CHALMERS
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Lignin Extraction from Black Liquor in a Softwood Pulping Plant

A Process Simulation and Evaluation of how much Lignin can be Extracted and its Impacts on the Plant

Master's thesis in Innovative and Sustainable Chemical Engineering

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CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

The industrial sector of pulp and paper production is one of the world's largest industries and is thus very energy demanding as well as a contributor to the rising environmental concerns. To meet the needs of the future, more raw materials need to substitute today's huge dependence on fossil fuels. The pulp and paper mills of today need to consider converting towards biorefineries, and thus lignin is an interesting by-product to be part of the solution. Lignin as a valuable product have start to pop up more and more during the last decade, however in a rather low production scale where approximately 25% of black liquor is extracted for lignin production. This master thesis is evaluating the possibilities of extracting more black liquor for the lignin recovery plant to produce more lignin, up to 50%. Also, consequences that the chemical recovery cycle and thus the plant may have will also be investigated. For this purpose, a model over a lignin recovery plant in the software Matlab Simulink have been used and further developed. Also, multiple analyses were conducted with the updated version of the model, supported by literature findings from deep literature studies. The results show that it would be possible to produce approximately 140 000 ton lignin per year when 50% of black liquor outtake is considered. However, whether it would be possible to run the plant in the same pace as today cannot be surely concluded from this study. This model still has uncertainties that needs to be further studied to fit reality better and to be able to be more certain about the impacts on the plant. An implementation of a lignin recovery plant will however decrease the useful electricity production. When approximately 50% of lignin was recovered in the model, the plant could not run by the energy produced only from the recovery boiler anymore and will thus need extra energy from example a biomass boiler. As more lignin is produced, the ratio of sodium (Na) and sulphur (S) will be disturbed. To keep the ratio constant, an implementation of an internal production of sulfuric acid can be a good solution. The economic feasibility of a lignin recovery plant is highly dependent on the lignin market. More economical studies are needed to be able to conclude the profitability of a lignin recovery plant in a near future. However, after this study, it can be concluded that there is a future for lignin production, but more research and effort is still needed to be more accurate about the outcome, both economically and the effects on the plant.

Keywords: Lignin, Kraft pulping process, Black liquor, Lignin precipitation, Na/S balance, Matlab Simulink

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Wilma Nilsson, Gothenburg, May 2023

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1

Introduction

This master's thesis will investigate the possibilities to recover lignin from a pulping plant in a larger extent than what is done today in commercial scale. This is done in collaboration with IVL Svenska Miljöinstitutet in Gothenburg, Sweden. This chapter will introduce the background of the thesis, the aim together with clarifications, the scope, and a short description of the structure of the report.

1.1 Background

The industry of pulp and paper is one of the largest industries in the world and contributed with about 192 million tons of pulp for paper production in 2021 [8]. Most of the pulp is produced in the United States, Brazil, and China. However, Sweden and Finland are contributing with a 5^{th} and 6^{th} place of the countries that are producing most pulp in the world, making Scandinavia very important when speaking of pulp production. The total energy demand in the pulp and paper sector were measured to 8.595 EJ in 2021 [9], and is predicted to grow with a yearly rate of 1.6% until 2030 [10]. In Europe, the pulp and paper industry is the fourth most energy intensive industry sector [11]. At the same time, the primary resources needed to produce energy are starting to become scarce. This concern is one of the major driving forces to research more renewable energy sources such as lignin being one of the possibilities, and thus the potential of further development of existing mills to become biorefineries of the future [10].

The remarkable growth in energy demand as well as a wide range of negative environmental effects have been witnessed during the last century. This is only some of the responses due to the fact that the world has entered the anthropogenic era where activities of humans are heavily affecting the Earth in a negative manner. The population in the world is growing and living standards are increasing, as well as the world's economy. At the same time, the raw materials that are utilized for these purposes are starting to become scarce which creates uncertainties for the future. If the extraction and utilization of primary resources continue in the same pace as today, many of the fossil resources will only last during the next century which will affect the next generations [10].

More renewable raw materials are needed on the market to minimize the hazardous greenhouse gases such as CO_2, being the largest villian. By 2050, the pulp and

paper industry in Europe expects a reduction in emissions of greenhouse gases by 62% compared to the levels of 2015 [11]. Therefore, it is important for a sustainable future to start developing new types of raw materials coming from suitable residuals and by-products. By utilizing secondary resources, less primary production of raw materials would be needed, which could pro-long the availability of those. Lignin is one possibility of a secondary resource of raw material that have the potential to substitute a wide range of different materials and fuels for various applications without having any negative environmental effects. Also, lignin does not contribute to the competition of resources for food. Lignin as an end product has good potential for the future, since lignin has very similar building blocks in its chemistry as petroleum-based materials. Therefore, lignin is a very interesting renewable raw material for replacement of fossil-based materials. However, lignin has more possibilities of application, such as thermoplastics, chemicals, resins, surface active agents, concrete additives, only mentioning some of the possibilities [12].

This master thesis work is done together with the research- and consultant based company IVL Svenska Miljöinstitutet in Gothenburg. One of their many divisions are right now looking deeply into the possibilities of making already existing pulp mills more sustainable and environmentally friendly. In other words, one of their objectives are to investigate if a completely CO_2 neutral pulp mill for the future is possible and what the consequences on the production would be. Thus, new process steps are investigated as well as the ability to make residuals from the core process into valuable products. Capturing of emitted CO_2 to the atmosphere is an interesting topic on their agenda as well. Also, the expectation is to make lignin a valuable product for the future, with a larger sales price compared with today's status, since it is not very valuable today due to the limited market in large scale [13].

1.2 Aim

The aim of this master thesis is to evaluate a pulping process with an integrated lignin recovery plant, with the goal of extracting more lignin than what is done today in commercial scale. This evaluation will be done with a literature study together with a process simulation in Matlab Simulink. The expectation is to extract 50% of the lignin that ends up in the black liquor in the pulping plant. However, by extracting a larger amount of lignin from the process will have effects on other important processing parameters and sections along the core process path. The purpose is to understand whether this amount of lignin extraction would be possible to achieve in reality or not, by studying the full picture of the plant.

Some of the questions that are aimed for to answer during this master thesis work are:

- Is it possible to run a pulping plant in the same order as an ordinary plant, if lignin is extracted by 50%?
- How will the recovery boiler be affected, and how much steam/electricity pro-

duction is lost?

- Is it economically feasible to have a lignin recovery plant, considering the self-sustainability of the plant?
- To what extent will the sodium (Na)/sulfur (S) balance in the plant be affected if lignin is extracted?

1.3 Scope

This master thesis has a time limitation of approximately 20 weeks, which will affect the extent of the work. Due to the limited amount of time, the main focus will be on the LignoBoost concept, and no other lignin extraction method will be further modelled. The model that will be used and further developed in this investigation is an already existing model in Matlab Simulink from an ongoing collaboration between IVL and a Swedish pulp mill. Thus, no other modelling software will be investigated. Also, no real-life experiments will be performed in the scope of this master thesis. The results, discussion, and the final conclusions will be fully based on the outcome of the Simulink model together with literature findings.

1.4 Report structure

This report begins with a brief introduction to the project, with a short background of why this project were conducted together with the aim as well as a short scope. The second chapter will describe the theory behind the topic. This chapter cover both knowledge about lignin, the pulp and paper industry as well as the extraction of lignin by different methods, but primarily regarding the LignoBoost concept. In chapter three, the method that have been used will be briefly explained with both further explanations of the model in Simulink as well as the general course of action of the project. In the fourth chapter, both the results and the discussion will be presented. Here, several figures and tables will be visualized, explained, and discussed before concluding the project with some final conclusions in the fifth chapter. Finally, a short conclusion of potential future work on this topic will be summarized.

2

Theory

In this chapter, some basic knowledge to give a deeper understanding to the topics that this thesis will cover is going to be introduced. First, the biorefinery concept is being discussed briefly, followed by a section of wood as biomass together with a deeper insight of the complex macromolecule called lignin. Also, the pulp and paper industry in general, as well as the kraft pulping process will be explained more in depth. A short description of the history and theory of lignin recovery will be presented. How lignin is extracted, its filterability, and finally the Na/S balance in the pulp mill will also be explained.

2.1 The biorefinery concept

A biorefinery can be compared with a conventional petroleum refinery, producing fuels, power, and chemicals by different integrated conversion processes [14]. The difference is that a biorefinery has its focus around biomass as the raw material, instead of crude oil. Depending on the pathway of the biorefinery, value-adding products like electricity, chemicals, biofuels, and other materials can be produced alongside to the conventional pulp and paper line. Only a yield of about 50% is going from wood to pulp in a traditional kraft method, thus the other 50% are available to produce all those things just mentioned [12]. So, instead of focusing on one main product, the goal with a biorefinery is to produce several main products and additional valuable by-products. Another goal is to replace fossil fuels with biomass for further production, and thus implement a great promise for reduced environmental impacts and for industries to become more environmentally friendly [4]. This makes the biorefinery concept very important, since the demand for energy and raw material is increasing, and at the same time, sources for energy and raw material starts to become more and more scarce, as mentioned in the introduction. The pulp and paper industry are promising to become the biorefineries of the future [4], due to the fact that they already use biomass as raw material, and the infrastructure already exist. However, to adapt and transform todays existing mills into biorefineries are going to be a trade-off to decide what will be the core business and most profitable in long terms. The advantage is thus that the pulp line as it is today can be kept in operation through the transition period, assuming that no changes that affects today's core business is done in a drastic manner [15]. Up until today, the pulping process type called acid sulphite have reached the furthest on

the path of transforming into a biorefinery concept, although this type of chemical pulping method is heavily undominating compared by the dominating type called kraft pulping, which produces approximately 95% of the pulp on the market [4], and is thus the type of process that will be further investigated in this project.

2.2 Wood as biomass

The raw material that is utilized in a pulp and paper mill is wood. Wood is one of the most abundant natural organic materials in the world. It consists mainly of three components; carbon, oxygen, and hydrogen, see Table 2.1. These are the components building up the polymers in the wood structure such as cellulose, hemicellulose, and lignin. Wood also contains about 1-5% extractives, such as terpenes and fatty acids among others [7].

Table 2.1: Elementary composition of wood [7].

Name	Element	Content [%]
Carbon	C	49
Oxygen	O_2	44
Hydrogen	H_2	6
Nitrogen	N_2	<1
Inorganic elements	Na,K,Ca,Mg,Si	«1

Depending on what type of wood the tree is built up of, it contains different amount of the main components cellulose, hemicellulose, and lignin, see Table 2.2. Softwood (mainly fir and pine) and hardwood (mainly birch and eucalyptus) are the two main categories of trees. These two have different characteristics, which will give different end products in a pulp and paper process. In this study, the softwood type will be of main interest since the pulp mill used for the study is producing pulp mostly from softwood.

Table 2.2: Chemical composition in different wood types [1].

Wood type	Cellulose [%]	Hemicellulose [%]	Lignin [%]
Softwood	40-45	25-30	25-30
Hardwood	40-45	30-35	20-25

2.2.1 Lignin

Lignin is a biopolymer that is found in all vascular plants. However, only lignin in wood materials will be further introduced here. Since wood is a very common material and lignin is a rather large part of wood, lignin becomes one of the most abundant biopolymers that exist [15]. The two different types of wood - softwood and hardwood - consist of different fractions of lignin as mentioned above. Softwood contains slightly more lignin compared to hardwood, 25-30% and 20-25% respectively, as shown in Table 2.2.

There are several biological functions of lignin. First, lignin gives stiffness to the cell walls in a tree. It is a fixating polymer that makes the fibers stiff and rigid in wood which makes it possible to serve as mechanical support to build up both the stem and the branches. Secondly, lignin glues together different cell types in the woody tissue, and it occurs together with hemicellulose, see Figure 2.1, where both glucomannan and xylan are two of the most commonly existing types of hemicellulose.

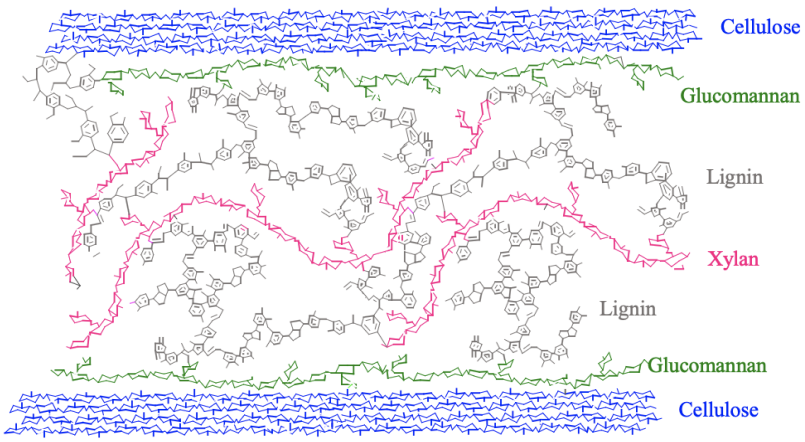

Figure 2.1: Distribution of cellulose, hemicellulose, and lignin on a molecular level [1].

Thirdly, lignin makes the cell wall hydrophobic. This makes up for efficient transport of water and nutrition's in trees. Lastly, lignin serves as protection against microbial degradation of wood [1]. Thus, lignin is a very important component of trees. However, at the same time lignin makes the process of extracting cellulose for the pulp and paper process complex and several thermochemical treatments are needed. Lignin is a very complex amorphous polymer, with a mix of aromatic and aliphatic moieties. The monomers, or namely monolignols, that are building up the lignin 3D structure are of three different types; sinapyl alcohol, p-coumaryl alcohol, and coniferyl alcohol, see Figure 2.2.

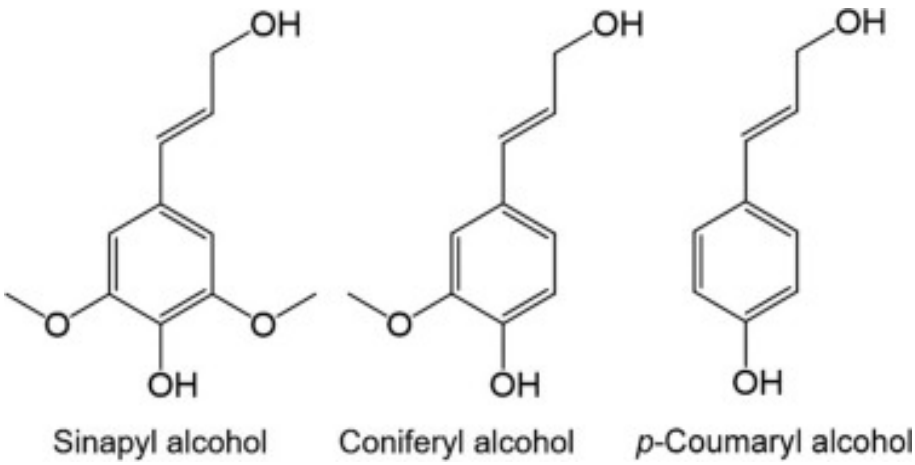

Figure 2.2: Three different types of lignin monolignols [2].

