

De-polymerization and Purification of Kraft Lignin Utilizing the Liquid-Lignin Phase

Production of lignin oil with the *SunCarbon* process

by

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Abstract

The effects of global warming are apparent and the work towards a sustainable future is underway. In order to reduce the environmental impact caused by the transportation sector, a transition from fossil fuels to those based on renewable resources are important. Using agricultural land to produce raw materials, e.g. wheat or corn, for biofuel is controversial as it competes with food production. Furthermore, a single process would not be able to keep up with the demand for biofuels. Using previously unused residual products or upgrading their use to increase efficiency and value is a great way forward. Black liquor is exactly that, a residual product in pulp mills that can be used more efficiently. A large portion of black liquor is lignin, a large and complex aromatic structure that when broken down into smaller units can function as fuel. However, black liquor contains all the cooking chemicals used during the cooking process and needs to be extracted.

There are already methods for extraction and purification of lignin from black liquor but more cost efficient methods are needed in order for a large-scale production of lignin-based biofuel. A new method developed by *SunCarbon* consists of four parts; membrane filtration of black liquor, base catalyzed de-polymerization of the complex structure, CO₂ induced precipitation of a heavy lignin-rich liquid-phase and purification with the Aqueous Lignin Purification with Hot Acids (ALPHA) process. The ALPHA process purifies lignin with mixtures of acetic acid and water which acts as an anti-solvent and phase separation between a heavy lignin-rich liquid-phase and a light phase occurs, where the metals prefer the light phase and the lignin is thus purified. The red line of this method is that the product and the intermediary products are kept liquid and can thus be pumped. This eliminates problems with lignin in powder form, which otherwise is common, and the final liquid product can be introduced to existing refineries without altering their process, i.e. a drop-in fuel. In this work, all but membrane filtration has been investigated experimentally and weight has been put on precipitation and purification.

It was found that base catalysis successfully de-polymerizes lignin at 220-240 °C and that an increase in temperature yields a higher degree of de-polymerization. 250 °C was also tested but the formation of solid material in the reactor made it un-pumpable. The largest lignin molecules (~100 kDa) are completely removed and instead lignin dimers and monomers are formed. It was also shown that a heavy lignin-rich liquid-phase forms at 110-150 °C and when pH was ~9 or lower. The lignin yield in the heavy liquid-phase was high; 76-85% of the initial lignin had precipitated and a lower temperature improved yield. The decanted light liquid-phase removed a large portion, 72%, of the initial ash content and again a lower temperature was preferable.

Initial attempts of purification with the ALPHA process on the precipitated lignin failed. A model substance, LignoBoost powder, was thus used to test the method. Purification with the model substance successfully separated in two liquid phases that could easily be separated. The viscosity of the heavy phase was too high to be pumped with, e.g. a centrifugal pump, but a screw pump could be used. A two-step purification of the model substance showed that a high yield can be expected, >92%, from the ALPHA process. Two-step purification of the precipitated lignin showed that ash content decreases but the formation of a heavy liquid phase is crucial for achieving a high yield.

Popular Science Summary - Lignin, a raw material for biofuel production with its roots in the Swedish forest

A new process hopes to produce a biofuel based on lignin, one of the world's most abundant molecules. In this work, parts of the new process were investigated and the results are promising.

Global warming is a hot topic and its effects, e.g. melting glaciers and increased intensity of hurricanes, are often discussed in media and terms like the *greenhouse effect* and *greenhouse gases* often comes up. Greenhouse gases in the atmosphere such as carbon dioxide, methane and nitrous oxide, are to a large extent responsible for the greenhouse effect [1]. Sunlight passes these gases on its way down to earth, but as they hit earth, the light energy transforms to heat energy, infrared radiation. Heat is constantly radiated from Earth's surface out into space but greenhouse gases hinder this by blocking the infrared radiation. This is the so-called greenhouse effect and because not all energy supplied by the sun is radiated back into space, it leads to an unbalance. More energy comes in than what comes out, which in turn leads to an increase in mean temperature around the globe; this is what is called global warming. The fight against global warming takes many shapes but maybe the best known is the transition from fossil fuel to a renewable alternative. Fossil fuels have been used heavily since the industrial revolution (1750) and the use, burning, of fossil fuels creates carbon dioxide which is the foremost greenhouse gas [1]. According to the U.S. Environmental Protection Agency (EPA) the emissions of carbon dioxide represents 81% of the total greenhouse gas emissions from the U.S. in the years 1990-2014 [2]. Reduction of carbon dioxide emission are a necessity if the fight against global warming is to be won. Reduction of carbon dioxide emissions require that fossil fuel is replaced with a sustainable and renewable alternative, e.g. electricity or biofuel. Electric cars may very well have an important role in this transition but heavier transportation such as trucks, ships and aircrafts will be needing liquid fuel, biofuels, in the foreseeable future.

A new process developed by *SunCarbon* aims to produce a biofuel which originates in the Swedish forest. 69% of Sweden's total land area is covered with forest and this has led to a strong and globally competitive pulp and paper industry [3-5]. During pulping a residual product called black liquor is produced, it contains the chemicals used for producing pulp from wood chips but also extracted wood substances [6]. The most interesting substance found in black liquor is lignin, one of the main building blocks of all trees, grasses and other plants [7]. Lignin is a large and complex molecule but when it's cut up in smaller fragments, it can function as a raw material for the production of biofuel [8]. However, the pulping chemicals found in black liquor needs to be removed in order to produce a biofuel. This is where the *SunCarbon process* comes in. A portion of the lignin in black liquor will be removed with filtration and then broken down into smaller fragments by heating it in a reactor together with catalysts. The smaller lignin fragments will be purified in two steps, first by using carbon dioxide that will purify the lignin by separating it from excess water and chemicals. In the next stage, hot acetic acid and water mixtures will be used to further purify the lignin. The result after the second purification stage is a heavy lignin-rich bio-oil that can be sent to existing refineries for final treatment.

The *SunCarbon process* was tested in this master thesis and the results seems promising. Lignin was successfully broken down into smaller fragments and purification with carbon dioxide removed 72% of the unwanted pulping chemicals while still recovering up to 85% of the lignin fragments. The second purification stage proved difficult to master but some successful experiments were preformed and showed that a high recovery of lignin can be expected.

Acknowledgments

Thinking back, five years is a long time. Then again, it feels like I started my studies at Lund University just recently. My time at the university have been filled with joyful moments and hair ripping moments, maybe more of the latter in recent time. Jokes aside, this thesis has been the most challenging, entertaining and educational experience of these five years. I am grateful to have been a part of this project and I would like to thank a number of people who have assisted me or otherwise been a part of the work.

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Abbreviations and symbols

Abbreviations

AC	Ash content (% w./w. dry basis)
ALPHA	Aqueous Lignin Purification with Hot Acids
GHG	Greenhouse gases
NF	Nano filtration
RF	Radiative forcing ($W m^{-2}$)
RO	Reverse osmosis
SEC	Size exclusion chromatography
SLRP	Sequential Liquid-Lignin Recovery and Purification
TDS	Total dry solids (% w./w.)
TLC	Total lignin content (% w./w.)

Symbols

C_{depol}	Lignin concentration in de-polymerized retentate
C_{light}	Lignin concentration in light phase
m_{depol}	Total mass of the de-polymerized retentate
m_{light}	Total mass of the collected light phase

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1 Introduction

More than two thirds of Sweden's total land area is covered by forest. 28 million hectares (69%) are covered by mostly spruce, pine and birch [3]. This have resulted in that the pulp and paper industry in Sweden for a long time have been an important industry which each year presents large revenues and employs many people. During 2015 the pulp and paper production was at 12 respectively 11 million tons which corresponds to more than 6% of the global production of both pulp and paper [5]. Looking at the export of pulp, paper and lumber, Sweden is at third place globally following Canada and USA. Sweden is thus an important export country for these products and the production volumes have been fairly constant the last 16 years which shows the stability of pulp and paper industry in Sweden [2, 3].

The fight against global warming requires that large industries, like the Swedish pulp and paper industry, adapts and continues the development of environmentally sustainable processes and products. Succeeding with this development would result in an attractive and contemporary process, keeping the Swedish pulp and paper industry globally competitive. In order for the pulp and paper industry to lower emissions of greenhouse gases (GHG), reduce waste and to find new sources of value in the production line; new processes are constantly developed and assessed. A way for the pulp and paper industry to continue the development is to utilize one of their by-products, black liquor, more efficiently.

An interesting component found in black liquor and one of the main components, is lignin. Together with cellulose and hemicellulose, lignin constitutes the primary building blocks in lignocellulosic biomass [7]. It is said to be the second most abundant organic polymer in nature, only trumped by cellulose and constitutes about 30% of the dry mass in woody biomass [9]. The structure is a complex grid of irregularly coupled aromatic phenol polymers and these aromatic structures puts lignin apart from other lignocellulosic polymers [7]. De-polymerizing lignin yields aromatic structures that are a suitable raw material for the production of renewable biofuels and chemicals [9]. Producing biofuels and chemicals from lignin would reduce the need for fossil resources such as oil, natural gas and coal, and in extension reduce the net emission of carbon dioxide (CO₂).

Today, black liquor is energy recycled by burning its organic content, mostly lignin, in the recovery boiler while pulping chemicals are recycled and reintroduced to the pulp mill [6, 7]. The recovery boiler is often a bottleneck in production and to reduce its load is of great value to pulp mills [11]. Extracting lignin from black liquor would reduce the load on the recovery boiler and as a result, the productivity of the pulp mill could be increased. The extracted lignin would be a new attractive product that broadens the product range while increasing the competitiveness of the pulp mill.

There are existing processes for the separation of lignin from black liquor that rely on acid precipitation [8, 9]. However, these processes uses relatively high quantities of chemicals, e.g. CO₂ and sulphuric acid (H₂SO₄) [11]. A new method for the extraction of purified lignin from kraft black liquor have been proposed by *SunCarbon*. The method aims to produce an economically competitive lignin-rich bio-oil that can be used in existing refineries for the production of a lignin-based biofuel.

1.1 Background

Human activities affect the Earth's surface and atmospheric conditions and by doing so, Earth's overall energy balance is shifted. Climate change is largely due to these changes and human activities plays an important role. The effects of global warming are becoming clear, melting ice caps and glaciers, rising sea levels, increasing precipitation and intensity of hurricanes and storms. Many species are threatened by these changes and none the least humans. These effects are due to a mean temperature increase of 0.85 °C and the best projections shows that by the end of the 21st century it is likely to exceed 1.5 °C [1].

Global warming is caused by an increase in radiative forcing (RF) which is the difference between insolation, solar irradiance absorbed by the earth, and the radiative energy reflected back into space. A positive RF means more energy is absorbed then reflected and thus the flux of energy is positive and we can conclude that energy is accumulated which causes a rise in temperature. GHGs such as CO₂, Methane (CH₄), Nitrous oxide (N₂O) and Halocarbons are the main reason for the increasing RF as these gases traps Earths outgoing infrared radiation causing the so-called *Greenhouse effect*. Other changes to the atmosphere like aerosols and particles and surface changes like deforestation and surface albedo also have an effect on the RF but the largest increase in RF are caused by greenhouse gases and that is where the focus of many studies are, this one included [1].

To battle global warming, emissions of greenhouse gases needs controlled and limited. During the 2015 Paris climate conference, 194 countries adopted a universal and legally binding climate agreement. It was agreed that the global average temperature increase, an effect of global warming, should be limited to well below 2 °C compared to pre-industrial levels and that the aim is to limit the increase to 1.5 °C [14]. In line with the Paris agreement, the EU have put up a plan for a low-carbon economy transition where the ultimate goal is to cut emissions of GHGs by 80-95% by the year 2050, compared to the level of emissions in 1990. This will be completed with milestone marks of 20% by 2020, 40% by 2030 and 60% by 2040 [15].

Carbon dioxide (CO₂) is the foremost GHG emitted to the atmosphere by human activity. According to the U.S. Environmental Protection Agency (EPA) the emissions of CO₂ represents 80.9% of the total GHG emissions from the U.S. in the years 1990-2014. The atmospheric levels of CO₂ were constant at ~280 ppm prior to the start of the industrial revolution in 1750. Since then increasing emissions have led to steadily increasing levels of atmospheric CO₂. In February 2017, the U.S. National Oceanic Atmospheric Administration measured the global annual mean CO₂ concentration to 406 ppm [16].

The International Panel of Climate Change (IPCC) states in their fifth assessment report (AR5) that "*Carbon dioxide concentrations have increased by 40% since pre-industrial times, primarily from fossil fuel emissions and secondarily from net land use change emissions*" [1]. To halt the steadily increasing levels of atmospheric CO₂ and therefore the effects of global warming, a change from fossil fuel to renewable biofuels are much needed.

1.1.1 SunCarbon

With the vast forest areal and the well-developed pulp and paper industry in Sweden a renewable biofuel based on lignin extracted from black liquor would be ideal. This is the vision of *SunCarbon*, a company founded in 2014 by *KIRAM, Hulteberg Chemistry & Engineering* and *Arkell Innovations*. *SunCarbon's* process idea to complete this is divided in three parts, membrane separation, hydrothermal treatment & purification and process integration. The membrane separation is on good way with a membrane pilot already running in a Swedish pulp and paper mill. A lot of research is put into the second part were this master thesis is aimed to aid. Process integration is on its way as *SunCarbon* works with companies in both the forest and petrochemical industry to meet their respective demands.

Process idea

The process is aimed to produce a lignin-rich bio-oil that can work as a drop-in raw material in existing refineries. A liquid and pumpable product is desirable as refineries cannot handle powder which otherwise is common among lignin products. It is also important to keep the ash content low, especially the sodium content (<25 ppm), as it otherwise poisons the refinery catalysts [17]. When black liquor is used as raw material, it is advantageous if the process is an extension on a pulp mill, a so-called bolt-on process.

