Katja Kuparinen

TRANSFORMING THE CHEMICAL PULP INDUSTRY – FROM AN EMITTER TO A SOURCE OF NEGATIVE CO_2 EMISSIONS

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Abstract

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The chemical pulp industry is an energy-intensive industrial sector. Modern kraft pulp mills are typically energy-independent, and fossil fuels are used mainly in lime kilns. Following the Paris Agreement, the pulp industry along with other industrial sectors is urged to take action to combat climate change. This requires the reduction of fossil fuel use and CO_2 emissions. The kraft pulp mill process offers several possibilities to achieve the desired environmental targets. This thesis evaluates the significance and possible routes of the chemical pulp industry in fulfilling the recently presented climate targets. The replacement of fossil fuels in lime kilns with renewable biomass or synthetic fuel and implementing CO_2 capture technologies offer pulp mills the possibility to operate nearly fossil fuel-free or even to become sources of negative CO_2 emissions.

Various biomass processes to convert solid biomass to biofuels are tested and used, but only a few of them in large scale. Kraft pulp mills have a globally significant role in converting biomass to energy due to recovery boilers, but not yet in biofuel production. New biomass conversion technologies, power-to-gas, and carbon capture are options to reduce fossil fuel use and fossil-based CO_2 emissions in kraft pulp mills. Renewable biomass-based fuels can, in many cases, fully substitute fossils in lime kilns in a feasible way. Kraft pulp mills have a significant potential to utilize biomass conversion for fossil fuel replacement. Hydrogen from an integrated electrolyser can replace part of the fossil fuels used in a lime kiln and simultaneously make separate oxygen production unnecessary. Electrolysis is most feasible in stand-alone mills when the electricity price is low. Carbon capture methods are still developing technologies. In kraft pulp mills, even a small capture can make the mill a negative CO_2 emitter, when wood raw material is from a sustainable origin. A part of the captured CO_2 can be utilized in existing processes. All of these technologies were found to be technically feasible. Economic feasibility depends on mill-specific details, technology development, and political decision-making, such as carbon taxes and possible incentives for carbon-neutral/-negative technologies.

Keywords: pulp mill, carbon dioxide emissions, climate change mitigation, negative CO_2, fossil fuel replacement, emission reduction, lime kiln

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Katja Kuparinen
September 2019
Lappeenranta, Finland

Contents

Publications

List of publications

This thesis is based on the following papers. The rights have been granted by publishers to include the papers in this dissertation.

I. Kuparinen, K., Heinimö, J., and Vakkilainen, E. (2014). World’s largest biofuel and pellet plants – Geographic distribution, capacity share, and feedstock supply. *Biofuels, Bioproducts and Biorefining*, 8(6), pp. 747–754.

II. Kuparinen, K., Vakkilainen, E., and Ryder, P. (2016). Integration of electrolysis to produce hydrogen and oxygen in a pulp mill process. *Appita Journal*, 69(1), pp. 81–88.

III. Kuparinen, K., and Vakkilainen, E. (2017). Green pulp mill: Renewable alternatives to fossil fuels in lime kiln operations. *BioResources*, 12(2), pp. 4031–4048.

IV. Kuparinen, K., Vakkilainen, E., and Hamaguchi, M. (2017). Analysis on fossil fuel-free operation in a northern pulp and paper mill. *Proceedings of 2017 International Chemical Recovery Conference*. 24–26 May 2017, Halifax, Nova Scotia, Canada.

V. Kuparinen, K., Vakkilainen, E., and Tynjälä, T. (2019). Biomass-based carbon capture and utilization in kraft pulp mills. *Mitigation and Adaptation Strategies for Global Change*. (Accepted).

Author's contribution

I. Publication I was written based on the idea of Dr Heinimö and Professor Vakkilainen. The author was the principal author and investigator. The author collected the data, was responsible for its analysis and wrote the manuscript. Professor Vakkilainen and Dr Heinimö supervised the work and gave valuable comments and suggestions during the course of the research. They also participated actively in revising the paper during the journal review process.

II. The author was the principal author and investigator in Publication II. Professor Vakkilainen participated actively as a technical advisor and provided ideas, guidance, and valuable remarks. Mr Ryder contributed by acting as a technical advisor considering the operational details of a eucalyptus kraft pulp mill process and made valuable remarks about the reference mill operations and the analysis of the results.

III. The author was the principal author and investigator in Publication III. The author was responsible for the calculations and writing the manuscript. Professor Vakkilainen supervised the calculations, provided expertise in the mill operations and made valuable comments and remarks during the process of writing.

IV. The author was the principal author and investigator in Publication IV. The author was responsible for the calculations and writing the manuscript. Professor Vakkilainen supervised the work, provided valuable information for the mill balance calculations and commented the manuscript. Dr Hamaguchi provided expertise in the mill operations and gave valuable comments and suggestions about the results and the manuscript.

V. The author was the corresponding author and responsible for the mill calculations and most of the writing in Publication V. The Publication was researched and written based on the idea of Professor Vakkilainen. He also contributed especially to the section on CO_2 utilization possibilities, supervised the work, and commented on the manuscript. Associate Professor Tynjälä wrote most of the section on carbon capture technologies, commented on the manuscript, and made valuable remarks on the results of the study.

Related publications (not included in the thesis)

Vakkilainen, E., Kuparinen, K., and Heinimö, J. (2013). Large industrial users of energy biomass. Report for IEA Bioenergy Task 40. 75 p.

Kuparinen K., Vakkilainen E., and Kärki, J. (2016). Electrolysis and biomass conversion as options to produce renewable alternatives for fossil lime kiln fuels. *Proceedings of 2016 Pulping, Engineering, Environmental, Recycling, Sustainability (PEERS) Conference*. 25–28 September 2016, Jacksonville, Florida, US.

Kuparinen, K., Vakkilainen, E., and Tynjälä, T. (2018). Pulp mill as BioCCU. *Proceedings of International Conference on Negative CO_2 Emissions*. 22–24 May 2018, Göteborg, Sweden.

Kuparinen K., Vakkilainen E., Tynjälä, T., and Cardoso, M. (2018). Reuse of CO_2 in pulp mills. *Proceedings of 2018 Pulping, Engineering, Environmental, Recycling, Sustainability (PEERS) Conference*. 28–31 October 2018, Portland, Oregon, US.

Nomenclature

Latin alphabet

M	molar mass	g/mol

Greek alphabet

η	efficiency	%

Subscripts

CC	carbon capture
CCU	carbon capture and utilization
e	electricity
f	fossil fuel
th	thermal

Abbreviations

ADt	air-dry ton
AEC	alkaline electrolysis
BB	biomass boiler
bbl	barrel
BDt	bone-dry ton
BECCS	bioenergy with carbon capture and storage
BECCU	bioenergy with carbon capture and utilization
BFB	bubbling fluidized bed
C	carbon
$CaCO_3$	calcium carbonate
CaL	calcium looping
CaO	calcium oxide
CC	carbon capture
CCU	carbon capture and utilization
CE	causticizing efficiency
CFB	circulating fluidized bed
ClO_2	chlorine dioxide
CO_2	carbon dioxide
CTO	crude tall oil
ETS	Emissions Trading System
EU	European Union
H_2	hydrogen
HHRR	hearth heat release rate
H_2O	water
H_2SO_4	sulphuric acid

IPCC	Intergovernmental Panel on Climate Change
KOH	potassium hydroxide
LHV	lower heating value
LK	lime kiln
MEA	monoethanolamine
MP	medium pressure
Na_2CO_3	sodium carbonate
NaOH	sodium hydroxide
NCG	non-condensable gas
O_2	oxygen
OEA	oxygen enriched air
OECD	Organisation for Economic Cooperation and Development
PCC	precipitated calcium carbonate
PtG	power-to-gas
PtX	power-to-X
RB	recovery boiler
SOEC	solid oxide electrolysis cell
tDS	ton dry solids
WL	white liquor
wt	weight

1 Introduction

1.1 Background

The pulp and paper industry is the fourth largest energy consumer in the industrial sector globally after the chemicals and petrochemicals, iron and steel, and cement industries (IEA, 2014). Sustainability, emission control, environmental regulations, corporate image, self-sufficiency of fuel supply, and the price of fossil fuels are among the many factors driving companies to reduce the usage of fossil fuels. Also pulp and paper mills are facing increasing demands to diminish fossil fuel use and carbon dioxide (CO_2) emissions. The Paris Agreement requires all participants to undertake efforts to combat climate change (UNFCCC, 2019). New technologies, the increased use of renewable energy, and expanding carbon sinks are included in the primary means to achieve the targets, not forgetting financial support for them.

Biomass and bio-based residues cover about 10% of the global primary energy consumption (IEA, 2018). A large part of biomass is used for residential purposes in developing countries. In industrialized countries, biomass use for industry, electricity and biofuels for transport is increasing with modern methods being adopted (Beurskens and Hekkenberg, 2011). Although biomass alone cannot solve the problem of climate change, it has the possibility to be a relevant part of the solution. In the pulp and paper sector, 42% of total energy consumption was covered with fossil fuels in the year 2014, and it is essential to find low-carbon options for these fuels (IEA, 2017).

Biomass is typically a locally limited resource, and especially large-scale users often have to transport feedstock from distant locations. A low energy density, heterogeneous consistency, and high moisture content are typical properties that increase transport costs and lower efficiency. Biomass conversion is a solution for biomass properties that limit the possibilities of biomass utilization. Conversion to solid, liquid, or gaseous fuels makes transportation easier and enables wider application, such as for transportation fuels and chemical feedstock. Biomass refining for energy purposes is becoming more common (Thrän *et al.*, 2014). Currently, only a few methods are used on a large scale and several methods are under research and development.

Pulp mills as large biomass users and in a need of measures to reduce carbon dioxide emissions should actively look to implement advanced methods to replace fossil fuels and reduce fossil CO_2 emissions. A kraft pulp mill produces heat and electricity using residual biomass from its own processes. In normal operation, modern mills are usually self-sufficient in energy, with the exception of lime kilns. The lime kiln is additionally the only unit operation utilizing fossil fuels during normal operation, and consequently, the main source of fossil fuel-based emissions. Fossil fuels are used to reduce lime mud to burnt lime, and they are also used during upsets, start-up and shut-down, and sometimes for safety reasons to secure non-condensable gas destruction (Vakkilainen and Kivistö, 2008; Vakkilainen and Kivistö, 2014). Substituting fossil fuels used in the lime kiln with renewable fuels produced at the mill would make normal kraft pulp mill operations nearly fossil fuel-free. This can be realized by utilizing existing side streams. Already some mills gasify bark while others fire small biomass particles in their lime kilns (Wadsborn *et al.*, 2007). Recently, a large Finnish pulp and paper company announced a target of fully fossil fuel-free operation by 2030 (Metsä Group, 2019). It can be expected that others will follow, especially considering the targets of the Paris Agreement (UNFCCC, 2019), and the findings of a recent report from the Intergovernmental Panel on Climate Change (IPCC) (2018) suggesting rapid actions to limit the global temperature rise. There is no universally agreed preferable single method to replace fossil fuel usage in the lime kiln. Therefore, there is a need to study various alternative options.

The chemical pulp industry as an energy-intensive industrial sector is a significant producer of CO_2 emissions. Most of these emissions originate from combustion processes, and due to a large share of biomass fuels, the emissions are largely biogenic. When biomass fuels are from a sustainable origin, carbon capture followed by storage or the on-site utilization of CO_2 could turn kraft pulp mills from CO_2 emitters to sources of negative CO_2 emissions. Bioenergy with carbon capture and storage (BECCS) is one of the often-proposed methods to mitigate climate change (de Coninck *et al.*, 2018). BECCS or bioenergy with carbon capture and utilization (BECCU) could offer the chemical pulp industry the possibility to act as a platform for negative CO_2 emissions.

1.2 Objective

The main objectives of the thesis were, firstly, to look at the role of the pulp and paper industry in combatting climate change, and secondly, to evaluate ways to react to future demands created by the Paris Agreement. Specifically, the thesis evaluated possibilities to reduce fossil CO_2 emissions in kraft pulp mill operations by utilizing existing resources, such as biomass residue and renewable electricity. The targets of the work can be specified with the following research questions.

Q1. What is the role of biomass conversion methods in energy generation, and how important are kraft pulp mills?
Q2. What can be done to increase biomass usage to minimize the use of fossil fuels in pulp mills?
Q3. How can pulp mills respond to the increasing demand to reduce fossil-based CO_2 emissions and to serve as sources of negative CO_2?
Q4. What are the future challenges of a modern pulp mill?
    a. Role of location; do *e.g.* eucalyptus mills differ from northern mills?
    b. What are the technical and economic issues to be considered?

Refining biomass into biofuels was studied in Publication I to understand how the processes are applied globally and how processing is distributed between various technologies. The studied technologies were pellet, biodiesel, ethanol, and charcoal production, together with torrefaction and pyrolysis. In addition to existing facilities, projects under planning were mapped to evaluate their effect on global biomass use and markets in the near future. Literature, statistics, databases, reports, and reviews were studied, most of them publicly available, complemented with information from personal communications mainly within the IEA Bioenergy Task 40 Sustainable International Bioenergy Trade: securing supply and demand.

Publications II and III examined the technical possibilities and constraints of fossil fuel replacement with existing side streams of a eucalyptus kraft pulp mill by calculating and analysing the mass and energy balances of an example mill. The calculations were based on theoretical fundamentals, literature data, and practical experience. Publication IV evaluates the replacement of fossil fuels in a softwood kraft pulp mill with integrated papermaking. Both example mills were analysed in Publication V to estimate the BECCU possibilities in kraft pulp mills. Figure 1.1 gives an overview of the kraft pulp mill by-products and the studied concepts, and Figure 1.2 clarifies the contribution of each publication within the studied fields.

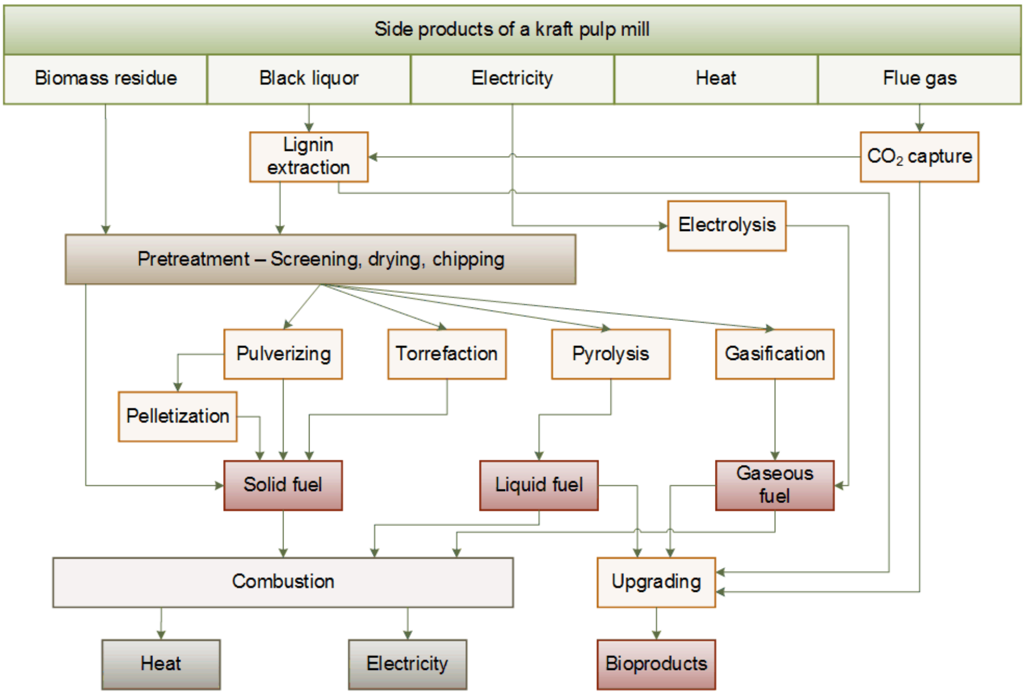


Figure 1.1. Concepts for utilization of kraft pulp mill side products.

The studied substitutes for fossil lime kiln fuels were hydrogen, biogas from biomass gasification, torrefied biomass, lignin, and pulverized woody biomass. These routes are not the only possible ones, but they have been chosen for this study as they were considered potential options based on literature. Pyrolysis is included in the figure, although it was not used in the integration studies because it is one of the commercially available conversion methods discussed in Publication I. Electrolysis was chosen because it is an exciting new alternative that was estimated to have integration benefits, especially in stand-alone pulp mills in distant locations. Hydrogen is a carbon-free fuel, it is already used in lime kilns, and its use furthers the targets of emission reduction. When produced using renewable electricity, it can also be considered renewable.

The integration of lime kiln fuel production into the kraft pulp mill process can bring synergy benefits that make the fuel production process more feasible compared with stand-alone operations. Apart from nearly fossil fuel-free operation, the integration concepts offer interesting new possibilities, such as increasing mill capacity and gaining additional revenue by the production of advanced bioproducts. In addition to technical evaluation, an economic analysis was conducted for the biofuel concepts to gain a comprehensive view on their feasibility.

The capture and on-site utilization of CO_2 was studied because it could offer the pulp and paper industry the possibility to act as a platform for negative CO_2 emissions, especially when captured biogenic CO_2 is reused in the production of further bioproducts. The studied possibilities for CO_2 utilization include tall oil manufacturing, lignin extraction, and the production of precipitated calcium carbonate (PCC), depending on local conditions and mill-specific details. In addition, the global potential of the chemical pulp industry to act as a source of negative CO_2 emissions through BECCS/U was assessed.

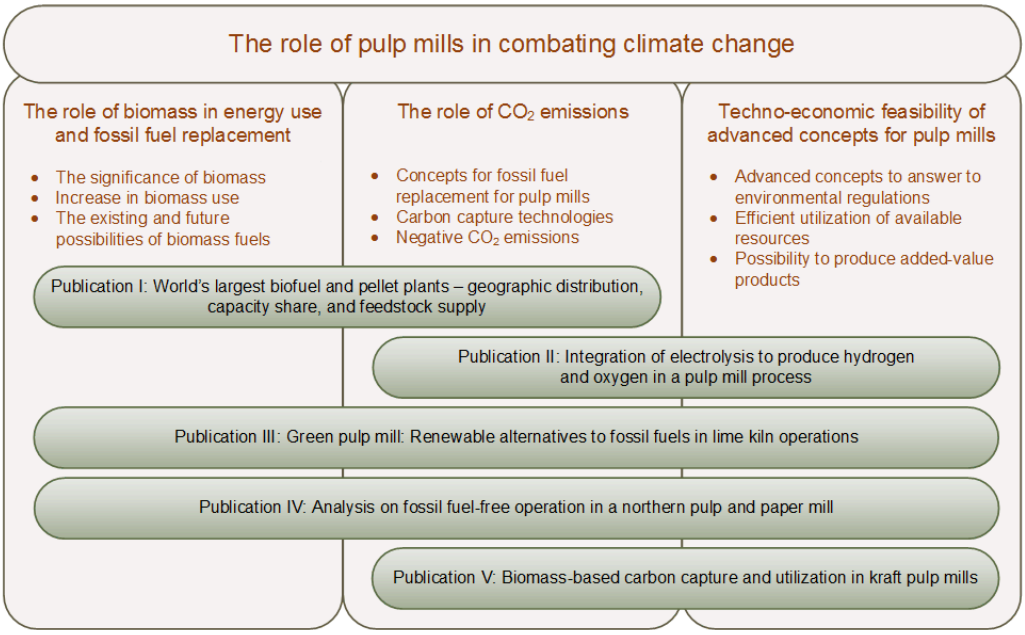


Figure 1.2. The contribution of each publication in the research areas of the thesis.

1.3 Outline of the thesis

This thesis is divided into seven sections. After this introduction, section 2 provides a brief description of biomass use for energy and the most significant conversion technologies from a global perspective. Section 3 introduces kraft pulp mill operations and the theoretical background of the studied conversion technologies. The section gives an overview of the possibilities of the technologies in a kraft pulp mill environment. Lime kiln operations are presented to examine current fuels used in lime kilns and the requirements the kiln operation sets for alternative fuels. Section 4 presents the theoretical background of the technologies that can make pulp mills a carbon sink. The primary carbon dioxide sources in a pulp mill, the state-of-the-art technologies for carbon capture, and existing possibilities to reuse carbon dioxide on-site are discussed. Water electrolysis is presented as a method to produce renewable carbon-free lime kiln fuel on-site.

Section 5 evaluates the implications of the studied processes for pulp mill operations by mass and energy balance calculations. The section introduces the basis for the calculations and the reference mill models employed, and evaluates the effect of alternative lime kiln fuels. Each process integration concept and its effect on the mill balances is presented. Section 6 presents and discusses the results of the thesis. The feasibility of the studied concepts is evaluated to determine the benefits and constraints of the processes, as well as their possibility to transform a pulp mill into a fossil fuel-free unit or even make it a carbon sink. The section also answers the research questions presented in the introduction. Finally, section 7 gives the conclusions.

2 Global view on biomass conversion for energy purposes

2.1 Biomass use for energy

Biomass is a material of biological origin including both plant- and animal-derived materials. More than 80% of biomass used for energy purposes globally is derived from wood (Chum *et al.*, 2011). The rest is from the agricultural sector with various waste and by-product streams. Modern biomass refining and processing systems use several species and types of biomass, whereas older existing bioenergy systems mainly use wood, residues, and waste for heat and power production and agricultural crops for liquid biofuels. Biomass is mainly available in low-density form, which is why it typically demands more storage space, transport, and handling than conventional fuels. Pre-treatment such as densification is required when biomass used for energy is transported longer distances (Uslu *et al.*, 2008; Tumuluru *et al.*, 2011).

In 2011, the total use of biomass for energy purposes was 55 EJ (IEA, 2018). About two-thirds of this was residential use mainly in developing countries. Industry and energy generation were the second largest user sectors with a consumption of 8 EJ, with the transportation sector (2 EJ) trailing. In the industrial sector, the biomass consisted almost entirely (98%) of primary solid biomass; this includes plant matter used directly as fuel or processed before combustion, covering also for example black liquor. Industrial biomass use is concentrated in a small number of countries. Fifteen countries use 80% of the global solid biomass usage in the industrial sector.

Biomass is typically a locally limited resource. Large users of biomass have often to import feedstock from larger and often expanding locations. Several studies have shown that international biomass trade for energy purposes is growing rapidly (Uslu *et al.*, 2008; Heinimö and Junginger, 2009; Oosterveer and Mol, 2010; Chum *et al.*, 2011; Cocchi *et al.*, 2011; Hoefnagels *et al.*, 2011; Tumuluru *et al.*, 2011; Lamers *et al.*, 2012; Goh *et al.*, 2013; Heinimö *et al.*, 2013).

2.2 Large-scale biomass conversion processes

In 2012, ethanol (1 790 PJ), biodiesel (700 PJ), and pellet (310 PJ) were the most important biomass refining processes for energy in terms of production volumes (Vakkilainen *et al.*, 2013). Charcoal production, about 1 EJ in 2011, was also notable, but limited mainly to small-scale facilities using traditional methods. Torrefaction and pyrolysis were developing technologies and the global capacity was negligible; together they accounted for less than 20 PJ/a. Current torrefaction and pyrolysis plants are primarily pilot and demonstration plants (Bridgwater, 2012; Balan *et al.*, 2013). Biomass gasification is a more widely used technology, but there are only a few industrial scale operational units (Vakkilainen *et al.*, 2013).

The USA and Brazil are the major fuel ethanol producers. In 2011, they accounted for 87% of the global production (RFA, 2012). In the USA, the annual production capacity was around 1.2 EJ in over 200 industrial ethanol mills. The primary feedstock is corn. In Brazil, the production capacity was around 0.9 EJ, and Barros (2011) estimated that 59% was in use. The mills are smaller than in the USA. Fuel ethanol was produced in over 440 mills in 2012, primarily from sugarcane. Ethanol mills are typically located close to feedstock sources, which indicates that they use local feedstock.

The global wood pellet production was estimated at 18.3 million tonnes (310 PJ) in 2011 (REN21, 2012), whereas the production capacity at the same time can be estimated at about 35 million tonnes (595 PJ). Thus, 52% of the capacity was in use. Pellet production is concentrated mainly in North America and Europe, where also the largest mills are located (Bioenergy International Magazine, 2013). Pellet mills primarily use local wood-based raw material (Vakkilainen *et al.*, 2013), but the production of the largest mills is mainly aimed at European markets – also from North American mills. In Europe, the pellet consumption has been increasing faster than production (Cocchi *et al.*, 2011).

Biodiesel production is geographically more divided than ethanol and pellet production, but most of the production is located in Europe. In 2011, the global production was around 18.8 Mt (700 PJ), of which 48% (9 Mt) was produced in the European Union (EU) (REN21, 2012; EIA, 2013; Eurostat, 2019). The fifteen largest plants used vegetable oils as feedstock, and their production capacity covered 13% of the global capacity. Feedstock was often imported, but also local sources were used. In Europe, rapeseed oil was primarily used, while in the USA, soybean was the main raw material. The share of soybean oil is increasing also in Europe, and smaller amounts of palm oil and fats are used.

3 Production and use of biomass fuels in kraft pulp mills

3.1 Kraft pulping process

Kraft (sulphate) pulping is the dominant chemical pulping process, covering 99% of chemical pulp production today (FAO, 2017). A kraft pulp mill consists of a fibre line and a chemical recovery system. The primary operations of a kraft pulp mill are depicted in Figure 3.1. Various wood species are used in kraft pulping processes. The differences between the properties of wood raw materials lead to different properties in produced pulp, *e.g.* pulp strength and opacity. Regardless of the varying properties of wood species, the pulping and bleaching processes for eucalyptus and softwoods are remarkably similar (Shackford, 2003).

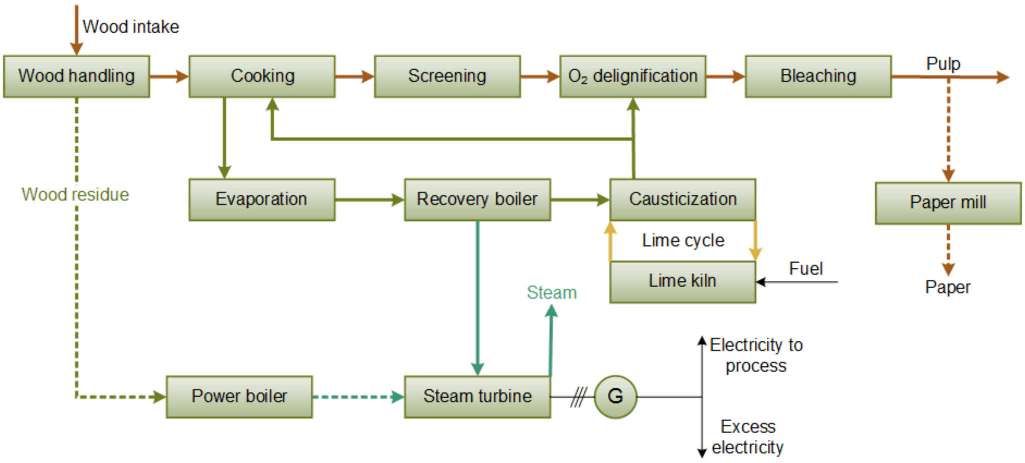


Figure 3.1. Kraft pulp mill operations.

The fibre line covers mill operations from wood handling to bleaching. The wood handling department produces bark-free wood chips for the cooking stage, where chemicals (white liquor) and heat are used to defibre them. In the cooking process, about half of the wood ends up in pulp. Subsequent washing, screening, O_2 delignification, and bleaching stages are used to attain the desired pulp quality. Pulp can then be dried for transportation or conveyed to an integrated paper mill.

The chemical recovery system consists of evaporation, a recovery boiler, and white liquor preparation, i.e. the lime cycle. Black liquor, including the cooking chemicals used and the residual wood, is evaporated and then combusted in the recovery boiler. The recovery boiler has two purposes: chemical recovery and steam production. The recovered chemicals in the form of green liquor are converted back to white liquor in a recausticization plant. White liquor is then used again in cooking. Lime is needed in causticization, and returned after process as lime mud to the lime kiln. The lime kiln converts lime mud to burnt lime for reuse. Typically fossil fuels are used to generate heat for the lime regeneration reaction. The operations of the lime kiln are introduced in more detail in section 3.3.

Kraft pulp mills produce steam in the recovery boiler and usually in a separate power boiler. Steam is used in the mill processes and excess steam is led to a turbogenerator for electricity generation. Modern mills are typically energy-independent (Vakkilainen and Kivistö, 2014).

3.2 Kraft pulp mills as users of energy biomass

In chemical pulping, wood is not only a raw material, but also a significant source of energy. Varying a little mainly due to differences in wood species, less than half of the incoming wood is used for the end product. The processing of wood prior to pulping creates biomass residues including bark, sticks, and fines. In most mills, woody residue is combusted in a biomass boiler for steam production.

In the pulping process, the cooking yield varies in the range of 44–54% depending on the wood species and process details. The rest of the wood, including mainly hemicelluloses and lignin, is combusted in the recovery boiler for steam generation. In 2016, the global sulphate pulp production was 137 million tons (FAO, 2017). This equals 206 million tons of black liquor dry solids combusted in recovery boilers (Tran and Vakkilainen, 2007), and approximately 1.8 EJ energy generated. In the industrial sector, recovery boilers were responsible for about a quarter of the global biomass-based energy generation in 2011 (Vakkilainen *et al.*, 2013). Figure 3.2 shows a comparison of global capacities of plants converting biomass for energy purposes in 2012; recovery boilers top the global capacity.

Renewable fuels can be produced at a kraft pulp mill using available biomass residues or renewable electricity generated at the mill. This thesis studies the integration of biofuel production in the pulp mill process to replace fossil lime kiln fuels. The studied concepts have been depicted in Figure 3.3.

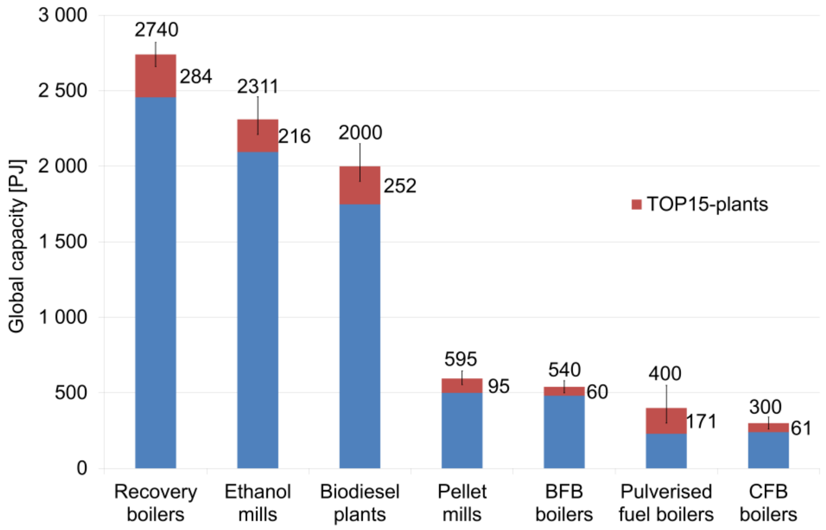


Figure 3.2. Comparison of the global capacities of various types of biomass plants (Vakkilainen *et al.*, 2013). BFB and CFB refer to a bubbling fluidized bed and circulating fluidized bed, respectively.

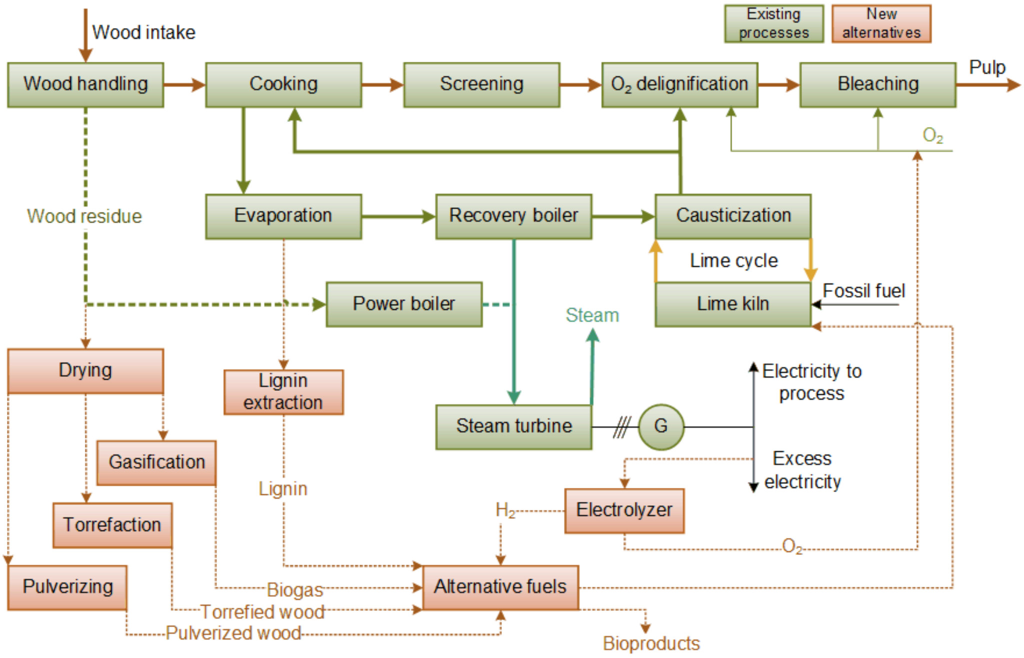


Figure 3.3. Kraft pulp mill operations and alternative biomass conversion concepts studied in the thesis.

The studied concepts are existing processes, and some of them have been used in pulp mills before. Hydrogen production from water using alkaline electrolysis is a well-known commercial process (Millet and Grigoriev, 2013; Lehner *et al.*, 2014). In a pulp mill, excess electricity can be used on-site for hydrogen production in electrolysers. The gasification of biomass followed by gas firing in a lime kiln is a known technology and has been used in a number of pulp mills in Scandinavia (Wadsborn *et al.*, 2007; Vakkilainen and Kivistö, 2008; Metsä Group, 2013). Torrefied biomass is produced by the mild heating of biomass in the absence of oxygen, and its properties resemble those of coal (Koppejan *et al.*, 2012). Torrefied biomass has not yet been used to fuel lime kilns in commercial operations, but the option has recently been studied, as has the possibility of integrating torrefaction in pulp mill processes (Hamaguchi *et al.*, 2013; Kukkonen, 2014). Lignin extraction from black liquor and its use for a wide range of purposes has been studied widely; a possible and easily achievable usage is as lime kiln fuel (Vakkilainen and Kivistö, 2008; Lundberg *et al.*, 2013; Manning and Tran, 2015; Björk, 2016). Dried and pulverized biomass can be easily combusted in lime kilns (Wadsborn *et al.*, 2007; Stora Enso, 2015).

The amount of residue from the wood handling process depends on the process details, the wood type, and local conditions. Eucalyptus is usually debarked in the forest, which decreases the amount of woody residue at the mill (Salmi and Vuojolainen, 2005). Electricity generation and use varies greatly depending on mill operations. Modern kraft pulp mills produce renewable electricity and heat in the form of steam and hot water during normal operations, typically in excess of their own needs (Vakkilainen and Kivistö, 2014). Excess electricity can be either sold or used internally for the production of chemicals or paper. Steam is utilized in pulp production, but in large modern mills, a condensing tail is used in a turbine to convert excess steam into electricity. Electricity and heat sale can be a significant source of income for a pulp mill. Sometimes in stand-alone mills in distant locations, a limited power transmission capacity weakens the possibilities to sell excess electricity. In integrated mills, papermaking is a large additional energy consumer.

3.3 Lime kiln fuels and operation

The lime kiln is a part of the chemical circulation that consists of recausticizing and lime mud re-burning processes. Lime is used in recausticizing to convert green liquor from the recovery boiler into white liquor. The lime kiln converts lime mud, which is largely composed of calcium carbonate ($CaCO_3$), into burnt lime, i.e. calcium oxide (CaO), and carbon dioxide (CO_2), according to reaction 3.1. This thermal decomposition reaction requires a high temperature and occurs spontaneously when the lime mud temperature exceeds approximately 800 °C in a gas atmosphere containing 20% CO_2. The gas temperature needs to be notably higher because of the poor heat transfer in the kiln (Arpalahti *et al.*, 2008).

$$CaCO_3 + (\text{heat}) \rightarrow CaO + CO_2 \tag{3.1}$$

Lime kilns are typically long, cylindrical rotary kilns. Lime mud is fed into the kiln at the feed end, from where the mud, because of kiln rotation and slight inclination, flows slowly through the drying and heating zones to the burning zone. External heat is brought into the kiln by combusting typically fossil fuels at the hot end of the kiln. Lime kilns are usually fired with oil or natural gas, and modern lime kilns are often equipped with burners suitable for both oil and gas combustion. Various alternative fuels originating from the pulp production process side streams are often co-combusted, but only in a few cases are they used as the main fuel (Francey *et al.*, 2011). For example, methanol, tall oil, strong odorous gases, tall oil pitch, hydrogen, and turpentine have all been co-combusted with fossil fuels in lime kilns. The operation of the lime kiln requires stable combustion conditions and an easily controllable temperature, and therefore the quality of fuel should be stable. A sufficiently high adiabatic flame temperature is also required to ensure adequate heat transfer in the kiln. The combustion of biomass-based fuels lowers the hot-end temperature in the kiln due to the lower adiabatic flame temperature (Isaksson, 2007). To maintain the kiln production capacity, higher firing rates are required, which causes an increase in the back-end temperature and higher flue gas heat loss. Therefore, an additional increase in fuel consumption needs to be considered in the case of biomass fuels.

Alternative solid fuels fired in lime kilns can include non-process elements as contaminants, which tend to accumulate in closed cycle processes such as the lime cycle (Hamaguchi and Vakkilainen, 2011). These impurities can cause corrosion, ring formation in the kiln, and adverse environmental effects, in addition to having an unfavourable effect on the quality of the lime. Increased amounts of contaminants can lead to increased use of make-up lime. A high fuel moisture content decreases the heating value of the fuel and the system efficiency and increases the amount of flue gas. The fuel heating value needs to be high enough to enable the desired flame temperature at the lime kiln hot-end (Vakkilainen and Kivistö, 2008).

3.4 Lignin

In kraft pulping, about half of the wood entering the cooking process is converted to pulp. The rest of the organics, including mainly hemicelluloses and lignin, are typically combusted in the recovery boiler with black liquor for energy production. In eucalyptus, the lignin content is typically 26–27% (*Eucalyptus grandis*, *E. saligna*; dry basis) (Almeida *et al.*, 2010). The lignin content in softwood is typically 25–30% (Alén, 2011). Lignin can be separated from black liquor before the recovery boiler to be used as fuel or to be refined further into other products (Björk, 2016). Possible lignin separation methods are membrane filtration after the digester and acidic precipitation and dewatering at the evaporation stage (Vakkilainen and Kivistö, 2008).

Lignin separation using an acidic precipitation method and combustion in a lime kiln have been tested in Sweden (Tomani, 2010), and the method is currently used in Finland (Björk, 2016). Sulphuric acid is typically used, and in many commercial processes, part of the acid is replaced by CO_2. Several studies have examined the effects of lignin separation on pulp mill operations and dimensioning (Axelsson *et al.*, 2006; Vakkilainen and Kivistö, 2008; Vakkilainen and Välimäki, 2009; Hamaguchi *et al.*, 2011).

The precipitation of lignin from black liquor is based on the decreased solubility of lignin when the pH is lowered. CO_2 and sulphuric acid (H_2SO_4) are used in a two-step process to lower the pH (Tomani, 2010; Gellerstedt *et al.*, 2013). CO_2 can be either purchased or separated from the flue gases of the lime kiln or the recovery boiler. Using the lime kiln flue gas as a source of CO_2 decreases the chemical cost by 20–25%.

Precipitated lignin is a hydrophobic filtercake with 30–40% moisture content (Tomani *et al.*, 2011), and it can be dried further and pulverized before utilization. Lignin includes free sodium and sulphur, which may cause ringing in the lime kiln. The sulphur content after the process is approximately 2–3%, and the sodium content can be decreased by washing to a level that is acceptable for lime kiln use (Gellerstedt *et al.*, 2013). Standard burner and feeding equipment can be used for lignin combustion in lime kilns. No notable adverse effects on lime kiln operation nor on emission levels were detected in trials conducted in a Swedish kraft pulp mill (Tomani *et al.*, 2011).

Lignin removal has several advantages in addition to the possibility to use it as a fuel. It decreases the steam load and flue gas production of the recovery boiler, which is often a bottleneck in the pulp production process. Therefore, it has been introduced as a method to enable an increase in pulp production capacity without an expensive upgrade of the recovery boiler (Axelsson *et al.*, 2006; Vakkilainen and Kivistö, 2008). Lignin is also a valuable raw material for many bioproducts, such as formaldehyde resins, carbon fibres, moisture barriers in packaging materials and upgraded fuel (Tomani, 2013).

The removal of lignin changes the properties of black liquor and thus affects the operation of the recovery boiler. If the mill production remains unchanged, steam production in the recovery boiler decreases and, as a result, electricity generation decreases as well. The washing of precipitated lignin increases the load of the evaporation plant because the washing filtrates are returned to the evaporation (Hamaguchi *et al.*, 2011).

3.5 Biomass conversion technologies

3.5.1 Biomass pretreatment

The pretreatment of biomass residue is required regardless of the following conversion process. Pretreatment reduces problems in the fuel feeding systems and improves the efficiency of the conversion or combustion processes. Undesired elements such as sand and metals need to be removed to prevent malfunctions in the processing equipment. Additionally, pretreatment includes drying, chipping, and grinding to fulfil the requirements of the conversion process. The desired moisture content, particle size, and other properties vary based on the chosen process.

3.5.2 Gasification

Biomass gasification for lime kiln use is a well-known process (Isaksson, 2007; Francey *et al.*, 2011; Metsä Group, 2013). In the 1980s, several gasifiers to produce biogas from wood for lime kiln use were built due to the increasing oil price (Isaksson, 2007). Currently, there are some newly built ones in use. Most of the gasifiers at pulp mill sites are circulating fluidized bed (CFB) gasifiers. A CFB gasifier can be atmospheric or pressurised. They have the advantage of being suitably sized for lime kiln operations. Compared to fixed bed gasifiers, fluidized bed gasifiers are more flexible regarding feed particle size. A suitable particle size for a CFB gasifier is around a 6 mm average diameter with moisture content at or below 15%. A typical heating value for biogas produced in a CFB gasifier is 3–7 MJ/kg, when air is used as a gasifying agent (Vakkilainen and Kivistö, 2008).

Biomass drying before gasification is essential to improve the efficiency of the process. Moisture in the fuel notably increases the amount of flue gas from the lime kiln (Isaksson, 2007). Particles like sand or metals should be removed in the biomass pretreatment process prior to gasification, and minor contaminants can be handled in the gasification process (Worley and Yale, 2012). A significant part of ash can be removed from the gasifier, which leads to less contaminants ending up in the fuel gas and onwards in the combustion process. The electricity consumption of a gasifier is moderate compared with other biomass conversion methods. In addition to biomass pretreatment, the gasifier air fans consume electricity.

Due to a lower adiabatic combustion temperature, biogas use increases the temperatures of the flue gas at exit in comparison with natural gas or fuel oil (Isaksson, 2007). Therefore, the flue gas heat losses are higher, and consequently, more fuel is needed.

3.5.3 Pulverizing

Pulverized wood has been tested and used as lime kiln fuel (Wadsborn *et al.*, 2007; Stora Enso, 2015). The combustion of unsorted wet wood and bark in a lime kiln is challenging due to a high moisture content, varying particle size and heating value, unpredictable flow characteristics, and the high content of non-process elements. Drying and pulverizing is therefore required for stable operation. Pulverized wood can be combusted using pulverized fuel burners or, when wood is used as additional fuel, pulverized wood can be mixed with lime. The characteristics of wood make pulverizing wood more energy-intensive than, for instance, the pulverization of coal or torrefied biomass.

