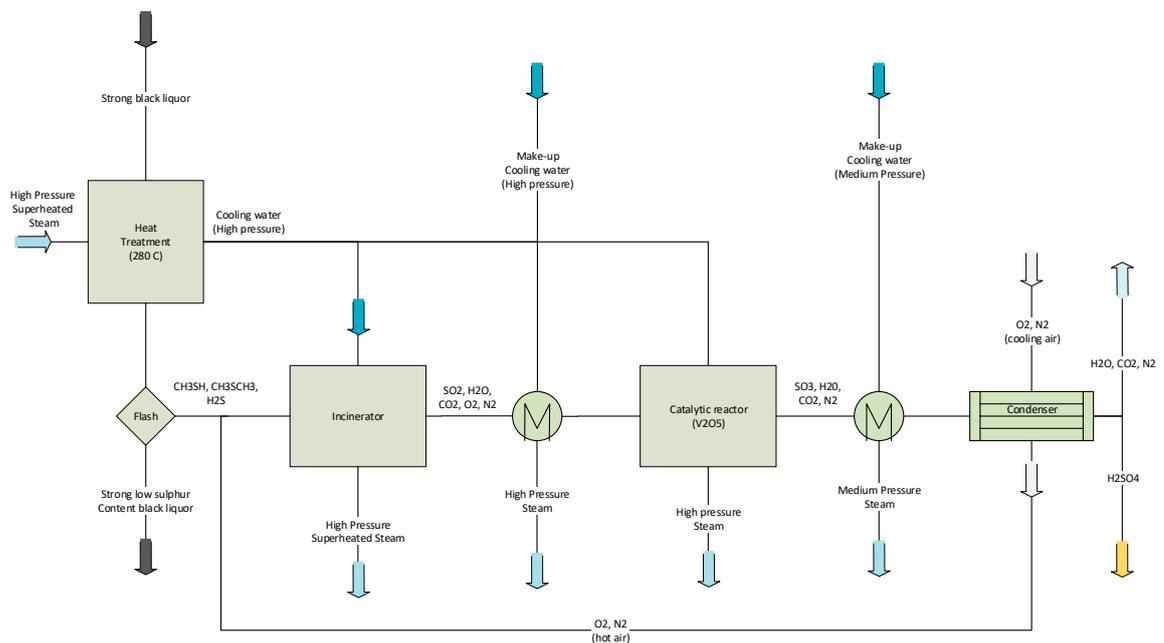


Raising the efficiency of black liquor lignin extraction



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by

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Foreword

First of all I would like to thank my family for their support during all these years at Lund University.

I would also like to thank Christer Gustavsson and Jonas Kihlman at Pöyry for giving me a chance to do this project and also providing me with answers when I was familiarizing myself with the topic.

Finally I would like to thank Christian Hulteberg for answering my many questions during the project.

Abstract

The aim of this report was to study possibilities of making the process of extracting lignin from black liquor at pulp and paper mills more efficient in the form of a literature study. Lignin is a commodity that is likely to become more valuable in the future due to work being done by a number of companies in utilizing it as for example a base for the production of renewable fuels and carbon fibre. At the current moment the extraction of lignin from black liquor is quite expensive so it is not yet common on an industrial scale thus it is important to find methods of reducing the costs. One of the more reliable methods of extracting lignin from black liquor is known as acid precipitation and involves utilizing mineral acids to lower the pH of the liquor and induce precipitation of solvated lignin into a solid form. Normally carbon dioxide is used in the initial precipitation step where the pH is lowered to 8-9 and then sulfuric acid is added reducing the pH of the lignin further to 2.5-3. Introducing sulfuric acid into the process however will affect the sodium-sulfur balance in the mill and excess sulfur must be purged to avoid reducing the quality of the pulp. Sulfur is commonly purged in the form of dust from the electrostatic precipitator with this dust also containing sodium compounds. This will in turn reduce the sodium content in the mill calling for the demand of make-up sodium which costs quite a bit more than sulfuric acid. By choosing to utilize pre-existing process streams of sulfur and carbon dioxide at the mill for use in acid precipitation one can potentially avoid additional chemical costs and avoid upsetting the sulfur balance. Thus the primary goal of this project has been to study the possibility of utilizing carbon dioxide at the mill for acid precipitation and determining a method of separating sulfuric compounds from black liquor and converting them into sulfuric acid.

It was found that the required carbon dioxide could be supplied from flue gases leaving both the lime kiln and recovery boiler. As the carbon dioxide needed must be of a high purity amine-based chemical absorption was the chosen method of separation. Unfortunately this also introduced a high steam cost due to the rather low concentration of carbon dioxide in the process streams, this coupled with the reasonably low costs of purchasing carbon dioxide from an outside source lead to the feasibility of this method being questionable.

From a number of separation methods it was found that the thermal treatment of black liquor was an efficient method of separating volatile organic sulfur compounds. The treatment itself involves exposing the black liquor to elevated temperatures during alkaline conditions leading to the formation of sulfuric off-gases. In addition the viscosity of the liquor is reducing causing additional benefits such as increased recovery boiler capacity.

The conversion of the sulfuric compounds was done through the wet sulfuric acid process and a preliminary simulation in Aspen was done to clarify that the process was reasonable. From the results it was found that even in a worst-case scenario enough sulfuric acid could be produced to cover a theoretical 70 mass% extraction of lignin.

The big question mark over the project was the thermal treatment of the liquor. If future work was done it should include studies on how high the heat demand for thermal treatment is and how varying parameters such as retention time and alkali charge effect off-gas formation.

Abstrakt

Målet med denna rapport har varit att studera möjligheten att göra processen för extraktionen av lignin ifrån svartlut på massabruk mer effektivt i form av en litteraturstudie. Lignin är en råvara som troligtvis kommer att bli mer värdefull i framtiden på av att många företag studerar idag möjligheten att använda den som en bas i produktionen av förnybara bränslen och kolfiber. För tillfället så är extraktionen av lignin ifrån svartlut dyrt och är inte vanlig på industrial skala därför är det viktigt att hitta metoder för att reducera kostnader. En av de mer pålitliga metoderna för ligninextraktion är utfällning med hjälp av syra och använder mineralsyror för att reducera pH av svartluten vilket leder till att det lösta ligninet fälls ut i en fast form. Vanligtvis används koldioxid i det första utfällningssteget då pHt reduceras till 8-9, följande detta används svavelsyra för att reducera pHt ytterligare till 2.5-3. Introduktionen av svavelsyra i processen kommer att påverka natrium-svavelbalansen i bruket och överskottet av svavlet måste separeras för att undvika att kvaliteten på producerad pappersmassa påverkas. Svavel separeras ofta i form elfilteraska, denna aska innehåller dock också natrium. Denna separation kommer leda till ett behov av en tillsats av natrium för att balansen skall regleras och är betydligt dyrare än svavelsyra. Genom att utnyttja svavel- och koldioxidhaltiga strömmar i massabruket så är det möjligt att reducera kemikaliekostnader och undvika att natrium-svavelbalansen rubbas. På grund av detta så är huvudmålet för detta projekt att undersöka möjligheten att utnyttja koldioxid på massabruket för syreutfällning och designa en process för att separera svavelhaltiga komponenter ifrån svartluten och omvandla dem till svavelsyra.

Det upptäcktes att gasströmmarna som lämnade både sodapannan och mesaugnen innehåller tillräckligt med koldioxid för en lämplig separation av lignin ifrån svartlut. Koldioxiden måste dock vara av hög renhet och därför valdes aminbaserad kemisk absorption. Tyvärr så introducerade detta en stor ångkostnad på grund av den låga koncentrationen av koldioxid i procesströmmarna. Detta tillsammans med de relativt låga kostnaderna för att köpa koldioxid ifrån en yttre källa ledde till att denna metod bedömdes som ej pålitlig.

Ifrån flera separationsmetoder så valdes värmebehandling av svartlut ut som den mest effektiva metoden för att separera organiska lättflyktiga svavelkomponenter. I själva behandlingen utsätts svartluten för höga temperaturer under alkaliska förhållanden vilket leder till att svavelhaltiga gaser bildas. Utöver detta så reduceras viskositeten av svartluten vilken medför fler fördelar som ökad kapacitet i sodapannan.

Omvandlingen av de svavelhaltiga komponenterna gjordes genom den våta svavelsyreprocessen och en preliminär simulering i Aspen gjordes för att bekräfta att processen av pålitlig. Ifrån beräkningsresultaten så visade det sig att även om separationen och omvandlingen av svavelgaser var låg så var det möjligt att uppnå en teoretisk separation av 70 mass% av lignin.

Det stora frågatecknet under arbetets gång har varit värmebehandlingen av svartlut. Om arbete görs i framtiden med ett liknande tema så vore det fördelaktigt om det studerades om hur högt värmebehovet för värmebehandling av svartlut är och hur olika parametrar som alkali laddning och retentionstid påverkar bildandet av svavelgaser.

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1. Introduction

In recent time's lignin as a resource has been a topic of particular interest. One of the reasons for this are the increased environmental legislations that are dedicated towards reducing the emissions of carbon dioxide.

One attractive source of lignin is from pulp and paper mills where it can be extracted from black liquor as a product in a series of process steps. Lignin extraction as a technology has been utilized on a laboratory scale for quite a while; however, beyond a few smaller start-up mills it is not yet common on an industrial scale. Part of the reason for this is simply that until recently lignin has not been in a particularly large demand but with more companies looking into the possibility of using lignin as a base for a bio-fuel in the future and even the production of carbon fibres this is likely to change soon. Extraction of lignin would also reduce the load on the recovery boiler allowing for the possibility of producing more pulp without it having to modify the boiler. [4,29]

Because of this it is of interest to study various possibilities to improve steps in the lignin extraction process to make it more profitable. This project as a whole is composed of a literature study regarding methods of improving the efficiency of process steps during lignin extractions and is performed in collaboration with Pöyry in Karlstad. Topics of particular interest include reducing the demand for chemicals from outside sources during extraction by utilizing pre-existing process streams at the mill. Other factors that will be looked into include the difference between the currently promising acid based lignin extraction methods, the mechanisms behind lignin precipitation, what volatile sulfurs exist in black liquor and how they are formed and the benefits of black liquor oxidation.