About 20-25% of the lignin in black liquor can be extracted without causing any problems with the recovery boiler [18]. In the first step, black liquor is passed through the membrane filtration pilot and lignin is concentrated from about 7% to 25%. The lignin molecules are too large to function as a fuel and needs to be de-polymerized. This is done with a base catalysis with pulp mill internal catalysts that breaks the large molecules apart into a mix of smaller components. After base catalysis the lignin components needs to be purified in order to lower the ash content to acceptable levels. Often this can be the most expensive operation but a new method aiming to lower costs and the requirement for chemicals have been proposed by *SunCarbon*. It relies on a combined use of the Sequential Liquid-Lignin Recovery and Purification (SLRP) process and the ALPHA process; these processes are further described in section 2.5 *Sequential Liquid-Lignin Recovery and Purification* and 2.6 *Aqueous Lignin Purification with Hot Acids*

The carbonization step in the SLRP process is used to precipitate lignin in black liquor into a lignin-rich heavy liquid-phase that can be separated from the remaining light liquid-phase by gravity. The precipitation and wash steps in the SLRP process are not used in the *SunCarbon* process. After the carbonization, the heavy liquid-phase is pumped to the ALPHA process and mixed with acetic acid (AcOH) and water (H₂O) at specific ratios. Acetic acid acts as an anti-solvent and forces lignin out of the water phase and into another heavy liquid-lignin phase while further removing ash with the lighter liquid-phase [19]. The heavy liquid-lignin phase can then be pumped or screwed to the next step. Remaining acetic acid and water is removed by evaporation and results in a lignin rich bio-oil with very low ash content.

Lignin-rich bio-oil is then mixed 50/50 with a fossil fuel source like vacuum gas oil (VGO) and about 2% surfactants are added. This is done to stabilize the product which otherwise can re-polymerize. By mixing with fossil fuel to the required renewable source quota, the supply of biofuels can be stretched to meet the demand in a transition towards fossil free fuel.

1.2 Aim and limitations

The aim of this project is to investigate the possibility of processing black liquor retentate from *SunCarbons* membrane filtration pilot into a de-polymerized lignin-rich low-ash product. The effect of temperature on de-polymerization will be investigated. The carbonization step in the SLRP process will be used and the effects of temperature and carbonation are to be studied. Purification of heavy liquid-phase from the SLRP carbonization will be done according to the ALPHA process and the potential of using the process in combination with the SLRP carbonization will be investigated.

Production of lignin-rich bio-oil require additional process-steps and is not investigated in this work. Performing trials on de-polymerized retentate is necessary as it alters lignin structure and properties, which could have an effect on down-stream processes like SLRP and ALPHA. However, it is not the main objective of this work and only the effect of temperature will be investigated.

2 Theory

2.1 Lignocellulosic biomass

Woody biomass is mainly constructed by three organic compounds: cellulose, hemicellulose and lignin. These compounds are often referred to as *lignocellulose* and when materials comprised by these compounds are used as biomass they are called *lignocellulosic biomass* [7].

Cellulose

Cellulose is the main constituent of the cell wall in plants and it is the most abundant organic substance present in nature. Hundreds of D-Glucose molecules interconnected with a β -1,4-glycosidic linkage forming long chains comprise the main structure of cellulose. Hydroxyl groups from one strand can form hydrogen bonds with other hydroxyl groups and thus connect several strands with each other forming a large and well-ordered crystal structure [20]. Figure 2.1 shows the cellulose structure and its interconnecting bonds.

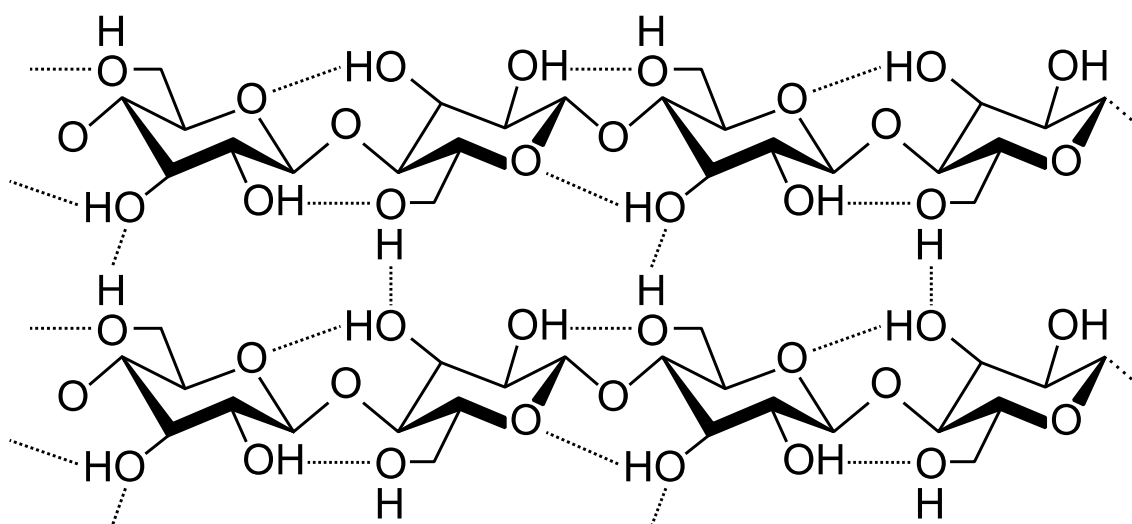


Figure 2.1. Chains comprised of β -1,4-glycosidic linked glucose units are interconnected with hydrogen bonds to form the structure of cellulose. Modified from [21].

Hemicellulose

Hemicellulose is group of branched polysaccharides with a more complex and diversified structure compared to cellulose. The function of hemicellulose in the cell wall is to add strength by interacting with cellulose and in some cases with lignin. What exactly is defined as hemicellulose is a discussed topic but most researchers consider it to be a polysaccharide which is neither cellulose nor pectin and have β -1,4-glycosidic bound units of glucose, mannose or xylose as backbone [22].

Lignin

After cellulose, lignin is the most abundant organic polymer and is found in all species of gymnosperms and angiosperms. In wood, lignin content is 20-40% and in grasses it is somewhat lower at 15-20% [7]. The function is mainly to supply support by interacting with cellulose and hemicellulose in different parts of the cell wall. Lignin is also vital in the vascular system where gaps are filled and with its hydrophobic attributes it waterproofs the cell wall and thus enables the transport of water and solutes [23].

Just like hemicellulose, lignin is a group of organic polymers with a common backbone. Structures differ between plant species but also between different parts of the plant. The structure is very complex and consists of irregularly coupled units of phenyl propane linked with C-C and C-O bonds. Three structural monomers make up the major part of lignin and divides lignin into three classes, p-hydroxyphenyl- (H), guaiacyl- (G) and syringyl lignin (S). These monomers are derived from p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, respectively. [7]. Figure 2.2 presents the structure of these monomers and the alcohol from which it is derived.

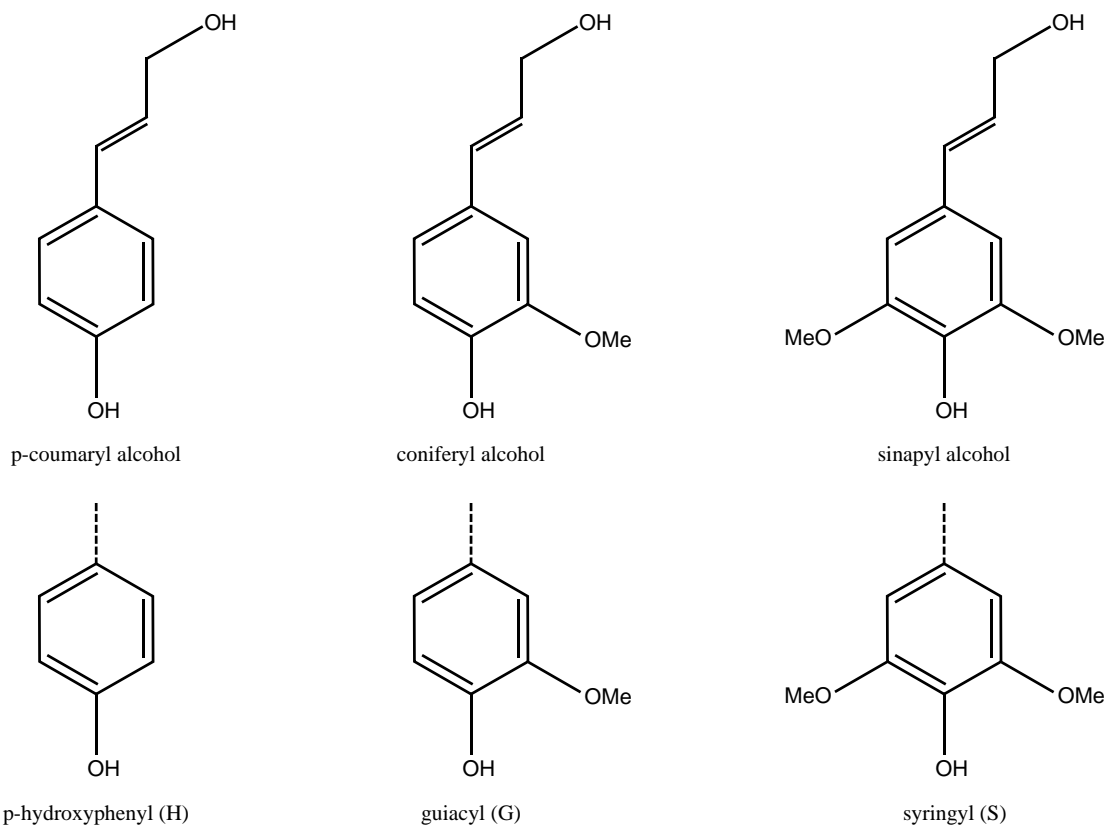


Figure 2.2. Three structural monomers divide lignin in three classes; H, G and S. These monomers are derived from the alcohol depicted above.

Wood from gymnosperms are often referred to as softwood while wood from dicot angiosperms are called hardwood. The lignin in softwoods have large amounts of guaiacyl monomers and small amounts of p-hydroxyphenyl monomers while hardwoods mainly are comprised of guaiacyl and syringyl monomers. These monomers are linked by a variety of bonds, up to 14 different types [24]. The most common bond type is ether bonds, which includes phenol-ether-, alkyl-ether-, dialkyl- and diaryl-ether bonds. 70-80 % of the ether bonds are phenol-ether bonds and this group includes the most common bond, arylglycerol- β -aryl ether bond (β -O-4). The group also includes the second most common bond, the arylglycerol- α -aryl ether bond (α -O-4). Examples of both bonds are depicted in Figure 2.3.

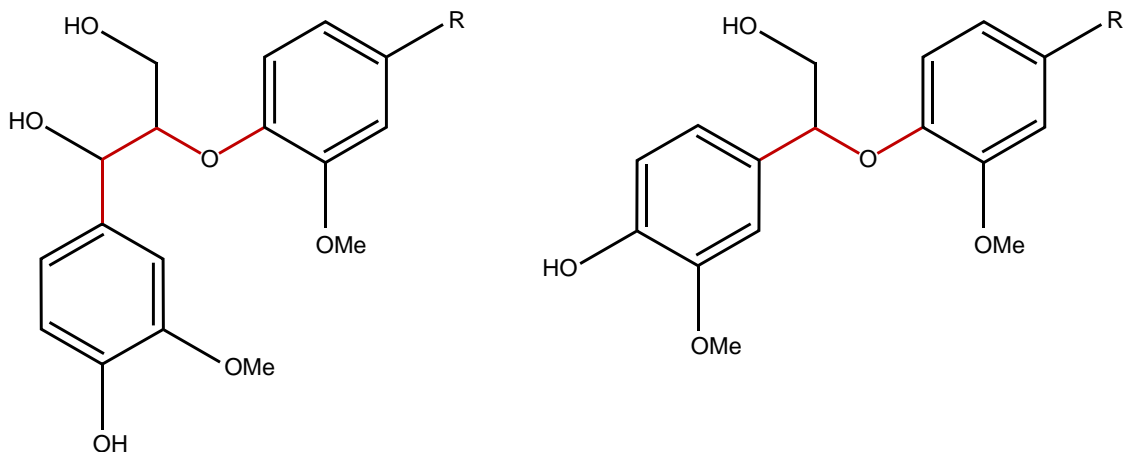


Figure 2.3. To the left, arylglycerol- β -aryl ether bond (β -O-4). To the right, arylglycerol- α -aryl ether bond (α -O-4).

2.2 Chemical pulping

The first step in chemical pulping is to chop the wood in a wood chipper. The wood chips are then cooked at elevated temperature and pressure together with a mix of chemicals (cooking liquor) meant to break couplings and thus dissolving the lignin so that the wood fibers are exposed. After the cooking process, the cooking liquor and the wood fibers are separated, washed and sieved before bleaching. Finally, the produced pulp is pressed and dried in several steps before it is packaged in bales. Some pulp mills also have an integrated paper mill and in that case the wet pulp can directly be pumped to the paper production without being dried [6].

2.2.1 The Kraft process

The most common chemical pulping process in use today is the *kraft process*, depicted in Figure 2.4. It has largely replaced the previous *sulfite process*, though this process still exists [2, 22, 23]. In the kraft process, wood chips are processed in a heated and pressurized vessel known as a digester. In the digester, wood chips are mixed with a cooking liquor called white liquor. The white liquor consists largely of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) dissolved in water. These are the active chemicals participating in the isolation of wood fibers during cooking. White liquor also contains other chemicals like sodium carbonate (Na₂CO₃) and sodium sulfate (Na₂SO₄). The cooking process is run either in batch mode or in a continuous mode. Temperature (~170 °C) and pressure are controlled according to a cooking scheme that is adapted after the wood resource used and the desired quality of the pulp. The cooking liquor is separated from the pulp and now contains lignin and other dissolved substances such as cellulose, hemicellulose, organic acids and rosin. This makes the liquor darker and it is now called black liquor. The black liquor is still hot and contains valuable energy, therefore it is sent to an expansion cyclone where it is used to produce steam which drive other parts of the process. Pulp from the cooking process is passed through a sieve in order to remove unwanted debris like twigs, bark, un-cooked wood chips and bundles of wood fibers. It is also washed in several steps to remove chemicals which otherwise can hamper the bleaching process, negatively affect pulp quality and to remove remaining dissolved lignin. Chemicals which are separated in the washing process are recycled and used again [22, 23].

