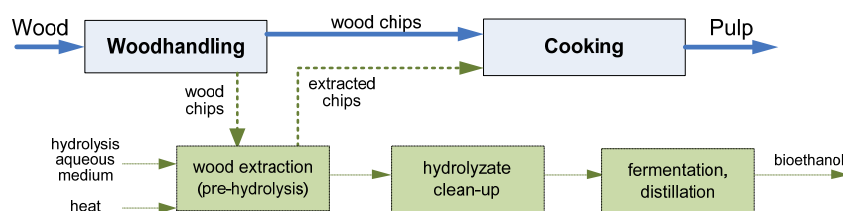
Applications of direct liquefaction of biomass are cited by Behrendt *et al.* [45]. One interesting example is the hydrothermal liquefaction (HTL), where water is an important reactant and catalyst, and thus the biomass can be directly converted without an energy consuming drying step [46]. In one application of this process, biomass is converted into an oily liquid by contacting water at elevated temperatures (300–350 °C) with high pressure (12–18 MPa) for a period between 5 and 20 min. The product yield (mass percentage of dry input material), is about 45% bio-oil, 25% gas (mostly CO₂), 20% water, and 10% dissolved organic materials [45]. The bio-oil yield and quality however depend on the biomass specie and on many process conditions such as final liquefaction temperature, residence time, rate of biomass heating, size of particles and type of solvent media [47]. Cheng *et al.* [48] for example showed that white pine sawdust can be effectively liquefied using co-solvent of 50 wt % aqueous alcohol (methanol or ethanol) at 300 °C for 15 min, which led to a bio-oil yield of 66 wt %.

In general the high heating values in these HTL oils are in the range of 30 and 37 MJ/kg [46]. The oil however still contains high percentage of oxygen, making it more polar than crude oil. This causes some disadvantages such as relatively high water content, corrosive properties or thermal instability. The quality of the oil can be improved by subsequent hydro-treatment, which will increase productions costs. Although the HTL process is still under development, it has attracted increasing interest in processing biomass streams containing high water content.

4.1.6. Bioethanol from Hemicellulose

The production of ethanol from corn or sugarcane is relatively straightforward. They concentrate natural sugars that are easily fermented. However, production of ethanol from lignocellulosic biomass presents considerable challenges. Cellulose and hemicellulose have long-chain molecules made up of linked glucose sugar. They need a treatment step called hydrolysis to break up the larger chain of sugars into mono sugars. Yeasts and bacteria can then process these to produce ethanol. In pulp mills, hemicellulose can be extracted prior to pulping via hydrolysis and used for producing bioethanol, Figure 7.

Figure 7. Overview of hemicellulose recovery and bioethanol production.



Different methods have been proposed for the aqueous phase extraction of hemicelluloses in combination with pulp production. In acidic pre-hydrolysis processes, hemicelluloses are hydrolyzed to oligomeric and monomeric sugars and dissolved in the hydrolyzate either in a dilute solution of a mineral acid, which acts as a catalyst of hydrolysis [49–51], or auto catalytically (auto-hydrolysis, AH or hydrothermal). In both processes, the hydrolysis is catalyzed by hydronium ions (H₃O⁺). In

auto-hydrolysis, the acidic conditions are created through the cleavage of acetyl groups from xylan backbone and consequent release of acetic acid in hot water at a temperature of 130–175 °C [50–56]. In alkaline conditions, hemicellulose extraction has been carried out with green liquor in a so-called near-neutral process [57], with strong alkaline solutions at low temperatures [12], or with white liquor [58].

Table 6 shows experimental results from different pre-hydrolysis conditions with subsequent pulping of hydrolyzed chips. It can be observed that the auto-hydrolysis (AH) has been frequently tested. This process was already studied in the 50's [59], but with more emphasis on the pulp quality improvement. Currently, the process is being considered as an alternative for pulp mills that pursue a more thorough valorization of lignocellulosic components. The use of hot water can be favorable for many reasons: the PHL contains a reasonable amount of hemicellulose dissolved; the core fraction (cellulose) can be only slightly degraded; expenses with extra chemicals can be reduced; the use of water as aqueous phase is less harmful to the environment. In spite of these advantages, impacts on the mill operation are expected and have to be investigated. These include impacts on the equipment utilization capacity [49,56] or the treatment of hydrolysis water to avoid the input of non-process elements such as potassium and chlorine.

Table 6. Impacts of different methods of pre-hydrolysis on the experimental cooking process.

Wood	Pre-hydrolysis conditions time, T, L:W, washing?	Extraction yield %	Pulping MaxT, sulfidity, EA ⁴ , L:W	Overall pulping yield without (with) extraction, %	Extracted matter analysis wt % or g/L
<i>E. globules</i> [51]	AH (hot water) 3 h, 150 °C, 4:1, yes	12.5	160 °C, 28%, 17.4%, 4:1	54.7 (45.1)	1–4 g/L, as ethanol conc.
	Acid (0.4 H ₂ SO ₄) ² 2 h, 140 °C, 4:1, yes	13.1	160 °C, 28%, 17.4%, 4:1	54.7 (39.7)	6.8–9.6 g/L, as ethanol conc.
<i>E. urograndis</i> [52]	AH (hot water) 0.5 h, 165 °C, 3.5:1, no	10.8	155 °C, 37%, 15.8%, 3.5:1	53.9 (41.9)	~40% of dry PHL as xylan
Birch [58]	AH (hot water) 1.5 h, 150 °C, 3:1, no	8.0	160 °C, 36%, 21%, 3.5:1	51.7 (43.2)	11.75 g/L as xylan
	Alkali (white liquor) 31 h, 160 °C, 3:1, no	9.0	160 °C, 36%, 18%, 3.5:1	51.7 (46.0)	3.62 g/L as xylan
North. hardw [57]	Alkali (green liquor) 1.8 h, 160 °C, 4:1, no	9.0	160 °C, 30%, 14%, 4:1	48.0 (46.0)	40%, as fermentable sugars
Aspen [12,50]	AH (hot water) 4.5 h, 150 °C, 4:1, no	19.0	160 °C, 25%, 21%, 4:1	53.3 (39.7)	46% as xylan
	Alkali (1.67 M NaOH) 4 h, 90 °C, 4:1, no	19.3	170 °C, 39.8%, 12%, 4:1	52.7 (53.3)	27.3% as xylan
Pine [49,56]	Acid (0.5 H ₂ SO ₄) ² 1 h, 150 °C, 5:1, yes	14.0	165 °C, 30%, 16%, 4:1	46.6 (36.5)	~70% carbohydrates (~50% hemicel.)
	AH (hot water) 1.7 h, 150 °C, 4:1, no	14.1	160 °C, 40%, 19.4%, 4:1	46.2 (40.0)	48% carbohydrates

¹ washing post hydrolysis, which may affect the cooking process due to PHL entrained in the pores; ² wt % on dry wood;

³ EA 3%; ⁴ as NaOH.