1.1 Aim and Scope

As mentioned above this project will mainly consist of studying various methods of extracting lignin from black liquor and how they can be made more efficient, the mechanisms behind lignin precipitation is also of interest.

The primary goal at hand is to determine the feasibility of utilizing existing process streams at the mill as a source of chemicals for lignin extraction. The chemicals that are of interest are carbon dioxide which is utilized for the initial precipitation of lignin from black liquor and sulfuric acid which is utilized in the acidification of the lignin and black liquor or lignin slurry based on chosen process for lignin extraction.

Carbon dioxide is mainly formed during combustion in the lime kiln and recovery boiler at the mill alongside other gases. In order for the carbon dioxide to be utilized it must be concentrated and have a higher purity which requires it to be separated from these flue gas streams. Topics of interest is how said carbon dioxide can be separated and if the chosen method is more feasible than simply purchasing CO₂.

During the kraft process highly volatile sulfurous compounds are formed and are known as Total Reduced Sulfurs (TRS). If not treated or separated these compounds will be emitted at various points at the mill. When sulfuric acid from an outside source is used during lignin

extraction it will also affect the sodium sulfur balance which can reduce pulp quality and increase TRS emissions. By choosing to separate the volatile sulfurs in black liquor and converting them into sulfuric acid for use during lignin extraction one not only reduces sulfur emissions at the mill but also avoids other issues with using sulfuric acid from an outside source such as a higher demand for make-up sodium.

Producing sulfurous off-gases through the use of thermal treatment or black liquor oxidation were the two initial suggestions for extracting the volatile sulfurs from the liquor. These were the methods that were looked into most in-depth. Black liquor oxidation was determined to not be a reliable method of producing sulfurous off-gases however as the process still provides many other benefits it was considered of interest to study further. In addition to this a preliminary simulation for the conversion of the separated sulfurs into sulfuric acid was to be designed in Aspen Plus in order to determine the feasibility of the process.

2 Background

2.1 The Kraft process

Today the most common method of producing pulp and paper from wood is through the Kraft process.

The wood used is debarked and chipped prior to being treated. The first step following this consists of mixing the wood chips in a chemical mixture known as white liquor in a digester where it is cooked allowing for the separation of much of the cellulose fibres present in the wood chips, the liquor itself mainly consists of sodium hydroxide and sodium sulphide solved in water. The cellulose fibres present in the wood are then separated from the cooking liquor and washed for pulp production.

Following this separation the now spent liquor becomes known as black liquor. [18]

2.2 Black liquor

As mentioned above black liquor is formed during the pulping process and is its main by-product. An important thing to note is that the composition of black liquor varies greatly based on a number of factors. As black liquor is formed as a result of the impregnation and cooking step of wood chips the main factor involved in determining its composition is the chemicals used in this step, the type of raw material processed and the operational conditions of the pulping step. This means that it is not possible to list a general chemical composition for black liquor as it not only varies based on the mill in question but could also vary based on day if the sulfidity is altered. The dry solid chemical composition of the liquor will also vary based on the point of the mill where it was measured, liquor in the same mill may for example possess a higher sodium sulfide concentration right after the digester compared to after a direct-contact evaporator. Black liquor that has been stored for a period of time may also be subjected to oxidation due to contact with air leading to a presence of dimethyl disulfide.

Black liquor is an aqueous solution composed of both organic and inorganic substances with a possible composition being displayed in table 2.1. The organic substances are to a large degree composed of hydrophilic lignin with varying molecular weight formed during the delignification step, additional organic fractions include hemicellulose and other organic compounds that were present in the wood. Inorganic compounds present include sodium sulfide, sodium hydroxide and varying other components including a number of salts that have been dissociated into ionic species giving black liquor a high ionic strength. [1]

Table 2.1. A possible composition of black liquor divided into organic and inorganic components. [24]

	Weight percentage
Organic	73.64
C	34.65
H	3.46
N	0.10
S	4.09
Na	21.40
K	2.20
Cl	0.15
O	33.95
Inorganics	26.36

2.3 Recovery cycle

In order to avoid wasting precious chemicals during the pulping process a recovery cycle is utilized in order to convert the now spent chemicals in black liquor so they can be reused.

In its initial state black liquor possesses a fairly low solid content where it is known as weak black liquor, to lessen the burden of the recovery boiler much of the water present is evaporated. Using a series of evaporators the solid content is raised to about 60-70% where it is known as strong black liquor.

Following this the concentrated black liquor is led into the recovery boiler where it is burnt producing a smelt of sodium carbonate and sodium sulfide. In addition to this as the solved lignin present has a high energy content a large quantity of heat is released which is utilized for steam generation. An excess of heat is normally generated which allows most mills to be self-sufficient in regards to steam demand. In certain cases steam is also used for the generation of electricity through the use of steam turbines.

The remaining smelt from the boiler is then dissolved in water leading to the formation of what is known as green liquor. The green liquor is then sent to the causticizing plant where it reacts with burnt lime produced in the limekiln. Together with the burnt lime sodium carbonate from the green liquor forms sodium hydroxide, in addition calcium carbonate or as it is also known "lime mud" is precipitated. The newly formed white liquor is reintroduced to the digester while the lime mud is sent to the limekiln where it is regenerated into CaO for further use. A flowsheet displaying said cycle can be seen in figure 2.1. [2]

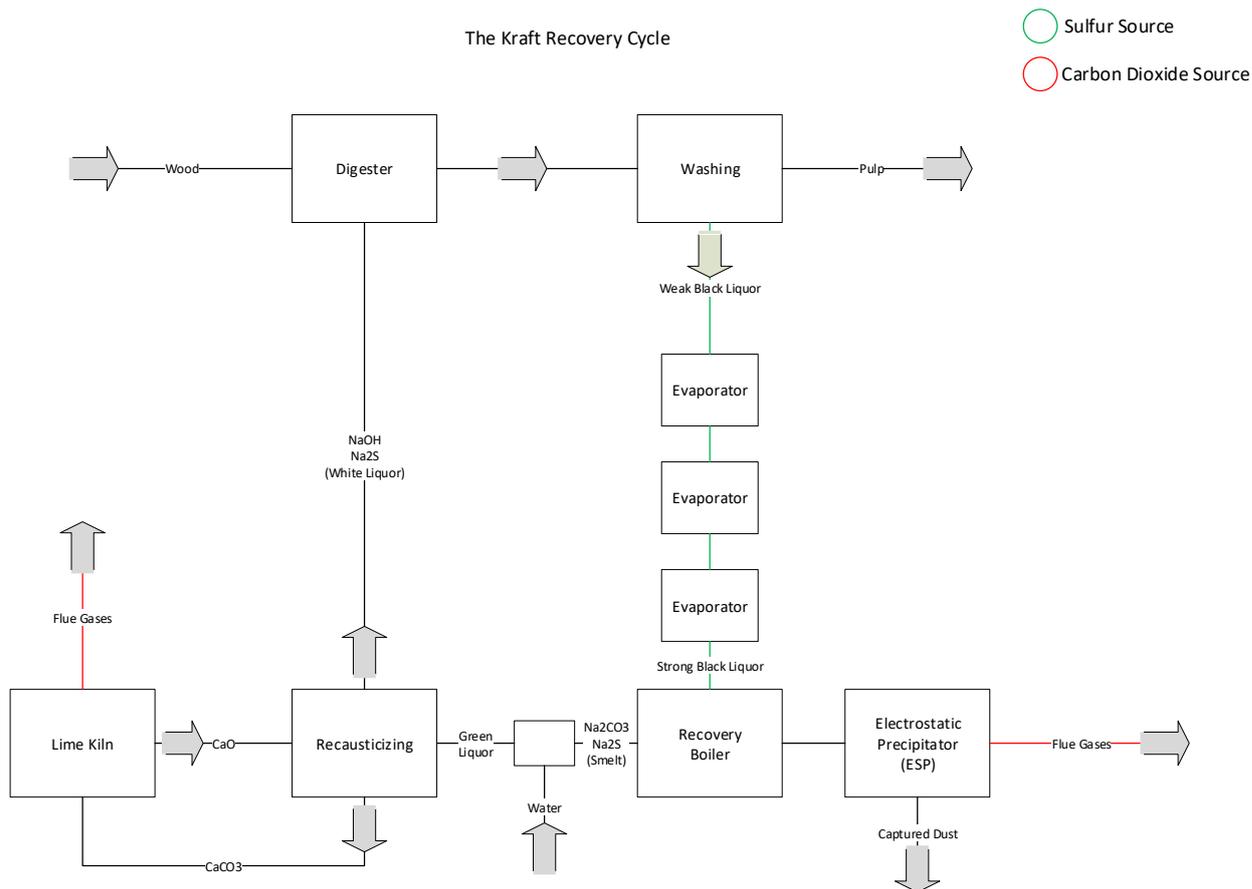


Figure 2.1. A flowsheet describing the kraft recovery cycle with the points of interest for sulfur and carbon dioxide separation. Modified after [18]

2.4 Organic sulfurs

A common problem for most pulp mills are the odorous sulfur containing compounds formed during varying process steps. Because of their volatility they are expelled at multiple points and are responsible for the characteristic odors present at paper mills. The volatile sulfurous substances formed are mainly hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3) and dimethyl disulfide (CH_3SSCH_3). Odor thresholds for said sulfurs are displayed in table 2.2.

The formation of hydrogen sulfide is the result of sodium sulfide reacting through a pH dependant hydrolysis. This reaction will only occur when the pH of black liquor is below 9 to 10 which happens mainly in direct contact evaporators where flue gases from the mill are used as a source of heat to concentrate the liquor. As these gases contain carbon dioxide the pH of the liquor will be reduced. This occurs according to the reaction presented below



In order to prevent this reaction from occurring it may be reasonable to concentrate untreated black liquor through the use of indirect heat exchangers.