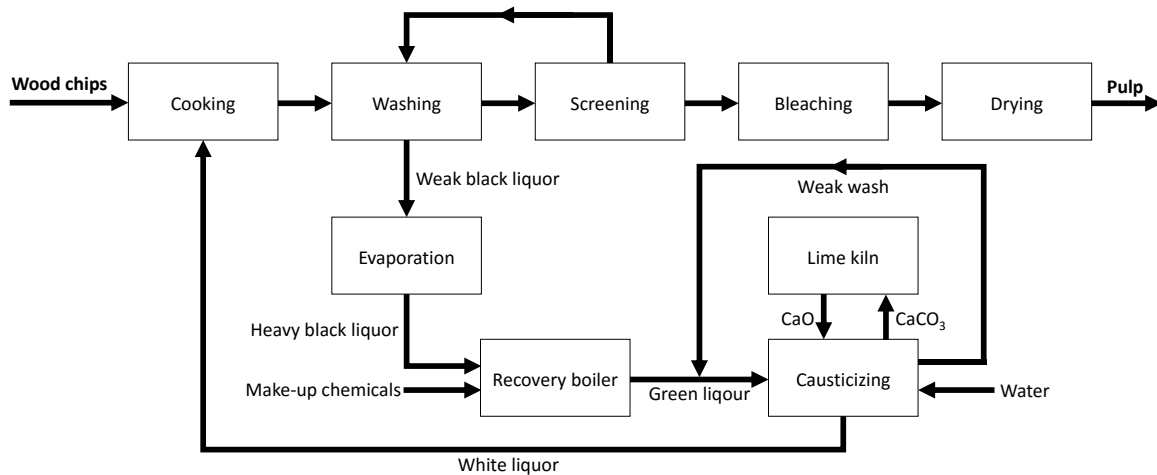


Figure 2.4. Scheme over the kraft process displaying important steps. Graphic modified from Jirvall [6].

If the pulp is to be bleached, it is done after the washing. Discolorations in the pulp are due to remaining lignin that have changed color during the cooking process. The bleaching process means either to bleach the lignin itself (brightening) or to remove the lignin (delignification) with chemicals so the natural white color of cellulose can come through. Brightening is mostly used for pulps high in lignin, e.g. mechanical pulp, as the amount of chemicals needed in a delignification process would be high. For chemical pulps where most of the lignin is already removed, delignification bleaching is common. Previously it was done with chlorine gas but as evident environmental impacts could be identified, it has been phased out and today there are methods using chlorine dioxide but also those that are completely chlorine free. Instead of chlorine; oxygen, peroxide, ozone and other chemicals/methods can be used in series to bleach the pulp [6].

The last step is drying and pressing of the pulp. In an integrated pulp- paper mill the wet pulp can be pumped directly to the paper production but if the pulp is to be transported it is dried and pressed into bales [6].

Cooking chemicals, lignin and other dissolved substances are found in the black liquor separated in the washing step. For process economic and environmental reasons, it is vital to recycle these chemicals. Lignin and other dissolved substances are energy recycled through combustion in the recovery boiler and thereby produce steam that often is enough to power the entire process or at least a large portion of the power demand. Recycling of the used cooking chemicals starts with the black liquor retrieved after the washing step. This liquor, known as weak black liquor, has a relatively low solids content, ~15%, and cannot be combusted as is. To increase the solids content, it is passed through an evaporator train where the solids are increased to 70-80% and the liquor is now known as heavy black liquor. Often a higher solids content is better for combustion in the recovery boiler as it gives better heat economy, lowers the amount of sulfur containing gases and results in a more efficient chemical recycling. During the evaporation, rosin soap is pushed out of solution due to the increasing ionic strength and can be skimmed off. The rosin soap is then further processed to, among other products, tall oil which in turn is used in soap and by *SunPine* for the production of bio-diesel [23, 24]. Heavy black liquor is sprayed into the recovery boiler where organic species are burned while the inorganic fall to the bottom and forms a smelt. The smelt flows out of the boiler and is solvated in a filtered liquor (weak wash) from a later step. After mixing, it is called green liquor. Carbon

dioxide formed in the boiler reacts with sodium and forms sodium carbonate, which is one of two main components in the green liquor. The other component is sodium sulfide and is formed by the reduction of sodium sulfate [22, 23]. Losses of active cooking chemicals are added before the recovery boiler as sodium sulfate then can be used as a make-up chemical for sodium sulfide [23].

The last step in the chemical recovery process is to causticize the sodium carbonate to form sodium hydroxide needed for the white liquor. Green liquor is filtered and a part of the liquor is used to solvate the smelt while the rest is pumped to the lime slaker where it is mixed with calcium oxide (CaO). Water in the green liquor reacts with lime to form calcium hydroxide (Ca(OH)₂). The mix is sent to causticizing where calcium hydroxide reacts with sodium carbonate and forms sodium hydroxide and calcium carbonate (CaCO₃). To complete the regeneration, calcium carbonate is filtered and then burned in a lime kiln where calcination occurs and calcium oxide is regenerated [22, 23].

2.3 Membrane filtration

Membrane filtration enables the separation of different solvated species in a liquid or gas stream. It means it is possible not only to separate solid particles from liquid but also to separate solvated species like salts, protein or other organic substances. Separation is accomplished by passing the stream through a membrane that selectively can separate different substances. Often the separation is based on size and the size of the membrane pores control the maximum size of substances that can penetrate. By doing so, the in-stream is separated into two out-streams. The stream which penetrates the membrane is called permeate and contains the solvent plus the substances which could penetrate the membrane. The stream that cannot penetrate the membrane is called retentate and it contains substances too large to pass through the membrane pores. Pressure differences between the two sides of the membrane is often used as the driving force of the process and is called transmembrane pressure [11].

Pressure driven membrane filtration in liquid-phase are often separated into four categories. The categories are based on the size of the substances for which the process is commonly used. Microfiltration is in the interval 50 nm to 10 µm and is foremost used to separate particles and cells. Ultrafiltration, 5-50 nm, can separate viruses and macromolecules like proteins. Nanofiltration, 1-3 nm, is used for separation of multivalent ions, sugars and other small organic substances. Reversed Osmosis is used on substances up to 2 nm in size and can separate univalent ions [7, 14].

A membrane does not have an exact point where all substances larger than the pores stay in the retentate. Instead, the retention of a membrane is given as a percentage of substance that stays in the retentate. This is used to define the term cut-off, which describes the size of the particles that to a large extent is stopped by the membrane. For ultrafiltration and nanofiltration a membranes cut-off is expressed as a molecular weight cut-off and is defined as the molecular weight (dalton) of a particle which is retained to 90% [11].

A filtration process can either be run batchwise where the retentate is fed back to the feed tank or continuously where retentate and permeate continuously is separated. In a continuous process several membrane filtration systems can be connected in series so the retentate/permeate from one system is the in-flow to the next. The flow in a membrane filtration system can be of two sorts, crossflow and dead-end. Crossflow means the flow direction is along the membrane were as dead-end means the flow direction is perpendicular to the membrane. Dead-end filtration has

a disadvantage in that there easily is a build-up of substances that cannot pass through the membrane and thus clogs it. It is therefore more common with crossflow filtration, shown in Figure 2.5.

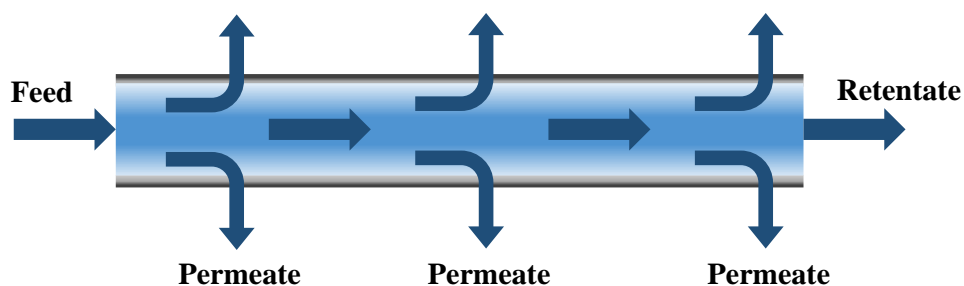


Figure 2.5. A tubular crossflow membrane has a flow that is horizontal with the membrane.

2.4 Base catalyzed de-polymerization

A base-catalyzed de-polymerization with pulp mill internal catalysts can be utilized to degrade the complex and large structure of lignin. Sodium hydroxide and sodium sulfide are the two active chemicals participating in the dissolution and de-polymerization of lignin during pulping. The most abundant of these chemicals are sodium hydroxide, which solubilizes lignin by increasing pH and thus de-protonating lignin making it soluble in the alkali solution. Sodium hydroxide also participates in the de-polymerization. Figure 2.6 presents a suggested mechanism of how NaOH participates in the cleavage of a β -O-4 bond [24].

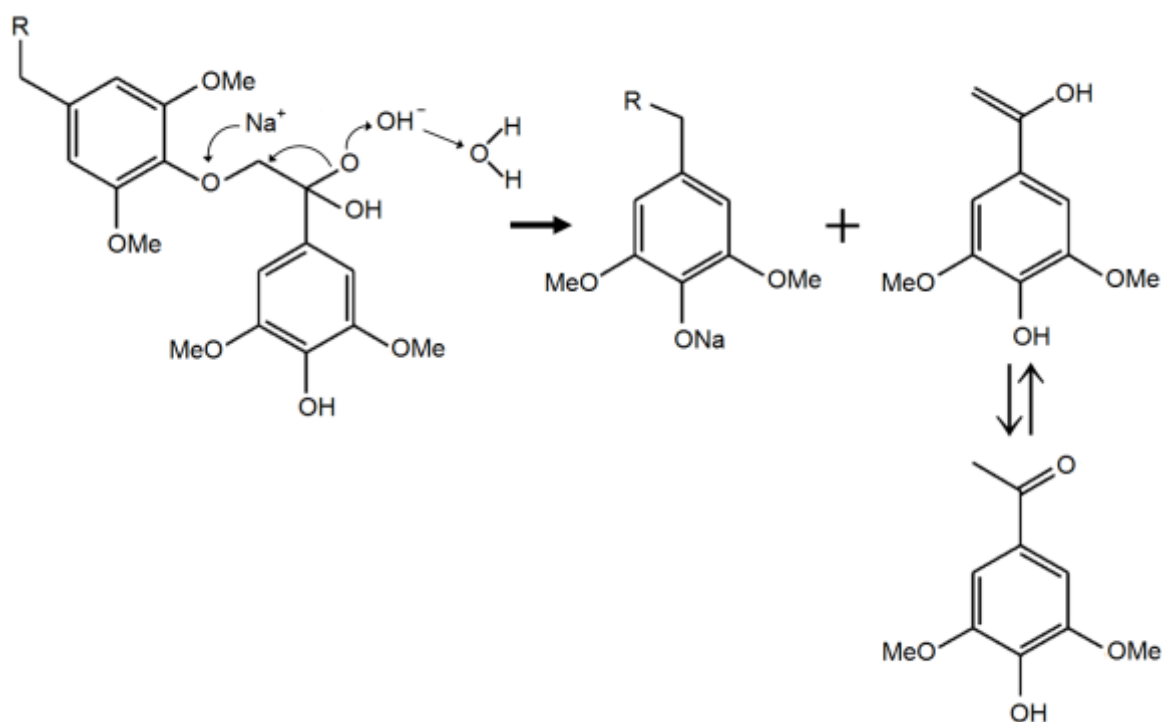


Figure 2.6. Lignin de-polymerization with NaOH as suggested by Roberts et. al. One of many possible reactions. Modified from [24].

2.5 Sequential Liquid-Lignin Recovery and Purification

In 2009, Michael Lake and John Blackburn at the *Liquid Lignin Company* were awarded a U.S. Department of Energy (DOE) grant. They were to develop a new and energy efficient process for extraction of lignin from black liquor. They based their new technology on the original lignin recovery process developed in the late 1930s by Tomlinson Sr. and Tomlinson Jr. The idea behind the new SLRP process was that at the right temperature, pressure and pH, lignin precipitates as a heavy liquid-phase [27]. As in LignoBoost and LignoForce [8, 9], carbon dioxide is used to lower pH in the incoming black liquor stream but unlike those processes, lignin does not precipitate as solid particles but as a heavy liquid-phase. This is because the reactor runs at elevated temperature (~115 °C) and at pressures, enough to prevent boiling, that allow the heavy liquid-phase to form. A lighter phase is also achieved and lignin is partitioned between the two phases but are concentrated in the heavy phase. The two phases are separated and the lighter phase is re-introduced to the pulp mill before the evaporators. The heavy phase is lignin rich and have lost some of the original water, cooking chemicals and ash [26–28].

In the next step, lignin in the heavy phase is washed and precipitated as solid particles by acidification with sulfuric acid to pH 2-3. The particles are separated from the bottom of the reactor and pressed in a filter press to further separate liquid before the lignin particles are washed, dried and finally, considered a finished product [27].

2.6 Aqueous Lignin Purification with Hot Acids

The Aqueous Lignin Purification with Hot Acids process also works on the basis of liquid-liquid phase separation. The process was developed by Thies, Klett and Bruce at the Department of Chemical and Biomolecular Engineering at Clemson University, USA, and is aimed to produce ultraclean lignin where the metal content is <100 ppm [16, 29]. Ultraclean lignin is used for certain applications when it is further processed to e.g. carbon fiber as metals in the lignin otherwise can cause problems for the process and imperfections in the product [19]. The researchers at Clemson University discovered that if lignin powder from the SLRP process is mixed with acetic acid and water at the right proportions and under appropriate conditions, it separates into two liquid-phases. A heavy lignin-rich phase and a light lignin-depleted phase is formed. Metals prefer the light liquid-phase and they can thus be separated from the main part of the lignin content, producing an ultraclean product [19]. For the liquid-liquid phase separation to occur, the temperature needs to be above the required phase-transition temperature. The required temperature increases as more water is used, ranging from 30-100 °C. Lignin concentrations of 5-36% are possible and the phase-transition temperature increases as concentration drops [16, 30]. By altering the H₂O/AcOH ratio, the lignin can be partitioned between the two phases based on their molecular weight [19].

The two phases are separated and the heavy liquid-phase have a drastically lowered (tenfold) metal content after one ALPHA stage. The process can be repeated on the resulting heavy liquid-phase to further decrease the metal content and thus produce an ultraclean lignin rich solution with <100 ppm metal content [19].

3 Method

Trials are separated in three parts, base catalysis, acidulation and purification. The first two was performed at *SunCarbon* in Tygelsjö and the purification was done at the Department of Chemical Engineering at Lunds University Faculty of Engineering.