These monolignols are different propylphenol derivatives, and they have different number of methoxy groups attached to the aromatic ring. The monolignols and the functional groups of lignin are connected to each other with either carbon-carbon (C-C) bonds or ether (C-O-C) bonds in a random order resulting in a 3D structured macromolecule, see Figure 2.3. The most frequent bond in lignin is an ether bond called β-O-4 and this bond appear with a frequency of 35-60% in softwood [1]. Since this is the most abundant bond, it is also the most important bond to break in the digestion process, in order to access the coveted cellulose. Lignin and large parts of hemicelluloses together with some extractives end up in a by-product from the cooking process called black liquor. The lignin in the black liquor is called kraft lignin when speaking of the kraft pulping process and will be further discussed.

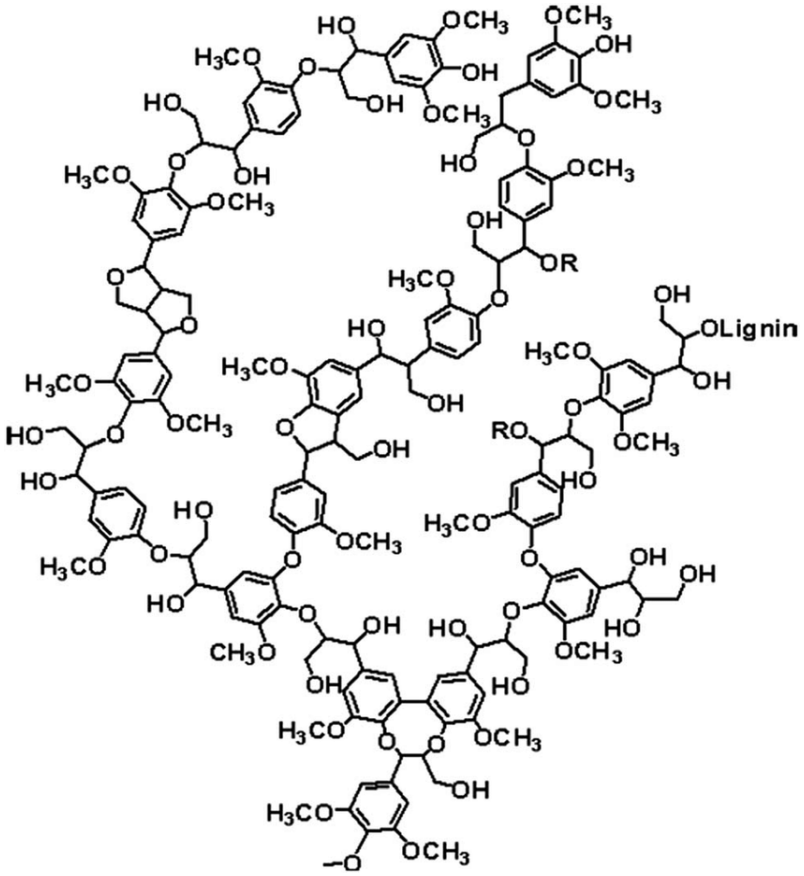

Figure 2.3: Chemical structure of an example of how the macromolecule lignin can look like [3].

2.3 The pulp and paper industry

Pulp and paper can be produced at the same site, or separately. To produce pulp and paper at an integrated pulp and paper mill would be the most advantageous and efficient option. This is because the wet pulp must be dried before it can be transported to a paper mill, since wet pulp is too heavy and expensive to transport. So, the wet pulp must be dried which demands large amounts of heat. However, if

the paper is produced at the same site, the drying process could possibly benefit from excess heat from the process which would decrease the demand of external utility [16].

There are two main processes to produce pulp, either by mechanical or chemical separation [4]. To mechanically release the cellulosic fibers from the wood, a pre-treatment by using steam, heat, or a weak chemical solution is often used prior to the mechanical equipment, which can be for example grinding the wood chips. The most dominating method instead, the chemical method, mainly relies on chemicals and heat to dissolve and soften the lignin from the chipped wood. Different types of chemical pulping that exist are kraft pulping (alkaline sulphate pulping), acid sulphite, or semichemical pulping [16]. Kraft pulping is the predominant type of chemical pulping methods and is the type of method that the pulping mill in question uses and will thus be of main focus in this project. In Figure 2.4, an overview of a conventional pulp mill is depicted, starting at the wood handling of trees, all the way to the final pulp often being shipped with boats in the right-hand side in the figure. To the left, the recovery cycle is visually explained with all its steps. Each step of the process will be briefly described in the sections below, with the perspective of a kraft pulping process stand-alone pulp mill.

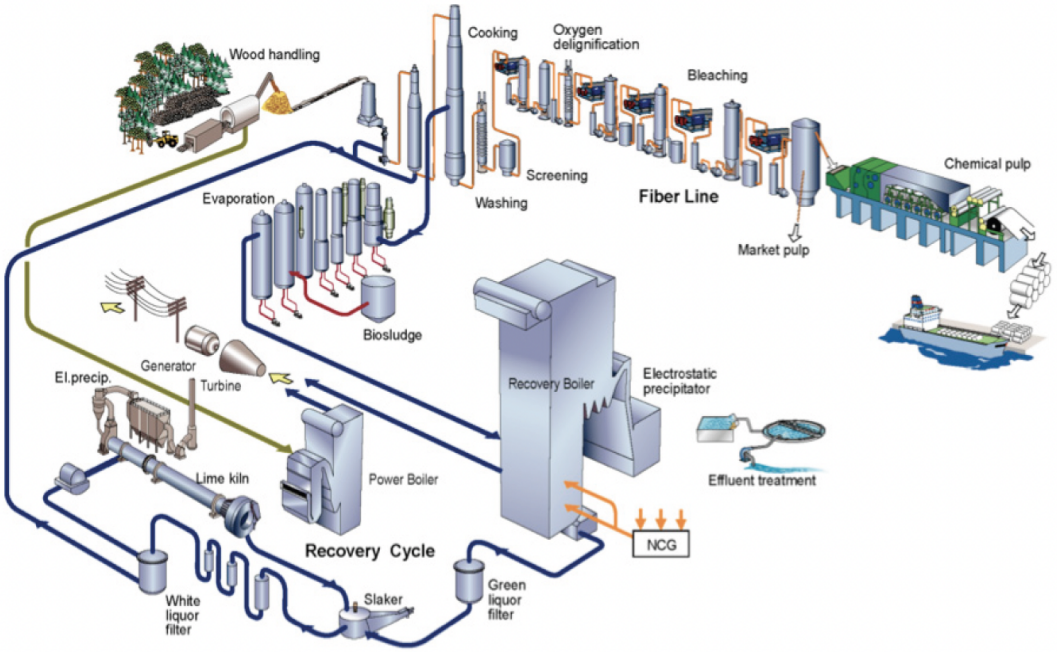

Figure 2.4: Overview of each step of a conventional pulp mill [4].

2.3.1 The kraft pulping process

The kraft pulping process consists of mainly four parts; handling of raw material, chemical delignification of wood chips together with chemical and energy recovery cycles, bleaching of the pulp, and a final system to handle wastewater [17]. The

kraft process uses chemicals such as sodium hydroxide (NaOH) and sodium sulphide (Na_2S) solved in water. These are the active components in the liquor that is used in the kraft pulping process during the cooking step, called white liquor [6].

After pre-treatments like logging and debarking of wood at the wood yard, the wood is chipped and sieved so that the chip size is homogeneous, for providing uniform treatment of the wood chips. They are pre-treated with steam, to get rid of air and extractives. A following impregnation step where white liquor is sprayed into the digester with wood chips is carried out before more white liquor is added, to make the wood chips delignified. In the white liquor that is added, NaOH and Na_2S are dissolved into active components in the form of hydroxide ions (OH^-) and hydrogen sulphide ions (HS^-). During the delignification, the cleavage of the abundant bond β-O-4 in lignin, and many other types of reactions, appear to dissolve lignin from the cellulose. The fiber and liquor mixture of cellulosic pulp proceeds for further treatment of several bleaching and drying steps, before it becomes the final pulp that is being shipped away to become saleable paper products. The solution of fragmented lignin, hemicelluloses, and spent white liquor becomes black liquor and is the first step in the chemical recovery cycle that can be seen in Figure 2.5. This part of the process is to recover and recycle cooking chemicals and to utilize the organic parts in the black liquor to produce useful energy [6]. This will be described more in depth in the following sections.

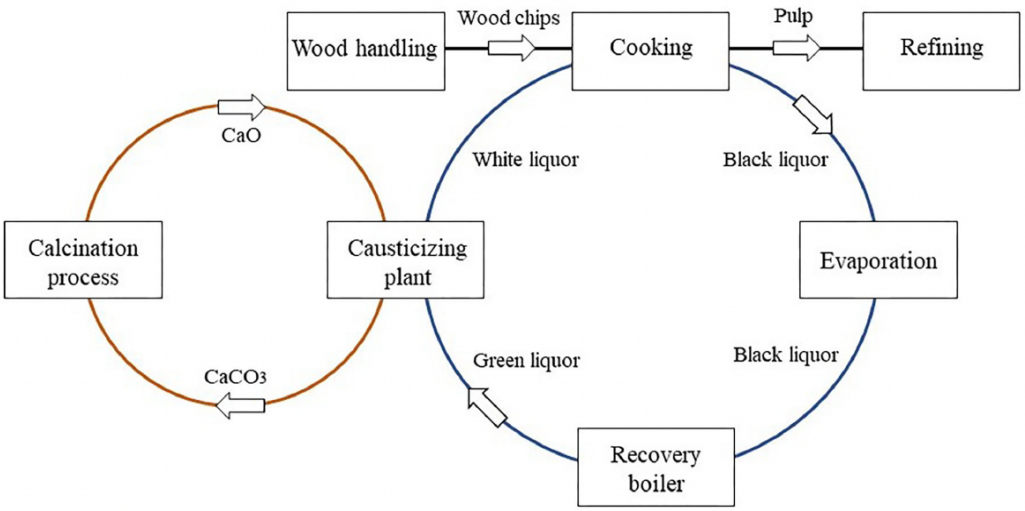

Figure 2.5: The chemical recovery cycle in a kraft process [5].

2.3.2 Black liquor evaporation

Black liquor is the waste liquor coming from the pulping process after the delignification is complete and is called weak black liquor due to its high water content. This weak black liquor consists of various organic components and some small share of inorganic materials besides the water, see a list of the main components in Table 2.3. The largest share is dissolved lignin consisting of sodium salts, but also a lot of carbohydrate derived residues together with some extractives exist in the weak

Table 2.3: Approximate chemical composition of dry substance of black liquor [6].

Element	Amount (weight %)	Organic material	Amount (weight %)
Carbon	34-39	Lignin	29-45
Hydrogen	3-5	Hydroxy acids	25-35
Oxygen	33-38	Extractives	3-5
Sodium	17-25	Formic acid	~ 5
Sulphur	3-7	Acetic acid	~ 3
Potassium	0.1-2	Methanol	~ 1
Chlorine	0.2-2		
Nitrogen	0.05-0.2		

black liquor. An approximation is that roughly 2/3 of the solids is organic material and the rest 1/3 is inorganic [6]. This complex liquid is highly alkaline and have a pH value around 13 [18]. Typically, the weak black liquor consists of 15-20% dry solids and 80-85% water [19]. This weak black liquor is sent to the evaporators. As a first step in the chemical recovery cycle, the weak black liquor enters the evaporation plant consisting of several evaporation units in a serial connection. A general description of the purpose of the evaporation step is to separate water from the weak black liquor, to be able to increase the heating value of the black liquor before it can be combusted in the next step [20]. So, weak black liquor gets concentrated to approximately 65-85% dry solids and 15-25% water [19], getting rid of mostly water but also some small amounts of organics such as sulphureous compounds and methanol that is condensated [6].

Evaporation units have both a heat exchanger and a separation device to enable the formed vapor and remaining black liquor to be separated. The steam that is formed in the separate evaporation unit is then passed on to the next unit for provide efficient heating. However, the flow of the steam can be either counter-current or co-current. The former is often the choice in modern systems. Several types of evaporation units can be used, for example a Kestner evaporator (rising film evaporator) or a falling film evaporator, the latter being the most frequently used type [6]. In the falling film evaporator, the weak black liquor is distributed at the top of the evaporation tower, heated as it falls in a vertical direction towards the bottom, where it is passed on to the next evaporation unit. Several evaporation units are preferred to be able to reach the desired degree of dry solids content, often six or seven evaporation units in series is recommended in a modern evaporation plant [6]. In the lignin recovery process, black liquor is extracted by a side-stream from the evaporation plant, containing about 30-45% dry solids content [21].

2.3.3 The recovery boiler and the causticization

In the recovery boiler's furnace, the concentrated strong black liquor is sprayed from the liquor guns, and particles are combusted, see Figure 2.6. The high heating value (HHV) of black liquor is a very important parameter in the recovery boiler as it defines how much heat that can be released once the black liquor particles

have been combusted, by the mass or volume of black liquor. Another important parameter is the hearth heat release rate (HHRR). This parameter is defined as an estimate of the capacity of the ability of the recovery boiler to effectively process the black liquor that is fired in relation to the air that is coming into the lower furnace. In other words, the heat input from the dry solids of black liquor, which is mostly lignin, that is fired in the furnace over a certain cross-section [22]. A third important parameter is the adiabatic combustion temperature. This is the temperature of a combustion reaction that loses no heat during the process, at constant pressure.

The organic content in the black liquor is what is being burnt, and thus heat can be recovered as stated above, by using heat exchangers. The produced heat can be used as high-pressure steam to produce electricity in a turbine, to utilize for heating applications in the pulp mill processes. Besides producing applicable steam, the recovery boiler also produces green liquor. Heavy particles fall into the lower part of the recovery boiler, the char bed, producing a smelt that consist mainly of sodium carbonate (Na_2CO_3) and Na_2S, and some residues of inorganics. This smelt is called the green liquor. The recovery boiler also recover dust from inorganic flue gases, to save make up chemicals in the process [23].

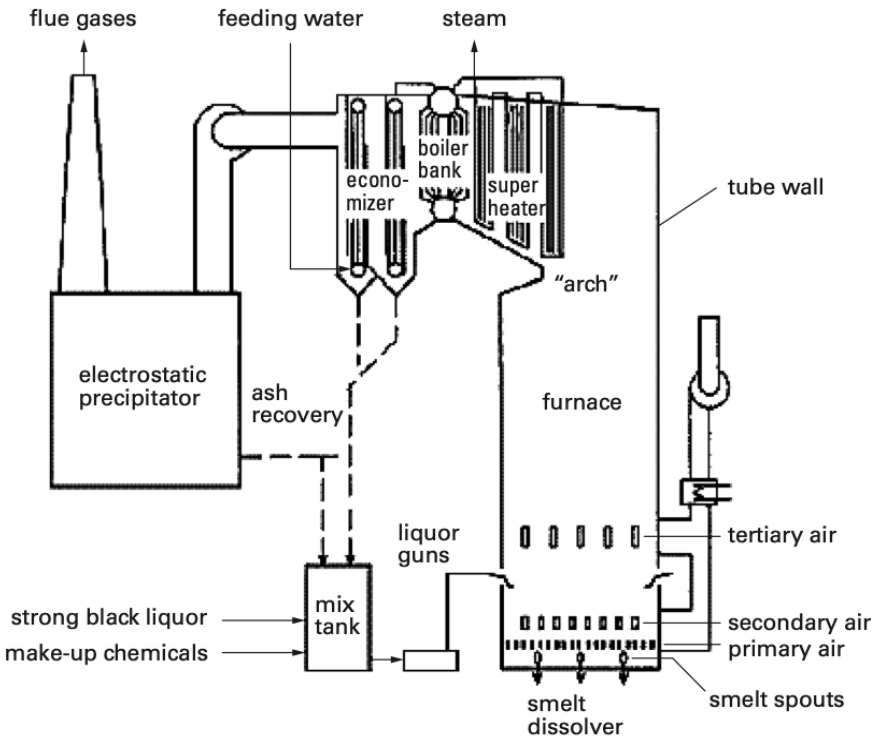

Figure 2.6: A visual description of the recovery boiler [6].