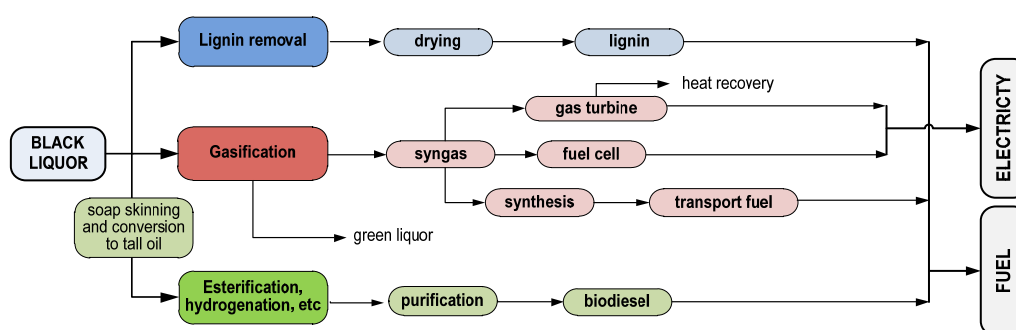
The auto-hydrolysis process has some drawbacks, which include high investment and energy costs of the water pre-hydrolysis step as well as the expensive waste disposal of the PHL caused by the formation of sticky precipitates [60]. The formation of these precipitates is attributed to condensation products created by fragments of lignin dissolved in the PHL. Their content is determined by the auto-hydrolysis duration. This change in the lignin reactivity during hydrolysis can make the processing of PHL very difficult, affecting also the efficiency of subsequent cooking operations [61]. Since the content of degradation products are determined by the auto-hydrolysis duration, the time becomes an important aspect for the feasibility study. Although the auto-hydrolysis can reduce the impacts on pulp quality, it requires a post-hydrolysis step to increase the concentration of fermentable sugars for ethanol production [51].

The temperature has also a great influence on the hydrolysis process. As an example, for the same extraction yield, the auto-hydrolysis time can be significantly reduced by increasing the water temperature. Drawing from Table 1, however, one can conclude that a preferable condition for hemicellulose extraction is still not clear. Although it shows that the overall pulping yield is less affected with alkaline pre-hydrolysis, the amount of recovered xylan can be significantly lower when compared to dilute acid or auto hydrolysis. In the case of dilute acid, the cellulose can be highly degraded depending on the hydrolysis conditions [49], which can lead to a poorer quality of pulp. It is important to bear in mind that since hemicelluloses are extracted prior to pulping, both the fiber line and chemical recovery can be affected. The specific effects therefore will strongly depend on the extraction process and the amount of wood extracted. The impact on the pulp yield will directly affect the specific consumption of wood and the black liquor yield.

4.2. Black Liquor-Based Technologies

The technologies presented in this section involve processing the black liquor to produce biofuels. They are divided into three processes: Lignin removal, gasification and processing of tall oil to produce biodiesel, Figure 8.

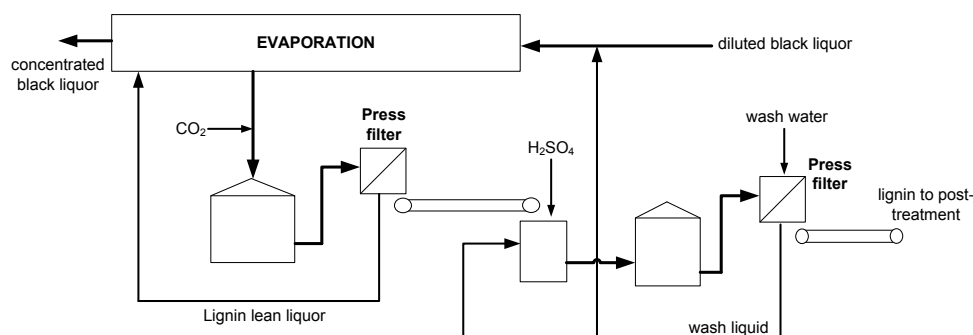
Figure 8. Technologies for biofuel production using black liquor as a source.



4.2.1. Lignin Removal

The idea of separating lignin from black liquor has been advocated since mid-1940s, when Tomlinson and Tomlinson [62] applied the liquor carbonation method using CO₂-containing gases. Since then, important contributions have been made towards improving the process [63–65]. The technology can be used not only to debottleneck overloaded recovery boilers but also to produce a solid biofuel with high energy density and low ash content. The most common separation process is the lignin precipitation from black liquor by acidification, which can be done by using mineral acid and CO₂. The method was improved jointly by STFI and Chalmers University of Technology [66], Figure 9. The black liquor from the evaporator is led into the acidification phase at a dry solids content of 30%–45%. In this phase, CO₂ is mixed into the liquor to reduce the pH, which results in the precipitation of lignin. The lignin is then dewatered using a press filter dissolved again with wash water. The pH is decreased during conditioning with sulfuric acid. The slurred lignin is filtered again and the filtrate is introduced back to the evaporation plant.

Figure 9. Overview of Lignoboost process.



The separated lignin can be used for producing biomaterials or chemicals. An immediate option is the combustion for heat and power generation. The burning of separated lignin in lime kilns was studied in the late 1980s [67] and is considered a viable option. It is important to point out however that the removal rates are limited by the impacts they cause on the mill operation. When lignin is removed, it will affect mostly the chemical recovery process and steam generation rate [39]. The reason is that about 60% of the black liquor heating value comes from the lignin. These impacts should be taken into consideration when being compared with the production of biofuels from the wood residues. Some variables are demonstrated in Table 7 for one eucalyptus pulp mill [16].

Table 7. Calculated values for different lignin removal rates in one eucalyptus pulp mill.

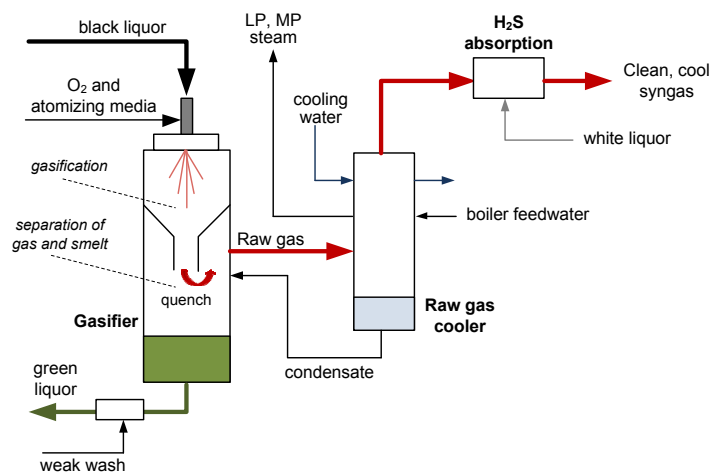
Variable	Percentage of Lignin Removal			
	0%	10%	20%	30%
Recovery boiler steam production, t/h	890	825	760	696
Heat load into recovery boiler, MW	948	889	831	772
Lignin/total dry solids in black liquor, wt %	36.3	33.9	31.3	28.5
Power generation, MW	192.9	174.9	156.4	137.5

4.2.2. Black Liquor Gasification (BLG)

The BLG is a specific application for kraft pulp mills. The residual liquor is gasified in a reactor under reducing conditions. There are two gasification processes that have been tried [68]: low temperature in the range from 600 °C to 850 °C, where the inorganic compounds are below their melting point, and high temperature 800 to 1200 °C which produces molten smelt. The generated gas is always separated from inorganic compounds (*i.e.*, ash). To recover heat the syngas and inorganic compounds are cooled and inorganics are dissolved in water (or weak white liquor) to form green liquor in an identical manner as in the dissolving tank of the traditional kraft pulp mill.