Methyl mercaptan and dimethyl sulfide are only formed in the digester and are emitted at varying points in the mill. The formation of methyl mercaptan is a result of a reaction between

a lignin methoxyl group and a hydrosulfide ion while the formation of dimethyl sulfide is formed by a lignin methoxyl group reacting with a methyl sulfide group. [1]

Dimethyl disulfide is formed from the oxidation of methyl mercaptan when the digester has been relieved to atmospheric pressure and through the oxidation of black liquor. [7]

Table 2.2. The odor thresholds for Total Reduced Sulfurs being emitted from the mill.[7]

Compound	Odor Threshold, ppb
H ₂ S	0.4-5
CH ₃ SH	2-3
CH ₃ SCH ₃	1
CH ₃ SSCH ₃	1-5

With increased environmental legislations recently there has been a greater effort to reduce the emissions of these compounds through various methods including the absorption of them through the utilization of white liquor or through incineration in for example the lime kiln or a dedicated incinerator. [19]

2.5 Sodium/sulfur balance

An important aspect of the chemical recovery cycle is to maintain the balance between the concentrations of sodium and sulfur. If the concentration of sodium hydroxide and sodium sulfide in the recycled white liquor has a moderate deviation from the initial composition used the quality and characteristics of the produced pulp can vary greatly. If the mill operates at a high sulfur content for example risks of equipment corrosion and increased emissions of Total Reduced Sulfurs are introduced.

Maintaining the sodium-sulfur balance can be a challenge due to the fact that the chemical recovery cycle features many points in which losses are present in the form of for example emissions. This in turn leads to the need of introducing make-up chemicals to the plant in order for balance to be maintained. [18]

One method of reducing the sulfur content of the mill is by purging electrostatic precipitator ash from the recovery boiler. It is important to note that sodium will also be purged through this method which means that sodium make-up will be necessary.

3 Lignin extraction

3.1 Precipitation of lignin

Lignin present in black liquor possesses different attributes compared to that of lignin in its normal state. For starters it is in a liquid hydrophilic form which means that it must be treated prior to separation steps. The solvated lignin in black liquor will under normal conditions take the form of large colloidal macromolecules although a small fraction is dissolved in the form of smaller molecules. As long as the alkaline conditions of black liquor are retained the behaviour of the colloidal lignin will depend on a balance between attractive and repulsive forces acting upon it. The attractive forces that affect the lignin particles consist of Van der Waal's forces.

The repulsive forces are the result of the ionizable groups present in the lignin macromolecules. At high pHs the lignin is kept stable and soluble due to ionized hydrophilic groups, with these mainly being phenolic hydroxyls and carboxyls.

Colloidal lignins will remain soluble as long as the repulsive forces caused by these ionized hydrophilic groups exceed the attractive forces between lignin particles. If the pH of the black liquor is allowed to be reduced however (pH=11) the repulsive forces will be reduced due to dissociated groups accepting protons and lignin will begin to precipitate. The majority of soluble lignin present will have precipitated upon the black liquor reaching a pH of 9 and below. [3]

With the lignin forming solid, non-soluble particles, the task of separating them will be significantly easier.

3.2 Lignin separation

A common method used for inducing the precipitation of lignin is through acid precipitation. By introducing a mineral acid or carbon dioxide to the black liquor to reduce its pH, it is possible to reduce the solubility of the lignin through the mechanics described above.

Carbon dioxide tends to be the preferable choice of chemical in inducing precipitation as unlike for example sulfuric acid it does not have a negative impact on the sodium sulfur balance nor does it introduce additional chemicals into the recovery cycle that will have to be separated at a later stage. Upon reaching the desired pH for precipitation the lignin is filtered with for example a filter press while being washed with water and acid (for example sulfuric acid). The biggest problem with this method of extracting lignin is the poor filtration rates. One alternative in improving filtration rates is the usage of a larger filtration area however this introduces a relatively large cost. In addition the lignin achieved through this method tends to have high levels of impurity which can make it unattractive for potential buyers. [4]

In recent times a number of methods have been developed to achieve superior filtration conditions, some of the more noteworthy methods are described below.

3.3 LignoBoost

The poor filtration rates and plugging of the filter cake during the separation of lignin is to a large degree caused by variations in lignin solubility. Due to a still rather high pH there exist ionic strength gradients in the lignin filter cake during washing. This can in turn lead to the lignin precipitating in the filter medium or returning to a colloidal form.

In the LignoBoost process designed by Innventia the black liquor is taken from the evaporation plant. Following this the pH of black liquor is reduced through the absorption of carbon dioxide inducing precipitation. The solid lignin is then separated from the liquor in a filtration step with the now lignin lean liquor being sent back to the evaporators. The lignin cake formed in the filtration step is then re-dispersed by mixing it with spent wash water, sulphuric acid is also added reducing the pH to about 2.5. During this second acidification step carbonate and sulphide ions present in the black liquor will form gaseous carbon dioxide and hydrogen sulfide which can be re-circulated to the first acidification step to reduce the demand for carbon dioxide. The acidified lignin slurry is then introduced to a second filtration step where it is also washed. The full process is seen in figure 3.1.[11]

The benefit this method provides compared to the one discussed above is through raising the acidity further there will be little to no changes in pH or ionic strength during the washing step minimizing the risk of changes in lignin solubility causing filter plugging. Instead this occurs during the second acidification step. This also reduces the quantity of wash water needed which in turn lessens the impact on the evaporation plant.

In addition to the improved filtration rates additional benefits include a lignin product with a higher content of dry solids and less ash and carbohydrates compared to earlier lignin separation methods where only one filter was utilized. [5]

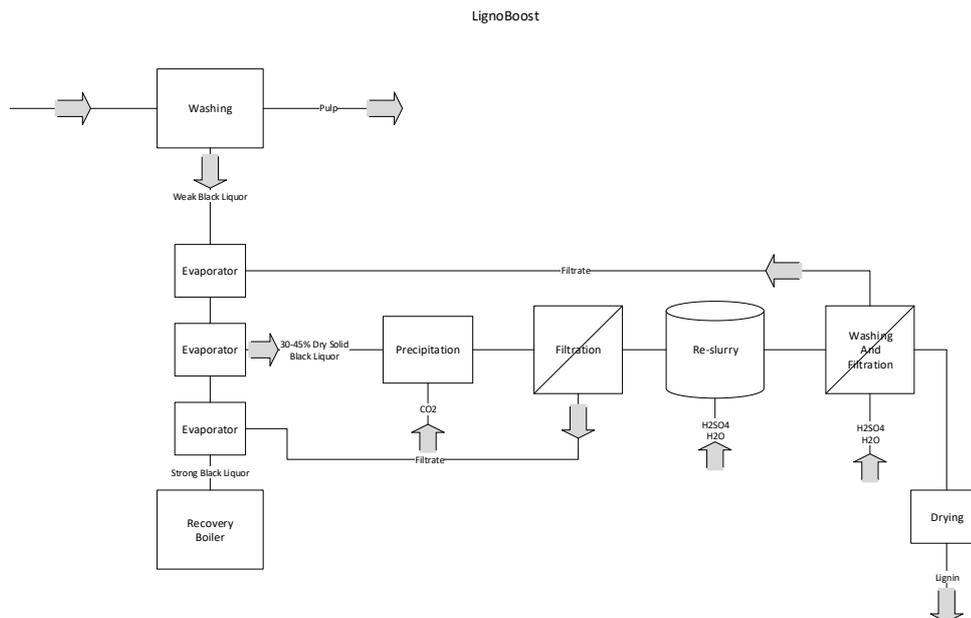


Figure 3.1. A flowsheet describing the LignoBoost process for separating lignin from black liquor through two-step filtration. Modified after [13]

3.4 LignoForce

In a further method known as LignoForce developed by FPInnovations the filtration conditions of black liquor are improved through oxidation.

After being extracted from the evaporators the black liquor is oxidized, acidified, filtered and washed with water and acid with the finished product then being solid lignin.

Due to oxidation reactions being exothermic heat is generated in the liquor in a well distributed fashion improving the conditions for the formation of larger lignin particles during precipitation. These larger lignin particles have been proven to achieve superior filtration rates compared to those achieved with untreated black liquor.

When black liquor is oxidized sugars are converted into organic acids which leads to an overall reduction of pH. Total reduced sulphurs also form non-volatile compounds such as dimethyl sulphone. As issues regarding lignin extraction from black liquor include high acid consumption and TRS emissions it can be seen that the LignoForce process not only improves the conditions for filtration but also reduces costs for acidification and sulphur emissions. The reduced chemical demand can be seen in table 3.1. and the full process in figure 3.2. [6]

Table 3.1. Demand for carbon dioxide and sulfuric acid during lignin separation from black liquor with and without black liquor oxidation. [6]

	Without BL oxidation	With BL oxidation
CO ₂ consumption (kg/kg of lignin)	0.5-0.6	0.2-0.4
H ₂ SO ₄ consumption (kg/kg of lignin)	0.3-0.4	0.2-0.3

Unlike the LignoBoost process less hydrogen sulfide or carbon dioxide is formed in the acidification step. This is due to the fact that a great deal of the formation of these compounds in this step is caused by sodium hydrosulfide reacting with sulfuric acid, however when black liquor has been oxidized sodium hydrosulfide and sodium sulfide are converted into sodium thiosulfate which does not form these compounds when reacting with sulfuric acid. It is worth noting however that sulfur dioxide is formed instead however it is in much smaller quantities and is generally not worth recycling to the acidification steps.[13]

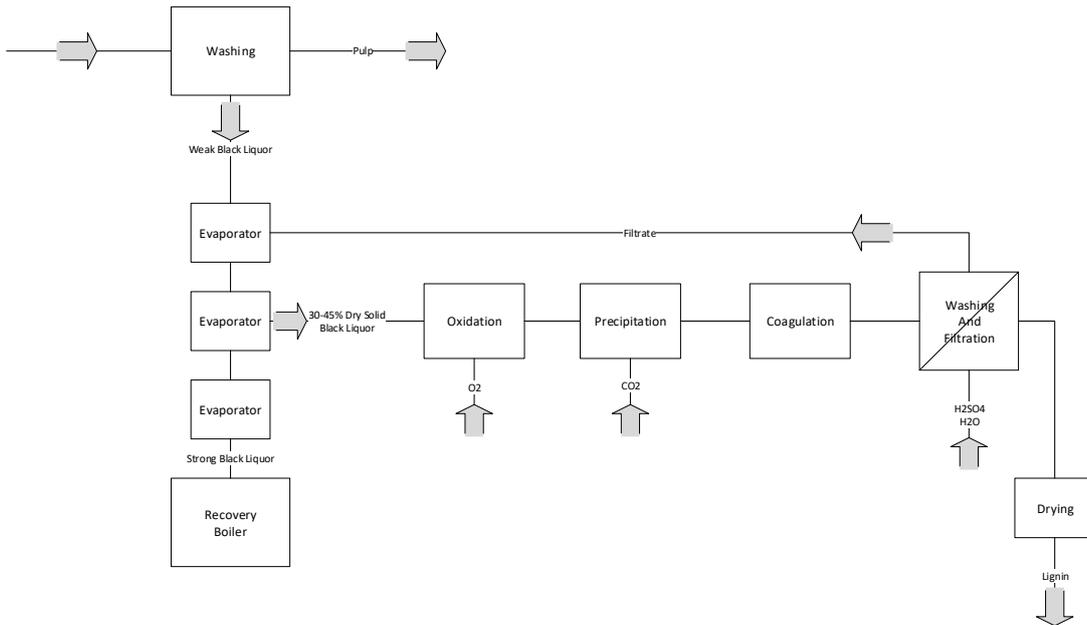


Figure 3.2. A flowsheet describing the LignoForce process for the separation of lignin from black liquor through black liquor oxidation. Modified after [6]

3.5 SLRP

The SLRP or Sequential Liquid-Lignin Recovery and Purification process utilizes a column reactor operating at an elevated temperature in order to continuously precipitate the lignin in black liquor through introduction of carbon dioxide. The pressure is also kept high enough to prevent boiling but is normally below 4 atmospheres.