The green liquor is proceeding to the causticizing plant where the goal is to recover chemicals to produce fresh white liquor to be used in the cooking process over again. The green liquor is first filtered and slaked, before entering the causticizing plant, where white liquor is separated and calcium carbonate ($CaCO_3$) is produced, called lime mud. $CaCO_3$ is washed before being calcinated in a lime kiln where the $CaCO_3$ is forming CaO, called lime, and flue gases in form of CO_2. The burnt CaO is then

utilized again in the slaker to close the loop, see the left hand side of Figure 2.5.

So, the recovery boiler is producing both steam for internal usage and electricity, as well as green liquor for fresh white liquor production. However, the recovery boiler is often the bottleneck of the process in a pulp mill [24]. If lignin from the black liquor is extracted, the capacity of the mill could be raised. In other words, more pulp can be produced at the same time as the by-product lignin can be produced and can be sold or potentially utilized at the site as a fossil-free fuel, for example in the lime kiln as an eco-friendlier alternative.

2.4 History and development of LignoBoost

Lignin recovery had its breakthrough in the early 2000s. Several bench- and pilot scale trials were conducted before the first start-up in 2006 [25]. In 2006, the first demonstration plant of the LignoBoost process was built in Bäckhammar, Sweden. The plant has a capacity to produce 8 000 ton lignin/year. Later, in 2012 in Plymouth at the pulp mill of Domtar, the first commercial plant was built and was up and running in 2013. This plant produces about 25 000 ton lignin/year. In 2015, the third plant was built in Finland at the plant Stora Enso Sunila Mill. They produce 50 000 ton lignin/year, and uses the lignin as a fuel in the lime kiln, instead of other fossil fuels [12]. Also, a small LignoBoost plant for experiments and small amount of lignin extractions for research have been built in 2019 in Klabin, Brazil, with a capacity of only 500 ton lignin/year. So, these are the four plants that are in operation today. The LignoBoost process and its patents is owned by Metso.

2.5 The lignin removal principle

The process of lignin removal is pictorially described in Figure 2.7. The process uses a side-stream of black liquor coming from the evaporation plant. To extract kraft lignin from the black liquor, several steps are followed, starting with a first precipitation step. The black liquor is around 30-45% dry solids content as mentioned earlier [21]. Acid is added to the black liquor to lower the pH, often and preferably in the form of CO_2. The pH of the highly alkaline black liquor is around 13 and is lowered by acidification, and thus, lignin starts to precipitate. The pH that is reached with only CO_2 is somewhere between 9-10. The slurry is filtered by a chamber press before the filter cake is re-dispersed with a second acidification step, where the acid added is H_2SO_4 instead. In this step, the pH is lowered even more, to reach a pH of about 2-3. This re-slurry is then filtered one more time, again with a chamber press and then washed by displacement washing, using acidified water. The lignin coming out from the washing step contain about 65-70% dry solids content and thus a final drying step is needed before the final lignin product is complete. Here the final lignin reaches up to 95 % dryness. This lignin can either be sold or utilized at the site. One example is for replacing fossil fuels used in the lime kiln as mentioned earlier. To summarize, the inlet flows to the lignin removal system are three; black liquor, chemicals in the form of the often used acids CO_2 and H_2SO_4, and water.

Also, three flows are leaving the system. Two of those are re-circulated back to the recovery cycle; lignin-lean black liquor and wash liquor are going back to the evaporation plant. The third component leaving the system is the final product of lignin.

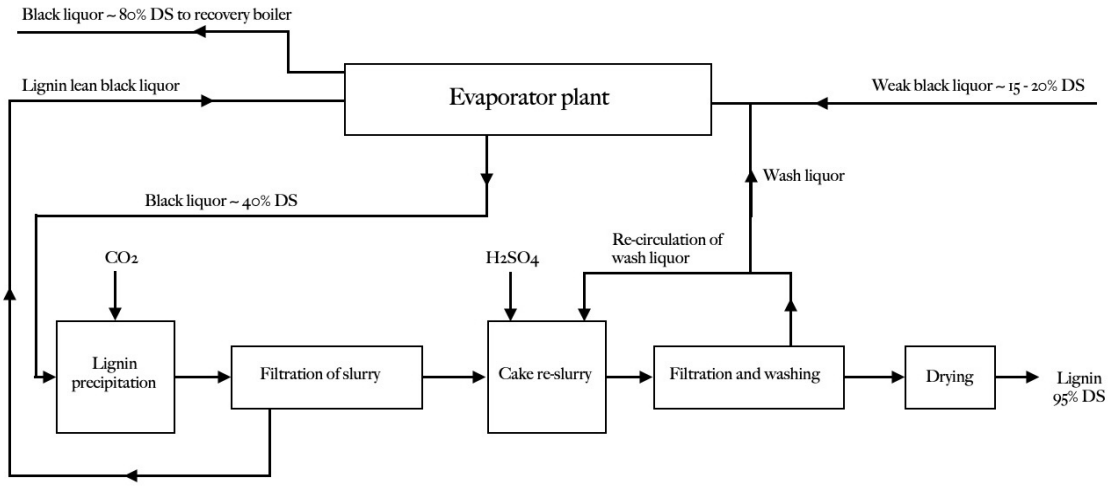

Figure 2.7: A schematic view of the lignin removal process.

2.5.1 Methods of lignin recovery besides LignoBoost

More alternatives of lignin recovery methods are available besides the LignoBoost process. The first discovered method to separate lignin from black liquor was *The West Vaco Process* in the late 1940s. In this method, the black liquor is separated from the evaporators in an earlier stage, 20-30% dry solids content [26], compared to the LignoBoost process. This process refers to indulin lignin, which is lignin coming from linerboard pulp.

Another method is called *LignoForce* and was first commercialised in 2016 in Canada. The difference from the LignoBoost process is that an extra filtration step as well as an oxidation step are added before the first precipitation step. Due to these additional steps, acids like acetic acid or lactic acid are formed, leading to a natural lowering of the pH. Also, lignin is oxidized and carboxylated lignin is formed. This carboxylated lignin have other solubility properties and have thus higher solubility in water which leads to a lower overall lignin yield of the final lignin product. Also, more CO_2 needs to be added to this process compared to LignoBoost. However, improvements of the filterability can be seen due to the additional steps in this method.

A third method is called *Sequantial Liquid-Lignin Recovery and Purification (SLRP)*. This method was patented in 2009. In this process, higher temperature and pressure are used, as well as lower amount of CO_2 added [26]. This method is however not yet used in any commercial scale. None of the above mentioned processes will be further investigated in this project.

2.6 The extraction of lignin

The black liquor where lignin is located is very alkaline, around pH 13-14 as mentioned earlier. In this alkaline solution, lignin has different attributes if comparing with its native state where lignin is broken down in smaller components. However, lignin has both polar and non-polar characteristics which are important factors to understand speaking of lignin separation from black liquor. The solubility of lignin decreases in water and decreasing pH. An acid is added to the black liquor to decrease the very alkaline pH. In the interval of pH above 7, protonation of phenolic -OH groups are making the lignin precipitate. In the second interval of pH 7 to 2, the further lignin precipitation is due to protonation of carboxylic acid groups in the black liquor that is associated with the lignin [27].

Lignin can be separated in different ways such as acidification, ultrafiltration, or electrolysis [27]. However, the most often used method is acidification. Both weak and strong acids can be used to lower the pH and thus precipitate lignin. Most often CO_2 is used as a weak acid, and H_2SO_4 as a strong acid. In the inital step of lowering pH from about 13, the weak acid CO_2 is preferred. This is due to the fact that CO_2 have no effect on the important Na/S balance in the pulp mill. Also, carbon dioxide does not introduce any additional chemicals that does not already exist in the recovery cycle. In a second precipitation step, the strong sulphuric acid is often added to decrease the pH further and recieve a higher yield of precipitated lignin. However, if both CO_2 and H_2SO_4 are going to be purchased externally, the lignin recovery process can be costly.

2.6.1 Filterability of lignin

The filterability of lignin is very important for the lignin recovery process. Due to research, good filterability is related to lower values of pH, thus it is consistent with improved protonation of lignin [27]. Initially, the process of lignin recovery only consisted of one stage of filtering, compared to the two stages used today. The disadvantage of only have one stage were struggling with filter cake plugging. The filter cake did not proper flow through of the wash liquor, thus the final lignin often had high content of sodium. High content of sodium in lignin is not advantageous since it can create corrosion and other problems when used as biofuel for example. However, the struggle with filter cake plugging happened because the gradient of ionic strength was high in the cake when it was being washed. This is why the process today consist of two stages where the filter cake is re-dispersed after the first filtration. The re-dispersion is happening in a liquor that has approximately the same pH as the final washing step, thus creating as small gradient as possible [28].

2.7 Sodium and sulphur balance in a pulp mill

In the alkaline sulphate pulping process, chemicals like NaOH and Na_2S are the active components as mentioned above. The ratio between sodium and sulphur

is important since the final pulp properties are affected by this ratio. Also, it is expensive to compensate with make-up chemicals if the losses are too large. So, the goal is to keep the ratio stable, and thus less need for make-up chemicals. However, if a lignin removal process is applied to the pulp and paper process and lignin is extracted from the otherwise rather closed loop, there is a risk of Na/S disturbance. Normally, the losses are to wastewater and the air. Sulphur emissions have a negative impact on the environment, which is also an important reason to try to keep the loop as closed as possible [29]. The form of sulphur losses to the air are most often as H_2S and SO_2 [30].

3

Method

In this chapter, the method that were used for conducting this master thesis will be presented. The procedure consisted of both a deep literature study as well as an evaluation and shaping of the Simulink model of the lignin recovery. Also, different analyses associated with the model have been conducted. In the following chapters, small illustrative figures are highlighted and then better viewed in full size in Appendix A, due to small detailed figures.

3.1 The approach of the project

This master thesis work was initiated with a deep literature study, where knowledge about the lignin macromolecule and its characteristics as well as the full picture of how a pulping process looks like in general were gained. Also, more specific knowledge about lignin extraction methods from previously done studies were gained. Literature about different processes of lignin recovery besides the LignoBoost concept were read for comparison, since this thesis is exclusively based on the LignoBoost concept of lignin recovery. The literature study followed through during the entire period since this project was exclusively based on literature studies and no real-life experiments were conducted.

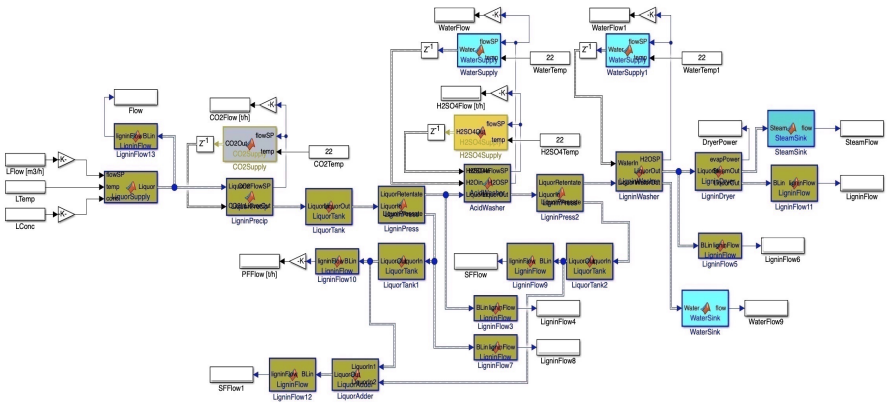

Figure 3.1: The draft Simulink model visualizing the lignin removal concept.

The main focus of this project was a built up model in Matlab Simulink representing a lignin recovery process originating from the conventional LignoBoost concept. The draft model is represented in Figure 3.1, and can be visualized in a larger picture in Appendix A in Figure A.1. This model is based on real life data from a Swedish pulp mill and were received as a draft from the ongoing collaboration between IVL and the pulp mill. Before receiving this model, an introduction of how Simulink is working was initiated. Several videos on YouTube were watched as well as instructions from the supervisors since no previous knowledge about Simulink existed. The progress of how the project has been conducted can be followed in accordance to Figure 3.2.

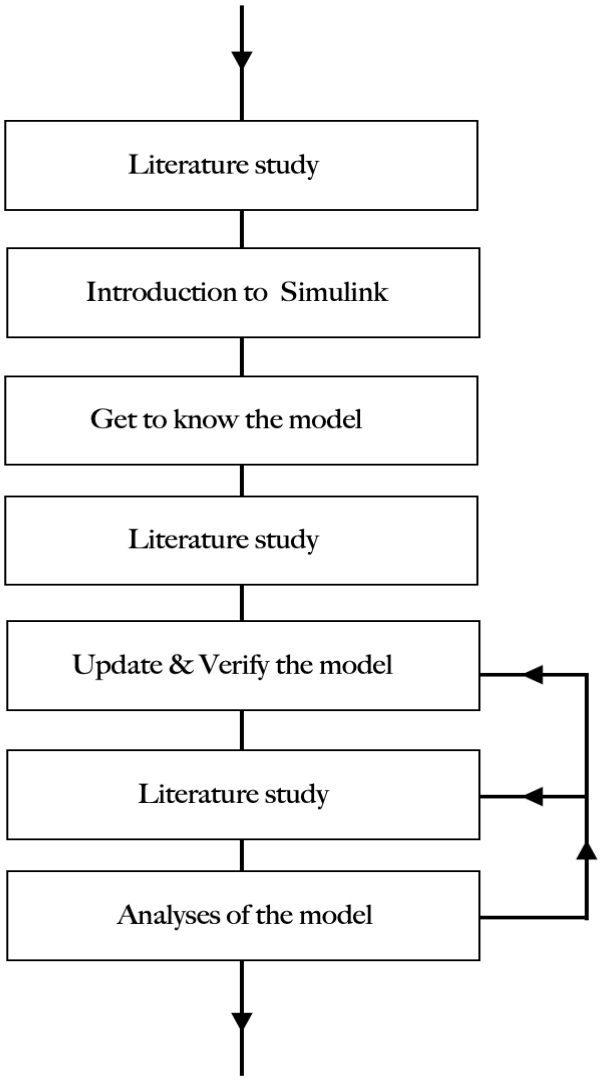

Figure 3.2: Flowchart of the progress of the project.