Different technologies for BLG are available, which include: Manufacturing and Technology Conversion International (MTCI) process, Direct Alkali Regeneration System (DARS) process, and the Chemrec process, each with its own distinctiveness. Others under development are the Supercritical Water Oxidation (SCWO) and BLG with direct causticization, which can be integrated without the need of the recausticizing unit. Figure 10 shows an example of Chemrec process [43]. The core units are the entrained flow reactor with the quench cooler, the counter current gas cooler, and heat exchangers for cooling the hot green liquor. Black liquor and oxygen is fed in the top of the reactor. The residence time in the reactor is about 5 seconds, with the temperature normally kept steadily slightly above 1000 °C. The H₂S in the cooled raw gas (1.4 vol %–2.5 vol %) is removed in the H₂S absorption unit.

Figure 10. Simplified diagram of Chemrec BLG.



Naqvi *et al.* [68] highlight the potential of the black liquor to generate fuel and energy and present a series of studies being developed in the area of BLG integrated in pulp and paper mills. One disadvantage of the recovery boiler is the great precautions that have to be taken to avoid explosions between water and smelt. This can be corrected with the implementation of the gasification system. Although recovery boiler processes can achieve as good efficiencies as gasification processes [69], the BLG allows the production of alternative fuels such as DME or methane [70]. In spite of these

benefits, there are still challenges in implementing the BLG. One is determining the appropriate choice of the best material for the refractory lining in the gasification reactor. There is a consensus that what we have today is not appropriate, in that the environment in the gasifier is very aggressive with high temperatures and alkalinity.

Another challenge is that in the conventional process, all of the sulfur is recovered in the process, however, in the BLG integrated in pulp and paper mills, only a portion of the sulfur is converted to Na_2S and the majority of the synthetic gas exits as H_2S and COS . This leaves excess sodium which leads to additional Na_2CO_3 to recausticizing. Therefore, alternatives are needed to recovery the sulfur in the form of H_2S or to avoid excessive overloading recausticizing in lime kiln. The direct causticizing is one option to be considered, although more research on the pulping step should be performed. Nohlgreen and Sinquefield [71] present the main reactions in the gasifier using titanium dioxide. In one of these steps, when the sodium oxide titane is leached in water, NaOH is directly formed.

4.2.3. Biodiesel from Tall-Oil

Crude tall oil (CTO) is the acidified product of soap and an important by-product in the kraft pulping of coniferous wood such as pine (“tall” in Swedish). These species have a reasonable amount of extractives. As a consequence, in alkaline conditions, sodium salts of fatty and resin acids are formed by saponification and become partly soluble in the black liquor [72]. The soap can be separated from black liquor due to density differences and the optimum dry solids content for the soap skimming is between 28% and 32%. The acidulation process is subsequently required to convert the soap into CTO. The yield per ton of pulp depends on the wood species, part of wood trunk, season, soil quality or storage period. For Scots pine, for example, it falls in a range of 20–100 kg/CTO/Adt. Typically, the CTO is depitched and then upgraded to produce more valuable products such as tall oil fatty acids and oil rosin [73]. Again, it is important to emphasize the relevance of wood species, since the content of fatty acids, Table 8, plays an important role in the production of biodiesel.

Table 8. Examples of distribution of tall oil extractives, wt % [74].

Component	N. American softwood	N. American hardwood	Scandinavian pine	Scandinavian spruce
Rosin acids	42	-	30–35	20–30
Fatty acids	47	76	50–55	35–55
Neutrals	11	24	5–10	18–25

Separation of soap from black liquor is important to avoid disturbances in the evaporators and in the fibre quality. The resulting tall oil can be used as auxiliary fuel or sold to outside companies to produce for example detergents, lubricants or varnishes. Production of biodiesel [75,76] is also an interesting tentative of adding more value to the CTO. The UPM group will start producing annually, in southeastern Finland, approximately 100,000 tons of biodiesel for transport using crude tall oil [77]. The industrial scale investment is the first of its kind globally.

In typical industrial applications, the vegetal triglyceride oils are converted to their lower viscosity methyl esters via acid or base transesterification to produce biodiesel. With tall oil, some strategic processes include acid-catalyzed esterification, enzymatic processes, hydrogenation and the use of

supercritical methanol [73]. The latter two seem to be a good choice. White *et al.* [78] investigated the reaction of methanol with tall oil at high temperature and supercritical pressures to produce fatty acid methyl esters (FAME). The process seems promising especially because the reaction proceeds without the need for additional catalysts. In addition, it has advantages when compared to catalytic or enzymatic processes in terms of reaction time and yield. The biodiesel produced by hydrogenation has a high cetane number (CN) close to 60. The process is demonstrated by Canada [73] and involves simultaneous catalytic hydrogenation and cracking of the depitched tall oil. Because the CN is related to the ignition delay time of a fuel upon injection into the combustion chamber, the resulting biodiesel can be used as cetane enhancer in petrodiesel blends.

5. Conclusions

This review shows that there is a potential for kraft pulp mills to produce alternative biofuels in addition to the traditional market pulp, with some technologies such as gasification, lignin removal or biodiesel from tall oil already operating or being implemented. The attractiveness of these processes depends on many factors such as wood species processed, energy policies, economic (prices of pulp, wood, biofuels or electricity), scale of production, process maturity, end-use requirements and effects that the integration would cause on existing mills. The case of ethanol from hemicellulose can be more critical due to the possible impacts on the pulp quality. In this sense, the use of wood residues and tall oil is more favorable. Regarding biodiesel, especially mills processing softwood have the potential to use the tall oil. Some options are still being improved to become more competitive. Examples include Fischer-Tropsch process, catalytic synthesis to produce hydrogen, upgrading of bio-oil or black liquor gasification. Others technologies, such as pelletizing, are well established but would have less value added when compared to liquid transportation fuels from biomass.

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Publication V

Hamaguchi, M., Saari, J., and Vakkilainen, E.

