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Eliminating greenhouse gas (GHG) emissions in pulping: sustainable solutions for lignin extraction

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ABSTRACT

Mitigating greenhouse gas (GHG) emissions is one of the most important challenges in various industries, including the pulp and paper industry. This thesis explores potential pathways for the separation of lignin and the recovery of pulping chemicals such as sodium hydroxide (NaOH), sodium sulfide (Na_2S), and calcium carbonate ($CaCO_3$) without generating GHG emissions. The research includes a comprehensive literature review of existing processes and interviews with experts in the Finnish bioproduct field.

Stora Enso is a partner in the Polestar 0 project, which aims to produce a completely climate-neutral car by 2030. This study focuses on producing lignin-based battery anode material, Lignode, by Stora Enso. Traditional kraft processes used for lignin separation involve combustion-based recovery methods that significantly contribute to carbon dioxide (CO_2) and other GHG emissions. The primary aim of this research is to conduct a comparative analysis of alternative methods to identify the most effective solutions for greenhouse gas-free lignin separation and chemical recovery.

Qualitative methods were employed to analyze various lignin separation and chemical recovery technologies. This process involves examining existing literature, conducting expert interviews, and analyzing case studies. The research identified several potential technologies that could significantly reduce or eliminate GHG emissions from pulp mills.

The study showed that replacing traditional lime kilns with electrical lime kilns could reduce CO_2 emissions, as electrical kilns do not require boilers, which use the combustion of biomasses or fossil fuels to generate heat. Furthermore, the research highlighted the potential of alternative lignin separation processes, such as the organosolv method, which can offer a more sustainable solution compared to the traditional kraft process.

Keywords: greenhouse gas emissions, kraft pulping chemicals, lignin separation, climate neutrality

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1 INTRODUCTION

Mitigating Greenhouse gas (GHG) emissions is one of the most important challenges in the industries. One of the major difficulties facing the pulp and paper industry is the recovery of pulping chemicals in a manner that aligns with emerging sustainable practices. This thesis explores the potential pathways for the separation of biomass in various technologies and evaluates solutions for recovering kraft pulping chemicals specifically sodium hydroxide (NaOH), sodium sulfide (Na_2S), and calcium carbonate ($CaCO_3$) without generating GHG emissions. Traditionally the kraft process most often used for lignin separation involves combustion-based recovery methods that significantly contribute to CO_2 and other GHG emissions. The thesis will include a literature review of potential processes and interviews with experts in the Finnish bioproduct field.

The context for this research is framed by the ambitious goals of the Polestar 0 project, which aims to produce a total climate-neutral car by 2030, necessitating innovations across the supply chain. Stora Enso, one of the key partners in the Polestar 0 project, is providing lignin-based hard carbon to serve as an active anode material in automotive batteries. Generally, graphite is a common raw material for battery anode material and Lignode can be a more sustainable solution for batteries because Lignode is made from trees. The primary aim of this research is to conduct a comparative analysis of alternative methods to identify the most effective solution for achieving totally greenhouse gas-free lignin separation and chemical recovery. This thesis focuses on the production of lignin-based battery anode material Lignode by Stora Enso.

The focus of this thesis is to address and eliminate both biogenic and fossil-based CO_2 emissions. Biogenic CO_2 emissions, which are part of the natural carbon cycle, originate from processes such as decomposition and biomass combustion. These emissions are typically considered carbon-neutral if the biomass is managed sustainably (Cherubini et al. 2011, 413-426). In contrast, fossil-based CO_2 emissions result from the combustion of long-stored fossil fuels, releasing carbon that disrupts the natural carbon balance and contributes significantly to climate change (IPCC 2014). By targeting both types of emissions, this thesis aims to develop comprehensive strategies to eliminate greenhouse gas emissions in pulp mills.

2 GREENHOUSE GAS EMISSIONS

Human activities, particularly greenhouse gas emissions, have caused global warming. From 2011 to 2020 the average global surface temperature was 1.1 °C higher than in the period from 1850 to 1900. Despite the efforts, global greenhouse gas emissions continued to rise from 2010 to 2019 fueled by unsustainable energy usage, land use changes, and varying consumption and production patterns across different regions and social strata. This warming has already influenced extreme weather and climate events worldwide adversely impacting food and water security, human health, economies, and societies (IPCC 2023). Figure 1 illustrates, that greenhouse gas emissions have risen significantly in the past 70 years.

The main greenhouse gases that naturally occur in the atmosphere include water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3). The primary gases in the atmosphere nitrogen and oxygen do not contribute to the greenhouse effect. Greenhouse gases have molecular structures that allow them to absorb thermal radiation at specific wavelengths. Once a greenhouse gas molecule absorbs energy, it can re-emit this energy as radiation. Some of this radiated energy returns to the Earth's surface warming it while the rest escapes into space. (Imasto-opas 2023)

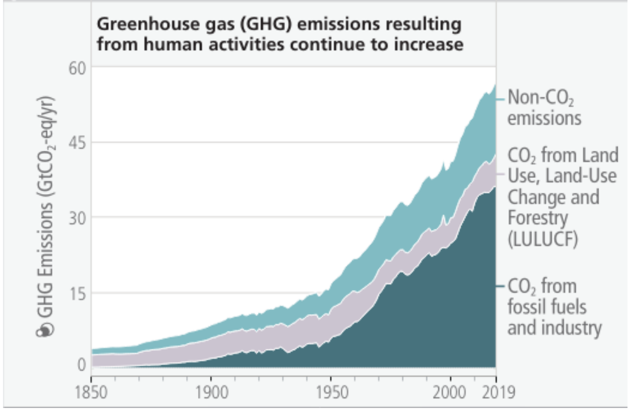

Figure 1. Greenhouse gas (GHG) emissions resulting from human activities (IPCC 2023)

3 GHG PROTOCOL AND CALCULATIONS

Greenhouse gas (GHG) protocol has scope 1, 2, and 3. This thesis focuses on scope 1 emissions. Scope 1 emissions are those that originate from sources that are owned or controlled by the organization (World Resource Institute, n.d.). According to statistics from Stora Enso's Sunila Mill (2022), the greatest emitters of the pulp mill are recovery boiler, bark boiler, and lime kiln. The recovery boiler emits almost 80 % of biogenic CO_2 emissions. This thesis consists of a carbon balance calculation, where the movement of the carbon through the process is calculated using data from Stora Enso's Sunila mill's statistics in 2022. After the carbon balance calculations, the thesis will calculate the impact of different alternative methods for the process.

4 KRAFT PROCESS

The kraft process also known as the sulfate process became the dominant method for producing pulp primarily due to its efficiency in breaking down particularly resilient wood species like resinous pine, which were less amenable to other pulping methods such as the sulfite process. It operates under high alkaline conditions with pH above 12, temperatures ranging 160-180°C, and steam pressure around 800 kPa for periods lasting between half an hour to three hours. Kraft process uses sodium hydroxide and sodium sulfide as cooking chemicals. (Biermann 1996, 86-88.)

4.1 Wood Handling

The transportation of wood is made by truck, train or ship. In this thesis, we can assume that transportation is made with green electric vehicles. A first process in pulp mill is debarking. Debarking in pulp mills involves removing bark from wood to the degree necessary for producing high-quality pulp. The efficiency of this process is often expressed as the "debarking degree," which indicates the presence of bark removed. For instance, in the Nordic countries achieving a 95 % degree means the wood chips contain typically only 0,5 % bark. (Willför 2011, 101-110.)

Some pulping processes, such as those producing softwood sulphite pulp, can tolerate a limited amount of bark, as some bark components can dissolve in the cooking acid. For bleached hardwood sulphate pulps, any residual bark, and its extractives like betulin from birch, can be problematic, necessitating even higher debarking standards. For mechanical pulps like groundwood pulp and thermomechanical pulp (TMP), where the wood is mechanically processed, the bark content should be kept very low (around 0.5% to 1% by weight) since no chemical process is used to remove the bark. (Willför 2011, 101-102.)

Figure 2 shows that the logs are moved through the drum gate to the chipper infeed line after the debarking process. The primary function of this chipper infeed line includes several critical steps to prepare the logs for chipping efficiently and safely. On the chipper infeed, there is the removal of metals, oversized logs, and stones and the washing of the logs. The second purpose of wood handling is chipping. The wood logs must be chipped for better cooking and absorbency of chemicals (KnowPulp, n.d.)