After Simulink had been introduced, the draft model was received, and a lot of effort were put into get to know the model and how it was built up. A further literature study was conducted to be able to make further progress with the model and verify the parameters building up the model. The following process was iterative; the

model was updated, more knowledge was gained, analyses was made from the model, and then this procedure was repeated several times to achieve the final results.

3.1.1 The software Matlab Simulink

The software that has been used for this master thesis is Matlab, in particular Simulink. This software is, as well as Matlab, a software developed by MathWorks. However, Simulink is "a block diagram environment used to design systems with multidomain models, simulate before moving to hardware..." [31]. The difference between Matlab and Simulink is that the latter is intended for visualization of simulations and modelling, rather than only relying on coding. This tool was chosen for this master thesis work because it was already in use in the collaboration project which made it favorable to proceed with the already existing draft.

3.2 Initial evaluations of the model

When the Simulink model had been familiarized, an initial analysis regarding the parameters in the model were conducted. The parameters were either verified by literature and left unchanged or updated in accordance with literature. For example, the parameters in the inlet of the model were evaluated, see in Figure 3.1 furthest to the left, or in Appendix A in Figure A.1 for better resolution and to facilitate the understanding of the following descriptions of the model. The dry solids (DS) content of black liquor was one parameter that was investigated and compared with literature (called BLConc in the model). Also, the temperature (BLTemp), of the black liquor in the system to achieve good filter properties was studied and verified by literature. The third inlet parameter, the flow of black liquor (BLFlow), was changed during the simulations to verify how much lignin the system could extract. Other important parameters such as lignin, sodium, and sulphur content and pH, in the incoming black liquor were compared with values from literature. Also, an investigation of how much acids that were needed in the model was done by varying the amount of added acid to the system and values were verified by literature.

As can be seen in Figure 3.1, each of the building blocks in the model are visualized as boxes. They were evaluated both regarding the code and specific values used in the boxes, such as press efficiencies and precipitating rates, for example. All the boxes in the model were evaluated deeper one by one and compared and verified with values from literature. The model was slightly updated in order to work well and fit the reality better. Some of the flows in the system were changed and will be visualized and presented in the next chapter.

3.3 Analyses of the model

As can be seen in Figure 3.2, the model was slightly updated and modified throughout the whole project. However, analyses of the model were initially conducted as well as after some time of evaluating the model. Analyses that have been done are

to utilize the model with different amounts of black liquor in the inlet flow, different amounts of added CO_2 and H_2SO_4, and evaluate how much lignin that can be extracted from the lignin recovery model hourly and yearly. Also, different analyses of the content of ash, sodium, and sulphur, in the final lignin product beside lignin have been done, based on literature values. Along with this study, it was also calculated how much sodium and sulphur that were left in the system due to added amounts of acids. Some final analyses regarding how much the steam and electricity production decreases when lignin is extracted were done. With this analysis, an economic analysis was also done. All the analyses that have been conducted in the project are based on the Simulink model with values from the Swedish pulp mill as well as values found in literature, with calculations made in Excel.

4

Results and discussion

In this chapter, both the results and the discussion will be presented together. Several results of the Simulink model will be presented both in words and illustrative by figures and tables with analytic discussions.

4.1 The outlook of the Simulink model

Here follows a description of the outlook of the model in Simulink, see Figure 4.1 or Appendix A in Figure A.2 for better resolution to facilitate the following description. In the first block of the model, called *Liquor Supply*, some parameters concerning the black liquor are defined, see Table 4.1 for the most interesting ones. The values of lignin, sodium, and sulphur concentration are the dry solids concentration. These values are defined from literature of how black liquor often are composed when considering a black liquor of approximately 30-45% dry solids content. These values were already in the draft model and were thus only confirmed by literature.

Table 4.1: Parameters of the inlet flow of black liquor.

Parameter	Value
pH	13
Lignin conc.	36%
Na conc.	21%
S conc.	5%

In the next block, called *Lignin Precipitation*, the inlet flow of black liquor together with the added amount of CO_2 are mixed and the approximated amount of lignin that can precipitate in this step is set to 70%, which can be achievable if this step is being carefully performed [32]. However, this number can vary quite a lot for different pulp mills and different black liquors, since every mill run on different conditions and the composition of black liquor can vary also within a mill depending on the process. How much lignin that can be precipitated also depends on what pH the reaction stops, which is also a question of cost of how much acids one a willing to put in. Thus, this 70% is an estimation for this model. In the next step, called *Lignin Press*, the slurry is filtered with a press efficiency that is set to 70%. This number could possibly be higher or lower, depending on what type of press that is being used. This 70% means that in this model, it is assumed that 70% of the lignin

in particulate form will proceed in the process and is called the retentate. The rest will be filtered out and re-circulated back to the evaporation plant in a lignin-lean black liquor flow, called pressate. The press efficiency will affect how much lignin that end up in the retentate and the pressate respectively. If the efficiency is higher, more lignin can be produced in the lignin recovery system. In this case, this is the desired outcome.

The step after the first press is where the strong acid H_2SO_4 as well as water is added to the filter cake. This is done in the block called *Acid Washer*. The re-slurry is then filtered in a second step, *Lignin Press 2*. Here, as well as in the first filter press, the press efficiency is assumed to be 70%. After the second filtration, the filter cake is washed in a displacement washing step, in the block called *Lignin Washer*. An approximation that is done in this model is that there is no re-circulation between the water that is added in the acidification step and in the displacement washing step. Comparing with Figure 2.7, where the flow of water is partly re-circulated between these steps to use less amount of water supply. Thus, the model is utilizing slightly more water than what could be the optimum. This implies that more water is being re-circulated back into the evaporation plant than what would be the case in real-life. As a final step, the lignin is dried up to 95% dryness with the block called *Lignin Dryer*, and thus, the final lignin product is complete. Due to confidentiality, only visual and verbal descriptions of the model will be presented, thus, no coding will be shown in this report.

4.1.1 Adjustments of the model

The model that was received from the ongoing collaboration between IVL and the pulp mill has been slightly updated from the draft. From the beginning, the two pressates coming from the two filter presses were added together as one flow from the lignin extraction model. The water that is added to the model was leaving the system as a single flow. This can be seen in Figure A.1. However, after a deeper literature study on how the outgoing flows from this type of system usually looks like in reality, it was found that these flows should be separated slightly different. The pressate from the first filter press where CO_2 is added, is called lignin-lean black liquor. This pressate should go back and enter the evaporation plant after the separation point of where black liquor for the lignin recovery is placed, in other words, right before the black liquor is entering the recovery boiler. This flow should be a single flow, and not added to the other pressate as it was modelled initially. This is shown in Figure 4.1 as the red circle to the left where the flow going back into the evaporation plant is called *Lignin-lean Flow*. As this pressate does not consist of any added possibly disturbing chemicals like sodium and sulphur, it is safe to re-circulate this alkaline pressate into the recovery boiler without impacting the Na/S balance. Also, this pressate contain the lignin that is not proceeding in the lignin recovery process as was discussed above. It is important to re-circulate as much lignin as possible to the recovery boiler since this is a large contributor to what is transformed into useful energy. The more black liquor that is extracted for the purpose of producing lignin, the less energy can be produced in the recovery boiler. Thus, it becomes important to benefit from all lignin available for the recovery

boiler.

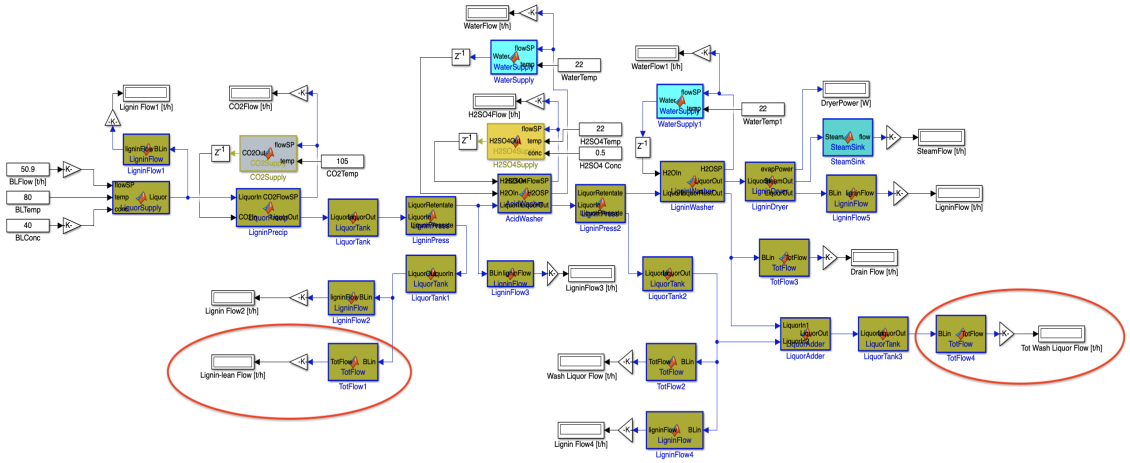

Figure 4.1: The Simulink model showing with red circles where the filter presses and water flows are changed.

However, the pressate from the second filter press, where H_2SO_4 and water is added, should go together with the waste stream of the *Lignin Washer* as one stream instead. This flow is wash liquor that is a mix of H_2SO_4 and water among other residual components, and should go as one stream back into the evaporator plant in an earlier stage, before the separation point of black liquor for the lignin recovery process, see Figure 2.7. In other words, this wash liquor flow should be mixed with the rather weak black liquor and is thus re-circulated into both the lignin recovery plant again but also the recovery boiler. This can be seen in Figure 4.1, in the red circle to the right instead. For a closer look at the model, see Figure A.2 in Appendix A.

Since this pressate from the second filter press contain the added sulfuric acid, it means that higher sulphur content will be re-circulated back into the evaporation plant. Depending on how much black liquor that is extracted for the lignin recovery, different quantities of sulphur is re-circulated. From a previously done study of black liquor from softwood, it was discovered that the content of sulphur went from 4.09% of the elemental composition of black liquor when considering 0% lignin production. This amount increased to 4.77% when considering 50% of black liquor extraction for the lignin production. The same increase could be seen for sodium, going from 21.71% to 24.98% [28]. This increase in sodium and sulphur in the black liquor composition is probably because of the re-circulation of the wash liquor into the recovery cycle. Since a pulp mill is very dependent on its ratio of Na/S to produce a pulp of good quality, this addition of the pressate can cause trouble for the recovery cycle. However, this will be further discussed in a couple of sections.

4.1.2 Analysis of parameters

The black liquor dry solids content (BLConc) in the flow into the lignin recovery plant was investigated. This BLConc is assumed to be the concentration of the black liquor in this model. However, it was quickly determined that the range of 30-45% dry solids content of the black liquor coming from the evaporator plant was the most reported [18, 21, 26, 33]. The decided value of dry solids content was set to 40% as an estimation of the interval. Also, the temperature of black liquor for precipitation were investigated. In terms of the filtration properties, the range of 60-80°C seemed to be the most reported [26, 34]. However, the model is not dependent on the temperature as it is today, and an approximation of the lignin recovery to be a closed system were done. Thus, the temperature was set to 80°C in the inlet of the model just to state that this parameter also is important in reality and should be taken into consideration.

The same thing was done for the amount of added acid to the system. Both the added amount CO_2 and H_2SO_4 were investigated deeper by further literature studies. One source stated that 200 kg CO_2/ton lignin were the desirable amount to add for lowering the pH from around 13 to 10 and make the lignin precipitate [18]. Another source stated that the interval of 150-300 kg CO_2/ton lignin were favorable [26]. According to Innventia, that also is part of the founder of the LignoBoost process, it was found that the added amount of CO_2 should be in an interval of 150-320 kg CO_2/ton lignin [25]. It was also stated that an average value of added amount of CO_2 should be 220 kg CO_2/ton lignin. For H_2SO_4, one source stated that 150 kg H_2SO_4/ton lignin was the desirable amount to add [18]. Additionally, according to Innventia, the amount of added H_2SO_4 was estimated to be in the interval of 120-255 kg H_2SO_4/ton lignin [25], with an averge value of 175 kg H_2SO_4/ton lignin. Thus, it could be concluded that the addition of acid to the system is proportional to the lignin content in the system. The more black liquor going into the system, the more lignin is entering the system, and thus more acid is needed. However, the range of how much acid per ton lignin that should be added is rather wide.

In the following sections, analyses have been made with varied amount of CO_2 and H_2SO_4. The amounts of CO_2 that have been tested are the highest recommended value of 320 kg as well as the average value of 220 kg. Regarding the amount of added H_2SO_4 to the system, 255 kg and 175 kg have been tested.

4.2 Lignin production dependency on black liquor flow and supply of acids

In the model, an analysis has been made by changing the inlet flow of black liquor between 10-50% of the total amount of produced black liquor in the plant. The total black liquor flow coming from the digester is assumed to be 1166 m^3/h according to values received from the pulp mill with a dry solids content of just below 17%. At the separation point where black liquor for the lignin recovery plant is extracted, the flow is 509 t/h, with a dry solids content of about 40%. The interval of the tested

percentage range that have been analysed can be seen in Figure 4.2. For the exact values of black liquor mass flows, see Appendix A Figure A.3. The values of black liquor inflow were calculated by the different percentages from the total amount of 509 t/h. These calculations were done in order to continue the analysis of how much lignin that could be produced by the lignin recovery plant when extracting different amounts of black liquor from the evaporation plant.

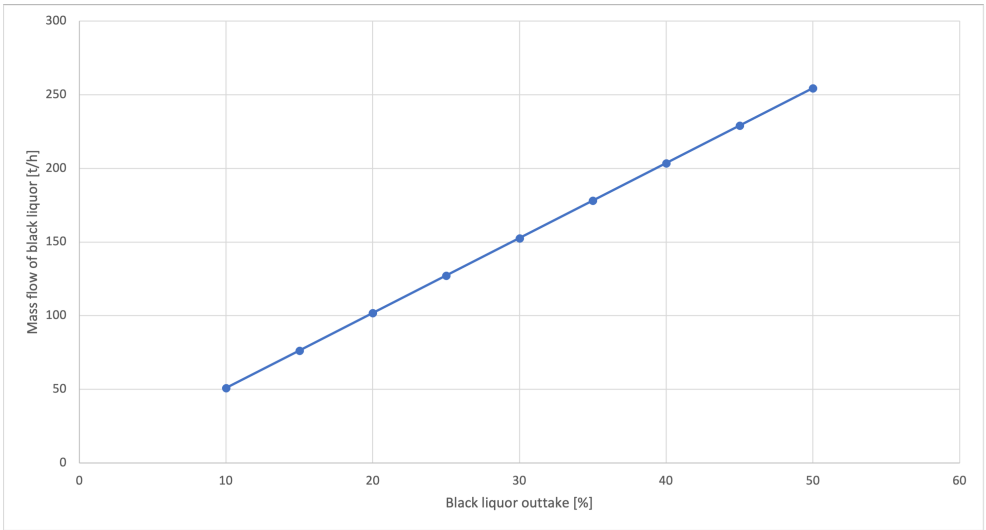

Figure 4.2: Amount of black liquor going into the lignin recovery boiler with different percentages of black liquor extraction.