The type and quality of wood affects the combustion process and the lime kiln operation. A high moisture content decreases the heating value of the fuel and the system efficiency and also increases the amount of flue gas. Woody biomass, especially bark, contains a relatively large amount of contaminants. The impurities can cause corrosion, ring formation in the kiln, and adverse environmental effects in addition to having an unfavourable effect on the quality of the lime. Thus, make-up lime use increases in proportion to the amount of contaminants fed in the lime kiln with fuel.

Problems in the renewable fuel system cause breaks in biofuel firing, which typically leads to occasional fossil fuel use. In Swedish mills, the biofuel system availability has been between 80 and 90% (Wadsborn *et al.*, 2007). The most common reasons for stoppages have been fires in the fuel feeding system and clogging in hammer mills. Fires are common especially when flue gas is used for drying; therefore, secondary heat instead of flue gas is recommended.

3.5.4 **Torrefaction**

Torrefaction is a mild pyrolysis process, which produces biomass with properties resembling those of coal, such as grindability and heating value (Koppejan *et al.*, 2012). Therefore, torrefied biomass can replace coal in many applications without notable modifications to the combustion equipment. Coal is a commonly used fuel in cement kilns, whose operation is similar to lime kilns in kraft pulp mills. The integration of torrefaction into a pulp mill process has been studied previously (Hamaguchi *et al.*, 2013; Kukkonen, 2014). Torrefied biomass can be combusted in a lime kiln as the main fuel by using pulverized fuel burners, or as additional fuel either mixed with lime mud or blown to the kiln from the burner end.

Torrefaction occurs at atmospheric pressure in the absence of oxygen. The operating temperature is approximately 200–300 °C with a residence time in the range of 0.5–2 h. Depending on the process details, biomass loses typically 30% of its mass and 10% of its energy content during torrefaction (Schorr *et al.*, 2012). Torrefaction reduces the moisture content of biomass and makes it hydrophobic and brittle. The behaviour of biomass in the torrefaction process depends on the type and composition of the biomass (Prins, 2005). The quality requirements of torrefaction feed are not strict (Schorr *et al.*, 2012), and residual biomass from pulp mills' woodhandling is well suited for processing.

4 Towards negative CO_2 emissions

4.1 CO_2 emissions in kraft pulp mills

In the chemical pulp industry, most CO_2 emissions originate from combustion processes. The primary CO_2 sources in a kraft pulp mill are the recovery boiler, the biomass boiler, and the lime kiln. Due to a high share of biomass-based fuels, CO_2 emissions are largely biogenic. Smaller CO_2 streams originate from other mill processes, such as non-condensable gas (NCG) destruction, but these are negligible sources. In some new mills, biosludge is treated to biogas, and subsequently, CO_2 is released. The biogas production can be 10–15 kWh/ADt (Metsä Group, 2016). This type of process can be expected to become more common, but currently, their CO_2 streams are minor compared to combustion processes. A simplified process diagram of a kraft pulp mill in Figure 4.1 shows the primary sources of CO_2.

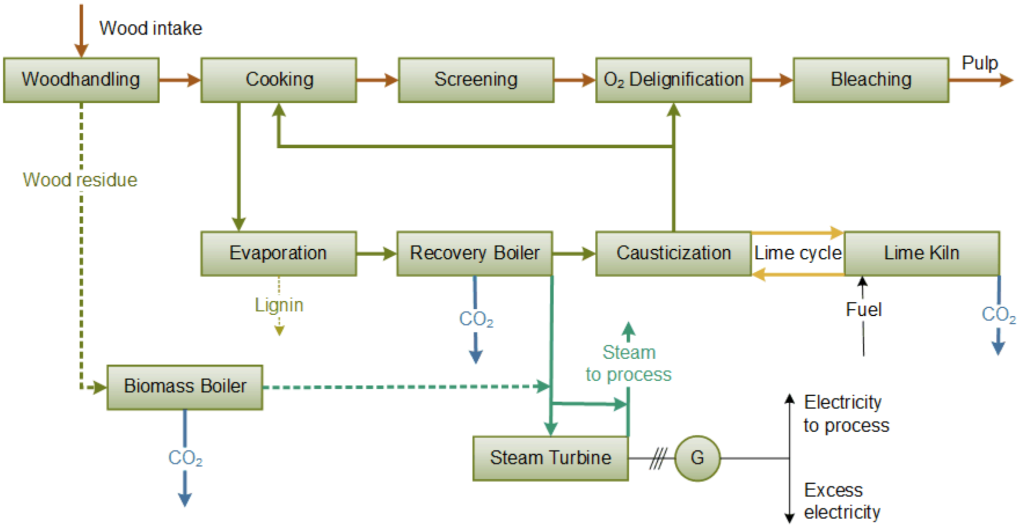


Figure 4.1. The primary CO_2 sources in a kraft pulp mill.

Biomass residue is combusted in a biomass boiler in nearly all pulp mills. A typical biomass boiler uses fossil fuels during start-up and shutdown. Additional auxiliary steam is also often generated using fossil fuels, especially in integrated mills including a paper machine. The fossil fuel usage in the biomass boiler produces at least 20 $kgCO_2$/ADt, but significantly larger quantities are possible.

The role of the recovery boiler is to burn organic residue from pulping and recover the used sodium-based cooking chemicals in the black liquor. After pulping, weak black liquor is concentrated in a multi-effect evaporator. Most of the water is removed, and concentrated black liquor is sprayed into the lower part of the recovery boiler. Organic residue including mostly hemicelluloses and lignin is combusted. Biogenic CO_2 forms in the combustion and exits from the stack of the recovery boiler. Fossil fuels, usually natural gas or oil, are used during start-up and shutdown, and occasionally due to sudden process upsets or equipment failure. Fossil CO_2 is formed in the amount of 10–20 kgCO_2/ADt, while the amounts of biogenic CO_2 are in the range of 1600–2400 kgCO_2/ADt.

In the lower part of the furnace of the recovery boiler, sodium sulphide (Na_2S) is formed in an oxygen-deficient environment. The extent of sulphide formation over sulphate is measured by the reduction efficiency, which is typically over 90%. The rest of the sodium reacts to carbonate. The sodium and sulphur are recovered as a molten smelt that consists mostly of Na_2S and sodium carbonate (Na_2CO_3). The molten smelt is dissolved in weak white liquor in a dissolving tank to form green liquor. Green liquor reacts with lime (CaO) in the recausticizing plant to form sodium hydroxide (NaOH) following the reactions:

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{4.1}$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2\ NaOH + CaCO_3 \tag{4.2}$$

Conversion is measured by the causticizing efficiency (CE), which is typically 80–85%. Calcium carbonate ($CaCO_3$) is converted back to CaO in the lime kiln (see section 3.3), following the reduction reaction 3.1. The reaction produces biogenic CO_2 that exits with the flue gases from the stack of the lime kiln. Make-up lime use may cause a small amount of fossil CO_2 emissions during the reaction, depending on the choice of make-up lime; either CaO or $CaCO_3$ can be used.

Typically, fossil fuels are combusted in the lime kiln to reach the required temperature for the reaction 3.1. Fossil fuel usage, mostly oil and natural gas, produces 100–250 kg CO_2/ADt. The lime kiln is then typically the largest source of fossil CO_2 emissions in a modern mill.

4.2 CO_2 capture technologies

Several methods can be used for CO_2 capture in pulp mills, including pre-combustion, post-combustion, and oxycombustion methods. A recent review on different CO_2 removal methods applied in industrial processes showed that capture processes are little studied in pulp mills (Leeson *et al.*, 2017). Benchmarking is difficult due to a lack of references.

CO_2 capture (CC) from lime kiln flue gases and subsequent use as calcium carbonate paper filler is a well-known and widely applied technology (Hirsch *et al.*, 2013). It is technically possible to retrofit post-combustion CC to an existing pulp or pulp and board mill recovery boiler or biomass boiler (IEAGHG, 2016). CO_2 capture processes use heat and power, which affects the energy balance of the mill. The adequacy of steam and electricity needs to be estimated based on mill-specific details and the requirements of the chosen CC process. For instance, when an amine-based post-combustion CO_2 capture process is used in stand-alone mills, increased steam consumption can be covered without an additional boiler (Onarheim *et al.*, 2017).

Amine-based post-combustion CO_2 capture systems are a proven technology that is commercially available. The CO_2 capture efficiency of the monoethanolamine (MEA) process is usually between 80–90%, and as a post-combustion method, it can be applied easily to existing plants. An aqueous solution (30 wt-%) of MEA can be considered as a reference solvent in the post-combustion capture process. CO_2 is absorbed at temperatures of 45–50 °C, and flue gases need to be cooled before amine absorption. Desorption occurs at 100–120 °C. Approximately 3.7 MJ/kgCO_2 heat is needed for sorbent regeneration. In addition, electricity is needed for the process, which increases the mill's own electricity use (Onarheim *et al.*, 2015).

A few studies have estimated the costs of CO_2 capture in pulp mills, mostly considering amine-based post-combustion processes (IEAGHG, 2016; Karjunen *et al.*, 2017; Leeson *et al.*, 2017). The results differ due to varying assumptions and case-specific details. A recent study (IEAGHG, 2016) estimated the cost of avoided CO_2 at 62–92 €/tCO_2 for a pulp mill and at 82–92 €/tCO_2 for an integrated pulp and board mill. The estimations are based on the modelling of cases where CO_2 capture is retrofitted in the hypothetical mills in Finland. The cases include MEA-based post-combustion capture from the flue gases of the recovery boiler, the multi-fuel boiler, the lime kiln, and combinations of these. Karjunen *et al.* (2017) studied the application of CO_2 capture, transport, and intermediate storage logistics for a Finnish energy system based on renewable energy sources. The cost of biogenic CO_2 for utilization varied between 40 and 44 €/tCO_2 depending on the applied future scenario. Costs were the lowest for the industrial scenario, where the largest amount of CO_2 was captured from large industrial (mainly pulp and paper) point sources. In the calculations, a conventional MEA capture process was taken as the reference capture method. The application of more advanced capture methods could reduce capture costs.

Oxycombustion processes (see *e.g.* Stanger *et al.* (2015)) applied to the recovery boiler, bark boiler or lime kiln are one option but require an oxygen source and possibly modifications to the flue gas passages. In oxycombustion processes, the reaction zones and gas atmosphere in the furnace will change, which may have implications on heat transfer and reactions. The main additional cost is the production of oxygen, which in kraft pulp mills can be quite affordable due to often pre-existing equipment on site.

In addition, pre-combustion processes based on black liquor gasification have been suggested for CO_2 capture, but these technologies have not yet been demonstrated successfully in commercial scale (Onarheim *et al.*, 2015).

Advanced hot solid looping technologies such as post-combustion calcium looping (CaL) (Martínez *et al.*, 2016) also offer interesting possibilities for CO_2 capture. In the CaL process, calcium oxide is used for CO_2 capture. In the case of kraft pulp mills, it has been proposed that lime mud from the lime kiln could be used as a sorbent for CO_2 capture

(Sun *et al.*, 2013; Tynjälä *et al.*, 2014). Even if lime mud as is were not a feasible choice for CO_2 capture, there would be other integration possibilities with the CaL process and lime kiln. The existing infrastructure for limestone acquisition and handling in a pulp mill could lead to further integration benefits. For the CaL process integrated with the lime kiln of a cement plant, Romano *et al.* (2013) estimated that the minimum cost of CO_2 avoided could be as low as 27 €/tCO_2.

4.3 On-site utilization possibilities for CO_2

The possibilities to utilize captured CO_2 as raw material for further bioproducts depend on mill-specific details, such as the chosen processes and the type of wood raw material. The studied alternatives for the on-site utilization of CO_2 are typically occurring large streams: lignin extraction, tall oil manufacturing, and production of precipitated calcium carbonate (PCC).

Lignin extraction was introduced in more detail in section 3.4. The process can be integrated into both hardwood and softwood mills. Typically, lignin is separated by acidifying part of the black liquor using sulphuric acid. The acid use is 50–100 kgH_2SO_4/t lignin (Tomani *et al.*, 2011). CO_2 can replace part of the sulphuric acid in the process. CO_2 is then needed approximately 150–250 kg per ton of separated lignin. If the lignin separation degree is 20% and the wood pulped is pine, then the CO_2 use can be estimated at 35 kg/ADt.

Crude tall oil (CTO) is the major chemical by-product of the kraft pulp industry (Gullichsen and Lindeberg, 1999). CTO is a sellable product that can also be refined further or used as fuel without purification for example in the lime kiln. Tall oil conversion to biodiesel is low-cost, which gives an advantage compared to, for example, vegetable oils (Aro and Fatehi, 2017).

Tall oil manufacturing can be considered as an option in softwood mills, but in hardwood and eucalyptus mills, tall oil is rarely recovered due to low levels of extractives (Shackford, 2003). The extractive content varies with wood species and is high especially in coniferous trees. Tall oil production can be estimated at 45 kg/ADt for Nordic pine, 25 kg/ADt for Nordic spruce, and below 20 kg/ADt for Nordic birch (Gullichsen and Lindeberg, 1999).

CTO is produced from extractives that form foamy material called soap during the cooking process. Soap can be separated and skimmed from weak black liquor. Raw soap is converted into CTO by acidulation, typically using sulphuric acid (H_2SO_4). Sulphuric acid consumption is 200–300 kg per ton of CTO (Aro and Fatehi, 2017). When the mill has a chlorine dioxide (ClO_2) plant, waste acid from the plant can be partially used. CO_2 can be used to partly replace sulphuric acid, and also commercial processes for it exist (Gullichsen and Lindeberg, 1999). CO_2 is a weaker acid, and therefore, only up to 50% replacement is possible. CO_2 use can then be calculated at 4–6 kg/ADt.

PCC is used as a paper filler and in coatings to whiten and smoothen the paper surface (Nanri *et al.*, 2008). In the case of an integrated pulp and paper mill, CO_2 can be used in PCC production (Teir *et al.*, 2005). PCC is produced by blowing for example lime kiln flue gas through a calcium hydroxide solution. Typically, lime kiln flue gases are bubbled through green liquor. PCC production is typically fixed to meet the local demand. A possible production level could be 33 kg$CaCO_3$/ADt, corresponding to a CO_2 use of 20 kg/ADt.

4.4 Water electrolysis

Power-to-gas (PtG) is a process, where electricity is transformed into gas (Lehner *et al.*, 2014; Götz *et al.*, 2016). Power-to-gas and gas-to-power technologies have been considered primarily as a chemical storage option for intermittent renewable energy. It can be expected that when intermittent power production, such as solar and wind power, increases, also variation in the electricity price increases. PtG processes can then be used to store energy in gaseous form or to regulate power production when production exceeds consumption or the price of electricity is low. PtG and PtX processes offer interesting alternatives for kraft pulp mills, especially if the power production exceeds the mill's own consumption. PtX includes a growing number of concepts to produce gas, liquids, or chemicals using power-based synthesis processes (Agora Energiewende, 2014). In this thesis, hydrogen production is examined as an option to substitute for fossil fuels, but developing technologies can be expected to offer more options in the future in the form of a wider product portfolio. As an example, the production of hydrogen and available CO_2 resources on-site enable a methanation process. Hydrogen can be refined further to methane, which has various usage possibilities both as fuel and as raw material for chemical products. Hydrogen can also be used *e.g.* in the conversion of tall oil into renewable diesel (UPM Biofuels, 2015).

Water electrolysis is a process where electricity is used to split water into hydrogen and oxygen through the following reaction:

$$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g) + \text{(heat)} \qquad (4.3)$$

The reaction is exothermic, and thus the electrolysers need cooling. Cooling water can be utilized for heating purposes. Typically, hydrogen is the main product, but the use or sale of oxygen increases the profitability of the process. Hydrogen can be used for energy or refined further into other chemicals, such as methane. When renewable electricity is used for electrolysis, the produced hydrogen is renewable.

Hydrogen is a colourless, odourless and highly flammable gas with a high energy content, around 119 MJ/kg (lower heating value, LHV). It burns in the air at a wide range of concentrations and can be used in various energy production applications. The combustion of hydrogen causes hardly any emissions; pure hydrogen combusted in oxygen releases only water. However, the flammability makes the storage and transportation of hydrogen difficult, and although it has a high energy content in relation to mass, its energy content in relation to volume is poor. Therefore, the best option is to use hydrogen near the source, if possible. In a pulp mill, an electrolyser can act as online equipment, which eliminates the need for storage or further transportation and makes the process simpler and safer.

Alkaline electrolysers are commercial technology and used typically in up to 10 MW_e units in hydrogen production (Zeng and Zhang, 2010; Lehner *et al.*, 2014). It is also the most frequently used technology for an industrial-scale water electrolysis process (Götz *et al.*, 2016), and has therefore been chosen as the reference method for this study. Alkaline electrolysis (AEC) has the advantage of producing hydrogen of a high purity. The challenges of the technology are related to energy consumption, cost, and maintenance. The operating temperatures of the commercial processes are typically in the range of 70–90 °C (Lehner *et al.*, 2014).

Steam electrolysis using a solid oxide electrolysis cell (SOEC) is a hydrogen production process under development. It operates at high temperature, at 550–800 °C (Zeng and Zhang, 2010). The electrical energy consumption of water electrolysis is around 4.5 kWh/Nm^3 (H_2), while the consumption for the SOEC process could be significantly smaller at about 3 kWh/Nm^3 (H_2) (Udagawa *et al.*, 2007).

The alkaline electrolysis cell is composed of two electrodes (anode and cathode) and a liquid electrolyte, which are typically enclosed in a steel container. The electrolyte is usually 25–30% aqueous potassium hydroxide (KOH) (Zeng and Zhang, 2010). Water is consumed during the process, but the amount of KOH decreases only slowly over time due to process losses. The efficiency of an electrolysis system varies according to the system pressure and size. The power-to-gas process efficiency from electricity to hydrogen varies between 50–75% (Lehner *et al.*, 2014). A conventional alkaline electrolyser can be operated between 20–100% of the nominal capacity, but operation below 60% capacity will reduce both the system efficiency and the quality of the gas produced (Lehner *et al.*, 2014). Current electrolysers are suitable for conventional purposes where stable hydrogen production is needed. However, dynamic operation, which is required to intermittently adjust the electricity production of renewable energy sources to electricity consumption, is still a problem due to lower efficiencies and lower gas quality.

Alkaline electrolysis can be easily integrated with an existing pulp mill process. Hydrogen can typically substitute traditional lime kiln fuels without significant modifications to the combustion equipment. Hydrogen has been used as an additional fuel in, for example, Finland (Sarja *et al.*, 2012) and Uruguay (Saarela *et al.*, 2008). In these cases, hydrogen is a by-product of chemical plants adjacent to the pulp mills. Quality requirements for the water used in the electrolyser vary depending on the electrolyser type. In general, it can be assumed that an existing water treatment plant of a pulp mill can produce water that meets the requirements for the electrolyser. Additional water flow to the electrolyser adds to the load of the water treatment plant. Figure 4.2 shows the electrolysis integration concept in a kraft pulp mill.

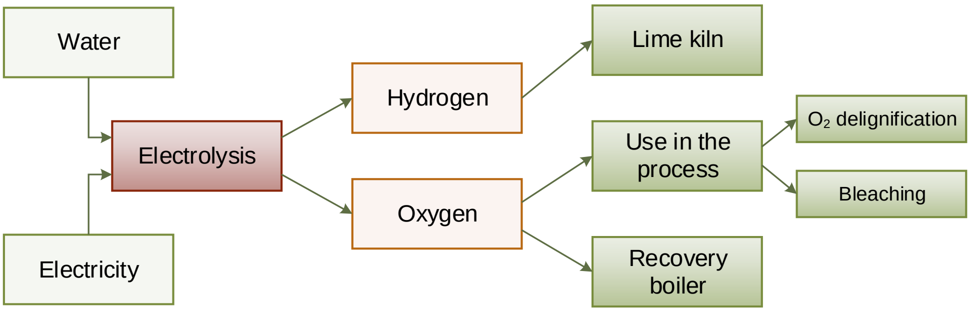


Figure 4.2. Water electrolyser as a part of the pulp mill process.

Pulp mills use oxygen in the pulping process, and it is often manufactured on-site. An integrated electrolyser can make separate oxygen production unnecessary. Oxygen is used in pulp mills for oxygen delignification and bleaching. The purpose of oxygen delignification is to remove residual lignin after cooking and before bleaching. Lignin is the primary factor influencing the pulp colour. Lignin removal before bleaching reduces emissions of the mill.

5 Implications

5.1 Basis for the reference mill calculations

5.1.1 Millflow

The effect of the studied concepts on pulp mill operations were studied by calculating mass and energy balances for chosen reference mills. The calculations were carried out using the updated Millflow programme, which is a mill spreadsheet including a detailed mass and energy balance. Millflow has been developed at Lappeenranta University of Technology (Vakkilainen and Kivistö, 2008; Hamaguchi *et al.*, 2011).

The Millflow balances are based on literature (Adams and Frederick, 1988; Grace and Malcolm, 1989; Gullichsen and Fogelholm, 1999a; Gullichsen and Fogelholm, 1999b), data from operating mills, and practical experience, *e.g.* the Gunns project (Jaakko Pöyry Oy, 2006). Millflow has previously been used to pulp mill design by equipment vendors and in preliminary studies for lignin removal, for example by Vakkilainen and Kivistö (2008). The accuracy of the models has been verified in projects with pulp and paper companies during the last decade by comparing the balance values with real operating values of existing mills. The models have also been compared with other pulp mill models, such as WinGems (Cardoso *et al*., 2009) and the model by Kangas *et al*. (2014).

Pulp mill balances consist of hundreds of calculations, which makes it challenging to introduce them in detail. The Millflow programme includes detailed balances for each mill department (Hamaguchi *et al.*, 2011). Figure 5.1 represents the primary inputs and outputs for each mill department. Table 5.1 gives the definitions for inputs and outputs presented in the figure.

In the programme, the pulping line is dimensioned based on the desired capacity of the mill. The wood demand is calculated based on the cooking yield and losses in the process stages, and the chemicals demand is calculated from the digester balance. The programme includes a black liquor calculation tool to define the inputs for the recovery boiler calculations, such as the dry solids flow, the composition, and the heating value of black liquor. The black liquor calculation tool is partly based on correlations from a black liquor database (Vakkilainen, 2000), and Hamaguchi *et al.* (2011) improved it by taking into account the lignin removal. The lime kiln calculations require that inputs such as the type of make-up lime, the amount of residual lime, and the availability of burnt lime be defined. Appendix B presents examples on the balance calculations: the cooking balance, the black liquor heating value calculations, and the balance of the evaporation plant.

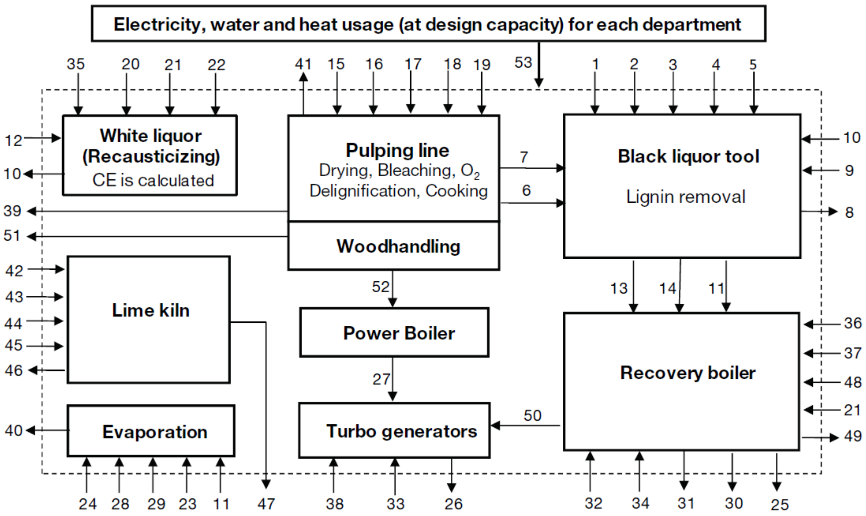


Figure 5.1. The main inputs and outputs for the Millflow balances. (Hamaguchi *et al.*, 2011)

Table 5.1. Description of inputs and outputs presented in Figure 5.1. Modified from Hamaguchi *et al.* (2011).

ID	Description	ID	Description
1	Lignin heating value, MJ/kg	27	HP steam flow, power boiler, t/h
2	Wood composition, wt-%	28	Strong liquor virgin concentration, %
3	Heating values of inorganics (Na_2S, K_2S)	29	Steam economy, kJ/kgH_2O
4	Organics heating values (acids, etc)	30	Flue gas generation, Nm^3/h
5	Washing efficiency of pulp, %	31	Air ratio, excess air, %
6	Dry wood demand, t/h	32	Blowdown and sootblowing, kg/s
7	Dry unbleached pulp, t/d	33	All steam requirements (kg/s, °C, bar)
8	Lignin in pulp, kg/ADt	34	HP steam parameters (°C, bar)
9	Lignin removal rate, %	35	Cl and K content in liquor, wt-%
10	Inorganic compounds in WL, kg/BDt	36	Combustion air temperatures, °C
11	Dry solids generation tDS/d	37	Recycled ash (% of variable 11)
12	Formation rate of $S_2O_3^{2-}$ and SO_3^{2-}, %	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, %	41	Pulping line required capacity, ADt/d
16	Equipment losses, %	42	Availability of burnt lime, %
17	Effective alkali charge as NaOH, %	43	Availability of make-up lime, %
18	Desired bleached pulp capacity, ADt/a	44	Residual lime and $CaCO_3$ in lime mud, %
19	Dilution water in pulp washing, kg/ADt	45	Kiln heat requirement, MJ/kg
20	Sulfidity, %	46	Amount of lignin to be burned, t/d
21	Reduction, %	47	Kiln required capacity, t lime/d
22	Active alkali charge, gNaOH/l	48	Recovery boiler furnace area, m^2
23	MP steam/total steam usage, %	49	HHRR and heat load, kW/m^2 and MW
24	Additional load to be evaporated, t/h	50	HP steam flow, recovery boiler, t/h
25	Smelt production, kg/s	51	Wood handling required capacity, m^3/d
26	Power generation, MW	52	Bark to burning, BDt/d

Millflow includes a comprehensive energy balance and is therefore well suited for use in this study. The electricity generation is calculated from the turbogenerator balances after defining the steam flows from the recovery boiler and the biomass boiler. The electricity and heat usage per unit of production in each department of the mill is used to define the steam balance. The condensing tail flow sets the steam balance. Typical departmental energy consumption values can be found in literature (Nieminen, 2007; Vakkilainen and Kivistö, 2014).

The energy balance and the changes in it due to the studied process integrations are in the focus of the thesis work. The actual pulp mill model was not modified during the work, and the main parameters of the pulping process act as input values. The pulp production remains unchanged, and thus the fibre line operations are kept constant. During this study, an electrolyser and a carbon capture unit were added to calculate how they affect the balances.

5.1.2 The reference mill processes

Two different types of reference mills were used during the course of the research. Biomass fuel and electrolysis concepts were calculated for a South American eucalyptus kraft pulp mill. Biogas and pulverized wood concepts were calculated also for a softwood kraft pulp mill located in Northern Europe. The CCU concept was estimated for the southern mill and for the northern mill. The mills represent typical modern mills in their chosen location.

The southern mill (Mill S) is a large stand-alone kraft pulp mill producing bleached pulp from eucalyptus. Its annual pulp production is 1.5 million ADt. The amount of wood residue was calculated based on the assumption that one third of the incoming wood is delivered at a bark content of 10 wt-% and two thirds at 2 wt-% due to forest-debarking. Additionally, wood losses of 1.5 wt-% in screening and 3 wt-% in debarking was taken into account. Steam is generated in the recovery boiler only, and no separate power boiler exists. The recovery boiler is able to cover the energy demand of the mill, which is typical for a modern stand-alone mill. Steam is used in the mill processes and for power generation in a turbogenerator. The lime kiln is fired with oil. Low temperature heat flows are abundantly available to, for example, dry biomass residue. The electricity generation exceeds the mill power requirements, and thus the sale of excess electricity is possible. Hamaguchi *et al.* (2011) presented a more detailed description on the design conditions of the southern mill. The main mass and energy flows of the southern mill are depicted in Figure 5.2.

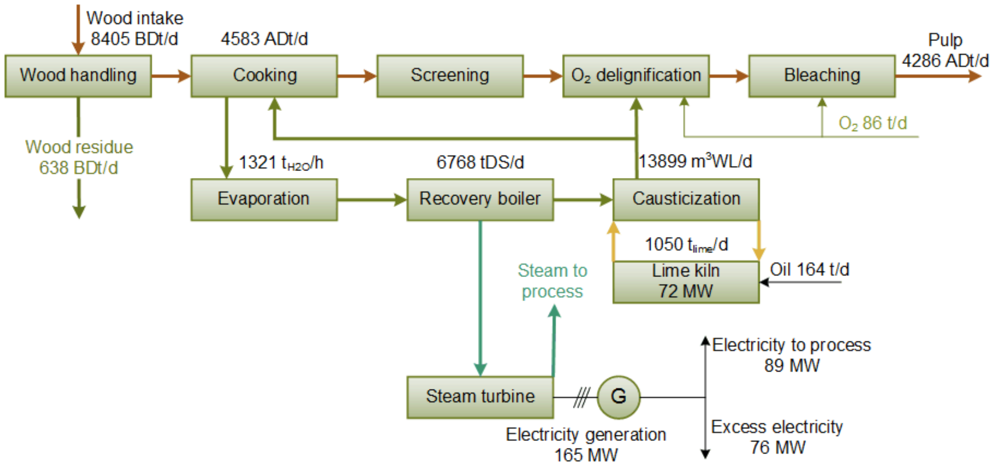


Figure 5.2. The operations and main mass flows of the southern reference mill (Mill S).

The northern mill (Mill N) is a large softwood kraft pulp mill with integrated papermaking. Its annual pulp production is 1.4 million ADt. The integrated paper mill produces coated and uncoated paper and is a notable additional energy consumer. The recovery boiler and a separate biomass boiler produce steam for use in pulp and paper production and for electricity generation in a turbogenerator. All residue from the wood handling process is combusted in the biomass boiler. The lime kiln is fuelled with natural gas, which is typical when the mill is located near the natural gas grid. Figure 5.3 shows a simplified block diagram of the northern reference mill. The main process values of the reference mills have been collected into Table 5.2. Appendix A presents the detailed balances of the reference mills.

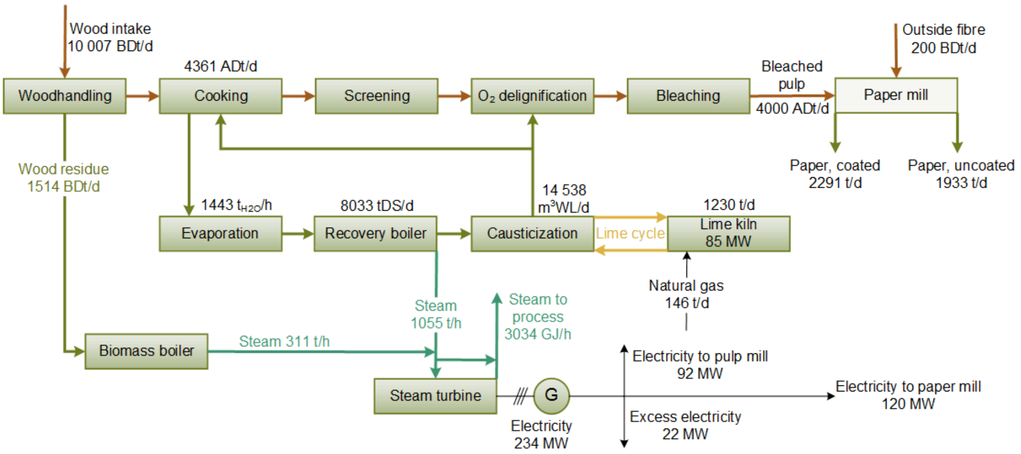


Figure 5.3. The operations and main mass flows of the northern reference mill (Mill N).

Table 5.2. The reference mill operations and the main process flows.

	Unit	Mill S	Mill N
Production			
Operating hours	h/a	8400	8400
Pulp production	ADt/d	4286	4000
Paper production	t/d	-	4224
Wood handling			
Wood income	BDt/d	8405	10 007
Residue	BDt/d	638	1541
Wood moisture	-	45%	50%
Recovery boiler			
Black liquor flow	tDS/d	6768	8033
Net steam flow	t/h	890	1055
CO_2 production	t/d	7524	8957
Biomass boiler			
Biomass fuel use	BDt/d	-	1514
Net steam flow	t/h	-	311
CO_2 production	t/d	-	3087
Lime kiln			
Lime production	t/d	1050	1230
Make-up limestone	t/d	77	60
Heat requirement	MW	72	85
Fuel consumption	t/d	164	146
CO_2 production	t/d	1099	1132
Share of biogenic CO_2	-	55%	64%
Energy			
Steam use, pulp mill	t/h	660	813
Steam use, paper mill	t/h	-	401
Power generation	kWh/ADt	925	1406
Power consumption, pulp mill	kWh/ADt	501	552
Power consumption, paper mill	kWh/t	-	681

5.1.3 Properties of alternative lime kiln fuels

Fuel properties affect the operation of the lime kiln. The properties of the studied renewable fuels were compared with the fossil fuels typically used in lime kilns; Table 5.3 shows the results. Lime kiln operation requires stable combustion conditions as well as an easily controllable hot-end temperature. Therefore, stable and consistent fuel quality is required. Variations in the fuel heating value and moisture affected the flow and temperature profile of the flue gas.

Table 5.3. Properties of the studied alternative fuels compared with the most commonly used fossil fuels (Alakangas, 2000; Moilanen *et al.*, 2002; Isaksson, 2007; Vakkilainen and Kivistö, 2008; Suomen Kaasuyhdistys, 2010; Torrec Oy, 2014).

Fuel	Lower heating value [MJ/kg]	Adiabatic flame temperature [°C]	Contaminants
Hydrogen	120	2210	No
Biogas	6-30	1870	Some
Torrefied biomass	20-30	1840	Substantial
Lignin	17-26	1980	No
Wood	12-19	1950	Substantial
Natural gas	50	2050	No
Oil	41	2210	Some

The combustion of biomass-based fuels lowers the hot-end temperature in the kiln due to the lower adiabatic flame temperature (Isaksson, 2007). To maintain the kiln production capacity, higher firing rates were required, which caused an increase in the back-end temperature and a higher flue gas heat loss. Therefore, in the case of biomass fuels, an additional increase of 3% in fuel consumption based on input lower heating value (LHV) was assumed.

5.2 Implementation of the studied concepts

5.2.1 Biomass processing

Flue gas or secondary heat in the form of hot or warm water as well as recovered steam from the pulping process can be used for drying. There is a considerable risk of fire in the fuel feeding system when flue gas is used for drying wood (Wadsborn *et al.*, 2007). Due to fire safety, the use of low pressure steam or hot water to heat the drying air is recommended. In the calculations, a moisture content of 45% was assumed for the received biomass residue in the southern mill and 50% in the northern mill. 65 °C water from the mill processes was used for drying. The biomass processes were scaled to meet the heat demand of the lime kiln, considering the available resources.

Electricity consumption in grinding depends on the type of material and required particle size. When a rotating grinder and a belt drier is chosen, the electricity consumption for pretreatment was estimated at 192 kWh/t based on proprietary vendor data.

For pulverized wood firing, the required average particle size is below 1 mm. The electricity consumption of pulverization using hammer mills is roughly 50 kW/MW_{th}, based on proprietary vendor data. In previous trials (Wadsborn *et al.*, 2007), the most common problems with pulverized wood firing were fires in the fuel feeding system and clogging in the hammer mills. Unplanned shutdowns of the fuel feeding system require the use of fossil fuels unless a backup renewable system exists, thus increasing costs. Make-up lime use increases due to contaminants in the fuel. In the case of pulverized wood, an increase of 3 kg/ADt was assumed for these calculations. The moisture content of the residue after drying is 10%. Figure 5.4 presents the pulverized wood firing concept for the southern reference mill and Figure 5.5 for the northern reference mill.

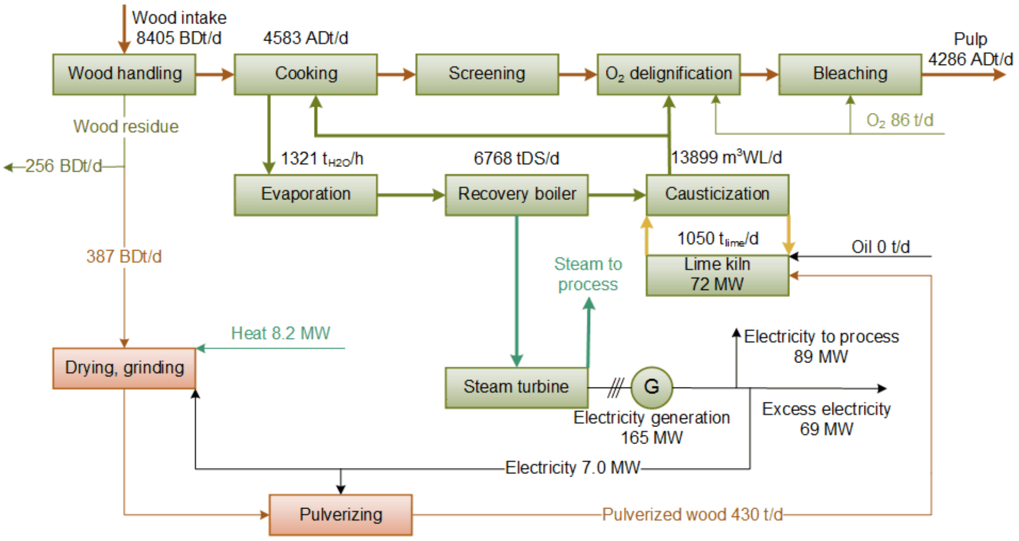


Figure 5.4. The pulverized wood concept for the southern reference mill.

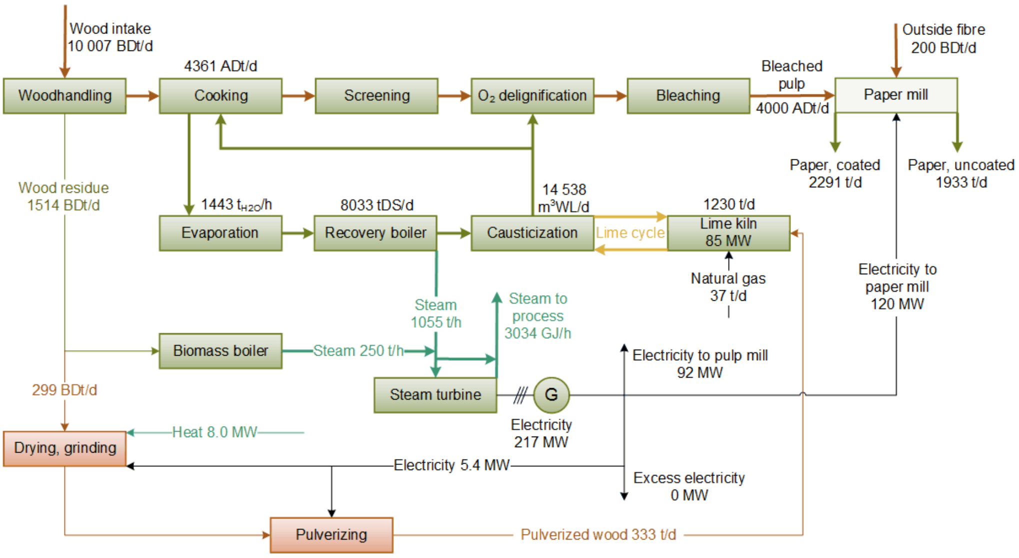


Figure 5.5. The pulverized wood concept for the northern reference mill.

In the torrefaction case, the energy content of the torrefied biomass was set at 18.7 MJ/kg (LHV) based on the experimental results of the torrefaction of eucalyptus (*Eucalyptus* *grandis*) wood and bark (Almeida *et al.*, 2010) with an operating temperature of 250 °C and a residence time of 1 h. The mass loss is estimated at 19% (dry basis) and the thermal efficiency (LHV) of the torrefaction process at 90% (Bergman, 2005; Basu, 2010; Schorr *et al.*, 2012). Size reduction is relatively easy for torrefied wood due to its brittleness. Size reduction of torrefied wood consumes 70–90% less energy than pulverized wood (Bergman, 2005). Figure 5.6 presents the torrefied biomass concept for the southern reference mill. The biomass is pre-dried before torrefaction, and pulverized torrefied biomass is fed into the lime kiln. Also for torrefied biomass, a make-up lime addition of 3 kg/ADt was estimated.

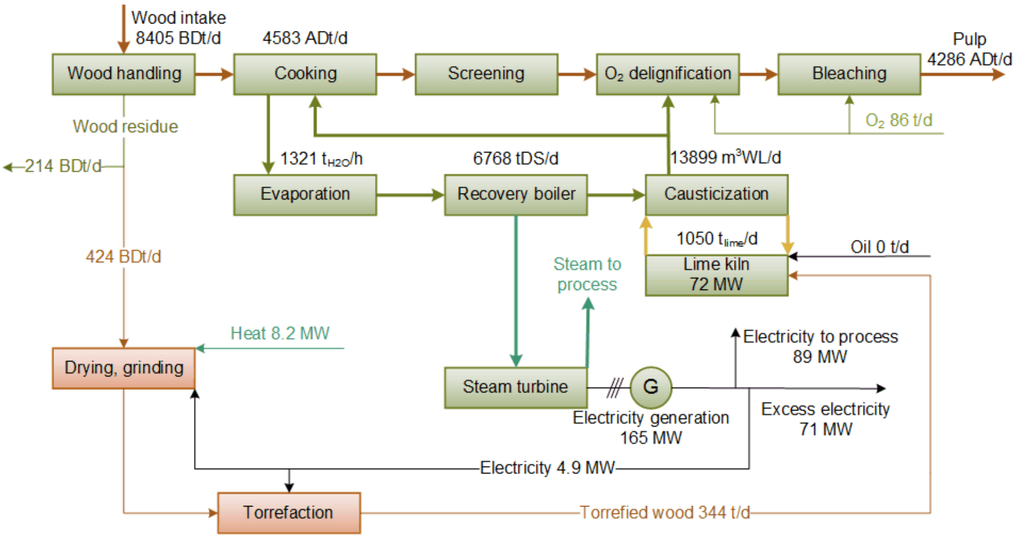


Figure 5.6. The torrefaction of biomass residue to fuel the lime kiln in the southern reference mill process.

When biomass is gasified, part of the ash exits the gasifier with the bottom ash. If 50% of the ash ends up in the lime kiln, which is a probable amount, the make-up lime use increases 50–100% compared with fossil fuel use (Isaksson, 2007). An increase of 2 kg/ADt was assumed for the calculations. Before the gasifier, a 15% moisture content and an average particle size of 6 mm were used. These are recommended values for a CFB gasifier (McKendry, 2002; Basu, 2010). The gasifier efficiency was estimated at 85% on LHV basis (Basu, 2010). Figure 5.7 displays the biomass gasification concept for the Mill S and Figure 5.8 for the Mill N.

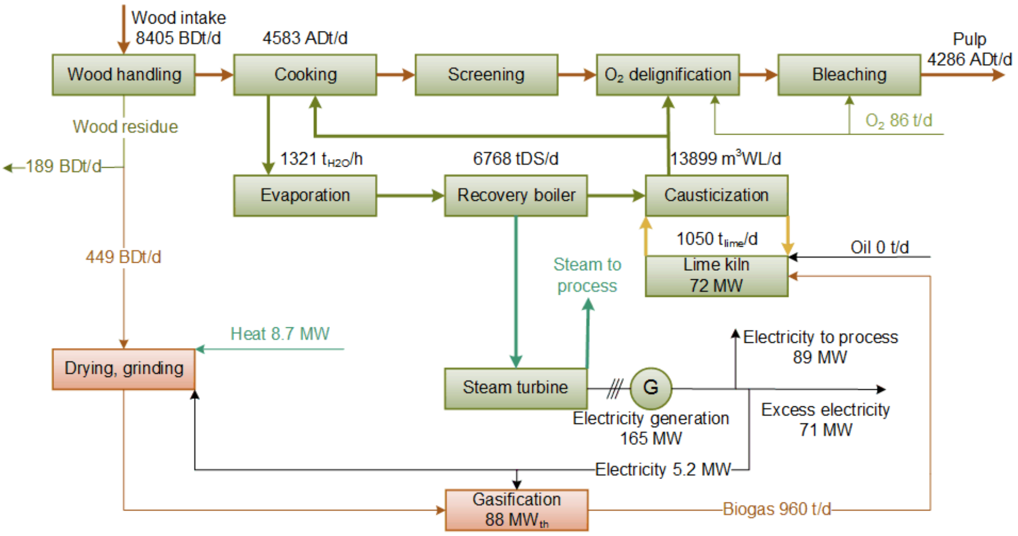


Figure 5.7. The biomass gasifier integrated in the southern reference mill process.