3.1 Materials

A Parr 4570 series reactor in a bench-top stand and a Parr 4848 reactor controller was used for the base catalysis and acidulation trials. The total volume of the reactor was 500 ml and it was rated for 500 °C and 345 bar. Temperature was measured with a J-type thermocouple inside a thermowell. Pressure was measured by both an analog manometer and a digital pressure gauge connected to the controller. Stirring was conducted by two turbine-type impellers. Heat was applied with a ceramic heater (part of the Parr bench-top stand) with 1400 watts of power at 115 volts. On the reactor-head were two needle valves used when pressurizing and depressurizing the reactor. For safety reasons the reactor had a bursting disc rated for 345 bar. It was connected with steel piping to an empty 200-liter barrel that in turn was connected to the ventilation. The barrel was used as an intermediate to hinder reactor content from reaching the ventilation. A computer running the associated Parr program was connected to the reactor controller and used to log temperature, pressure and stirrer speed data during trials. Gas flasks were chained nearby and connected with a braided steel hose. Figure 3.1 shows photos of the reactor and the complete setup used during trials.

The entire reactor was weighed regularly during trials to keep track of weight changes, for this a Scandscale QHC-15+ with a resolution of 0.2g was used. All other weight measurements in Tygelsjö were performed on a KERN PCB1000-2 with a resolution of 0.01g. At Lunds University a Mettler Toledo AE240 with a resolution of 0.0001 g were used for SEC dilutions, total dry substance and ash content. A KERN KB1200-2N with a resolution of 0.01 g was used for all other weight measurements.

pH measurements were performed on a Metrohm 877 Titrino plus using a Metrohm Solvotrode electrode filled with TEABr 0.4 mol/l. On each day of trials, the setup was calibrated with three pH buffers, 7, 10 and 13.

For the purification trials, a heated water bath, Julabo 5B, was used in combination with a mantled beaker. Silicone hose connected the water bath with the mantle and hot water could be pumped through by the combined heater and pump, Julabo EM, in the water bath. A rubber stopper with a glass outlet pipe was used to hinder evaporation without building pressure. Temperature in the water bath and in the beaker was monitored with a 4-channel K-type thermocouple thermometer, TSURUGA Model 3527. The beaker was placed on a heated stir plate, IKA WERKE RCT Basic. The heater function was not used during trials. Other equipment used was a ceramic mortar, 100 ml Schott bottles and Pasteur pipettes. Figure 3.2 shows a photo of the setup used during trials.



Figure 3.1. On the right is the Parr reactor used during trials and to the left is the entire setup as it was during an experiment.



Figure 3.2. Equipment setup used for the ALPHA purification trials. A heated water bath pumps hot water through a mantled beaker that is placed on a stir plate.

3.1.1 Chemicals

- Acetic Acid, 99-100%, VWR
- Sulfuric Acid, 95-97%, Scharlau
- INDULIN AT, powder, MeadWestvaco
- NaOH, 50%, Merck
- NaOH, BioChemica pellets, AppliChem
- CO₂ (g), Strandmøllen
- N₂ (g), Strandmøllen
- pH buffer, pH 7 & 10, Thermo Scientific
- Titrisol buffer concentrate, pH 13, Merck
- LignoBoost, powder, STFI-Packforsk (now RISE Bioekonomi)

3.2 Base catalysis

The effect of temperature on base catalysis was examined by testing temperatures between 220-250 °C according to the method presented below with the exception that 250 ml retentate was used, the reactor was not weighed and heating was controlled manually. The results from these initial experiments were then used when deciding the temperature used for the acidulation trials.

Method

The reactor was visually checked for faults and residues from previous trials and any issues were sorted. The reactor was weighed empty, filled with approximately 300 g (260 ml) of black liquor retentate and then weighed again. pH of the unprocessed retentate was measured before each trial. The reactor was closed and then placed in the bench-top stand and all cables and fittings were attached. Reactor temperature was set to 240 °C and stirring was commenced with 400 RPM. To ensure repeatable heating and de-polymerization between the experiments, the controllers PID was used to control the heating. A PID auto tuning at 240 °C was made according to the controller manual prior to the first experiment. Heating to 240 °C took approximately an hour and once the temperature had been reached, it was held for 15 min before the reactor was cooled. Cooling was accelerated with a desk fan and it took 45 min to reach 60 °C. The reactor was weighed before being opened and then stirred to ensure a homogenous liquid. After each base catalysis, 15 ml sample was taken and pH was measured before the sample was placed in a freezer. Afterwards the reactor was weighed again to quantify the sample taken.

3.3 Acidulation

To test the effect of differing temperature and CO₂ volume, an experimental series with three temperatures and three pressures to a total of nine combinations were tested. All combinations are presented in Table 3.1. Trials are named after temperature, pressure and possible phase separations. As an example, the heavy phase of 110 °C with 10 bar will be shortened to 110/10/H. For the light phase it would be 110/10/L and 110/10 is the trial as a whole.

Table 3.1. Nine combinations were tested during acidulation trials.

Temperature [°C]	Pressures [bar]
110	5, 10, 15
130	5, 10, 15
150	5, 10, 15

Method

Acidulation trials were started immediately after base catalysis. The reactor was closed and re-fitted in the bench-top stand. In order to achieve an inert atmosphere and to keep water in its liquid state during heating, a nitrogen (N₂) pressure of 6-6.5 bar was applied. Stirring was set to 400 RPM and the temperature to 110, 130 or 150 °C. A second PID auto tuning at 120 °C was made prior to the experiments. A stable temperature was reached after 30-45 minutes and at this time, stirring was stopped. CO₂ was then quickly injected into the headspace of the reactor until a pre-determined pressure differential of 5, 10 or 15 bar was achieved. Pressure readings were taken while stirring was turned off, the needle valve to the gas flask was shut and when a stable pressure had been recorded for ~10 seconds. Stirring was re-commenced at 300 RPM, a lower RPM was used to allow settling of a heavy liquid-phase but still high enough to limit scorching at the reactor walls. The reactor was left to allow CO₂ to dissolve and react, after 1-2 hours a stable pressure was achieved and at this point stirring was turned off. A stable pressure was defined as no change in the first decimal, 0.1 bar, for 15 minutes. The reactor was then left for an hour at temperature and pressure to allow the liquid-phase to settle. After the hour had passed, heating was turned off and cooling was commenced. The reactor was left for another hour, after which the temperature was ~50 °C and the reactor was weighed and then opened. A light liquid-phase could be poured into a beaker and weighed. A 50 ml sample was kept frozen for analysis. The reactor was weighed again to determine the mass of the solidified heavy liquid-phase in the bottom of the reactor and on the impellers. The solid phase was then scooped out and kept frozen for analysis and further trials. Afterwards, the reactor was first cleaned with water and then filled with a NaOH solution and left overnight.

3.4 Purification

To test the purification of the solid phase collected in the acidulation trials a mix from several experiments was made. 25g of solidified heavy phase from four acidulation experiments, 110/10/H, 110/15/H, 130/10/H and 130/15/H, were mixed together in a ceramic mortar and air dried to form a powder, further on called acidulation powder, which could be used in the method described below. Other lignin powders used were supplied as a powder and was used as they were.

Method

A solution with 70/30% of H₂O/AcOH with 10% lignin powder added was prepared by mixing 44g distilled water, 19 g acetic acid and 7 g lignin powder in a Schott bottle. pH of the mixture was if necessary adjusted to ~2.5 by additions of concentrated sulfuric acid. The mixture was poured into the mantled beaker, the rubber stopper was closed and stirring was commenced at ~200 RPM. The beaker was connected to the water bath, which had been heated to 80-90 °C, and water circulation was started. Once phase separation occurred the phases were left for 15 minutes with stirring turned off in order for them to fully separate. Light phase was drawn off

with a pipette and saved for further analysis. The heavy phase was collected, weighed and placed in a centrifuge tube to cool. As the heavy phase cools it solidifies and after cooling it was crushed in a mortar into a powder. All crushed heavy phase was placed in the beaker and weighed again, as some material is lost in the mortar. A fresh solution of 63g H₂O/AcOH (70% water) was poured into the beaker and the process above was repeated.

3.5 Analysis

3.5.1 Total dry substance and ash content

Measurements of TDS was made according to a method evaluated in previous work by Anders Arkell. Clean crucibles were stored in an oven at 105 °C (at least 24 h) to ensure that they are completely dry. When handling the crucibles, a plier or gloves were used to avoid adding weight in the form of moisture and finger grease. For each sample a crucible was taken out of the oven and kept in a desiccator for 30 min, a Whatman filter was placed in the crucible and the crucible with filter was then weighed to establish a base weight. Approximately 3 ml or 2 g of sample was added onto the filter and the crucible was then weighed again before being placed in 105 °C. After 24 hours at temperature, the crucibles were placed in a desiccator for 30 min to cool before being weighed.

Directly after TDS measurements, the crucibles were moved to another oven for AC measurements. During 9 hours the temperature in the oven was ramped from room temperature to 900 °C and the final temperature was then held for 3 hours. After the oven had cooled to 200 °C the crucibles were placed in a desiccator for 30 min to cool before being weighed. A short discussion about the use of UV measurements for lignin quantification can be found in section *4.1 Methods for analysis*.

3.5.2 Total lignin content

Total lignin content (TLC) was measured with a Shimadzu UV-160A spectrophotometer and quartz cuvettes. A wavelength of 280 nm was utilized and all samples were diluted with NaOH 5 g/l until the absorbance was between 0.6 and 0.9. Solidified heavy phase was diluted to 20x based on weight, the rest of dilutions were based on volume and made with automatic pipettes. An absorbance extinction factor of 21.1 (l g⁻¹ cm⁻¹) for hardwood and 24.6 (l g⁻¹ cm⁻¹) for softwood was weighted with the respective mass percentages of hardwood/softwood used at the pulp mill [31, 32]. The weighted extinction factor used was 23.6 (l g⁻¹ cm⁻¹).

3.5.3 Size Exclusion Chromatography

Size Exclusion Chromatography (SEC) have been used to analyze the mass distribution in the samples. A non-polar column separates species in the sample solely on size, which correlates to its mass. For this, a Waters 600E chromatography system was used with a refractive index detector (Waters 2414), used for calibration, and a UV detector (Waters 486), used for lignin measurements at 280 nm. The column was packed with 30 cm Superdex 30 and another 30 cm of Superdex 200, both supplied by GE Healthcare. Mobile phase was 5 g/L NaOH that holds a pH of ~13 and thus keeps lignin dissolved. Polyethylene glycol (PEG), supplied by Merck, with peak molecular masses at 0.4, 4, 10 and 35 kDa were used as standards. All samples were filtered through a 0.2 µm syringe filter (Schleicher & Schuell) and the injection volume was 500 µl.

All samples are diluted based on mass with mobile phase to an absorbance of ~1. For retentate- and de-polymerization samples, a dilution of 100x was used. Solidified heavy phase was diluted to 25x and put on a heater with a stirrer bar to dissolve all solids fully before being further

diluted to 250x. Light liquid-phase was diluted to 40x. Dilutions were made in maximum steps of 10x, except for the first dilution of heavy phase where a higher dilution was necessary to dissolve all solids.

In this report the SEC response of different samples have been normalized so that the highest peak of each sample has the same response. This minimize the influence that response has on the interpretation of the results and facilitates for easier comparisons between samples. A short discussion about the response can be found in section *4.1 Methods for analysis*.

4 Results & Discussion

4.1 Methods for analysis

UV 280 nm

Measuring lignin content with UV is a fast and easy method for quick lignin concentration determination. However, as UV measures conjugated double bonds and the idea of de-polymerization is to break bonds and thus change the structure of lignin, it is not a very exact method. Still its ease makes it a valuable method and most interesting is how different samples compare to each other, which should be more reliable as all samples should be similarly affected.

SEC

Taking a known amount of two differently sized lignin molecules and run those through the SEC would of course yield two different responses. Integrating these responses, knowing the amount of lignin is the same, will not yield the same total area. Some lignin molecules will give a higher response at 280 nm relative to their size, mass or structure than others will. Thus, SEC is suited as a qualitative analysis and not a quantitative. Despite this, the response can tell some tales but it has to be interpreted as merely an indication.

The use of PEG as standard can be discussed. The two molecules, lignin and PEG, are not similar. PEG is a linear polyether while lignin is a bulky and aromatic compound. A more suitable standard might be polystyrene, which is still a linear polymer but it is aromatic and thus more similar to lignin. The use of polystyrene as a standard in SEC analysis of lignin has been reported in literature [9, 33, 34]. However, it needs to be remembered that SEC is a relative method and that the actual molecular weight might differ. Thus, it is still a good method for determining which process or parameter that affects de-polymerization and to what degree.

4.2 Retentate analysis

To get an idea of the starting material, analysis results of the black liquor retentate is presented below in Table 4.1.

Table 4.1. Results from analyzes made on black liquor retentate.

Total dry substance [% w./w.]	Ash content [% w./w. dry basis]	Total lignin content [% w./w.]	pH
33.1	7.7	21.8	13.4 ± 0.1

4.3 De-polymerization

Four temperatures were tested, 220, 230, 240 and 250 °C and below in Table 4.2 are results from the trials compiled. When looking at heating time it is important to take into account that the starting temperature differed between the experiments. 220, 230 and 240 °C were run in direct succession and thus the reactor was still warm from previous experiments and thus the heating time is lower for 230 °C and 240 °C compared to 220 °C. The following day 250 °C was run and the cold reactor combined with the highest temperature resulted in the longest heating time.

Table 4.2. *Compilation of experiments performed when testing temperature dependency of de-polymerization.*

Temperature [°C]	Heating time [min]	Max pressure [bar]	pH (depol.)	Characteristics
220	49	21.6	11.4	Glossy finish, crackles when drying
230	43	26.2	11.0	Glossy finish. Highly viscous
240	40	31.8	10.9	Matte finish and small particles
250	53	37.5	10.7	Solids in reactor and on impeller

Overall, the heating time does not change much for the different experiments and with the same starting conditions all experiments would have about 50 min heating time. It is not believed that the difference in heating time has any effect on the de-polymerization as the highest temperature held for a prolonged time (3-5 min) have been shown to be the deciding factor [15]. As expected pressure increased with temperature and was mainly used to make sure the reactor was not leaking. As the liquid is mainly water, which is incompressible, the pressure is not believed to have much of an effect on the de-polymerization except for allowing the high temperatures. The pressure for all experiments are constantly somewhat lower than the vapor pressure for pure water at the corresponding temperature, as is reasonable with the retentate being approximately 70% water. pH measurements made after the de-polymerization are interesting results as the de-polymerization consumes sodium hydroxide which should lead to a decrease in pH [21, 33]. However, there are also organic acids formed from cleavage of hemicellulose and CO₂ from lignin cleavage that also can lower pH [15]. The retentate has a pH of 13.4 and the de-polymerized samples have a pH ranging from 11.4 (220 °C) to 10.7 °C (250 °C) which shows that the pH drops 2-3 units during base catalysis. The theory that a higher temperature results in a more de-polymerized product is substantiated by the pH measurements as the pH drops when the temperature is increased.