Also, the added amount of CO_2 and H_2SO_4 was tested at both the highest recommended value and the average value according to the source mentioned previously. In other words, 320 kg CO_2/ton lignin and 220 kg CO_2/ton lignin were the values tested for added amount of CO_2, and 255 kg H_2SO_4/ton lignin and 175 kg H_2SO_4/ton lignin for added amount of H_2SO_4. The reasoning why the highest value was tested was to see how much more lignin it was possible to extract for the final product, since the goal of the lignin production is to produce as large quantity as possible. The average value was tested to compare how large of a different it made in the model, of the final lignin production. These assumptions were made since no real-life experiments on how much CO_2 and H_2SO_4 were the optimum were conducted. However, it can be questionable if more lignin will be produced if more acids are added, or if the lowering of the pH will just happen faster, and thus the precipitation will happen faster, and more lignin could be produced in the same timeframe. Thus, there is also a trade-off of how much acids one is willing to put into the process, since this becomes a question of cost. However, the acids lower the pH, and it will be a trade-off between how much lignin will precipitate and how much acids that are put into the system [32].

The result of the first analysis with the highest recommended added amount of CO_2 and H_2SO_4 to decrease the pH and thus precipitate lignin, can be seen in Figure 4.3. The values of the full analysis with more values from the model can be seen in Figure A.3 in Appendix A. In this analysis, the amount of lignin produced annually is approximated to an operation time of 8400 hours per year. This approximation

is done to take into consideration maintenance work and other kind of activities that forces the production to interrupt. As can be seen in Figure 4.3, the lignin production obviously increases as more black liquor is entering the lignin recovery plant. At 50% black liquor removal for lignin production, it can be stated that just below 140 000 ton/year could possibly be produced according to the model. The increasing production of lignin is advantageous if the market of lignin is attractive and thus have a high market value. Today, the market of lignin is not very large but hopefully this will change in a near future. Otherwise, this lignin can be utilized internally in the mill to exchange the fuel for the lime kiln as being done at the plant Sunila Mill in Finland. Lignin would be a renewable option instead of using fossil fuels as most plants do today. However, a deeper analysis and trade-off to state if this would be a cost-effective option is needed, since the lignin recovery plant comes with both a capital cost, rather large operational costs, as well as possible side-effects of the conventional pulp mill that must be taken into consideration.

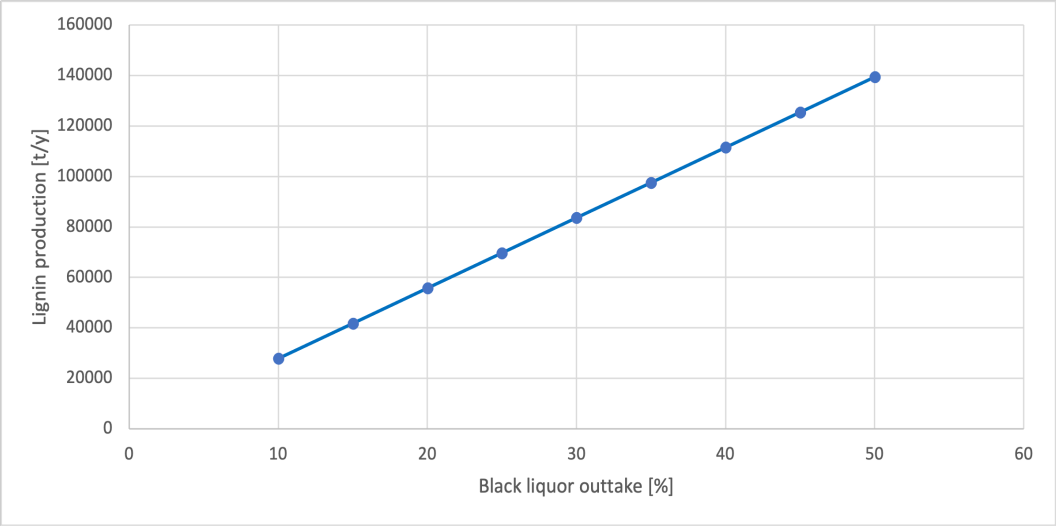

Figure 4.3: Produced lignin from the model with supply of 320 kg CO_2/ton lignin and 255 kg H_2SO_4/ton lignin.

The same analysis was done but with the average values of added acids instead, in other words, 220 kg CO_2/ton lignin and 175 kg H_2SO_4/ton lignin. The result of how much lignin it would be possible to produce in this analysis can be seen in Figure 4.4. The values of the full analysis with more values from the model can be seen in Figure A.4 in Appendix A. What can be concluded from this analysis with the average values of added acids is that slightly less lignin would be produced per ton of black liquor inflow according to the model. With a decrease of 100 kg CO_2/ton lignin and 80 kg H_2SO_4/ton lignin added, the production would decrease with approximately 10 500 ton/year in the case where 50% extracted black liquor are assigned for the lignin recovery.

The re-circulation of wash liquor to the evaporation plant should be approximately 2 m^3/ton lignin according to literature [35]. However, this model was found to have a re-circulation flow of approximately 4 m^3/ton which is double that value. This probably has to do with that this model is simplified without any re-circulation of

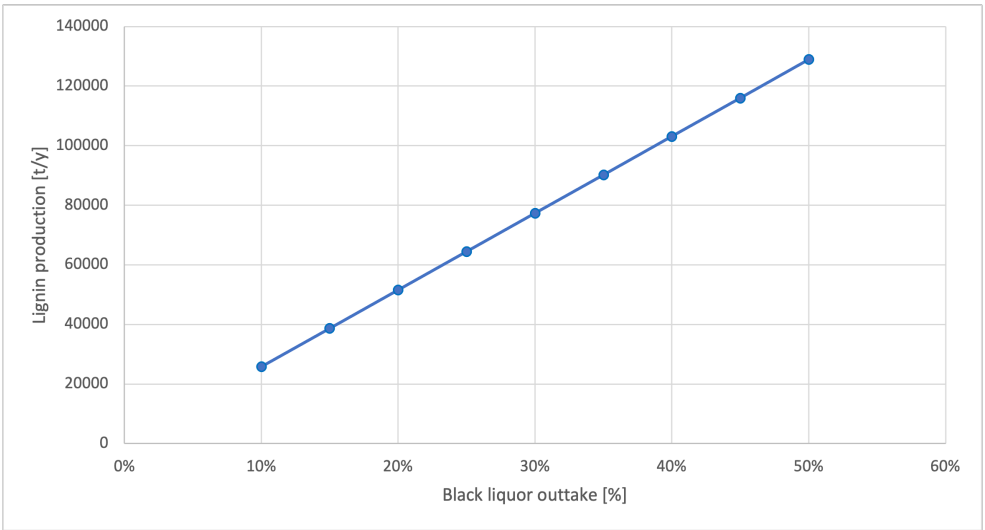

Figure 4.4: Produced lignin from the model with supply of 220 kg CO_2/ton lignin and 175 kg H_2SO_4/ton lignin.

the water and H_2SO_4 mixed liquor between the box of *Acid Washer* and *Lignin Washer*. Thus, the influence that the lignin recovery will have on the evaporation plant in this model is a slight over-estimation from the optimum. From a previous study, it was found that the required capacity of the evaporation plant increased with 3% when 30% of lignin was removed [36]. Thus, more steam and cooling water will be needed for the evaporation at the plant, but the changes are not very large. When 50% is the desired amount of lignin to be extracted, the increase of steam and cooling water will increase and put even higher pressure on the evaporators. However, it is hard to conclude whether this would be a big obstacle for the plant or not, with no further experiments done on the pulp mill in question.

4.3 Ash, sodium, and sulphur content of the final lignin

An analysis was conducted to investigate how large content of ash, sodium, and sulphur that the final lignin product of the model contains, based on literature values. Results from different studies that were gathered in order to make a good approximation of how much of the different components that appear can be seen in Table 4.2.

The source of Tomani and Innventia [25] were chosen to use in the analysis since this source included all three values compared to the other findings. The calculations that were done in this analysis were based on the average value from the intervals of ash, sodium, and sulphur content. In other words, the ash content was assumed to be 0.8% of the final lignin product, the sodium content were assumed to be 175 g/kg ash, and the sulphur content were assumed to be 2.5%. However, the chosen source has done the analysis of lignin with a DS content of 65-70% which is slightly lower than the same value of this study, which is set to be 95% dryness of the final lignin

Table 4.2: Summary of literature findings regarding ash, sodium, and sulphur contents of the final lignin product.

Ash content	Sodium content	Sulphur content	Source
0.2-1.4%	120-230 g/kg ash	1.8-3.2%	[25]
		2-3%	[27]
	0.5%	1-3%	[37]
0.6%			[38]

product. However, this should not impact the final result since the DS content is just a value of how much water content the lignin slurry have.

The important parts of the result of this analysis with 320 kg CO_2/ton lignin and 255 kg H_2SO_4/ton lignin is presented in Figure 4.5, and the full table with all values can be seen in Appendix A in Table A.5. From this analysis, approximate values for ash, sodium, and sulphur content for the different black liquor outtakes were gained. As expected, the values of all parameters increases as more lignin is produced, and thus the amount of the different contents increases since it is a percentual calculation.

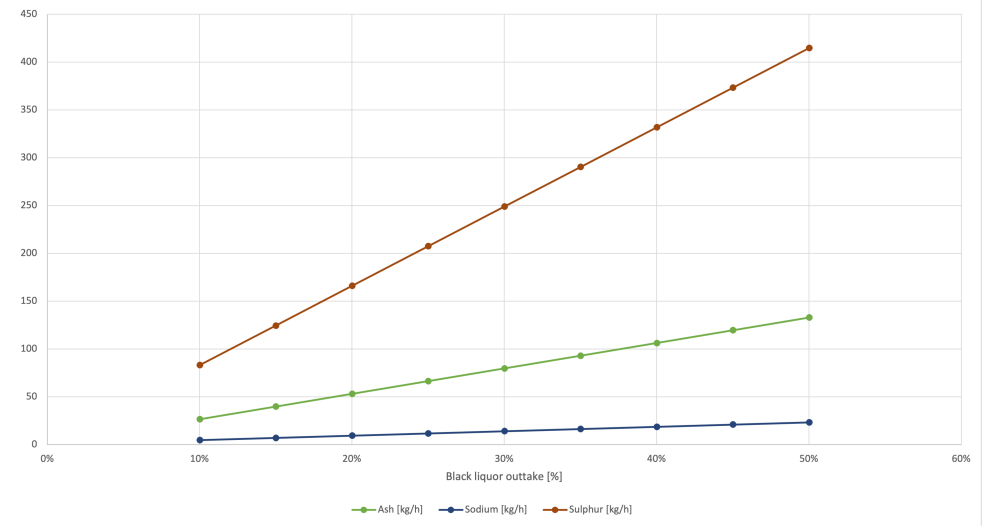

Figure 4.5: Ash, sodium, and sulphur content in the final lignin with 320 kg CO_2/ton lignin and 255 kg H_2SO_4/ton lignin.

The same analysis was done with 220 kg CO_2 and 175 kg H_2SO_4/ton lignin, see Figure 4.6 and the full table with all values can be seen in Appendix A in Table A.6. The same thing can be concluded here, that the different amounts of the parameters increases as the lignin production increases. However, these values are slightly lower than the values in Figure 4.5 since these calculations are done with the case where less acids are added, and thus, slightly lower amount of lignin is produced as the model is defined.

The results from Figure 4.5 and Figure 4.6 were used to do further calculations to analyse how much sulphur and sodium that is left in the system after the lignin recovery process. Both the case with the highest recommended amount of added

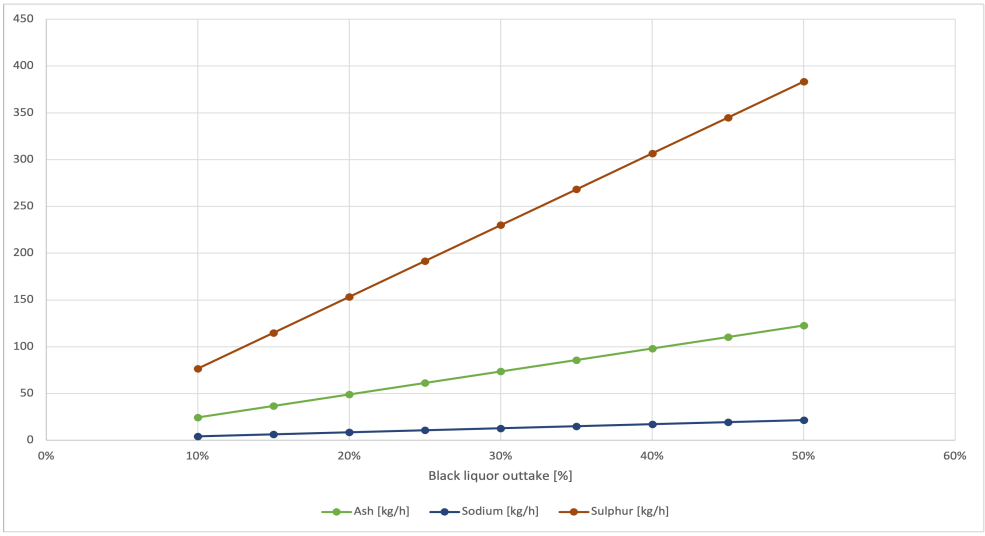

Figure 4.6: Ash, sodium, and sulphur content in the final lignin with 220 kg CO_2/ton lignin and 175 kg H_2SO_4/ton lignin.

CO_2 and H_2SO_4 as well as with the average amounts were analysed. The first mentioned case where sulphur and sodium contents were analysed can be seen in Table 4.3 and Table 4.4. The amount of sodium/sulphur that is entering the system in the black liquor is assumed to be 5% and 21% of the total amount respectively, as mentioned earlier. With the results of the previous analysis of how much sodium and sulphur that is leaving the system in the lignin product is then used to calculate the difference between these, and thus get a value of how much sodium and sulphur that is left in the system.

Table 4.3: Analysis of sulphur content left in the system in the case of the highest recommended amount of CO_2 and H_2SO_4.

BL outtake [%]	S in BL flow [t/h]	S in final lignin [t/h]	S left in the system [t/h]
10	2.55	0.0830	2.4620
15	3.82	0.1243	3.6906
20	5.09	0.1659	4.9241
25	6.36	0.2074	6.1551
30	7.64	0.2489	7.3861
35	8.91	0.2903	8.6173
40	10.18	0.3318	9.8483
45	11.45	0.3733	11.079
50	12.73	0.4148	12.310

It can be concluded that the amount of sulphur increases as the black liquor flow into the lignin recovery system increases, and thus, more sulphur will be left in the system and will be returned back into the evaporators, and further enter the recovery boiler. The sulphur that is left in the final lignin product is mostly sulphur that is chemically bonded with lignin from chemical reactions taking place during the delignification process in the digester when lignin is separated from the cellulose.