The ship screening system in a pulp mill is tailored based on the quality of incoming wood chips and the specific chip quality demands of the subsequent processing stages. The decision to process oversized and over-thick chips involves balancing the costs of additional equipment, the operational expenses of screening, and the potential loss of material. The quality of chips post-screening is determined by the pulp production process's necessities and the associated screening costs. For continuous and stable production, adequate chip storage is crucial. Most pulp mills utilize open pile storage systems where the chips are kept before being transported for screening and further processing. (KnowPulp, n.d.)

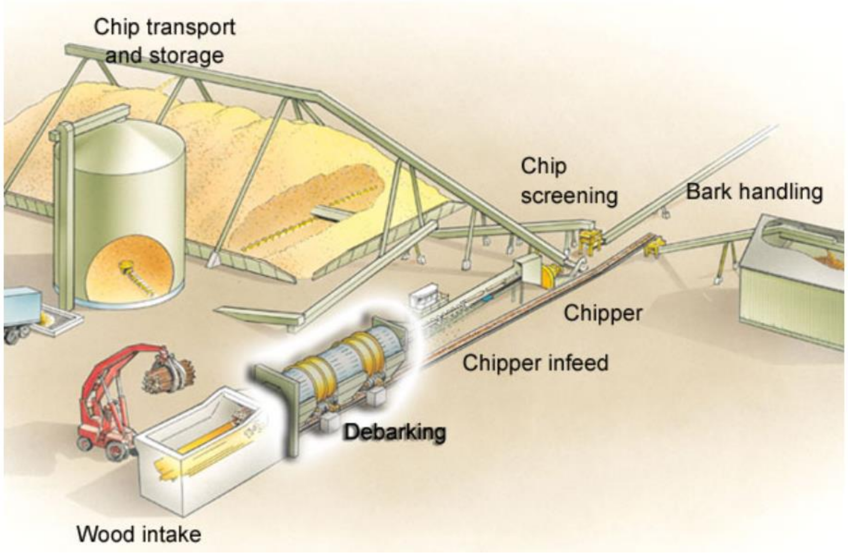

Figure 2. Wood handling (KnowPulp n.d.)

4.2 Cooking

This thesis focuses on only continuous cooking because the Lignode process is linked with continuous cooking. All pulp delignification reactions occur within a single cooking container in the continuous cooking process. Wood chips are introduced at the top of the digester and progressively descend through the digester. During their descent, circulating heated liquor acts upon the chips effectively breaking them down into pulp by the time they arrive at the lower end of the digester. (KnowPulp, n.d.)

Suitable chips from wood handling are directed to the pressurized digester, which first involves steaming to expel as much air as possible enhancing the chemical effectiveness during cooking. The chips are submerged in a mixture known as white liquor a blend of regenerated and spent black liquor, which contains active chemicals primarily composed of hydroxide and sulfide ions. The cooking temperature within the digester is raised to between 150°C and 170°C, either through direct steam or by a steam liquor heat exchanger which helps in recirculating the liquor. This maintains a uniform temperature and chemical concentration throughout the digester facilitating a more homogeneous delignification process. (Willför 2011, 192-197.)

4.3 Chemical Recovery

The kraft chemical recovery process is a crucial technology in the pulp industry focusing on recycling pulping chemicals and converting black liquor into steam and electricity. Despite its benefits, the process faces significant environmental and operational challenges such as controlling air emissions and managing effluent discharge, which are critical to maintaining compliance with environmental regulations and improving the overall ecological footprint of pulp production. (Vakkilainen & Honghi 2016,1-2.)

Sodium hydroxide (NaOH) and sodium sulfide (Na_2S) are the pulping chemicals in the kraft process. The liquor consisting of these pulping chemicals is named white liquor. The yield of the pulp in the pulp mill is about 50 %. The other half is mostly lignin, carbohydrates, and pulping chemicals that are called weak black liquor. The kraft pulping process generates about 10 tons of weak black liquor for every ton of pulp produced. (Vakkilainen & Honghi, 2016, 2-3.)

Chemical recovery has three main purposes. The first purpose is to recover as much as possible pulping chemicals (NaOH and Na_2S). The second purpose is to generate steam and electricity. The third purpose is to minimize the environmental impact of waste materials and implement a circular economy as well as possible. (Vakkilainen & Honghi, 2016, 2-3.)

According to Vakkilainen (2008, 41-42), the kraft recovery process includes several key operations. Black liquor is evaporated to capture more pulping chemicals and raise its dry solids content. As demonstrated in Figure 3, this concentrated black liquor is then burned in a recovery boiler, where it undergoes a chemical transformation to produce sodium sulfide and sodium carbonate. Subsequently, the sodium carbonate is converted into sodium hydroxide through a causticizing process. Finally, lime mud, a byproduct of this process, is regenerated in a lime kiln to complete the cycle.

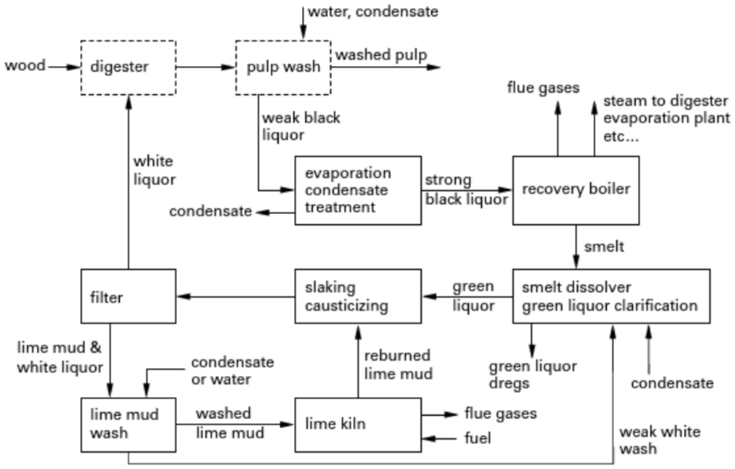

Figure 3.Chemical recovery at the pulp mill (Ek et al. 2009)

4.3.1 Evaporation

According to Parviainen et al. (2008, 38), in the pulp production process at the cooking plant, wood chips are processed into organic materials such as lignin and hemicelluloses, and a small amount of cellulose dissolves into the cooking liquor. This mixture forms what is known as black liquor. The black liquor is rich in chemical energy, which is recovered and utilized as fuel in the recovery boiler. Simultaneously the inorganic materials in the liquor are also recovered and reprocessed at the recausticizing plant making them reusable in the cooking process.

During the washing phase, black liquor is separated from the pulp as a watery solution with a dry solids content ranging from 14 % to 18 %. Due to its high water content this weak black liquor cannot be directly used as fuel. It is sent to an evaporation plant where liquor is concentrated to 70 % to 80 % dry solids. The concentration process is critical as it prepares the black liquor for efficient combustion in the recovery boiler (Parviainen et al. 2008, 38.)

The evaporation plant not only focuses on water removal but also plays a critical role in recovering valuable by-products produced during the cooking process. Key by-products include methanol, turpentine, and soap, which need to be effectively captured and processed. (KnowPulp, n.d.)

As Figure 4 shows, an evaporation unit includes a heat exchanger and a device to separate the vapor from the remaining liquor. The steam generated in one unit is used as heating steam in the second unit and the process repeats through subsequent units. This recycling of condensation energy makes the process efficient. The more units the evaporation plant includes the greater the energy efficiency. A modern evaporation plant consists of six or seven evaporation units. (Ek et al. 2009, 300-302.)

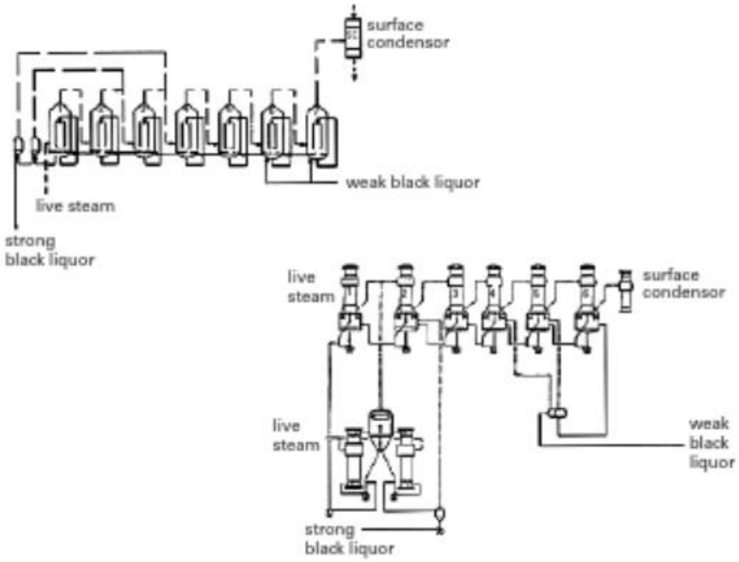

Figure 4. Common evaporation plants. (Ek et al. 2009)

4.3.2 Recovery boiler

Strong black liquor is combusted in the recovery boiler. The main purpose of a recovery boiler is to generate heat, salt smelt, and flue gases. The liberated heat is utilized to produce high-pressure steam. The steam is used to rotate the turbine to generate electricity. The steam from the recovery boiler is also used in different sections of the process. According to Vakkilainen (2005, 1-2) low pressure steam is used for process heating and medium-pressure steam is used in cooking, sootblowing, and evaporation plants.