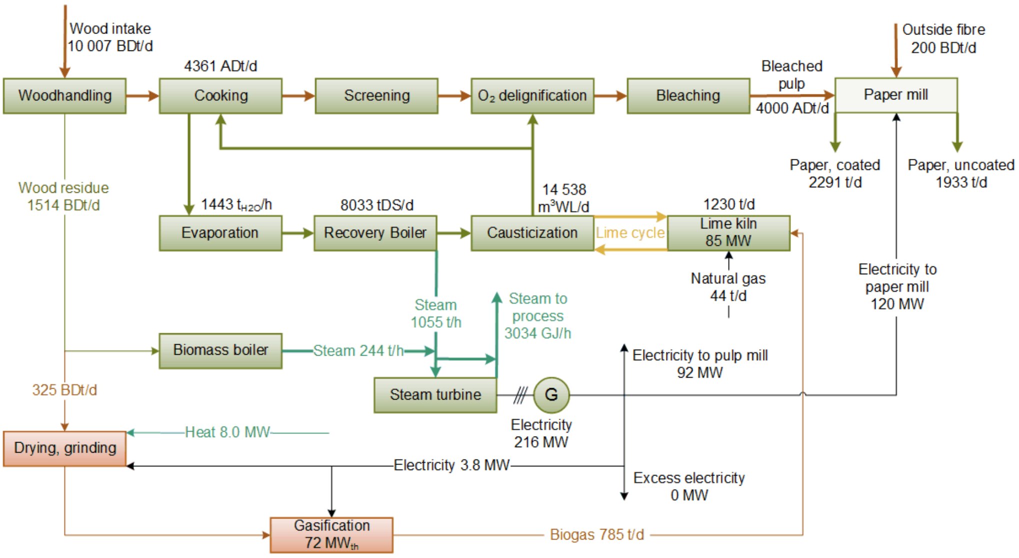


Figure 5.8. The biomass gasifier integrated in the northern reference mill process.

5.2.2 Lignin extraction

Lignin extraction affects the properties of black liquor and reduces the steam generation at the recovery boiler. Also, the washing of precipitated lignin increases the load of the evaporation plant because the washing filtrates are returned to the evaporation (Hamaguchi *et al.*, 2011). In the calculations in this work, an increase of 2 kg per kg of extracted lignin was taken into account, but it was assumed that the nominal capacity of the evaporation plant could be kept unchanged.

Electricity consumption in the lignin removal process was estimated at 80 kWh/t (Laaksometsä *et al.*, 2009). Additional electricity consumption of 0.3 MW for drying and pulverizing was included. In the studied concept, lignin removal was scaled to meet the lime kiln heat demand, and pulp production was kept at the base case level. Figure 5.9 depicts the main mass and energy flows. To fire the lime kiln, 280 t/d lignin at 10% moisture was needed. This was equal to a 16% extraction rate from black liquor.

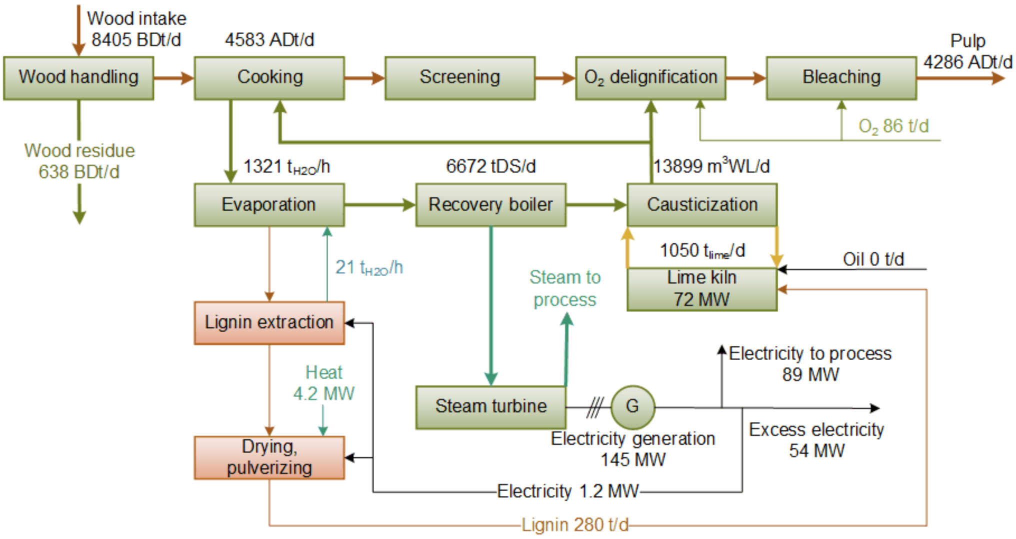


Figure 5.9. The main process flows of the lignin extraction process integrated in the southern reference mill.

5.2.3 Electrolysis

The alkaline electrolyser was modelled based on literature (Ulleberg, 2003; Diéguez *et al.*, 2008; Zhou and Francois, 2009). The following assumptions were made:

- The oxygen and hydrogen produced were considered pure and ideal gases.
- The feed water quality was considered to meet the requirements for boiler water. Requirements for water quality vary with the type of electrolyser (Ivy, 2004).
- The gas and liquid phases were assumed to be kept separate.
- Atmospheric pressure was assumed. The operating pressure has an influence on the cell voltage, but it is small (Lehner *et al.*, 2014).
- The system temperature was considered constant; all heat generated during the process was assumed to be removed with cooling water.
- The electricity requirement of auxiliary systems was assumed at 8% of the electrolyser capacity (Mohseni *et al.*, 2012).

The electricity consumption in relation to the hydrogen production is approximately 50 kWh/kgH_2 with this model, corresponding to the recent state of electrolyser development (Bertuccioli *et al.*, 2014). In the future, the efficiency can be expected to increase along with process development and more advanced technologies (Götz *et al.*, 2016), which will affect the feasibility of the processes accordingly.

In the southern reference mill case, electrolysis is an alternative to power sale. The amount of excess electricity limits the size of the electrolyser. As only the recovery boiler is used for steam generation but residual biomass is available, additional electricity could be produced using a biomass boiler.

Two electrolysis cases of different configurations were studied:

A. The electrolysis process is scaled to meet the oxygen demand of the mill. Hydrogen is combusted in the lime kiln to replace as much fossil fuel as possible.
B. The electrolysis process is scaled to meet the lime kiln fuel demand, considering the maximum amount of electricity available for electrolysis. The generated oxygen is used firstly at the mill, and secondly, to boost the recovery boiler by use of oxygen enriched air combustion (Verloop *et al.*, 2001).

In the calculations, the cooling of the electrolyser is integrated as a part of the mill water system, and the generated heat can be utilized at the mill, if needed. The cooling water inlet temperature is 45 °C and the outlet temperature 75 °C, with a reaction temperature of 80 °C. The feed water for the electrolyser comes from the pre-existing water treatment plant of the mill.

The estimated oxygen charge in the delignification process is 16 kg/ADt, which corresponds to a typical charge (Gullichsen, 1999a); in addition, 2 kg/ADt is used for oxidized white liquor. During bleaching, 2 kg/ADt is assumed after also considering caustic make-up as a charge to the oxygen delignification stage. Oxygen use in the Mill S is then 86 t/d.

Oxygen can be separated from air using a cryogenic separation process or by absorption. Cryogenic separation is more common in pulp mills. Cryogenic separation produces oxygen of a high maximum purity of 99.9%, while the maximum purity of on-site installed absorption processes is 95% (Gullichsen, 1999b). The specific power demand for the cryogenic process varies between 200 and 550 kWh/tO_2, depending on the unit size and required oxygen purity, and for the absorption process between 265 and 350 kWh/tO_2 (Gullichsen, 1999b; Kauranen, 2008; Janusz-Szymańska and Dryjańska, 2015).

Oxygen enriched air technology (OEA) was presented by Verloop *et al.* (2001) as a method to increase the oxygen content in a boiler inlet from the 21% in plain air. This resulted in a smaller amount of flue gases and the possibility to increase the capacity of an existing recovery boiler. OEA was found to increase a boiler's black liquor dry solids burning capacity by approximately 10–20% by using nominally 25% oxygen at the secondary and tertiary air levels. The technology increased the combustion temperature, which resulted in more rapid and stable combustion and less emissions; namely, lower total reduced sulphur, sulphur dioxide, and carbon monoxide levels.

Figure 5.10 depicts the main process flows for the hydrogen case A. To cover the oxygen demand, the required electrolysis power is 22.4 MW. With auxiliary systems consuming 8% of the electrolysis capacity, the electricity consumption of the process is 24.2 MW. Hydrogen production is 10.8 t/d, which covers 21% of the fuel demand of the lime kiln. The oil demand is thus 131 t/d. The electricity consumption in mill processes decreases by 3.3 MW due to no need for separate oxygen production.

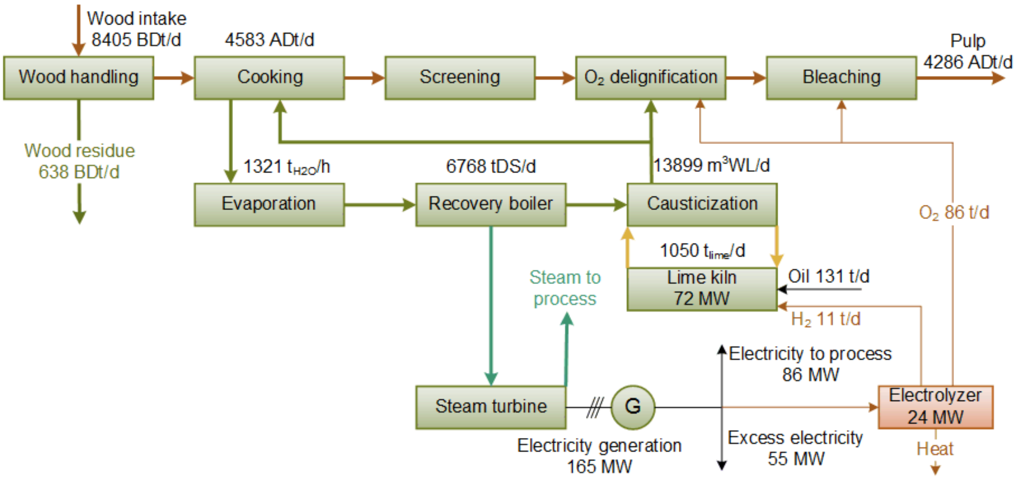


Figure 5.10. The main process flows in the hydrogen case A, where the electrolyser capacity is scaled to meet the oxygen demand of the mill.

In the hydrogen case B, the amount of available electricity limits the electrolyser capacity. The lime kiln heat requirement is 72 MW. To fully replace fossil fuels in the kiln, 52 t/d hydrogen is required, which corresponds to electrolyser power of 108 MW. Without additional electricity generation, 79 MW is the maximum amount available for the electrolyser, including the use of auxiliary equipment. Hydrogen production can then be calculated at 38 t/d, which covers 73% of the kiln heat demand. The oil demand for the kiln is 45 t/d. The oxygen production from the electrolyser is 302 t/d. Figure 5.11 depicts case B. Table 5.4 compares the main process values between cases A and B.

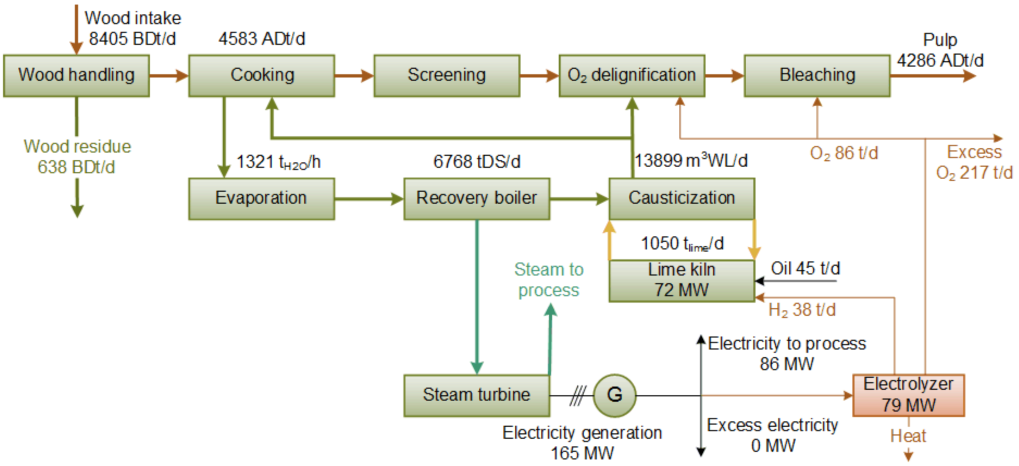


Figure 5.11. The main process flows of the hydrogen case B, where the amount of available electricity limits the electrolyser capacity.

Table 5.4. The main process variable in the hydrogen cases.

Variable	Unit	Case A	Case B
Electrolysis power consumption	MW	24.2	79
Hydrogen production	t/d	10.8	38.1
Oxygen production	t/d	85.7	302.4
Feed water flow	t/d	97	343
Cooling water flow	t/d	5 078	14 019
Cooling water inlet temperature	°C	45	45
Cooling water outlet temperature	°C	75	75
Reaction temperature	°C	80	80
Electricity for sale	MW	55	0
Oil requirement for the lime kiln	t/d	131	45
Reduction in CO_2 emissions[1]	tCO_2/a	35 450	124 060

[1] Compared with the case without an electrolyser.

5.2.4 CO_2 capture

The potential to capture and reuse CO_2 was analysed by calculating the both reference mill cases. The primary CO_2 streams from the mill operations are shown in Figure 5.12 for the southern mill and in Figure 5.13 for the northern mill. The primary CO_2 sources are the combustion processes, namely, the recovery boiler and the lime kiln, and in the northern mill, also the biomass boiler. The recovery boiler is the largest of these point sources. The biomass boiler in the northern mill is assumed to combust all generated biomass residue, and the amount of CO_2 is calculated accordingly. The figures represent a normal operation situation, and therefore, fossil fuels used during start-ups and shutdowns are not shown. The CO_2 from fossil fuels used during start-up and shutdown can be estimated at 10–20 $kgCO_2/ADt$. The lime kiln produces both fossil, fuel-based

CO_2, and biogenic CO_2 originating from the lime reburning reaction. In the reference mill cases, 55% of lime kiln CO_2 is biogenic in the southern mill, and 64% in the northern mill.

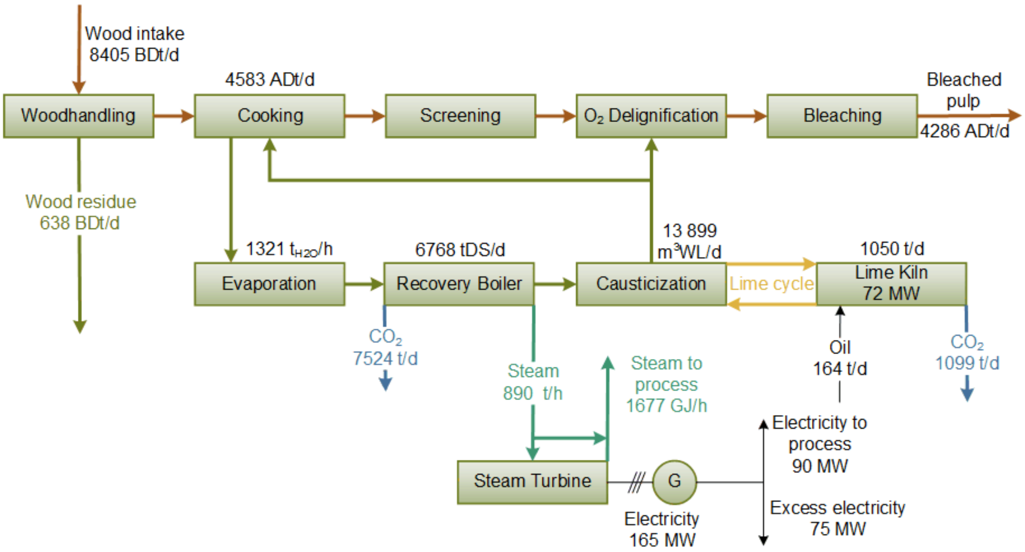


Figure 5.12. The primary CO_2 sources in the southern mill.

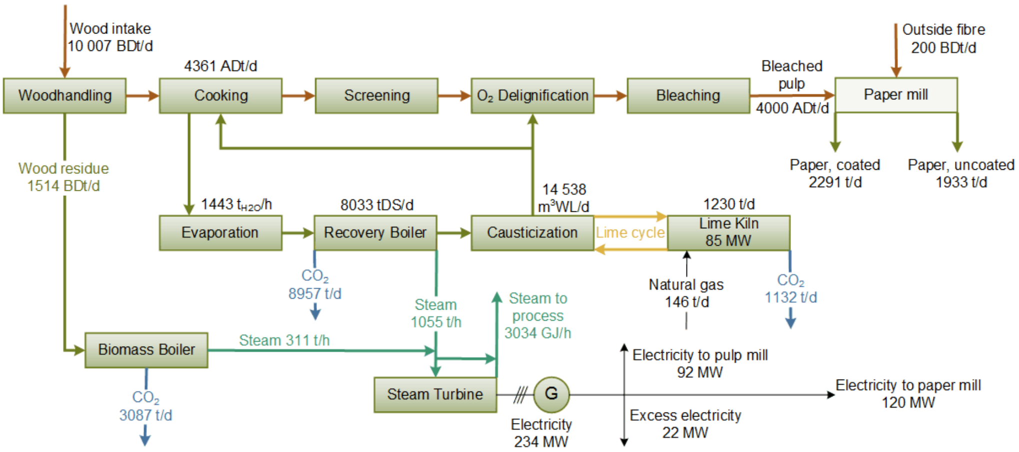


Figure 5.13. The primary CO_2 sources in the northern mill with integrated papermaking.

Considering only carbon flows across the plant borders presented in the figures above, a simplified carbon balance and net CO_2 emissions from the process ($CO_{2,net}$) can be defined for the process as follows:

$$CO_{2,net} = (C_f + C_{CaCO3})\frac{M_{CO2}}{M_C} - \eta_{CCU}\eta_{CC}CO_{2,total} \quad (5.1)$$

where η_{CC} is the share of CO_2 removed from the total CO_2 emissions ($CO_{2,total}$) and depends on the capture method and how it is applied. η_{CCU} gives the effect of selected CO_2 utilization and storage route on CO_2 emissions, where 100% means that all captured CO_2 is permanently removed from the atmosphere without additional emissions from the storage or utilization process. C_f and C_{CaCO3} are carbon flows into the plant in fossil fuel and limestone makeup streams. M_{CO2} and M_C refer to molar masses of CO_2 and C.

It is most likely not feasible to apply CO_2 removal to all possible CO_2 streams, but rather to consider only the largest one(s). For example, in the northern mill and the southern mill, the shares of total emissions from the recovery boiler are 68% and 87%, respectively. If the efficiency of the CO_2 capture process is 90%, it follows that for the northern mill, $\eta_{CC,N}$ = 61%, and for the southern mill, $\eta_{CC,S}$ = 78%. Depending on the CO_2 source and emissions of electricity production, in CO_2 to fuels conversion, emissions in the CCU route may exceed the fossil emissions (Abanades *et al.*, 2017). Net negative CO_2 emissions can be reached only if at least part of the captured CO_2 is permanently removed from the atmosphere. For the two studied mill types where the capture process is applied only to the recovery boiler, the net specific CO_2 emission curves show substantial recovery potential for a single mill (Figure 5.14). Specific emissions vary largely depending on the capture process efficiency and the CO_2 emissions of the utilization route.

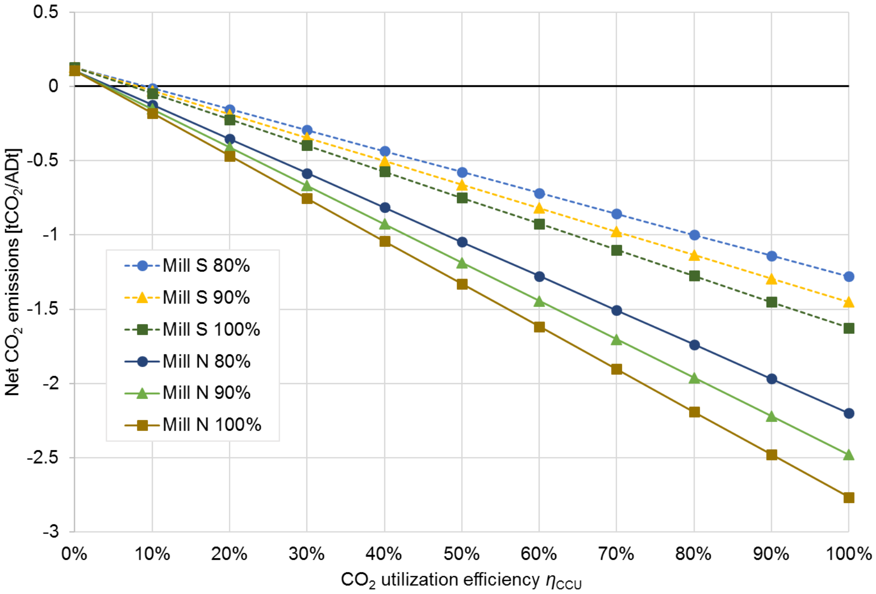


Figure 5.14. Net CO_2 emissions per produced air-dry ton of pulp from the reference mills for different capture efficiencies (80%, 90%, 100%), when CO_2 capture is applied only to recovery boiler flue gases.

CO_2 capture processes are energy-intensive, and therefore, the effect of the process on the reference mill energy balances was estimated. Table 5.5 presents the results. An MEA-based post-combustion process and capture from the recovery boiler flue gas flow were chosen for the calculations. The consumption of low-pressure steam, cooling water and electricity was estimated based on a previous study (Onarheim *et al.*, 2015).

Due to integrated paper production, the northern mill is a large energy consumer compared with a stand-alone pulp mill. Additional steam used in CO_2 capture reduces electricity generation. If the energy use is limited to the mill's own production, availability of electricity sets the maximum limits for the capture process. Without additional electricity, 21% of CO_2 in the recovery boiler flue gas flow can be captured. This equals 14% of the total CO_2 of the mill. If carbon capture is used together with another process influencing the energy balance, such as lignin extraction, energy adequacy may become an issue.

The southern mill is a stand-alone pulp mill where electricity is produced substantially in excess of the mill’s own use. In this case, the limiting factor is the adequacy of steam, when steam is produced only in the recovery boiler and no additional boiler exists. The capture process consumes low-pressure steam. Based on the steam balance calculations, the maximum capture rate from the recovery boiler flue gas flow is 32%, which equals a capture rate of 28% of the total CO_2 emissions of the mill. The mill steam consumption then increases by 22%. Electricity consumption increases by 12% and production decreases by 10%.

Table 5.5. The effect of the carbon capture process in the energy balances of reference mills, when an MEA-based post-combustion process is used to capture CO_2 from recovery boiler flue gas.

	Unit	**Mill N Base**	**Mill N CC**	**Mill S Base**	**Mill S CC**
CO_2 capture	t/d	-	1881	-	2378
Mill steam use	t/h	1109	1225	860	807
Power generation	MW	234	221	195	149
Power consumption	MW	212	221	90	101

5.2.5 CO_2 utilization

On-site utilization of CO_2 was estimated considering the existing utilization routes presented in section 4.3. Tall oil production was considered only for the northern mill because in eucalyptus mills, tall oil is rarely recovered due to pulp properties. PCC production was also considered for the northern mill due to integrated paper production. A lignin separation rate of 20% was chosen for both mills.

Compared with carbon capture potential, the utilization possibilities are currently small. Considering the CO_2 requirement of the above-mentioned utilization processes, the required carbon capture rates at the reference mills vary from 0.2% to 21.6% depending on the chosen process/processes and the CO_2 source (Table 5.6).

Table 5.6. Required CO_2 capture rates to cover selected CO_2 utilization processes in the reference mills. Capture rates are calculated for the flue gases from the recovery boiler, the biomass boiler, and the lime kiln.

	CO_2 capture rate		
Mill N	**Recovery boiler**	**Biomass boiler**	**Lime kiln**
Tall oil production	0.2–0.3%	0.5–0.8%	1.4–2.1%
PCC production	0.9%	2.6%	7.1%
Lignin separation	1.6%	4.5%	12.4%
Tall oil + PCC + Lignin	2.7%	7.9%	21.6%
Mill S			
Lignin separation	1.1–1.8%	-	7.0–11.7%

The main process flows with integrated CCU processes are presented in Figure 5.15 for the northern mill and in Figure 5.16 for the southern mill. For the northern mill, the three possible options are shown, although the implementation of each of them simultaneously would require the generation or purchase of additional electricity. This results from increased electricity consumption due to new processes and a decrease in steam generation in the recovery boiler due to lignin extraction. Capture from the recovery boiler flue gas was chosen except for PCC production, where the use of lime kiln flue gas is a customary choice.

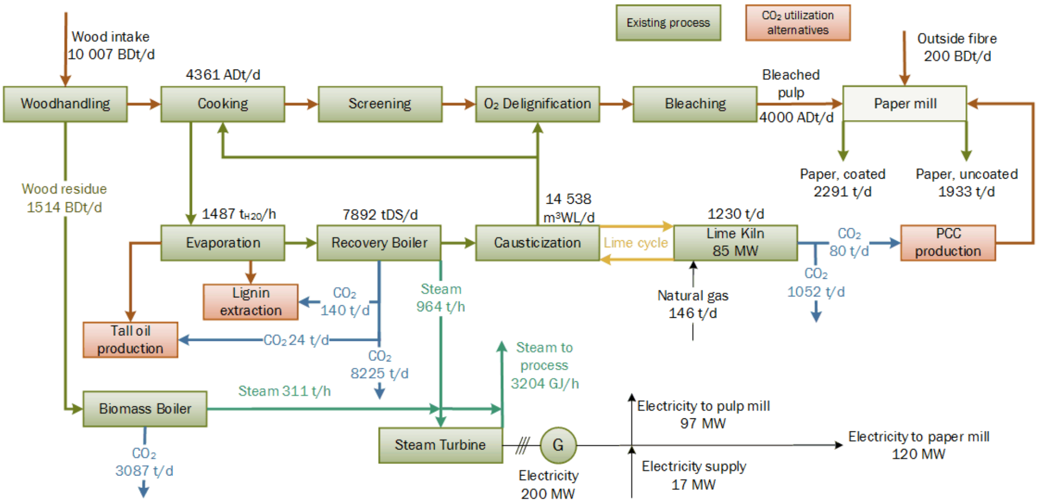


Figure 5.15. The main process flows for Mill N with the studied CCU processes.

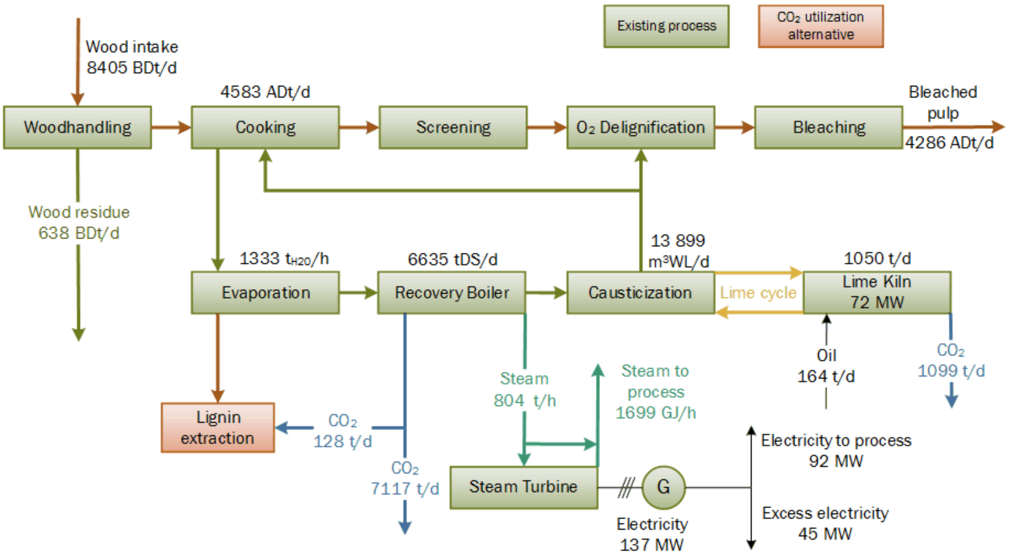


Figure 5.16. The main process flows for Mill S when CO_2 from the recovery boiler is utilized for lignin extraction.

5.3 Evaluation of economic feasibility

The costs of each renewable lime kiln fuel scenario depend on the needed process and auxiliary equipment including possible storages. Figure 5.17 compares the process stages in each studied concept. For biomass fuels, the pretreatment processes have considerable impact on the process costs. Hydrogen production using alkaline electrolysis is a developing technology, and it can be expected that the price will decrease in the near future as power-to-gas processes become more common.

Investment and operational costs for the selected processes were estimated based on information from recent projects and proprietary vendor data. None of the studied wood residue based processes is commonly used. Electrolysers have not been previously used in pulp mills on this scale, nor for this purpose. The economic evaluation of the concepts is challenging due to uncertainties and a lack of references related to prices, local conditions, and the size of required storage. Consequently, the results should be considered as best estimates with no better than ±30% accuracy.

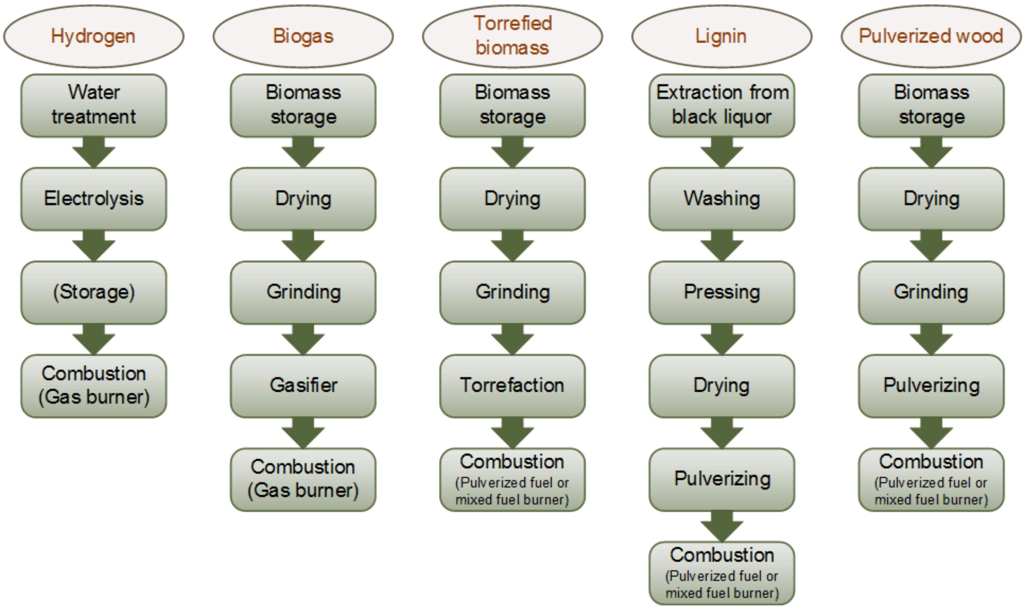


Figure 5.17. The process stages for each of the studied renewable lime kiln fuel options.

A lifetime of 20 years, an interest rate of 10%, an operation time of 8400 h/a, and operation and management costs in the range of 5% of the investment were assumed for all the cases. Table 5.7 gives other assumptions made for the economic analysis. Possible incentives for renewable fuel use or savings from costs of carbon dioxide emissions can affect the cost-effectiveness of the fuel choice, but these were not taken into account in the southern mill calculations. Although there are plans for emissions trading in South America, they have not yet been put into action (ICAP, 2018). In the EU, the Emissions Trading System (ETS) has the purpose of guiding industrial operators towards emission reduction. Therefore, the EU ETS allowance price was taken into account in the northern mill calculations based on the recent market development at the time of writing.

In the southern mill calculations, it was assumed that biomass has a market value. This value, however, can vary depending on the local conditions, and it may even have a disposal cost instead. The northern mill uses biomass for electricity generation; the value of biomass was then estimated based on the electricity sale price. The value of replaced oxygen is case-specific and dependent on sourcing because oxygen can be produced on-site or purchased. When comparing the investment costs, it should be noted that some renewable fuel options cover the heat demand of the lime kiln only partly, while the others were considered as the sole fuel to be fired.

Table 5.7. Basis for the economic evaluation for the lime kiln fuel concepts.

	Unit	**Hydrogen A**	**Hydrogen B**	**Biogas**	**Torrefied biomass**	**Lignin**	**Pulverized wood**
Investment –Mill S	M€	16.1	56.2	35.0	35.7	63.1	38.0
Investment –Mill N	M€			28.7			33.2
Biomass	€/BDt	-	-	40	40	-	40
Water	€/m^3	0.4	0.4	-	-	-	-
Oxygen	€/t	43	43	-	-	-	-
Make-up lime	€/t	300	300	300	300	-	300
H_2SO_4	€/t	-	-	-	-	160	-
EU ETS price	€/tCO_2			24			24

The economic feasibility of CCU processes was not evaluated for the reference mill cases. Carbon capture processes as well as the utilization possibilities are emerging technology, and economic analysis is therefore a challenging task. Price estimates for captured CO_2 were given in section 4.2. The studied utilization processes are commercial processes, although not widely applied.

6 Results and discussion

6.1 The status and prospects of refining biomass into biofuels

The largest plants converting biomass into biofuels are located in a small number of countries. Figure 6.1 shows how the capacity of the largest plants is distributed between these counties. The 15 largest plants accounted for about 30% of the global biodiesel production, for ethanol mills the share of the largest mills was about 10% and for pellet mills about 16%.

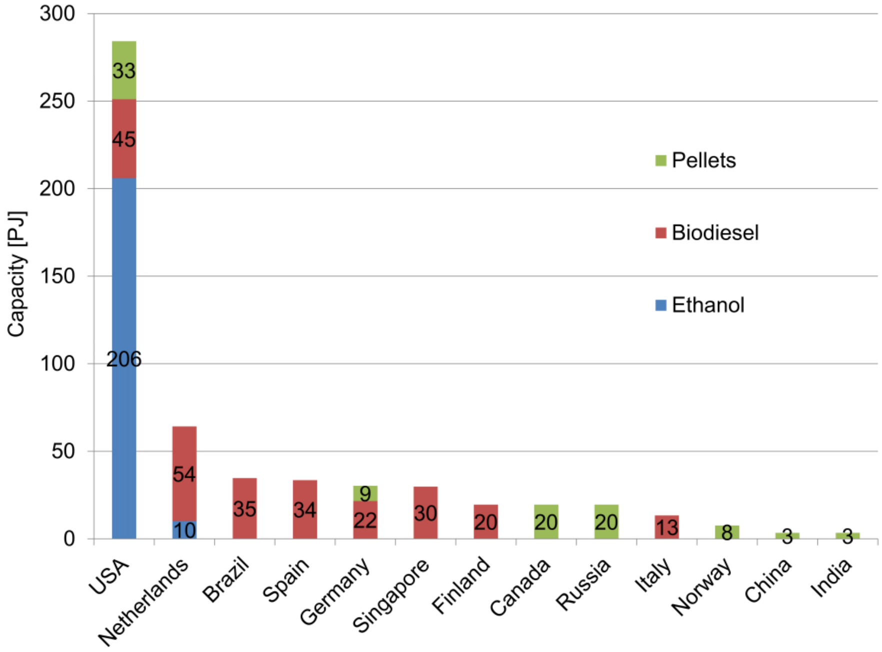


Figure 6.1. The geographical distribution of fifteen largest plants converting biomass to biofuels.

Figure 6.2 compares the global production capacity and actual production (estimated or known) of ethanol, biodiesel, and pellet plants in 2012, and shows the share of the 15 largest plants in each sector. The utilization rate of the ethanol production capacity is quite high, about 80%, whereas only about a third of the biodiesel capacity and about half of the pellet capacity was utilized. The share of the largest plants of the capacity and production is fairly similar for the studied biofuels. An exception is biodiesel production; the fifteen largest plants produced as much as 29% of the global production. This means that the refining of biomass into biofuels at global level is distributed widely, not concentrated on the largest units. However, the results show that in a single country a large plant can have a dominant role.

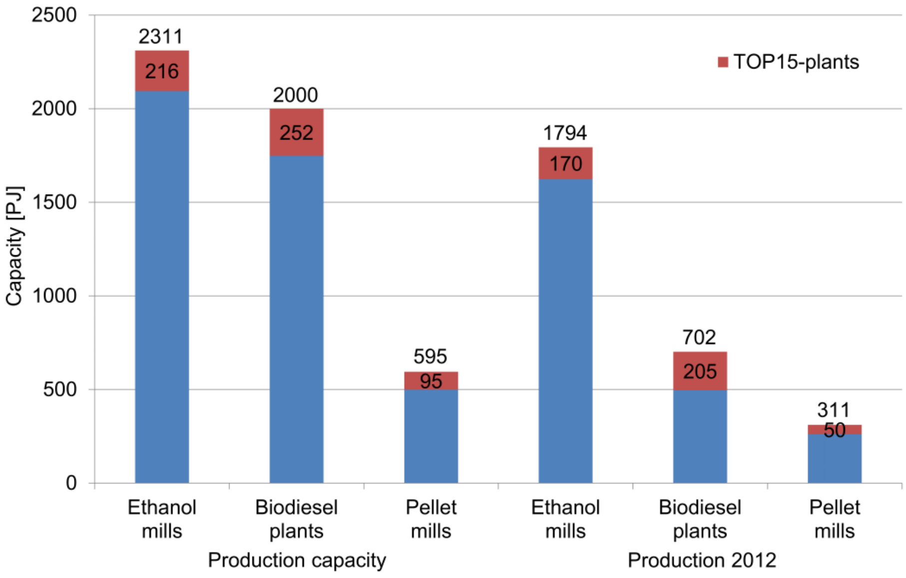


Figure 6.2. The global production capacity and actual production of ethanol, biodiesel, and pellet plants in 2012, and the share of the fifteen largest plants in each sector.

Publication I also estimated the future development of the global biomass refining capacity. Due to a lack of comprehensive, timely information and the fact that not every plan is realized, the results should be considered indicative and used with care. The results show that like the existing facilities, also the planned projects concentrate on a small number of countries. New products have not yet appeared in volume, but a few renewable diesel production projects as well as some pyrolysis plants were found.

Currently, biomass is processed primarily near the biomass source using local feedstock. Imported feedstock was used most commonly in biodiesel plants. The raw biomass use seems to remain local also in the near future, but the trade of refined biofuels will likely continue to increase. The USA and Canada are planning several large pellet mills, and their production aims mostly for markets in Europe, but also in Asia.

Although advanced biomass conversion processes are still minor compared with the more established technologies, the increasing need to substitute fossil fuels and products with renewables creates demand for them. Kraft pulp mills are potential players in these markets due to biomass-based side streams as well as existing transportation infrastructure and synergy benefits of the existing processes.

The chemical pulp industry already has a significant role in biomass conversion into energy via black liquor combustion, as Figure 3.2 showed. The global capacity of recovery boilers exceeds the combined capacity of other boilers that combust biomass. Thus, it is useful to develop new pulp and paper mills towards greater energy efficiency and lower fossil CO_2 emissions.

Most of the converted biomass in the markets is ethanol, biodiesel, and wood pellets, which do not offer a feasible solution for fossil fuel replacement in a lime kiln. Therefore, kraft pulp mills are forced to look for options for their own lime kiln fuel production.

6.2 Fossil fuel-free lime kiln operations

The main use of fossil fuel in modern pulp mills is heat generation to convert lime mud to burnt lime in the lime kiln. The full or partial replacement of fossil fuel in lime kilns utilizing existing side streams, such as residual biomass or excess electricity, is both technically and commercially possible. The studied processes can be integrated into a pulp mill without adverse effects on the actual pulp production process. Table 6.1 gives the main parameters from the integrated mill calculations in the case of the southern reference mill. All concepts except for the electrolyser concepts enable the full substitution of fossil fuels in the lime kiln. Using the electrolyser and all available excess electricity, oil is still needed to cover at least 28% of the kiln's heat demand.

Table 6.1. The main results from the calculations when lime kiln fuel production is integrated with the southern reference mill.

	Unit	**Hydrogen A**	**Hydrogen B**	**Biogas**	**Torrefied biomass**	**Lignin**	**Pulverized wood**
Lower heating value	MJ/kg	120.0	120.0	6.7	18.7	23.0	15.0
Fuel production	t/d	10.8	38	960	344	280	430
Share of kiln energy	-	21%	72%	100%	100%	100%	100%
Power consumption	MW_e	24.2	79.1	5.2	5.3	1.2	7.0
Biomass use	BDt/d	-	-	449	424	-	387
Low value heat use/production[1]	MW_{th}	7.4	20.3	-8.7	-8.2	-4.2	-8.2
Pure water consumption	t/d	97	343	-	-	-	-
Increase in make-up lime usage	t/d	-	-	8.6	12.9	-	12.9
Difference in sellable power	MW_e	-20.8	-75.8	-5.2	-5.3	-21.5	-7.0
Reduction in CO_2 emissions[2]	1000 tCO_2/a	35	124	172	172	172	172

[1] Negative values refer to heat consumption

[2] Refers to fossil fuel-based CO_2 emissions

The power balance of the mill is affected by the renewable fuel production, and the amount of sellable electricity decreases in all of the cases. In the hydrogen B case, all excess electricity is used for renewable lime kiln fuel production. Lignin extraction does not only consume electricity, but also decreases the amount of organics ending up in the recovery boiler, and therefore, markedly less steam and electricity is generated.

In the southern mill, the biomass residue generated in the wood handling process of the mill is sufficient to cover the lime kiln heat demand. There is actually excess biomass available in all of the cases. The combustion of biomass residue in a power boiler would offer a possible increase in the amount of produced electricity. Especially in the hydrogen cases, a power boiler could be used to increase hydrogen production or to produce electricity for sale.

In the lignin extraction case, lignin removal affects the recovery boiler balance and causes a decrease in electricity production. On the other hand, lignin extraction offers a possibility to increase the capacity of the recovery boiler, which is often a bottleneck in pulp production. Consequently, additional revenue could be gained by increasing the pulp production of the mill without expensive modifications to the recovery boiler.

The hydrogen cases make separate oxygen production unnecessary. Oxygen enriched air combustion was presented as an option to utilize excess oxygen from the electrolyser. The oxygen requirement for combustion in the recovery boiler of the reference mill is 0.85 m^3_n per kg of black liquor dry solids. The combustion air flow to the boiler is then 27 Mm^3/d, of which 77% comes as secondary and tertiary air. If excess oxygen from hydrogen case B is added to the secondary and tertiary air flows, oxygen content in these flows increases from 21.0% to 21.6%. This can be considered as an insignificant change in the operation of the recovery boiler.

Water purification for the electrolyser adds to the load of the mill’s water treatment plant. The increase is 3% and 12% for the hydrogen cases A and B, respectively. The cooling water for electrolysis is part of the mill’s water cycle. Heating water by cooling the electrolyser reduces the amount of water heated with steam. In Case A, the alkaline electrolyser produces 12% of the 75 °C water used at the mill, and in Case B, 34%.

Table 6.2 gives the main parameters from the calculations when lime kiln fuel is produced from biomass at the northern reference mill. Due to integrated paper production, the northern mill is a large energy consumer compared with a stand-alone pulp mill. Biomass use for biofuel production reduces electricity generation. In the calculations, the energy use is limited to the mill's own production. Therefore, availability of electricity limits the production of biofuels in both cases. Without additional electricity or biomass, 70% and 75% of the heat demand of the lime kiln can be covered with biogas and pulverized wood, respectively. Additionally, side streams such as tall oil pitch or methanol can be combusted to increase the share of renewable fuels in the lime kiln.