4.3.1 Visual comparison

220 °C resulted in a homogenous black liquid with somewhat higher viscosity than the starting retentate at room temperature. The finish was glossy and when the liquid dried on the glass wall of a beaker it crackled and a “cracked glass” pattern formed in the dried material. 230 °C became a highly viscous liquid; at room temperature a spoon could be left standing upright in a beaker without falling. The finish was similar to the lower temperature of 220 °C and the same pattern could be seen when the liquid dried. 240 °C had a lower viscosity than the two lower temperatures and lower than the starting retentate. The finish was matte and grainy, small particles could be seen if the liquid was smeared on the wall of a glass beaker. However, the particles did not separate and fall to the bottom, neither did they stick to the reactor wall or the impeller. The highest temperature, 250 °C, resulted in solid material in the bottom of the reactor and on the impeller. The liquid had a lower viscosity than the retentate, similar to 240 °C, and showed a matte and grainy finish with particles. Figure 4.1 presents pictures taken during trials. The “cracked glass” pattern can be seen to the left, the highly viscous properties of 230 °C are seen on the middle picture and the matte and grainy finish of 240 °C are shown on the left.

These results suggest that 220 and 230 °C has all lignin completely dissolved in the alkali solution, thus the clear and glossy finish completely free of solid particles. At 240 °C, lignin has started to precipitate and as an effect, the viscosity is lower. The very viscous 230 °C would thus be on the verge where lignin starts to precipitate. Possibly, lignin-lignin molecule interactions are stronger in this state and clings to each other, resulting in a very viscous liquid.



Figure 4.1. Left: 220 °C, Middle: 230 °C, Right: 240 °C.

4.3.2 Mass distribution

The decrease of pH coincide with the SEC analysis of these samples, presented in Figure 4.2. 250 °C were left out as it resulted in a solid material sticking to the walls of the reactor and to the impeller. This is not desirable as the solids would not be pumpable and would lead to further processing difficulties. De-polymerization peaks at ~3 kDa compared to retentate which peaks at 4 kDa. One of the most important results is seen at high molecular weights. The retentate does not reach zero response until after 100 kDa while the de-polymerized samples reaches this at ~12 kDa. Thus, the base catalysis has been very successful at splitting these very large molecules and completely removed them from the retentate. At the lower end of the mass scale, ~0.4 kDa, a small peak is found. As 400 dalton corresponds in mass to dimers of p-coumaryl-, coniferyl- and sinapyl alcohol, it that means that the base catalysis has yielded lignin dimers. At the lower end of the mass scale, it can also be seen that there is tailing occurring in the de-polymerized samples that does not occur in the retentate. As it only occurs in these samples and at very low molecular masses, it is probable that the de-polymerization has yielded lignin monomers and that the SEC column do not have the resolution to separate these molecules. The effect of this lack in resolution is tailing of the monomers into parts of the mass scale that would correspond to single atoms, and of course, this is not the case.

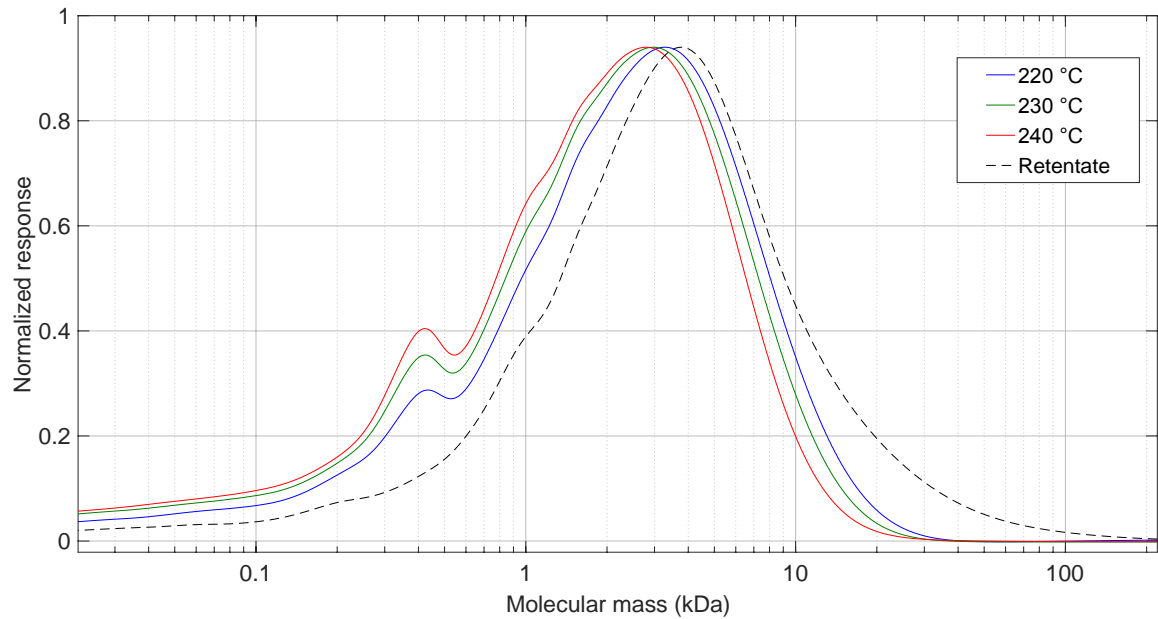


Figure 4.2. SEC analysis of the de-polymerization experiments. A higher temperature results in a shift towards lower molecular weight products.

4.3.3 Temperature dependency

The results show how the molecular mass distribution is shifted towards lower molecular weights with increasing de-polymerization temperature. The small peak at 0.4 kDa has a higher response and the difference between the peak and the following valley is more pronounced at higher temperatures. The tailing response is also increasing with temperature and these differences suggests that a higher temperature is preferable as it yields a higher degree of de-polymerization. The highest temperature that yielded a pumpable liquid with no substantial amount of solid phase (240 °C) was chosen for the acidulation trials.

4.4 Acidulation trials

4.4.1 De-polymerization

At the start of each acidulation trial, a base catalysis was performed as described in section 3.2 *Base catalysis*. pH of the retentate, amount of retentate used in each trial, average temperature during de-polymerization, time above 240 °C and pH of de-polymerized retentate is presented in Table 4.3.

Table 4.3. Parameters tracked during initial base catalysis. Explanation of the trial abbreviations are found in section 3.3 Acidulation.

Trial	pH (retentate)	Retentate [g]	Temp [°C]	Time [min]	pH (depol.)
110/5	13.47	307.8	240.4	15.3	10.85
110/10	13.38	303.0	240.8	15.8	10.77
110/15	13.23	299.2	240.8	15.9	10.86
130/5	13.54	302.2	240.9	16.0	10.86
130/10	13.44	303.7	240.9	15.2	10.85
130/15	13.44	300.0	240.6	16.0	10.80
150/5	13.31	299.8	240.2	15.2	10.81
150/10	13.22	303.0	240.6	16.5	10.75
150/15	13.31	301.8	240.0	15.8	10.75
Mean	13.37 ± 0.111	-	-	-	10.81 ± 0.046

As can be seen, the base catalysis data is consistent for all trials. pH of the retentate have some variations which is believed to be due to properties of the retentate and measuring uncertainties of the equipment. The standard deviation is deemed satisfactory. Amount of retentate and temperature during base catalysis are stable for all trials. Residence time at temperature is between 15.3-16.5 minutes and the small difference is not believed to have much of an impact on de-polymerization. Previous experiments at Lund University have shown that a residence time above 3-5 minutes have little impact on de-polymerization [15]. pH measurements of de-polymerized retentate are consistent and shows a lower standard deviation compared to measurements in the starting retentate.

Three de-polymerized samples were analyzed with SEC in order to investigate the repeatability of the method. Results are shown in Figure 4.3. Two of the samples, 130/15 and 150/15, show little or no difference while 110/15 is similar but shows a small shift towards lower molecular weights. The difference is small and the three samples shows a very similar mass distribution, thus an average of the three samples were made (Depol.) and further on this is what will be presented as comparison in figures.

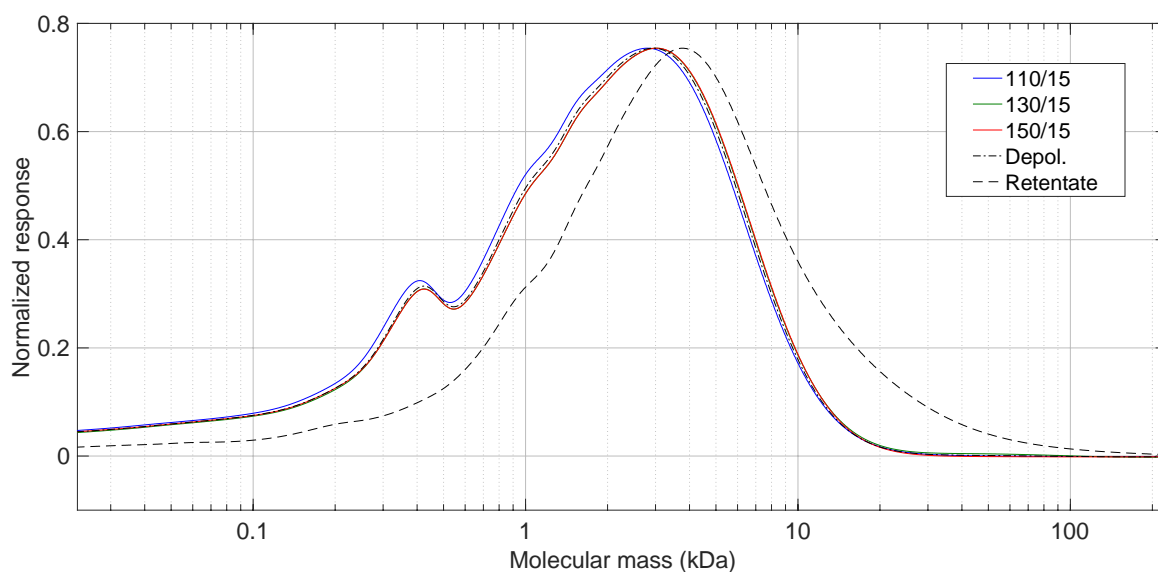


Figure 4.3. Three de-polymerized samples were analyzed and all three shows similar mass distribution. An average of the three (Depol.) will be used further on.

4.4.2 Acidulation

CO₂ data

Parameters correlating to the CO₂ addition is presented in Table 4.4.

Table 4.4. Temperature and CO₂ data collected during trials. CO₂ consumed is given as mg CO₂ per g of retentate. Explanation of the trial abbreviations are found in section 3.3 Acidulation.

Trial	Temperature [°C]	Time with CO₂ [min]	ΔP_{ac} [bar]	CO₂ consumed [mg/g]	pH (CO₂)
110/5	110.2	142	4.3	15.5	9.6
110/10	110.3	180	9.4	35.0	8.4
110/15	110.2	178	11.7	44.8	8.1
130/5	130.0	132	4.4	14.0	9.7
130/10	130.0	167	9.1	28.6	9.1
130/15	130.0	206	11.5	37.0	8.4
150/5	150.1	133	4.2	11.7	9.7
150/10	150.1	165	9.0	24.6	9.1
150/15	149.7	202	10.7	29.5	8.6

Temperature is kept at the set value (± 1 °C) during the entirety of each trial. Time required to reach a stable pressure after CO₂ have been added increases with the amount of CO₂ added. The actual differential pressure (ΔP_{ac}) was calculated as the pressure difference between maximum pressure after CO₂ addition and the final pressure before cooling. It is assumed that during cooling only a small amount of CO₂ is consumed as the pressure have been stable for 15 minutes and stirring is turned off. Thus, any CO₂ consumption during cooling is neglected. Comparing the actual differential pressure to the added differential pressures of 5, 10 and 15 bar, it can be seen that in 5 and 10 bar experiments the added CO₂ is mostly consumed. In the 15 bar trials the actual differential pressure is further away from the added differential pressure, thus more CO₂ are left unreacted in the reactor.

These results suggest that some kind of equilibrium is achieved or that some reaction is halted. An experiment at 110 °C with an added differential pressure of 25 bar was conducted to test if any more CO₂ could be consumed and for pH to drop further. The actual differential pressure of this experiment was 12.5 and pH was 7.94, which further suggests that a maximum have been reached for the current conditions. CO₂ dissolved in water forms carbonic acid (H₂CO₃) which have disassociation states HCO₃⁻ and CO₃²⁻ with pK_a values of 6.4 and 10.3 at 25 °C and ionic strength=0 [35]. CO₂ have the ability to further lower pH than what is the case in the acidulation trials. It is believed that ionic strength plays an important role and limits the effects of CO₂. Ionic strength in the retentate is high due to the various dissolved salts, especially Na₂CO₃ and Na₂SO₄, which originates from the black liquor and the pulping process. The theory is that already existing carbonates and ions inhibits further disassociation and thus the solution is saturated with CO₂ preventing further dissolution.

Actual differential pressure was recalculated to mg consumed CO₂ per g of retentate by using the ideal gas law with the corresponding reactor temperature, the known headspace volume and the molar mass of CO₂. With increasing temperature, the amount of consumed CO₂ at each added differential pressure drops due to the increasing volume of the gas. pH was also measured in the light phase after the reactor had been opened and in Figure 4.4 pH is plotted against dissolved CO₂. A linear relationship can be seen and it seems reasonable as the solubility is low and the reaction of dissolved CO₂ should be fast in the alkali solution, which means little or no CO₂ can be dissolved without reacting. In addition, there is no buffering capacity that can counteract the effects of CO₂ without hindering its dissolution. Thus, any consumed CO₂ will lower pH and a linear or close to linear relationship is plausible.