As illustrated in Figure 5, the recovery boiler consists of a furnace, convection surfaces (superheater, boilers, and economizer), electrostatic precipitation filters, and a mixing tank. In the recovery boiler, concentrated black liquor is introduced into a mixing tank along with fly ash sourced from the electrostatic precipitator and supplementary make-up chemicals as required. The mixture is subsequently preheated and conveyed to the liquor guns. These guns spray the black liquor into fine droplets each a few millimeters in diameter, which are then injected into the recovery boiler's combustion chamber. (Ek et al. 2009, 315-316.)

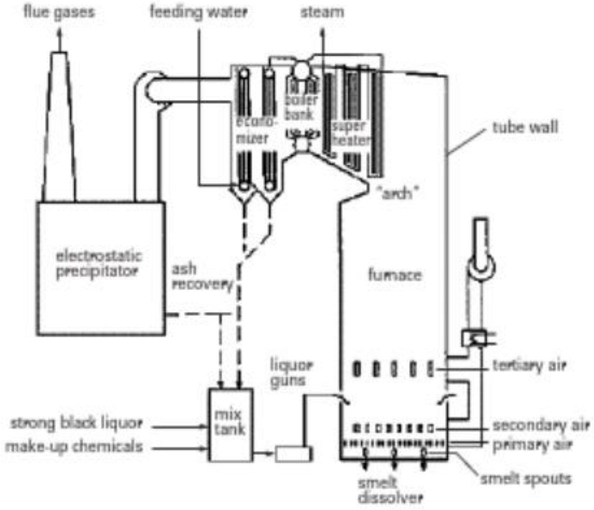

Figure 5. Recovery boiler (Ek et al. 2009)

As these droplets descend within the combustion chamber, they undergo a four-stage sequence of transformations starting with drying and devolatilization during which char is formed. This char may either partially or fully combust depending on the conditions within the furnace. Eventually, the final product on the bottom of the furnace is smelt. (Ek et al. 2009, 316-317.)

The composition of the resulting char primarily includes carbon along with three inorganic salts: Sodium Carbonate, Sodium Sulphate, and Sodium Sulphide. Specifically, the char consists of roughly half of the carbon, and the other half consists of the three mentioned inorganic salts. Carbon has a notable role in the reduction reaction. During the char combustion, sodium sulphate (Na_2SO_4) reacts with carbon to generate sodium sulfide (Na_2S). (Vakkilainen 2008, 101-102.)
The sodium sulfide reacting with oxygen make Sodium Sulphate in reaction 1:

$$Na_2S + 2O_2 \rightarrow Na_2SO_4 \tag{1}$$

The sodium sulphate then reacts with carbon to make sodium sulfide and carbon dioxide in reaction 2:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \tag{2}$$

Sodium sulfate reaction with carbon generates sodium sulfide and carbon monoxide in reaction 3:

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO \tag{3}$$

4.3.3 White Liquor Preparation

White liquor preparation is one of the main processes in chemical recovery. Causticizing is part of the lime circulation and one of the main units to regenerate white liquor. The pulping chemicals are sodium hydroxide and sodium sulfide and the goal is to recover as much as possible of these chemicals. The smelt from the recovery boiler consists of sodium carbonate and sodium sulfide as inorganic products. The main goal of the causticizing part is to form sodium carbonate ($NaCO_3$) to sodium hydroxide (NaOH). As seen in Figure 6, the regeneration of white liquor starts when the smelt from the recovery boiler mixes with weak white liquor to create green liquor. (KnowPulp, n.d.)

Dominant compounds in green liquor are sodium carbonate ($NaCO_3$) and sodium sulfide (Na_2S). Green liquor contains small amounts of other sodium compounds such as sodium chloride (NaCl), sodium sulfate ($NaSO_4$), and sodium hydroxide (NaOH). (KnowPulp, n.d.)

As Arpalahti et al. (2008, 125-126) outlined, the initial step in the white liquor preparation process is the removal of dregs from green liquor, which is achieved using a green liquor filter. This filter separates dregs from the raw green liquor resulting in a cleaner liquor.

The next step involves the slaking of lime. In this reaction, water in green liquor reacts with calcium oxide (CaO) from burnt lime. The product of this reaction is calcium hydroxide ($Ca(OH)_2$). This slaked lime then reacts with sodium carbonate which begins the causticizing reaction in lime milk. The unslaked lime and grits are removed as waste with a classifier screw. (Arpalahti et al. 2008, 126-127.)

Following slaking, the causticizing reaction occurs where causticizers complete the reaction between lime milk and green liquor yielding white liquor and lime mud. (Arpalahti et al. 2008, 126-127.)

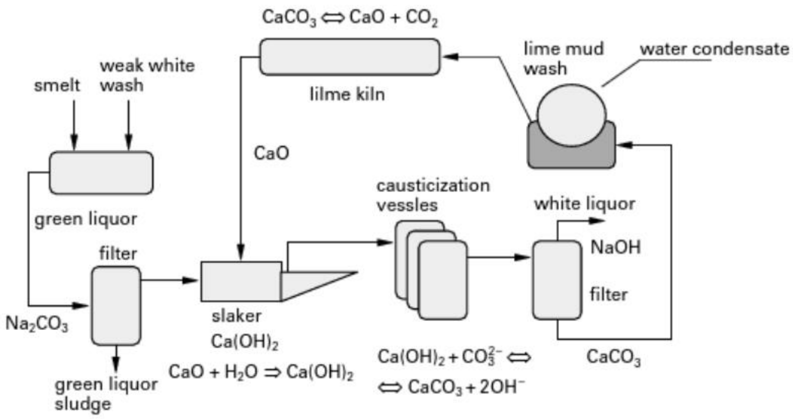

Figure 6. White liquor preparation plant (Ek et al. 2009)

4.3.4 Lime Reburning Process

Lime is needed to convert green liquor to active white liquor for the cooking process. The point of the lime kiln is to convert calcium carbonate ($CaCO_3$) to calcium oxide (CaO), while CO_2 is the by-product of this process. The calcium oxide is also known as burnt lime. The burnt lime from the lime kiln is then used in a slaker to manufacture calcium hydroxide ($Ca(OH)_2$). (KnowPulp, n.d.)

As noted by Ek et al. (2009, 355-356), the first step of lime circulation is the separation of lime mud from white liquor. Normally white liquor and lime mud are separated by filtration in a CD filter. The white liquor is ready for a white liquor storage tank and the lime mud continues to lime circulation. After the separation of white liquor, lime mud is washed trying to capture as much white liquor as possible knowing the lime mud contains a small amount of white liquor. The washed lime mud then is transported to the lime mud reburning system. In the reburning system, the lime mud is dried and heated to above 850 ºC. The calcium carbonate transforms into calcium oxide and carbon dioxide (CO_2) in the following reaction 4:

$$CaCO3 \leftrightarrow CaO + CO2 \qquad (4)$$

5 FUTURE PULP MILL

A future pulp mill will have a much better conversion rate. According to Harlin (2024), an average pulp mill in Finland produces 1,8 times more energy than their own use. That allows for recovery for other products using 56 % of lignin and keeping the mill self-sufficient. If the conversion rate is higher there is no need for big recovery boilers and CO_2 emissions will be lower. When the CO_2 emissions are lower the carbon capture systems will be easier to handle.

Energy and electricity are crucial for pulp mills. Future pulp mills can generate electricity without burning black liquor. Potential ways for electricity generation would be to own solar plants or windmills. That would allow greater use of lignin for products. Lignin greatly impacts reducing the CO_2 emissions of products such as bitum, concrete, and carbon fiber. (Harlin 2024.)