Table 6.2. The main results from the calculations when lime kiln fuel is produced from biomass at the northern reference mill.

	Unit	Biogas	Pulverized wood
Lower heating value	MJ/kg	6.7	17.0
Fuel production	t/d	785	333
Share of kiln energy	-	70%	75%
Power consumption	MW_e	3.8	5.4
Biomass use	BDt/d	325	299
Low value heat use/production[1]	MW_{th}	-8.0	-8.0
Increase in make-up lime usage	t/d	8.0	12.0
Difference in sellable power	MW_e	-22	-22
Reduction in CO_2 emissions[2]	1000 tCO_2/a	98	105

[1] Negative values refer to heat consumption

[2] Refers to fossil fuel-based CO_2 emissions

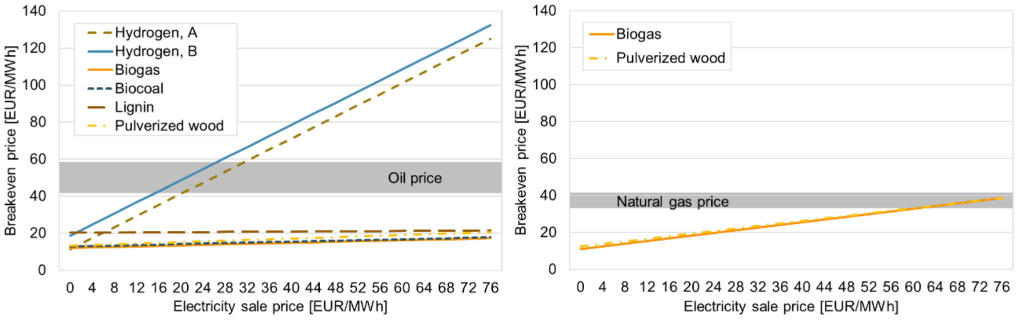
The main concern of the biomass-based lime kiln fuel concepts is unforeseen stoppages in the fuel feeding and pretreatment systems. Additionally, the fire risk needs to be considered, especially if flue gas instead of water or steam is used for biomass drying. Stoppages are quite common in biomass processes, and they reduce the availability of the system. Consequently, occasional fossil fuel use or biofuel storage is required to maintain mill operations during unforeseen breaks. The costs of possible biofuel storage or increase of occasional fossil fuel use were not included in the cost calculations.

All of the integrated processes either produce or use low temperature heat in the form of hot water. Secondary heat is an abundant resource in modern kraft pulping processes, and as a result, the need for heat does not substantially affect the cost of the process. Biomass-based fuels include contaminants that mix with lime and may accumulate in the lime cycle. This can be mitigated by increasing lime replacement by adding make-up lime use.

6.3 Economic feasibility of the lime kiln fuel alternatives

The electricity price and fossil fuel price are the main factors when evaluating the profitability of the fossil fuel replacement concepts. The feasibility depends on mill-specific details and local conditions, such as the possibility to sell excess electricity and whether the mill is an operating or a greenfield mill.

The profitability of the studied concepts can be viewed as the difference between the renewable fuel production cost and the cost of the replaced fossil fuel. Figure 6.3 presents the breakeven lime kiln fuel price for each case as a function of electricity price. When the fossil fuel price exceeds the calculated breakeven price, the case is considered economically feasible.



(a) (b)

Figure 6.3. The breakeven lime kiln fuel price in the studied alternative fuel concepts as a function of electricity sale price for the southern reference mill (a) and for the northern reference mill (b). The grey areas indicate the recent price levels of oil and natural gas at the time of writing.

In the lignin case, the breakeven price is approximately 20–22 €/MWh. In the biomass conversion cases, the breakeven prices are in the range of 12 to 22 €/MWh in the southern mill case and in the range of 11 to 39 €/MWh in the northern mill case. The lowest renewable fuel price can be found in the biogas cases, but the results of the biomass conversion cases are close to each other. The OECD (2018) estimates the crude oil price in 2019 and 2020 at 80 USD/bbl (approximately 40 €/MWh). For a pulp mill, the refinery margin, cost of transport, and taxes need to be added to the price calculations. Recent natural gas prices in the EU area have been around 35–40 €/MWh or even higher, including taxes and levies (Eurostat, 2019). All the biomass cases seem to be profitable considering the current fossil fuel price development. Choosing a biomass-based heat source for the lime kiln has recently been seen as a trend in the some new and retrofitted mills.

The profitability of the hydrogen concept is highly dependent on the price of electricity. Considering recent oil prices (OECD, 2018) at the time of writing, the cases are unlikely to be profitable when the alternative is to sell electricity. However, when selling electricity is not possible due to local conditions, for instance, if the mill is located in a remote area or the local electricity price is low, then the integration of an electrolyser can offer a reasonable alternative for savings in operational costs. In the studied cases, oxygen production was assumed to already exist for the full demand. Therefore, only the operating electricity consumption decrease affected costs. If a need to increase oxygen production capacity exists, then alkaline electrolysis offers an alternative possibility that could save in operating costs.

The profitability of the gasification, torrefaction, lignin and wood pulverizing concepts depends primarily on the fossil fuel price, and secondly on the investment cost. The investment cost and the cost of biomass are highly dependent on the local conditions. Therefore, each case needs to be evaluated separately. The payback period for the southern mill cases as a function of oil price was calculated to gain insight on the profitability of the cases. Two electricity prices, 35 €/MWh and 65 €/MWh, were used. Figure 6.4 presents the results. In the biomass cases, the electricity price affects the profitability when oil price is low, below 35 €/MWh (approximately 69 USD/bbl), whereas in the lignin case, the change in the electricity price does not change the profitability notably.

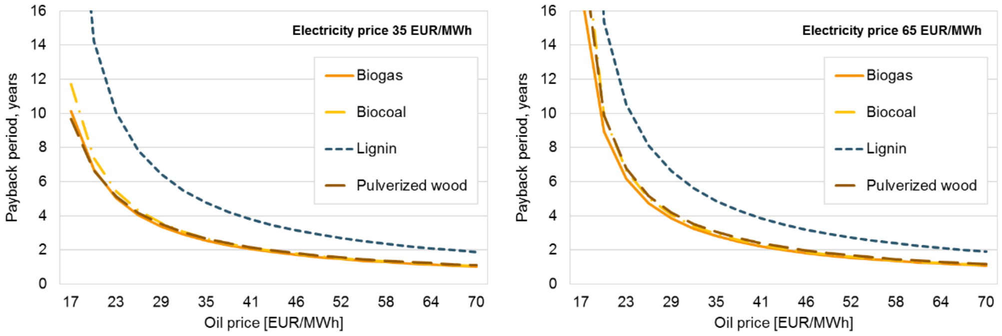


Figure 6.4. The payback period for biogas, torrefied biomass, lignin, and pulverized fuel cases as a function of oil price in the southern reference mill when the electricity price is 35 or 65 €/MWh.

Similarly, Figure 6.5 presents the payback period for the gasification and wood pulverizing cases as a function of natural gas price for the northern reference mill. Only a small difference can be detected between the cases, except with low natural gas prices, below 25 €/MWh. Publication IV presents also a sensitivity analysis, which shows that a low fossil fuel price leads to the fast increase of the payback period unless the carbon price is high.

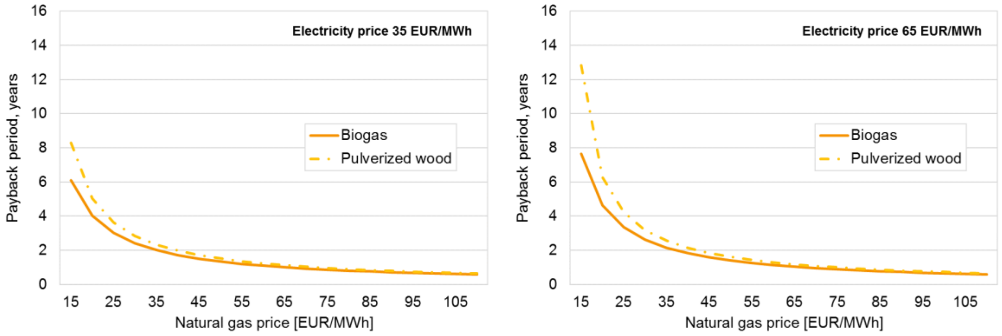


Figure 6.5. The payback period for biogas and pulverized fuel cases as a function of natural gas price in the northern reference mill when the electricity price is 35 or 65 €/MWh.

6.4 Pulp mill as a source of negative CO_2 emissions

Due to a large share of biomass-based fuels, carbon capture from flue gas followed by storage or utilization enables pulp mills to act as carbon sinks. Pulp mills have a significant carbon capture potential, but the current utilization potential is notably smaller considering available technologies.

Publication V assesses the global technical potential of the kraft pulp industry to act as a source of negative CO_2 emissions. Rough estimates are given based on recent production data from the year 2016 (FAO 2017) and the reference mill calculations presented in this work. The results are collected into Table 6.3. The carbon capture potential was estimated at 100 and 35 $MtCO_2/a$ for bleached and unbleached sulphate pulp, respectively. The technical potential to utilize CO_2 in the mill processes using technologies mentioned earlier was estimated at about 12 and 4 $MtCO_2/a$.

Table 6.3. Global technical potential to capture CO_2 from recovery boilers (RB), biomass boilers (BB), and lime kilns (LK) and on-site utilization potential, estimations based on sulphate pulp production data from the year 2016 (FAO 2017) and the reference mill calculations.

	CO_2 capture potential 1000 tCO_2/a			**CO_2 utilization potential** 1000 tCO_2/a		
	RB	BB	LK	Tall oil	PCC	Lignin
Bleached pulp	76 264	14 731	10 297	1102	4409	7149
Unbleached pulp	26 909	5198	3633	389	1556	2522
	Share of total CO_2 from sulphate pulp production					
Bleached pulp	21%	4%	3%	0.3%	1.2%	2.0%
Unbleached pulp	7%	1%	1%	0.1%	0.4%	0.7%

Total capture potential 137 $MtCO_2/a$

The global technical potential to capture CO_2 from pulp mills is substantial. With rather conventional assumptions presented above, the total amount of about 140 $MtCO_2/a$ could be removed from the atmosphere from existing pulp mills without additional biomass harvesting at a price level well below 50 €/tCO_2. With currently available technologies, only a small part of produced CO_2 can be utilized on-site. The potential for both capture and utilization can be estimated to increase along with both technology development and the steady increase of pulp production capacity due to new mills. However, this study did not estimate the commercial potential of CO_2 utilization routes.

In recent mitigation scenarios for climate change, BECCS has been presented as one of the key technologies, as it offers a way to negative CO_2 emissions (IPCC, 2018; Fridahl and Lehtveer, 2018). The global annual BECCS potential has been estimated at or below 5 $GtCO_2$ (de Coninck *et al.*, 2018). Based on the estimate above, capture from the chemical pulp industry can cover at least 3% of the global potential. The technology is not yet mature, but it is tested and used on a small scale. The deployment of BECCS/U in the pulp industry does not affect the wood use of the mills, and therefore has no effect on forest or land use when applied to existing mills. Socio-political issues are the primary constraints on the way to BECCS and its large-scale use (Fridahl and Lehtveer, 2018).

The capture processes are energy-intensive, and the costs depend on the chosen method and process integration possibilities. In addition to the investment and operational costs, the economic feasibility of BECCS/U is greatly dependent on the avoided CO_2 costs – primarily taxes and emissions credit collected on fossil-based emissions. It should be noted that as currently CO_2 in chemicals is counted at the production source, the use of biogenic CO_2 replacing fossil CO_2 would give the mill no credits. Therefore, apart from the development of carbon utilization technologies, the future of BECCS/U depends on political decisions. Incentives for negative emissions would be a probable way to encourage producers to adopt these processes. The utilization of biogenic CO_2 in the processes of an emission producer is a novel concept, and thus unknown as a legislative issue.

6.5 Does a modern eucalyptus pulp mill differ from northern pulp mills

The operational differences between northern and southern kraft pulp mills arise mainly from differences in the properties of wood raw material and local weather conditions. The local regulations and the operational environment set different boundaries for the operation of the mills. The operational differences are, however, not crucial when solutions for fossil fuel-free operation are sought.

Significantly more pulp mills are built in South America and Asia than in Northern Europe and America. New South American mills are more often stand-alone mills than the northern ones. Typically, they are more than self-sufficient in electricity generation, but in some cases, local conditions make electricity sales challenging. The starting point for process integration is then different from the northern mills, where electricity and heat sales are commonly a significant source of income when they are not used for integrated papermaking, which is often the case.

The pulping processes of eucalyptus and Nordic softwood are rather similar regardless of the differences in the raw material properties. The main differences regarding the integration of the studied processes are related to energy generation and the amount of biomass residue. The pulp yield is typically higher with hardwood and eucalyptus than with softwoods due to a lower hemicellulose content. A high yield leads to a smaller amount of organics in black liquor, and subsequently, less steam is produced. The northern mills more often combust biomass for steam production in a separate boiler for two reasons: firstly, they are more often integrated mills where energy is needed in papermaking, and secondly, wood is typically debarked at the mill site resulting in a significant amount of biomass residue. Unlike for the northern wood species, for eucalyptus forest-debarking is commonly used because the delay makes the process notably more challenging and increases the amount of wood losses.

The biomass concepts studied in this thesis can be implemented in both mill types. In a stand-alone eucalyptus mill, the biomass concepts can fully substitute for fossil lime kiln fuels. In a mill where biomass residue is usually combusted in a boiler for additional steam production, the use of biomass for lime kiln fuel production decreases the amount of produced steam and electricity. The results of Publication IV show that also in a modern integrated mill such as the northern reference mill, more than two thirds of fossil fuels in a lime kiln can be replaced with biomass fuels without additional electricity. Some of the studied biomass concepts are already in use in new and retrofitted mills in *e.g.* Scandinavia.

An electrolyser could be a feasible option to convert electricity into a form where it can be stored, combusted, or refined into further bioproducts when electricity sale is not an option, such as in stand-alone mills in remote areas. It is unlikely that the concept would be profitable in northern mills in the near future. In Europe, electrolysers have been presented as an option to convert intermittent renewable energy into a storable form, and therefore, the process has been under research and development and also discussed widely. Similar interest in PtG processes is not yet seen in South America.

The attitude towards emission reductions and fossil fuel replacement varies from country to country. In northern mills, new technologies have been implemented faster, while mills in South America tend to rely on existing technologies and concentrate on efficient pulp production using traditional methods. Local conditions, such as the prevailing attitude towards the new technologies and how necessary they are, have an effect on the attractiveness of investments. Financial issues are in an important role in investment decisions, and therefore, the decisions are governed by market demand, but also political decision-making. In the EU, *e.g.* the Emissions Trading System (ETS) has the purpose of guiding industrial operators towards emission reduction. A similar system is not yet in use in *e.g.* Brazil, although it has been planned.

6.6 Main findings

The key observations in response to the research questions stated at the beginning of the thesis can be summarized as follows.

> *Q1. What is the role of biomass conversion methods in energy generation, and how important are kraft pulp mills?*

Several methods to convert biomass into energy are in global use, but only a few of them on a large scale. In the order of magnitude they are recovery boilers, ethanol mills, biodiesel plants, pellet plants, BFB boilers, pulverized fuel boilers and CFB boilers. Pulp mills (recovery boilers with a part of BFB and CFB boilers) are the largest industrial application that converts biomass into energy. Refining biomass into liquid biofuels takes place primarily by means of first generation conversion into ethanol and biodiesel. Pellet production is growing fast, but the global capacity is significantly smaller than that of biodiesel and ethanol. The capacity utilization rate is lower for biodiesel than for ethanol or pellets. Biomass torrefaction and pyrolysis are still in the development phase, and it seems that in the coming few years, pyrolysis oil and torrefied biomass will not become global biomass commodities similar to pellets, ethanol and biodiesel.

The large-scale refining of biomass is concentrated in a small number of countries. Biomass processing for energy purposes is increasing, and new plants are being planned, mostly in the industrialised countries and near feedstock sources similarly to the existing ones. While the use of raw biomass seems to remain local, the trade of refined biofuels will likely continue to increase in the near future.

Kraft pulp mills are significant users of energy biomass via combustion in the recovery boilers, as Figure 3.2 demonstrated. Pulp mills convert biomass locally and do not stand out in the global bioenergy trade. Currently, the role of pulp mills in the biomass markets limits primarily to wood sourcing and the sale of conventional products, namely, pulp, paper, and board. The product portfolio of many mills includes also bioenergy in the form of electricity, and especially in Scandinavia, heat can be sold to the surrounding community. In the future, kraft pulp mills can become important players in the market as producers of advanced bioproducts.

Q2. What can be done to increase biomass usage to minimize the use of fossil fuels in pulp mills?

The lime kiln is the primary fossil fuel user in kraft pulp mills, and in modern mills during the normal operational process also the only one. Therefore, lime kiln fuel replacement is the most significant action to minimize the remaining use of fossil fuels in pulp mills. The results of Publication I show that biomass-based fuels available on the markets offer limited possibilities for pulp mills to substitute for lime kiln fossil fuels. Therefore, other solutions for lime kiln fuel replacement are needed.

Publications II, III, and IV studied various fossil fuel replacement alternatives. These renewable fuel production concepts can be integrated into pulp mill processes without a noticeable effect on pulp production. Based on the reference mill calculations, processing residual biomass into biofuels (biogas, torrefied biomass, pulverized wood) as well as lignin extraction from black liquor for combustion in a lime kiln are technically and economically feasible concepts. In a typical South American kraft pulp mill, these options can be used to fully substitute for fossil fuels in the lime kiln during normal operation. In a northern mill with integrated papermaking, biogas or pulverized wood can cover more than two thirds of the lime kiln heat requirement without additional electricity or biomass. The attractiveness of each concept is highly dependent on the price of fossil fuels and the taxes levied. The most favourable alternative for each mill depends on the local conditions and the operational specifics, and an individually customised solution is therefore needed.

The integration of an alkaline electrolyser to produce hydrogen for fuel use could offer a partial substitution for fossil lime kiln fuels. The concept is technically feasible, but economic viability requires specific conditions, such as low electricity prices, limited possibilities to sell excess electricity, or a need for additional oxygen production in the mill. In remote stand-alone mills, such as some new mills in South America, uses for excess electricity are sometimes needed. Electrolysis can be seen as an alternative for producing market power. Electrolysers are also an emerging technology, and the investment costs can be expected to decrease when the implementation of the technology becomes more common. Additionally, more advanced technologies than alkaline electrolysers, such as SOEC, are under research and may permit more efficient integration concepts in the future.

Q3. How can pulp mills respond to the increasing demand to reduce fossil-based CO_2 emissions and serve as sources of negative CO_2?

Pulp mills produce CO_2 primarily in combustion processes. The largest sources are the recovery boiler, the lime kiln, and in most mills, the biomass boiler. A large part of the CO_2 formed in the pulping process is biogenic, and the primary source of fossil-based CO_2 is the lime kiln. The use of renewable alternatives for fossil fuels in the lime kiln significantly reduce the amount of fossil CO_2 emissions. The biomass-based alternatives produce biogenic CO_2 when combusted, but hydrogen is a carbon-free fuel.

The pulp and paper industry could be one of the largest sources of capturing and converting CO_2 from modern bioenergy use. The results of Publication V show that carbon capture offers pulp mills the possibility to act as a platform for negative CO_2 emissions, provided that the biomass raw material is from a sustainable origin and biogenic CO_2 is permanently removed from the atmosphere. Captured CO_2 can be stored or utilised as raw material for further bioproducts. Even a small carbon capture in a kraft pulp mill can make the mill a carbon sink.

The technical potential to capture CO_2 from pulp mills is substantial. Considering currently available technologies, the utilization possibilities in pulp mills are minor compared with the capture potential. Pulp mills alone are not the answer to high negative emission targets, but they can be one significant component in the palette. Bioenergy with carbon capture or utilization has been recognized as one of the key technologies in recent scenarios on climate change mitigation. The technical potential for carbon capture in pulp mills can be estimated at 137 $MtCO_2/a$, which covers approximately 3% of the global capture potential for bioenergy. Technology development and global growth in pulp production capacity will likely increase the potential to both capture and reuse CO_2.

The cost-effectiveness of BECCS/U is primarily dependent on the avoidance of costs of fossil CO_2 emissions. In the future, the feasibility will depend both on the technological development of CO_2 utilization possibilities, and on political decision-making regarding emission taxes and possible incentives encouraging CO_2-negative solutions.

Q4. What are the future challenges of a modern pulp mill?
  a. Role of location; do e.g. eucalyptus mills differ from northern mills?
  b. What are the technical and economic issues to be considered?

Differences between northern and southern pulp mills are not limited to differences such as raw material and physical location. The socio-political environment is also different. Based on the literature review conducted during this research, European mills are more eager to implement new technologies and look for new business opportunities than the mills in *e.g.* South America.

The increasing demand for sustainability makes it necessary for pulp mills to transform towards higher sustainability. Also the significance of paper is decreasing. Biomass-based by-streams and existing infrastructure together with requirements for sustainability encourage pulp mills to invest in new processes. In addition to fossil fuel replacement, the studied renewable fuel concepts offer a further possibility to integrate downstream processes to convert biomass or hydrogen into biofuels or biochemicals in order to find new revenue streams. For example, lignin is not only a fuel but also a valuable resource for further use as a bio-based raw material. It is, however, essential to evaluate the effects of the processes on the pulping process in order to ensure an undisturbed pulping process and to maintain pulp quality. For many pulp mills, energy is also a significant source of income, and it is obvious that the implementation of a new process affects the energy balance of the mill. The feasible options for each pulp mill depend on local conditions and operational details, and each concept needs a case-specific evaluation.

An important but often challenging question is what the value of the new process for the mill is. In addition to the prevailing market situation, national and international politics have a significant role in the future challenges of pulp mills. The situation of biomass, its energy use, and whether it can be considered carbon-neutral, is not clear. Environmental politics make long-term planning challenging due to uncertainties. The viability of developing technologies can be dependent on socio-political issues.

7 Conclusions

The chemical pulp industry along with other industries is urged to take action to combat the climate change, following the targets of the Paris Agreement. This thesis offers a view on how kraft pulp mills could respond to the increasing demands of sustainability and climate change mitigation. The thesis compares the currently available technologies to minimize fossil fuel use in lime kilns and a pathway that can lead to carbon-neutral or even carbon-negative solutions in kraft pulp mills.

The thesis assessed the magnitude of the various routes used in biomass conversion to biofuels to give an overview of the scale and distribution of the conversion processes. Many processes are used globally, but only a few of them on a large scale. In kraft pulp mill recovery and fluidized bed boilers, biomass is converted into steam, making chemical pulping one of the largest users of biomass for energy. Refining biomass into liquid biofuels takes place primarily by means of first generation conversion into ethanol and biodiesel. Pellet production is growing fast, but the global capacity is significantly smaller than that of biodiesel and ethanol. Biomass torrefaction and pyrolysis are still in the development phase, and it seems that in the coming few years, pyrolysis oil and torrefied biomass will not become similar global biomass commodities as pellets, ethanol and biodiesel currently are.

Biomass-based by-product streams in large volumes, the existing infrastructure, and a growing need for more sustainable production make the chemical pulp industry a significant player in finding solutions for climate change mitigation. This research gives valuable information on novel concepts on the way to fossil-free, climate-friendly kraft pulp production. The pulp industry is facing new challenges due to growing urge to diminish fossil fuel usage and CO_2 emissions; mapping the existing and viable possibilities is essential for decision-makers in companies as well as in politics. This thesis discusses the role of the chemical pulp industry in the conversion of biomass into energy to form an understanding of the significance of the pulp industry in combating climate change. Fossil fuel replacement concepts and carbon capture and utilization were evaluated to give a basis for mill-level analyses.

The lime kiln is the primary fossil fuel user in kraft pulp mills, and in modern mills during the normal operational process also the only one. Lime kiln fuel replacement is then the most significant action to minimize the use of fossil fuels. Biomass trade does not offer a solution for lime kiln fuel replacement due to a lack of feasible options on the market. Therefore, local solutions are needed.

Several technically feasible alternatives to produce renewable fuels for the lime kiln were found. These processes can be integrated into the pulp mill and can make use of by-products of the pulping process. Processing biomass into biofuels and extracting lignin from black liquor for use as a renewable lime kiln fuel can be implemented in a technically and economically feasible way. In a typical South American kraft pulp mill, all of the studied options could be used to fully substitute fossil fuel in the lime kiln during normal operation. In a northern mill with integrated papermaking, biomass-based fuels can cover majority of the lime kiln heat requirement without additional electricity or biomass. The integration of an alkaline electrolyser to produce hydrogen for fuel use could be a feasible alternative when electricity prices are low, when electricity cannot be sold due to local conditions, or when additional oxygen production capacity is needed in the mill. The attractiveness of each integration concept is highly dependent on the price of fossil fuels and the taxes levied. The most favourable alternative for each mill depends on the local conditions and the operational specifics, and an individually customized solution is therefore needed.

Pulp mills are large biomass users and *e.g.* in Finland can easily retain significant negative CO_2 possibilities. Carbon capture with storage or utilization has been presented as one of the key technologies by the IPCC. In recent climate change mitigation scenarios, the significance of BECCS/U has been highlighted due to their realistic possibility to remove CO_2 from the atmosphere, i.e. negative CO_2 emissions. For pulp mills, carbon capture offers the possibility to act as platform for negative CO_2 emissions if biogenic CO_2 is permanently removed from the atmosphere by utilizing it as raw material for further bioproducts or by storing it.

The accuracy of the results and conclusions is affected by several factors. The conclusions drawn based on statistical data and available literature reflect the prevailing situation at the time the research was conducted. The energy field is changing rapidly and new ideas emerge continuously; therefore, the results should be considered as indicative and used with care. The results and conclusions based on the pulp mill models and calculations in this thesis are valid within the assumed conditions; there are no universally correct answers for the stated research questions, unless the concepts are employed in real plants. The economic evaluation is valid within the given assumptions. The economic evaluation was based on timely information on recent investments and product prices, but varying price levels, the limited availability of public cost data, and the changing economic environment reduce its accuracy. The studied concepts are in different stages of maturity; some of them are commercial, well-known technologies, such as biomass gasification, and some are newly introduced, promising alternatives, such as electrolysis. A varying operational environment as well as political decision-making affect the profitability of the presented concepts. Each concept has its own uncertainty factors.

The calculations performed during the course of this research are limited to the effect of the studied concepts and material flows inside the plant borders; although the processes considered primarily utilize existing resources in the mill and the products are targeted for on-site use, they also affect preceding and subsequent stages in the production chain beyond the plant. Life cycle analysis is essential when new products are produced, as is an analysis of the effects of the concepts beyond the plant environment. Further research is also needed on the material and energy efficiency of the pulping process as well as the new concepts, such as PtX processes. Efficient material and energy use is crucial to control the environmental impacts of an industrial process.

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Appendix A: Balances of the reference mills

MILL BALANCE OVERVIEW

Project Name		Euca Base	Softwood Base
Client name		Mill S	Mill N
Location		South America	Scandinavia
Bleached Pulp production	ADt/a	1500000	1400000
Operating days		350	350
Average daily production	ADt/d	4286	4000

1.0 COOKING AND BLEACHING

Bleached Pulp production	ADt/a	**1500000**	**1400000**
Bleached Pulp production	BDt/a	1350000	1260000
Pulp moisture	BDt/ADt	90 %	90 %
Bleached Pulp Production	BDt/d	3857	3600
	ADt/d	4286	4000
Shrinkage from unbleached to dried pulp	%	3.1	4.0
Unbleached pulp	ADt/d	4424	4167
Oxygen delignification shrinkage	%	1.5	1.5
Screened brown stock	ADt/d	4491	4230
Screening and knotting losses	%	2.0	3.0
Unscreened brown stock	ADt/d	4583	4361
Unscreened brown stock	BDt/d	4125	3925
Cooking yield	%	53	46
Kappa after cooking		18	28
Kappa after oxygen delignification		9.000084	14.0
Chips to digester	BDt/d	7782	8532
Chips to digester	BDt/a	2723714	2986301
Loss in drying machine	%	0.12	1.00
Bleached plant yield loss	%	3.00	3.00
Lignin removal	%	0.00	0.00
Hydrolysis Extraction yield	%	0.00	0.00
Lignin removal	kg/ADt	0.00	0.00
PHL that remained in the wood pores	kg/ADt	0.00	0.00
PHL that was removed	t/d	0.00	0.00
Part of green liquor as alkali	%	0.00	0.00

2.0 WOOD HANDLING		Mill S	Mill N
2.1 Wood processing			
Wood species		Eucalyptus	Softwood
log length	m	2...4	2...4
log diameter	cm	10...40	10...40
Wood moisture	%	45	50
Bark content average	%	5	11
Chips to digester	BDt/d	7782	8532
Days of operation	d/a	350	350
Annual chip requirement	BDt/a	2723727	2986314
Fines	%	2	2
Fines removed at screening	BDt/a	41478	60945
Chips to screening	BDt/a	2765205	3047259
Debris at debarking	%	1	2
Bark and debris at debarking	BDt/a	176504	455338
Logs to barking drum	BDt/a	2941709	3502597
Logs to woodroom	BDt/a	2941709	3502597
Woodyard wood intake	BDt/d	8405	10007
Wood density	BDkg/m^{3}sob	540	410
Woodyard wood intake	m^{3}sob/d	15565	24408
Wood consumption /ADt	m^{3}sob/h	3.63	6.10
Design factor	%	75 %	75 %
Woodyard wood intake, design	m^{3}sob/d	20753	32544
Woodyard wood intake, design	m^{3}sob/h	1297	2034
Chip weight	kgBD/m^{3}l	189	144
Wood loose/solid	m^{3}l/m^{3}s	3	3
Woodyard chipping	m^{3}sub/d	14397	20747
Chip storage time	days	14	14
Chip storage volume	m^3	574000	828000
Wood handling operating time	d/week	7	7
Wood handling operating time	h/d	16	16
2.2 Hog fuel processing			
Bark and debris at debarking	BDt/a	176504	455338
Fines removed at screening	BDt/a	41478	60945
Losses in the woodyard	%	3	3
Losses in the woodyard	BDt/a	5295	13660
TOTAL to bark handling	BDt/a	223277	529943
	BDt/d	638	1514
Bark density	kgBD/m^{3}l	335	335
Bark volume	m^{3}l/d	1904	4520
Storage time	days	4	4
Storage volume	m^3	7618	18079

3.0 WHITE LIQUOR REQUIREMENTS		Mill S	Mill N
3.1 Cooking			
Active alkali charge as Na_2O	%	18 %	17 %
Active alkali charge, as NaOH	%	24 %	23 %
Chips to digester	BDt/d	7782	8532
Active alkali charge as Na_2O	BDt/d	1421	1490
Active alkali charge, as NaOH	BDt/d	1834	1924
Caustic in oxidized white liquor	kg/m^3	140	140
White liquor flow to cooking plant	m^3/d	13100	13740
Real chemicals in white liquor	kg/m^3	178	182
White liquor solids to digester	BDt/d	2326	2504
3.2 Oxygen delignification			
Caustic charge	kg NaOH/ADt	18	21
Oxygen charge	kg O_2/ADt	18	19
Caustic in oxidized white liquor	kg/m^3	97	105
White liquor flow	m^3/d	799	798
Real chemicals in oxidized white liquor	kg/m^3	214	212
Oxidized white liquor solids to O2 reactor	BDt/d	171	169
3.3 Total white liquor required			
White liquor to cooking plant	m^3/d	13100	13740
Oxidized white liquor to ox delignification	m^3/d	799	798
Oxidized white liquor to bleaching plant	m^3/d	0	0
Oxidized white liquor total	m^3/d	799	798
TOTAL	m^3/d	13899	14538
4.0 BLACK LIQUOR CALCULATION			
4.1 Cooking			
Chips to digester	BDt/d	7782	8532
Cooking yield	%	53	46
Blown stock	BDt/d	4124	3925
Organic solids generated	BDt/d	3658	4607
White liquor solids to digester	BDt/d	2326	2504
Water loss, as % of inorganic	%	6 %	6 %
Water loss	BDt/d	140	150
White liquor solids to black liquor	BDt/d	2186	2353
Green liquor solids to black liquor	BDt/d	0	0
Total solids to black liquor	BDt/d	5758	6867
4.2 Oxygen delignification			
Pulp to reactor	BDt/d	4124	3925
Oxygenated pulp	BDt/d	4042	3807
Organic solids to black liquor	BDt/d	82	118
Oxidized white liquor solids to O2 reactor	BDt/d	171	169
Total solids to black liquor	BDt/d	331	361

4.3 Total solids in Black Liquor

		Mill S	Mill N
Total solids to black liquor	BDt/d	6089	7228

5.0 BLEACHING CHEMICALS PREPARATION

5.1 Bleaching requirement

Delignification stage	Kappa in	14	14
	kappa out	9	9
O2 delinification stage	kg/ADt	18	19
Chemical charge DED bleaching	at kappa	8.5	8.5
ClO_2	kg/ADt	26	63
NaOH	kg/ADt	17	10
O_2	kg/ADt	2	3
HCl	kg/ADt	0	0
hydrogenperoxide, H_2O_2	kg/ADt	8	3
$NaHSO_3$	kg/ADt	3	0
Antichlor as SO_2	kg/ADt	0	1
H_2SO_4	kg/ADt	15	5
$MgSO_4$	kg/ADt	3	0
Talc	kg/ADt	2	0
Oxidized white liquor to bleaching plant	m^3/d	0	0

5.2 Bleaching chemicals demand

Oxygen for ox delignif and bleaching	BDt/d	86	86
Oxygen for white liquor oxidation	BDt/d	0	0
Oxygen total	BDt/d	86	86
ClO_2	BDt/d	111	252
HCl	BDt/d	0	0
NaOH for bleaching	BDt/d	73	40
NaOH for scrubber	BDt/d	0	0
NaOH required total	BDt/d	73	40
NaOH produced in balance	BDt/d	137	309
NaOH in imbalance	BDt/d	-64	-269
$NaHSO_3$	t/d	13	0
Antichlor as SO_2	BDt/d	0	5
H_2SO_4	t/d	64	20
$MgSO_4$	t/d	13	0
Talc	BDt/d	6	0
hydrogenperoxide	BDt/d	34	12

6.0 RECAUSTICIZING PLANT

Flow of white liquor	m^3/d	13899	14538
Sulfidity	%	43 %	35 %
Reduction	%	94 %	94 %
Causticizing efficiency	%	83 %	80 %
Active alkali in white liquor	g/l	140	140

7.0 LIME REBURNING PLANT		Mill S	Mill N
Causticizing power of burnt lime	%	83 %	83 %
Kiln product	t/d	1050	1230
Burnt lime for waste water neutralization	t/d	0	0
Kiln product total	t/d	1050	1230

8.0 EVAPORATION PLANT

Black liquor dry solids	BDt/d	6097	7237
Weak black liquor conc	%	15 %	17 %
Strong black liquor concentration	%	79 %	85 %
As fired black liquor concentration	%	81 %	86 %
Evaporation capacity	t/h	1321	1443
Spills	t/h	0	0
Evaporation capacity total	t/h	1321	1443
Total solids to as fired black liquor	tDS/d	6768	8033
Total as fired black liquor	tBL/d	8389	9310
Steam economy with stripper	kg/kg	5.89	5.37
MP steam usage	%	19 %	24 %
MP Steam requirement	kg/s	12	18
LP Steam requirement	kg/s	50	57
Stripper TRS removal efficiency	%	95 %	95 %
Stripper methanol removal efficiency	%	90 %	90 %

9.0 RECOVERY BOILER

Black liquor solids capacity, as fired	BDt/d	6768	8033
Black liquor solids capacity, virgin	BDt/d	6097	7237
Strong black liquor concentration	%	81 %	86 %
Elemental analysis:			
Sodium	%	16.6 %	20.0 %
Hydrogen	%	3.6 %	3.4 %
Carbon	%	35.8 %	34.5 %
Oxygen	%	35.0 %	35.4 %
Sulfur	%	5.8 %	4.1 %
Potassium	%	2.0 %	2.2 %
Chloride	%	1.0 %	0.2 %
Nitrogen	%	0.1 %	0.1 %
Silica	%	0.021 %	0.021 %
Aluminium	%	0.002 %	0.002 %
Total inert	%	0.1 %	0.1 %
TOTAL		100 %	100 %

		Mill S	Mill N
Higher heat value	MJ/kgDS	14.69	14.07
Superheated steam			
Temperature	°C	504	510
Pressure	bar(a)	102	115
Steam generation	kg/s / kgDS/s	3.77	3.64
Net steam flow	t/h	890	1055
	kg/s	247	293

10.0 POWER BOILER

Continuous rating with hog fuel	t/h	0.0	311.2
	kg/s	0.0	86.4

Hog fuel

Hog fuel available	BDt/d	0.1	1514.1
Hog fuel steam generation	t_{steam}/h / BDt/d	0.000	0.206

11.0 TURBINE GENERATOR

Total power generation	MW	165.10	234.40

12.0 FRESH WATER HANDLING

Design flow	m^3/d	205220	191538
	m^3/ADt	48	48
	m^3/d	89571	83600
Balance	m^3/ADt	21	21

13.0 WASTE WATER TREATMENT

Effluent from Bleached Plant	m^3/d	62143	58000
Effluent from Woodhandling	m^3/d	12429	11600
Pulp Dryer	m^3/d	4286	4000
Miscellaneous	m^3/d	27857	26000
TOTAL	m^3/d	106714	99600
Balance	m^3/ADt	25	25
Design factor	%	52 %	52 %
Waste water treatment, Design	m^3/d	205220	191538
	m^3/ADt	48	48

14.0 STEAM BALANCE		Mill S	Mill N
14.1 Departmental steam usage			
Woodhandling	kg/s	0.00	7.92
Cooking & O2	kg/s	35.77	68.07
Bleaching	kg/s	11.27	14.25
Drying	kg/s	40.16	9.99
Evaporation	kg/s	61.63	73.88
Recovery Boiler	kg/s	17.46	18.95
Causticization	kg/s	0.98	1.07
Lime reburning	kg/s	0.96	1.13
Raw water	kg/s	0.51	0.48
Effluent treatment	kg/s	0.51	0.48
NCG	kg/s	1.49	1.39
Auxiliary condenser	kg/s	3.16	2.95
Auxiliary departments	kg/s	6.73	17.03
14.2 Mill steam usage and production			
Pulping steam usage total	kg/s	180.64	217.58
ClO2+O2 Plant	kg/s	2.28	2.28
Paper mill	kg/s	0.00	111.32
Saw mill	kg/s	0.00	0.00
Power Boiler	kg/s	0.00	5.38
Steam for heating water	kg/s	5.00	5.00
NCG-Boiler	kg/s	0.00	0.00
Auxiliary Production	kg/s	-4.61	-4.30
Mill net steam usage total	kg/s	183.31	307.97
14.3 Steam production			
Power Boiler	kg/s	0.00	86.43
Recovery Boiler	kg/s	247.14	293.08
Condensing tail	kg/s	-41.78	-45.15
Spraying	kg/s	1.66	3.52
To feedwater preheating in feedwater tank	kg/s	-23.73	-29.92
Steam to consumers	kg/s	183.61	307.97

15.0 ELECTRICITY BALANCE		Mill S	Mill N
15.1 Departmental electricity usage			
Woodhandling	MW	1.75	11.66
Cooking	MW	7.05	6.72
O2 delignification	MW	4.87	4.58
Screening	MW	6.05	5.76
Washing	MW	3.83	3.65
Bleaching	MW	8.34	6.00
Drying	MW	21.86	5.03
Evaporation	MW	4.93	5.98
Recovery Boiler	MW	11.97	14.21
Causticization	MW	3.12	2.11
Lime reburning	MW	2.03	1.90
Raw water	MW	1.67	1.87
Effluent treatment	MW	3.92	4.18
NCG	MW	0.28	1.62
Cooling towers	MW	0.67	1.33
Compressed air	MW	0.63	1.25
Miscellaneous	MW	2.80	7.63
15.2 Mill electricity usage			
Pulping usage total	MW	85.75	85.47
Power Boiler	MW	0.00	2.95
Turbine	MW	0.22	0.31
ClO2 production	MW	0.18	0.18
Paper mill	MW	0.00	119.86
Saw mill	MW	0.00	0.00
Oxygen+peroxide	MW	3.35	3.17
Mill total usage	MW	89.49	211.93
15.2 Mill electricity production			
Condensing turbine	MW	105.12	164.10
Back pressure turbine	MW	59.98	70.29
Electricity production total	MW	165.10	234.40

Appendix B: Balance calculation examples

THE COOKING BALANCE – THE SOUTHERN REFERENCE MILL (MILL S)

Wood species		
Operating days	d/a	350
Bleached pulp production	ADt/d	4286
Pulp moisture	BDt/ADt	180 %
Total white liquor required	m^3/d	13899
White liquor flow to cooking plant	m^3/d	13100
White liquor flow to oxidation	m^3/d	799
Total green liquor required	m^3/d	0
Oxidized white liquor to bleaching plant	m^3/d	0
Total solids to weak black liquor	tDS/d	6089
Total weak black liquor flow	t/d	39627
Effective alkali in white liquor	kg NaOH/m^3	219.8
Active alkali in white liquor	kg NaOH/m^3	280.0
Effective alkali in green liquor	kg NaOH/m^3	92.9
Active alkali in green liquor	kg NaOH/m^3	153.1
Wood moisture	%	95
Chips to digester	BDt/d	7782
Dry solids from fibreline	%	30 %
Unbleached pulp	BDt/d	3981
Oxygen delignification yield loss	%	4.0
Kappa after cooking		18
Kappa after oxygen delignification		9
Specific gravity, white liquor	g/l	2304.8
Chemicals in white liquor	kg/m^3_{WL}	355
Water in white liquor	kg/m^3_{WL}	1950
Chemicals in oxidized white liquor	kg/m^3_{WL}	429
Water in oxidized white liquor	kg/m^3_{WL}	1950
Chemicals in green liquor	kg/m^3_{GL}	413
Water in green liquor	kg/m^3_{GL}	1950
Caustic in oxidized white liquor	kg/m^3_{WL}	193
Sulfidity	%	86 %
Oxygen charge in oxygen delignification	kg/ADt	34
Lignin removal	%	0 %
Hydrolysis Extraction yield	%	0 %
Lignin removal	kg/ADt	0.0
PHL that remained in the wood pores	kg/ADt	0.0
PHL that was removed	t/d	0.0
Active alkali charge as Na_2O	BDt/d	36.5 %
Part of green liquor as alkali	%	0 %

1.0b Cooking

Brown stock from pulping	BDt/d	4124
	ADt/d	4583
Cooking yield	%	53.0
Chips to digester	BDt/d	7782
Chips to digester	BDt/a	2723714

1.0c Screening

Unbleached pulp	BDt/d	3981
	ADt/d	4424
Screening and knotting losses	%	1.5
Unscreened brown stock	BDt/d	4042
Exit pulp consistency	%	14.0

1.0d O2 delignification

Pulp from oxygen	BDt/d	4042
	ADt/d	4491
Oxygen delignification yield loss	%	2
Brown stock from pulping	BDt/d	4125
	ADt/d	4583

1.0e Washing

Washed brown stock	BDt/d	4125
	ADt/d	4583

3.1 WHITE LIQUOR REQUIREMENTS

3.1.1 Cooking

Effective alkali charge, as NaOH	%	18.5 %
Part of green liquor as alkali	%	0.0 %
Active alkali charge, as Na_2O	%	18.3 %
Active alkali charge, as NaOH	%	23.6 %

Chips to digester	BDt/d	7782
Effective alkali charge, as NaOH	BDt/d	1440
Active alkali charge as Na_2O	BDt/d	1421
Active alkali charge, as NaOH	BDt/d	1834
Active alkali in white liquor	kg NaOH/m^3	140.0
Active alkali in green liquor	kg NaOH/m^3	76.5
White liquor flow to cooking plant	m^3/d	13100
Green liquor flow to cooking plant	m^3/d	0
Real chemicals in white liquor	kg/m^3	177.5
White liquor solids to digester	BDt/d	2326
Real chemicals in green liquor	kg/m^3	206.6
Green liquor solids to digester	BDt/d	0
Kappa after cooking		18.0