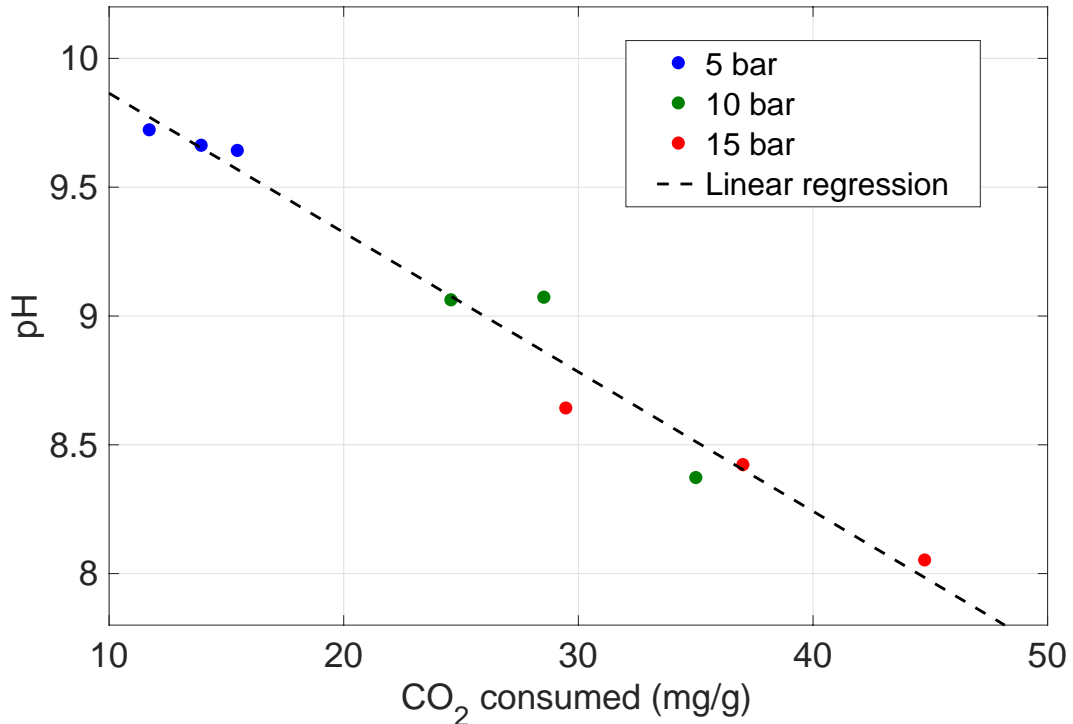


Figure 4.4. pH vs CO₂ consumed shows a linear behavior. Linear regression $y = -0.0541 \cdot x + 10.4$ with $R^2 = 0.966$.

Phase separation

The idea of the chosen precipitation method is to separate the lignin as a heavy liquid-phase and it is thus important that this phase is formed during these trials. When the reactor is opened, the heavy liquid-phase will have solidified and thus its appearance is important as it will show if the liquid-phase have formed or not. The reactor and stirrer was photographed after each trial, below in Figure 4.5 to Figure 4.7 are some of these photos.

All trials with 10 and 15 bars of CO₂ showed evidence of a heavy liquid-phase. 130/15 showed clearly that a heavy liquid-phase had been formed both in the bottom of the reactor where imprints of the stirrer can be seen and on the stirrer where it can be seen how the heavy liquid has run down along the stirrer and dripped to the bottom of the reactor. This have probably happened during the period when stirring was turned off but heating was still on, thus some of the heavy phase have stuck to the stirrer and then flowed downwards still surrounded by light phase. When the reactor was cooled, the heavy liquid-phase solidified either while flowing or the flow had already stopped and heavy liquid-phase still stuck on the stirrer have solidified in place.



Figure 4.5. 130/15 shows clear evidence of the heavy liquid-phase. A smooth surface in the reactor bottom and solidified droplets hanging from the stirrer.



Figure 4.6. 110/15 was stored in the fridge overnight and the top of the solidified heavy liquid-phase had been dissolved by the light liquid-phase.

For one experiment, 110/15, the last step of cooling and emptying was not completed at the end of the day so it was stored in a refrigerator overnight and emptied the following morning. A heavy phase had formed but had started to dissolve into the lighter liquid-phase. Figure 4.6 shows a photo of the heavy phase. Only the top layer of the heavy phase had been affected and had a brown color similar to lignin precipitated with sulfuric acid. When emptying the heavy phase, a hard and dark solid phase similar to other 10 and 15 bar trials was found underneath the brown material. Thus, it is believed that the heavy liquid-phase had formed but the top layer has been dissolved by the light liquid-phase. This affects the experiment mainly by increasing the water content in the heavy liquid-phase. It is not believed that the light liquid-phase have been affected to the same degree as it is probably the light liquid-phase that have mixed into the heavy liquid-phase and not the other way around. Another plausible theory is that during refrigeration more lignin has precipitated due to the drop in temperature, which often leads to lower solubility for many compounds. If this were the case, the light liquid-phase would be affected and this should be seen in analyses presented further below.

The 5 bar experiments did not result in any indications of a heavy liquid-phase, see Figure 4.7. Instead, a wet sand mixed mud with a brown color was the results. A liquid-phase could be poured of but it also contained some solid particles still suspended in the liquid. The stirrer was clogged and spun heavily. The structure of the solid seems porous and when touched with a glove it seemed to dissolve upon contact with liquid pouring out and the solid material almost completely vanishes. It is believed that the amount of actual solid material is low compared what the picture tells and that the porous structure holds liquid, which then pours out when the structure is disturbed. The solid material in the bottom of the reactor behaved in a similar way and what seemed to be a relatively dry solid material fell apart upon contact and became a watery mud. Weight of the heavy phase was taken before anything was done with the solid material, only liquid that could be poured of with gravity alone was removed.



Figure 4.7. 5 bar differential pressure did not yield a heavy liquid-phase for any temperature. This can be seen as the precipitate in the reactor bottom are not smooth and the stirrer has no solidified droplets. Photos are of 130/5.

Comparing pH of the trials to the expression heavy liquid-phase or not suggests that all temperatures allows the heavy liquid-phase to exist. However, when using less CO₂, the solids which precipitate doesn't form a liquid-phase, which might suggest that the precipitated lignin lacks the correct properties, e.g. size. It could also be that the lignin in the solution requires a certain pH where the functional acidic groups of lignin are present both in their salt and acidic form which would affect the hydrophobicity of the molecules and potentially push most of the water out. The results suggest that a pH around 9 or lower is desirable.

Another observation during trials is that a higher temperature results in less solids on the stirrer, probably the heavy liquid-phase is less viscous at a higher temperature and thus more easily can separate to the bottom of the reactor. Figure 4.8 shows trial 150/15 and it can be seen that the amount of solids on the stirrer is quite low. The bottom impeller is halfway submerged in the heavy liquid-phase as it solidifies and thus it was disregarded when comparing solid quantities on the stirrer. The photo also shows how the top impeller has gotten a "hat", this was also seen for 150/10. From the bottom of the hat are small droplets hanging and on the reactor wall, seen at the line where the liquid level has been, are some similar flakes. It seems like a phase have been floating on top of the light liquid-phase and solidified, thus forming a thin layer which broke as the reactor was opened.



Figure 4.8. 150/15 shows the least amount of solids on the stirrer. The top stirrer has a "hat" with small droplets hanging underneath.

Gravimetric analysis

Weight of the light and heavy phase, their combined weight and the difference compared to the starting weight of retentate is presented in Table 4.5. Differences in weight is mainly due to small spills and differences in empty reactor weight. When connecting and disconnecting the reactor different amounts of cooling water for the stirrer and digital pressure gauge (total amount ~30 ml) can be trapped in the system and thus affect weight. With increasing CO₂ pressures the weight of separated light phase increases while the weight of heavy phase declines. The only exception is 110/15, which have been affected by the refrigerated storage. It

might seem counter-intuitive that more CO₂, which means lower pH, results in less heavy phase when more lignin should precipitate at the lower pH. This is because it is important to account for the difference in dry substance, presented in next section.

Table 4.5. Weight of light and heavy phase, their combined mass and the difference compared to the starting weight of retentate. Samples taken have been accounted for. Explanation of the trial abbreviations are found in section 3.3 Acidulation.

Trial	Light phase [g]	Heavy phase [g]	Total [g]	Diff. [g]
110/5	172.8	129.6	317.4	9.6
110/10	200.3	83.6	303.7	0.7
110/15	188.0	98.2	301.2	2.0
130/5	171.7	106.4	296.5	-5.7
130/10	197.2	91.0	303.8	0.1
130/15	202.6	81.6	302.7	2.8
150/5	168.5	114.6	299.7	-0.1
150/10	201.3	82.0	301.7	-1.3
150/15	203.4	79.9	301.5	-0.3

Total dry solids, ash content and total lignin content

In Figure 4.9 on the following page are TDS, AC and TLC measurements for both phases presented. In general, it looks like the TDS in the heavy phase is increased with an increased CO₂ pressure. The low number of 110/15/H is as previously stated due to the refrigeration storage that seemed to dissolve some of the solidified heavy phase and thus increasing its water content. The light liquid-phase shows clearly how a higher CO₂ pressure results in a lower TDS. 110/15/L doesn't seem to deviate far from the trend, possibly it's somewhat lower but not by much. This reconnects with the theories about the effect refrigeration had on 110/15, as the heavy phase resulted in a TDS lower than the trend and the light phase seems to follow the trend, it's more probable that the heavy phase has been dissolved by the light phase than that more lignin has precipitated as this would lower TDS.

TLC has the same appearance as TDS measurements and it is good to see that the UV measurements are reflected in the more reliable TDS measurements and therefore are deemed more reliable. The use of UV for lignin quantification was discussed previously in section 4.1 *Methods for analysis*.

The starting ash content in the retentate is 23.3% on dry basis. A decrease can be seen in the heavy phase and the ash content is instead found in the light phase, which has an increased ash content compared to the retentate. Taking an average of the 10 and 15 bar experiments the ash content and the respective phase weight it can be seen that 72% of the total ash content is removed with the light liquid-phase. The figures look like the TDS measurements have been horizontally flipped which is reassuring as a large portion of the ash are dissolved salts. These salts are dissolved in the water and a higher TDS means less water that in turn results in the horizontally flipped behavior.

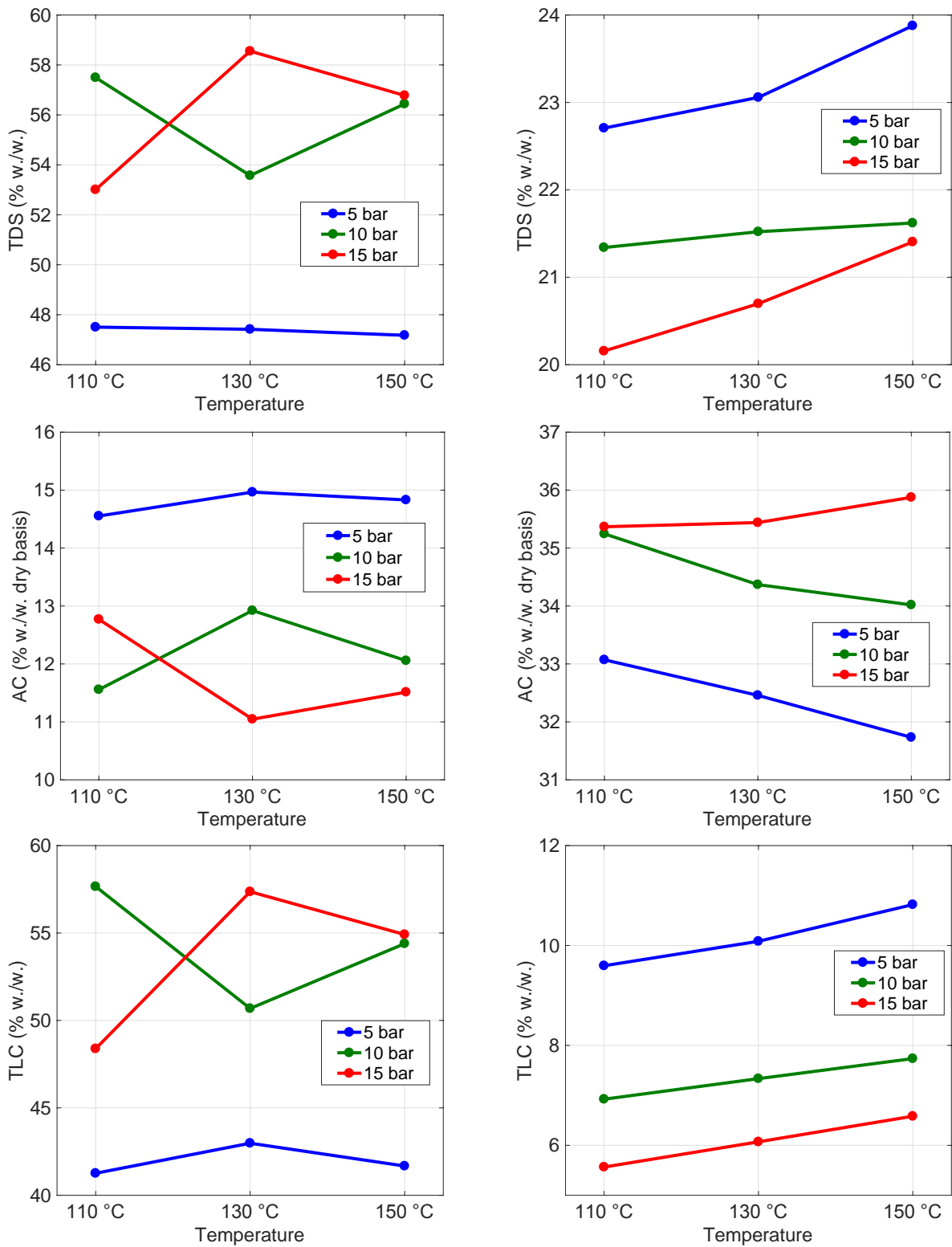


Figure 4.9. Left column shows the solidified heavy liquid-phase and the right the light liquid-phase. The crossing of 10 and 15 bar between 110 and 130 °C seen in the heavy phase cannot be seen in the light phase. Ash content resembles the TDS figures but horizontally flipped. TLC is very similar to TDS; their absolute values are also similar.