Hydrogen is a potential replacement fuel in the recovery boiler. The use of hydrogen enables more lignin to be extracted before the recovery boiler. That enhances the conversion rate of the mill and lowers the emissions. According to the European Technology and Innovation Platform (n.d.), the heating value of hydrogen is 2 to 4 times more than that of methane, gasoline, and coal. Hydrogen has a massive benefit over other raw materials in combustion because its only by-product is water. If hydrogen can be integrated into the recovery boiler, that would be a great advantage in reducing carbon emissions. An interview with Antti Arasto revealed that VTT has been conducting research in hydrogen recovery boilers and integrating hydrogen into pulp mills.

According to Ramboll (2023), Power to X refers to technologies that convert electricity into carbon-neutral synthetic fuels like hydrogen, synthetic natural gas, or liquid fuels. These fuels can be used in hard-to-decarbonize sectors and stored for later use. The key advantages include replacing fossil fuels, reducing CO_2 emissions, and providing long-term energy storage. As shown in Figure 7, Green hydrogen is central to this transition. For example, aviation is facing strong pressure to reduce emissions. The Finnish Forest Industry has a lot of biobased CO_2 that can be utilized for e-aviation fuels. The e-aviation fuel market is expected to grow and pulp mills can add more value to its products (VTT & Luke 2024).

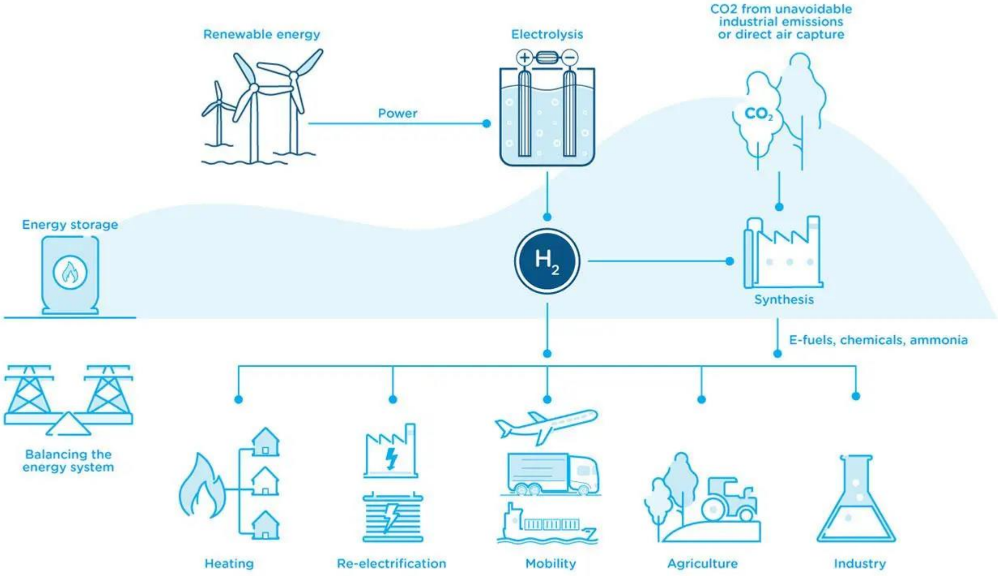

Figure 7. Power to X (Ramboll. 2023)

6 ELECTRIC CHEMICAL RECOVERY

VTT has successfully tested an electric rotary lime kiln. The lime kiln needs about 1000 ºC temperatures to convert calcium carbonate to calcium oxide. (VTT 2022). In conventional lime kilns the energy source is typically fossil fuels or biomass. In VTT’s electric rotary kiln, the heat is created by electricity. According to VTT, the lime kiln is air-tight to capture the carbon from the lime reburning process easily. Some modern pulp mills have gasification processes for wood bark to produce flue gas for lime kilns (KnowPulp, n.d.). After using an electric lime kiln there is no need for a bark-burning plant. This can reduce CO_2 emissions if pulp mills figure out objects of use for that bark.

Renewable power-to-heat technologies convert renewable electricity into heat for buildings and industrial processes using heat pumps or electric boilers. Electric boilers heat water with electricity, which is then circulated for space heating or stored for later use. According to a UPM (2023) article, UPM is investing in electrical boilers in its paper mills. It is said to reduce emissions and fuel costs in time. Electric boilers can be an interesting alternative way to generate heat and steam to process if the electricity to the boiler is made from renewable sources.

7 CARBON CAPTURING SYSTEMS

Carbon capture and storage (CCS) and carbon capture and utilization (CCU) are ways to collect the CO_2 emissions from flue gasses. These two techniques can help companies to create carbon-neutral processes. According to Neste (2021) today CCS technology can prevent almost 40 million tons of CO_2 per year. Both technologies have a capturing system. The CCS process is for storing CO_2 permanently and CCU is for utilizing the captured CO_2.

8 ALTERNATIVE SEPARATION OF LIGNIN

Lignin can be separated via different methods. The most common way is alkaline hydrolysis (kraft process). In 1995 lignin production was 20 million metric tons only from the kraft process and was used mostly for energy (Flores et al. 2015, 127). In recent years, lignin has gained new applications, and it can be used more than just for energy. The environmental impact of pulp mills has put pressure on companies and lignin must be separated in more sustainable ways. In the past, pulp quality and yield were the main parameters, but now the bioproduct mills must produce as many by-products as possible.

Figure 8 shows, that there are a lot of different ways for the isolation of lignin. Normally, lignin is a by-product, but in this work, lignin can be considered as a mainstream and there is no need to think about the quality of pulp. If some lignin separation process is environmentally better than the kraft process and has good lignin yield, it can replace the kraft process.

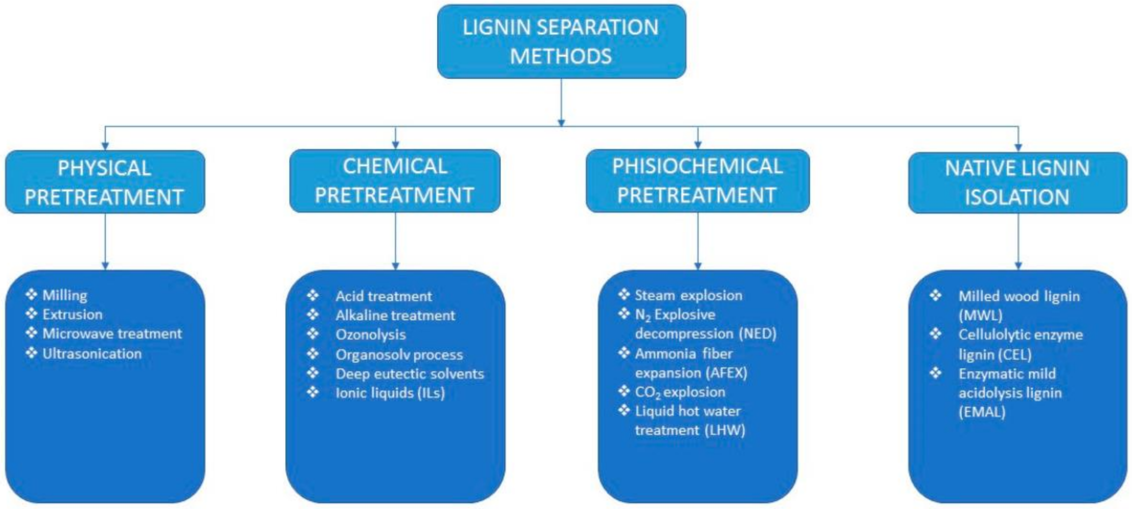

Figure 8. The role of ionic liquids in the lignin separation from lignocellulosic biomass (Hasanov, Raud, M & Kikas, T. 2020)

8.1 Soda pulping

In soda pulping lignin is dissolved from fibers using only NaOH as a pulping chemical. Garcia et al. (2010) had a life cycle assessment (LCA) about non-wood-based pulp production using a soda-anthraquinone (SQ) pulping process. The SQ process uses fewer chemicals than the kraft process. The chemical recovery process can have a better environmental impact when the process is only recovering NaOH. The recovery of only one pulping chemical may be easier to handle.

The delignification efficiency of soda method is less efficient than in kraft process when soda pulping does not have Na_2S. Anthraquinone (AQ) as a catalyst can improve the delignification efficiency. (Ek et al. 2009, 92-93.)

As research by Grace (1987) reported, the soda recovery process involves burning black liquor, which converts sodium compounds into sodium carbonate. This sodium carbonate can then be causticized with lime to produce sodium hydroxide. The recovery process is much like the kraft process but does not involve any sulfides.