The lignin in this process is kept in a liquid phase where the liquid lignin droplets collide while moving down the column and coalesce forming a dense liquid-lignin phase which can be separated by gravity. The liquid-lignin phase is then continuously reacted with sulfuric acid reducing the pH to 2-3 in a similar fashion to above acidifications forming solid lignin in the form of large particles. The off-gases formed during the carbonation include hydrogen sulfide and carbon dioxide and are vented efficiently due to the absence of air which would impede mass transfer of the gases. The solid lignin phase can then be filtered and washed.

In addition to the precipitation process being continuous the carbonation system in the SLRP process is very efficient and little carbon dioxide goes to waste. Vented off-gases can also be recycled in a similar fashion to the LignoBoost process leading to reduced CO₂ consumption compared to batch processes such as LignoBoost. According to work done by Michael A. Lake and John C. Blackburn the carbon dioxide usage rates can be up to 30% lower than more traditional methods. [12]

3.6 Benefits and consequences from separation

In most cases the recovery boiler is the main bottleneck at a Kraft pulping mill. Separating lignin from black liquor is one method of circumventing this limitation and would allow for a greater quantity of pulp to be produced.

One major consequence for the separation of lignin from black liquor is the increased operating costs. Additional water is used during the washing of the lignin filter cake which introduces an additional load on the evaporators in which the demand of steam is increased.

In addition there is a chemical cost in the form of carbon dioxide and sulfuric acid for the acidification and washing. A large chemical cost is represented by sodium hydroxide which is used in order to adjust the sodium sulfur balance which is affected by the usage of sulfuric acid during the washing step during certain lignin extraction processes.

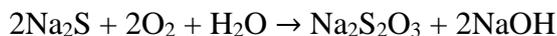
A factor that is important to consider is the ratio of organic and inorganic compounds present in the lignin-lean black liquor. If organic contents are too low there will be consequences on the combustion properties leading to operating problems in the recovery boiler. [9]

4 Black liquor oxidation

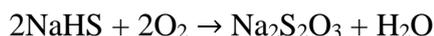
In addition to the benefits discussed above there are a number of other values related to oxidizing black liquor and example being that a portion of the heating value is released leading to a reduced load on the boiler thus allowing a larger capacity of pulp to be processed.

The choice of oxidant is also of importance, common choices are air or molecular oxygen with both possessing benefits either in the form of environmental or economical. In most cases oxygen tends to be the preferred choice due to a few reasons. Such as the speed of reaction, oxidation through the use of air can take over an hour which in turn leads to the demand for a large oxidation tank, pure oxygen however will react with black liquor in seconds meaning that the oxidation system will be much smaller. As air is also composed of 79% inert gas, a large amount must be vented from the oxidation system which can form a source of sulfur emissions and cause foaming in the liquor. In addition the heat formed during oxidation in the presence of air is mostly stripped from the system by the vented gases. Unlike air oxygen is fully consumed meaning that a venting system is not necessary. [23]

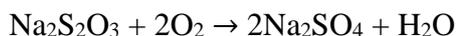
The primary reaction that takes place during the oxidation of black liquor is the oxidation of sodium sulfide into sodium thiosulfate, due to the complexity of the reactions the overall reaction has been simplified to



It's important to note however that a large quantity of Na_2S has been converted into NaHS , this means that the primary reaction is as follows



Continued oxidation will lead to the formation of sodium sulfate through the reaction



While this reaction does not necessarily lead to any issues for the recovery cycle or cause unwanted emissions it is generally a unneeded reaction that should be avoided as it leads to excessive oxygen consumption.

The conversion of sodium hydrosulfide into sodium thiosulfate is one of the contributors to the reduction of pH in black liquor during oxidation as sodium hydrosulfide is an alkaline salt while $\text{Na}_2\text{S}_2\text{O}_3$ is not. [3]

In addition to the reduction in pH the conversion of sodium sulfide and sodium hydrosulfide through oxidation provides another important benefit in that it prevents further formation of the total reduced sulfur hydrogen sulfide. Under normal conditions black liquor is highly alkaline and the TRS present will be in sodium form and thus non-volatile however when the pH is reduced during evaporation with direct-contact evaporators or when acidified the sodium bound sulfurs including sodium hydrosulfide (NaHS) will begin to form hydrogen sulfide. [13]

Unlike sodium sulfide and sodium hydrosulfide, sodium thiosulfate is non-volatile and will not experience hydrolysis when black liquor pH is reduced. Not only will this prevent hydrogen sulfide formation during lignin precipitation and in the black liquor evaporators but also in the recovery boiler. It is important to note however that there can be difficulties in achieving a permanent conversion of sulfide to thiosulfate as if the oxidation does not occur at a high enough temperature (above 80 C) there is a risk of elemental sulfur forming. This sulfur will slowly dissolve and will cause the reformation of sulfides during black liquor evaporation or storage. [7]

In addition to these reactions the oxidation of the organic sulfur compounds or as they are also referred to Total Reduced Sulfurs present in black liquor will take place. As the quantity of organic sulfurs present in black liquor is quite low a small amount of oxygen is consumed. The oxidation of methyl mercaptan is quite complex and one possible reaction forms a regeneration cycle. In its first step, methyl mercaptan will be oxidized into dimethyl disulfide according to



Once dimethyl disulfide is formed hydrolysis can occur leading to the formation of methane sulfinic acid or methane sulfonic acid and also the reformation of methyl mercaptan. It is important to note however that this is only one of the reactions that can occur during the oxidation of methyl mercaptan as according to McKean et al the reactions that occur depend on multiple factors including temperature and concentration of sodium sulfide, other noteworthy reactions include the formation of mono, di- and tri-thiopolyphenols from lignin structures. It has been found that higher oxidation temperatures result in a smaller formation of dimethyl disulfide, higher oxidation temperatures do present the downside of increased oxygen consumption however. [7]

The lignins and carbohydrates present in black liquor will also undergo oxidation. Due to the complexity and variation of lignin structures present a large number of compounds are formed during oxidation, these include methanol, acetone and a large number of low molecular weight acids. [3]

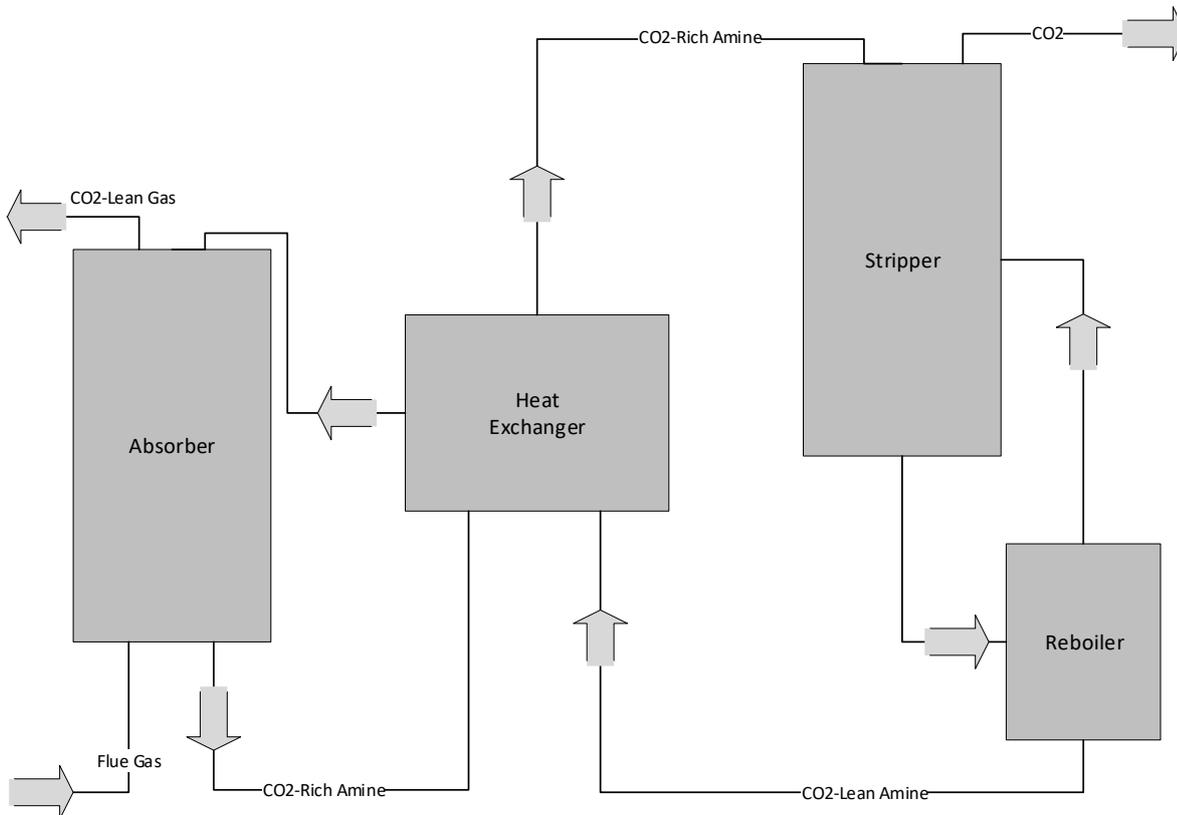
As a whole black liquor oxidation provides many benefits during the pulping process even though many reactions that occur are not well known and conversions can be difficult to predict.