**Bio-oil and Biochar as Additional Revenue Streams in South American
Kraft Pulp Mills**

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Bioresources

Vol. 9, pp. 3399–3413, 2013

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Bio-oil and Biochar as Additional Revenue Streams in South American Kraft Pulp Mills

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Pulp and paper companies are seeking opportunities beyond the traditional production of market pulp. One interesting alternative is to expand their revenue streams by adding value to the wood residues that they generate. Considering that excess heat and electricity can be used for biomass pre-treatment and conversion, the aim of this work is to show how the integrated production of bio-oil or biochar would affect the operation of a 1.5M t/a kraft pulp mill in South America. Detailed balances with a focus on modern eucalyptus mills are then developed for this purpose. Since the attractiveness of increasing renewable energy is often influenced by energy policies or local market development for the new products, the target was not to determine the best investment decision. Nevertheless, an economic analysis was performed to observe the main variables affecting the viability of these technologies. The results showed that satisfactory internal rates of return can be achieved for multiple technologies depending on the price of electricity, torrefied pellets, or bio-oil.

Keywords: Biochar; Fast pyrolysis; Pulp mill; Torrefaction; Wood residues

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INTRODUCTION

Brazil and Uruguay together produced approximately 13.3 million tons of bleached eucalyptus pulp in 2010 (92% in Brazil) (FAO 2010). This represents an increase of 52.6% in comparison with 2005, mostly attributed to the start-up of several large standalone mills during this period. Given the potential productivity of eucalyptus in South America, single line pulp mills designed to produce up to 1.75 million tons per year of pulp are currently under study or being implemented (Pöyry 2011; Labigalini 2011). These mills can produce a considerable amount of excess heat, enabling them to generate and export surplus electricity. This, however, might not be the most profitable option. Firstly, the price per kWh in the local electricity market may not be attractive, especially without renewable incentives. Secondly, if condensing electricity is produced, then a considerable fraction of steam enthalpy is not converted into work, but is lost in the condenser. Thirdly, many mills are being built in remote areas and would require additional investment in electricity transmission infra-structure.

In this scenario, the integrated production of alternative fuels for export might make economic sense, especially when wood residues can be used as raw materials. The attractiveness, however, will depend on critical factors such as the possibility to invest, the required internal rate of return, the maturity of the process, and, especially, the renewables market development for the new products.

Wood-based oil has been assessed as a promising biofuel alternative over the past few years. The result is a considerable growth of activities, either with innovation in the types of reactor (Bridgwater 2012) or in attempts to find optimum process conditions. For achieving high liquid yields, pyrolysis reactors require temperatures of 450 to 500 °C, residence times of 0.5 to 2 s, and high heating rates (~1000 °C/s) (Demirbas 2009). These conditions, combined with the chemical composition, moisture, and particle size of biomass, are key factors to be considered when studying the quality and potential of bio-oil production. Alternatively, fuel can be exported in the form of torrefied pellets (Pirraglia *et al.* 2012) or pyrolysis char, both classified here as biochar.

Torrefaction occurs between 220 and 300 °C, with typical reaction times ranging from 0.5 to 2 h. The optimal parameters depend on the feedstock composition, but torrefaction is characterized by low particle heating rates (<50 °C/min) (Bergman *et al.* 2005). Under these conditions, the moisture is removed and hemicellulose is decomposed, causing the release of volatile compounds (Prins *et al.* 2006). The resulting material becomes brittle and hydrophobic, with intermediate characteristics between coal and untreated biomass.

Increasing generation of electricity from kraft pulp mills has been reported (Raukola *et al.* 2002; Vakkilainen 2005; Kankkonen *et al.* 2010). Techno-economical analysis of transport biofuel production in pulp mills has been presented by Frederick (2009). Integration of processes has been analysed by *e.g.* Sadhukhan *et al.* (2009) and Ng and Sadhukhan (2011). In the present work, the fast pyrolysis and torrefaction are considered alternative pathways for kraft pulp mills to convert the wood residues into sellable products. This choice will be compared to more traditional ways of increasing electricity generation.

Availability of Wood Residues

The amount of bark entering the Brazilian pulp mills for incineration depends essentially on the electricity demand (Pöyry 2011). This includes, for example, the existence or not of a sodium chlorate unit, integrated paper machine, or supply agreement with nearby communities. For standalone pulp production, modern recovery boilers are able to generate much more steam than what is required in the process. As a result, there is no actual need for wood residues as additional fuel. However, the biomass boiler can bring some other advantages such as elimination of residues and production of steam for equipment start-up.

Maximizing the debarking efficiency can lead to a better quality of pulp, but also to higher operational costs and wood losses (Foelkel 2007). It is then usual to define an allowable content of bark that can enter the digester, typically less than 1 wt% of dry chips. The debarking process, either at the forest or mill, leaves the logs susceptible to losses of 3 to 5 wt.% (dry), depending on the debarking methods applied (*e.g.* rotary drums, harvesters, or manual). When forest-debarked, some residual bark still enters the mill, which in case of eucalyptus, may be shed in long strings and unbroken strips during the conveying of logs. Afterwards, a reasonable amount of fines are generated during the chipping and screening stages, estimated as 1 to 2% of dry incoming wood (Foelkel 2010). It is important to point out that the wood consumption per ton of pulp varies between pulp mills. This is mostly attributed to the cooking yield required for each wood species (Hamaguchi *et al.* 2012), which also results in a varying amount of wood residues generated.

Bio-oil from Forest Residues

Forest residues contain higher amounts of extractives and alkali metal salts when compared to bark-free wood (Werkelin *et al.* 2005). Since mineral salts are known to catalyze thermal decomposition reactions, their presence can result in i) accelerated conversion rates, ii) lower temperatures at which pyrolytic decomposition proceeds, iii) decreases in the bio-oil molecular weight, and iv) significant impacts on the product yields.

The organic liquid yield in fast pyrolysis can be up to 65 wt.% for sawdust, 46 to 55 wt.% for forest residues, and less than 40 wt.% for straw and hay (Oasmaa *et al.* 2010). Eucalyptus bark contains 2 to 10 wt.% (dry basis) of mineral ash (Foelkel 2010), depending on the varying composition of inner and outer parts. The crude bio-oils from the residues can also exhibit a separated top layer, originating mainly from extractive derivatives (Manuel *et al.* 2006). However, this might be reduced by adding few percentage points of alcohol (Oasmaa *et al.* 2004) such as methanol.

METHODS

In the kraft pulping process, white liquor is consumed during the cooking of wood chips. The result is the production of wood pulp containing dissolved organic and soluble inorganic materials. After a washing stage, the pulp is sent to be screened, and the separated liquid, known as black liquor, is sent to the evaporators. The concentrated black liquor is then burned in the recovery boiler for the regeneration of pulping chemicals, and in turn, for the production of steam. The high-pressure steam generated is sent to the turbo generators to produce electricity and heat.

The reference mill in study is designed to produce 1.5 M Adt/a of bleached eucalyptus pulp in Brazil, operating at 8400 h/a. The amount of residues generated is based on an average pulping yield of 52.5%, as shown in Table 1. Following the forest debarking trends in South America, one third of logs are delivered with 10 wt.% of bark, with the remaining logs (forest-debarked) carrying 2 wt.% of residual bark. The calculations were performed using the Millflow spreadsheet, which is useful for designing pulp mills by equipment vendors and for evaluating new processes alternatives (Hamaguchi *et al.* 2011). Different steam levels serve the mill: LP (160 °C, 5.4 bar), MP (200 °C, 12 bar), and MP2 (330 °C, 30 bar), with pressure units indicated as absolute values. The recovery boiler produces steam at 486 °C and 86 bar. Examples of operational data for steam and electricity generation in South American mills can be found elsewhere (Germiniani 2011; Fernandez 2011).