8.2 Organosolv

Organosolv is a general name for many fractional treatments where organic solvents are combined with water and a catalyst to separate cellulose, hemicellulose, and lignin. Figure 9 demonstrates an organosolv process. The most common organic solvents are ethanol, acetone, formic acid, and acetic acid. The organosolv process offers flexibility in selecting organic solvents and adjusting reaction conditions such as time, temperature, and the ratio of organic solvents to water. This adaptability makes it suitable for processing various lignocellulosic biomasses including wood, grasses, agricultural residues, and wastepaper. (Tofani et al. 2024.)

A key advantage of the organosolv methodology is its ability to extract and valorize all main components of lignocellulose extractives celluloses, hemicelluloses, and lignin into biomaterials. Notably, it enables the isolation of highly pure lignin. Organosolv allows lignin extraction from various sources including cardboard, wood, grasses, cornstalks, and other agricultural residues. Organosolv fractionations employ solutions of organic acids, alcohols, and ketones. The process can be further optimized by adding organic or inorganic acidic or alkaline catalysts to enhance fractionation yields. (Tofani et al. 2024.)

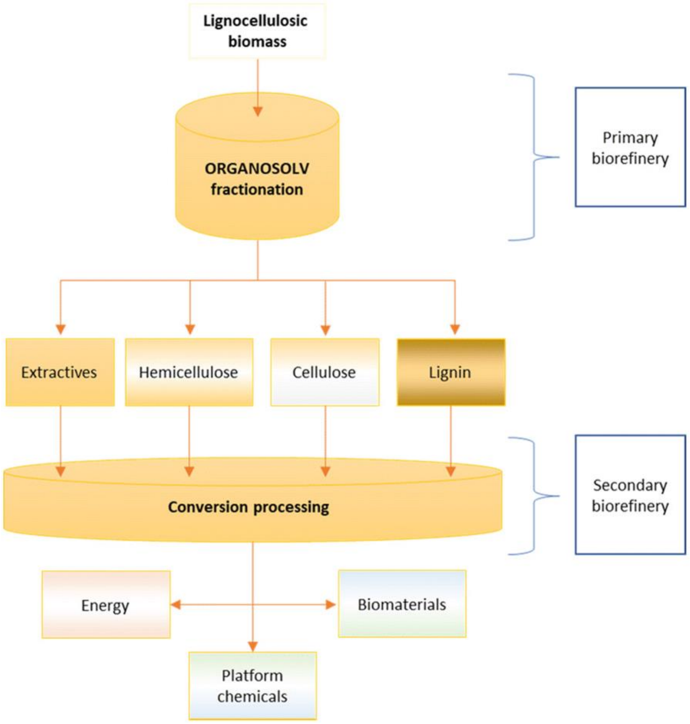

Figure 9. Organosolv process. Royal Society of Chemistry (Tofani et al. 2023)

As stated by Granatier et al. (2023), the lower viscosity of organic solvents allows for more effective lignin removal and reduces its recondensation due to the buffering effect of the acids involved. This results in better bleachability of organosolv pulps compared to kraft pulps. Kleinert's initial success with ethanol-water mixtures led to the development of the Alcell process. (Flores et al. 2015, 123). Table 1 depicts various organic solvents, including acetic acid (Acetocell), formic acid (Formacell), performing acid (MILOX), and methanol (Organocell), which were later proposed, but many did not meet sustainable biorefinery requirements. Recent advancements, such as gamma-valerolactone and systems like SO_2-ethanol-water (SEW) and Clean Fraction (methyl isobutyl ketone-ethanol-water), have renewed interest in pulping. Although no organosolv processes have been commercialized yet, the Bio2X process, based on Chempolis organosolv technology, is currently in the pilot phase.

Lignin type	Solvent
Alcell	EtOH/water
Acetocell	Acetic acid/water
ASAM	Alkaline sulfite/anthraquinone/MeOH
Batelle/Geneva phenol	Phenol/acid/water
Formacell	Acetic acid/formic acid/water
Milox	Formic acid/H_2O_2
Organocell	MeOH/NaOH/anthraquinone

Table 1. Different organosolv processes (Flores et all. 2015)

8.2.1 Alcell

The University of Pennsylvania and General Electric Company discovered a way to treat biomass using organosolv ethanol process in the 1970s. This process got a commercial name known as Alcell (Xie & Gathergood 2012, 242-243). The Alcell process as seen in Figure 11, uses ethanol and water-based solvent. The biomass separation is completed by a 1:1 mixture of water and EtOH at 175-195°C. The produced lignins are sulfur-free and have high purity. Furfural is a by-product of this process (Flores et al. 2015, 134). The recovery of ethanol can be made by distillation or flash evaporation (Xie & Gathergood 2012, 247-249).

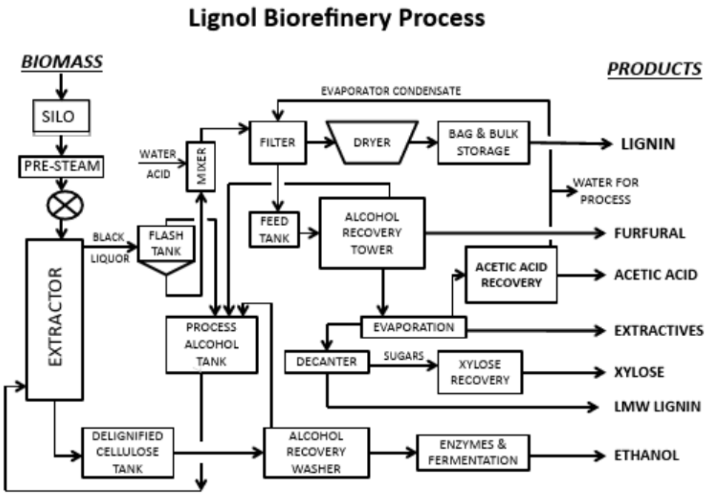

Figure 10. Alcell process (Imhof & van der Waal 2013)

8.2.2 Acetosolv

In the Acetosolv process, lignin is extracted by acetic acid using HCl as the catalyst. The isolation of lignin is made using an acid/water mixture. The recovery of acetic and HCl can be done by evaporation (Flores et al. 2015, 134-135).

As noted by Marks & Viell (2021), the use of acetic-based pretreatment liquids presents an advantage over alcohols due to their great lignin solubility, facilitating pretreatment under mild conditions such as temperatures below 100 degrees and atmospheric pressure. High concentrations of acetic acid are particularly effective in lignin removal, and a catalyst enhances this effect.

8.2.3 Gamma-valerolactone solvent

Gamma-valerolactone (GVL), a biomass-derived solvent, is an organic solvent that separates lignin and hemicelluloses from cellulose. GVL can be used as an intermediate in chemical synthesis, liquid fuel, or food additive. GVL has been recognized as a promising solvent for various applications. The synthesis of GVL does not involve any hazardous halogenated or phosphorus compounds. Recently, GVL has demonstrated significant potential as an environmentally friendly solvent for the fractionation of lignocellulosic biomass. (Yang et al. 2020.)

GVL, known for its use in food and cosmetics, is emerging in biomass fractionation. Initially highlighted for sustainable fuel production, GVL is a lactone with notable properties: non-toxic, low volatility, and high water solubility without forming an azeotrope. With a solid acid catalyst, GVL dissolves cellulose, producing levulinic acid, which can be hydrogenated back into GVL. It remains stable under various conditions, though it can partially hydrolyze into 4-hydroxyvaleric acid. GVL is an effective lignin solvent in pulping. (Granatier et al. 2023.) The GVL process is sulfur-free. It offers high pulp bleachability, enabling completely chlorine-free bleaching (Le 2018).

Figure 12 presents, the recovery of GVL consisting of CO_2 extraction where fresh CO_2 is added to the reactor. Reaction products are extract (GVL with CO_2) and raffinate which includes mostly H_2O and a small amount of GVL and acetic acid. Raffinate continues to flashing and stripping and finally to further handling. The extract continues to extract flashing, where the CO_2 is removed, and the CO_2-free extract proceeds to GVL stripping. The reaction products of GVL stripping are gas tripping and extract. Extract continues to GVL distillation and recovery of GVL is done. The yield of the recovered purified GVL is high. According to studies, GVL recovery rate can be nearly 99 %, if there are more equilibrium stages. (Granatier et al. 2023.)