Mass distribution

Molecular mass distribution of all 15 bar trials were analyzed with SEC as these experiments formed a heavy liquid phase, they had the highest TDS/TLC and the lowest AC/pH and thus they seemed most promising. The starting retentate and one heavy phase at 10 bar was also analyzed, 130/10/H. Figure 4.10 presents the molecular mass distribution of the heavy phase and Figure 4.11 for the light phase.

The mass distribution for the heavy phases closely follows that of the de-polymerization average which means lignin of all size found in de-polymerization also can be found in the heavy phase. By following the de-polymerization average so closely, it also indicates that there is little or no occurrence of re-polymerization during the long residence time at moderately high temperatures, which is excellent in a process perspective.

Looking at the light phase it is clear that the average molecular weight is lower, the highest peak is found at ~1 kDa. Most interesting too look for in the light phase is what will be removed from the product (heavy phase) and returned to the evaporators in the pulp mill. The largest molecules at ~11 kDa are completely gone from the light phase but surprisingly so is the tailing which can be seen in the heavy phase and de-polymerization average. The small peak containing dimers is still there but smoothed out and drops fast toward zero response as towards lower molecular mass. Looking at the same part on the heavy phase it follows the de-polymerization average and does not reach zero response. This would suggest that monomers are not found in the light liquid-phase but in the heavy phase. Expectations were to find the smallest molecules in the light liquid-phase, as they were thought to be more hydrophilic and required a lower pH in order to precipitate.

130/10/H displays a different mass distribution compared to the 15 bar trials and the de-polymerization average. It is shifted towards larger molecular weights and the small peak at ~0.4 kDa is flattened out to a plateau. On the right side of the highest peak it is easy to be fooled that 130/10/H contains large molecules which aren't found in the de-polymerization average. This would suggest re-polymerization and contradict the previous statement that this does not seem to occur. Looking closely it can be seen that both 130/10/H and the 15 bar trials reach zero response at the same molecular mass, ~12 kDa. This means all sizes lower than 12 kDa exist in both samples and it is merely the response that differs. The difference that can be seen in response is probably due to that these larger molecules makes up a larger portion of the total content relative to the highest peak compared to the 15 bar trials. However, as previously stated in 3.5.3 *Size Exclusion Chromatography*, the response needs to be taken lightly.

A temperature effect can be seen for both phases when comparing the 15 bar trials. With a decrease in temperature, a shift towards lower molecular weights can be seen. However, the shift is probably not truly an effect of temperature but of pH. On a molar basis 15 bar of CO₂ at 110 °C contains more CO₂ than 15 bar at 150 °C, thus less CO₂ is supplied as the temperature increases. This can also be seen in Table 4.4 where CO₂ consumed drops and pH increases with an increase in temperature, as discussed earlier in 4.4.2 *Acidulation* under CO₂ d. To investigate if there are any true temperature effects, trials with constant pH are needed. This would require further equipment to monitor CO₂ additions and pH, which were not available at the time of these trials. If there were any temperature effects in this interval they would be small, as otherwise they should be seen in these trials and thus there would be nothing to gain from a mass distribution perspective by using a higher temperature than what's necessary to form the heavy liquid-phase.

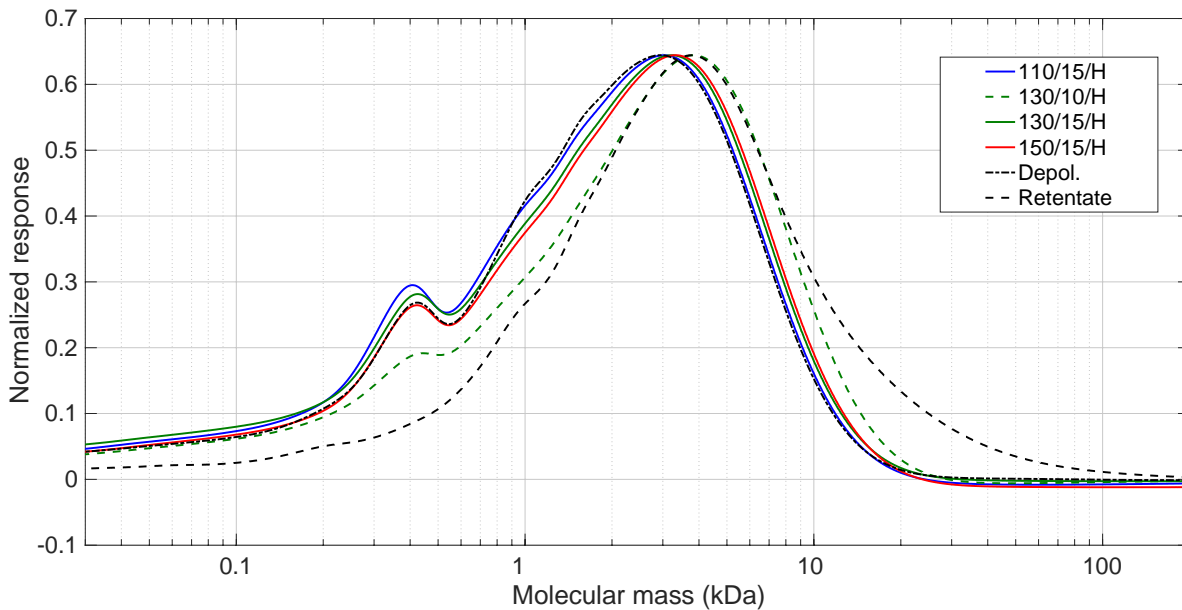


Figure 4.10. Molecular mass distribution for the heavy phase.

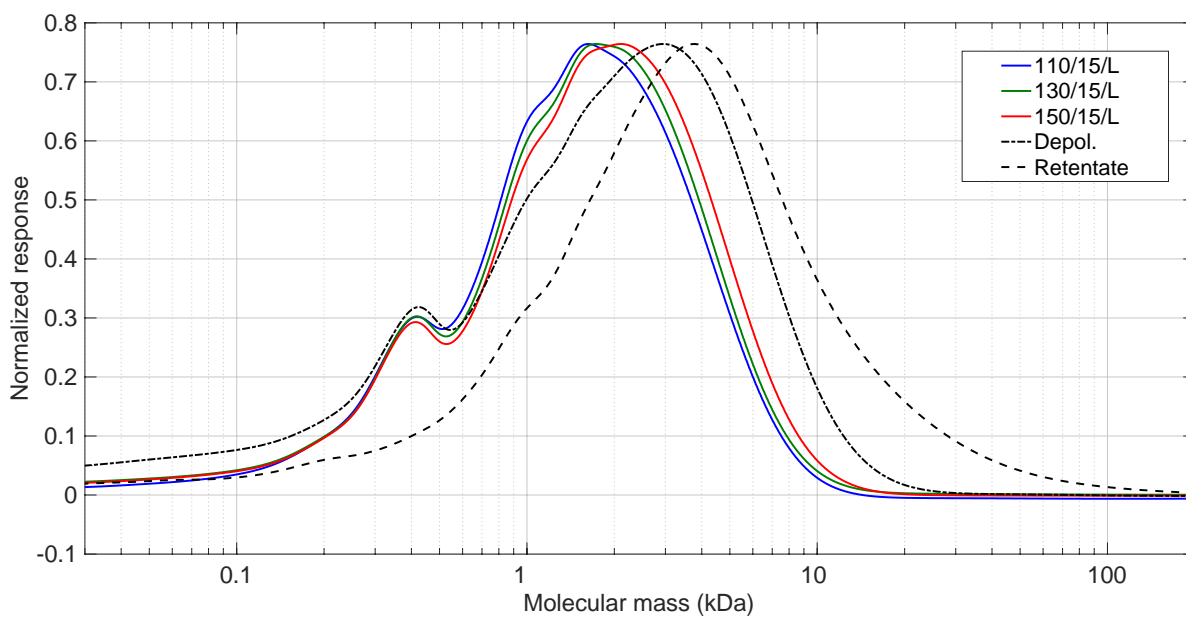


Figure 4.11. Molecular mass distribution for the light phase.

Yield

Since the light and heavy phase are interlocked, it entails that if TDS, lignin content or ash in the light phase is lowered, the same species in the heavy phase must increase. Thus in theory the results from either phase should tell the same story. However, the solidified heavy phase is more difficult to analyze as it has to be dissolved in NaOH before lignin content analysis. It is also more sensitive to storage and handling, as seen with trial 110/15, differences in how long the reactor have been sitting with both phases can greatly affect the solidified heavy phase. Because of this, yield calculations are based on analyzes made on the light liquid-phase.

Yield presented to the left in Figure 4.12 is calculated from lignin concentration in the liquid-phase and in the de-polymerized retentate. As the total mass of both phases are known yield can be calculated. CO₂ yield was similarly calculated by using the previously calculated CO₂ consumption which was calculated as mg CO₂ per g retentate. Below are these calculations compiled.

$$\text{light phase lignin} = m_{\text{light}} \cdot c_{\text{light}} \qquad \text{total lignin} = m_{\text{depol}} \cdot c_{\text{depol}}$$

$$\text{heavy phase lignin} = \text{total lignin} - \text{light phase lignin}$$

$$\text{total CO}_2 \text{ consumed} = m_{\text{retentate}} \cdot \frac{\text{CO}_2 \text{ consumption}}{1000}$$

$$\text{yield} = \frac{\text{heavy phase lignin}}{\text{total lignin}}$$

$$\text{yield}_{\text{CO}_2} = \frac{\text{heavy phase lignin}}{\text{total CO}_2 \text{ consumed}}$$

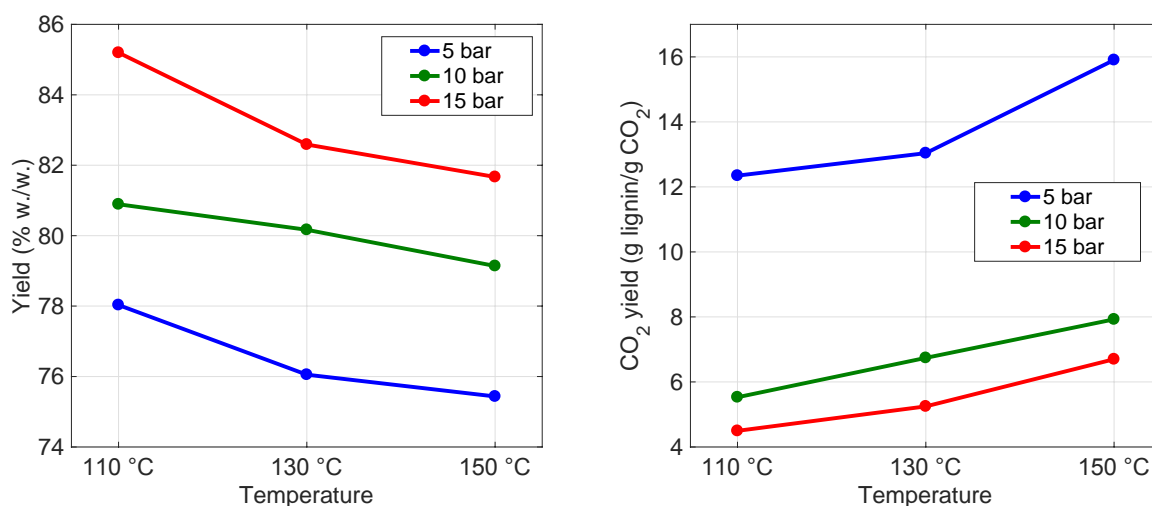


Figure 4.12. The left figure shows the lignin yield as the percentage of the total lignin found in the heavy phase. The right figure presents lignin yield based on CO₂ consumption.

As could be expected the yield is increased when the CO₂ pressure is increased. More CO₂ means a lower pH and thus more lignin precipitates. A temperature effect can also be seen; at a lower temperature the yield is increased. However, as discussed in *Mass distribution* above the pH probably have an important role in this. Though in the case of yield it is a little different. Temperature can affect solubility and for most substances solubility increases with temperature. An increase in solubility would counteract CO₂, which means to lower solubility by affecting pH. 110/5 and 130/5 have very similar pH and 130/10 and 150/10 also have similar pH, as seen in Table 4.4. Looking at the yield of these experiments it can be seen that the yield is lower at a higher temperature even though the pH is the same. This would suggest that a true temperature effect can be seen and that yield is lowered as the temperature is increased.

Looking at the CO₂ based yield it can be seen that the amount of lignin per CO₂ consumed decreases as more CO₂ is added. This is reasonable as most of the lignin has a relatively large mass and will precipitate at a pH around 9-10. Lowering pH is linear, as seen in Figure 4.4, but as pH is lowered, less and less lignin will precipitate which causes the lignin/CO₂ yield to decrease. There will be a trade-off between CO₂ consumption and lignin yield but as will be seen in the next section 4.5 *Purification*, pH needs to be lowered further and thus it will be the

cost of lowering pH which will decide how low pH is taken with CO₂ and when other chemicals will be used. The yield also seems to be increasing with temperature and the reason for this behavior is unknown but it could be caused by false assumptions. Calculations on CO₂ consumption are based on the ideal gas law where the temperature have been assumed to be that of the reactor, thus much of the results rely on this assumption. The starting pressure greatly depends on the temperature of the gas in the reactor headspace. During calculations, the temperature have been assumed that of the liquid i.e. 110, 130 or 150 °C. The CO₂ holds 20 °C and ~50 bar in the gas bottle, when this is injected its depressurized to 10-15 bars, depending on which experiment is run, which would further cool it down. If this gas is not heated to reactor temperature before the starting pressure is read, i.e. the assumption that it does is wrong, the amount of injected CO₂ would be underestimated, as the temperature assumed is higher than the actual value. Then if this effect increases with temperature, i.e. that the headspace temperature is at its lowest compared to the reactor temperature in the 150 °C trials, the amount of injected CO₂ will be more underestimated when the temperature is increased. The effect of this when calculating CO₂ yield would be that the CO₂ consumption which the heavy phase lignin is divided with would be underestimated and it would be more underestimated as temperature increased which could cause the behavior seen in Figure 4.12.