5 Utilization of plant gas streams

As has been discussed above one noteworthy cost when separating lignin from black liquor through acid precipitation is the demand for carbon dioxide. In normal cases it can prove to be quite costly to acquire carbon dioxide from an outside source both due to the costs of the chemical itself but also transport and storage. Most if not all pulp mills utilize a chemical recovery cycle where carbon dioxide is produced meaning that it will always be at hand and implementation of a few process steps would allow it to be used for acid precipitation.

As can be seen in the earlier figure 2.1 there are two major sources of carbon dioxide in the recovery cycle of a pulp and paper mill, the recovery boiler and the lime kiln.

As the gas streams containing carbon dioxide have a low concentration it will be necessary to capture and concentrate it through for example chemical absorption. An advantage of this method is that if the recovery boiler is used as the source of CO₂ it is not necessary to make any modifications to it. Other possible options include pressure swing adsorption however this method may not fulfill the strict demands for high purity carbon dioxide and it performs best at low temperatures and high pressure which makes it less than optimal for gases formed post combustion.[28]



5.1. Flowsheet describing the separation of carbon dioxide from flue gas streams through amine-based absorption. [25]

The standard method of capturing carbon dioxide from flue gas utilizing MEA is done by allowing the gas to enter an absorber where it comes in contact with a counter-current flow of absorbent which capture the CO₂. The absorbent now containing carbon dioxide is heated with previously used absorbent and is then regenerated through the use of steam. Through this a stream of high CO₂ concentration is formed and remaining heat can be used in order to produce medium- or low-pressure steam. The separation method can be seen in figure 5.1. The energy demand for the regeneration of the absorbant is related to the initial concentration of carbon dioxide in the flue gas stream, this poses an issue as the carbon dioxide concentration in the gases leaving the lime kiln and recovery boiler are somewhat low. [25]

Chemical absorption does however introduce an additional demand for low-pressure steam in order to regenerate the absorbent that ranges between 2.9-4.5 MJ/kg of CO₂. In order to cover this steam demand it may be necessary to burn additional fuel or introduce a process integration. [9,8]

As mentioned above both the emissions from the recovery boiler and limekiln can be used as a source of carbon dioxide. The main difference between the two is that the flue gases leaving the recovery boiler have a higher flow rate while the gases leaving the limekiln have a higher fraction of carbon dioxide. Regardless of the chosen stream are capable of supplying enough carbon dioxide to allow a reasonable lignin separation. Flow rates and fractions are from the reference case by Périn-Levasseur et al with 50 t/d lignin being extracted and 400 tons of pulp being produced per day and can be seen in table 5.1. [9]

Table 5.1. Flow rates and carbon dioxide concentration in flue gases emitted from the recovery boiler and lime kiln in a reference case by Périn-Levasseur et al. [9]

Chemicals	Available mass fraction (%)	Flow Rate (kg/s)
CO ₂ from the recovery boiler	22.3	14.7
CO ₂ from the lime kiln	35.6	1.7

Important factors to consider are the conditions and purity of the absorbed carbon dioxide. According to the start-up of the first commercial LignoBoost plant in Plymouth, North Carolina it is necessary to have stable conditions when black liquor absorbs carbon dioxide during the precipitation step as otherwise the quality of the formed alkaline slurry will vary. This means that it may be necessary to introduce a cleaning step following the desorption of carbon dioxide adding to costs. As the concentration of carbon dioxide in the flue gas streams will depend on black liquor composition it may be important to perform a sensitivity analysis on how varying black liquor composition will affect both the produced flue gases and the purity of desorbed carbon dioxide. [8]

One possible method of making the flue gas streams easier to process would be by implementing oxy-fuel combustion in the recovery boiler. In oxy-fuel combustion the air that is normally used in the recovery boiler is replaced by pure oxygen, this will in turn lead to the formation of flue gases with a lower flowrate and a higher concentration of carbon dioxide as no nitrogen will be present. This will in turn reduce the energy demands for the desorption of carbon dioxide in the carbon capture process, it is of course important to note that using pure oxygen will form an additional cost that must be considered. [25]

A benefit in this case is that the carbon dioxide that has been captured is utilized immediately and thus does not require any storage and transportation which normally make up over half the cost of carbon capturing. By utilizing it on-site the costs relating to the cooling and compression are not present as well.

From a design perspective the usage of limekiln and recovery boiler flue-gases as a source of carbon dioxide appears to be reasonable as absorption of carbon dioxide from flue gases is a common practice, there are of course questions that must be answered regarding how varying CO₂ purity affects precipitation. From an economic perspective however it becomes difficult to determine how reliable this method really is. Currently there are no known MEA absorption systems being utilized at any pulp and paper mills which means that start-up costs are mostly unknown. Most of the previous studies regarding the topic have also assumed that the majority of emitted carbon dioxide is captured with the goal of mitigating climate change, due to this in many cases it is assumed that grants have been given or a fraction of the start-up cost has been paid for in compensation, with only a small part of the CO₂ being captured in this case it seems unreasonable to assume that these benefits would be given making the option even less attractive. While costs for the steam required to regenerate the absorbant is lower than that for purchased carbon dioxide there is little knowledge on the costs required for the absorbant system itself and maintenance of it which adds a large degree of uncertainty to this process. [10]

6 Separating sulfur from black liquor

In addition to utilizing flue gas streams for a source of carbon dioxide it would be of interest to study the possibility of separating some of the more volatile sulfurs from black liquor and use these as a base for the production of sulfuric acid. While some work is present regarding taking advantage of sulfur-heavy waste gas streams from for example the digester there is very little covering the possibilities of separating reduced sulfurs from the black liquor itself. The points in which the separation of sulfur from black liquor is considered can be seen in figure 2.1.

In addition to the costs for purchasing sulfuric acid from an outside source there is also the issue of upsetting the sodium sulfur balance when separating lignin from black liquor through acid precipitation. This in turn will introduce the necessity of purging the added sulfur from the system; this can be done by for example removing precipitator dust formed from the recovery boiler. This dust is mainly in the form of Na_2SO_4 which means that when this dust is purged the concentration of sodium will also be reduced meaning that using sulfuric acid from an outside source will also introduce an additional cost for make-up sodium which is even more expensive.

Because of the high costs related to sulfuric acid and make-up chemicals upsetting the sodium/sulfur balance it is of interest to study methods of separating and utilizing the organic sulfurs already present in black liquor for sulfuric acid production, in addition if it can be separated from the black liquor before precipitation less sulfur will be present in the finished lignin allowing for a product of higher purity and value, this is especially interesting as certain developing products from lignin include carbon fibre which requires lignin of very high purity to produce.

As the separation of lignin from black liquor has only been a hot topic for a short period of time so far separating TRS compounds from the black liquor itself is a topic that has not been studied to a large extent.

6.1 Steam stripping

Steam stripping is one possible method of separating volatile sulfurs that has been locked into the liquor. Steam stripping uses steam in order to separate steam volatile organic compounds from aqueous black liquor streams. Compounds separated include alcohols such as methanol and ethanol, terpenes, ketones, sulfur bearing compounds and phenolic compounds. Steam stripping is capable of reducing the quantity of the more volatile constituents present in the liquor however in order to separate methyl mercaptan with this method the pH of the liquor must be below 12. At a pH of 11 it has been shown to be possible to strip 90% of all methyl mercaptan from the black liquor with a liquor feed to steam ratio of 30:1, if a larger separation of methyl mercaptan is necessary the height of the used stripper columns must be increased.

While a large degree of the methyl mercaptan present can be separated through this method the other TRS compounds are not to easily removed. At a pH of 11 the hydrogen sulfide removal did not exceed 12%, as a large quantity of sulfide is still in sodium form and thus non-volatile at this pH this appears to be reasonable. [14]

As the goal is to find a separation method that allows for an efficient separation of a large quantity of the volatile sulfurs in black liquor the usefulness of this method is debatable. While a large quantity of methyl mercaptan can be removed, little information has been presented on how much dimethyl sulfide can be removed and hydrogen sulfide separation is quite poor. In addition there appears to be a need for a large number of separation methods following the steam stripping of the liquor as many compounds besides TRS are removed. As internal sulfuric acid production is considered in order to reduce operation costs, the addition of a large and potentially expensive separation system seems counter-intuitive.

6.2 Black liquor oxidation with air as an oxidant

Another although somewhat unorthodox separation method is by using air as an oxidant during black liquor oxidation. While oxidizing the black liquor the inert parts of the air will strip away fractions of the more volatile compounds present including TRS gases and methanol formed during oxidation. These chemicals could then be collected and separated from the off-gases leaving the oxidation reactor. This method should not be considered a viable method of separating sulfur on it's own as it is not that effective due to a large amount of the TRS compounds that haven't been stripped forming less volatile sulfurs during oxidation, these compounds will then be significantly harder to separate. [23]

6.3 Heat treatment of black liquor

A common theme among these two above separation methods is their lack of ability to discriminate. While a moderate quantity of sulfur can be separated there is a large number of different compounds present in the separated stream which would demand a complex series of separation steps before the sulfur itself could be utilized for the production of sulfuric acid. Because of this neither method is regarded as optimal as the end goal is a method of separation that separates most of the organic sulfur and does not remove many other compounds from the liquor in order to avoid the necessity of additional complex separation steps to produce a reasonably pure stream of sulfuric compounds. An additional factor that has not been mentioned so far are the free sulfides that are solved in the liquor which are not separated with the above methods

It has been found that exposing black liquor to an elevated temperature and pressure has an impact on its chemical and physical characteristics.

According to work done by Soderhjelm et al when black liquor is exposed to elevated temperatures under alkaline conditions the polysaccharide chains will break resulting in a notable reduction of viscosity in the heat treated black liquor. The reduction of

polysaccharides is promoted by the presence of hydroxide ions so the reducing of viscosity is more efficient when the residual alkali charge is high.