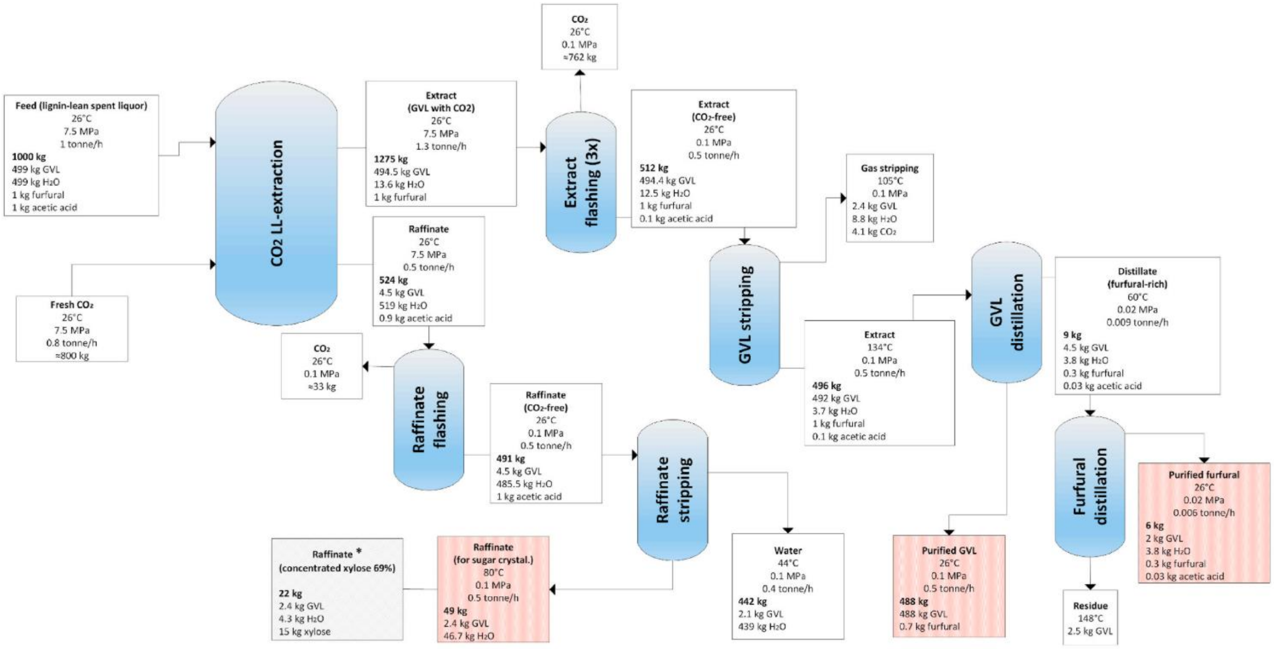

Figure 11. Recovery of GVL. (Granatier et al. 2023)

8.3 Steam Explosion

Steam explosion is one method to separate the wood components. The technology involves treating wood with high-temperature steam 180-230 degrees and pressure 1,38-3,00 MPa for short periods of 1 to 20 minutes, followed by rapid decompression with certain chemicals. This process degrades hemicellulose and partially hydrolyzes lignin, resulting in water-insoluble lignin with low levels of carbohydrates and impurities. (Flores et al. 2015, 125-126.)

Key advantages include minimal chemical use, high yields of hemicelluloses with low degradation by-products, and reduced equipment corrosion due to the mild pH of the reaction. Additionally, the process eliminates the need for acid handling and recycling. Research indicates that steam explosion, particularly with the addition of chemicals like sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4), enhances lignin extraction. (Flores et al. 2015, 125-126.)

Steam explosion is an initial step for enzymatic or acid hydrolysis. Hydrolysis involves breaking down the complex polysaccharides, cellulose, and hemicellulose, into simpler sugar units using enzymes or acids. Hydrolysis is a common process for making bioethanol. (Celignis 2023.)

9 ALTERNATIVE KRAFT RECOVERY SYSTEMS

9.1 Direct Alkali Recovery System

According to Bajpai (2017, 183-185), ferric oxide (Fe_2O_3) has gained interest in pulping industry. The commercially known Direct Alkali Recovery System (DARS) is based on Fe_2O_3. In the DARS process, black liquor is burned with ferric oxide particles in a fluidized bed combustor forming sodium ferrite ($Na_2Fe_2O_4$) through reaction 5:

$$Na_2CO_3 + Fe_2O_3 \rightarrow Na_2Fe_2O_4 + CO_2 \tag{5}$$

The sodium ferrite is then leached with hot water to make sodium hydroxide and regenerate ferric oxide.

9.2 Borate-Based Autocausticizing

Autocausticizing is an advanced method in the chemical recovery phase of pulping facilitating the conversion of sodium carbonate (Na_2CO_3) to sodium hydroxide (NaOH) directly within the recovery boiler system. Sodium borates, due to their amphoteric oxide nature dissolve rapidly in aqueous solutions reducing the system's dead load and enhancing economic viability. The process produces sodium hydroxide and sodium metaborate ($NaBO_2$) reducing the burden on traditional causticizing equipment such as slakers and causticizers (Bajpai 2017).

The sodium metaborate reacting with sodium carbonate generates sodium borate (Na_3BO_3) and CO_2 in the following reaction 6:

$$NaBO_2 + Na_2CO_3 \rightarrow Na_3BO_3 + CO_2 \qquad (6)$$

The natrium borate then reacts with water to generate sodium hydroxide and sodium metaborate in the following reaction 7:

$$Na_3BO_3 + H_2O \rightarrow 2NaOH + NaBO_2 \qquad (7)$$

The implementation of borate autocausticizing in recovery boilers has demonstrated increased efficiency and reduced lime requirements, offering significant cost savings and environmental benefits by lowering greenhouse gas emissions. This method supports Kraft pulp mills in optimizing their chemical recovery processes, aligning with sustainability goals by minimizing reliance on conventional lime-based causticizing and its associated emissions. (Bajpai 2017.) This process is promising and will reduce a lot of emissions. This process still involves a combustion step that generates CO_2.

10 CARBON BALANCE

The practical part of this thesis includes the carbon balance calculations of each process unit. The focus is to calculate a carbon balance in today's pulp mill following calculations of different alternative methods for common kraft process units. The goal is to find solutions towards zero CO_2 emissions.

Carbon balance calculations have been done using data from Stora Enso and literature. The calculations are not exact, but show the guidelines, for how carbon moves in the process. The carbon balance calculates the total carbon balance in debarking, cooking, evaporation, recovery boiler, causticizing, lime kiln, and bark boiler operations. Total carbon represents the entire amount of carbon in the process. Initially, most of the carbon is contained in the wood, but the lime kiln also introduces additional carbon into the system. Figure 13 illustrates the movement of carbon throughout the process. The calculations assume a pulp yield of 47 %, meaning roughly 40 % of carbon is stored in pulp. Additionally, about 4 % is extracted from the process through lignin extraction. The removed bark from debarking is burned in the bark boiler.