3.1.2 Oxygen delignification

Caustic charge per Oxygen delignification production	kg NaOH/ADt	18.0
Oxygen charge	kg O_2/Adt	18.0
Caustic in oxidized white liquor	kg/m^3	96.5
White liquor flow	m^3/d	799.3
Real chemicals in oxidized white liquor	kg/m^3	214.3
Oxidized white liquor solids to O_2 reactor	BDt/d	171.3
Kappa after oxygen delignification		9.0
Washing loss organic		0.0
Washing loss inorganic		0.0
$MgSO_4$		0.0

3.1.3 Total white liquor required

Green liquor solids to digester	BDt/d	0
White liquor to cooking plant	m^3/d	13100
Oxidized white liquor to ox delignification	m^3/d	799
Oxidized white liquor to bleaching plant	m^3/d	0
Oxidized white liquor total	m^3/d	799
Total white liquor required	m^3/d	13899

3.2 BLACK LIQUOR CALCULATION

3.2.1 Cooking

Chips to digester	BDt/d	7782.0
Cooking yield	%	53.0
Blown stock	BDt/d	4124.5
Organic solids generated	BDt/d	3657.6
White liquor solids to digester	BDt/d	2325.6
Green liquor solids to digester	BDt/d	0.0
Water loss, as % of inorganic	%	6 %
Water loss	BDt/d	139.5
White liquor solids to black liquor	BDt/d	2186.1
Reaction water loss	BDt/d	85.6
Green liquor solids to black liquor	BDt/d	0.0
Lignin removal	kg/ADt	0.0
PHL that remained in the wood pores	kg/ADt	0.0
Total solids to black liquor	BDt/d	5758.0

3.2.2 Oxygen delignification

Pulp from reaction	BDt/d	4124.5
Oxygenated pulp	BDt/d	4042.0
Organic solids to black liquor	BDt/d	82.5
Bound O_2	BDt/d	77.1
Oxidized white liquor solids to O2 reactor	BDt/d	171.3
$MgSO_4$		
Total solids to black liquor	BDt/d	330.9
Solids lost to bleaching		0.0

3.2.3 Total solids in Black Liquor

Total solids to black liquor	BDt/d	6089.0
	kgDS/ADt	1420.8

Water with black liquor

Water with wood	kg/t Bleached pulp	1485.7
Dilution water (in pulp washing)	kg/t Bleached pulp	2500.0
Water in white liquor	kg/t Bleached pulp	2979.8
Water in green liquor	kg/t Bleached pulp	0.0
Water in oxidized white liquor	kg/t Bleached pulp	181.8
Reaction water with wood	%	1.1 %
	kg/t Bleached pulp	20.0
Steam condensate	kg/t Bleached pulp	212.4
Water leakages(sealing water etc)	kg/t Bleached pulp	446.0
Total water	kg/t Bleached pulp	7825.7
Dry solids from fibreline	%	15.4 %

BLACK LIQUOR HEATING VALUE – MILL S

Wood species in cooking		Euca
Chemical composition of wood		
Cellulose	%	45
Hemicellulose	%	23
Lignin	%	29
Extractives	%	3
Total	%	100
Wood type		hardwood
Bleached pulp production	BDt/d	3981
Yield from wood to cooking to dry unbleached cellulose	%	51
Washing efficiency unbleached pulp	%	99
Washing efficiency bleached pulp	%	99
Soap recovery efficiency	%	0
Water created by neutralization of acids in wood	kg/BDt	67
NCG generation during cook	% wood	3
Sulfur in NCG	kg/BDt	2
Methanol formation in Oxygen deliginification	kg/t Bleached pulp	0.2
Lignin removal	%	0 %
Hydrolysis Extraction yield	%	0 %
Lignin removal	kg/ADt	0
PHL that remained in the wood pores	kg/ADt	0
PHL that was removed	t/d	0

Organic balance		
Air dry bleached pulp	t/24h	4286
Dry bleached pulp	t/24h	3857
Dry unbleached cellulose	t/24h	3981
Dry wood demand to cooking	t/24h	7782
Dry wood demand to extraction	t/24h	7782
Hydrolysis Extraction yield	%	0.0
Wood requirement to produce 1000 kg unbleached cellulose	kg/BDt UB	1955
Loss and volatiles (incl. TRS-compounds)	kg/BDt	59
TRS-compounds lost (as methylmercaptan)	kg/BDt	3
Water generation as acids are neutralized	kg/BDt	67
Organic compounds to black liquor	kg/BDt	899
Organic compounds to pulp	kg/BDt	995
Lignin in wood used to produce one ton of unbleached pulp	kg/BDt	567
Lignin in unbleached pulp	kg/BDt	28
Lignin removed	kg/BDt	0
Lignin to black liquor	kg/BDt	539
Talloil content in wood	kg/BDt	2
Talloil stays in pulp	kg/BDt	0
Talloil recovered	kg/BDt	0
Talloil to black liquor	kg/BDt	2

other organic compounds generation (3 % wood)	kg/BDt	59
other organic compounds to pulp	kg/BDt	1
other organic compounds to black liquor	kg/BDt	58
PHL that was generated	kg/BDt	0
PHL that remained in the wood pores	kg/BDt	0
Organic acids to black liquor incl. PHL in pores	kg/BDt	300
organic matter to black liquor	kg/BDt	899
Heating value of Lignin	kJ/BDt	13530
Heating value of fatty and raisin acids	kJ/BDt	75
Heating value of organic acids	kJ/BDt	4158
Heating value of other organic compounds	kJ/BDt	1100
Heating value of PHL in pores	kJ/BDt	0
Heating value of all organic compounds	kJ/BDt	18863

White liquor

Active alkali as NaOH-% per wood	%	23.3
Active alkali kg/tn unbleaced pulp, Na_2O	kg/BDt	357
Active alkali kg/tn unbleaced pulp, NaOH	kg/BDt	455
NaOH charge as Na_2O	kg/BDt	203
NaOH charge as NaOH	kg/BDt	263
Na_2S charge as Na_2O	kg/BDt	153
Na_2S charge as NaOH	kg/BDt	198
Active alkali concentration, Na_2O	g/l	112
Active alkali concentration, NaOH	g/l	145
White liquor density (estimate)	g/l	1169
Na_2CO_3-quantity in white liquor Na_2O	kg/BDt	35
Na_2SO_4-quantity in white liquor Na_2O	kg/BDt	9
Inorganic compounds in white liquor	kg/BDt	557
Inorganic compounds in white liquor as Na_2O	kg/BDt	422

Green liquor

Active alkali as NaOH-% per wood	%	0
Active alkali kg/tn unbleaced pulp, Na_2O	kg/BDt	0
Active alkali kg/tn unbleaced pulp, NaOH	kg/BDt	0
NaOH charge as Na_2O	kg/BDt	0
NaOH charge as NaOH	kg/BDt	0
Na_2S charge as Na_2O	kg/BDt	0
Na_2S charge as NaOH	kg/BDt	0
Active alkali concentration, Na_2O	g/l	1574173
Active alkali concentration, NaOH	g/l	2031733
White liquor density (estimate)	g/l	1169
Na_2CO_3-quantity in green liquor Na_2O	kg/BDt	0
Na_2SO_4-quantity in green liquor Na_2O	kg/BDt	0
Inorganic compounds in green liquor	kg/BDt	0
Inorganic compounds in green liquor as Na_2O	kg/BDt	0

Black liquor

NaOH in black liquor	kg/BDt	113
Organically bound Na in black liquor	kg/BDt	88
Na_2S in black liquor	kg/BDt	186
Na_2CO_3 in black liquor	kg/BDt	60
Na_2SO_4 in black liquor	kg/BDt	21
Inerts from white liquor	kg/BDt	18
Inorganics in black liquor	kg/BDt	485
Heat in inorganics, (Na_2S heating value)	kJ/BDt	2403

Inorganics in pulp

NaOH in pulp	kg/BDt	1
Organically bound Na in pulp	kg/BDt	1
Na_2S in pulp	kg/BDt	2
Na_2CO_3 in pulp	kg/BDt	1
Na_2SO_4 in pulp	kg/BDt	0
Inorganics in pulp	kg/BDt	5
Black liquor dry solids formed during cook	kg/BDt	1384
	tDS/d	5340

Oxygen delignification

Bleached pulp	kg/BDt	980
Inorganic compounds in bleached pulp	kg/BDt	5
Organic compounds in bleached pulp	kg/BDt	975
Loss from unbleached pulp during bleaching	kg/BDt	20
Lignin in bleached pulp	kg/BDt	16
Lignin dissolved to bleaching effluent	kg/BDt	12
Methanol creation	kg/BDt	0.2
Organic acids to bleaching effluent	kg/BDt	8
Organics to bleaching effluent	kg/BDt	40

Oxidized white liquor

Reaction in white liquor oxidation: $2Na_2S + 2O_2 + H_2O \Rightarrow Na_2S_2O_3 + 2NaOH$

Use of oxidized white liquor in oxygen delignification	kg NaOH/BDt	18
Dry solids in unoxidized white liquor	%	15
Dry solids in unoxidized white liquor	kg/t WL unoxidized	150
Water in unoxidized white liquor	kg/t WL unoxidized	850
Na_2S-content in unoxidized white liquor	%	35
NaOH-content in unoxidized white liquor	%	47
Na_2CO_3-content in unoxidized white liquor	%	11
Na_2SO_4-content in unoxidized white liquor	%	4
TOTAL	%	96

Oxidizing reaction: $2Na_2S + 2O_2 + H_2O \Rightarrow Na_2S_2O_3 + 2NaOH$

Na_2S quantity in ton of unoxidized white liquor	kg/t WL unoxidized	52
Quantity of created $Na_2S_2O_3$	kg/t WL unoxidized	53
Quantity of created NaOH	kg/t WL unoxidized	27
Quantity of destructed water	kg/t WL unoxidized	6

NaOH in oxidized white liquor	kg/t WL oxidized	97
$Na_2S_2O_3$ in oxidized white liquor	kg/t WL oxidized	53
Na_2CO_3 in oxidized white liquor	kg/t WL oxidized	16
Na_2SO_4 in oxidized white liquor	kg/t WL oxidized	6
Water in oxidized white liquor	kg/t WL oxidized	844
Total oxidized white liquor	kg	1016

Oxygen delignification
$Na_2S_2O_3$ oxidizes completely into Na_2SO_4
$Na_2S_2O_3 + 2O_2 + 2NaOH \Rightarrow 2Na_2SO_4 + H_2O$

Oxygen deliginification thiosulfate oxidizing reaction destruction of NaOH	kg/kg WL oxidized	27
Oxygen deliginificationthiosulfate oxidizing reaction creation of Na_2SO_4	kg/t WL oxidized	95
Oxygen deliginification thiosulfate oxidizing reaction creation of H_2O	kg/t WL oxidized	6
Inorganics and water in effluent	kg	1090

Use of oxidized white liquor	kg/BDt	185
NaOH in oxygen delignification effluent	kg/BDt	12
$Na_2S_2O_3$ in oxygen delignification effluent	kg/BDt	0
Na_2CO_3 in oxygen delignification effluent	kg/BDt	3
Na_2SO_4 in oxygen delignification effluent	kg/BDt	17
Bound O_2	kg/BDt	19
Sum of inorganics to effluent	kg/BDt	51
Dry solids in bleachplant effluent	kg/BDt	*91*

Heating value in bleachplant effluent

Effluent heating value from lignin	kJ/BDt	299
Effluent heating value from organic acids	kJ/BDt	109
Effluent heating value from $Na_2S_2O_3$	kJ/BDt	0
Heating value in effluent	kJ/BDt	408
Sum of black liquor and effluent organics dry solids	kgDS/BDt	1475
	kgDS/ADt	1371
Total heating value of black liquor	kJ/BDt	**21675**
Heating value of black liquor dry solids	kJ/kg BLDS	**14692**

Dry solids to recovery boiler	kg/BDt UB	1475
Organics in dry solids	%	63.63
Total black liquor to recovery boiler (incl. Water)	kg/BDt	1864
Black liquor density (estimate)	g/l	1400
Heat into recovery boiler	GJ/BDt	**21.68**
	GJ/s	**0.999**

EVAPORATION PLANT BALANCE – MILL S

Black liquor dry solids (virgin)	tDS/d	6097
Weak black liquor conc	%	15 %
Strong black liquor virgin concentration	%	79 %
As fired black liquor concentration	%	81 %
Evaporation capacity	t/h	1321
IPPC BAT Spills	% extra	0 %
	t/h	0
Required evaporation capacity IPPC total	t/h	1321
Total solids to as fired black liquor	tDS/d	6768
Total as fired black liquor	tBL/d	8389
Evaporation capacity	kg/s	367
Steam economy with stripper	kJ/kg$_{H2O}$	415.0
MP steam usage	%	19 %
MP Steam requirement	kJ/kg$_{H2O}$	78.9
LP Steam requirement	kJ/kg$_{H2O}$	336.2
MP Steam requirement	kg/s	12
	kg steam/kg evap.	0.033
LP Steam requirement	kg/s	50
	kg steam/kg evap.	0.137
Steam economy with stripper	kg/kg	5.89
Stripper TRS removal efficiency	%	95 %
Stripper methanol removal efficiency	%	90 %
Heat economy for hot water usage	kg/kg	0.29

Publication I

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World's largest biofuel and pellet plants – Geographic distribution, capacity share, and feedstock supply

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Perspective

World's largest biofuel and pellet plants – geographic distribution, capacity share, and feedstock supply

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Abstract: Biomass can be used for energy purposes by either combustion to heat and power or refining into solid and liquid biofuels. The majority of biomass is used for residential purposes in developing countries. Modern biomass use in industrialized countries is increasing, and more and more biomass is also traded to be used for energy purposes. The purpose of this paper is to locate the 15 largest ethanol, biodiesel, and wood pellet plants. Facilities generating heat, steam and electricity were left out. Secondly it is not generally known what share of biomass users are large plants. Also an effort is made to find out how much these large-scale biomass refining plants use imported feedstock. For the most part, very large industrial processing facilities are found in a small number of countries. The largest ethanol mills are found almost exclusively in the United States, with one very large plant in the Netherlands. The distribution of biodiesel and wood pellet plants is more dispersed. The countries with the most large biodiesel plants include the USA, Brazil, Spain, and the Netherlands. The countries with the most very large wood pellet plants include the USA, Canada, Russia, and Germany. Torrefaction and pyrolysis technologies are still rarely used on industrial scale. Ethanol and wood pellet plants tend to be sourced from local feedstocks, while biodiesel plants are much more likely to use imported feedstocks or a mix of imports and local biomass. All of these fuels are increasingly traded through the international market. © 2014 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: biomass; biofuels; biomass refining; large-scale biomass processing plants; industrial use of biomass

Introduction

Currently, biomass and waste covers about 10%* (55 EJ) of the global primary energy consumption (Fig. 1).[1] Biomass use for energy is increasing especially in the industrialized countries, where modern methods for biomass utilization are being adopted.[3] For example, in the EU biomass-based energy is playing an important role within the year 2020 climate targets set.[4]

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*This represents IEA category biomass and wastes. The IEA does not provide more detailed data of biomass. Despite waste consists partly of non-organic material we assume the portion of non-organic material to be negligible.[2]

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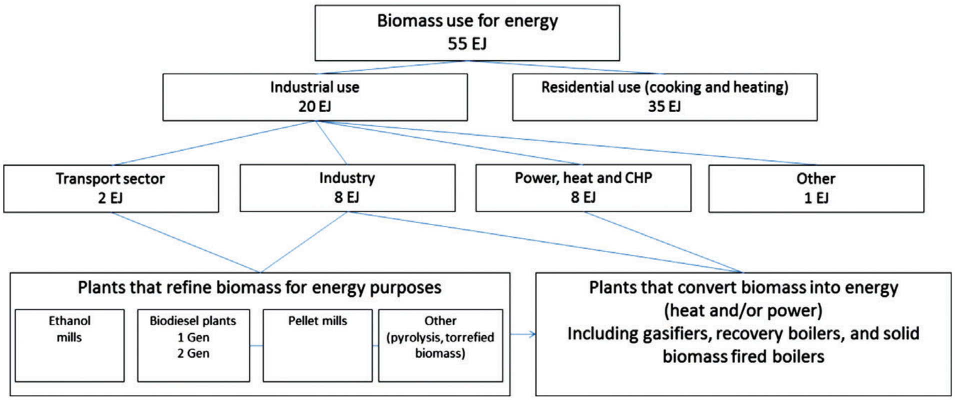

Figure 1. Categorization of biomass users and biomass consumption by sector in the year 2011. Biomass use figures are from the IEA.[1]

Increase in biomass use in industrial-scale applications has had many obstacles due to biomass properties, such as low energy density, high moisture content and heterogeneous consistency. Creating a suitable biomass supply chain can create large problems.[5] Pre-processing and refining of raw biomass improves significantly the utilization possibilities. Refined biomass in solid, liquid, or gaseous form can be transported more easily than raw and unprocessed biomass and used in a wider range of applications than before. Biomass refining for energy purposes is becoming more widely used.[6] There are several large-scale plants currently in operation and under planning.[2]

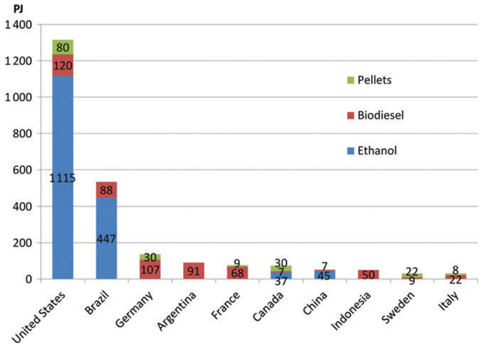

Figure 2. The 10 largest biofuel (ethanol, biodiesel, and pellet) producer countries in 2011. The countries produced 85% of the global ethanol, biodiesel, and pellet production.

Biomass processing for energy purposes is concentrated in a small number of countries (Fig. 2). Currently (in 2012), ethanol (1 790 PJ), biodiesel (700 PJ), and pellet (310 PJ) are the most important biomass refining processes for energy in terms of production volumes. Significant amounts of charcoal (about 1 EJ in 2011) are also produced, but primarily on a small scale using traditional methods. Brazil is the largest charcoal producer covering 14% of the global production in 2011.[17] Torrefaction and pyrolysis are still developing technologies and the global capacity is negligible, together they account for less than 20 PJ/a. Current torrefaction and pyrolysis plants are primarily pilot and demonstration plants.[18,19]

Because biomass is typically a locally limited resource, large users of biomass have often to import feedstock from larger and often expanding locations. Several studies have shown that international biomass trade for energy purposes is growing rapidly.[7–16] Industrialized comprehensive energy statistics and country specific studies[†] in particular give good overviews of biomass use for energy and biomass markets. However, no studies available summarize up to date information about biomass use at plant level in various sectors. Specifically this study wanted to find out the proportion of the 15 largest plants, which use imported feedstocks as opposed to locally grown biomass, for processing to solid and liquid biofuels. Plants that directly convert biomass to energy (heat, steam and electricity) were left out.

[†] Such as country reports of IEA Bioenergy Task 40, www.bioenergytrade.org/publications

In this study, the objective is to find out how processes for biomass refining into biofuels are used globally and how processing is distributed between different technologies. The studied technologies are pellet, biodiesel, ethanol, and charcoal production, together with torrefaction and pyrolysis. An effort was made to find out whether the large biomass users (which was arbitrarily set as the 15 largest plants found) use local or imported biomass. Biomass refining and processing facilities under planning were studied to evaluate their effect on global biomass use and markets in the near future. The information used reflects the state at the end of the year 2012. The plant-level situation is changing rapidly as new capacity is being added. Comprehensive and accurate information of the plants has been challenging to find; therefore the results should be considered as indicative. The study was done using literature, statistics, databases, reports, and reviews, most of them publicly available complemented with information from personal communications mainly within IEA Bioenergy Task 40 Sustainable International Bioenergy Trade: securing supply and demand.

Biomass conversion for energy purposes

Biomass is a material of biological origin including both plant- and animal-derived materials. More than 80% of biomass used for energy purposes globally is derived from wood.[13] The rest is from the agricultural sector with various waste and by-product streams. Modern biomass refining and processing systems use several species and types of biomass, whereas older existing bioenergy systems use mainly wood, residues, and waste for heat and power production and agricultural crops for liquid biofuels. Biomass is mainly available in low-density form, which is why it typically demands more storage space, transport, and handling than conventional fuels. Pre-treatment such as densification is required when biomass used for energy is transported longer distances.[15,16]

In 2011, the total use of biomass for energy purposes was 55 EJ.[1] About two-thirds of the biomass use was residential, mainly in developing countries for cooking and heating purposes. Industry and energy generation were the second largest user sectors with consumption of 8 EJ, with the transportation sector (2 EJ) trailing. In the industrial sector, used biomass consisted almost entirely (98%) of primary solid biomass; this includes plant matter used directly as fuel or processed before combustion, covering also for example charcoal and black liquor. Industrial biomass use is concentrated in a small number of countries. Fifteen countries use 80% of the global solid biomass usage in industrial sector. Figure 1 presents the categorization of biomass users used in this study. The focus of this paper is on those plants that process or refine biomass into solid or liquid biofuels. The resulting fuels can be further refined to other bioproducts or used as chemicals (methanol, fertilizers, synthetic fiber), energy (heat, electricity) or as transportation fuels.

Large-scale processing and refining of biomass for energy at country and plant level

The USA and Brazil are the major fuel ethanol producers. In 2011, the USA and Brazil produced as much as 87% of the global fuel ethanol production.[20] In the USA, there are over 200 industrial ethanol mills using mainly corn as raw material. The annual ethanol production capacity is about 1.2 EJ.[20] In Brazil, ethanol production is based on sugarcane and there were over 440 mills producing ethanol in 2012. The ethanol production capacity in Brazil was about 0.9 EJ, of which Barros[21] estimates that 59% was in use. Based on these capacities it is estimated here that the global ethanol production capacity is around 2.3 E J/a. According to this estimation, the average utilization rate was about 80% in 2011. The mills can be assumed to use local feedstock, due to their location near feedstock sources. Lignocellulosic (second-generation) ethanol production technologies are still in developing phase. Brazilian mills are typically smaller than the mills in the USA; one of the 15 largest operational ethanol mills globally is located in the Netherlands, all the others are in the USA. The capacity of the 15 largest ethanol mills is about 216 PJ/a equaling to 9% of global production capacity. The 15 largest ethanol mills are depicted in Table 1.

The global wood pellet production was estimated at 18.3 million tonnes (310 PJ) in 2011.[22] The global production capacity at the same time can be estimated to be about 35 million tonnes (595 PJ). This means that 52% of the capacity was in use. Most of pellet production takes place in North America and Europe. Also the largest pellet mills are located mainly in Northern America and Europe.[23] Global pellet production capacity in 2012 can be estimated to be around 40 million tons (680 PJ/a), of which the capacity of the 15 largest mills covers 14% (95 PJ/a) (Table 2). The largest pellet mills use primarily local feedstock, mainly sawdust and various other wood residues.[24] The production of the largest mills is mainly aimed for European markets, both from Europe and Northern

Table 1. The largest ethanol mills at the end of 2012.[15,26]

No.	Mill	Production capacity	
		Ml/a	PJ/a
1	Archer Daniels Midland, Columbus, NE, USA	1 136	24
2	Archer Daniels Midland, Decatur, IL, USA	1 098	23
3	Archer Daniels Midland, Cedar Rapids, IA, USA	1 041	22
4	Archer Daniels Midland, Cedar Rapids, IA, USA	908	19
5	Archer Daniels Midland, Clinton, IA, USA	897	19
6	Cargill, Blair, NE, USA	738	16
7	Aventine Renewable Energy, Pekin, IL, USA[a]	606	13
8	Tharaldson Ethanol, Casselton, ND, USA	568	12
9	Valero Renewable Fuels, Jefferson Junction, WI, USA	492	10
10	Abengoa Bioenergy Netherlands, Rotterdam, Netherlands	480	10
11	Green Plains Renewable Energy, Bluffton, IN, USA	454	10
12	Green Plains Renewable Energy, Obion, TN, USA	454	10
13	Valero Renewable Fuels, Aurora, SD, USA	454	10
14	Absolute Energy, St. Ansgar, IA, USA	435	9
15	BioFuel Energy - Buffalo Lake Energy, Fairmont, MN, USA[a]	435	9

[a]Halted in September 2012 due to lack of feedstock.

Table 2. The largest biodiesel plants at the end of 2012. Feedstock origin: L (Local), I (Import), M (Mixed),? (Not known).[19,27–29]

No.	Company, Location	Feedstock origin	Production capacity	
			1000 t/yr	PJ/yr
1	Neste Oil, Rotterdam, Netherlands	I	800	30
2	Neste Oil, Singapore, Singapore	I	800	30
3	Biopetrol, Rotterdam, Netherlands	?	650	24
4	Infinita Renovables, Castellon, Spain	M	600	22
5	Archer Daniels Midland, Hamburg, Germany	?	580	22
6	Neste Oil, Porvoo, Finland	I	525	20
7	Ital Green Oil, Verona, Italy	?	360	13
8	Imperium Grays Harbor, Hoquiam, WA, USA	M	333	12
9	Oleoplan, Veranópolis, RS, Brazil	L	333	12
10	ADM, Rondonópolis, MT, Brazil	?	303	11
11	Infinita Renovables, El Ferrol, Spain	M	300	11
12	Green Earth Fuels of Houston, LLC, Galena Park, TX, USA	?	300	11
13	Granol, Cachoeira do Sul, RS, Brazil	L	296	11
14	Louis Dreyfus Agricultural Industries, Claypool, IN, USA	L	293	11
15	Archer Daniels Midland, Velva, ND, USA	L	283	11

America. European pellet production covered in 2010 still the EU demand, but the consumption is increasing faster than the production.[8]

Biodiesel is produced more in Europe than in other continents. The 15 largest biodiesel plants are located in Europe, Singapore, Brazil, and the USA. The global biodiesel production in 2011 was around 18.8 Mt (700 PJ), of which 48% (9 Mt) was produced in the EU.[22,25,26] The Global Biofuels Center[27] has estimated that biodiesel production capacity in 25 largest producer countries is 57 billion liters equaling to 1.9 EJ. Global biodiesel capacity can thus be estimated to be about 2.0 EJ, which means that about one-third of the production capacity was in use in 2011. The 15 largest biodiesel plants use vegetable oils as feedstock, and their production capacity covers about 13% of the global biodiesel capacity (Table 3). Many of the largest plants use imported feedstock. Some of them use both imported and local raw material. In Europe, biodiesel has been produced primarily from rapeseed oil, and in the USA from soybean. The share of soybean oil is increasing also in Europe. Smaller amounts of palm oil and fats are used.

Figure 3 compares the global production capacity and actual production (estimated or known) of ethanol, biodiesel, and pellet plants in 2012, and shows the share of the 15 largest plants in each sector. Utilization rate of the ethanol production capacity is quite high, about 80%, whereas only about a third of the biodiesel capacity and about half of the pellet capacity was utilized. The 15 largest plants produced about 30% of the global biodiesel production, as for ethanol mills the share of the largest mills was about 10% and for

Table 3. The largest pellet producers at the end of 2012. Feedstock origin local (L), imported (I), mixed (M), or not known (?).[18,19,30]

No.	Company, Location	Feedstock origin	Production capacity	
			1000 t/a	PJ/a
1	Vyborgskay Cellose, Leningrad Region, Russia	L	900	15
2	Georgia Biomass (RWE), Waycross GA, USA	L	800	14
3	Green Circle (JCE Group), Cottondale FL, USA	L	550	9
4	Biowood, Averøy, Norway[a]	I	450	8
5	Pinnacle Pellet, Burns Lake BC, Canada	L	400	7
6	Enviva, Hertford, Ahoskie, NC, USA	?	380	6
7	Pacific BioEnergy, Prince George BC, Canada	L	360	6
8	German Pellets, Wismar, Germany	?	256	4
9	German Pellets, Herbrechtingen, Germany	?	256	4
10	Arkaim, Khabarovsk, Russia	L	250	4
11	Fram Renewable Fuels, Appling Country Pellets, Baxley, GA, USA	L	220	4
12	Pinnacle Pellet Meadowbank, Strathnaver BC, Canada	L	200	3
13	Ankit, Bengaloouru, India	?	200	3
14	Hongyi Biofuels, Linyl, Shandong, China	?	200	3
15	Premium Pellet, Vanderhoof BC, Canada	L	190	3

[a]Production ended in 2013.

pellet mills about 16%. The largest plants are concentrated in a small number of countries. Figure 4 shows how the capacity of the largest plants is distributed between these counties.

Even though the largest part of the biomass processing capacity for energy is ethanol followed by biodiesel and pellet, the share of large plants of the total is fairly similar. Although for biodiesel production in 2012 the share of largest plants was high. This means that the processing of biomass for energy at global level is not concentrated on large plants but is distributed widely. However, it is fairly evident that at single country level a single plant (i.e., biodiesel production in Singapore) can have a dominant production role.

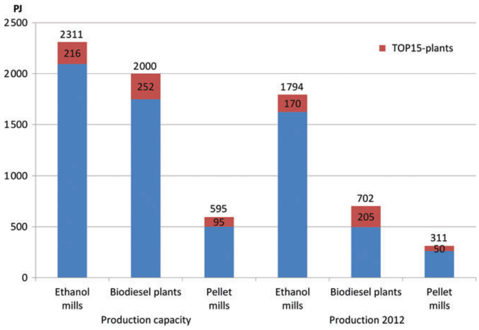

Figure 3. Comparison of global capacity and estimated or known production in 2012 of ethanol, biodiesel, and pellet production and the share of the 15 largest plants in each sector.

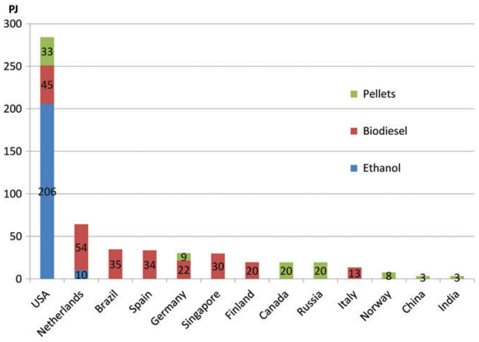

Figure 4. The distribution of the production capacity (PJ) of the 15 largest ethanol, biodiesel, and pellet plants between countries at the end of the year 2012.

Biomass used in the largest plants is typically not imported but from local sources. Imported biomass is used variably in different plants. Plants using imported, or a mixture of imported and local biomass, cover 50% of the capacity of the 15 largest biodiesel plants. In ethanol production 95% of the feedstock was from local source, and 5% remained unknown. Pellets are produced mainly from locally sourced biomass.[28] So except for biodiesel plants, the tendency still seems to be to build plants that utilize local biomass and sell refined biomass instead of building refining plants near final usage and import biomass.

Prospects for biomass refining to biofuels

The future development (next 2–5 years) of biomass refining capacity can be estimated via examination of refining plants planned or under construction. The analysis is based on the prevailing situation at the end of the year 2012. Due to the lack of comprehensive, timely information, and the fact that not every plan is realized, the results should be considered indicative and used with care. Figure 5 shows how projects under planning would, if realized, affect the global ethanol, biodiesel and pellets production capacity. Like the existing capacity, also the planned projects are located in a small number of countries; the distribution of the planned capacity between the countries can be seen in Fig. 5. The largest ethanol production projects planned or under construction are located primarily in the USA; some projects are planned also in Europe and Brazil. The investments in new ethanol mills in Brazil have been decreasing recently and at the same time the ethanol imports from the USA have been increasing.[29,30] Global ethanol capacity is estimated to increase with about 80 PJ. Figure 5 shows that there is significantly more capacity using mostly local biomass resources planned for biodiesel than for pellet or ethanol production.[31–35] However, the majority of planned biodiesel capacity is in two projects in India. Planned biodiesel capacity is around 630 PJ. Excluding the Indian projects, the capacity would be around 120 PJ. There are several pellet mills under planning, especially in the USA and Canada. The mills are located in areas with large forest biomass resources, and pellet production is mostly aimed for export to Europe but also to Asia. The planned pellet capacity in this study is estimated at about 250 PJ.

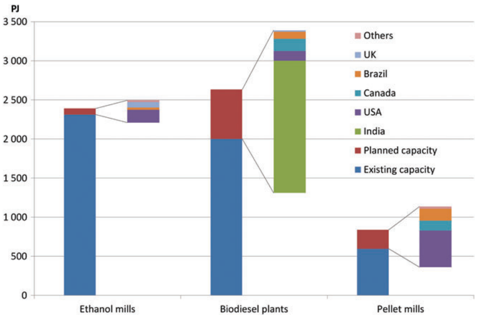

Figure 5. Biomass refining capacity planned or under construction, its effect on the existing capacity, and the distribution of the planned capacity between countries. The figure reflects the situation at the end of the year 2012. It should be noticed that all the plans will not be realised, and that majority of the planned biodiesel capacity consists of the capacity of two projects.

New products have not yet appeared in volume. A few renewable diesel production projects were also found, capacity in total is around 15 PJ. These are located in Finland and France. Plants producing pyrolysis oil from woody biomass are under planning in Europe, Canada, and Australia. The total capacity of these is less than 10 PJ. It seems that the predicted trade of refined biofuels to EU will likely continue to increase in the near future.[36,37] It seems that feedstock availability will define where and whether new plants will be built. There is a huge difference in economics and most probably also on biomass sourcing for different size plants. The initial assumption was that large plants would be first to use imported biomass, therefore this study was limited to those. In the future, expanding the field to smaller plants would make an important contribution.

Conclusions

Biomass refining to liquid biofuels takes place primarily by means of first-generation conversion to ethanol and biodiesel. Pellet production is growing fast, but the global capacity is significantly smaller than that of biodiesel and ethanol. The capacity utilization rate is lower for biodiesel than for ethanol or pellets. Biomass torrefaction and pyrolysis are still in the development phase, and it seems that in the coming few years pyrolysis oil and torrefied biomass will not become similar global biomass commodities as pellets, ethanol, and biodiesel currently are. Large-scale refining of biomass is concentrated in a small number of countries. A significant part of the total capacity is in the USA because the majority of large ethanol mills are located there. Pellets are produced mainly in Europe and North America, and the largest biodiesel plants are located in the EU area and Singapore. Currently biomass is processed primarily near the biomass source using local feedstock. Biodiesel production is the exception. Biomass processing for energy purposes is increasing, and new plants are planned, mostly in the industrialized countries and near feedstock sources like the existing ones. While the use of raw biomass seems to remain local, the trade of refined biofuels will likely continue to increase in the near future. Pellet mill capacity in the USA and Canada can be expected to increase, and the production of the new mills is primarily aimed for export to Europe. The share of largest 15 plants both capacity and production wise was small for all categories, roughly between 10 and 30%. The share was largest for biodiesel plants and smallest for ethanol mills.

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Publication II

Kuparinen, K., Vakkilainen, E., and Ryder, P.
Integration of electrolysis to produce hydrogen and oxygen in a pulp mill process

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Integration of electrolysis to produce hydrogen and oxygen in a pulp mill process

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SUMMARY

The pulp and paper industry faces demand for totally carbon free production. Due to local conditions, there are challenges to sell produced additional electricity. A novel way, generating hydrogen and oxygen through the electrolysis of water can decarbonize the largest fossil carbon dioxide producing equipment, the lime kiln. The oxygen produced can be used for generation of bleaching chemicals, and also for effluent treatment. The operation and capacity of the recovery boiler can be improved by oxygen use. Using excess electricity of a typical, large South-American pulp mill, 73% of the heat demand of the lime kiln can be covered with hydrogen and the produced amount of oxygen exceeds the mill's oxygen requirement. The profitability of the integration depends on the other possible uses for electricity. When sales price for electricity is low or purchased oil price is high electrolysis can decrease the operating costs of a modern pulp mill.

KEYWORDS

Water electrolysis, hydrogen, oxygen, lime kiln, recovery boiler

INTRODUCTION

The pulp and paper industry is an energy-intensive industry. Globally, the pulp and paper sector is the fourth largest industrial sector in terms of energy consumption *(1)*. The share of renewables is high in both energy production and consumption in this sector, but fossil fuels are however still used. It is essential to find substitutes for fossil fuels in order to reduce carbon dioxide emissions and consequently the environmental impacts of the processes. Modern pulp mills produce heat and electricity during the normal operation process using residual biomass. Typically, all or nearly all the energy used in the process is from the mills own production *(2)*. Many pulp mills also produce heat and electricity in excess of their own requirements.

When considering modern pulp production, the lime kiln is typically the only user of fossil fuels during normal operational process. Lime kilns are mainly fired with natural gas, or fuel oil when natural gas is not available. Previous studies on fossil fuel free pulp mill concepts include lime kiln fuel replacement with gas from biomass gasification or lignin extracted from black liquor *(3)*. An example of this is bark gasification at the Metsä Fibre Joutseno pulp mill *(4)*.

The objective of this study is to explore an exciting new alternative of producing hydrogen and oxygen at a pulp mill using water electrolysis. As electricity at the pulp mill is renewable, then hydrogen produced is a renewable fuel. If this hydrogen is then burned in the lime kiln, the main source of fossil fuel based emissions at the pulp mill can be replaced. The effects of electrolysis integration on the mass and energy balances of the mill are calculated, and possibilities for the use of oxygen and hydrogen are assessed. The study evaluates possible routes to use the electricity in a water electrolysis process to produce hydrogen and oxygen (Fig. 1).

The feasibility is evaluated by reviewing the available technologies as well as the mass and energy balance calculations. Oxygen is used at pulp mills for various purposes, such as for delignification and bleaching, and it is therefore either produced at the mill or purchased. With a suitably sized electrolysis plant, a separate oxygen production plant would not be needed. Oxygen is also used in the production of ozone and hydrogen peroxide which can be used in the bleaching process and also for effluent treatment. However in these cases the requirement for oxygen may necessitate an oxygen plant.

Hydrogen could be a possible full substitute for fossil fuels used in the lime kiln. Hydrogen has been burnt in lime kilns, as a complement to natural gas at some pulp mills. For instance at Stora Enso Oulu mill in Finland, 2000 tons of hydrogen is used in the lime kiln annually; about 250 TJ energy is thus produced *(5)*. UPM pulp mill at Fray Bentos, Uruguay also uses hydrogen and methanol as lime kiln fuels in addition to heavy fuel oil. Hydrogen comes from the chlorate plant which is located on-site and operated by the supplier company, Kemira. Due to higher combustion temperatures and limited liner brick resistance, these additional fuels are not used continuously *(6)*.

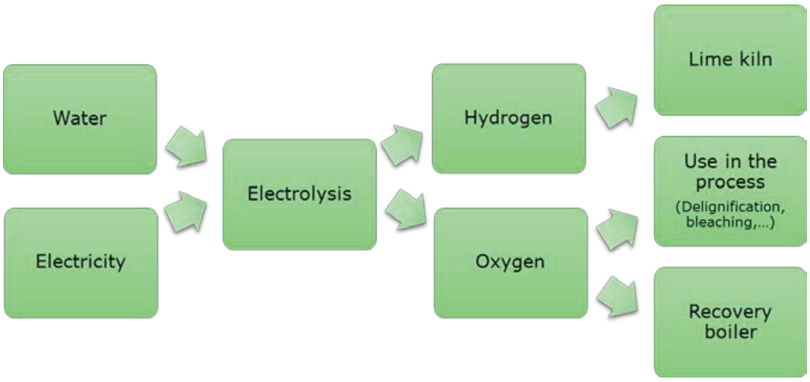

Fig. 1. Studied concept – water electrolysis integration with the pulp mill process

METHODS AND MATERIAL

Millflow

The pulp mill mass and energy flows have been calculated using the *MillFlow* program. This is a mill spreadsheet including a detailed mass and energy balance, and it has been developed and updated at LUT Energy *(3, 7)*. More detailed description of *MillFlow* can be found in *(7)*.

Case selection

The target of this study is to evaluate the technical feasibility of the selected cases. The example mill studied, in this case, is a modern eucalyptus mill located in South America. The annual pulp production is 1.5 million ADt. This base case has been introduced in detail in the previous study *(7)*. In such modern pulp mills, excess electricity of renewable origin is produced at the mill, but the lime kiln requires externally supplied fuel oil. Two cases of different configuration are studied in order to find out how electrolysis integration would affect the main mill mass and energy balances:

A. In case A the electrolysis process is scaled to meet the oxygen demand of the mill. Hydrogen is combusted in the lime kiln to replace as much fossil fuel as possible.
B. In case B the electrolysis process is scaled to meet the lime kiln fuel demand, considering the maximum amount of electricity available for electrolysis. The generated oxygen is used firstly at the mill, and then secondly to boost the recovery boiler (oxygen enriched air combustion) *(8)*.

Lime kiln operations

In a pulp production process, the lime kiln is a part of the chemical circulation called the lime circuit. The lime cycle consists of causticizing and lime mud re-burning processes *(9)*. Lime is used to convert green liquor from the recovery boiler into white liquor in the causticizing process. Calcium oxide (CaO) reacts with sodium carbonate (Na_2CO_3) in green liquor to form sodium hydroxide (NaOH) and calcium carbonate ($CaCO_3$). Lime reburning in the lime kiln converts calcium carbonate back into calcium oxide according to reaction 1. The re-burning process requires external heat for the reaction, to increase calcium carbonate to the typical final temperature of about 900 to 1300 °C, to dry the water containing lime mud and for process heat losses. Typically, lime kilns are fired with fuel oil or natural gas, but often small amounts of alternative fuels, such as methanol, tall oil, strong odorous gases and turpentine are also used. A few lime kilns are fired with alternative fuels; bark and oil pitch *(10)*. The lime kiln operation requires stable combustion conditions as well as easily controllable temperature; therefore the homogeneous consistency of the fuel used is highly relevant. A modern lime kiln is often equipped with burners suitable for both gas and oil combustion. Hydrogen can substitute natural gas in lime kiln without significant modifications in the combustion equipment *(11)*.

$$CaCO_3 \rightarrow CaO + CO_2 \quad [1]$$

Power-to-gas processes and hydrogen production via electrolysis

Power-to-gas is a process, whereby electricity is transformed into gas *(12)*. The first step is to use electricity to split water or steam to hydrogen and oxygen in a water electrolysis process. Water electrolysis is the link between electrical and chemical energy in power-to-gas processes. Typically, hydrogen is the main product, but use or sale of oxygen increases the profitability of the process. Hydrogen can be used for energy or as feedstock, stored, or refined further into methane.

Power-to-gas and gas-to-power technologies are envisioned to make use of intermittent solar and wind power more flexible and usable. It is expected, that when solar and wind power production increases, the variation in electricity prices will also increase. Power-to-gas technologies can then increase the profitability of electricity production; gas can be produced when electricity price is low.

Hydrogen (H_2) is a colourless, odourless and highly flammable gas with high energy content, around 119 MJ/kg. It burns in air at a wide range of concentrations, and can be used in various energy production applications. However, the flammability makes storage and transportation of hydrogen difficult, and although it has a high energy content in relation to mass, the energy content in relation to volume is poor. Therefore, the best option is to use hydrogen near the source, if possible. Water electrolysis is a method to split water into oxygen and hydrogen using electricity, following reaction 2.

$$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g) \qquad [2]$$

Alkaline electrolysis (AEC) is a simple, commercial process with the advantage of high purity of the produced hydrogen. Typically, it is used for hydrogen production on a small scale *(13)*. The production challenges are related to energy consumption, cost, and maintenance. The operating temperatures of the commercial processes are typically in the range of 70 to 90 °C *(12)*. Steam electrolysis using solid oxide electrolysis cell (SOEC) is currently a hydrogen production process under development. It operates at high temperature, from 550 to 800 °C *(13)*. The electrical energy consumption of water electrolysis is around 4.5 kWh/Nm^3 (H_2), while the consumption for the SOEC process could be significantly smaller at about 3 kWh/Nm^3 (H_2) *(14)*. Sunfire GmbH in Germany is currently developing a SOEC electrolysis system with operating temperature over 700 °C *(15)*.