The total generated residues are indicated in Table 1 and represent approximately 125 MW_{th} of biomass input. The target is to evaluate four integration cases, described in this section as: **BB**) Incineration of the wood residues in a biomass boiler with generation of additional steam and electricity; **T**) Torrefaction of wood residues with biochar for sale; **FP**) Fast pyrolysis of wood residues with bio-oil and biochar for sale; and **FP2**) Fast pyrolysis of bark-free biomass and incineration of wood residues with bio-oil for sale. A comparative analysis involving the three first cases can be performed for the reference mill. The FP2 scenario is specifically applicable to existing mills already operating with a biomass boiler and is, therefore, treated as an isolated case.

Table 1. Generation of Wood Residues and Energy Balance for Reference Mill

Residues, dry	Unit	Values	Observations
Bark	t/d (MW _{th})	368.0 (67.2)	Debarking loss of 3wt% for 1/3 of logs. For forest-debarked logs, 0.5wt% loss
Fines	t/d (MW _{th})	120.0 (24.1)	1.5wt% of loss as fines
Other losses ^a	t/d (MW _{th})	182.0 (33.3)	bark in chips: 0.6 wt%
Energy Balance			T_{ref} : 25°C
Recovery boiler steam	t/h (MW _{th})	890.0 (693.0)	Black liquor: 927MW _{th} (14.1MJ/kg)
Power consumption	MWe	106.3	NaClO ₃ unit disregarded
Power generation	MWe	150.8	Steam to TGs: 483°C, 84 bar
Exportable power	MWe	44.5	Without biomass boiler

^a Higher wood losses when rotary drums are used for logs debarking

Biomass Boiler: BB

The incineration of wood residues in this study is considered as an alternative. The steam flow is calculated based on a eucalyptus wood dry composition of 49% carbon, 5.3% hydrogen, 0.3% nitrogen, and 0.05% sulphur, with an ash content of 5% for bark and 1% for fines. The oxygen content is calculated by difference. The moisture content is 45%, with a lower heating value (LHV, dry) of 17.4 MJ/kg for fines and 15.8 MJ/kg for bark and other losses. The average temperature of the combustion air, with 25% excess ratio, is 150 °C. The boiler thermal efficiency can be calculated by an indirect method (EN12952-15 2003), with boiler feed water entering at 130 °C and flue gas exiting at 190 °C. The steam is generated at 486 °C and 86 bar.

Biomass Pre-treatment

Feedstock preparation is crucial to minimize feeding instabilities and to improve the efficiency of torrefaction or pyrolysis processes. Firstly, a dedicated area for cleaning is required to remove the undesirable particles such as sand, dust, or metals. Afterwards, a drying step is needed to reduce the biomass moisture content, which is not necessary in the case of direct combustion in a biomass boiler. It is assumed that low-pressure steam is utilized for drying and that the condensate is fully returned for boiler feed water treatment. Although modern dryers allow the use of hot water at 65 to 90 °C as a heat source, this option is not considered in the present work. The energy requirement of biomass dryers, H_{DSt} , is obtained from,

$$H_{DSt} = \frac{1}{\eta_{dryer}} \dot{m}_{ut} \left\{ (MC_{ut} - MC_d)(h_{wL,in} - h_{wV,out}) + [(1 - MC_{ut})c_{p,dry} + MC_d c_{p,wL}](T_{out} - T_{in}) \right\} \quad (1)$$

where h is enthalpy [kJ/kg], c_p the specific heat [kJ/kgK], and MC is the moisture content [kg_{H2O}/kg_{total}]. The subscripts ut and d refer to untreated and dried biomass and wL and wV to liquid and vapour-phase water, respectively. A $c_{p,dry}$ value of 1.6 kJ/kg is assumed for the biomass, with water enthalpies estimated according to temperature. The moisture content is reduced from 45% (MC_{ut}) to 10% (MC_d) and a dryer efficiency (η_{dryer}) of 60%

is considered. The exhaust moist air exits at 70 °C, resulting in a dryer heat requirement of approximately 1.2 kWh/kg of evaporated water (Salo 2011).

After drying, the biomass has to be ground. This will enable the fast heat up of the particles to the optimum temperature, providing as short as possible exposure at lower temperature. For fast pyrolysis, reports show that suitable particle sizes range from 0.5 to 2 mm (Oasmaa *et al.* 2010; Manuel *et al.* 2008; Kumar *et al.* 2010). In the case of torrefaction, different sizes have been tested, ranging from less than 1 mm (Prins *et al.* 2006) to more than 50 mm (Almeida *et al.* 2010). The electricity required for biomass crushing/chipping depends on the final particle size (Wright *et al.* 2010).

Fast Pyrolysis

Several types of reactors have been developed for fast pyrolysis tests (Hulet *et al.* 2005; Brown 2005). Currently, one of the most favored options is to utilize hot sand as a heat carrier, since high heating rates can be achieved. The fluidized bed pyrolyzer types have, therefore, good technological strength and market attractiveness for large-scale units. They can be classified into bubbling fluidized bed (BFB), with the bed material remaining suspended in one reactor, or circulating fluidized bed (CFB). The latter, sometimes referred to as transport bed, often has a separate combustion reactor used to re-heat the sand, which is continuously recirculated. Gas exiting from the pyrolysis reactor contains entrained particles that are separated through cyclones. Examples of companies that commercialize fluidized bed technology are Envergent, Metso, and Dynamotive.

After the cleaned gases exit the cyclone unit, they must be cooled for the formation of bio-oil and separation of non-condensable pyrolysis gases to prevent further detrimental reactions from taking place. The non-condensable gases can be used as fluidizing agents, although other gases such as N₂ can also be applied for this purpose. In a typical continuous process, the oil can be cooled, recirculated, and sprayed to quench the gases through direct contact heat transfer.

It is important to point out that there will always be a challenge of using the sub-products in an optimum manner (Oasmaa *et al.* 2010), suggesting that modifications to the char/gas handling can be very common. Taking into account that steam is required for biomass drying, and that residues are to be pyrolyzed, the following configurations are presented, as seen in Fig. 1.