When the lignin dissolved in the black liquor is exposed to temperatures of about 140-190 degrees Celsius, residual alkali present will degrade it into smaller fragments. In addition free sulfides present in the liquor will react with methoxy groups present in the degraded lignin forming organic sulfurous compounds such as methyl mercaptan and dimethyl sulfide in a similar fashion to the pulp mill digester and cook. [15]

According to a patent by Ryham et al by heating black liquor in the manner explained above it is possible to produce large volumes of off-gases containing organic sulfur compounds. The heat treatment itself can be carried out at a temperature between 170-350 degrees Celsius and a pressure between 8 to 165 bar with varying temperature controlling the amount of sulfur leaving the black liquor. The retention times for this treatment vary based on temperature and the composition of the liquor but standard times are somewhere between the interval of 20-40 minutes. Almost all organic sulfurs present in the liquor can be separated if treatment is performed at a temperature between 190-290 degrees Celsius. At a heat treatment temperature of 280 degrees Celsius the sulfuric gas stream apparently had a composition that can be seen in table 6.1. [20,21]

Table 6.1. Composition of sulfurous gases from thermal treatment of black liquor at a temperature of 280 degrees Celsius. [20]

Sulfuric compound	%
Dimethyl Sulfide	65
Methyl Mercaptan	34
Hydrogen Sulfide	1

Available data on gas streams formed during heat treatment of black liquor is quite restricted at the moment so there are difficulties in determining how heat treatment temperature affects the composition, it is however reasonable to assume that a higher temperature will lead to a greater fragmentation of solvated lignin allowing for the formation of more methoxy groups for free sulfides to react with. It is important to note that in order for proper sulfur separation occur the heat treatment must be followed by sufficient flashing. [17]

It is however important to determine how the heat treatment of black liquor will affect the quality of the precipitated and separated lignin. According to work done by McKeough if black liquor is heated at a temperature of 350-400 degrees Celsius for 45 minutes it will lead to the formation of a homogenous oil-like phase. As no work has been done in determining how the formation of this oil-product will affect the quality of the precipitated lignin it is reasonable to set the maximum heat treatment temperature for black liquor when separating sulfuric compounds to 300 degrees Celsius for the time being until further work on this topic has been done. [16]

In a study done by Tiainen et al it was found that when heat treatment is performed using intermediate pressure steam (13 bar, 195 degrees Celsius) and lignin was then extracted from the liquor the operating costs would increase by about 50% compared to if lignin was extracted without prior heat treatment of the liquor. Because of this reason the viability of black liquor heat treatment should be based on how much the demand of chemicals can be

reduced by utilizing the separated sulfur gas stream and the increased value of the lignin itself as heat treated lignin appears to possess a higher purity. [17]

The reduction of viscosity that occurs during black liquor heat treatment also provides other benefits. These include the possibility of concentrating black liquor up to 80% prior to entering the recovery boiler reducing it's load and improving it's capacity.[26]

Of the studied alternatives thermal treatment of black liquor appears to be the most promising of the bunch. The relatively simple composition of the sulfuric gas stream separated from the liquor means that the conversion into sulfuric acid should be possible without any major hitches as no complex secondary separation methods are required.

There are still a few question marks present relating to the profitability of this method compared to simply purchasing sulfuric acid and make-up sodium from an outside source however. As mentioned above even when heat treatment was done utilizing steam at a temperature of 195 degrees Celsius the increased cost was equal to 50% of that required for precipitating lignin from black liquor, this including indirect costs for make-up chemicals and reduced steam production. A positive note however is that this study did not include an internal sulfuric acid production so the money saved on make-up chemicals and sulfuric acid may exceed the steam demand costs. For the theoretical separation of sulfurs utilizing heat treatment at 300 degrees Celsius the cost of steam would be much higher. There may also be a risk that sulfur stream data is a bit to optimistic as black liquor possesses certain compounds such as methanol and acetone with low boiling points that could potentially be flashed alongside the odorous sulfur gases.

7 Internal sulfuric acid production

7.1 Thermal oxidation

Through the aforementioned heat treatment method off gases composed of methyl mercaptan, dimethyl sulfide and hydrogen sulfide is formed. The first step in converting these compounds into sulfuric acid is through thermal oxidation. While it is possible to combust the sulfurous gases in the lime kiln, power boiler or recovery boiler it is preferable to use a dedicated incinerator.

Standard incineration conditions for these off-gases are

- Temperature of at least 871 C
- Residence time of 0.75 seconds
- Excess oxygen content of 3-4%

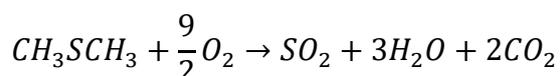
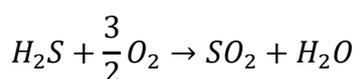
A thing that must be considered when treating sulfuric off-gases in the presence of air is the risk of an explosion. Table 7.1 lists the upper and lower explosive limits of the present compounds. These limits describe the minimum and maximum volume concentration of gas that when in the presence of air will burn.

Table 7.1. The upper and lower explosive limits of hydrogen sulfide, methyl mercaptan and dimethyl sulfide. [19]

	Lower explosive limit (% Vol)	Upper explosive limit (% Vol)
H ₂ S	4.3	45
CH ₃ SH	3.9	21.8
CH ₃ SCH ₃	2.2	19.7

In order for an explosion to occur however there must also be an ignition source present so it is of importance to make sure that vessels containing the gases are properly grounded to prevent static electricity. Other risks include the formation of sparks from used fans. [19]

The reactions that occur when the off-gases enter the incinerator are the following

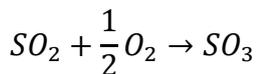


In addition to sulfur dioxide the incineration will also lead to the formation of water and carbon dioxide. The carbon dioxide can be treated as an inert in the following process steps and its removal is thus not necessary. Depending on the chosen method of producing sulfuric acid however it may be necessary to remove formed water.

7.2 Wet sulfuric acid process process

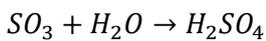
Due to the fact that the combustion of the sulfuric off-gases also leads to the formation of water the wet sulfuric acid process is the chosen method for producing sulfuric acid as there are no necessary condensation or separation steps that must be performed prior to the conversion. With less separation steps involved this also minimizes the losses of sulfuric compounds during the process.

Following incineration the process stream enters a reactor which contains a series of beds containing vanadium pentoxide (V_2O_5) catalyst where sulfur dioxide is converted into sulfur trioxide according to



The reactor is kept at a temperature of 400 degrees Celsius and as the reaction itself is exothermic will require a supply of cooling water which allows for the possibility of producing superheated steam. This is a topic of particular interest as the formed steam could possibly offset some of the steam consumed during the black liquor heat treatment step.

The gas stream then leaves the catalytic beds and is cooled leading to the formation of sulfuric acid through the reaction between water vapour and sulfur trioxide.



Finally the process stream enters a dedicated wet sulfuric acid condenser. The condenser itself is often in the form of a vertical shell and tube type falling film condenser, the tubes themselves are made of boron silicate glass to resist corrosion from formed acid. The sulfuric gas is cooled using ambient air which upon leaving the condenser has a temperature of about 200 degrees Celsius and can be sent to the incinerator as a source of oxygen. [22]

8 Aspen Simulation

8.1 Design and specifications

With a method of converting the sulfur off-gases into sulfuric acid planned a preliminary design of the process was done in Aspen plus. As the wet sulfuric acid process is well developed and work featuring gas streams similar to the ones formed during heat treatment are present the main topics of interest during this simulation is to confirm that no oddities take place during the reaction and also determine how much heat can be generated.

Prior to designing the flowsheet the included chemical components are specified. In addition an appropriate physical property model must be selected. This property was chosen through a method developed by Carlson et al. [27] As there are polar compounds present in the simulation and sulfuric acid is considered an electrolyte the chosen property method is ELECNRTL.

As the chemical reactions that occur during the thermal treatment of black liquor are complex and rather poorly documented the streams that enter the process are those of the sulfurous off-gases with a pre-specified composition and a heated stream of air to be used during incineration and catalytic oxidation.

The two streams are mixed and then enter the first reactor in which incineration occurs at a temperature of 1000 degrees Celsius. The reactor models used in this case are of the RGIBBS variant, this reactor utilizes Gibbs free energy to determine the reactions that occur and the extent of them, this is particularly useful as it is not necessary to specify reaction constants.

Following the incineration the gas stream is cooled to a temperature of 400 degrees Celsius prior to entering the second reactor in which the catalytic oxidation of sulfur dioxide into sulfur trioxide occurs, a portion of sulfuric acid is also formed.

The sulfur trioxide and other gases are then cooled to a temperature of 200 degrees Celsius and remaining sulfur trioxide is converted into sulfuric acid. Finally the stream is cooled to a temperature of 100 degrees Celsius allowing most of the sulfuric acid to condense and the formed liquid is separated from the gas through the use of a flash unit with the full process being seen in figure 8.1.

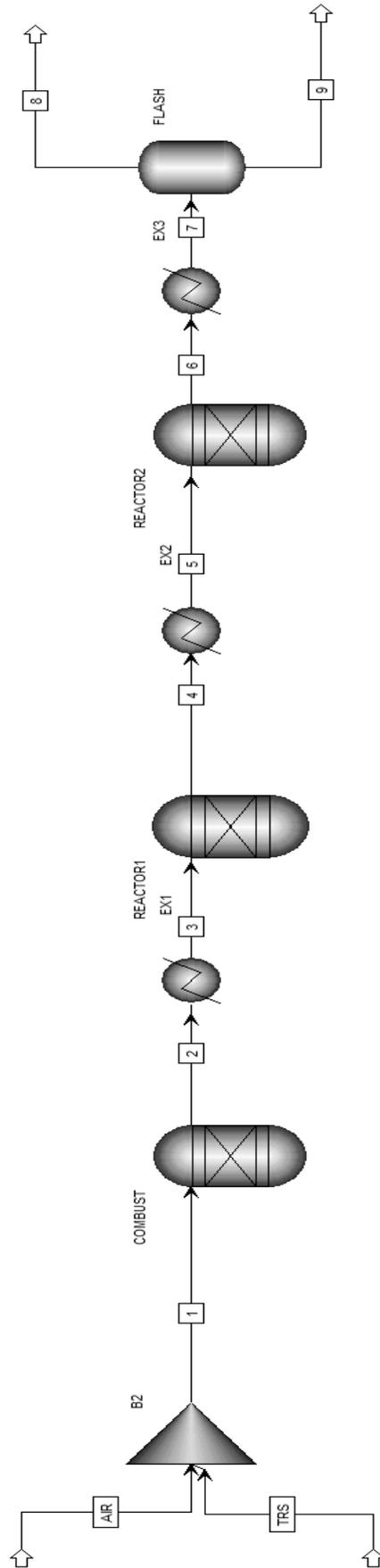


Figure 8.1. Flowsheet for the simulated wet sulfuric acid process.