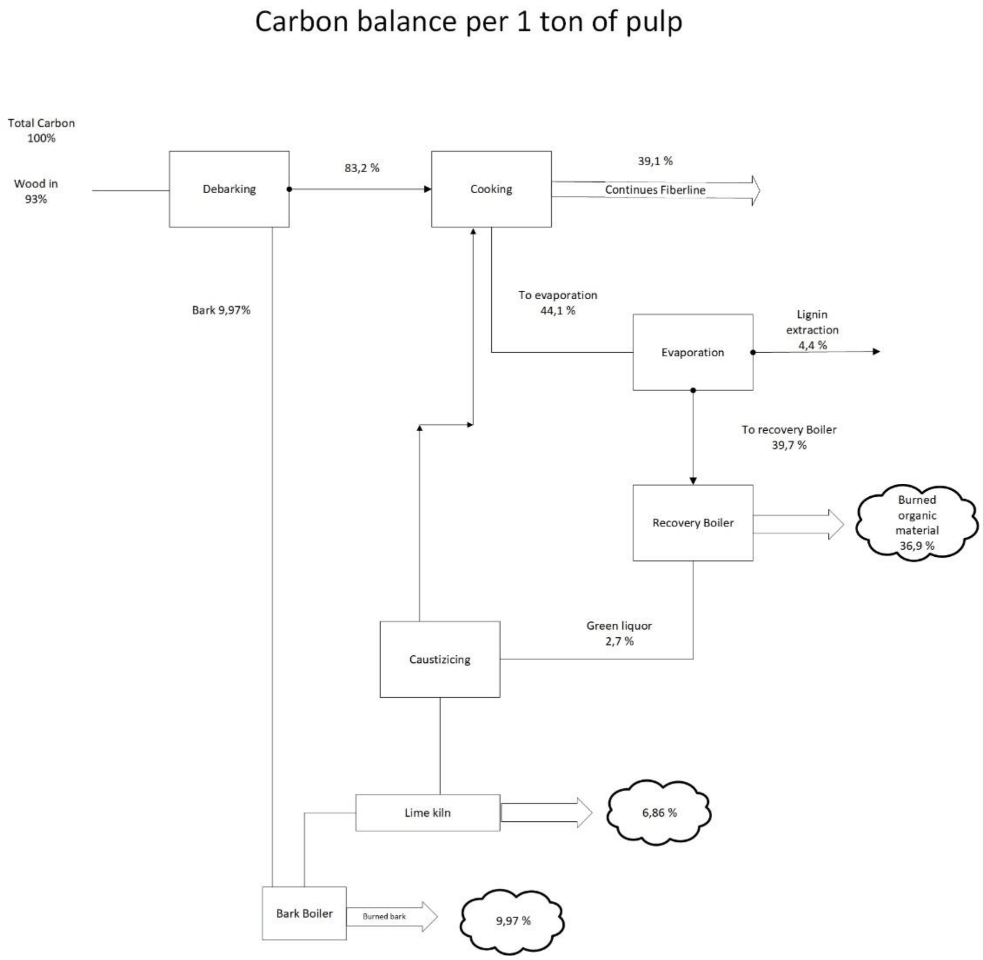

Figure 12. Carbon balance per 1 ton of pulp

Replacing a traditional lime kiln with an electrical one offers a significant advantage in reducing CO_2 emissions. Unlike the conventional method, an electrical lime kiln does not require a fossil-based boiler or bark gasification plant. However, even with electrical lime kilns, pulp mills may still need a bark boiler. The pulp industry must develop markets for bark utilization, otherwise, burning it remains the most viable utilization solution.

In this section, the thesis considers different scenarios for the kraft pulping process to tackle emissions. These scenarios are not precise, but they give thoughts on what can happen. Scenario 1, as illustrated in Figure 14, is the starting point where pulp yield is 47 % and lignin extraction from black liquor is 10 %.

Scenario 1

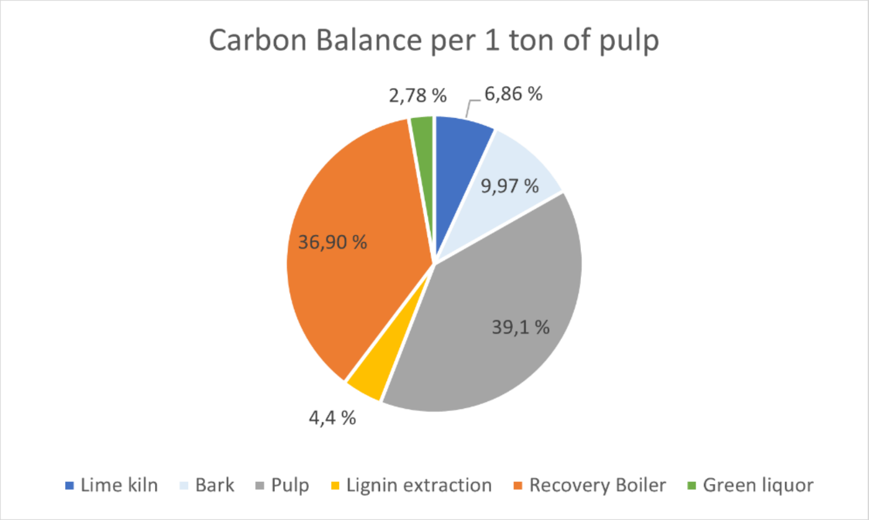

Figure 13. Scenario 1. Pulp yield 47 % and lignin extraction 10 from black liquor 10 %

In scenario 2 pulp yield rises to 55 % and lignin extraction stays the same. When pulp yield is higher the amount of carbon in pulp rises as well. Scenario 2 is seen in Figure 15.

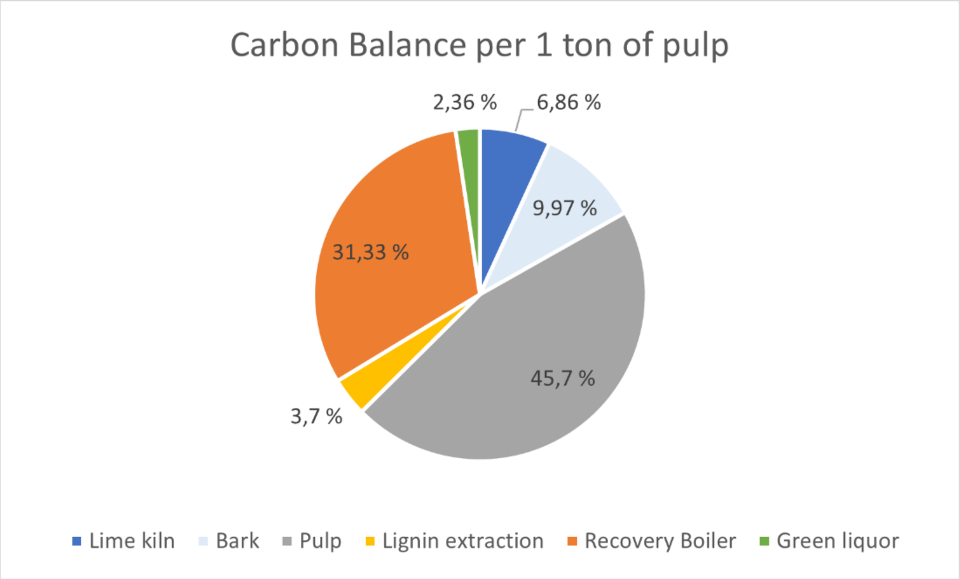

Figure 14. Scenario 2. Pulp yield 55 % and lignin extraction from black liquor 10 %

Figure 16 presents scenario 3. The pulp yield remains 55 % and lignin extraction from black liquor rises to 20 %. This stores even more carbon in products.

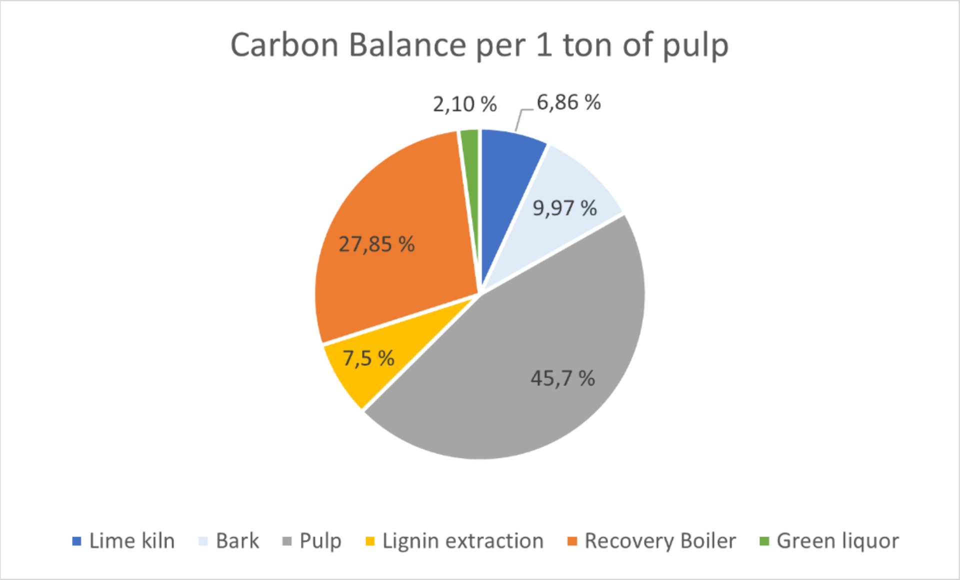

Figure 15. Scenario 3. Pulp yield 55 %, lignin extraction from black liquor 20 %

In scenario 4 a lignin extraction from the process is 30 %, pulp yield stays at 55 %, and the mill uses an electric lime kiln. As seen in Figure 17, about 67 % of total carbon can be stored in the product. The remaining 33 % is burning in some combustion processes such as recovery boiler and lime kiln.