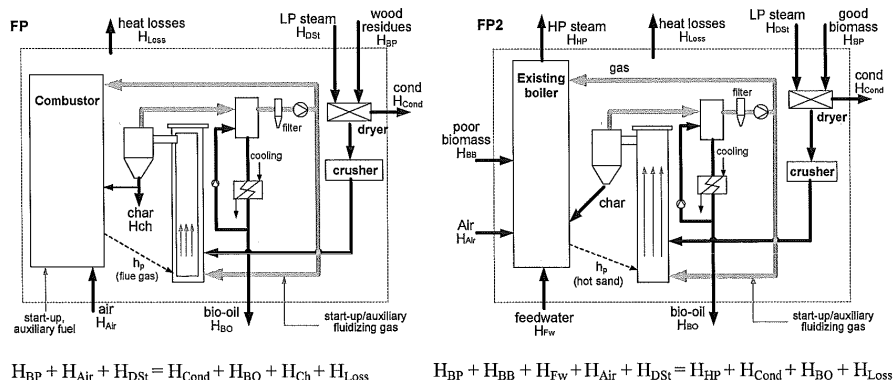


Fig. 1. Overall balances of integrated combustion and pyrolysis

FP: Co-production of biochar

Fractions of pyrolysis by-products are burned to produce hot flue gases, which are subsequently used to indirectly heat the bed material through, for example, a reactor jacket (Hulet *et al.* 2005). The hot sand acts as a heat carrier for the pyrolysis reactions. Since forest residues are used as feedstock, the quality and yield of bio-oil are expected to be lower when compared to bark-free wood. In this configuration with the BFB concept, the biochar is not fully mixed with the recirculating sand and can be alternatively recovered (Dynamotive 2013). As a result, biochar becomes a sellable high heating value by-product.

FP2: Co-production of steam

This scenario is suitable for existing mills already operating with fluidized bed boilers. Therefore, a separate combustor for the pyrolysis by-products would not be necessary. The idea is to maintain the same heat load that would be achieved with a standalone biomass boiler (BB case). With the integration of a CFB pyrolysis unit, the biochar, wood residues, and part of the pyrolysis gases are burned to generate high-pressure steam and also to provide the heat for pyrolysis through sand recirculation. This concept has been developed by VTT in Finland (Oasmaa *et al.* 2010). The bio-oil production would be limited to the boiler heat load and solids recirculation capacities.

Key assumptions

Discrepancies between yields of pyrolysis products are usually observed in the literature. This can be attributed to the differences in biomass composition, process conditions, apparatus reliability, and measurement errors. The average values however, including commercial scale units, are in the range of 60 to 70% of crude bio-oil (Badger *et al.* 2012; Envergent 2012; Dynamotive 2013; Oasmaa *et al.* 2010; Kumar *et al.* 2010), with lower yields expected for forest residues.

The heat for pyrolysis (h_p), for example, is dependent on the biomass species, reactor temperature, and consequently, on the changes in the pyrolysis reaction chemistry. Since large scale units processing eucalyptus are not presently in operation, exact h_p values are difficult to access. Therefore, the feasibility study relies on reported values for different biomass species (Daugaard and Brown 2003; Oasmaa *et al.* 2010). The assumptions for the balance are summarized in Table 2.

Table 2. Assumptions for Pyrolysis Balance

Stage	Assumptions	Ref
Pyrolysis and char removal	Yields: 70/60% bio-oil, 12/18% gas and 18/22% char; h_p for bark-free-wood/residues: 1.6/1.5MJ/kg; Efficiency of indirect heat exchange in FP1: 90%; Char removal efficiency of 95%	(Envergent 2012, Daugaard and Brown 2003, Dynamotive 2013)
Combustion	Biochar heating value: 26MJ/kg for FP and 30.6MJ/kg for FP2. These values are based on the balance between biomass input and products output; 70% of gas is burned; Flue gas to stack at 190°C.	(Demirbas 2004, Wright <i>et al.</i> 2010)
Oil recovery	Quench, collection of aerosols (gas): 95%; Bio-oil heating value for bark-free-wood/residues: 15.6/14.9 MJ/kg;	(Oasmaa <i>et al.</i> 2010, Wright <i>et al.</i> 2010)

In the FP2 case, the pyrolyzer-to-boiler feed ratio should be balanced to avoid possible instabilities in the continuous recirculation of sand. Although different ratios can be expected for each application, experimental values between 0.55 and 0.65 (MW%) have been reported (Oasmaa *et al.* 2010). Taking this issue into account, the present work assumes that the poor biomass (bark and debris) available is incinerated and that approximately 280 t(dry)/d of bark-free biomass enter the pyrolyzer. This represents 2% of additional logs to complement the fines fraction, with a proportional increase in wood losses. On the other hand, improvement in the bio-oil quality is expected.

Torrefaction: T

The severity of the torrefaction process depends on the biomass type, residence time, and temperature. The effect of temperature is significant, with mass and energy losses increasing fast above 250 °C (Bergman *et al.* 2005). Severe torrefaction would result in higher mass losses and increased brittleness of the product, which could bring problems for integrity of the produced pellets. Hence, a relatively mild torrefaction temperature of 250 °C was assumed in this study. At this temperature, most experiments have resulted in 90 to 95% of the energy and 80 to 90% of the mass of the untreated dry biomass retained in the product (Prins *et al.* 2006; Almeida *et al.* 2010; Arias *et al.* 2008; Chew and Doshi 2011; Zanzi *et al.* 2004; Oliveira and Rousset 2009). The higher loss of mass than energy leads to slightly increased LHV.

One important issue is to determine the appropriate design for the heat integration. For this purpose, different configurations can be suggested, either by indirect or direct heating (Bergman *et al.* 2005). In this work, steam at pressure level used for boiler sootblowers (MP2) is assumed to provide indirect heat to the torrefaction reactor. The integration also allows the released non-condensable volatiles to be incinerated in the recovery boiler, as seen in Fig. 2.

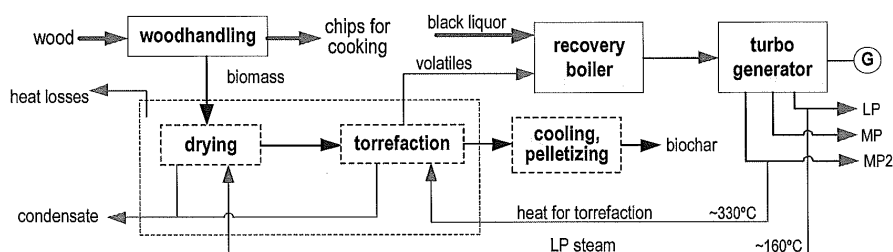


Fig. 2. Overall balance of integrated torrefaction

The torrefaction model was developed using IPSEpro, which is an equation-oriented stationary-state software developed by SimTech for power plant simulation. IPSEpro is a flexible tool for simulation, modeling, analysis, and design of components and processes in energy and process engineering (SimTech 2012). SimTech Simulation Technology is an Austrian firm providing the IPSEpro tool for a wide range of power and process industries. IPSEpro is used for this research to create the required models where needed. In addition to a library of common components used in thermal power plants, IPSEpro provides a Model Development Kit (MDK) by which the designer can build new models or modify the existing models according to the project's requirements. The steam

and power balance of the reference mill was reproduced with the objective of evaluating the possible changes after integration. The model is based on the assumptions of negligible energy needed in devolatilization reactions and negligible loss of heating value through partial combustion of the biomass. The energy requirement of torrefaction, H_{Torr} , is therefore obtained from:

$$H_{\text{Torr}} = \frac{1}{\eta_{\text{torr}}} \dot{m}_{\text{d}} \{ MC_{\text{d}} (h_{\text{wL,in}} - h_{\text{wV,out}}) + (1 - MC_{\text{d}}) c_{\text{p,dry}} (T_{\text{out}} - T_{\text{in}}) \} \quad (2)$$