AEC is the most developed water electrolysis technology *(12)*. Currently, it is also the most used commercially available technology for an industrial-scale electrolysis process and has therefore been used for this study. The alkaline electrolysis cell is composed of two electrodes (anode and cathode) and a liquid electrolyte, which are typically enclosed in a steel container. The electrolyte is usually 25 to 30% aqueous potassium hydroxide *(13)*. Water is consumed during the process, but the amount of potassium hydroxide decreases only slowly over time due to process losses. The efficiency of an electrolysis system varies according to the system pressure and size. The power-to-gas process efficiency from electricity to hydrogen varies between 50 to 75% *(12)*. A conventional alkaline electrolyser can be operated between 20 to 100% of the nominal capacity, but operation below 60% capacity will reduce both the system efficiency and the quality of the gas produced *(12)*. Currently electrolysers are suitable for conventional purposes where stable hydrogen production is needed. However dynamic operation, where it is required to intermittently adjust the electricity production of renewable energy sources to electricity consumption, is still a problem due to lower efficiencies and lower gas quality.

Hydrogen and oxygen production and use at pulp mill using electrolysis

Alkaline electrolysis is the chosen method for hydrogen and oxygen production as it can be easily integrated with an existing pulp mill process. The availability of water treatment equipment and the existing use of oxygen in the process reduces the auxiliary equipment investment requirement. If an electrolyser acts as an online unit and produces hydrogen directly to be used in the lime kiln, there is no need for hydrogen storage. This makes the process more straightforward and safer, and decreases investment cost.

Oxygen is used at pulp mills for delignification and bleaching, and it is often manufactured on-site. Oxygen can be separated from air using a cryogenic separation process or by absorption, but cryogenic separation is more common. Cryogenic separation produces oxygen of high maximum purity of 99.9%, while the maximum purity of on-site installed absorption processes is 95%. Specific power demand for cryogenic oxygen production varies from 200 to 550 kWh/t (O_2) depending on unit size and required oxygen purity, and for absorption processes from 265 to 350 kWh/t (O_2) *(16-18)*.

The purpose of oxygen delignification is to remove residual lignin after cooking and before bleaching. Lignin is the primary factor influencing the pulp colour. Lignin removal before bleaching reduces mill emissions. The chosen oxygen charge in the example delignification process is 16 kg/ADt, which corresponds to a typical charge *(19)*; in addition 2 kg/ADt is used for oxidized white liquor. During bleaching 2 kg/ADt is assumed.

Oxygen enriched combustion in a recovery boiler

Oxygen enriched air technology (OEA) is used to increase the oxygen content in boiler inlet from the 21% in plain air. This results in a lower amount of flue gases and the possibility to increase the capacity of an existing recovery boiler. OEA has been found to increase a boiler's black liquor dry solids burning capacity by approximately 10 to 20% over the previous capacity by using nominally 25% oxygen at the secondary and tertiary air levels *(8)*. Oxygen enrichment increases the combustion temperature in the boiler, which results in more rapid and stable combustion *(8)*. The combustion temperature affects the amount of volatile combustible gas emissions, such as total reduced sulfur, sulfur dioxide, and carbon monoxide emissions, so these are expected to be reduced with the implementation of OEA.

Basis for the calculations

The calculations are based on *MillFlow* mill balances and literature data. The pulp mill calculations using *MillFlow* have been presented earlier *(7)*. The alkaline electrolysis process has been modelled based on thermodynamics, empirical electrochemical kinetics and heat transfer theory *(20-22)*. For the alkaline electrolysis process, the following assumptions have been made:

- Oxygen and hydrogen produced have been considered pure.
- Feed water quality has been considered to meet the requirements of boiler water. Requirements for water quality vary with the type of electrolyser *(23)*.
- Water has been considered as an incompressible fluid.
- Hydrogen and oxygen are considered as ideal gases.
- Gas and liquid phases are assumed to be kept as separated.
- Atmospheric pressure has been assumed. The operating pressure has an influence on the cell voltage, but it is small *(12)*.
- The electrolyser consists of identical cells connected in series.
- All heat generated during the process is assumed to be removed with cooling water. System temperature is therefore considered constant.
- The auxiliary systems electricity requirement is assumed to be 8% of the electrolyser capacity *(24)*.

The electrical consumption in relation to the hydrogen production is approximately 50 kWh/kg (H_2) with this model, which corresponds to the current state of electrolyser development *(25)*. In the future, the efficiency is expected to increase, which will affect the profitability of the processes accordingly.

The electrolysis reaction generates heat; therefore the electrolyser needs cooling. Cooling is in these cases part of the mill water system, and the heat generated could be utilised at the mill. In the example cases, cooling water inlet temperature is 45 °C and outlet temperature 75 °C, when the electrolysis reaction temperature is 80 °C. The amount of heat generated as well as the required cooling water flow is calculated for both cases. The feed water for electrolysis is assumed to come from the existing mill water treatment plant, and the amount is calculated for each case.

Electricity is generated at the mill using steam from the recovery boiler. A separate biomass boiler for power generation is not considered for the studied case. However, it is possible to increase electricity generation by using a separate biomass boiler for power production if residual biomass is available. This may not always be the case. For instance in Brazil, eucalyptus is typically debarked in the forest, which means that bark is not available for energy generation at the mill *(26)*.

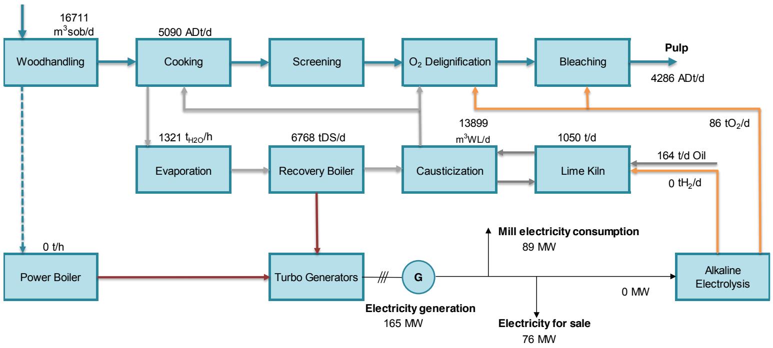

Fig. 2. Main process flows in the Base Case – No electrolysis.

RESULTS AND DISCUSSION

Effects of electrolysis integration on mill operation in the selected cases A and B

In the studied cases, excess electricity is produced at the mill and it can be used for electrolysis process as an alternative to selling. The studied mill produces 1,500,000 ADt eucalyptus pulp annually, equivalent to 4286 ADt/d with 350 operating days per year. Oxygen use for delignification and bleaching is 86 t/d, arising from 16 kg/ADt oxygen charge for oxygen delignification, 2 kg/ADt for oxidized white liquor preparation, and 2 kg/ADt charge for bleaching, after also considering caustic make-up as a charge to the oxygen delignification stage.

The Base Case represents the situation without integrated electrolysis. Lime kiln heat demand is 72 MW, which is covered by using fuel oil 164 t/d, the heating value of the oil being 38 MJ/kg. The total electricity generation is 165 MW, of which 89 MW is used in the mill process. This results in 76 MW excess electricity production. The process flows in the Base Case are depicted in Figure 2. Electricity use for oxygen production is calculated at 3.4 MW, which means that without separate oxygen production approximately 79 MW is available to be used in the electrolyser.

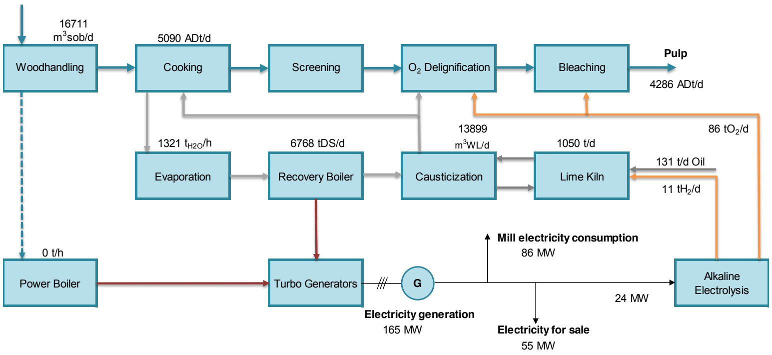

Fig. 3. Main process flows in Case A, where electrolysis capacity is scaled according to the oxygen requirement of the process.

In the first studied case, Case A, the electrolysis process is scaled to meet the oxygen demand of the studied mill. Hydrogen is burnt in the lime kiln to replace fuel oil as much as possible. To cover the oxygen demand, the required electrolysis power is 22.4 MW. With auxiliary systems consuming 8% of the electrolysis capacity, the electricity consumption of the process is 24.2 MW. Hydrogen production is in this case 10.8 t/d, which covers 21% of the fuel demand of the lime kiln; fuel oil demand is thus 131 t/d. The main process flows in Case A are represented in Figure 3.

Case B evaluates the situation, where electrolysis is scaled to make maximum hydrogen for fuel demand of the lime kiln. Oxygen is used at the mill for delignification and bleaching, and excess oxygen is used to boost the recovery boiler (oxygen enriched air combustion). The lime kiln heat requirement being 72 MW, the required hydrogen amount to fully supply this amount of heat, can be calculated at 52 t/d with 119 MJ/kg as lower heating value of hydrogen. The electrolysis power consumption to produce this amount is 108 MW, which exceeds the amount of excess electricity produced at the mill. Electrolysis is thus scaled back to 79 MW electricity consumption including the consumption of the auxiliary equipment. Hydrogen production can correspondingly be calculated at 38 t/d, and oxygen production at 302 t/d. This means that 45 t/d oil is still needed for the lime kiln, because combustion of hydrogen covers 73% of the lime kiln heat demand. Figure 4 presents the mill main balances in the Case B. Table 1 compares the main process values in the Base Case and Cases A and B.

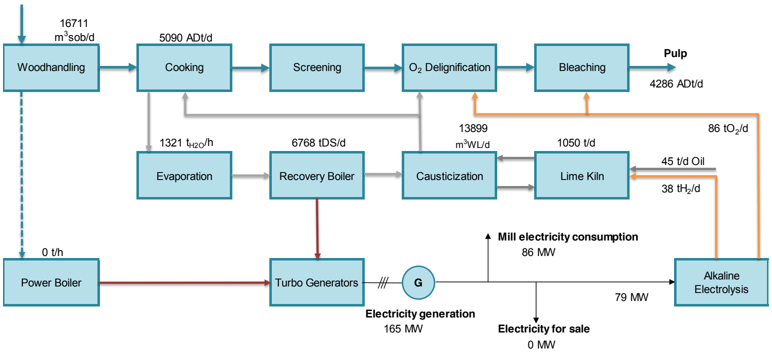

Fig. 4. Main process flows in Case B, where electrolysis is scaled according to the maximum electricity production of the mill.

Table 1. Main process variables in the Base Case and Cases A and B				
Variable	**Unit**	**Base**	**Case A**	**Case B**
Electrolysis power consumption	MW	0	24.2	79.1
- Hydrogen production	t/d	-	10.8	38.1
- Oxygen production	t/d	-	85.7	302.4
- Feed water flow	t/d	-	97	343
- Cooling water flow	t/d	-	5,078	14,019
- Cooling water inlet temperature	°C	-	45	45
- Cooling water outlet temperature	°C	-	75	75
- Reaction temperature	°C	-	80	80
Electricity for sale	MW	76	55	0
Oil requirement for the lime kiln	t/d	164	131	45

Fossil fuels used in the lime kiln can be substituted partly with hydrogen produced using water and excess electricity. To give up fossil fuels completely during normal operation, more electricity generation is needed; if biomass is available, this could be done with a separate biomass fired power boiler.

Hydrogen production from water affects the water flows at the mill. Feed water to electrolysis has the same quality requirements to boiler water, and it is therefore assumed to be purified using the existing water treatment equipment. This increases the water flow at the water treatment plant by 3% in Case A and 12% in Case B compared with the Base Case. Cooling water for the electrolyser is part of the mill's water cycle. Hot water production by cooling the electrolyser reduces the amount of hot water produced with steam. In Case A the alkaline electrolyser produces 12% of the 75 °C water used at the mill, and in Case B 34%.

The oxygen requirement for combustion in the recovery boiler is 0.85 Nm^3per kg of black liquor dry solids in the example cases. This means that, dry solids flow being 6768 tDS/d, the air flow to the boiler without oxygen enrichment (Base Case and Case A) is 27 Mm^3/d. Secondary and tertiary air flows are assumed to account for 77% of the combustion air flow. In Case B, 217 t/d excess oxygen is produced. If this is added to the secondary and tertiary combustion air flows, it means that oxygen content in the air flows increases from 21.0% to 21.6%. It is assumed that change in recovery boiler is insignificant.

Evaluation of economic feasibility of the selected cases

The electricity price and the possibility to sell excess electricity, together with fossil fuel price are the main factors when evaluating the profitability of integration of electrolysis in the selected cases. The profitability has been roughly evaluated using various electricity and fuel oil prices, in order to find conditions where electrolysis process integration would be reasonable. The profitability for both studied cases is depicted in Figure 5. Investment cost has not been evaluated here, but it can be assumed that in an existing mill it is not reasonable to invest in electrolysis process when oxygen production equipment has already been installed. Considering a new greenfield mill, investment is more probably reasonable, especially in the cases where local conditions make selling of additional electricity challenging.

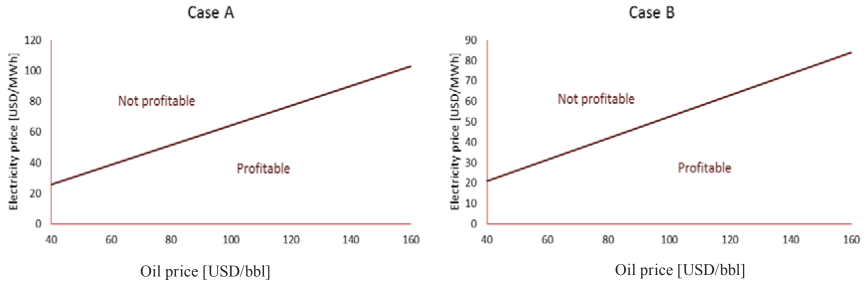

Fig. 5. The profitability of electricity use for electrolysis to substitute fuel oil with different oil and electricity prices in studied cases A and B.

At the time of writing, crude oil spot price has been around 60 USD/bbl, varying from 45 to 130 USD/bbl during the recent year *(27)*. For pulp mill fuel oil price one needs to add the refinery margin, cost of transport, and taxes. In Brazil, electricity price without taxes has been varying between 55 and 115 USD/MWh during the year 2014 and the beginning of the year 2015, depending on the region and electricity producer *(28)*. The average was approximately 91 USD/MWh. Under these circumstances, electricity use to substitute oil is rarely profitable, if electricity can be sold. Limited possibilities to sell additional electricity however change the situation.

In the studied cases, oxygen production was assumed to already exist for the full demand. Therefore, only the operating electricity consumption decrease affected costs. If a need to increase oxygen production capacity exists, then alkaline electrolysis offers an alternative possibility that could save in operating costs.

Future options

Power-to-gas process integration in pulp mill operations enables other possible process integrations and concepts for added value processes or products. Production of hydrogen and available carbon dioxide resources on-site enable a methanation process to refine hydrogen further to methane, which has various usage possibilities both as fuel and as raw material for chemical products. Hydrogen can also be used when the mill processes tall oil into transport fuels *(29)*. It could also be significant in the biorefinery concept of future pulp mills.

Continuous development on the electrolysis systems is expected to develop new electrolysers other than AEC available for industrial use. A conservative estimate on the profitability of a SOEC system shows, that SOEC would make the studied cases profitable even with recent electricity and oil price levels. Electricity consumption using SOEC is about 1.5 kWh/Nm^3 (H_2) lower than with AEC. As a consequence, the profitability curve shown in Figure 5 shifts higher, so that the cost-effectiveness improves markedly. With average oil and electricity prices represented earlier for the case of Brazil, SOEC system would be close to profitable. Due to lower electricity consumption, SOEC would also enable full replacement of fuel oil in the lime kiln at the example mill.

CONCLUSIONS

Water electrolysis integration into a pulp mill process to produce hydrogen and oxygen for use at the mill is a possible way to substitute part or all of fossil fuel used at the mill. The amount of excess electricity produced at a typical large-scale South-American pulp mill is enough to cover the oxygen demand at the mill and make separate oxygen production unnecessary. Also, hydrogen can be produced to cover 73% of the heat demand of the lime kiln, which is the only fossil fuel user at a modern pulp mill during normal operation. Electrolysis is an alternative for producing market electricity; therefore the profitability of the integration is dependent on the possibilities for selling, which are often limited at modern pulp mills such as the example cases presented in this study.

ACKNOWLEDGEMENTS

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Publication III

Kuparinen, K., and Vakkilainen, E.

Green pulp mill: Renewable alternatives to fossil fuels in lime kiln operations

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Green Pulp Mill: Renewable Alternatives to Fossil Fuels in Lime Kiln Operations

Katja Kuparinen* and Esa Vakkilainen

Pulp mills are making increasing efforts to reduce fossil fuel use and carbon dioxide emissions. Lime kilns, which are typically fired with fuel oil or natural gas, use the most fossil fuel in modern pulp mills. A modern kraft pulp mill can be fossil fuel-free during normal operation if fossil-based lime kiln fuels are substituted with renewable alternatives. This study compared the production and use of various renewable fuels, namely, hydrogen, producer gas, torrefied biomass, lignin, and pulverized biomass, in lime kiln operations in a 1.5 Mt/a kraft pulp mill in South America to define the techno-economic optimum for the fossil fuel-free operation of the pulp mill. The attractiveness of each of the concepts was dependent on local conditions and especially the prices of fossil fuels and electricity. The results showed, however, that feasible options exist for the replacement of fossil fuels in lime kiln operations.

Keywords: Fossil fuel replacement; Pulp mill; Lime kiln; Water electrolysis; Gasification; Torrefaction; Biocoal; Lignin; Wood residue

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INTRODUCTION

Sustainability, emission control, environmental regulations, corporate image, self-sufficiency of fuel supply, and the price of fossil fuels are among the many factors driving companies to reduce usage of fossil fuels. In the pulp industry, a large share of energy use is already biomass-based (IEA 2014), and in normal operations, modern kraft pulp mills are usually self-sufficient in energy, with the exception of lime kiln operations. Fossil fuels are primarily used to reduce lime mud to burnt lime, and they are also used during upsets, start-up and shut-down, as well as sometimes for safety reasons to secure non-condensable gas destruction (Vakkilainen and Kivistö 2008, 2014). Thus, the lime kiln is typically the only unit operation utilizing fossil fuels during normal operations, and, consequently, the only source of fossil fuel-based emissions. Substituting fossil fuels used in the lime kiln with renewable fuels produced at the mill, especially if existing side streams are used, would make normal kraft pulp mill operations nearly fossil fuel-free. This study evaluated the techno-economic feasibility of integrating renewable lime kiln fuel production into the kraft pulp production process.

The lime kiln in a kraft pulp mill converts lime mud, which is largely composed of calcium carbonate ($CaCO_3$), into burnt lime, *i.e.*, calcium oxide (CaO), and carbon dioxide (CO_2). This thermal decomposition reaction requires a high temperature and occurs spontaneously when the lime mud temperature exceeds approximately 800 °C in a gas atmosphere containing 20% CO_2. The gas temperature needs to be notably higher because of the poor heat transfer in the kiln (Arpalahti *et al*. 2008). Lime kilns are typically long, cylindrical rotary kilns. Lime mud is fed into the kiln at the feed end, from where the mud, because of kiln rotation and slight inclination, flows slowly through the drying and heating zones to the burning zone. External heat is brought into the kiln by combusting fuels in a flame at the hot end of the kiln. Lime kilns are usually fired with oil and natural gas. Alternative fuels originating from the pulp production process side streams are often co-combusted, but only in a few cases are they used as the main fuel (Francey *et al*. 2011). For example, methanol, tall oil, strong odorous gases, tall oil pitch, hydrogen, and turpentine have all been co-combusted with fossil fuels in lime kilns.

Renewable fuels can be produced at the mill from available biomass residues or produced using renewable electricity from pulp mill operations. The processing of wood typically creates biomass residues such as bark, sticks, and fines. The amount of residue depends on the process, the wood type, and local conditions. For example, eucalyptus is usually debarked in the forest, which decreases the amount of woody residue at the mill. Modern kraft pulp mills produce excess renewable electricity and heat in the form of steam and hot water during normal operations (Vakkilainen and Kivistö 2014). This excess electricity can be either sold or used internally for the production of chemicals or paper production. Part of the steam is used for pulp production, but in large modern mills, the condensing tail is used in a turbine to convert excess steam into electricity.

The integration of fuel production for the lime kiln into the kraft mill process can bring synergistic benefits that make the fuel production process more feasible compared with stand-alone operations. The lime kiln fuel replacements considered in this study were hydrogen, producer gas, torrefied biomass, lignin, and pulverized biomass. Some of these—hydrogen and producer gas—have been successfully used in lime kilns before, and some can be regarded as newly introduced promising alternatives. Apart from fossil fuel-free operation, the integration of biofuel production processes offers interesting new possibilities for increasing mill capacity and gaining additional revenue by the production of advanced bioproducts.

Hydrogen production from water using alkaline electrolysis is a well-known commercial process (Millet and Grigoriev 2013; Lehner *et al*. 2014). In a pulp mill, excess electricity can be used on-site for hydrogen production in electrolyzers (Kuparinen *et al*. 2016b). Gasification of biomass followed by producer gas firing in a lime kiln is a known technology and has been used in a number of pulp mills in Scandinavia (Wadsborn *et al*. 2007; Vakkilainen and Kivistö 2008; Metsä Group 2013). Torrefied biomass is produced by the mild heating of biomass in the absence of oxygen, and its properties resemble those of coal (Koppejan *et al*. 2012). Torrefied biomass has not yet been used to fuel lime kilns in commercial operations, but the option has recently been studied, as has the possibility of integrating torrefaction in pulp mill processes (Hamaguchi *et al*. 2013; Kukkonen 2014). Lignin extraction from black liquor and its use for a wide range of purposes has been studied widely; a possible and easily achievable usage is as lime kiln fuel (Vakkilainen and Kivistö 2008; Lundberg *et al.* 2013; Manning and Tran 2015). Dried and pulverized biomass can be easily combusted in lime kilns (Wadsborn *et al*. 2007; Stora Enso 2015).

The objective of this study was firstly, to analyze the technical possibilities and constraints of integrating renewable lime kiln fuel production into the pulp production process and secondly, to estimate the economic feasibility of the chosen concepts. The techno-economic effects of the above-listed integration concepts on the pulp production process were examined by analyzing the mass and energy balances of an example mill. Figure 1 presents an overview of the studied kraft pulp mill operations and technologies. The mill considered in this work was a large kraft pulp mill located in South America producing 1.5 million air-dry tons of bleached eucalyptus pulp annually. Several mills of this type have started operation recently. Potential advantages and disadvantages of the integration for existing pulp production process operations, along with requirements of a framework for feasible concepts, were assessed.

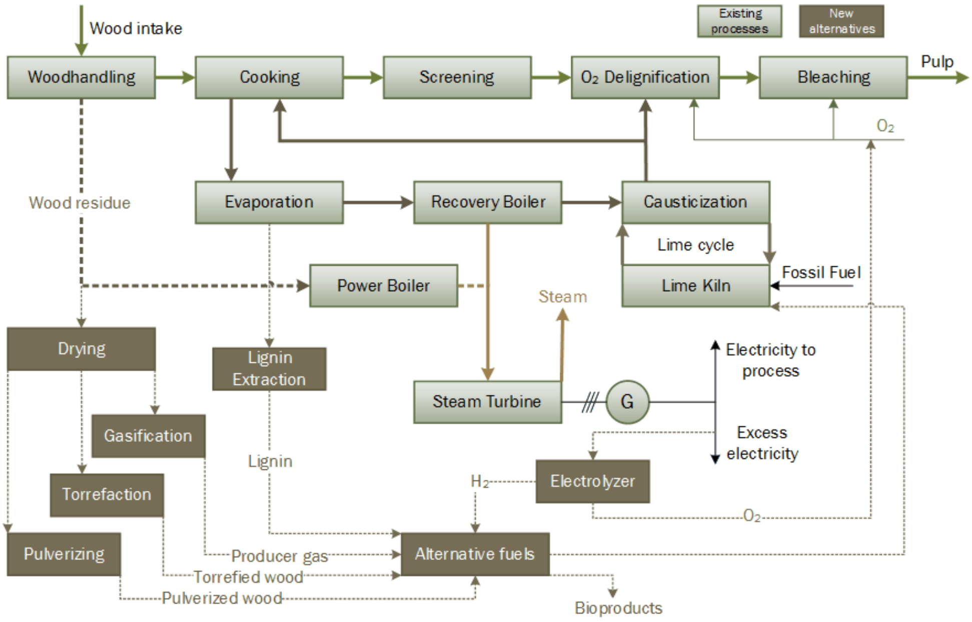

Fig. 1. Kraft pulp mill operations and alternative integration concepts studied

METHODS

The Reference Mill Process

The selected renewable fuel concepts to enable fossil fuel-free pulp mill operations were studied by calculating mass and energy balances for a reference mill. The main parameters and mass and energy flows of the reference mill operations are presented in Fig. 2. A more detailed description of the reference mill can be found in previous work (Hamaguchi *et al*. 2011; Kuparinen *et al*. 2016a,b). Calculations were made using an updated Millflow spreadsheet that included detailed mass and energy balances for a pulp mill. A more detailed description of Millflow can be found in earlier work (Vakkilainen and Kivistö 2008; Hamaguchi *et al*. 2011).

Biomass residue was generated in the wood handling processes of the pulp mill, and, in addition to bark, the biomass residues contained other particles such as fines and wood lost during mill debarking. Steam was generated only in the recovery boiler. Because of the small wood residue flow, there was no separate power boiler and therefore no use for the biomass residue generated. Steam was used for power generation and in the mill processes. There were abundantly available low temperature heat flows that were used, for example, to dry biomass residue. Electricity generation exceeded the mill power requirements, and thus the sale of excess electricity was possible.

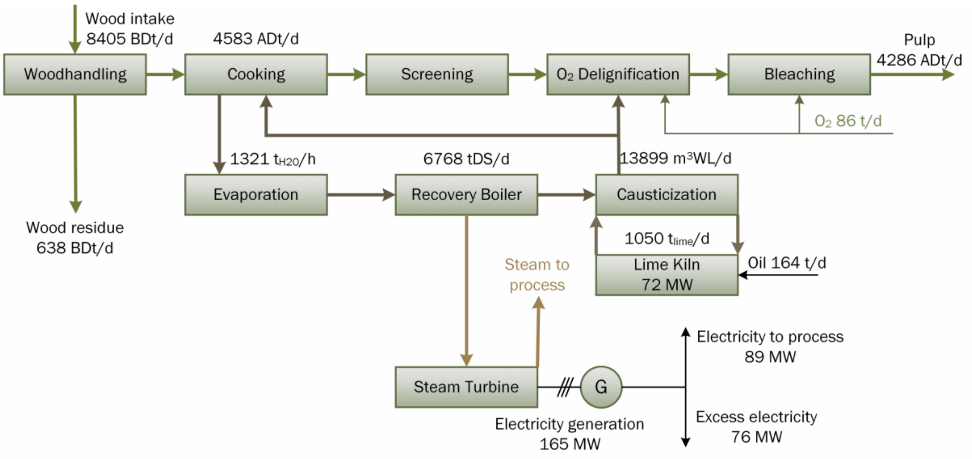

Fig. 2. The reference mill operations and the main process flows

Alternative Lime Kiln Fuels

Fuel properties affect the operation of the lime kiln. The properties of the studied renewable fuels were compared with the fossil fuels typically used in lime kilns; the results are shown in Table 1. Lime kiln operation requires stable combustion conditions as well as easily controllable hot-end temperature. Therefore, fuel quality should be stable and consistent. Variations in fuel heating value and moisture affected the flow and temperature profile of the flue gas.

Table 1. Properties of the Studied Alternative Fuels Compared with the Most Commonly Used Fossil Fuels

Fuel	Lower Heating Value (MJ/kgAF)	Adiabatic Flame Temperature (°C)	Contaminants
Hydrogen	120	2210	No
Producer gas	6-30	1870	Some
Torrefied biomass	20-30	1840	Substantial
Lignin	17-26	1980	No
Wood	12-19	1950	Substantial
Natural Gas	50	2050	No
Oil	41	2210	Some

Alternative solid fuels fired in lime kilns can include non-process elements as contaminants, which tend to accumulate in closed cycle processes such as the lime cycle (Hamaguchi and Vakkilainen 2011). These impurities can cause corrosion, ring formation in the kiln, and adverse environmental effects, in addition to having an unfavorable effect on the quality of the lime. Increased amounts of contaminants can lead to increased use of make-up lime. High fuel moisture content decreases the heating value of the fuel and the system efficiency and also increases the amount of flue gas. The fuel heating value needs to be high enough to enable the desired flame temperature at the lime kiln hot-end (Vakkilainen and Kivistö 2008).

Combustion of biomass-based fuels lowers the hot-end temperature in the kiln due to the lower adiabatic flame temperature (Isaksson 2007). To maintain the kiln production capacity, higher firing rates were required, which caused an increase in the back-end temperature and higher flue gas heat loss. Therefore, in the case of biomass fuels, an additional increase of 3% in fuel consumption based on input lower heating value (LHV) was assumed.

Biomass Pretreatment

Pretreatment of biomass residue is required whether the residue is gasified, torrefied, or pulverized for fuel use. Pretreatment reduces problems in the fuel feeding systems and improves the efficiency of the conversion or combustion processes. Undesired elements such as sand and metals need to be removed to prevent problems in the equipment during processing. Biomass pretreatment includes drying, chipping, and grinding in order to achieve the desired moisture content and particle size, which vary according to the chosen conversion process.

Flue gas or secondary heat in the form of hot or warm water as well as recovered steam from the pulping process can be used for drying. There is considerable risk of fire in the fuel feeding system when flue gas is used for drying wood (Wadsborn *et al*. 2007). Therefore, from the viewpoint of fire safety, the use of steam or hot water is recommended. In the calculations of this work, a moisture content of 45% was assumed for the received biomass residue, and 65 °C water from the mill processes was used for drying. Electricity consumption in grinding depended on the type of material and required particle size. When a rotating grinder and a belt drier was chosen, the electricity consumption for pretreatment was estimated at 192 kWh/t based on vendor data.

Hydrogen

Hydrogen can be produced from water by using water electrolysis. Alkaline electrolyzers are commercial technology and used currently in up to 10 MW_e units in hydrogen production (Zeng and Zhang 2010; Lehner *et al*. 2014). In an electrolyzer, water is split into hydrogen and oxygen following reaction 1:

$$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g) + heat \qquad (1)$$

Integration of water electrolysis in a pulp mill followed by hydrogen combustion in the lime kiln has been previously studied (Kuparinen *et al*. 2016a,b). The integration concept with main data for the reference mill is presented in Fig. 3. Renewable excess electricity produced in the mill was used in the electrolyzer, replacing the 3.4 MW that was needed for oxygen production in the base case. With the electrolyzer, separate oxygen production was not needed.

The production of hydrogen was limited by the availability of electricity; in the studied case the electrolyzer covered 72% of the heat demand of the lime kiln. The oxygen requirement of the pulping process was 20 kg/ADt (Kuparinen *et al*. 2016b), which was only a part of the oxygen produced by the electrolyzer. Cooling of the electrolyzer produced heat in the form of +75 °C hot water, which could be utilized if there were demand for heating. Hot water production from cooling of the electrolyzer could be replaced by the production of low pressure steam by a reboiler. Water for the electrolyzer can be purified using the existing water treatment facility, which would increase the load at the mill’s water treatment plant in the example case by 12%.

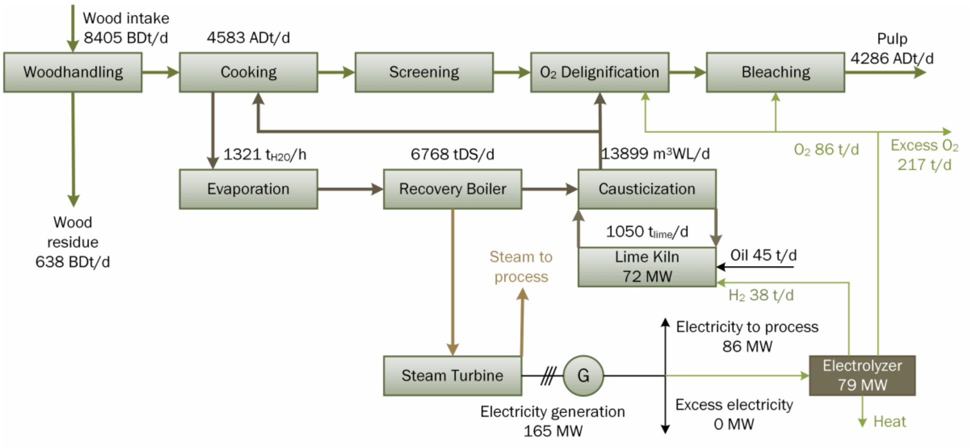

Fig. 3. The reference mill operations with an integrated alkaline electrolyzer to produce hydrogen and oxygen for mill processes

Producer Gas

Biomass gasification for lime kiln use is a well-known process (Isaksson 2007; Francey *et al*. 2011; Metsä Group 2013). The producer gas concept for the reference mill, including the main mass and energy flows, is depicted in Fig. 4.

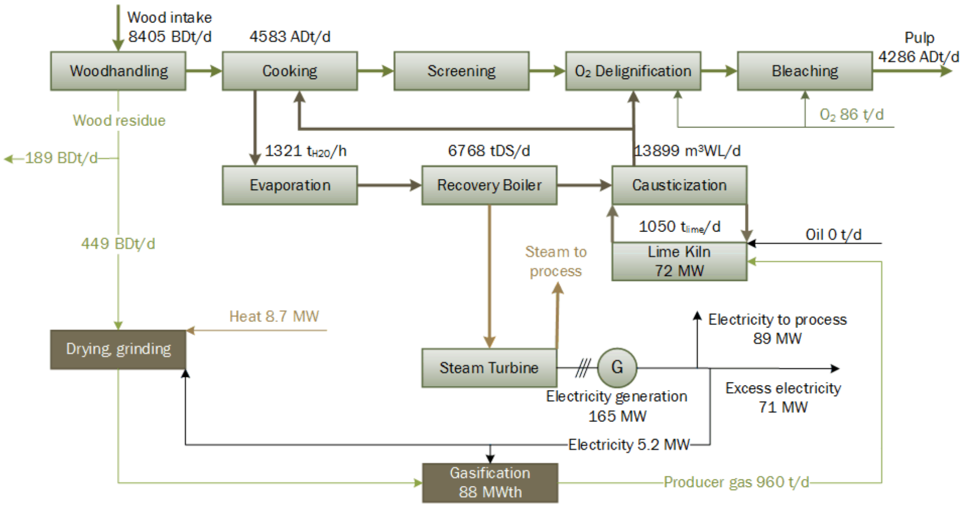

Fig. 4. The biomass gasifier integrated in the reference mill process

Biomass drying before gasification is essential to improve the efficiency of the process. Moisture in the fuel notably increases the amount of flue gas from the lime kiln (Isaksson 2007). In these calculations, 15% moisture content and an average particle size of 6 mm before gasification were used. These are recommended values for a circulating fluidized bed (CFB) gasifier (McKendry 2002; Basu 2010). The calculations are based on CFB gasifiers that are the most used commercial gasifiers and able to gasify biomass of varying quality. Particles like sand or metals are removed in the biomass pretreatment process prior to gasification, and minor contaminants can be handled in the gasification process (Worley and Yale 2012).

The integrated gasifier increased the amount of electricity used at the mill. The increase was mainly from biomass pretreatment, but also from the gasifier air fans, whose consumption was estimated at 1.1% of the thermal power of the gasifier. In the gasification process, part of the contaminants of the biomass exited the gasifier with the bottom ash, and therefore the amount of non-process elements that ended up in the lime cycle was lower than with, for example, wood combustion. Make-up lime increase due to contaminants was assumed at 2 kg/ADt (Isaksson 2007).

Torrefied Biomass

Upgraded biomass can be produced by torrefaction, which is a mild pyrolysis process occurring at atmospheric pressure in the absence of oxygen. The operating temperature is approximately 200 to 300 °C with a residence time in the range of 0.5 to 2 h. Torrefaction increases the energy density of biomass, reduces its moisture content, and makes it hydrophobic and brittle. Typically, biomass loses 30% of its mass and 10% of its energy content during torrefaction, depending on the process details (Schorr *et al*. 2012).

The behavior of biomass in the torrefaction process depends on the type and composition of the biomass (Prins 2005). Because they are processed, raw material quality requirements are not strict (Schorr *et al*. 2012). Therefore, residual biomass from pulp production is a material well suited for torrefaction. Integration of torrefaction into a pulp mill process has been studied previously (Hamaguchi *et al*. 2013; Kukkonen 2014).

The properties of torrefied biomass are close to those of coal, and, therefore, torrefied biomass can replace coal in many applications without notable modifications to the combustion equipment. Coal is commonly used in cement kilns, which resemble the lime kilns found in pulp mills. Torrefied biomass can be combusted as a main fuel in lime kilns using pulverized fuel burners. When used as additional fuel, torrefied biomass can either be mixed with lime mud or blown to the kiln from the burner end.

In the example case, the energy content of the torrefied biomass was set at 18.7 MJ/kg (LHV) based on the experimental results of torrefaction of eucalyptus (*Eucalyptus grandis*) wood and bark (Almeida *et al*. 2010), when operating temperature was 250 °C and residence time 1 h. Size reduction is relatively easy for torrefied wood due to its brittleness; size reduction of torrefied wood consumes 70% to 90% less energy than pulverized wood (Bergman 2005).

The torrefied biomass concept for the reference mill is presented in Fig. 5. The biomass was pre-dried before torrefaction, and pulverized torrefied biomass was fed into the lime kiln. The process was scaled to meet the heat demand of the lime kiln. Torrefied biomass ash included elements that could be harmful in the lime cycle, but problems can be prevented by increasing the make-up lime addition. In this case, an addition of 3 kg/ADt was estimated.

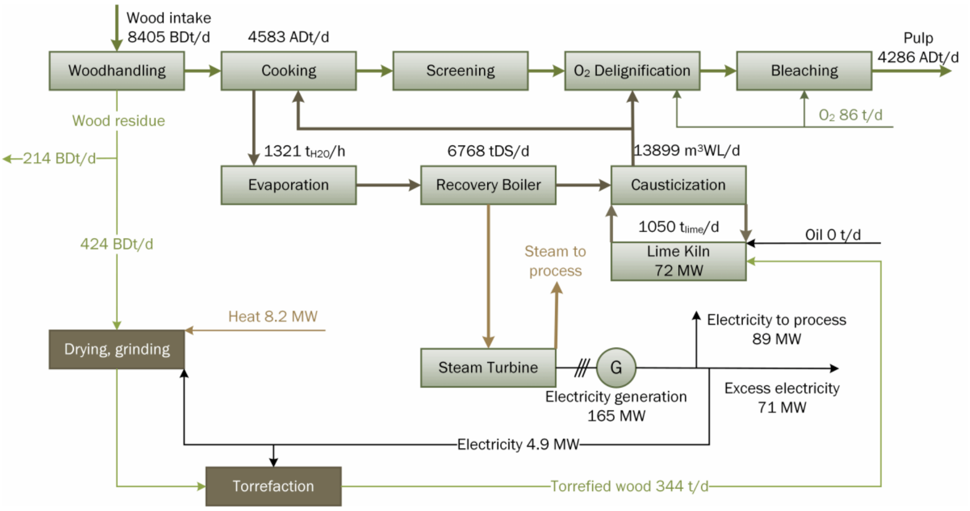

Fig. 5. The torrefaction of biomass residue to fuel the lime kiln in the reference mill process

Lignin

Lignin content in eucalyptus is typically 26% to 27% (*E. grandis*, *E. saligna*; dry basis) (Almeida *et al*. 2010). In the kraft pulp production process, approximately half of the wood entering the cooking process is converted to pulp, and the rest of the organics are typically combusted in the recovery boiler for energy production. Lignin can be separated from black liquor, before the recovery boiler, to be used as fuel or to be refined further into other products (Björk 2016). Possible lignin separation methods are membrane filtration after the digester and acidic precipitation and dewatering at the evaporation stage (Vakkilainen and Kivistö 2008).

Lignin separation using an acidic precipitation method called LignoBoost and combustion in a lime kiln have been tested in Sweden (Tomani 2010). The method is currently in use in Finland (Björk 2016). Several studies have been made to examine the effects of lignin separation on pulp mill operations and dimensioning (Axelsson *et al*. 2006; Vakkilainen and Kivistö 2008; Vakkilainen and Välimäki 2009; Hamaguchi *et al*. 2011).

Precipitation of lignin from black liquor is based on the decreased solubility of lignin when the pH is lowered. In the LignoBoost process, CO_2 with H_2SO_4 are used in a two-step process to lower the pH (Tomani 2010; Gellerstedt *et al*. 2012). CO_2 can be either purchased or separated from the lime kiln or recovery boiler flue gases. Using lime kiln flue gas as a source of CO_2 decreases the chemical cost by 20% to 25%. Precipitated lignin is a hydrophobic filtercake with 30% to 40% moisture content (Tomani *et al*. 2011), and it can be dried further and pulverized before utilization. Lignin includes free sodium and sulfur, which may cause ringing in the lime kiln. Sulfur content after the LignoBoost process is approximately 2% to 3%, and its sodium content can be decreased by washing to a level acceptable for lime kiln use (Gellerstedt *et al*. 2012). Standard burner and feeding equipment can be used for lignin combustion in lime kilns. No notable adverse effects to lime kiln operation nor to emission levels were detected in trials conducted in a Swedish kraft pulp mill (Tomani *et al*. 2011).

Lignin removal affects the properties of black liquor and, consequently, the operation of the recovery boiler. Lignin removal decreases the steam load and flue gas production of the recovery boiler, which is often a bottleneck in the pulp production process. Therefore, it has been introduced as a method to enable an increase in pulp production capacity without an expensive upgrade of the recovery boiler (Axelsson *et al*. 2006; Vakkilainen and Kivistö 2008). If the mill production remains unchanged, steam production at the recovery boiler decreases and, as a result, electricity generation decreases as well. The addition of sulfuric acid affects the mill Na-S balances. The washing of precipitated lignin increases the load of the evaporation plant because the washing filtrates are returned to the evaporation (Hamaguchi *et al*. 2011). In the calculations in this work, an increase of 2 kg per kg of extracted lignin was taken into account, but it was assumed that the nominal capacity of the evaporation plant could be kept unchanged.

In the studied concept, lignin removal was scaled to meet the lime kiln heat demand, and pulp production was kept at the base case level. The main mass and energy flows are depicted in Fig. 6. To fire the lime kiln, 280 t/d lignin at 10% moisture was needed. This was equal to a 16% extraction rate from black liquor. Electricity consumption in the lignin removal process was estimated at 80 kWh/t (Laaksometsä *et al*. 2009). Additional electricity consumption of 0.3 MW for drying and pulverizing was included.