Thus, almost all of the sulphur that is added as H_2SO_4 to the system, is filtered and re-circulated. This sulphur is transformed into sulphate SO_2^{4-} and will appear in this chemical form all the way back to the recovery boiler, where it is transformed into sulphide and finally converted back into the important process chemical Na_2S which is a part of the white liquor. It is also here, in the lower recovery boiler, sulphur can be extracted from the process if the ratio of Na/S is not satisfied. This is done by an electrostatic precipitator (ESP), making it possible to control the ratio. This parameter is considered to be the most important parameter to be able to control the balance of Na/S in a pulp mill today [32]. The most common form that the sulphur is removed is by sodium sulphate (Na_2SO_4) [39]. However, this precipitator dust removal also causes losses of sodium, thus this have to be compensated by make-up chemicals, either in the form of NaOH or Na_2CO_3. It was found that this ratio could possibly be maintained by adding a certain amount of NaOH, in particular 122 kg NaOH/ton lignin produced [18].

Table 4.4: Sodium content left in the system in the case of the highest recommended amount of CO_2 and H_2SO_4.

BL outtake [%]	Na in BL flow [t/h]	Na in final lignin [t/h]	Na left in the system [t/h]
10	10.69	0.00465	10.684
15	16.02	0.00697	16.016
20	21.38	0.00929	21.369
25	26.72	0.01161	26.711
30	32.07	0.01394	32.053
35	37.41	0.01625	37.395
40	42.76	0.01858	42.737
45	48.10	0.02090	48.080
50	53.45	0.02323	53.422

As well as for sulphur, the amount of sodium also increases as the black liquor flow into the lignin recovery system increases. However, the amount of sodium in the final lignin product is much less compared to sulphur, since there is not any chemical reaction, as for sulphur, taking place with sodium in the prior steps. However, there is much more sodium in the system compared with the sulphur, due to the fact that it exist approximately 4-5 times much sodium in the black liquor entering the lignin recovery system.

Also, the ratio of carbonates to sulphates are impacted when the lignin content of black liquor is decreased. A previous study were conducted on lignin removal of 60%, and the amount of sulphates, thiosulphates, and carbonates were increased as the lignin content decreased [40]. It is these elements that cause the phenomenon *scaling* in the evaporators, namely sodium carbonate (Na_2CO_3) and sodium sulphate (Na_2SO_4). In ordinary black liquor, more carbonates exist compared to sulphates, but in the lignin-lean black liquor, these amounts were almost equal which resulted in a different molar ratio than usual. Problems with scaling is that these salt crystals are growing on the inside of the evaporator walls, and the more carbonates and sulphates that exist, the faster this process will go. Thus, the scaling problems

will increase when more and more lignin are removed from the black liquor. To remove scaling from the walls, maintenance work is needed, and thus the production needs to be paused, leading to less production and less profitability. However, how large effects these scaling problems will have in the particular plant is very hard to determine without any real-life experiments.

The case with the average values of CO_2 and H_2SO_4 can be seen in Table 4.5 and Table 4.6. The same analysis can be done in this case; higher amounts of sulphur and sodium are left in the system as we are letting larger shares of black liquor enter the lignin recovery system.

Table 4.5: Sulphur content left in the system in the case of the average amount of CO_2 and H_2SO_4.

BL outtake [%]	S in BL flow [t/h]	S in final lignin [t/h]	S left in the system [t/h]
10	2.55	0.0767	2.4683
15	3.82	0.1150	3.7001
20	5.09	0.1534	4.9367
25	6.36	0.1917	6.1708
30	7.64	0.2300	7.4050
35	8.91	0.2683	8.6393
40	10.18	0.3068	9.8732
45	11.45	0.3450	11.108
50	12.73	0.3835	12.342

Table 4.6: Sodium content left in the system in the case of the average amount of CO_2 and H_2SO_4.

BL outtake [%]	Na in BL flow [t/h]	Na in final lignin [t/h]	Na left in the system [t/h]
10	10.69	0.00429	10.6847
15	16.02	0.00644	16.0166
20	21.38	0.00859	21.3694
25	26.72	0.01074	26.7118
30	32.07	0.01288	32.0541
35	37.41	0.01502	37.3965
40	42.76	0.01718	42.7388
45	48.10	0.01932	48.0812
50	53.45	0.02148	53.4235

When defining sodium and sulphur in the model, they were approximated by elements, and not by the actual molecules that sodium and sulphur are splitted into in reality, since no real-life experiment on the actual composition of the black liquor were done. The assumption was that the black liquor was composed of 21% sodium and 5% sulphur as mentioned above. However, out of these 21 and 5% respectively, the elements could potentially be split up in the following order for a typical black liquor; 35-40% Na_2CO_3, 5-10% NaOH, 15-20% Na_2S, 5-10% Na_2SO_3, 15-20% $Na_2S_2O_3$, 10-15% Na_2SO_4, and about 10% others [27]. Since sulphur is a very important parameter, both for the recovery boiler and the causticizing plant and how

they are being controlled, it will be important to take all those different molecules containing sulphur into consideration more in depth than this approximation that has been done in this project.

4.4 The effects on steam, electricity and lignin production

An analysis on the dependence of the increasing share of black liquor outtake to the lignin recovery process on produced steam, electricity, and lignin was conducted. As the share of black liquor outtake from the evaporation plant increases, more lignin is produced in the lignin recovery plant. However, this increase in lignin product, has affects elsewhere in the plant. The less amount of black liquor that enters the recovery boiler to be burnt and turned into useful energy get a lower high heating value (HHV) as the black liquor contains less amount of lignin, and thus the heat load into the boiler decreases. Also, the amount of black liquor to the recovery boiler decreases if no adjustments of the flow were done. Thus, before removing too much lignin from the black liquor, it is important to be aware of how much that is possible to remove to keep the process going. This might make the HHV of black liquor the bottleneck of how much lignin that is possible to extract. In an ordinary black liquor, this value is about 14 MJ/kg DS [24, 41], but will be lower for the case when lignin is extracted from the black liquor. Other important parameters are the hearth heat release rate (HHRR) and adiabatic combustion temperature. In a case study that has been conducted on hardwood, the HHRR value were the limiting factor when no adjustment of the heat load into the boiler were done, and the operating of the recovery boiler was limited when the lignin removal was 50%. However, when the heat load into the recovery boiler was constant, thus having a controlled flow of black liquor into the recovery boiler, neither the HHRR nor the adiabatic combustion temperature were the limiting factors. Instead, the mass flow rate of smelt out from the recovery boiler was limiting the process. It was also found that the adiabatic combustion temperature, that is highly dependent on the HHV and dry solids content, could be restored with an increased dry solids content of the black liquor at higher lignin removal rates [24]. However, softwood is the main focus of this analysis, but the content of the study can still be applied also in this case. However, no specific conclusions on how the recovery boiler will act in this specific case were made.

Since less heat is available in the recovery boiler, less steam will be produced when more lignin is produced. This can be seen in Figure 4.7, where the red line indicates the increasing lignin production [kt/year] with increasing black liquor outtake, and the green line is the decreasing amount of steam produced from the recovery boiler [kg/s]. As can be stated, with 0% lignin production, the recovery boiler produces above 200 kg/s of steam. However, at a lignin production of 50%, the mass flow of steam from the recovery boiler is just above 100 kg/s. This indicates that the loss of steam production is approximately 50% when 50% of black liquor for lignin production is extracted. What happens when the steam flow is lowered, is that less

electricity can be produced. This electricity is what makes it possible for pulping plants to often be self-sufficient in electricity. Also, some electricity can also be sold if there is a surplus of produced electricity, which is most often the case in pulp mills. The pulp mill in question here have two generators that provides the plant with enough electricity and also gives a surplus most of the year. The two generators together have an effect of just below 150 MW when considering 0% of lignin production, see the blue line in Figure 4.7. However, since this is correlated with the steam production, also the effect of how much electricity the generators can produce is decreasing with increased lignin production. To take into consideration is that this model is rather a linear model, and thus the mass flow of steam as well as the electricity production decreases linearly with the increasing production of lignin, which is an approximation to the reality. From this analysis, it could be stated that

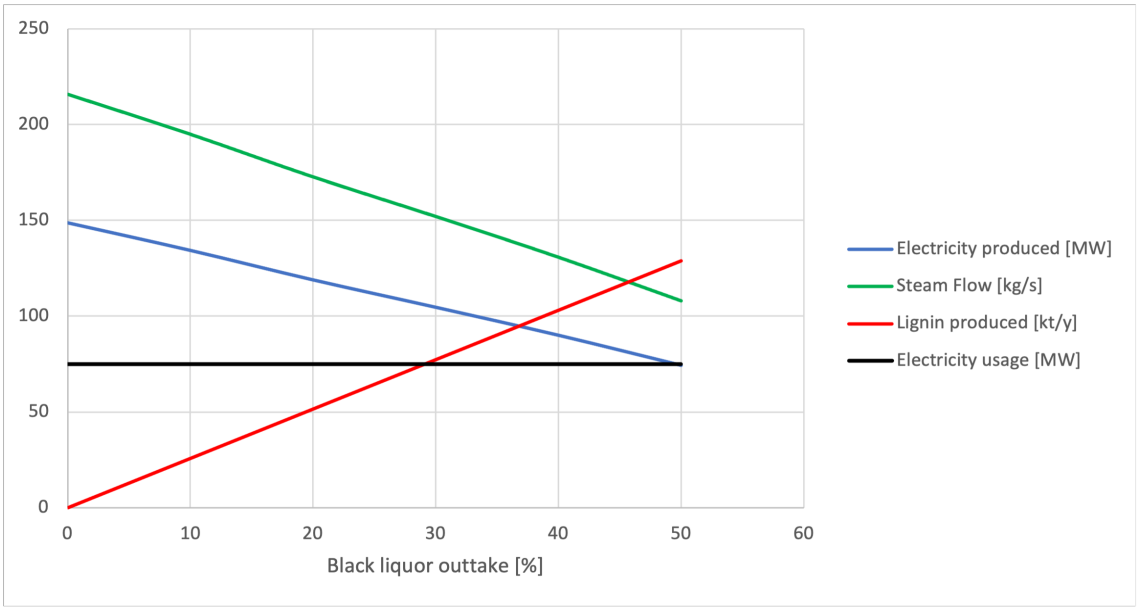

Figure 4.7: Steam, electricity and lignin produced in relation to black liquor outtake. The black line indicates the electricity usage of the mill.

approximately 2.2 kg/s of steam is lost with every % increase of lignin production. Also, approximately 1.5 MW of net power is lost for every % increase of lignin production. The total electricity usage at the pulp mill is about 75 MW and can also be seen in Figure 4.7, see the black line. The amount of electricity usage is approximated to a constant value in this study, but is decreasing slightly in reality, as a consequence of the increasing black liquor outtake. From this line, it can be analysed when the plant is producing too little energy for its self-sustainability. It can barely be seen in the figure, but at 50% of lignin removal, too little energy is produced for the mill to be run only by the energy produced by the recovery boiler. Thus, energy from example a biomass boiler will be needed to sustain the plant with enough energy. The decrease in produced electricity by every % of increased lignin production, less electricity can be sold to the grid. However, in this study, there is an available surplus to be sold up to just before 50% of lignin removal.

4.5 The expenses of acids

It can be concluded that having a lignin recovery plant requires a lot of added amount of acids in the form of CO_2 and H_2SO_4. This means that the operating costs of the lignin recovery will probably be quite high. However, CO_2 could potentially be used from the flue gases from the recovery boiler or from the lime kiln at the plant. These flue gases could be used without any treatment [42]. However, it has also been discovered that the pureness of CO_2 is very important and affects the time of pH decrease and thus precipitation [25]. Pure CO_2 of 99,7% pureness precipitates lignin much faster than CO_2 coming from the flue gases or potentially from an ethanol production site according to the study. From previously done studies on this topic, it was concluded that up to 50% of the operational costs could be saved by using the CO_2 that is produced internally [26]. However, challenges were discovered with the black liquor when using the CO_2 produced internally, since it caused foaming.

However, the thought behind this project is that the CO_2 is supposed to be recovered internally, to be able to keep the cost of purchasing CO_2 down. An alternative to be able to recover CO_2 internally is with an electric plasma calcination instead of an ordinary lime kiln, provided by a master thesis at IVL in previous years [43]. From this electric plasma calcination, CO_2 could be extracted by a cyclone in a very pure state and be stored before being utilized in for example a lignin recovery plant. Thus, the cost of CO_2 will be assumed to be zero in this case. However, this electric plasma calcination would also require a certain amount of electricity input to be utilized, which would decrease the amount of available electricity for the core process as well as for the case of lignin extraction and also the amount of electricity surplus to be sold.

The cost of H_2SO_4 is however even higher, but is used in a slightly smaller amount compared to CO_2. In March 2023, H_2SO_4 was estimated to a cost of approximately 2264 SEK/t [44]. For the case where the lignin production would be able to reach 50%, about 30 700 t/y of H_2SO_4 would be needed, see calculations of this in Appendix A in Table A.1. This would give an approximate operational cost of 69.9 MSEK per year. Upon this cost, also water will be needed for this process, both in the second filtration step and the displacement washing step. More water content means that more heat will be needed to dry the product, in this case up to 95% dryness.

Another analysis of the incomes and costs of the lignin recovery plant have been conducted. In Figure 4.8, the total incomes and costs can be seen. The incomes are approximated to the profit of sold lignin of a price of 3934 SEK/ton lignin [13], and the profit of sold electricity at a price of 124 SEK/MWh [45]. The costs are approximated to the cost of purchased H_2SO_4 of a price of 2264 SEK/t as mentioned above, and the cost of NaOH of 5625 SEK/t [46]. 122 kg of NaOH is assumed to be needed to keep the ratio of Na/S as mentioned above. It can be concluded that the incomes are larger than the costs in this case. This is mainly due to the fact that in this analysis, all lignin is assumed to be sold. However, as the market of lignin is

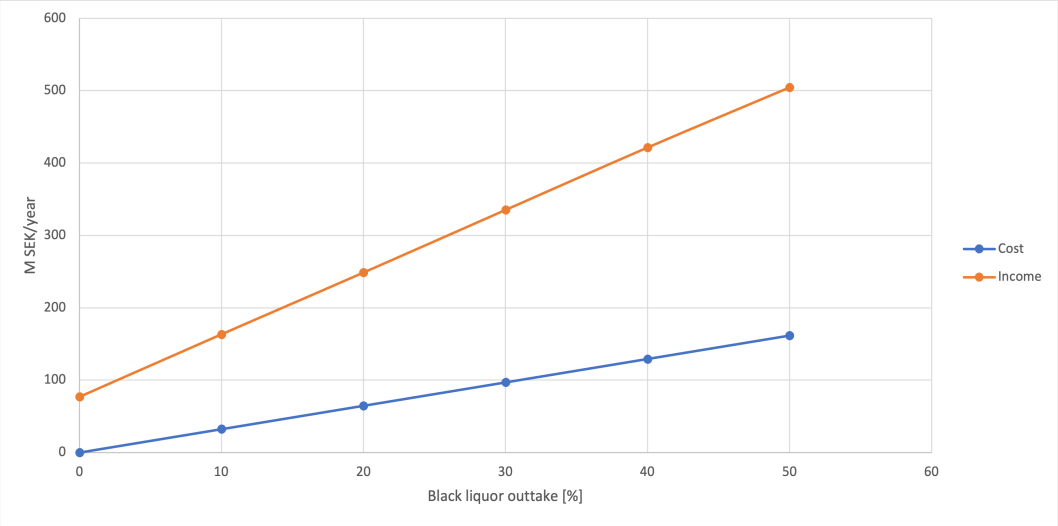

Figure 4.8: Incomes and costs of the lignin recovery plant.

not very attractive today, probably all produced lignin would not be sold in reality, and thus the profit would be considered lower. The amount of water and steam needed for the lignin recovery were not accounted for in this analysis.