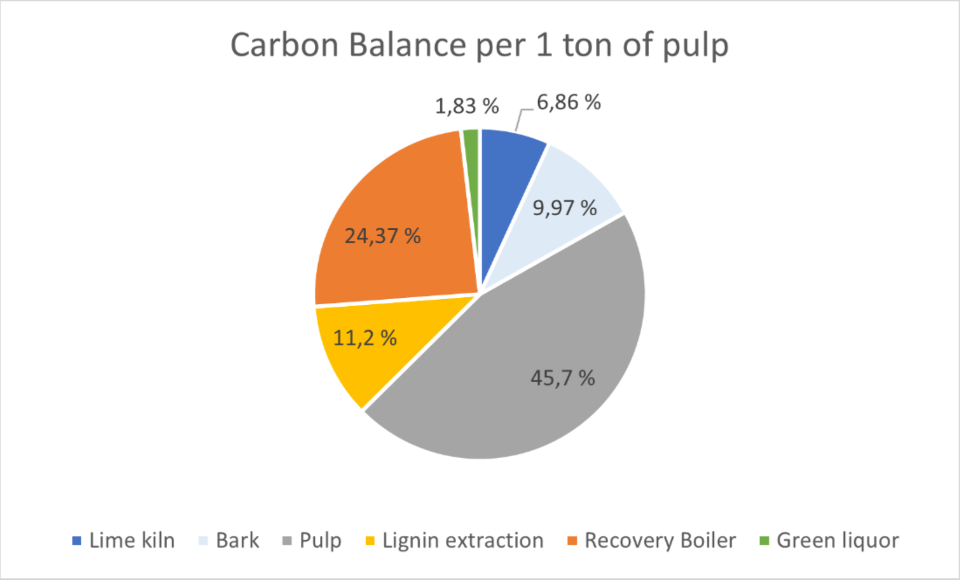

Figure 16. Scenario 4. Pulp yield 55 %, lignin extraction from black liquor 30 %

11 INTERVIEWS

This thesis includes interviews with professionals from various Finnish bioproduct companies such as Valmet, Andritz, Stora Enso, VTT, Afry, and LUT Esa Vakkilainen. The objective was to gather information about current efforts by Finnish forest companies to achieve net zero CO_2 emissions.

The first question was about what their company has done for this and whether they have ready concepts. Companies have similar things going on. The primary focus of the companies was on tackling fossil fuels. There was a general lack of interest in addressing biogenic CO_2. One of the main reasons companies are hesitant to address biogenic CO_2 is the current approach to its carbon accounting. At present, biogenic CO_2 emissions are calculated as having zero impact, which simplifies reporting but does not encourage efforts to reduce these emissions. Another reason is its huge potential for being the raw material for example in e-fuels. VTT together with Stora Enso and other industrial companies has initiated an emissions-free pulping program involving many of the major Finnish forest companies. The program aims to challenge traditional pulping processes trying to get more sustainable pulping.

The next question was about how it is possible to reach total emission-free kraft regeneration and what is the greatest alternative biomass separation processes. Nobody has a clear answer for that, and it is nearly impossible. The most viable current solution appears to be carbon capture.

The next question dealt with an alternative separation of biomass. The question was about the best alternative separation method for biomass. Interviewees don’t have clear answers for that and seems like most of them don’t research these methods. Only VTT has research about alternative separation of biomass (i.e. Emission-free pulping program). The kraft process is dominant in Finland, with only a few alternative biomass separation mills existing in the country. The only known alternative process mentioned is Chempolis, which does have an organosolv facility in Finland. Considering alternative separation of biomass is not necessary because the traditional kraft process is practical for making pulp and currently does not have any competition with alternative biomass treatment processes.

The last question was about what future pulp mills will be like. The interviewees foresee future pulp mills being more sustainable and producing a wider range of products. They expected an increase in the utilization ratio of the mills. Confidence in traditional pulp production remains strong due to the sustained demand for pulp-based products. There is a focus on better utilization of byproducts and creating an ecosystem for biobased products that can compete with fossil-based products.

Finnish forest companies are predominantly focusing on reducing fossil fuel use to achieve net zero CO_2 emissions. There is minimal interest in tackling biogenic CO_2 emissions because it can be a potential raw material for new products such as e-fuels.

Innovations like the Emissions-free pulping program represent significant steps toward a sustainable pulping process. However, achieving total emission-free kraft regeneration remains a challenge, with carbon capture being the most practical solution currently. The future of pulp mills is envisioned to be more sustainable, with an emphasis on increased product diversity and better utilization of byproducts, maintaining confidence in traditional pulp production methods.

12 CONCLUSIONS

The pressing need to mitigate climate change has driven significant advancements in industrial practices aimed at tackling greenhouse gas emissions. The pulp and paper industry, a substantial emitter of GHGs, faces a critical challenge in aligning its chemical recovery processes with emission-free practices. This thesis has investigated potential pathways for the isolation of lignin and recovery of pulping chemicals in various methods such as the kraft, soda, and organosolv processes, without generating GHG emissions.

This study challenges us to think about the process differently. If lignin is the mainstream and carbohydrates are the by-products, is the kraft process still the most dominant process? According to Tofani et al. (2024) organosolv process is an interesting alternative to the kraft process, offering more eco-sustainable solutions for valorization of all the components of biomass. Investigation of Flores et al. (2015) shows that organic solvents can be recovered by distillation which is a great advantage compared to the kraft process in terms of sustainability.

There are several potential ways to reach total greenhouse gas-free pulping processes. According to Simo Mertanen’s Valmet interview, he noted that the simplest route to get CO_2 free process is through carbon capture technology. Valmet has developed technology capable of theoretically capturing 100 % of CO_2 emissions. Additionally, VTT has its own technology for capturing CO_2 and carbon capture (CCS) and utilization (CCU). However, CCS and CCU have their own challenges. When captured carbon is used as an e-fuel, it still emits CO_2. VTT is also conducting promising research on electric lime kilns and electrical chemical recovery. These methods offer a big advantage compared to normal chemical recovery because (e.g.) lime kilns energy is made by natural gas or gasified bark from a pulp mill's own use (Stora Enso 2022).

Alternative separation of lignin shows promising methods for literature. Different organosolv processes such as Alcell are potential ways for reaching (GHG) free processes because the process does not have any combustion steps. The Alcell process uses ethanol as a solvent and the recovery of ethanol is way easier than (e.g.) sodium hydroxide and sodium sulfide. The main challenge with alternative lignin separation methods is that they are not yet commercially available and have not been scaled to meet the requirements of large industries.

The Kraft process presents significant challenges in achieving a completely greenhouse gas-free operation. While there are some methods to reduce emissions, no existing Kraft processes are entirely CO_2-free. According to Esa Vakkilainen's LUT interview, no processes in this field have a 100 % utilization rate, meaning there is always waste that needs to be disposed of. The question arises: what can we do with this waste if we cannot burn it?

Alternative recovery systems such as direct alkali causticizing and borate-based autocaustizicing offer different approaches to recovering pulping chemicals. Autocausticizing, for example, simplifies chemical recovery by eliminating the need for slakers and caustizers, with sodium borates reacting with H_2O to produce NaOH. However, both DARS and autocausticizing do not give the results the thesis needs, because they still emit CO_2.
Electrification of chemical recovery will give an advantage to reach CO_2-free chemical recovery. Electric lime kilns and boilers can eliminate the use of combustion-based energy methods. However, recovery of pulping chemicals needs high temperatures, and burning biomass is known good for that purpose. Equipment suppliers Valmet and Andritz share similar visions for achieving CO_2-free chemical recovery. Currently, carbon capture remains the most feasible alternative. Additionally, the Kraft pulping process can be modified to improve a much better pulp yield, thereby storing more carbon in products. Furthermore, increasing lignin extraction from black liquor reduces the amount of carbon that needs to be burned in the recovery boiler.

Green hydrogen gives high hopes for the reduction of CO_2 emissions. As noted by the European Technology and Innovation Platform (n.d.), The heating value of hydrogen can be multiple compared to fuels. The primary advantage of green hydrogen is that when it is burned, it generates only water as a by-product. If lignin is removed from the process, the pulp mill still needs the energy. Green hydrogen can be one solution if it can be integrated into a recovery boiler.

The Finnish Forest Industries face a crucial decision regarding their direction. If they aim for complete greenhouse gas-free processes, they must abandon Power-to-X concepts. This is because producing e-fuels necessitates generating CO_2. Consequently, the industry’s future path remains uncertain. Most interviews and literature suggest that continuing to generate CO_2 and utilizing it efficiently may be the best approach. In this thesis the aim was to find total CO_2-free processes. The forest sector must calculate and determine the most profitable methods to achieve its goals.

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LIST OF FIGURES AND TABLES

Appendix 1

List of interview questions

1. What has your company done for this topic? Do you have any ready concepts?
2. What is your company’s view on how to reach emissions-free pulping?
3. How to reach greenhouse gas-free kraft regeneration?
4. What is the greatest alternative biomass separation or extraction process?
5. What will the pulp mill of the future be like?