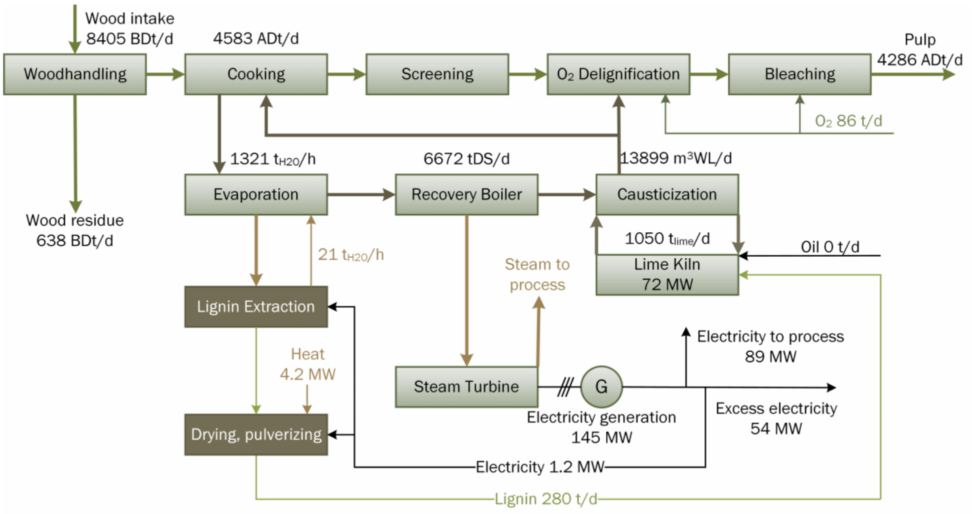

Fig. 6. The main process flows of the lignin extraction process integrated in the reference mill

Pulverized Wood

Pulverized wood has been tested and used as lime kiln fuel (Wadsborn *et al*. 2007; Stora Enso 2015). The combustion of unsorted wet wood and bark in a lime kiln is challenging due to high moisture content, varying particle size and heating value, unpredictable flow characteristics, and the high content of non-process elements. Drying and pulverizing the biomass is required for stable operation. Pulverized fuel burners can be used, or when wood is used as additional fuel, pulverized biomass can be mixed with lime. The characteristics of wood make pulverizing wood more energy-intensive than, for instance, the pulverization of coal or torrefied biomass.

A pulverized wood case for the reference mill was evaluated in previous work (Kuparinen *et al*. 2016a). Figure 7 shows the main process flows of the concept. Make-up lime use increased due to contaminants in the wood; an increase of 3 kg/ADt was assumed for these calculations. The moisture content of the residue after drying was 15%.

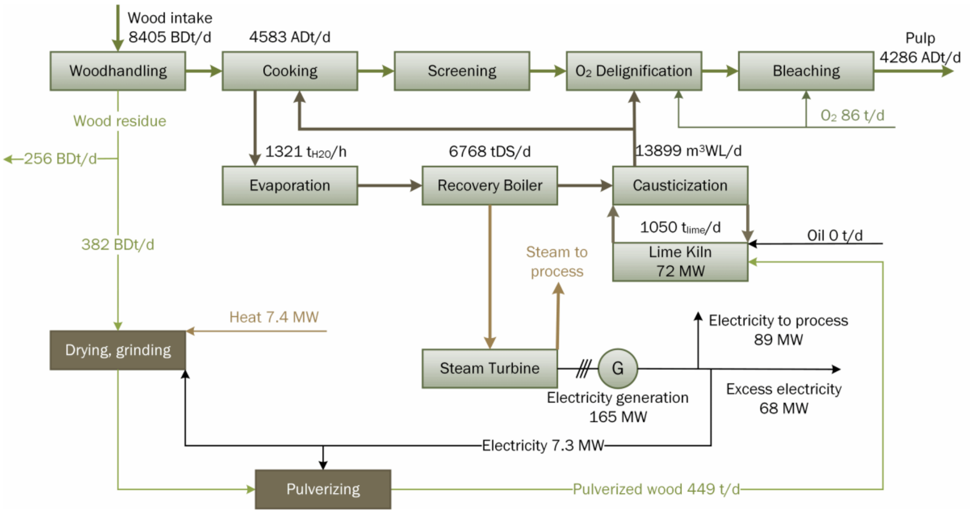

Fig. 7. The pulverized wood concept for the reference mill

For pulverized wood firing, the required average particle size is below 1 mm. The electricity consumption of pulverization using hammer mills is roughly 50 kW/MW_{th}. In previous trials, the most common problems with pulverized wood firing were fires in the fuel feeding system and clogging in the hammer mills (Wadsborn *et al*. 2007). Unplanned shutdowns of the fuel feeding system require the use of fossil fuels unless a backup renewable system exists, thus increasing costs.

Evaluation of Economic Feasibility

The costs of each renewable lime kiln fuel scenario depend on the process equipment and required auxiliary equipment, as well as the storage facilities needed. Figure 8 compares the process stages in each studied concept. For biomass fuels, the pretreatment processes had considerable impact on the process costs. Hydrogen production using alkaline electrolysis is a developing technology, and it can be expected that the price will decrease in the near future as power-to-gas processes become more common.

Investment and operational costs for selected processes were estimated based on information from recent projects and vendor data. None of the studied wood residue based processes are commonly used. Electrolyzers have not been previously used in pulp mills on this scale, nor for this purpose. The economic evaluation of the concepts is challenging due to uncertainties and a lack of references related to prices, local conditions, and the size of required storage. Consequently, the results should be considered as best estimates with no better than ±30% accuracy.

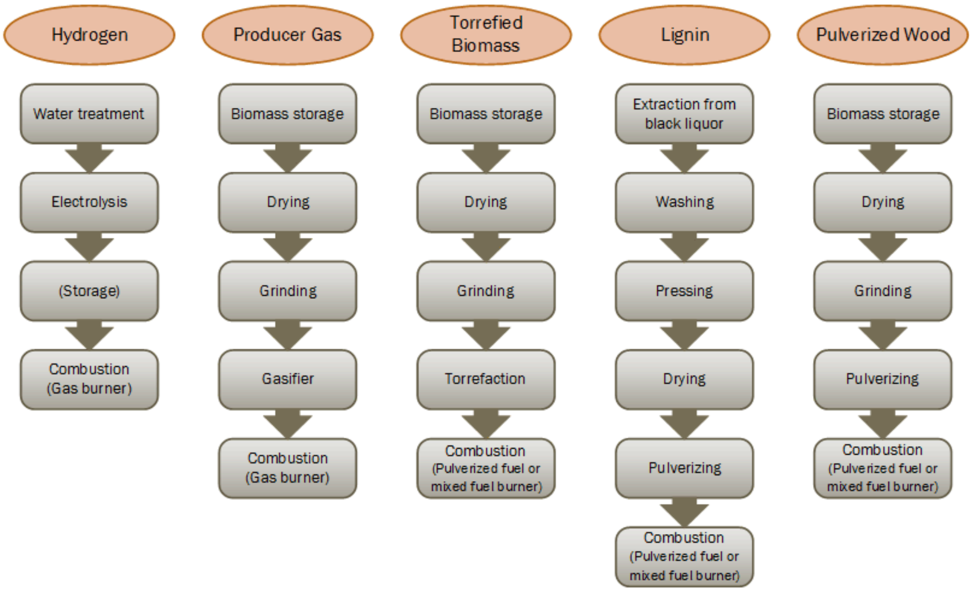

Fig. 8. The process stages for each of the studied renewable lime kiln fuel options

A lifetime of 20 years, an interest rate of 10%, an operation time of 8400 h/a, and operation and management costs in the range of 5% of the investment were assumed for all the cases. Other assumptions made for the economic analysis are given in Table 2. Possible incentives for renewable fuel use or savings from costs of carbon dioxide emissions can affect the cost-effectiveness of the fuel choice, but these were not taken into account in the calculations. Although there are plans for emissions trading in South America, they have not yet been put into action (ICAP 2016). It was assumed that biomass has a market value; this value, however, can vary depending on the local conditions, and it may even have a disposal cost instead. The value of replaced oxygen is case-specific and dependent on sourcing, because oxygen can be produced on-site or purchased. When comparing the investment costs, it should be noted that hydrogen covered the heat demand of the lime kiln only partly (72% of total kiln energy), while the other fuels were considered as the sole fuel to be fired.

Table 2. Basis for the Economic Evaluation

	Unit	Hydrogen	Producer Gas	Torrefied Biomass	Lignin	Pulverized Wood
Investment	MUS$	69.4	40.3	41.0	73.0	43.2
Biomass price	US$/BDt	-	50	50	-	50
Water price	US$/m^3	0.5	-	-	-	-
Oxygen price	US$/t O_2	50	-	-	-	-
Make-up lime price	US$/t	350	350	350	-	350
H_2SO_4 price	US$/t	-	-	-	160	-

RESULTS AND DISCUSSION

The technical implementation of all of the studied processes is possible and feasible, and they can be integrated in a pulp mill without adverse effects on the actual pulp production process. Full or partial fossil fuel replacement utilizing existing side streams, namely residual biomass or excess electricity, is technically possible. The main parameters from the integrated mill calculations are given in Table 3. In the reference mill, all the concepts except for the electrolyzer concept offered the possibility of fully substituting fossil fuels in lime kiln. Using the electrolyzer, 45 t/d of oil was still needed to cover 28% of the kiln heat demand.

The power balance of the mill was affected by the renewable fuel production, and the amount of sellable electricity decreased in all of the cases. In the hydrogen case, all excess electricity was used for renewable lime kiln fuel production. Lignin extraction decreased the amount of organics ending up in the recovery boiler, and therefore markedly less steam and electricity was generated.

Table 3. The Main Results from the Integrated Mill Calculations

	Unit	Hydrogen	Producer Gas	Torrefied Biomass	Lignin	Pulverized Wood
Lower heating value	MJ/kg	120.0	6.7	18.7	23.0	14.3
Fuel production	t/d	38	960	344	280	449
Share of kiln energy	-	72%	100%	100%	100%	100%
Power consumption	MW_e	79	5.2	5.3	1.2	7.3
Biomass use	BDt/d	-	449	424	-	382
Low value heat use/production	MW_{th}	20.0	-8.7	-8.2	-4.2	-7.4
Pure water consumption	t/d	338	-	-	-	-
Increase in make-up lime consumption	t/d	-	8.6	12.9	-	12.9
Difference in sellable power	MW_e	-75.8	-5.2	-5.3	-21.5	-7.3

In the studied case, the biomass residue generated in the wood handling process of the mill was sufficient to cover the lime kiln heat demand. There was actually excess biomass available in all of the cases. Combustion of biomass residue in a power boiler would offer a possible increase in the amount of produced electricity. Especially in the hydrogen case, a power boiler could be used to increase hydrogen production or to produce electricity for sale.

In the lignin extraction case, lignin removal affected the recovery boiler balance and caused a decrease in electricity production. On the other hand, lignin extraction offered a possibility to increase the capacity of the recovery boiler, which is often a bottleneck in pulp production. Consequently, additional revenue could be gained by increasing the pulp production of the mill without the need for expensive modifications to the recovery boiler.

The main concern of the biomass-based lime kiln fuel concepts was unforeseen stoppages in the fuel feeding and pretreatment systems. Additionally, the fire risk needed to be considered, especially if flue gas instead of water or steam were used for biomass drying. Stoppages are quite common in biomass processes, and they reduce the availability of the system. Consequently, occasional fossil fuel use or biofuel storage is required to maintain mill operations during unforeseen breaks. The costs of possible biofuel storage or increase of occasional fossil fuel use were not included in the cost calculations.

All the integrated processes either produce or use low temperature heat in the form of hot water. Secondary heat is an abundant resource in modern kraft pulping processes and, as a result, the need for heat does not substantially affect the cost of the process. Biomass-based fuels include contaminants that mix with lime and may accumulate in the lime cycle. This can be mitigated by increasing lime replacement by adding make-up lime use.

The profitability of the studied concepts depends primarily on the difference between the renewable fuel production cost and the cost of the replaced fossil fuel—in this case, fuel oil. In Fig. 9, the breakeven lime kiln fuel price for each case is presented as a function of electricity price. When the oil price exceeds the calculated breakeven price, the case is considered economically feasible.

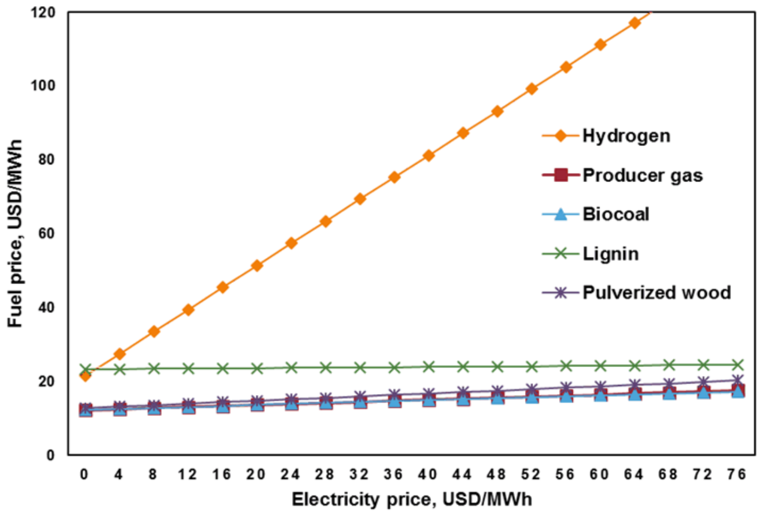

Fig. 9. The breakeven lime kiln fuel price for the studied concepts as a function of electricity price

In the lignin case, the breakeven price varies in the range of 23 to 25 US$/MWh (40 to 43 US$/bbl). In the biomass conversion cases, the breakeven prices were in the range of 12 to 20 US$/MWh (20 to 35 US$/bbl). The lowest renewable fuel price was found in the producer gas case, but the results of the biomass conversion cases were close to each other. The profitability of the hydrogen concept is highly dependent on the price of electricity, which should be remarkably lower than current levels in, for example, Brazil, thus making the concept profitable considering current oil prices. The OECD (2016) estimates the crude oil price in 2017 and 2018 at 45 US$/bbl, which equals 26 US$/MWh. For a pulp mill, the refinery margin, cost of transport, and taxes need to be added to the price calculations. The biomass cases seem to be profitable considering the current oil price development.

The hydrogen case seems to be feasible only with a low electricity price or high oil price. Considering recent oil price developments at the time of writing, the case is unlikely to be profitable when the alternative is to sell electricity. However, when selling electricity is not possible due to local conditions, for instance, if the mill is located in a remote area or the local electricity price is low, then the integration of an electrolyzer can offer a reasonable alternative for savings in operational costs.

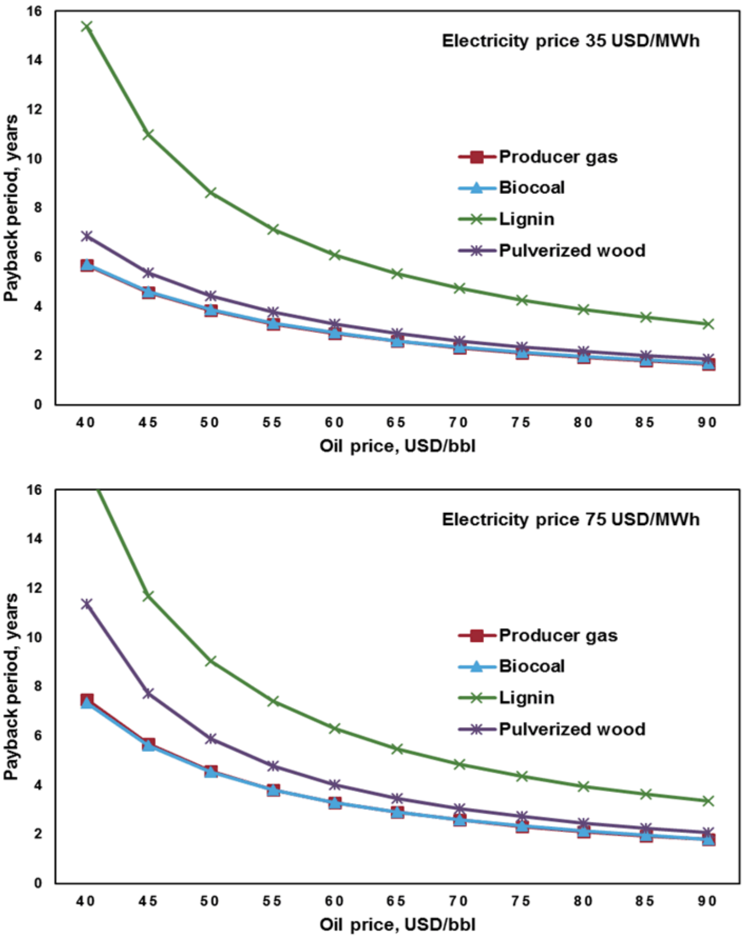

Fig. 10. The payback period for producer gas, torrefied biomass, lignin, and pulverized fuel cases as a function of oil price when the electricity price is 35 or 75 US$/MWh

The benefits of the electrolyzer concept in the example case include savings from the replacement of separately produced oxygen. The more efficient utilization for oxygen from the electrolysis process would increase the profitability of the concept. Only 28% of the produced oxygen is used in the pulping process, and excess oxygen is vented to the atmosphere in the example case. The purity of oxygen produced in an alkaline electrolyzer is high, and additional revenue can be gained by selling it when there is market demand. Another option is to utilize the oxygen in mill processes to, for example, increase the capacity of the recovery boiler by way of oxygen-enriched air combustion (Verloop *et al.* 2001).

The profitability of the producer gas, torrefied biomass, lignin, and pulverized wood cases depends primarily on the fossil fuel price, and secondly on the investment cost, while the impact of the electricity price is less noticeable. The payback period for these cases as a function of oil price was calculated in order to compare the profitability of the cases. Two electricity prices, 35 US$/MWh and 75 US$/MWh, were used. The results are presented in Fig. 10.

The results of the producer gas and torrefied biomass cases were close to each other due to investment costs being of the same order. They were also the most profitable concepts in the example mill case. The lignin concept was more sensitive to variation in the price of oil, while the pulverized wood case was the most sensitive concept in relation to the electricity price. The impact of changes in the electricity price reduces as the price of oil increases.

Electrolyzers are an emerging technology, and the investment costs of alkaline electrolyzers can be expected to decrease when implementation of the technology becomes more common. Additionally, more advanced technologies such as solid oxide electrolysis cells (SOEC) are under research, and these may permit more efficient integration concepts in the future.

In addition to fossil fuel replacement, the studied technologies offer a possibility to integrate downstream processes to convert biomass or hydrogen into biofuels or biochemicals in order to find new revenue streams. Lignin is not only a fuel but also a valuable resource for further use as a bio-based raw material.

CONCLUSIONS

1. Several technically possible ways to replace fossil fuels in modern kraft pulp mill lime kilns were found by utilizing the existing side streams of the mill process, such as biomass residues and excess electricity produced at the mill. These renewable fuel production processes were integrated into pulp mill processes without noticeable effect on pulp production.
2. The attractiveness of each integration concept was highly dependent on the price of fossil fuels and the taxes levied. The most favorable alternative for each mill depended on the local conditions and the operational specifics, and an individually customized solution is therefore needed.
3. Processing biomass into biofuels and extracting lignin from black liquor for use as a renewable lime kiln fuel were implemented in a technically and economically feasible way. In a typical South American kraft pulp mill, all of the studied options could be used to fully substitute fossil fuel in the lime kiln during normal operation.
4. The integration of an alkaline electrolyzer to produce hydrogen for fuel use could be a feasible alternative when electricity prices are low, when electricity cannot be sold due to local conditions, or when additional oxygen production capacity is needed in the mill.

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Publication IV

Kuparinen, K., Vakkilainen, E., and Hamaguchi, M.
Analysis on fossil fuel-free operation in a northern pulp and paper mill

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ANALYSIS ON FOSSIL FUEL-FREE OPERATION IN A NORTHERN PULP AND PAPER MILL

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Abstract: Paris COP21 encouraged pulp and paper mills to look at options of reducing fossil fuel based carbon dioxide emissions. At a modern pulp mill, renewable heat and electricity are produced in excess of the own process requirement and the lime kiln is the only fossil fuel user during normal operation. Integrated paper production creates need for additional fossil fuel input. Biogas and pulverized wood can be produced at the mill by processing woody biomass residue. These biofuels can then be combusted in the lime kiln to replace fossil fuels. The results of this study show, that a large part of fossil fuels in the lime kiln can be replaced in a feasible way by biomass fuels also when paper production is integrated in a Northern pulp mill operation.

Keywords: Pulp mill, Lime kiln, Biorefinery, Gasification, Pulverized wood firing

INTRODUCTION

The targets of the Paris 2015 Agreement have encouraged also pulp and paper industry to look for options of reducing fossil fuel based carbon dioxide emissions. In modern kraft pulp mills, a large share of energy is biomass-based as fossil fuels are primarily used in lime kilns and during upsets, start-up, and shutdown [1, 2]. The lime kiln is a significant energy consumer and during normal operation, also the only fossil fuel user in a modern kraft pulp mill. When a renewable alternative is substituted for fossil lime kiln fuels, a kraft pulp mill can run fossil fuel-free.

A typical, large Northern integrated pulp and paper mill produces a substantial part of the required heat and electricity using its own biomass-based by-streams. In the modern kraft pulp production process, heat and electricity are produced in excess of own requirement. When paper making is integrated with pulp production, a significant additional fuel usage, often fossil fuel usage, is required to cover the energy usage of paper making. In this study, the technical and economic possibilities to replace fossil lime kiln fuels with biogas or pulverized woody biomass in a large new Northern integrated pulp and paper mill are evaluated.

The lime kiln in a kraft pulp mill is used to convert lime mud into burnt lime to enable its re-use in the pulping process. The reducing reaction requires high temperature, above 900°C. Therefore, external heat is generated by combusting fuels in the kiln. Lime kilns are typically fired with fossil oil or natural gas. Alternative fuels, such as methanol, tall oil, strong odorous gases, tall oil pitch, hydrogen, and turpentine are often co-combusted, but rarely used as the main fuel [3].

Biogas and pulverized wood can be produced at a pulp mill using existing resources. Wood processing for pulping produces woody biomass residue including e.g. bark and fines, and this residue can be processed further to be used for example as a fuel. Gasification of biomass followed by biogas firing in lime kiln is a known technology and has been used before in pulp mills in Scandinavia [4]. Dried and pulverized biomass has been fired in lime kilns in for example Sweden [5], as well as in cement kilns [6], whose operation is similar to pulp mill lime kilns.

The studied mill of this work is a large bioproduct mill based loosely on the concept of the mill currently under construction by Metsä Group in Äänekoski, Finland [7]. In addition, data from similar Finnpulp Oy bioproduct mill planned to be constructed in Kuopio, Finland, was utilized [8]. Integrated paper making is added into the bioproduct mill model to analyze the chosen concepts. Substituting lime kiln fuels with renewables has been studied before in the case of kraft pulp mill [4, 5, 9, 10, 11], but integrated paper making together with more efficient side stream utilization within the bioproduct mill concept notably changes the approach. The primary benefit of this study lies in the need to find a suitable fossil fuel-free mill concept for a Northern integrated pulp and paper mill. In Scandinavia, integrated pulp and paper mills are more common than stand-alone pulp mills. Conclusions on the feasibility of the concepts cannot be drawn from studies that are made for stand-alone pulp mills.

The technical feasibility of the options can be evaluated by studying the effects of the process integration on the operation of a pulp and paper mill. In this study, the calculated mass and energy balances of the example mill are analyzed for the gasification and wood pulverizing cases in order to find out the benefits and constraints of the concepts. Economic analysis is made by evaluating the capital and operational costs of the integration concepts, and by comparing them with the expected profit. The majority of the profit is expected to come from the decrease in fossil fuel supply.

METHODS AND MATERIAL

The Bioproduct Mill Concept

The bioproduct mill concept includes a large pulp mill with integrated operations to produce both well-known and new products utilizing the side streams and resources of the pulp mill, for example existing infrastructure and heat and power streams. A traditional pulp mill produces e.g. woody residue for biofuel use, turpentine, tall oil, and bioenergy in the form of heat and electricity, along with pulp production. In a bioproduct mill, the product portfolio can additionally include for instance bioenergy in other forms such as biogas, bioethanol, or bio-oil, tailored pulps, biomaterials such as biocomposites and textiles, biochemicals, and fertilizers [7, 12]. The aim is to utilize resources more effectively than before and, at the same time, produce new, advanced products that can substitute for fossil fuel based products or meet new customer needs. In the future, the side products can be expected to increase their share of the turnover of a pulp mill.

Biogas and Pulverized Wood as Lime Kiln Fuels

Lime kiln operations and pulp quality are affected by lime kiln fuel properties. The operation of a lime kiln requires stable combustion conditions and easily controllable hot end temperature. Fluctuating fuel heating value and moisture content affects the flow and temperature profile of the lime kiln flue gas. Compared with fossil fuels, the moisture content of biomass-based fuels is typically higher and adiabatic flame temperature is lower. Table 1 compares the primary differences of biogas and pulverized wood with the properties of natural gas and fuel oil. Higher moisture content decreases the system efficiency and increases significantly the amount of flue gas from the kiln [13]. Lower adiabatic flame temperature leads to increase in flue gas temperature in the kiln exit. The use of biomass-based fuels lowers the firing end temperature in the kiln, which leads to requirement for higher firing rates in order to maintain the production capacity at the same level [4]. In these calculations, an increase of 3% in fuel consumption was assumed for biogas and pulverized wood compared with fossil oil.

Table 1. Comparison of lime kiln fuel properties

	Lower heating value (MJ/kg)	Adiabatic flame temperature (°C)	Contaminants
Heavy fuel oil	40.6	2210	No
Natural gas	50.0	2050	No
Biogas	6.7	1870	Some
Pulverized wood	14.3	1950	Significant

Solid fuels often include non-process elements that may cause ring formation and lime quality problems and they also tend to accumulate in the lime cycle. Therefore, solid fuel use leads to increased use of make-up lime. When biomass is gasified, a part of its contaminants is removed with the bottom ash of the gasifier. Consequently, the amount of harmful elements ending up in the lime cycle reduces. In these calculations, a make-up lime use increase of 3 kg/ADt was assumed for pulverized wood, and 2 kg/ADt for biogas based on earlier studies [4, 13].

The use of biomass residue requires feedstock pretreatment including removal of undesired elements such as sand and metals, drying, chipping, and grinding. Pretreatment is essential to improve the efficiency of the process and prevent problems in the fuel feeding systems. In a pulp mill, there are several low value heat streams that can be used for biomass drying, such as flue gas and secondary heat in the form of steam and hot water. Fire risk in the fuel handling systems is a common reason for system breaks, and it can be decreased by use of water or steam instead of flue gas [5]. In these calculations, moisture content of received biomass residue is 50%. Biomass is dried into 15% moisture before gasification and 10% moisture before pulverizing. Hot secondary water stream at temperature of 65°C is used for drying. Electricity consumption in biomass grinding is assumed at 192 kWh/t based on vendor data.

Biomass gasification is a well-known process, and it has been used before in pulp mills to fire lime kilns, for example in Finland in the beginning of the 1980s'. Recently, it has gained interest again due to increasing demand on fossil fuel replacement and utilization of biomass residue. Circulating fluidized bed (CFB) gasifiers are typically suitable for pulp mill integrations due to their size and ability to gasify biomass residue of varying quality. For a CFB gasifier, biomass moisture content should be at or below 15% and average particle size at maximum 6 mm [14, 15]. Electricity use in the pulp mill increases along with gasifier integration due to biomass processing and gasifier electricity consumption. The main part of power used by the gasifier is due to air fans; the consumption can be estimated at 1.1% of the thermal power of the gasifier.

Heterogeneous consistency of woody biomass residue makes its combustion in lime kiln challenging. When biomass is dried and pulverized, it can be combusted in lime kilns either using pulverized fuel burners or by mixing it with lime. Pulverized fuel burners are chosen when wood is used as the main fuel. Pulverized wood has been tested in lime kilns for example in Sweden [5], and used in cement kilns whose operation is similar to pulp mill lime kilns. For combustion in a lime kiln, the average wood particle size is to be below 1 mm. Pulverizing is energy-intensive due to wood properties. When hammer mills are chosen, the power consumption of pulverizing can be estimated at 50 kW/MW$_{th}$ based on vendor data. Unplanned shutdowns due to fires in fuel feeding system or clogging of hammer mills were found to be the main drawbacks when pulverized wood was tested in Swedish mills [5].

Operations and Modeling of the Reference Mill

The studied reference mill produces softwood pulp 1.4 MADt in 350 annual operating days. Paper production is 4224 t/d, where 50% of the produced pulp is used for coated and 50% for uncoated paper making. The wood handling unit processes incoming softwood 24 408 m^{3}sob/d, and produces woody residue including bark, saw dust and fines from screening. The reference mill was modeled using an updated Millflow spreadsheet. Millflow includes detailed mill mass and energy balances and is introduced in more detail in previous work [4, 16]. The possibilities of lime kiln fuel replacement were estimated based on the lime kiln heat demand considering the amount of available resources. The main operating values for the reference mill are represented in Table 2.

Table 2 Main process values for the reference mill

	Unit	Base case mill
Production		
-Operating hours	h/a	8400
-Bleached pulp production	ADt/d	4000
-Paper production, coated	t/d	2291
-Paper production, uncoated	t/d	1933
Wood handling		
-Wood income	m^{3}sob/d	24 408
-Residue generated	BDt/d	1514
-Wood moisture	-	50%
Recovery boiler		
-Solids as fired	BDt/d	8033
-Net steam flow	t/h	1055
Power boiler		
-Woody biomass fuel use	BDt/d	1514
-Net steam flow	t/h	311
Lime kiln		
-Product	t/d	1230
-Heat requirement	MW	85
-Oil consumption	t/d	193
Energy		
-Steam use in pulp mill	t/h	813
-Steam use in paper mill	t/h	401
-Power generation	MW	234
-Power consumption in pulp mill	kWh/ADt	552
-Power consumption in paper making	kWh/t	681

Steam is generated in the recovery boiler and in a separate power boiler. Power boiler is fired with woody residue from the wood handling process. Steam is used in steam turbines for electricity generation and for heating purposes in the pulp and paper production processes. There is abundantly low value heat available in the form of steam and water flows. On demand, these flows can be utilized for heating purposes, such as for biomass drying. Electricity generation exceeds the mill power demand in the case of a modern stand-alone pulp mill. With integrated paper making, external electricity may be needed depending on process details. In the reference mill operations, power consumption was estimated based on the public data of Metsä Group Äänekoski mill [7] and literature data [17]. In the base case, all available biomass residue is combusted in the power boiler for steam generation to maximize power generation.

Lignin extraction from black liquor has been considered as an option in both bioproduct mills under planning in Finland [7, 8]. Lignin can be either combusted in lime kiln to substitute for fossil fuels or refined further [18, 19]. Lignin is a valuable raw material that can be used for several bioproducts. Lignin extraction decreases the amount of organics entering the recovery boiler and affects the properties of black liquor, and therefore, steam production decreases. Consequently, less electricity can be generated. Lignin extraction was excluded from this study to secure power generation for integrated paper making. In addition, the further refining of lignin to value-added products has been considered the preferred pathway in the future mills.

The theoretical CaO requirement in the example mill process is 926 t/d. Considering unreacted lime, losses and make-up lime, the kiln product can be calculated at 1230 t/d and the lime kiln heat demand at 85.2 MW. In the base case, oil is used to fire the lime kiln, and make-up lime requirement is 15 kg/ADt.

Basis for the Economic Evaluation

The costs of the studied concepts depend on the process planning and the needed equipment. The costs increase when for instance storage facilities or backup system for unplanned system breaks is desired. Three scenarios were estimated for both biogas and pulverized wood cases. These are neutral, optimistic, and pessimistic scenario. In the scenarios, the values for investment cost, interest rate, fuel oil price, and EU ETS carbon price were varied to estimate the effect of uncertainties in these factors on the feasibility of the concepts. The initial values used in the calculations are presented in Table 3.

Table 3 Initial values for evaluation of economic feasibility of the studied concepts

	Unit	Gasification			Pulverizing		
Scenario		Neutral	Optimistic	Pessimistic	Neutral	Optimistic	Pessimistic
Lifetime	a	20	20	20	20	20	20
Interest rate	-	10	8	12	10	8	12
Investment	MUSD	30.4	22.8	38.1	36.4	27.3	45.6
Oil price	USD/l	0.40	0.50	0.30	0.40	0.50	0.30
EU ETS price	USD/t CO_2	5.75	8.75	2.75	5.75	8.75	2.75
Make-up lime price	USD/t	180	180	180	180	180	180

The capital and operational costs for the studied cases were estimated based on recent investments in Scandinavia and vendor data. The examined processes are not commonly used, and therefore, lack of references makes economic evaluation challenging. There are also uncertainties related to for instance fossil fuel prices, which affect the profitability of the concepts. Therefore, the results should be considered as best estimates.

Biomass price is not taken into account in the calculations, because the value of biomass depends on local conditions; it can have a sale price, but in some cases it may cause disposal cost. Also cost for heat used for biomass drying was not taken into account due to copious low value heat sources available in the mill. In the Nordic countries, pulp mills often sell excess heat to district heating network, and in these cases, also low temperature heat can be a source of income. The reduction of CO_2 emissions when fossil oil is replaced by renewables was taken into account by estimating cost savings from EU ETS.

RESULTS AND DISCUSSION

Biogas and pulverized wood processes are technically possible to integrate in a pulp and paper mill process. In this study, energy-independency was set as the target, and thus electricity or biomass was not purchased. In these conditions, lime kiln heat demand cannot be covered fully with biogas or pulverized wood, because biomass is used to produce electricity in the power boiler to cover the power requirement of the integrated pulp and paper production. According to the calculations, biogas and pulverized wood can cover 69.8% and 74.6% of the kiln heat demand, respectively. Additionally, tall oil pitch, methanol, and other side streams of the pulping process can be used to fire the kiln on order to meet the target of fossil fuel-free operation. Otherwise, fossil fuel use up to 30% of the kiln heat requirement is needed. For existing lime kilns already operating with fossil fuel, some vendors recommend a replacement rate of max 80-90% in order to keep the kiln capacity at the same level. The main parameters from the integrated mill calculations are presented and compared with the base case in Table 4.

Table 4 Effect of integration of lime kiln fuel production on the reference mill process

	Unit	Base case	Gasification case	Pulverizing case
Production				
-Operating hours	h/a	8400	8400	8400
-Bleached pulp production	ADt/d	4000	4000	4000
-Paper production, coated	t/d	2291	2291	2291
-Paper production, uncoated	t/d	1933	1933	1933
Wood handling				
-Wood income	m^{3}sob/d	24 408	24 408	24 408
-Residue generated	BDt/d	1514	1514	1514
-Wood moisture	-	50%	50%	50%
Recovery boiler				
-Solids as fired	BDt/d	8033	8033	8033
-Net steam flow	t/h	1055	1055	1055
Power boiler				
-Woody biomass fuel use	BDt/d	1514	1189	1214
-Net steam flow	t/h	311	244	250
Lime kiln				
-Product	t/d	1230	1230	1230
-Heat requirement	MW	85	85	85
-Make-up lime use	kg/ADt	15	17	18
-Oil consumption	t/d	193	-	-
-Biogas consumption	t/d	-	785	-
-Pulverized wood consumption	t/d	-	-	299
-Biofuel share of kiln energy	-	-	69.8%	74.6%
-Reduction in fossil CO_2 emissions	tCO_2/a	-	140 900	150 600
Biofuel production				
-Power consumption	MW$_e$	-	3.8	5.4
-Energy for drying	MW$_{th}$	-	8.0	8.0
Energy				
-Power generation	MW	234	216	217
-Power consumption, total	MW	211	215	217
-Excess power production	GWh/a	189	2	1

Mass and energy balances of the mill are affected when gasification or pulverized wood process is integrated in the pulp and paper mill process. However, the new processes do not affect the actual pulp or paper production or the quality of the products. The major effect of the studied concepts is the increased amount of non-process elements in the lime cycle, which leads to increase in the use make-up lime. In a modern, energy-efficient mill it is possible to produce the major part of lime kiln fuel by utilizing existing side streams and secondary heat.

In addition to lime kiln use, fossil fuels are used in a pulp mill during upsets, start-up, and shutdown. Substituting renewables for fossil lime kiln fuels will therefore make the mill approximately 90% fossil fuel-free. In order to run a pulp mill entirely without fossil fuels, a renewable option for the auxiliary fuels is required. Pyrolysis oil or ethanol, for instance, could be used for this purpose, but the implementation needs further studies.

The economic evaluation for both cases in the three scenarios was made by calculating payback period and breakeven lime kiln fuel price. The profitability of the concepts was estimated in relation to electricity sale price, because selling of electricity was considered as an option for biofuel production. The results show, that both the cases are economically feasible, and that there is only a small difference between the profitability of the cases. Higher investment cost makes the pulverizing case more expensive, even though the operating costs are lower than in the gasification case. The differences are however small and do not exceed the margin of error of the calculations. The differences are also highly dependent on mill-specific solutions, for example desired storage capacities and possible backup systems in case of unplanned shutdowns of the biofuel production facilities.

The payback period for the studied cases as a function of electricity sale price is represented in Fig. 1. The results show, that neutral and optimistic scenarios give highly promising results. In the pessimistic scenario, where the price of replaced oil and the ETS carbon price were considered lower than in other scenarios, and the investment cost as well as the interest rate higher, the payback period increases fast when electricity sale price increases. Low oil cost leads to a low benefit from the fuel replacement, unless cost of fossil CO_2 emissions is high at the same time.

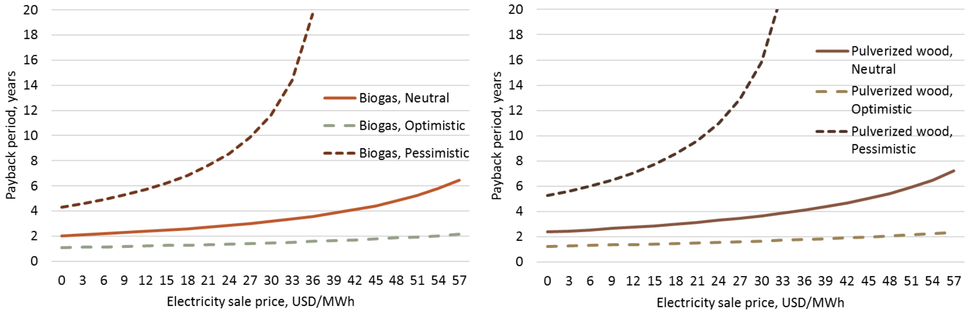

Fig. 1 Payback period for gasification and wood pulverizing cases in neutral, optimistic, and pessimistic scenarios as a function of electricity sale price

The breakeven lime kiln fuel price as a function of electricity sale price for the gasification and pulverizing cases is represented in Fig. 2. A case can be considered profitable, when the price of replaced fuel exceeds the calculated breakeven price. In the beginning of the year 2017, crude oil price has been around 55 USD/bbl [20], equaling to 32 USD/MWh. The oil price for an industrial user including e.g. taxes, is higher. At the same time, the average spot price in the Nord Pool power market has been approximately 33 EUR/MWh [21], which equals to 35 USD/MWh. Considering recent oil and electricity prices, the studied concepts are profitable. The investment cost and interest rate are the most significant factors when breakeven price is calculated. The ETS price and the make-up lime price have only a small influence.

The purpose of the economic evaluation in this study is merely to compare the presented concepts. The profitability of each concept is highly dependent on the mill processes and local conditions. In the future, fossil fuel-free solutions are needed in every mill, and then the decisions will be made based on mill-specific details and considering the political situation, namely, which solutions are encouraged and possibly subsidized based on political decisions.

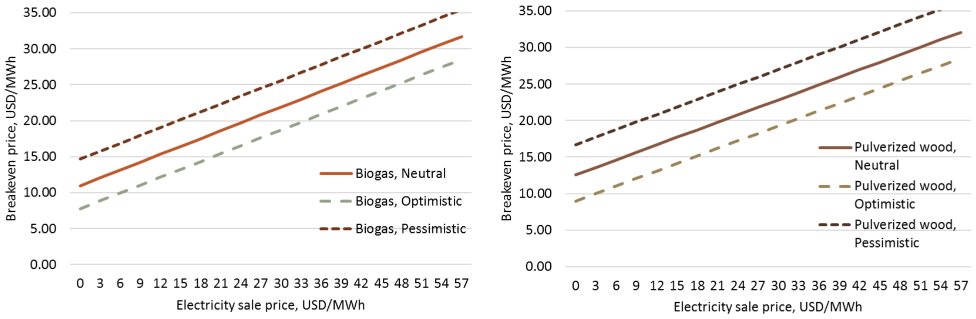

Fig. 2 Breakeven lime kiln fuel price in neutral, optimistic, and pessimistic scenarios as a function of electricity sale price

CONCLUSIONS

The results of this study show, that it is technically possible to produce renewable fuels in a modern, integrated pulp and paper mill to cover the major part of lime kiln fuel requirement. The studied integration concepts affect the pulp mill mass and energy balances, but there is no significant effect on the actual pulp production. To ensure the power production for the mill processes including the energy-intensive paper making, biomass combustion in a power boiler is necessary. Thus, there is a lack of biomass if the target is to fully substitute biomass-based fuels for fossil fuels in the lime kiln. In order to run a fossil fuel-free pulp and paper mill, additional biomass or other side streams, such as methanol, can be used to increase the share of bio-based fuels in the lime kiln. Otherwise, up to 30% of lime kiln heat demand needs to be covered with fossil fuels. Since approximately 10% of pulp mill fossil fuel use is auxiliary fuel use during e.g. start-up, an entirely fossil fuel-free pulp mill concept is possible only if also these fuels are substituted with renewables, such as pyrolysis oil.

The studied cases were found economically feasible, assuming that biofuel production is an option for electricity sale, and that fossil fuel price and EU ETS price are at recent level. In the future, the most feasible option for fossil fuel-free pulp and paper production depends not only from fossil fuel and electricity prices, but also on political decisions and possible incentives for the options.

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ORIGINAL ARTICLE

Biomass-based carbon capture and utilization in kraft pulp mills

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Abstract

Corporate image, European Emission Trading System and Environmental Regulations, encourage pulp industry to reduce carbon dioxide (CO_2) emissions. Kraft pulp mills produce CO_2 mainly in combustion processes. The largest sources are the recovery boiler, the biomass boiler, and the lime kiln. Due to utilizing mostly biomass-based fuels, the CO_2 is largely biogenic. Capture and storage of CO_2 (CCS) could offer pulp and paper industry the possibility to act as site for negative CO_2 emissions. In addition, captured biogenic CO_2 can be used as a raw material for bioproducts. Possibilities for CO_2 utilization include tall oil manufacturing, lignin extraction, and production of precipitated calcium carbonate (PCC), depending on local conditions and mill-specific details. In this study, total biomass-based CO_2 capture and storage potential (BECCS) and potential to implement capture and utilization of biomass-based CO_2 (BECCU) in kraft pulp mills were estimated by analyzing the impacts of the processes on the operation of two modern reference mills, a Nordic softwood kraft pulp mill with integrated paper production and a Southern eucalyptus kraft pulp mill. CO_2 capture is energy-intensive, and thus the effects on the energy balances of the mills were estimated. When papermaking is integrated in the mill operations, energy adequacy can be a limiting factor for carbon capture implementation. Global carbon capture potential was estimated based on pulp production data. Kraft pulp mills have notable CO_2 capture potential, while the on-site utilization potential using currently available technologies is lower. The future of these processes depends on technology development, desire to reuse CO_2, and prospective changes in legislation.

Keywords Bioenergy with carbon capture and storage BECCS · Bioenergy with carbon capture and utilization BECCU · Kraft pulp mill · Climate change mitigation · Negative CO_2

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1 Introduction

Pulp and paper production is one of the largest industrial energy users (IEA 2014). The raw material used in chemical pulping is mainly woody biomass. Over 80% of the carbon dioxide (CO_2) emissions are from burning of residual biomass. Of the global capacity, a significant portion is at forest industry sites (Vakkilainen et al. 2013). Comparison of global capacities of plants converting biomass for energy purposes shows that recovery boiler capacity is much larger than other biomass boiler capacities (Fig. 1).

Sustainability, emission trading and control, environmental regulations, corporate image, self-sufficiency of fuel supply, and the price of fossil fuels are among the many factors driving companies to reduce usage of fossil fuels. In the chemical pulp industry, a large share of energy use is already biomass-based, and in normal operations, modern kraft pulp mills are usually self-sufficient in energy, with the exception of lime kiln operations. Fossil fuels are primarily used to reduce lime mud to burnt lime. They are also used during upsets, start-up and shut-down, as well as sometimes for safety reasons, e.g., to secure non-condensable gas destruction (Vakkilainen and Kivistö 2008; Vakkilainen and Kivistö 2014). The lime kiln is typically the only unit operation utilizing fossil fuels during normal operations, and, consequently, the main source of fossil fuel-based emissions. When the woody raw material is from a sustainable origin, the mill operations can be considered carbon-neutral except for fossil fuel use. Substituting fossil fuels used in the lime kiln with renewable fuels produced at the mill, especially if existing side streams are used, would make normal kraft pulp mill operations nearly fossil fuel-free. Feasible options to integrate renewable lime kiln fuel production into the kraft pulp production process exist (Kuparinen and Vakkilainen 2017).