4.5.1 Internal production of sulphuric acid

However, also the H_2SO_4 can be produced internally, and thus decrease the operational costs of the lignin recovery process. Another benefit of having an internal production of H_2SO_4 is that the excess of sulphur in the system can be extracted and utilized for the purpose of producing H_2SO_4. "For sulphidity control of lignin recovery of high yields, it have been discovered that an in-mill production of sulfuric acid is the best option to control the sulphidity" [39]. So, having an internal production of H_2SO_4 might be able to facilitate the situation of the excess of sulphur that will be caused by lignin extraction, and as well as the high operational costs. However, also this H_2SO_4 production plant comes with a capital cost that needs to be taken into consideration.

One method that have been proposed by Valmet, is to produce H_2SO_4 from concentrated non-condensable gases (CNCGs) [29]. The gases are collected in a tank and further pumped into a boiler where total reduced sulphur (TRS) compounds are oxidized to SO_2. From the boiler, the flue gases are entering a catalytic reaction vessel where SO_2 is oxidized into SO_3 by reaction 4.1.

$$2\,SO_2 + O_2 \longleftrightarrow 2\,SO_3 + heat \tag{4.1}$$

Further in the process, this SO_3 in the flue gases reacts with water, see reaction 4.2.

$$SO_3 + H_2O \longleftrightarrow H_2SO_4 + heat \tag{4.2}$$

Thus, H_2SO_4 is produced at the mill. The first installation of this type were in operation in 2017 in Finland and can be concluded to be "an environmental investment with a tangible financial payback in chemical savings" [47].

5

Conclusion

Up to 70% of black liquor outtake is theoretically possible to remove by using the LignoBoost process by Metso [24]. However, yet no one has succeeded to reach such high degree of lignin extraction in real life. In this project, up to 50% of black liquor extraction was the desired amount that was simulated. According to the model when adding 320 kg CO_2/ton lignin and 255 kg H_2SO_4/ton lignin, up to 139 356 ton lignin per year was possible to produce. However, this model is based on several assumptions that needs to be further investigated, to be able to make the model as accurate as possible.

According to this study and the model, this plant would have enough energy to run the plant almost all the way down to 50% of lignin extraction. To be able to go down to 50%, some extra energy would be needed to be produced from for example a biomass boiler. However, no extra energy can be sold as electricity since no surplus will be available at 50% extraction level. Less and less amount of electricity production will be the result of a higher lignin production. This results in lower income from electricity sold, compared to what the plant is used to which will affect the profits.

Whether this is feasible or not from an economic point of view, the profitability is highly dependent on the lignin market. Also, if the necessary acids can be produced internally or need to be bought will affect the profit. In the case where it is assumed that all lignin produced is sold, and acids are utilized from in-mill production, the future of lignin production seems to be economically beneficial. However, no capital cost for the lignin recovery plant was investigated in this project, nor the total costs of producing in-mill acids. If the lignin is thought to be used in-mill, as a fuel for the lime kiln, more investigations are needed to state the profitability. So, whether it is possible to run a pulping plant with an integrated lignin recovery, in the same pace as today, cannot be stated surely after this investigation, but further investigations need to be done. Since the pulp mill is a very large and modern plant, the chances to success are definitely there, hopefully in a near future.

6

Future work

Since this project is an ongoing collaboration between IVL and this pulp mill, to be able to make a well functioning digital twin of the actual plant, more time and effort is needed to be put on the model. Many assumptions have been made, due to the fact that the topic of lignin and lignin extraction processes are a rather new topic in the industry. Not many mills have implemented this method, which make the shared knowledge very limited. For example, the temperature has been concluded important for the filterability of lignin, but have not been very implemented into the model, thus this can be one thing that need to be more investigated for the future. To be more certain about the temperature, a good solution can be analyses in the lab of how filterability depends on temperature in different steps throughout the process. Also, experiments on what the HHV of this specific case would end up being if 50% black liquor was extracted for lignin production would be of interest. Also, the HHRR and adiabatic combustion temperature are related to the HHV and would also be needed to be further investigated for this specific case. Another thing that needs to be studied more in depth if the lignin recovery plant is to be built in the future, is more precise investigations of how much CO_2 and H_2SO_4 that is optimal to use. In this project, the recommended highest values and average values were chosen, due to limited knowledge. However, an optimum between added amount of acid, time, and price paid should exist for every ton of lignin that is extracted.

To make the model even more accurate, real-life experiments need to be conducted, to fit the real plant as good as possible. The composition of black liquor is one thing that should be analysed to be more certain instead of relying too much on other studies and literature values. However, even if experiments with the black liquor from the specific pulp mill were conducted, the liquor changes in composition also within the plant, depending on how the plant is performing.

Also, problems with scaling in the evaporation plant is a question to further investigate for the future. The best solution right now seems to have an internal production of H_2SO_4, to get rid of excess sulphur that contributes to the build up of scaling, to keep the Na/S ratio, and to keep the operational costs down.

Bibliography

[1] Göran Gellerstedt, Monica Ek, and Gunnar Henriksson. *Wood chemistry and biotechnology*. 2009. doi: 10.1515/9783110213409.

[2] Iqra Zubair Awan, Nathalie Tanchoux, Françoise Quignard, Stefania Albonetti, Fabrizio Cavani, and Francesco Di Renzo. Heterogeneous Catalysis as a Tool for Production of Aromatic Compounds from Lignin. In *Studies in Surface Science and Catalysis*, volume 178. 2019. doi: 10.1016/B978-0-444-64127-4.00013-6.

[3] B. Prieur, M. Meub, M. Wittemann, R. Klein, S. Bellayer, G. Fontaine, and S. Bourbigot. Phosphorylation of lignin: characterization and investigation of the thermal decomposition. *RSC Advances*, 7(27), 2017. ISSN 20462069. doi: 10.1039/c7ra00295e.

[4] Karin Pettersson, Maryam Mahmoudkhani, and Anna von Schenck. Opportunities for biorefineries in the pulping industry. *Systems Perspectives on Biorefineries, Björn A. Sandén (ed.)*, 2012.

[5] Elin Svensson, Holger Wiertzema, and Simon Harvey. Potential for Negative Emissions by Carbon Capture and Storage From a Novel Electric Plasma Calcination Process for Pulp and Paper Mills. *Frontiers in Climate*, 3, 2021. ISSN 26249553. doi: 10.3389/fclim.2021.705032.

[6] Monica Ek, Göran Gellerstedt, and Gunnar Henriksson. *Pulping chemistry and technology*. 2009. doi: 10.1515/9783110213423.

[7] Herbert Sixta. *Handbook of Pulp*, volume 1-2. 2008. doi: 10.1002/9783527619887.

[8] Global pulp production by type 2021 | Statista. URL `https://www.statista.com/statistics/1177461/global-pulp-production-by-type/`.

[9] Pulp & paper - Fuels & Technologies - IEA. URL `https://www.iea.org/fuels-and-technologies/pulp-paper`.

[10] Himadri Roy Ghatak. Biorefineries from the perspective of sustainability: Feedstocks, products, and processes, 2011. ISSN 13640321.

[11] How EU pulp and paper industry can reduce greenhouse gas emissions. URL https://joint-research-centre.ec.europa.eu/jrc-news-and-updates/how-eu-pulp-and-paper-industry-can-reduce-greenhouse-gas-emissions-2018-09-25_en.

[12] Valmet. The next generation LignoBoost – tailor-maid lignin production for different lignin bioproduct markets. *Valmet*, May 26, 2017.

[13] Hodásová Ludmila, Jablonský Michal, Škulcova Andrea, and Ház Aleš. Lignin, potential products and their market value. *Wood Research*, 60(6), 2015. ISSN 13364561.

[14] Melih Soner Celiktas and Fikret Muge Alptekin. Biorefinery concept : Current status and future prospects. *International Conference on Engineering Technologies*, (December 2017), 2019.

[15] Kau Se, / En, / Vipp, and Jonas Kihlman. VIPP VALUES CREATED IN FIBRE-BASED PROCESSES AND PRODUCTS On the resource effi ciency of kraft lignin extraction. URL http://www.diva-portal.org/smash/get/diva2:1503636/FULLTEXT02.pdf.

[16] Pratima Bajpai. The Pulp and Paper Industry. In *Pulp and Paper Industry*. 2017. doi: 10.1016/b978-0-12-811099-7.00002-2.

[17] Kraft Pulp Mill Process | Encyclopedia MDPI. URL https://encyclopedia.pub/entry/602.

[18] Davide Di Francesco, Christian Dahlstrand, Joakim Löfstedt, Alexander Orebom, Johan Verendel, Christopher Carrick, Åsa Håkansson, Sören Eriksson, Henrik Rådberg, Henrik Wallmo, Martin Wimby, Florian Huber, Christopher Federsel, Mattias Backmark, and Joseph S.M. Samec. Debottlenecking a Pulp Mill by Producing Biofuels from Black Liquor in Three Steps. *ChemSusChem*, 14(11), 2021. ISSN 1864564X. doi: 10.1002/cssc.202100496.

[19] David T. Clay. EVAPORATION PRINCIPLES AND BLACK LIQUOR PROPERTIES. URL https://www.tappi.org/content/events/08kros/manuscripts/3-1.pdf.

[20] Marcus R Olsson. Thesis for the Degree of Doctor of Philosophy Simulations of Evaporation Plants in Kraft Pulp Mills Including Lignin Extraction and Use of Excess Heat. 2009. URL https://core.ac.uk/download/pdf/70579798.pdf.

[21] Per Tomani. The lignoboost process. In *Cellulose Chemistry and Technology*, volume 44, 2010.

[22] Keijo Salmenoja. Development of Kraft Recovery Boilers-What have been the Main Development Steps?

[23] Esa Kari Vakkilainen. Recovery Boiler. In *Steam Generation from Biomass*, pages 237–259. Elsevier, 2017. doi: 10.1016/b978-0-12-804389-9.00011-3.

[24] Erkki Välimäki, Piia Niemi, and Kari Haaga. A case study on the effects of lignin recovery on recovery boiler operation. In *International Chemical Recovery Conference*, volume 2, 2010.

[25] Per Tomani. Lignin extraction from black liquor , 2010. URL `https://www.celso-foelkel.com.br/artigos/outros/03_Lignin%20extraction_Per%20Tomani_Innventia.pdf`.

[26] Marlene Kienberger, Silvia Maitz, Thomas Pichler, and Paul Demmelmayer. Systematic review on isolation processes for technical lignin. *Processes*, 9(5), 2021. ISSN 22279717. doi: 10.3390/pr9050804.

[27] Martin A. Hubbe, Raimo Alén, Michael Paleologou, Miyuru Kannangara, and Jonas Kihlman. Lignin recovery from spent alkaline pulping liquors using acidification, membrane separation, and related processing steps: A review, 2019. ISSN 19302126.

[28] Esa Vakkilainen and Erkki Välimäki. Effect of lignin separation to black liquor and recovery boiler operation. In *TAPPI Press - TAPPI Engineering, Pulping and Environmental Conference 2009 - Innovations in Energy, Fiber and Compliance*, volume 3, 2009.

[29] Valmet. Control of suldifity in a modern kraft pulp mill. *Valmet*, May 26, 2017.

[30] Markus Persson. Mapping of sodium/sulphur-balances A study on losses in a kraft pulp mill.

[31] Simulink - Simulation and Model-Based Design. URL `https://se.mathworks.com/products/simulink.html`.

[32] Rickard Wadsborn. Personal communication, 2023.

[33] Julie Durruty. On the Local Filtration Properties of LignoBoost Lignin, Studies of the influence of xylan and ionic strength, 2017. URL `https://publications.lib.chalmers.se/records/fulltext/253312/253312.pdf`.

[34] Öhman Fredrik and Hans Theliander. Filtration properties of lignin precipitated from black liquor. *Tappi Journal*, 6(7), 2007.

[35] Henrik Wallmo, Martin Wimby, and Anders Larsson. Increase production in your recovery boiler with LignoBoost. In *TAPPI Press - TAPPI Engineering, Pulping and Environmental Conference 2009 - Innovations in Energy, Fiber and Compliance*, volume 4, 2009.

[36] Marcelo Hamaguchi and Esa K Vakkilainen. the Influence of Lignin Removal on the Energy Balance of. *XXI TECNICELPA Conference and Exhibition / VI CIADICYP 2010*, (October), 2010.

[37] Wenwen Fang, Marina Alekhina, Olga Ershova, Sami Heikkinen, and Herbert Sixta. Purification and characterization of kraft lignin. *Holzforschung*, 69(8), 2015. ISSN 1437434X. doi: 10.1515/hf-2014-0200.

[38] Ayumu Tagami, Claudio Gioia, Maris Lauberts, Tetyana Budnyak, Rosana Moriana, Mikael E. Lindström, and Olena Sevastyanova. Solvent fractionation of softwood and hardwood kraft lignins for more efficient uses: Compositional, structural, thermal, antioxidant and adsorption properties. *Industrial Crops and Products*, 129, 2019. ISSN 09266690. doi: 10.1016/j.indcrop.2018.11.067.

[39] Venla Partanen. Separation of Lignin in Pulp Mill Process and its Effect on Sodium Sulphur Balance , 2015. URL https://lutpub.lut.fi/bitstream/handle/10024/117328/Separation%20of%20lignin%20in%20Pulp%20Mill%20process%20and%20its%20effect%20on%20sodium-sulphur%20balance.pdf;jsessionid=CC4442F58A8D7CCD136D15A79A8BA1BA?sequence=2.

[40] Henrik Wallmo, Ulf Andersson, Mathias Gourdon, and Martin Wimby. Evaporation of lignin-lean black liquor, 2015. ISSN 07341415.

[41] Pratima Bajpai. *Pulp and Paper Industry: Energy Conservation*. 2016. doi: 10.1016/C2014-0-02105-3.

[42] H Loutfi, B Blackwell, and V Uloth. Lignin recovery from kraft black liquor : preliminary process design. *Tappi journal*, 74(1), 1991. ISSN 0734-1415.

[43] Elin Andersson and Arvid Skogström. Process Integration of Electric Plasma Calcination in Pulp and Paper Plants Techno-economic and greenhouse gas emission assessment includ-ing CO 2 utilisation options Master's thesis in Sustainable Energy Systems. 2020.

[44] US Producer Price Index: Chemicals and Allied Products: Sulfuric Acid. URL https://ycharts.com/indicators/us_producer_price_index_chemicals_and_allied_products_sulfuric_acid.