As the composition of the sulfurous off-gases formed during black liquor heat treatment do not directly specify if it is in weight or molar percentage a simulation of each case is done. In both cases the flowrate of sulfurous off-gases entering the first reactor is 1 kg/s. Enough air is supplied so about 10 mole% of oxygen remains unreacted, this to speed up reaction times during catalytic oxidation and minimize the theoretical risk of an explosion.

Unlike the standard wet sulfuric acid process this simulation lacks a few defining features. In real life applications it is difficult to cool the catalytic oxidation of sulfur dioxide into sulfur trioxide so it maintains a reasonable reaction temperature in a single reactor. Because of this the catalytic oxidation often takes place in a series of reactors with intercooling steps inbetween. A possible alternative to using a series of reactors is to use a large excess of air during the reaction which allows the reaction to occur quicker and with more gases to be heated during the oxidation the temperature will not be as high, this does however introduce the demand for a larger reactor. During the simulation however it is assumed that the reactor is maintained at a constant temperature of 400 degrees Celsius however the heat generated from the reaction and the degree of conversion should be similar to if a series of reactors was used. As discussed above the standard wet sulfuric acid condenser is quite a bit more complex and efficient than what was simulated as in this case the gas stream containing sulfur trioxide is simply cooled, allowed to react with steam to form sulfuric acid, cooled again with the gas and liquid phases separated with a flash unit. [22] The main reason for not further improving the condenser aspect of the simulation further was due to time constraints and the fact that the assumptions made regarding the quantity of sulfur that can be separated from black liquor are likely to have a much larger impact on the quantity of acid that can be produced than the degree of variation caused by the simplified condenser.

8.2 Simulation results

The results from the simulation as seen in the appendix appear to satisfactory. Compared to data presented from Haldor Topsoe the sulfuric acid from the simulation possesses a lower concentration of about 92.4 mole%, this is simply due to the fact that the simulated method of separating sulfuric acid from the remaining components is much simpler and in this case mainly used to determine the feasibility of the process. [22] Another noteworthy issue is the small quantity of sulfur trioxide formed during the incineration of sulfur off-gases. This is due to the fact that unless specified Aspen will take all possible reactions into consideration when the RGIBBS reactor is used, because the incineration chamber will of course not have any form of catalyst present the formation of sulfur trioxide will not occur in this step. However as the heat generated from the formation of sulfur trioxide is quite a bit lower compared to the incineration of sulfuric off-gases it does not interfere to much with heat generation. The %-yield was also calculated based on moles according to

$$\frac{H_2SO_4(\text{moles})}{CH_3SH(\text{moles}) + CH_3SCH_3(\text{moles}) + H_2S(\text{moles})} \cdot 100\%$$

The yield in both cases ended up being quite high at about 98.8 mole% of the available sulfur being converted and successfully separated during condensation.

Currently it has not been determined how large the reduction in sodium make-up demand is for the extraction of larger quantities of lignin with internally produced acid. Earlier work done by Venla Partanen however has shown that for the extraction of 20 wt% of lignin in black liquor the demand of sodium becomes similar to a mill without lignin extraction if acid is produced internally. [4]

With the simulation completed it appears to be feasible to produce sulfuric acid through this method. In addition a reasonable amount of heat is generated from the incineration and first heat exchanger which should be taken advantage of. Noteworthy data from the simulation can be seen in table 8.1.

Table 8.1. Sulfuric acid yield, concentration of formed sulfuric acid and heat generated during the thermal oxidation of the sulfurous off-gases formed during heat treatment of black liquor.

	Sulfurous Off-gases		Yield (mole)		Concentration (mole)		Heat generated from combustion	
Case A	1	kg/s	98.72	Mole%	92.44	Mole%	16730	kW
Case B	1	kg/s	98.86	Mole%	92.40	Mole%	16854	kW

9. Process calculations

9.1 Sulfuric acid production

As the conversion of the black liquor off-gases into sulfuric acid has been shown to be feasible a reasonable next step is to determine how much sulfuric acid can be produced and how much lignin it can separate from the liquor through acidification.

According to Rolf Ryham about 4-6 weight% of dry solids from the liquor can be converted into gases through heat treatment. As the results from case A and B ended up being reasonably similar the off-gases are assumed to have the composition of case A which is 65 wt% dimethyl sulfide, 34 wt% methyl mercaptan and 1 wt% hydrogen sulfide. Based on this composition it can be determined that 1 gram of off-gases contains 0.571 grams of elemental sulfur. Assuming that about 2 wt% of the sulfur is lost during the conversion process this means that 1 gram of sulfur can produce about 3 grams of sulfuric acid. [20]

As liquor composition and treatment methods vary it is assumed that the lignin content in the liquor is equal to 20-35 wt% of the dry solid content and that for each gram of lignin extracted 0.2 grams of sulfuric acid is required. This is of course just a preliminary assesment and should be taken with a grain of salt as studies show that the sulfuric acid consumption can be as high as 0,35 grams per gram lignin or as low as 0,09 grams per gram lignin, this will vary based on liquor composition and precipitation method. [30]

A sensitivity analysis is done based on how much lignin can be extracted according to the amount of off-gases produced. In this case it is assumed that 1 kg of dry solid black liquor is treated and the off-gases produced are equal to 3-6 wt% of the total dry solids of the liquor.

Table 9.1. Quantity of sulfuric acid formed and amount of lignin that can be separated with said acid at varying degrees of sulfurous off-gas formation.

Off gases		Sulfur content		Acid produced		Possible lignin separation		Lignin separated	
30	Gram	17.1	Gram	51.4	Gram	257	Gram	73-129	%
40	Gram	22.8	Gram	68.5	Gram	342.5	Gram	98-171	%
50	Gram	28.6	Gram	85.7	Gram	428.5	Gram	122-214	%
60	Gram	34.3	Gram	102.8	Gram	514	Gram	147-257	%

Based on the results in table 9.1. it appears that even during poor off-gas formation more than enough acid is formed to cover necessary lignin extraction. In most cases the maximum amount of lignin extracted from black liquor is in the 30-50 wt% range as if these numbers are exceeded there will be issues with the recovery boiler including problematic behaviour from the lower furnace and a steam superheating limit. Judging from these results it may be preferable to treat the liquor at a lower temperature than previously suggested as the acid demand would still be likely to be met.[24]

9.2 Steam generation

As the results from above imply that acid demands can be met through heat treatment and the wet sulfuric acid process the only other question at hand is how high the energy demand is for the separation and production method.

It is assumed that the thermal treatment of black liquor utilizes high pressure steam, during the heating process the steam will be condensed and then leave the thermal exchange unit. As the incineration step of sulfuric off-gases during the wet sulfuric acid process is highly exothermic the heat generated may be utilized to re-evaporate and superheat the water previously used during the heat treatment step. Based on how much steam can be generated it may be necessary to supply additional cooling water.

A preliminary attempt is made in determining how much steam is consumed during the thermal treatment process and how much steam can be generated from high pressure water during the off-gas incineration step. As data on thermal treatment is scarce and many reactions that occur, some of which are exothermic as a result of the depolymerisation of certain polysaccharides are not well documented the heat demand is assumed to be the energy that must be supplied to the liquor to raise its temperature from 70 to 280 degrees Celsius. The specific heat of the liquor varies based on composition, temperature and dry solid content between 2.7-3.9 kJ/(kg K) and is in this case assumed to be a higher constant value of 3.5 kJ/(kg K). Once again this is simply used as a preliminary assessment to determine how steam generation during sulfuric acid production relates to steam consumption.

The high pressure steam utilized in order to heat the liquor is assumed to have a pressure of 92 bar and is superheated to a temperature of 490 degrees Celsius. During the heat exchange the steam will be cooled, condensed and then cooled to a temperature of 290 degrees Celsius. The amount of heat supplied (E) from 1 kg of steam is calculated below.

$$E = H_V - (h_l - (c_p * (T_2 - T_1)))$$

With H_V being the enthalpy of the superheated steam, h_l being the enthalpy of the water following condensation and $c_p*(T_2-T_1)$ being the heat released when the pressurized cooling water has its temperature reduced from its boiling point of 305 degrees Celsius to 290 degrees Celsius.

$$H_V = 3350 \text{ kJ/kg}$$

$$h_l = 1373 \text{ kJ/kg}$$

$$c_p = 5.3 \text{ kJ/kg C}$$

It is thus determined that 1 kg of high pressure steam supplies 2,056 kJ.

The liquor is assumed to have a dry solid contents of 40% and an initial temperature of 70 degrees Celsius. The heat treatment is also assumed to be performed at an elevated pressure preventing evaporation of any water. The amount of steam needed to heat 1 kg of liquor (S) is calculated below.

$$S = \frac{cp * (T2 - T1)}{E}$$

$$Cp = 3.5 \text{ kJ/kg C}$$

$$T1 = 70 \text{ C}$$

$$T2 = 280 \text{ C}$$

It is determined that heating 1 kg of black liquor to the needed temperature requires 357 grams of high pressure steam.

With the steam demand known the next step is to determine how much superheated high pressure steam that can be generated. Based on the simulation of Case A 16730 kW of heat is generated from 1 kg/s of sulfuric off-gases in the incinerator, as this is the only point in the process where the temperature is at 490 degrees or higher it is the only point where high pressure steam superheated to 490 degrees Celsius can be produced. As discussed in the previous section in Case A 1 kg of off-gases contains 571 grams of elemental sulfur, through this it can be determined that off-gases containing a total of 1 gram sulfur is enough the generate 29.3 kJ of heat through incineration. Through this the amount of superheated high-pressure steam that can be formed from 1 gram of sulfur is calculated

$$\frac{29.3}{E}$$

It is thus determined that 1 gram of elemental sulfur (or 1.75 g off-gases) is enough to generate 14.25 grams of high pressure steam.

A feasibility study similar to the above case is done regarding steam generation with 3-6 wt% of black liquor dry solids being separated however as a dry solid content of 40% is assumed 1 kg of black liquor will release less off-gases than the above example where 1 kg of dry solid liquor was assumed.