This study provides an assessment of the global potential of pulp and paper industry to act as site for negative CO_2 emissions through biomass-based CO_2 capture and storage (BECCS) and what could be the share of internally utilized CO_2 (biomass-based CO_2 capture and utilization, BECCU). To clarify the potential to capture CO_2, an analysis of modern Nordic

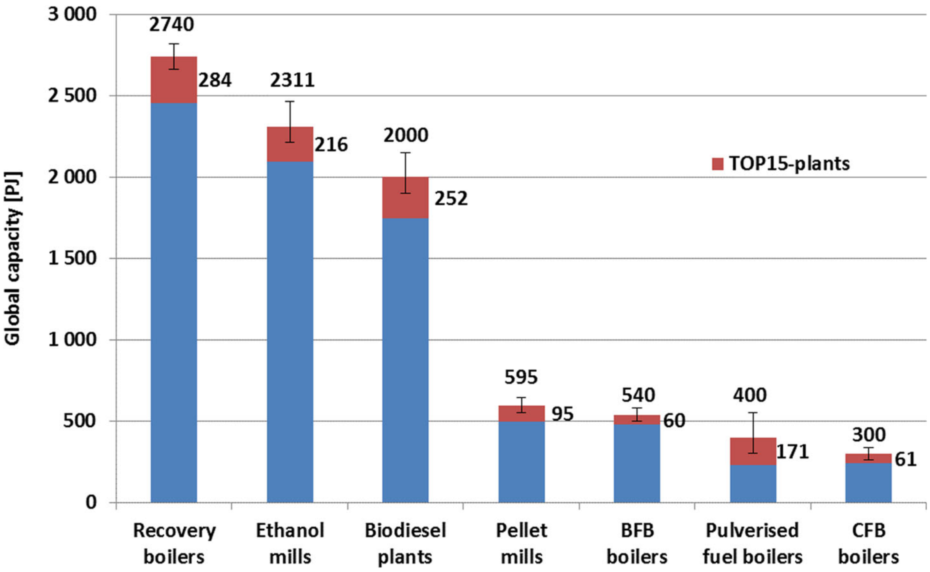

Fig. 1 Comparison of the global capacities (petajoules, PJ) of various types of biomass plants (Vakkilainen et al. 2013). BFB and CFB refer to bubbling fluidized bed and circulating fluidized bed, respectively

Softwood Kraft Pulp Mill (Kuparinen et al. 2017) and Southern Eucalyptus Kraft Pulp Mill potential with alternative sources captured and the effect to their energy production is shown and discussed. The possibility to utilize captured CO_2 as raw material for further bioproducts is explored.

2 CO_2 sources in kraft pulp mills

The operation of a modern Nordic Softwood Kraft Pulp Mill and a Southern Eucalyptus Kraft Pulp Mill is analyzed, to clarify the potential to capture CO_2 and the effect to their energy balances is shown and discussed. The magnitude of the recovery process is often not fully appreciated. The global sulfate pulp production was 137 million tons (t) in 2016 (FAO 2017). Consequently, more than 1300 million tons of weak black liquor was processed in recovery boilers globally and 206 million tons of black liquor dry solids was combusted (Tran and Vakkilainen 2007). The global energy generation in recovery boilers was thus approximately 1.8 exajoules (EJ). Based on statistics (IEA 2018), this makes black liquor the fifth most important fuel in the world after coal, oil, natural gas, and gasoline. In the industrial sector, recovery boilers were responsible for about a quarter of the global biomass-based energy generation in 2011 (Vakkilainen et al. 2013).

Carbon dioxide capture (CC) from lime kiln flue gasses and subsequent use as calcium carbonate paper filler is a well-known and widely applied technology (Hirsch et al. 2013). It is technically possible to retrofit post-combustion CC to an existing pulp or pulp and board mill recovery boiler or biomass boiler (IEAGHG 2016). Carbon dioxide capture processes use heat and power, which affects the energy balance of the mill. The adequacy of steam and electricity needs to be estimated based on mill-specific details and the requirements of the chosen CC process. Estimation on the effects of CC process implementation can be made by analyzing example mill processes. For instance, when amine-based post-combustion CO_2 capture process is used in stand-alone mills, added steam use can be covered without need for an additional boiler (Onarheim et al. 2017).

2.1 Sources of CO_2

CO_2 is formed in kraft pulp mills primarily during combustion, when carbon (C) in the fuel oxidizes. The primary reaction is

$$C + O_2 \rightarrow CO_2.$$

The main CO_2 sources are the recovery boiler, the biomass boiler, and the lime kiln. Non-condensable gas (NCG) destruction with several vents is also a CO_2 source, but a negligible one. Of these, typically, the lime kiln is the only fossil CO_2 source. A simplified process diagram of a kraft pulp mill showing the main CO_2 sources is depicted in (Fig. 2).

2.2 Biomass boiler

Biomass residue is generated in the wood handling processes of the pulp mill, and, in addition to bark, the biomass residues contain other particles such as fines and wood lost during mill debarking. Almost all pulp mills burn this residue at site in the biomass boiler.

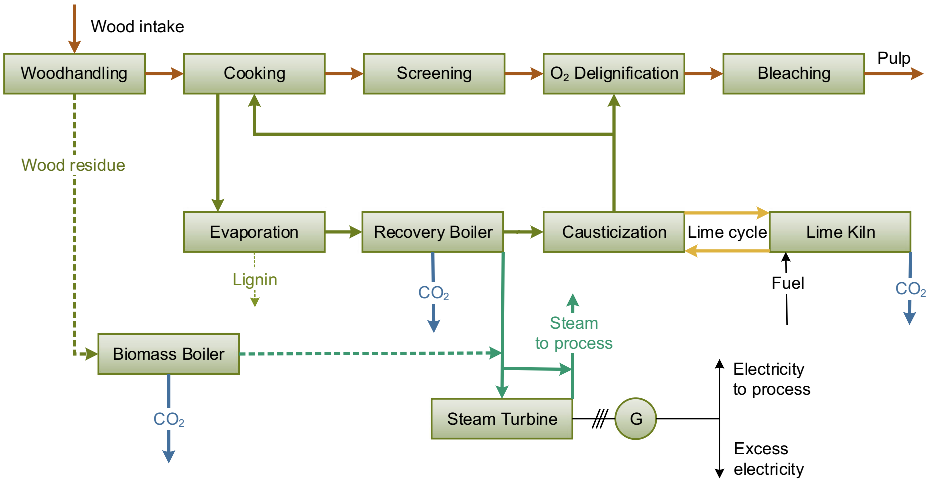

Fig. 2 Kraft pulp mill operations and alternative CO_2-removal streams studied

Biomass boiler uses fossil fuels during startup and shutdown. In many mills, additional auxiliary steam is generated with fossil fuels especially if the mill is an integrated mill. Integrated mill combines the pulp mill and the paper machine. For pulp mill, the fossil fuel usage produces at least 20 kilograms (kg) CO_2 per air-dry pulp ton (ADt), but can be significantly larger.

2.3 Recovery boiler

Weak black liquor from brown stock washers after pulping is concentrated in multi-effect evaporator. Most of the water is removed, and concentrated black liquor, at 10–35% water content, is burned in a recovery boiler. The role of the recovery boiler is to burn organic residue from pulping and recover used sodium-based pulping chemicals in the black liquor. As concentrated black liquor is sprayed into the lower part of the recovery boiler, the parts of wood, not used for pulp, are burned. In the lower part of the furnace, an oxygen deficient environment is maintained so that sodium sulfide (Na_2S) is preferably formed. The extent of sulfide formation over sulfate is measured by the reduction efficiency, typically over 90%. The rest of the sodium reacts to carbonate. The inorganic sodium and sulfur are recovered as a molten smelt, which consists mostly of Na_2S and sodium carbonate (Na_2CO_3). The molten smelt enters a dissolving tank where it is dissolved in almost water-like weak white liquor to form green liquor. Carbon dioxide in the carbonate is thus from biogenic source (Kuparinen and Vakkilainen 2017). Biogenic CO_2 from the recovery boiler exits from the stack of the recovery boiler with the flue gas. Typically fossil fuels are used during startup and shutdown. Occasionally due sudden and large process upsets or equipment failure fossil fuels, mostly oil and natural gas are burned. Fossil fuel usage produces 10–20 kg CO_2/ADt. Biogenic CO_2 produced is 1600–2400 kg CO_2/ADt.

2.4 Lime kiln

The green liquor from the recovery boiler is sent to the causticizing plant, where it reacts with lime (CaO) to convert the Na_2CO_3 to sodium hydroxide (NaOH) following the reactions

$$\begin{aligned}&CaO + H_2O \rightarrow Ca(OH)_2\\&Na_2CO_3 + Ca(OH)_2 \rightarrow 2\ NaOH + CaCO_3.\end{aligned}$$

Conversion is measured by causticizing efficiency, typically 80 to 85%. Reaction product calcium carbonate ($CaCO_3$) is regenerated to CaO in the lime kiln with heat from burning typically fossil fuel according to the reduction reaction:

$$CaCO_3 + (heat) \rightarrow CaO + CO_2.$$

The reduction reaction produces biogenic CO_2 that exits with the flue gasses from the stack of the lime kiln. Typically, fossil fuels are used to reach the required temperature, at least 850 °C. Fossil fuel usage, mostly oil and natural gas, produces 100–250 kg CO_2/ADt.

2.5 Biogas production

Liquid effluents from pulp mill are treated to high degree. Effluent flows contain small biomass particles (fiber sludge) that settle down. Separated material is called primary sludge. Very often the next step is biological treatment where remaining organics in the effluent are eaten by micro-organisms creating biosludge.

In some new mills, biosludge recovered is treated to biogas. Biogas production can be 10–15 kilowatt hours (kWh) per ADt (Metsä Group 2016). CO_2 emissions from biogas production can be estimated growing, but of minor significance in relation to above-mentioned combustion processes.

2.6 Studied mills

The potential to capture CO_2 within kraft pulp mill operations has been analyzed via case studies. The mass and energy balances of two reference mills were calculated and the most important CO_2 sources were defined to estimate the CC potential and the effect of the implementation of the capture processes on the mill operations. The following reference mills were studied:

- Mill A

  A modern softwood kraft pulp mill located in Northern Europe
  Annual pulp production 1,400,000 ADt
  Residue from woodhandling process combusted in a power boiler
  Integrated paper mill producing coated and uncoated paper

- Mill B

  A modern eucalyptus kraft pulp mill located in South America
  Annual pulp production 1,500,000 ADt

The mills represent typical mills in their chosen location. Three hundred and fifty annual operating days was estimated for the both mills. The mill balances were calculated using an updated *MillFlow* program. The program includes detailed mass and energy balances and has been used to design pulp mills and to evaluate new process alternatives (Vakkilainen and

Kivistö 2008; Hamaguchi et al. 2011). The Millflow balances include hundreds of calculations, which were introduced in more detail earlier (Hamaguchi et al. 2011). In the program, the pulping line is dimensioned based on the desired capacity of the mill. The wood demand is calculated based on the cooking yield and losses in the process stages, and the chemical demand is calculated from the digester balance. The program includes a black liquor calculation tool to define the inputs for the recovery boiler calculations, such as the dry solids flow, the composition, and the heating value of black liquor. The electricity generation is calculated from turbo generator balances after defining the steam flows from the recovery boiler and the biomass boiler. The electricity and heat usage in each department of the mill is used to define the steam balance. The lime kiln calculations require that inputs such as the type of make-up lime, the amount of residual lime, and the availability of burnt lime are defined. During this study, a carbon capture unit was added to calculate how carbon capture affects the balances of the reference mills.

Mill A is a large integrated pulp and paper mill located in Northern Europe. The recovery boiler and a separate biomass boiler produce steam for use in mill processes and for electricity generation in a steam turbine. The integrated paper mill is a notable steam and electricity consumer. Biomass boiler is fueled with woody residue from the wood handling process of the mill. The recovery boiler combusting black liquor and the biomass boiler produce biogenic CO_2 due to biomass-based fuels. Natural gas is used as lime kiln fuel. A more detailed description of the Northern reference mill operations can be found in a previous work (Kuparinen et al. 2017).

Mill B is a South American stand-alone kraft pulp mill producing market pulp from eucalyptus (*Eucalyptus globulus*). Steam is generated in the recovery boiler that is able to cover the heat and electricity demand of the mill, and a separate biomass boiler is not used. Eucalyptus is typically debarked in the forest, and therefore the amount of on-site woody residue is relatively small compared with Northern mills. The lime kiln is fired with oil, which is typical when the mill is not located near the natural gas grid. Earlier studies introduced the operations of this reference mill in more detail (Kuparinen and Vakkilainen 2017; Hamaguchi et al. 2011).

Simplified block diagrams of Mill A and Mill B (Figs. 3 and 4) show the primary CO_2 sources in the reference mills. The main process values of the reference mills are typical for new mills (Table 1). The biomass boiler in Mill A is assumed to combust all biomass residues generated, and the amount of CO_2 is calculated accordingly. The figures represent a normal operation situation, and therefore, fossil fuels used during startups and shutdowns are not shown in the figures. The CO_2 from fossil fuels used during startup and shutdown can be estimated at 10–20 kg CO_2/ADt. The lime kiln produces both fossil, fuel-based CO_2, and biogenic CO_2 originating from the lime reburning reaction. In the reference mill cases, 64% of lime kiln CO_2 is biogenic for Mill A, and 55% for Mill B.

3 CO_2 removal

As described above, the main CO_2 emission sources in a kraft pulp mill arise from the recovery boiler, the biomass boiler (when present), and the lime kiln, from which the recovery boiler is the largest point source. CO_2 removal is energy intensive and removal cost depends on removal method and process integration possibilities. Considering only carbon flows across the plant borders presented (Figs. 3 and 4), a

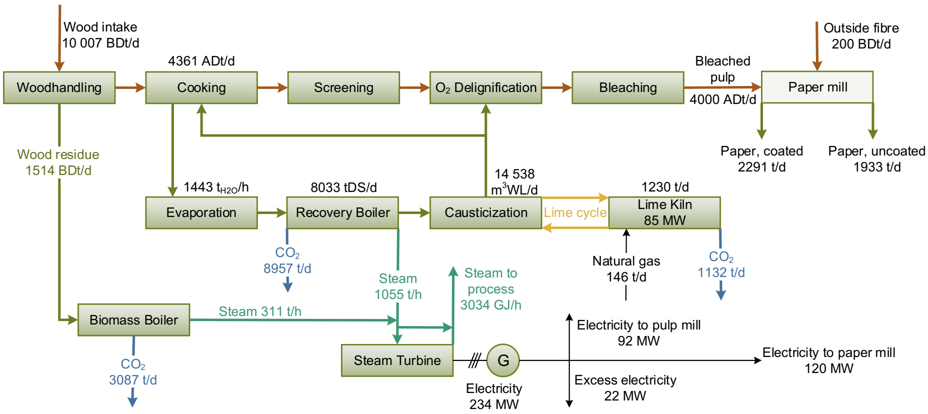

Fig. 3 Simplified block diagram of the operations of Mill A, a modern softwood kraft pulp mill located in Northern Europe. The values are given on hourly (h) or daily (d) basis. AD refers to air-dry, BD to bone-dry, DS to dry solids, and WL to white liquor

simplified carbon balance and net CO_2 emissions from the process ($CO_{2,net}$) can be defined for the process as follows

$$CO_{2,net} = (C_f + C_{CaCO3})\frac{M_{CO2}}{M_C} - \eta_{CCU}\eta_{CC}CO_{2,total}$$

where η_{CC} is the share of CO_2 removed from the total CO_2 emissions ($CO_{2,total}$) and depends on capture method and how it is applied. Most likely it is not feasible to apply CO_2 removal for all possible CO_2 streams, but rather to consider only the largest one(s). For example in Mill A and Mill B, the share of total emissions from the recovery boiler are 68% and 87%, respectively. If the efficiency of CO_2 capture process is 90%, it follows that $\eta_{CC,A} = 61\%$ and $\eta_{CC,B} = 78\%$. Depending on CO_2

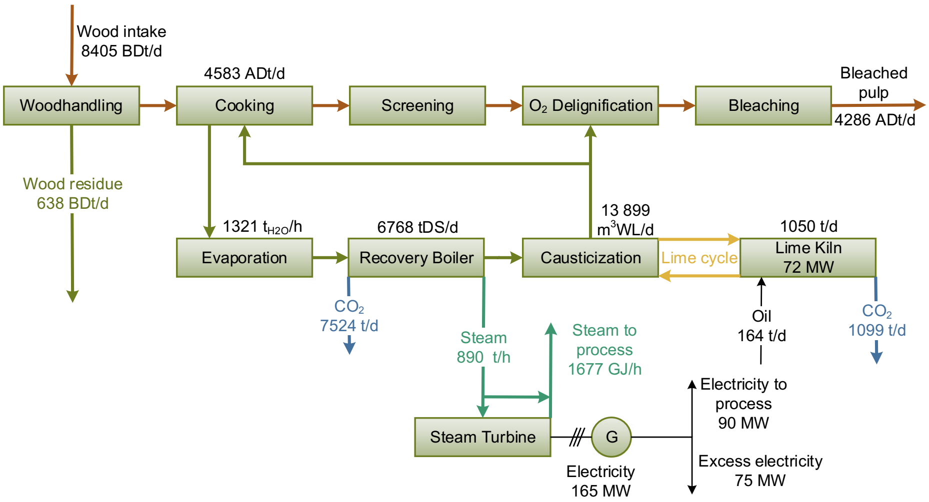

Fig. 4 Simplified block diagram of the operations of Mill B, a modern eucalyptus kraft pulp mill located in South America. The values are given on hourly (h) or daily (d) basis. AD refers to air-dry, BD to bone-dry, DS to dry solids, and WL to white liquor

Table 1 The main process values and CO_2 sources of the reference mills. The values are given on annual (a), daily (d), or hourly (h) basis. MW refers to megawatt

	Unit	Mill A	Mill B
Production			
-Operating hours	h/a	8400	8400
-Pulp production	ADt/d	4000	4286
-Paper production	t/d	4224	–
Recovery boiler			
-Black liquor flow, dry matter	tDS/d	8033	6768
-Net steam flow	t/h	1055	890
-CO_2 production	t/d	8957	7524
Biomass boiler			
-Biomass fuel use	BDt/d	1514	–
-Net steam flow	t/h	311	–
-CO_2 production	t/d	3087	–
Lime kiln			
Lime production	t/d	1230	1050
Makeup limestone	t/d	60	77
Fuel consumption	t/d	146	164
CO_2 production	t/d	1132	1099
Energy			
-Mill steam use	t/h	1109	660
-Power generation	MW	234	165
-Mill power consumption	MW	212	90

source and emissions of electricity production, in CO_2 to fuel conversion emissions in CCU route may exceed the fossil emissions (Abanades et al. 2017). Net negative CO_2 emissions can be reached only, if at least part of the captured CO_2 will be permanently removed from the atmosphere. η_{CCU} gives the CO_2 emission effect of selected CO_2 utilization and storage route, where 100% means that all captured CO_2 is permanently removed from the atmosphere, without additional emissions from the storage/utilization process. C_f and C_{CaCO3} are carbon flows into the plant in fossil fuel and limestone makeup streams. M_{CO2} and M_C refer to molar masses of CO_2 and C. For two studied Mill types where the capture process is applied only on recovery boiler, the net specific CO_2 emission curves show substantial recovery potential for a single mill (Fig. 5). Specific emissions have large variation, depending on capture process efficiency and the CO_2 emissions of the utilization route. When global potential for negative emissions is estimated roughly in Section 5, average specific emissions of −1 t CO_2/ADt is used for a general kraft pulp mill with CO_2 capture and utilization.

3.1 CO_2 removal methods

Different technologies based on pre-, post- or oxy-combustion processes can be utilized for CO_2 capture from pulp mills. Leeson et al. (2017) recently presented techno-economic analysis and review of different CO_2 removal methods applied to different industrial CO_2 sources. Also, pulp and paper industries were touched and it was determined that not many detailed studies have been applied to pulp mills. It was also noticed that there is no single winning technology in terms of costs and that benchmarking is difficult due to inconsistent literature.

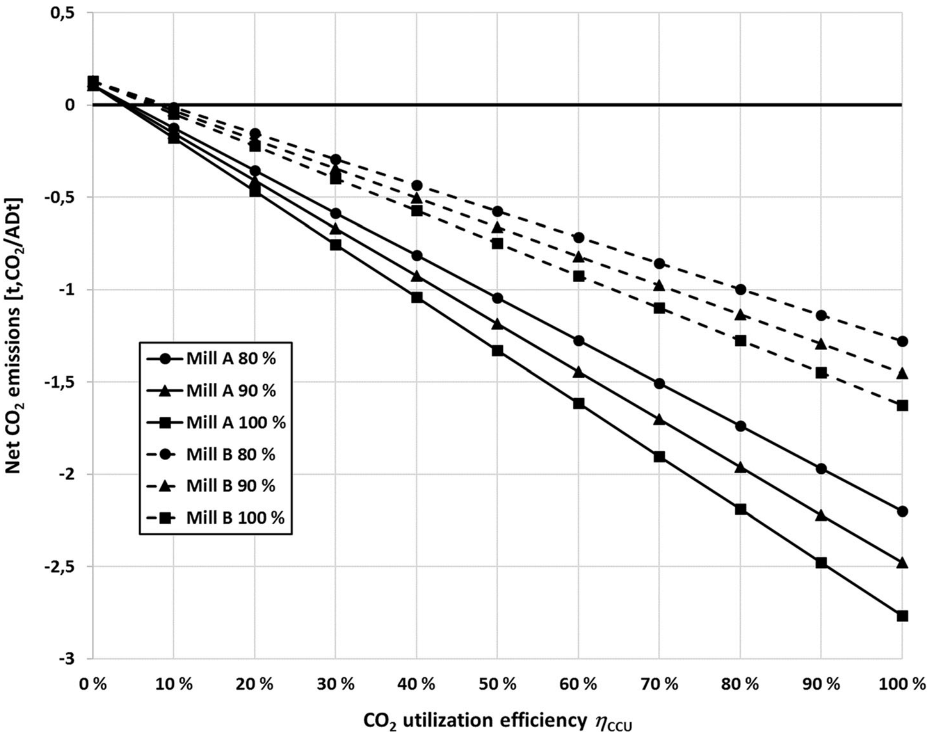

Fig. 5 Net CO_2 emissions per produced dry ton of pulp from Mill A and Mill B for different capture efficiencies (80%, 90%, 100%), when CO_2 capture is applied only on recovery boiler flue gasses. In this work, average specific emissions of − 1 t,CO_2/ADt is used for a general kraft pulp mill with CO_2 capture and utilization

Amine-based post combustion CO_2 capture systems are a proven technology that is commercially available. CO_2 capture efficiency of monoethanolamine (MEA) process is usually between 80 and 90% and as a post combustion method, it can be applied easily to existing plants. Aqueous solution (30 percentage by weight) of MEA can be considered as a reference solvent in post combustion capture process. CO_2 is absorbed at temperature 45–50 °C and flue gasses need to be cooled before amine absorption. Desorption occurs at 100–120 °C and approximately 3.7 megajoules (MJ) per kg,CO_2 heat is needed for sorbent regeneration. In addition, some electricity is needed for the process, which increases own electricity use of the mill (Onarheim et al. 2015).

In recent study, Karjunen et al. (2017) studied the application of CO_2 capture, transport, and intermediate storage logistics for Finnish energy system based on renewable energy sources. The cost of biogenic CO_2 for utilization varied between 40 and 44 €/t,CO_2 depending on applied future scenario. Costs were lowest for industrial scenario, where the largest amount of CO_2 was captured from large industrial (mainly pulp and paper) point sources. In the calculations, conventional MEA capture process was taken as reference capture method. Application of more advanced capture methods could lead to lower capture costs.

Oxycombustion processes (see e.g., Stanger et al. 2015) applied to recovery boiler, bark boiler, or lime kiln are one option but require oxygen source and possibly modifications to the flue gas passages. In oxycombustion processes, reaction zones and gas atmosphere in the furnace will change, which may have implications on heat transfer and reactions that should be taken into account. Main additional cost is production of oxygen, which in case of kraft pulp mills can be quite affordable due to often preexisting equipment on site. In addition, precombustion processes based on black liquor gasification have been suggested for CO_2 capture but these technologies have not yet been demonstrated successfully commercially (Onarheim et al. 2015).

Advanced hot solid looping technologies such as post-combustion calcium looping (CaL) (Martínez et al. 2016) offer also interesting possibilities for CO_2 capture. In CaL, process calcium oxide is used for CO_2 capture. In the case of kraft pulp mill, it has been proposed that lime mud from the lime kiln could be used as a sorbent for CO_2 capture in pulp mills (Sun et al. 2013; Tynjälä et al. 2014). Even if lime mud as is would not be feasible choice for CO_2 capture, there are other integration possibilities with CaL process and lime kiln, and also existing infrastructure for limestone acquisition and handling in a pulp mill, which could lead to further integration benefits. For CaL process integrated to lime kiln of a cement plant, Romano et al. (2013) estimated that the minimum cost of CO_2 avoided could be as low as 27 €/t,CO_2.

3.2 Effect of capture to energy use

CO_2 capture processes are energy-intensive, and therefore, the effect of the process on the reference mill energy balances was estimated. MEA-based post-combustion process and capture from recovery boiler flue gas flow were chosen for the calculations. The consumption of low-pressure steam, cooling water, and electricity were estimated based on a previous study (Onarheim et al. 2015). The effect of capture process to energy use in reference mills is presented in Table 2.

Due to integrated paper production, Mill A is a large energy consumer compared with a stand-alone pulp mill. Additional steam used in CO_2 capture reduces electricity generation. If the energy use is limited to mill's own production, availability of electricity sets the maximum limits for the capture process. Without additional electricity, 21% of CO_2 in the recovery boiler flue gas flow can be captured without additional energy generation. This equals to 14% of the total CO_2 of the mill. If carbon capture is used together with another process influencing the energy balance, such as lignin extraction, energy adequacy may become an issue.

Mill B is a stand-alone pulp mill where electricity is produced substantially in excess of own use. In this case, the limiting factor is the adequacy of steam, when steam production is limited to the recovery boiler and no additional boiler exists. The capture process consumes low-pressure steam. Based on the steam balance calculations, the maximum capture rate from recovery boiler flue gas flow is 32%, which equals to a capture rate of 28% of the total CO_2 emissions of the mill. The mill steam consumption increases then by 22%. Electricity consumption increases by 12% and production decreases by 10%.

Table 2 The effect of carbon capture process in the energy balances of reference mills, when MEA based post-combustion process is used to capture CO_2 from recovery boiler flue gas

	Unit	Mill A Base	Mill A CO_2 capture	Mill B Base	Mill B CO_2 capture
CO_2 capture	t/d	–	1881	–	2378
Mill steam use	t/h	1109	1225	860	807
Power generation	MW	234	221	195	149
Power consumption	MW	212	221	90	101

4 CO_2 utilization in kraft pulp mills

The possibility to utilize captured CO_2 as raw material for further bioproducts is explored. The possibilities depend on mill-specific details, such as the chosen processes and the type of wood raw material. The studied alternatives for on-site utilization of CO_2 are typically occurring large streams; tall oil manufacturing, lignin extraction, and production of precipitated calcium carbonate (PCC). Tall oil manufacturing can be considered as an option in softwood mills, but in hardwood and eucalyptus mills tall oil recovery is rarely done due to low levels of extractives (Shackford 2003). Lignin extraction can be integrated in both hardwood and softwood mills. There are several uses for the separated lignin; formaldehyde resins, carbon fibers, moisture barriers in packaging materials and upgraded fuel (Tomani 2013). In the case of an integrated pulp and paper mill, CO_2 can be used in PCC production (Teir et al. 2005).

4.1 Tall oil manufacture

After pulping, weak black liquor contains fatty and rosin acid extractives as foamy material called soap. Especially, coniferous trees have high extractive content. Soap in black liquor is separated and skimmed from feed and intermediate liquor tanks in the evaporation plant. Raw soap is converted to crude tall oil (CTO) by acidulation in the tall oil plant. Tall oil production varies and can be estimated as 45 kg/ADt for Nordic pine (*Pinus sylvestris*), 25 kg/ADt for Nordic spruce (*Picea abies*) and less than 20 kg/ADt for Nordic birch (*Betula pendula, Betula pubescens*) (Gullichsen and Lindeberg 2000). Acidulation is typically done using sulfuric acid. Acid use is 200–300 kg of sulfuric acid per ton of crude tall oil. Sometimes rest acid from chlorine dioxide (ClO_2) plant can be partially used. Part of the acid can be replaced by the use of CO_2. Because CO_2 is weaker acid only about 50% of acid use can be replaced. CO_2 use corresponds to 4–6 kg/ADt.

Due to the environmental footprint associated with the use of fossil fuels, it is of great economic importance to produce fuels from other sources. Tall oil can be converted to a renewable fuel at a low cost and offers competitive advantage against alternative biomaterials, such as vegetable oil (Aro and Fatehi 2017).

4.2 PCC production

In integrated mills, part of the coating materials for paper production can be produced by blowing, e.g., lime kiln flue gas through slurry of calcium hydroxide solution. Produced calcium carbonate is then used to whiten and smoothen the paper surface (Nanri et al. 2008).

Typically, lime kiln flue gasses are bubbled through green liquor. The amount of calcium carbonate produced is typically fixed to correspond the local demand. A possible production level could be 33 kg$CaCO_3$/ADt corresponding to CO_2 use of 20 kg/ADt.

4.3 Lignin separation

Major wood components are cellulose 40–50%, hemicellulose 23–32%, and lignin 15–30%. About half of the original wood, most of the cellulose and some hemicelluloses is converted to kraft pulp and the rest of the organics in wood are led through evaporation plant to energy production in recovery boiler.

The separation of lignin from residual black liquor is an option that is considered by the pulp mills for several reasons. Firstly, the heat transfer capacity of the recovery boiler is often a bottleneck that limits pulp production. Removing part of the lignin from the black liquor decreases the heat load on the recovery boiler and more pulp can be produced. The separated lignin could be sold or used to replace, e.g., fuel oil or natural gas in the lime kilns or be combusted in a power boiler if the energy is required. Secondly, the modern pulp mills have energy surplus and this energy surplus can be exported to other users in the form of biofuel. Thirdly, separated lignin can be used as a raw material in chemicals (Hamaguchi et al. 2013).

Typically, lignin is separated by acidifying part of the black liquor. Sulfuric acid is used for acidification. The use is 50–100 kg per ton of separated lignin. In many commercial processes, part of the acidification is done by CO_2. The CO_2 use is then 150–250 kg per ton of separated lignin. If lignin separation degree is 20% and the wood pulped is pine, then the CO_2 use is about 35 kg/ADt.

4.4 CO_2 utilization processes in the reference mills

Compared with carbon capture potential, the utilization possibilities are currently small. Considering the CO_2 requirement of the above-mentioned utilization processes, required carbon capture rates at the reference mills vary from 0.2 to 21.6% depending on the chosen process/processes and CO_2 source (Table 3). Tall oil production was considered only for Mill A, because in eucalyptus mills tall oil recovery is rarely done due to pulp properties. PCC production was also considered for Mill A due to integrated paper production. Lignin separation rate was chosen at 20% for both mills.

The main process flows of Mills A and B with integrated CCU processes are presented in Figs. 6 and 7. For Mill A, all the three possible options are shown, although implementation of each of them would require generation or purchase of additional electricity. This results from increased electricity consumption due to new processes and decrease in steam generation in the recovery boiler due to lignin extraction. Capture from recovery boiler flue gas was chosen except for PCC production, where lime kiln flue gas is used.

5 Global potential

This study provides an assessment of the global potential of pulp and paper industry to act as site for negative CO_2 emissions. Estimates are given based on recent production data (FAO

Table 3 Required CO_2 capture rates to cover for selected CO_2 utilization processes in reference mills A and B. Capture rates calculated for the flue gasses from the recovery boiler (RB), biomass boiler (BB), and lime kiln (LK)

	CO_2 capture rate		
	RB (%)	BB	LK (%)
Mill A			
Tall oil production	0.2–0.3	0.5–0.8%	1.4–2.1
PCC production	0.9	2.6%	7.1
Lignin separation	1.6	4.5%	12.4
Tall oil+PCC+lignin	2.7	7.9%	21.6
Mill B			
Lignin separation	1.1–1.8	–	7.0–11.7

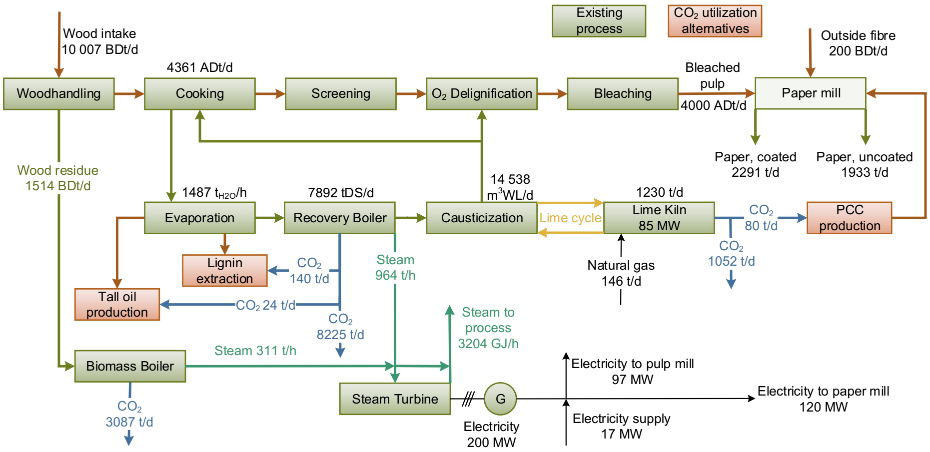

Fig. 6 The main process flows for Mill A when the studied CCU processes are implemented

2017). The development trend of the global chemical wood pulp production from the year 1961 to 2016 shows almost constant growth (Fig. 8).

The estimated CO_2 production of the 15 largest unbleached and bleached sulfate pulp producer countries based on production in the year 2016 is more than 300 megatons (Mt) (Fig. 9). These countries produced 93% of the global sulfate pulp production and therefore, substantial CCU potential can be expected.

The global technical potential to capture CO_2 from kraft pulp mill recovery boilers, lime kilns, and biomass boilers was estimated based on chemical pulp production data from the year 2016 (FAO 2017). The estimates were made for bleached and unbleached sulfate pulp, and were about 100 and 35 $MtCO_2$/a respectively (Table 4). Technical potential to utilize CO_2 in the mill processes using above-mentioned technologies was estimated about 12 and 4 $MtCO_2$/a respectively (Table 4).

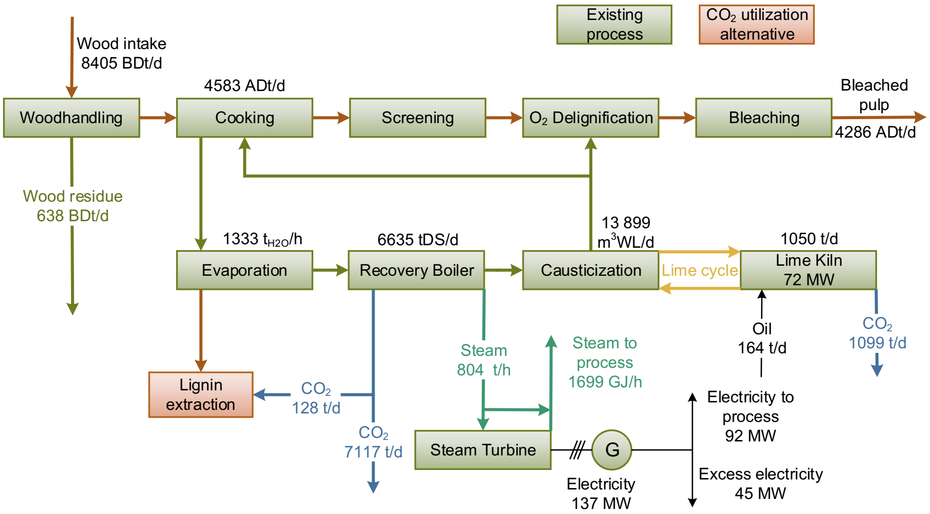

Fig. 7 The main process flows for Mill B when CO_2 from the recovery boiler is utilized for lignin separation

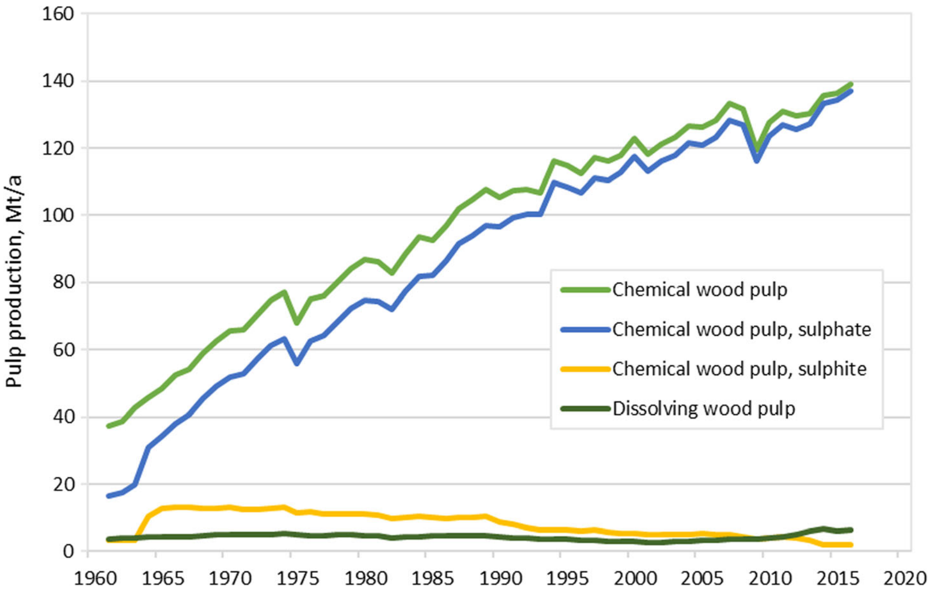

Fig. 8 World wood chemical pulp production, data from FAO 2017

Technical potential to capture CO_2 from pulp mills is substantial. With rather conventional assumptions presented above, total amount of about 135 $MtCO_2$/a could be removed from the atmosphere from existing pulp mills, without additional biomass harvesting at price levels well below 50 €/t,CO_2. Pulp mills alone are not answer to high negative emission targets but they can be one significant component in the palette. With currently available technologies, only a

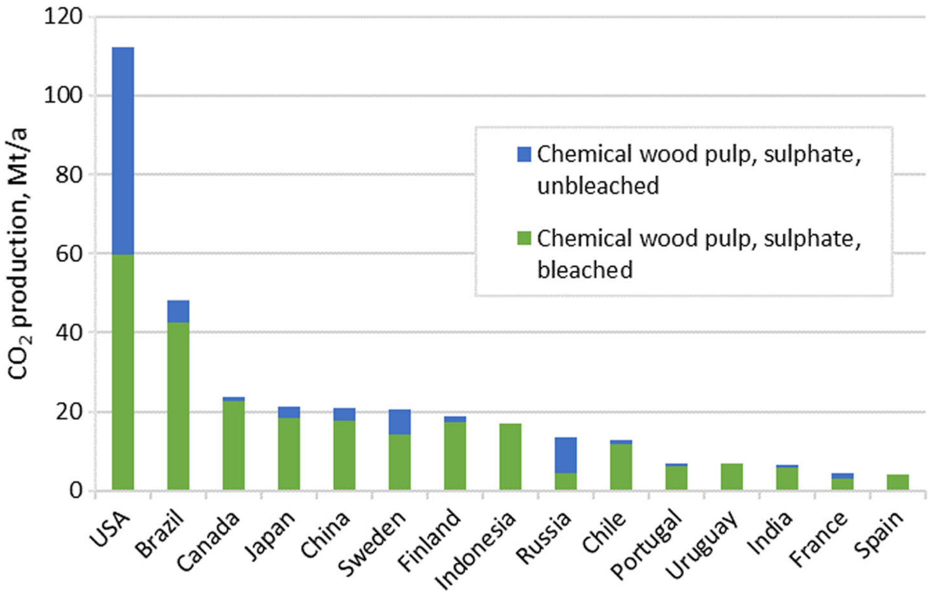

Fig. 9 CO_2 production, including both biogenic and fossil-based CO_2, of the largest sulfate pulp producer countries in the year 2016. Estimation based on pulp production data (FAO 2017)

Table 4 Global technical potential to capture CO_2 from recovery boilers (RB), biomass boilers (BB), and lime kilns (LK) and on-site utilization potential, estimations based on sulfate pulp production data from the year 2016 (FAO 2017)

	CO_2 capture potential			CO_2 utilization potential		
	1000 tCO_2/a			1000 tCO_2/a		
	RB	BB	LK	Tall oil	PCC	Lignin
Bleached sulfate pulp	76,264	14,731	10,297	1102	4409	7149
Unbleached sulfate pulp	26,909	5198	3633	389	1556	2522
	Share of total CO_2 from sulfate pulp production					
Bleached sulfate pulp	21%	4%	3%	0.3%	1.2%	2.0%
Unbleached sulfate pulp	7%	1%	1%	0.1%	0.4%	0.7%

Total capture potential 137 $MtCO_2/a$

small part of produced CO_2 can be utilized on-site. The potential for both capture and utilization can be estimated to increase along with technology development as well as the steady increase of pulp production capacity with new mills. Commercial potential of CO_2 utilization routes was not estimated in this study.

In recent mitigation strategies for climate change, BECCS has been presented as one of the key technologies, as it offers a way to negative CO_2 emissions (Fridahl and Lehtveer 2018; IPCC 2018). The global annual BECCS potential has been estimated at or below 5 gigatons (Gt) CO_2 (de Coninck et al. 2018). Based on the estimation above, capture from chemical pulp industry can cover at least 3% of the global potential. Technology is not yet mature, but it is tested and used in small scale. The deployment of BECCS/CCU in the pulp industry does not affect the wood use of the mills, and therefore has no effect on forest or land use when applied to existing mills. Sociopolitical issues are the primary constraints on the way to BECCS and its large-scale use (Fridahl and Lehtveer 2018).

In addition to the investment and operational costs, the economic feasibility of BECCS/CCU is greatly dependent on the avoided CO_2 costs, primarily taxes and emissions credit collected on fossil-based emissions. It should be noted that as currently, CO_2 in chemicals is counted at production source; therefore, use of biogenic CO_2 replacing fossil CO_2 would give the mill no credits. Therefore, apart from development of carbon utilization technologies, the future of BECCS/CCU depends on political decisions. Incentives for negative emissions would be a probable way to encourage producers to adopt these processes. Utilization of biogenic CO_2 in the processes of an emission producer is a novel concept, and thus unknown as a legislative issue.

6 Conclusions

This study evaluated the possibilities of CO_2 capture and on-site utilization in pulp mills. Bioenergy with carbon capture and storage or utilization has been recognized as one of the key technologies in recent strategies on climate change mitigation. In kraft pulp mills, three main CO_2 sources can be identified as the recovery boiler, the lime kiln, and in most mills, the biomass boiler. Large part of CO_2 formed in the pulping process is biogenic, and the primary source of fossil-based CO_2 is the lime kiln. Therefore, carbon capture offers pulp mills the possibility to act as site for negative CO_2 emissions, if biogenic CO_2 is permanently removed from the atmosphere by utilizing it as raw material for further bioproducts. The technical potential for carbon capture in pulp mills is notable, and it can be estimated to cover 3% of the global capture potential from bioenergy. Considering currently available technologies, the utilization possibilities in pulp mills are minor compared with the capture potential. Therefore, the possibilities for climate change mitigation using carbon capture in the chemical pulp industry center on carbon storage, and utilization possibilities require more research to become a notable option. The cost-effectiveness of BECCS/CCU is primarily dependent on the avoidance of cost of fossil CO_2 emissions. In the future, the feasibility will depend both on technology development on CO_2 utilization possibilities, and on political decision-making regarding emission taxes and possible incentives encouraging CO_2-negative solutions.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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