An efficiency of $\eta_{\text{torr}} = 0.9$ was assumed, with the gas exiting at 250 °C from the reactor. The module was adjusted to produce a solid product, with mass and energy contents obtained experimentally from the torrefaction tests of *E. grandis* (Almeida *et al.* 2010) for both wood and bark. The solid mass flow rates and LHV values are given on a dry ash-free basis (daf). Therefore, with the net loss of heating value negligible, the LHV of gas phase becomes:

$$LHV_{\text{g}} = \frac{(\dot{m}_{\text{ut}} LHV_{\text{ut}} - \dot{m}_{\text{torr}} LHV_{\text{torr}})_{\text{daf}}}{\dot{m}_{\text{g}}} \quad (3)$$

Economic Analysis

Investment and operational costs for fast pyrolysis or torrefaction are not easy to access. One reason is attributed to the lack of references for large-scale units. Predicting future renewable energy prices is also subject to considerable uncertainty, since the market for the products is still developing and may vary between countries. The results of the economic analysis are presented in the form of series of curves at different investment costs, showing internal rate return (IRR) as a function of energy price. Fixed payback period of 10 years, NPV zero at the end of payback time and annual operating time of 8400 h/a, same as for the reference mill, are considered for all cases. When economical parameters were not treated as variables, the values presented in Table 3 were used. The analysis was based on solving for the interest rate by finding such present value factor a that yields a NPV (net present value) of zero with the chosen interest rate.

$$NPV = a(C_{\text{e}} + C_{\text{product}} - C_{\text{O\&M}} \pm C_{\text{wood}}) - C_{\text{inv}} \quad (4)$$

The variable $C_{\text{e}} = \Delta P_{\text{e}} \cdot t \cdot c_{\text{e}}$ represents the difference in annual value obtained from exported electricity in comparison with the reference mill. In the specific case of FP2, the C_{e} value is compared to the BB scenario. C_{product} is the annual value of produced fuels for sale, $C_{\text{O\&M}}$ the annual operating and maintenance cost, and C_{inv} the total investment cost ($C_{\text{O\&M}} / C_{\text{inv}}$ of 5% is considered). The parameter C_{wood} refers to the cost for disposing the residues or for the additional wood brought from the forest.

In the reference mill, a minimum amount of residues is generated and have to be preferably disposed if not processed. With the integration of BB, T, or FP cases, the cost with disposal would be saved. For FP2, there is an extra expense with additional wood, as seen in Table 3. The investment cost analysis is not presented in detail, as this was done previously by Bagramov (2010) and Starck (2011). The values were derived from a confidential joint project involving the equipment vendors and one of the largest forest product companies.

Table 3. Basis for the Economic Analysis

		BB	T	FP	FP2	Based on
Investment cost C_{inv}	M US\$	50±15	40±15	85±20	45±15	(Bagramov 2010, Starck 2011, vendor quotes)
Construction	M US\$	8.0	4.5	11.0	4.4	
Equipment	M US\$	31.6	28.8	55.1	33.8	
Piping, electrification and automation	M US\$	4.1	3.1	6.5	3.6	
Engineering and project management	M US\$	6.3	3.6	7.4	3.2	
Residues disposal	US\$/BDt	30	30	30	0	(Foelkel 2007)
Electricity price, c_e	US\$/MWh	35-80	30/60	50	30/60	(FGV 2011)
Additional wood	US\$/MWh	0	0	0	10	(Foelkel 2010)
Biochar price	US\$/MWh	0	10-30	15/30	0	-
Bio-oil price	US\$/MWh	0	0	20-60	45-85	-

The torrefaction and pyrolysis equipment prices as well as other major parts such as pyrolysis oil tanks and product silos are based on vendor quotes for piping, building, electricity, engineering, and project management costs with similar actual project data. The investment costs were compared to literature values (Felix 2005; Bergman 2005; Jones and Zhu 2009). Since actual project reference costs are still unknown, one should realize that the presented investment costs are to be considered as best estimates. The investment cost for the BB case includes the boiler facility and the increased costs with turbo generators and steam piping. However, the biomass pre-treatment can be disregarded.

For the FP2 case, the combustor is not needed, although additional wood and minor modifications in the existing boiler structure are required. A power consumption of 210 kWh per ton of dry input biomass and 300 kWh per ton of pellets were considered for pyrolysis and torrefaction, respectively. To evaluate the influence of the selling electricity prices on the PBP, two scenarios are considered for T and FP2, as indicated in Table 3. In the FP case, 50 USD/MWh is assumed for two different market prices for biochar. The revenue from pulp sales has no effects on the IRR calculation.

RESULTS AND DISCUSSION

A great advantage of processing the wood residues for additional income comes from the fact that the pulping process, sales, and pulp quality are not affected. The integrated technologies will require heat and electricity. For BB and FP2 cases, additional steam is generated. These differences result in varying amounts of exportable electricity that will affect the economic calculations.

The attractiveness of the processes in study will strongly depend on how the selling price of the new products sets itself in the market. Therefore, the purpose of the economic analysis is not to define the option with the highest revenue, but rather to show the main variables affecting the viability of each option. Table 4 summarizes the main results from the integrated mill balances.

Table 4. Results of Integrated Mill Calculations

		BB	T	FP	FP2
Main inputs					
LP steam (dryer)	MW _{th}	3.7	24.1	24.1	10.1
MP2 steam (torrefaction)	MW _{th}	-	4.9	-	-
Heat load to boiler/combustor	MW _{th}	124.7	-	13.2 ^a	120.3 ^a
Pyrolysis/torrefaction feed	MW _{th}	-	124.7	124.7	56.4
Main outputs					
Steam generation	MW _{th}	102.4	-	-	95.9
Volatiles	MW _{th}	-	4.1 ^b	-	-
Bio-oil	MW _{th}	-	-	69.3	35.4
Biochar for export	MW _{th}	-	121.1	37.7	-
Power balance					
Diff in power generation ^c	MW _e	+34.2	-4.3	-4.0	-4.1
Net power diff, ΔP_e ^c	MW _e	+32.2	-10.3	-9.0	-7.1
Sellable power	MW _e	76.7	34.2	35.5	69.6

^a It includes the partial incineration of pyrolysis sub-products.

^b Torrefaction gases as additional heat load to recovery boiler.

^c In comparison with reference case for BB, T or FP, and with BB case for FP2.