Table 9.2. Amount of steam that can be generated from thermal oxidation and it's relation to the steam demand during heat treatment at varying degrees of sulfurous off-gas formation.

Off-gases		Elemental sulfur		Steam generated		Steam coverage	
12	Gram	6.9	Gram	97.6	Gram	27.4	%
16	Gram	9.1	Gram	130.2	Gram	54.7	%
20	Gram	11.4	Gram	162.7	Gram	45.6	%
24	Gram	13.7	Gram	195.3	Gram	54.7	%

Based on the above results in table 9.2 it appears as if the maximum amount of off-gases can be produced the incineration step generates about half of the steam required to offset the steam demand of the thermal black liquor treatment. It is however noteworthy that a large amount of heat is also generated through the heat exchanger used to cool the gas stream leaving the incinerator to a temperature of 400 degrees Celsius, this can also be used to generate superheated high pressure steam albeit at a maximum temperature of 400 degrees Celsius. In addition heat generated from the catalytic oxidation and second heat exchanger can be used to generate medium or low pressure steam. As the viscosity of the liquor is

reduced during heat treatment it may be possible to use a higher dry solid content than 40wt% which would in turn lessen the heat heat load during treatment as less water would be heated.

As the steam generated is significant it is something that should without a doubt be utilized if this acid production method is considered. A flowsheet displaying a preliminary design on utilizing generated heat can be seen below in figure 9.1.

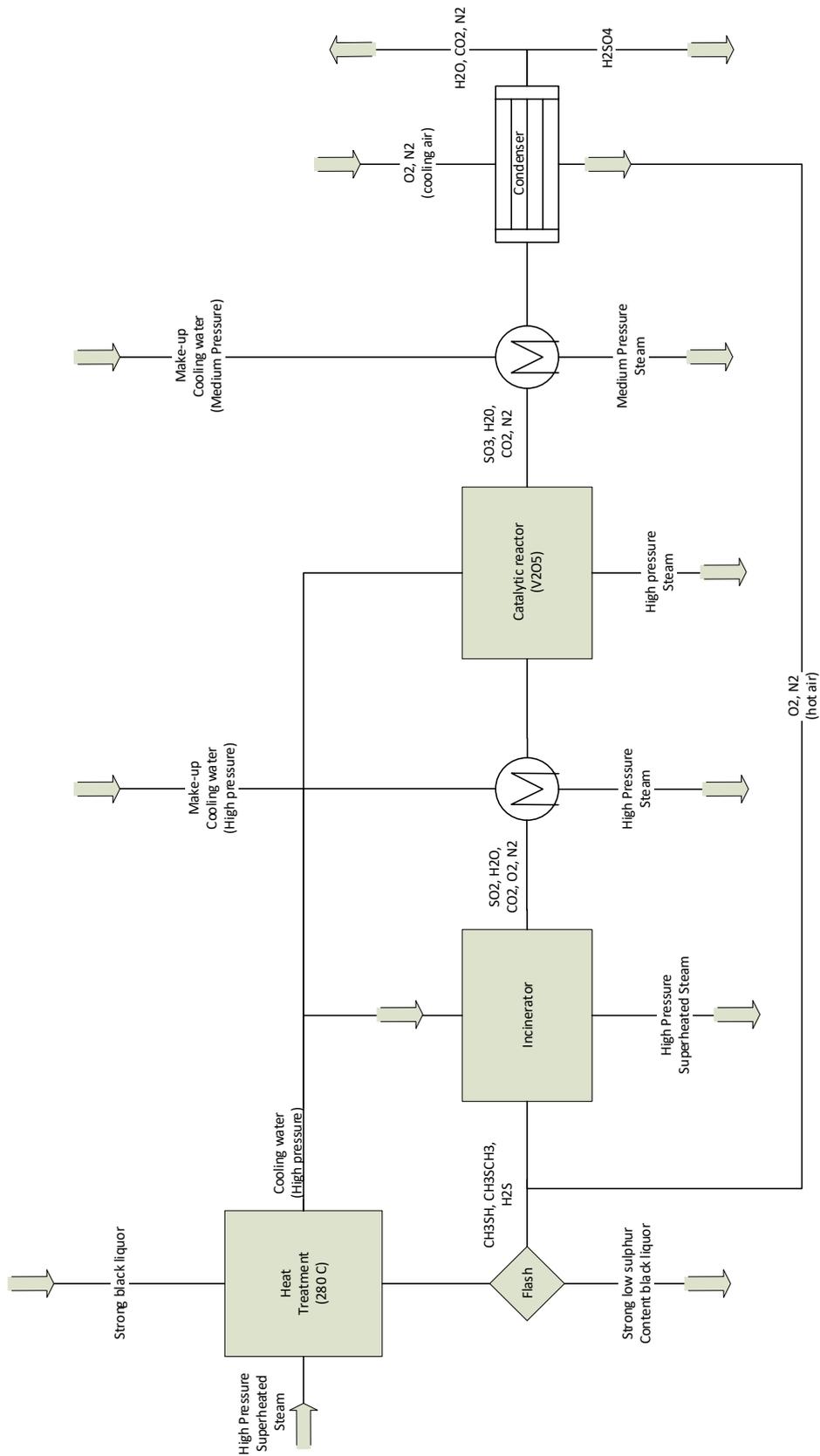


Figure 9.1. A flowsheet describing the suggested method of separating sulfur from black liquor through heat treatment and converting it into sulfuric acid through the wet sulfuric acid process

10. Summary

10.1 Conclusions

The project as a whole has had a number of goals surrounding the topic of lignin extraction. Topics such as determining the mechanisms behind lignin precipitation, studying various lignin extraction methods and determining the volatile sulfurs in black liquor and how they form have been reasonably straightforward and the results satisfactory.

The design of a method of separating the volatile sulfurs offered an interesting and at times demanding challenge due to difficult to find and at times contradictory information. It has however been determined that treating black liquor at an elevated temperature is one of the more promising methods of separating a fairly large degree of the volatile sulfurs from the liquor. Unlike other methods what makes heat treatment promising is that in addition to separating sulfurs it provides additional benefits by reducing the viscosity of the liquor which allows it to be evaporated to a higher solid content prior to entering the recovery boiler.

Converting the sulfurous off-gases into sulfuric acid with the wet sulfuric acid process has been determined to be relatively straightforward with the simulation produced in Aspen confirming this belief. Even if the separation of sulfur from liquor is half as large as it is implied in literature the quantity of acid produced still allows for a theoretical 70 mass% of lignin to be extracted. A surprisingly large quantity of steam can also be produced which means that the heat demand for separating the sulfur in the heat treatment step will not be as high as previously assumed. As the cost for purchased sulfuric acid is quite low the primary benefits from this process is the avoided costs for make-up sodium which poses a much higher cost than sulfuric acid and the aforementioned benefits of reduced black liquor viscosity.

Utilizing flue-gas streams containing carbon dioxide is an interesting concept however at the moment its usefulness is debatable. Prior to being utilized the carbon dioxide must be concentrated through the use of amine-based carbon dioxide absorption, which introduces a large steam cost. In addition there are questions present regarding if the carbon dioxide requires additional treatment prior to being utilized. Unlike internal sulfuric acid produced at the mill capturing carbon dioxide for use at the mill does not provide any additional benefits. The carbon dioxide captured is equal to a small fraction of carbon dioxide emitted from the mill which means the mitigation of climate change will be small and the odds of economic reimbursement low.

10.2 Future work

As has been stated a few times it has been necessary to make a number of assumptions when determining the quantity of sulfur that can be separated from black liquor through heat treatment. Because of this it would fill in many blanks, if work was done in determining how temperature, retention time and alkali charge affects the formation of sulfurous off-gases. In

addition it may be of interest to determine the heat demand when the liquor is treated with the use of for example a calorimeter

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Appendix

Case A: Mass fraction, Sulfur off-gas mass flow: 1 kg/s

Component	Unit	TRS	AIR	2	4	6	8	9
CH3SCH3	KMOL/HR	37.76	0	0	0	0	0	0
CH3SH	KMOL/HR	25.44	0	0	0	0	0	0
H2S	KMOL/HR	1.06	0	0	0	0	0	0
H2O	KMOL/HR	0	0	164.92	158.56	101.37	96.2	5.17
CO2	KMOL/HR	0	0	100.76	100.76	100.76	100.74	0.02
SO3	KMOL/HR	0	0	1.86	57.09	0.61	0.60	0
H2SO4	KMOL/HR	0	0	0	6.36	63.55	0.11	63.44
O2	KMOL/HR	0	309.10	60.79	29.30	29.65	29.64	0
N2	KMOL/HR	0	1034.83	1034.73	1034.83	1034.83	1034.79	0.03
SO2	KMOL/HR	0	0	62.29	0.70	0	0	0

	Unit	Combust	Ex1	Reactor1	Ex2	Reactor 2	Ex3
Temperature	Celsius	1000	400	400	200	200	100
Pressure	Bar	1	1	1	1	1	1
Heat generated	kw	16730	8555	1857	2605	1558	2344

Case B: Mole fraction, Sulfur off-gas mass flow:1 kg/s

Component	Unit	TRS	AIR	2	4	6	8	9
CH3SCH3	KMOL/HR	41.00	0	0	0	0	0	0
CH3SH	KMOL/HR	21.44	0	0	0	0	0	0
H2S	KMOL/HR	0.63	0	0	0	0	0	0
H2O	KMOL/HR	0	0	166.49	160.27	104.02	98.91	5.11
CO2	KMOL/HR	0	0	103.42	103.42	103.42	103.40	0.02
SO3	KMOL/HR	0	0	1.86	56.20	0.60	0.60	0
H2SO4	KMOL/HR	0	0	0	6.21	62.47	0.12	62.35
O2	KMOL/HR	0	314.83	64.17	33.90	33.57	33.57	0
N2	KMOL/HR	0	1054.00	1054.00	1054.00	1054.00	1054.00	0.03
SO2	KMOL/HR	0	0	61.20	0.66	0	0	0

	Unit	Combust	Ex1	Reactor1	Ex2	Reactor2	Ex3
Temperature	Celsius	1000	400	400	200	200	100
Pressure	Bar	1	1	1	1	1	1
Heat generated	kW	16854	8703	1824	2650	1531	2347