[45] Electricity prices in Sweden. URL https://euenergy.live/country.php?a2=SE2&utm_content=cmp-true.

[46] Caustic Soda Prices: Pricing, Chart, Latest Price, Market Analysis. URL https://www.procurementresource.com/resource-center/caustic-soda-price-trends.

[47] Valmet. Valmet Sulfuric Acid Plant - Savings and improved environmental performance. URL https://www.valmet.com/pulp/other-value-adding-processes/sulfuric-acid-plant/.

A

Appendix 1

A.1 The Simulink model

In this section, full pictures of the model in Simulink will be shown. Figure A.1 visualizes the draft model. In other words, how the model looked like when it was first received. This is the same as Figure 3.1 but in a better resolution to facilitate the understanding and actually see what the different boxes says. Figure A.2 visualizes the updated model, after some adjustments were done. This is the same as Figure 4.1 with the same explanation as above, to better see what the boxes actually says. The red circles in this figure shows how the pressate flows are splitted. The circle to the left represents the lignin-lean black liquor flow from the first filter press, that is re-circulated back into the evaporation plant just before the black liquor enters the recovery boiler. The circle to the right shows the wash liquor for re-circulation that will be re-circulated back to the evaporation plant in an earlier stage, before black liquor for lignin recovery is extracted.

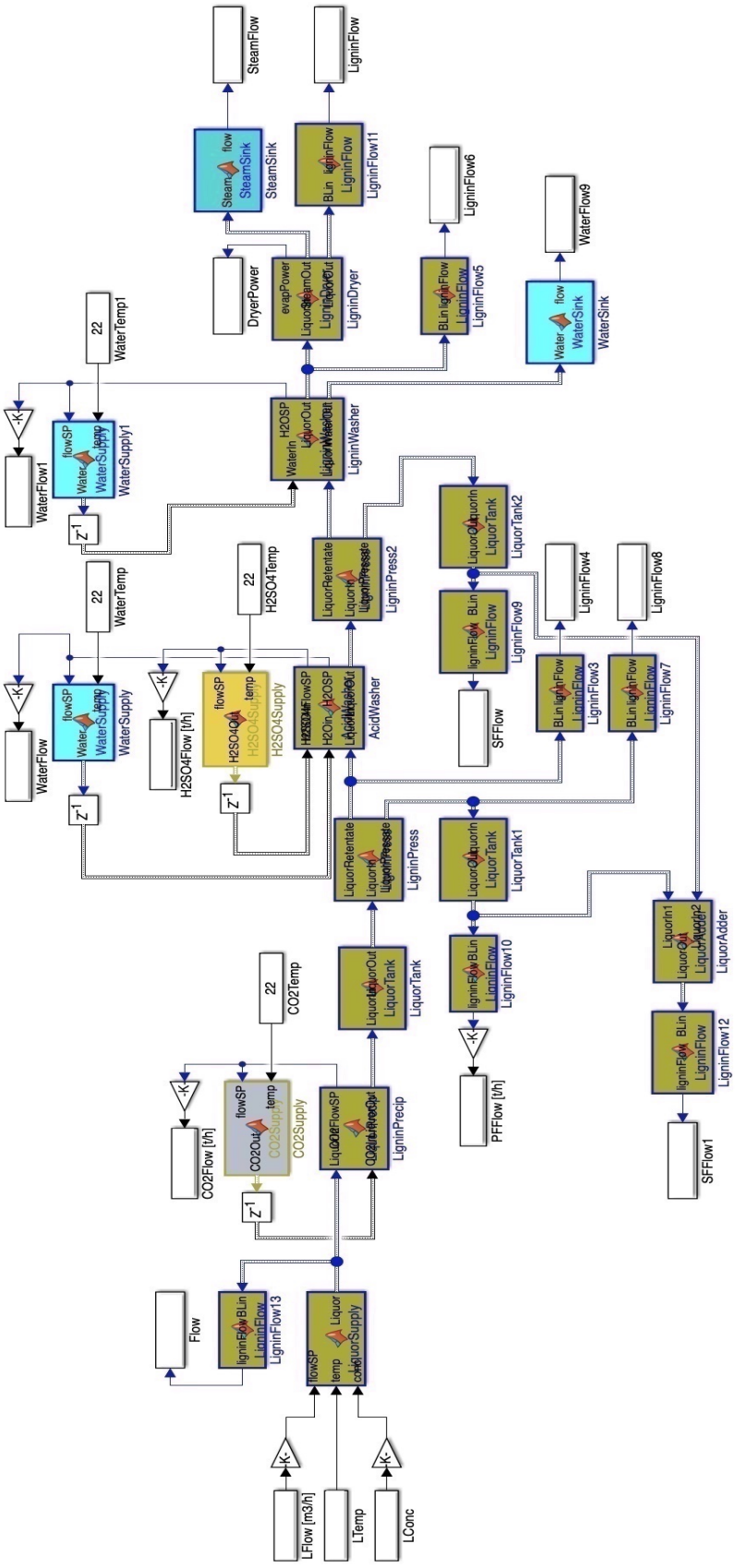

Figure A.1: The Simulink model from the beginning.

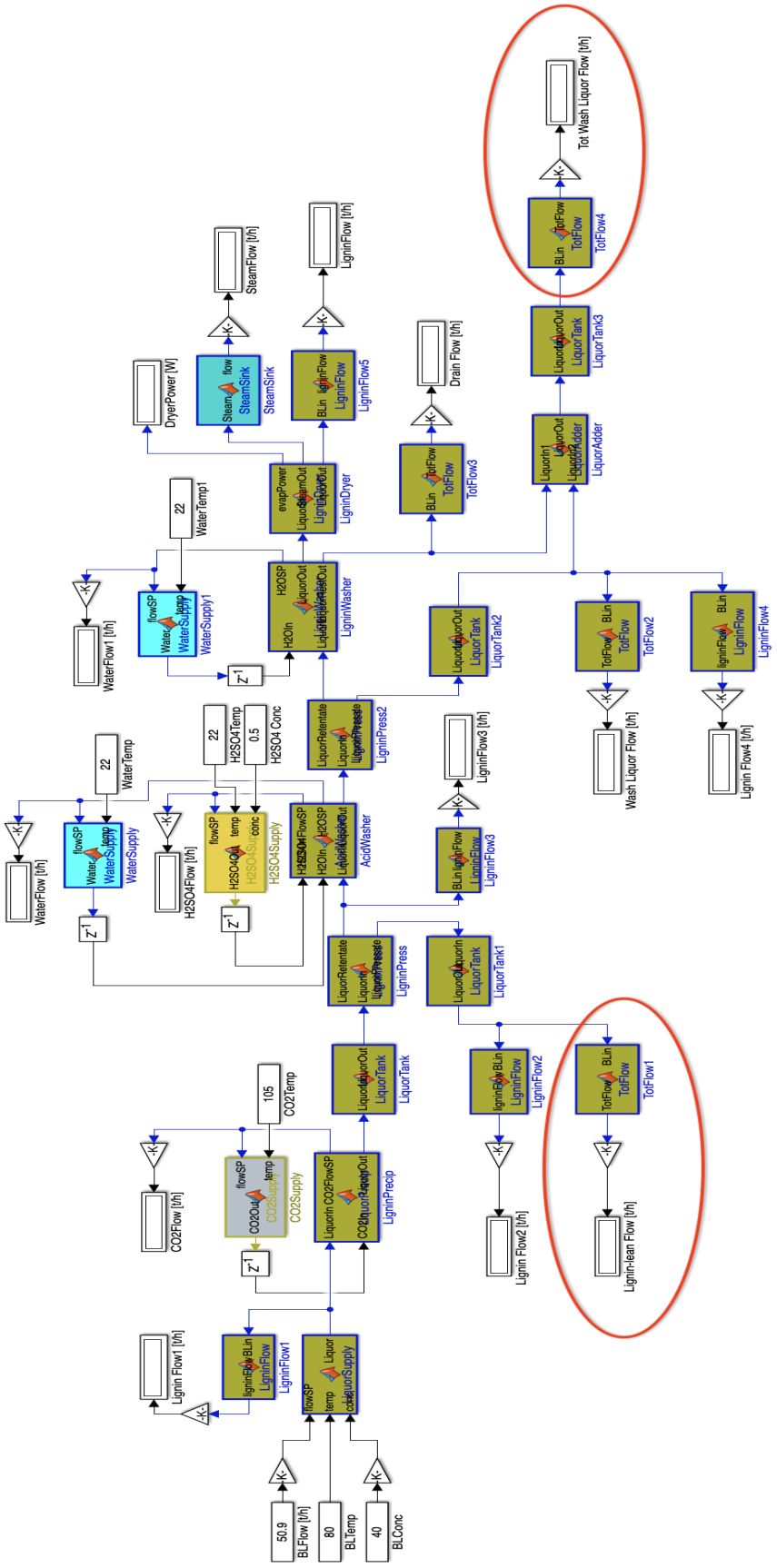

Figure A.2: The Simulink model with updated waste flows.

A.2 Full tables from analyses

In this section, the full tables from some analyses in the results shown up in the main text are shown. Figure A.3 is a summary of more values from the analysis that were conducted with the model in Simulink when using 320 kg CO_2/ton lignin and 255 kg H_2SO_4/ton lignin. Most of the values in the table are in the unit [t/h], except from the dryer power with the unit [W]. The same analysis have been made in Figure A.4, but with 220 kg CO_2/ton lignin and 175 kg H_2SO_4/ton lignin instead.

Figure A.5 is a summary of values used in the analysis with ash, sodium, and sulphur content when using 320 kg CO_2/ton lignin and 255 kg H_2SO_4/ton lignin. As can be seen, this is rather an extension of the analysis in Figure A.3 and Figure A.4. The same analysis have been made in Figure A.6, but with 220 kg CO_2/ton lignin and 175 kg H_2SO_4/ton lignin instead.

BL outtake	BL in	CO2 Supply	H2SO4 Supply	Lignin-lean flow	Total water supply	Wash liquor recirc	Dryer Power	Steam Flow	Lignin t/h	Lignin t/year
10%	50,9	0,32	0,255	47,27	27,798	34,41	121 600	0,1941	3,319	27879,6
15%	76,3	0,32	0,255	70,86	41,672	51,59	182 300	0,2909	4,975	41790
20%	101,8	0,32	0,255	94,55	55,61	68,83	243 300	0,3881	6,637	55750,8
25%	127,25	0,32	0,255	118,2	69,51	86,03	304 100	0,4852	8,296	69686,4
30%	152,7	0,32	0,255	141,8	83,41	103,2	364 900	0,5822	9,956	83630,4
35%	178,15	0,32	0,255	165,5	97,3	120,4	425 700	0,6792	11,61	97524
40%	203,6	0,32	0,255	189,1	111,2	137,7	486 500	0,7763	13,27	111468
45%	229,05	0,32	0,255	212,7	125,11	154,9	547 400	0,8733	14,93	125412
50%	254,5	0,32	0,255	236,4	138,99	172,1	608 200	0,9703	16,59	139356

Figure A.3: Summary of values gained from the model with the highest recommended values of added acids.

BL outtake	BL in	CO2 Supply	H2SO4 Supply	Lignin-lean flow	Total water supply	Wash liquor recirc	Dryer Power	Steam Sink	Lignin t/h	Lignin t/year
10%	50,9	0,22	0,175	47,16	25,698	31,42	112 400	0,1794	3,067	25762,8
15%	76,3	0,22	0,175	70,69	38,517	47,09	168 500	0,2689	4,598	38623,2
20%	101,8	0,22	0,175	94,32	51,4	62,83	224 800	0,3587	6,134	51525,6
25%	127,25	0,22	0,175	117,9	64,24	78,54	281 100	0,4484	7,668	64411,2
30%	152,7	0,22	0,175	141,5	77,08	94,25	337 300	0,5381	9,201	77288,4
35%	178,15	0,22	0,175	165,1	89,94	110	393 500	0,6278	10,73	90132
40%	203,6	0,22	0,175	188,6	102,78	125,7	449 700	0,7175	12,27	103068
45%	229,05	0,22	0,175	212,2	115,63	141,4	505 900	0,8071	13,8	115920
50%	254,5	0,22	0,175	235,8	128,44	157,1	562 100	0,8968	15,34	128856

Figure A.4: Summary of values gained from the model with the recommended average values of added acids.

BL outtake	BL in	CO2 Supply	H2SO4 Supply	Lignin t/h	Lignin t/year	Ash [kg/h]	Sodium [kg/h]	Sulphur [kg/h]
10%	50,9	0,32	0,255	3,319	27879,6	26,552	4,6466	82,975
15%	76,3	0,32	0,255	4,975	41790	39,8	6,965	124,375
20%	101,8	0,32	0,255	6,637	55750,8	53,096	9,2918	165,925
25%	127,25	0,32	0,255	8,296	69686,4	66,368	11,6144	207,4
30%	152,7	0,32	0,255	9,956	83630,4	79,648	13,9384	248,9
35%	178,15	0,32	0,255	11,61	97524	92,88	16,254	290,25
40%	203,6	0,32	0,255	13,27	111468	106,16	18,578	331,75
45%	229,05	0,32	0,255	14,93	125412	119,44	20,902	373,25
50%	254,5	0,32	0,255	16,59	139356	132,72	23,226	414,75

Figure A.5: Summary of calculated amounts of ash, sodium, and sulphur content in the final lignin with the highest recommended values of added amount of acids.

BL outtake	BL in	CO2 Supply	H2SO4 Supply	Lignin t/h	Lignin t/year	Ash [kg/h]	Sodium [kg/h]	Sulphur [kg/h]
10%	50,9	0,22	0,175	3,067	25762,8	24,536	4,2938	76,675
15%	76,3	0,22	0,175	4,598	38623,2	36,784	6,4372	114,95
20%	101,8	0,22	0,175	6,134	51525,6	49,072	8,5876	153,35
25%	127,25	0,22	0,175	7,668	64411,2	61,344	10,7352	191,7
30%	152,7	0,22	0,175	9,201	77288,4	73,608	12,8814	230,025
35%	178,15	0,22	0,175	10,73	90132	85,84	15,022	268,25
40%	203,6	0,22	0,175	12,27	103068	98,16	17,178	306,75
45%	229,05	0,22	0,175	13,8	115920	110,4	19,32	345
50%	254,5	0,22	0,175	15,34	128856	122,72	21,476	383,5

Figure A.6: Summary of calculated amounts of ash, sodium, and sulphur content in the final lignin with the recommended average values of added amount of acids.

A.3 Calculations of the flow of acids

To be able to calculate some economics regarding the needed amounts of acids, some simple calculations were conducted. The flow of H_2SO_4 were calculated in t/y by multiplying the flows in Table A.1 with 8400 h/y.

Table A.1: Flow of H_2SO_4 for the case with 220 kg CO_2/ton lignin and 175 kg H_2SO_4/ton lignin.

BL outtake [%]	H_2SO_4 flow [t/h]
10	0.7669
20	1.5335
30	2.2995
40	3.0678
50	3.8343

For this case with 220 kg CO_2/ton lignin and 175 kg H_2SO_4/ton lignin, it was calculated that for 50% of black liquor outtake would need a flow of 30 674 tH_2SO_4/y.

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