The decrease in power generation is mainly attributed to the heat requirements for biomass drying, torrefaction, or pyrolysis processes. As expected, the ΔP_e values are negative for T and FP, and positive for the BB case. If incentives are offered for selling bioelectricity, the surplus amount can be increased almost 72% by installing a biomass boiler. When the residues are fully torrefied or pyrolyzed, the surplus amount of electricity is decreased by 23 or 20%, respectively. Nevertheless, approximately 35 MW_e can still be sold to the grid.

Heat is inevitably lost during several stages. In drying, steam is required to heat the ambient air and the wet biomass and also to vaporize the water. The condensate is fully returned to the boiler water treatment area, but the moist exhaust air is counted as a loss. In combustion, the losses are mostly attributed to hot flue gas, radiation/convection, and carbon in ash. In pyrolysis, heat will be lost during the bio-oil recovery (cooling) or radiation in the reactor and cyclones.

Figure 3 shows satisfactory prospects for new investments, reminding that FP2 is not comparable to any other but to the BB case. It can be observed that with a torrefied pellet price of over 17 USD/MWh, an IRR of higher than 10% can be achieved for the estimated range of investment costs. The figure also shows that torrefaction becomes more viable when electricity prices are not attractive for sale. The same concept is valid for the FP scenario, where there is also a challenge to assess the market values for two sellable products. In order to achieve an IRR of over 10% with biochar at 15 USD/MWh, the price of bio-oil would range from 20 to 26 USD/MWh. It is important to emphasize that the graphs do not indicate which technology is more economically attractive. The final decision will strongly depend on the local market requirements.

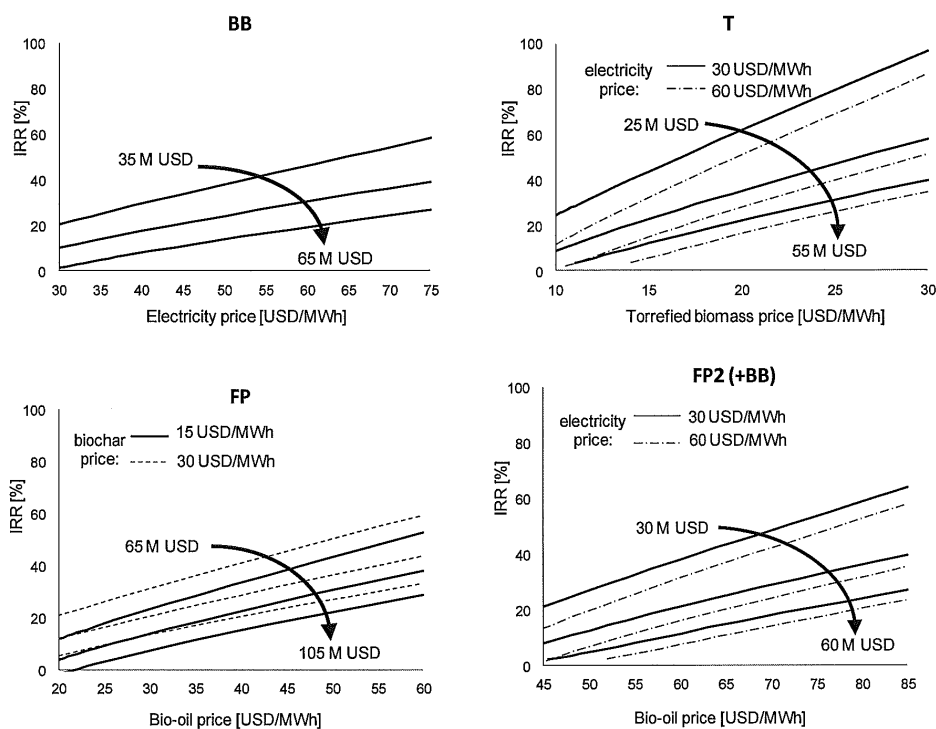


Fig. 3. Internal return rate for the different cases

The steam generation in the FP2 case is 6.4% lower compared to the BB scenario. The biomass flow to pyrolysis should be approximately 50% higher to achieve the same BB steam rate, considering that only the poor biomass (fines excluded) is incinerated. This would result in a high pyrolyzer-to-boiler feed ratio, leading to probable instabilities in the recirculation of bed material. The new stream revenue has to then compensate for the decrease in exportable electricity and for the extra wood. In addition, the cost of disposal is not accounted for. When the price of FP2 bio-oil is 48 USD/MWh or higher for electricity price 30 USD/MWh, or 54 USD/MWh or higher for electricity price 60 USD/MWh, the IRR of over 10% is achieved for the estimated investment cost. For upper bound of the investment price, a bio-oil price of 58 USD/MWh to 64 USD/MWh is required to achieve an IRR of over 10%. On the other hand, bark-free wood is used as feedstock and a better quality for the bio-oil is expected.

Regarding market development, the biochar has been already utilized for many years. Some applications for torrefied wood can include bakery ovens and replacement of coal in existing power plants. Bio-oil is still not well established as a sellable fuel. Bringing a new technology to market can be very challenging and expensive. In the same time there is a need to increase the familiarity of users, with companies eager to provide the resources or fortitude to progress beyond availability testing.

At mid-short term, bio-oil can be used as direct substitute to fossil fuels in power plants or in the industry of different segments. However, the substitution is not straight-

forward. Modifications in the feeding system are still required due to the higher density and lower heating value compared to light fuel oil. The adaptation of equipment material is also relevant, given the higher bio-oil acidity and the presence of ash. A promising option in the future is the upgrading to transport fuels such as diesel, gasoline, kerosene, methane, or jet fuels. For this purpose, full de-oxygenation followed by conventional refining would be required, since crude bio-oil contains high levels of oxygen and water.

CONCLUSIONS

1. Evaluating the future market value of the new products is challenging but indispensable to assess the feasibility of the technologies in study. The renewables incentives and selling electricity price are also important factors affecting the attractiveness.
2. Approximately 121 MW_{th} of torrefied pellets (T) or 107 MW_{th} of bio-oil and biochar (FP) can be produced in the pulp mill, but with the amount of exportable electricity reduced by 23 or 20%, respectively. As one alternative, the residues can be incinerated (BB) to generate steam and increase the surplus electricity by 72%.
3. In case a pyrolysis unit is attached to the biomass boiler (FP2), 158 t(dry)/d of additional wood is brought from the forest for pyrolysis. This results in a projected 35 MW_{th} of bio-oil but in 9.3% reduction in surplus electricity, attributed also to the limiting value assumed for the pyrolyzer-to-boiler feed ratio.
4. The results showed that investing in the production of bio-oil or torrefied pellets can bring satisfactory results regarding IRR. In order to achieve an IRR of *e.g.* over 10 % for the estimated investment cost, the price of electricity, pellets, and bio-oil should be approximately 30, 13, and 26 USD/MWh for BB, T, and FP cases, respectively. The selling price of FP2 bio-oil has to be higher to compensate for the additional wood and decrease in electricity generation.

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Article submitted: January 11, 2013; Peer review completed: March 10, 2013; revised version received and accepted: May 6, 2013; Published: May 10, 2013.

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