4.5 Purification

4.5.1 Model substance

Successful experiments were conducted with a model substance, LignoBoost powder, and the photos from these experiments are presented below in Figure 4.13. The initial color of the water, AcOH and lignin mixture was a light brown chocolate color. At ~60 °C lignin particles started to swell and the mixture darkened in color. At ~70 °C the swollen particles started to congregate and stirring was turned off to allow for the phases to separate. The heavy phase is very thick and sticky, similar to fudge. The fluidity is low but if the heavy phase is left in the reactor at 70-80 °C it flows out on the bottom of the reactor. It can be picked up with a pair of tweezers, see Figure 4.14, and its slowly dragged out and elongated by its own weight forming gold colored fibers. With this fluidity, it would not be pumpable with e.g. a centrifugal pump but a screw would be a viable option.

Experiments where H₂O/AcOH ratio was modified to 50/50 and 80/20 was conducted with LignoBoost powder and both were successful. A ratio of 50/50 yielded a darker light phase suggesting more lignin is dissolved. The heavy phase had a higher fluidity compared to 70/30 experiments but still could be picked up with a pair of tweezers. With a ratio of 80/20 results were very similar to 70/30, no distinct difference could be noticed. Though the results showed that the process worked with less acetic acid, which is good in an economical perspective. An experiment with H₂O/AcOH of 70/30 but with twice the amount of LignoBoost powder (20 %w./w.) was also performed and was successful. It resulted somewhat darker light liquid-phase and the heavy phase seemed to have a higher fluidity but is probably a result of the increased volume and mass of the heavy phase.



Figure 4.13. Experiments using LignoBoost powder successfully separated into two phases.



Figure 4.14. The heavy phase can be picked up with a pair of tweezers and is slowly dragged out by its own weight. The light phase is very clear after the heavy phase have been removed.

4.5.2 Influence of pH

Initial experiments using INDULIN AT and acidulation powder with the ALPHA process was unsuccessful. LignoBoost powder was then tested and worked immediately. To find potential causes of the problems the pH of the lignin powders was tested by mixing 4g powder in 36g distilled water. pH of LignoBoost was found to be lowest at pH 2.9, INDULIN AT had a pH of 7.0 and the heavy phase powder reached a pH of 8.7. Acetic acid has a pK_a value of 4.76 [36] and would disassociate to some degree when mixed with INDULIN AT and the heavy phase powder. Probably it would disassociate fully but pH after mixing with acetic acid was not measured. The role of acetic acid in the ALPHA process is to act as an anti-solvent which forces lignin out from the light liquid-phase, potentially the disassociation state of acetic acid can play a vital part in this effect. A new experiment with INDULIN AT was made but this time pH was adjusted to ~2.5 by additions of sulfuric acid to the lignin water mixture prior to addition of acetic acid. The pH-adjusted mixture proved to separate into two phases much like the LignoBoost experiment and it can be concluded that pH indeed plays an important role in the ALPHA process.

Acidulation powder

Testing the same approach on the acidulation powder was mostly unsuccessful. The color is pitch black as seen in Figure 4.15. At the same temperature where previous experiments coagulated and formed a heavy phase the acidulation powder transitioned from being a turbid mixture to showing clearly visible particles. It seemed like a portion of the lignin had formed a heavy sticky phase similar to the previous successful experiments with INDULIN AT and LignoBoost. The heavy phase attracted much of the remaining lignin powder and formed a grainy cake at the bottom of the beaker. Most of the particles precipitated to the bottom and left a black and clear light liquid-phase, though not as clear as previous experiments with INDULIN AT and LignoBoost. On top of the light liquid-phase, an oil film could be seen as of the typical rainbow colors seen in Figure 4.15. The oil is probably tall oil, which largely is removed in the retentate but not completely.

In an attempt to get a working process a new experiment was set up and during heating more acetic acid was added, the amount was not measured precisely but 10-15 ml was added which would put the ratio at 40-45% AcOH. A few drops sulfuric acid was also added as pH had increased during heating, probably because lignin and salts are dissolving during heating. The experiment was a success and a black heavy liquid-phase without solid particles was achieved. The heavy phase had a higher fluidity than previous experiments with LignoBoost and when picked up with a small spatula it flowed down with a thick syrup texture, see Figure 4.16. One experiment with acidulation powder was successful and yielded a liquid heavy phase. Figure 4.16. Later attempts to replicate these results failed for unknown reasons. It is unknown what causes the experiments with acidulation powder to have such varied success. Possibly a very specific combination of temperature, pH and H₂O/AcOH ratio is required.

In further attempts to find a reason for the many unsuccessful experiments, lignin was precipitated from black liquor retentate and washed with sulfuric acid. The washed lignin was dried and the ALPHA process was tested again without success. This was done to test if the high ash content or the de-polymerization had any impact on the ALPHA process.

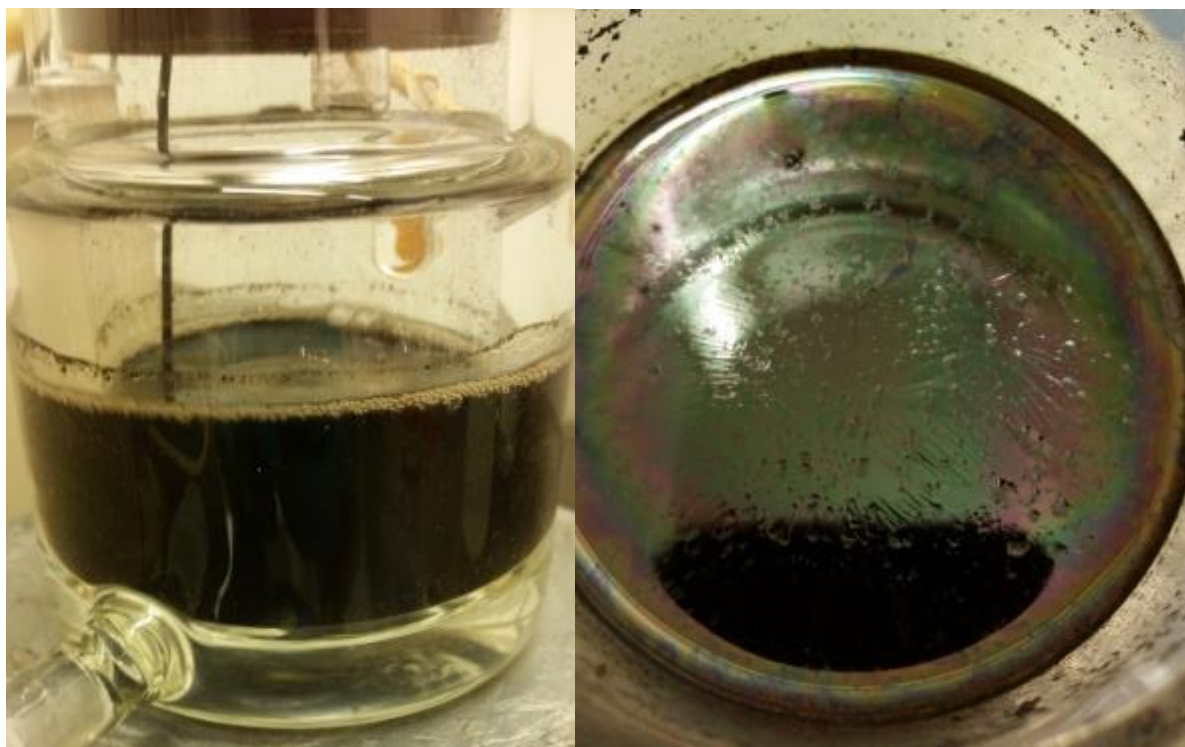


Figure 4.15. Experiments with acidulation powder was very dark. After heating, an oil film could be seen in the beaker.



Figure 4.16. One experiment with acidulation powder was successful and yielded a liquid heavy phase.

4.5.3 Two-step purification

A two-step purification was completed for the LignoBoost and acidulation powder, see Table 4.6. The LignoBoost powder yielded a heavy liquid-phase that was easily separated after both washing steps. Acidulation powder yielded some heavy phase but separated as a grainy cake, described above in the section *Acidulation powder*.

Table 4.6. Compiled data from the two-step purification trials. AC on dry basis.

Phase	Lignin Powder	Step	TDS (% w./w.)	AC (% w./w.)	TLC (% w./w.)	Yield (% w./w.)
-	LignoBoost	Initial	94.7	0.630	-	-
-	Acidulation	Initial	74.4	11.5	-	-
Heavy	LignoBoost	Wash 1	53.7	0.548	-	94.6
		Wash 2	53.0	-0.002	-	92.9
	Acidulation	Wash 1	31.0	4.37	-	71.1
		Wash 2	22.8	2.47	-	54.1
Light	LignoBoost	Wash 1	1.83	10.4	0.968	-
		Wash 2	0.854	7.43	0.333	-
	Acidulation	Wash 1	3.40	26.2	0.569	-
		Wash 2	1.39	57.0	0.265	-

TDS in the LignoBoost heavy phase is in the same range as where the heavy phase after acidulations were. However, in these experiments the heavy phase is much softer and behaves like a fluid at 60-70 °C whereas in the acidulation trials the heavy phase was a solid at 60 °C and had to be carved out with a screwdriver. Thus, the H₂O/AcOH mixture seems to lower the required temperature for a liquid heavy phase to form. When the phases were left to separate the temperature kept increasing as water still was circulating and when the temperature increased so did the fluidity of the heavy phase. TDS in the acidulation heavy phase is lower compared to LignoBoost as the liquid heavy phase did not form properly and water was not pushed out from the grainy bottom cake.

Ash content for LignoBoost heavy phase is very low. After the first wash, it has dropped slightly but after the second wash the weight of the crucible was lower than the starting weight causing the ash content to be negative and thus leading to the conclusion that the method used is not precise enough to measure such low ash contents reliably. In the light liquid-phase, higher ash contents are seen which indicates that ash has been washed from the LignoBoost powder. Again, the measurements do not seem right. When calculating the total ash content found in the light liquid-phase after the first wash, it is found to be four times more ash in this phase than what is in the initial LignoBoost powder.

The acidulation powder have a higher ash content and the initial ash content is reasonable when comparing it to the ash content of the four acidulation heavy phases it's made from, see Figure 4.9. After the first wash, it is more than halved and after a second wash, it is halved again. As the process has not worked properly, a tenfold decrease in ash content as reported in literature cannot be expected [17]. The yield that has been calculated is based on TDS and is accumulative so it compares to the total TDS content in the initial lignin powder added. Yield is high for the LignoBoost experiments showing that small losses can be expected in the ALPHA process. It is much lower for the acidulation powder as the liquid heavy phase did not form properly. The

higher difference in ash content would also affect the yield and cause it to be lower as ash weight found in the initial total TDS now will be found in the light liquid-phase. Measuring the lignin concentration would have been more accurate but as the process did not work properly, it was not of interest. A rough estimate on where the yield could be found was enough.

Coloration

Below in Figure 4.17 are photos of the light liquid-phases collected. The second wash step yields a less colored phase that probably is caused by lower ash and lignin concentrations, though this cannot readily be seen in the above measurements. TLC was measured in the light phases and was found to be very low, less than 1%, which seems low compared with losses in TDS (yield) previously seen. The samples had been stored in a fridge overnight and a lignin precipitate was found in the bottom of the sample tubes. The precipitate was light brown in color for all samples, including the very dark liquid-phase from the acidulation powder. The samples were clear before refrigeration and centrifugation did not yield any precipitate. This precipitate alone is more than 1% of the total weight and thus it seems UV measurements are not suited for this application. A gravimetric approach of deciding lignin content could work better.

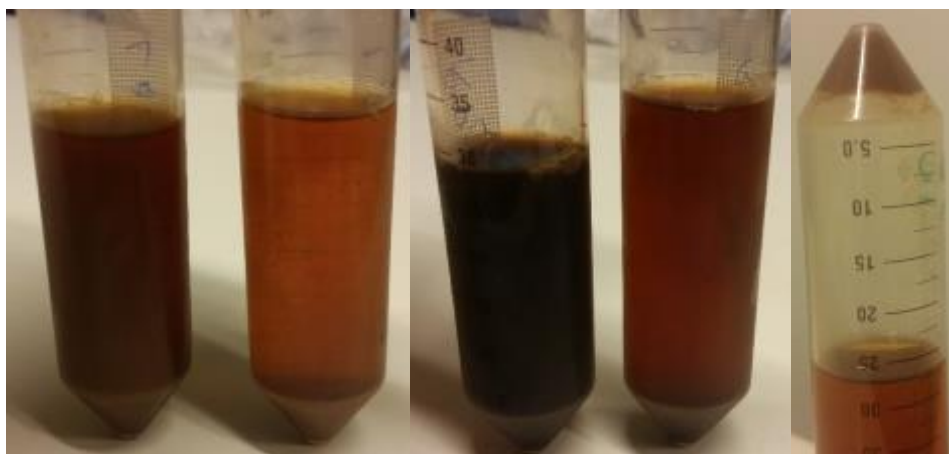


Figure 4.17. From the left, LignoBoost wash 1 and 2, acidulation powder wash 1 and 2 and to the right a precipitate found after refrigeration of the samples.

5 Conclusions and Future Work

The results presented in this work might not be the most accurate and the analysis of the samples could be improved by developing methods that are more precise and by upgrading to equipment that is more suitable. However, in this work, the most interesting thing is how samples compare to each other and when comparing two samples their absolute values are of little interest. The methods used can still give good appreciation of the actual values but are not necessarily completely correct. As most conclusions are drawn from comparing samples to each other, any analysis errors due to, e.g. PEG standards behave differently than lignin, should have little effect on the conclusions.

5.1 Conclusions

Increasing the temperature in the region of 220-240 °C showed to increase the degree of de-polymerization in the base catalysis, as seen by the shift in mass distribution. At all temperatures, base catalysis removed all larger molecules (~100 kDa) and yields a smaller peak and tailing, both not seen in the retentate. The smaller peak, which corresponds in mass to dimers, is more pronounced as temperature increases. Tailing, believed to be caused by monomers not being separated efficiently by the SEC column, also increases with temperature. These results could gain from using a different standard and possibly column for the SEC analysis, as much of the large lignin molecules that are removed and the tailing monomers are outside of the calibrated area, thus their mass is uncertain. Even though 240 °C yielded solids, they remained suspended and the liquid would be pumpable. However, these solids might cause processing problems by e.g. clogging pumps. 250 °C was not pumpable and therefore 240 °C was chosen for the remaining experiments.

A heavy lignin-rich liquid-phase was formed in all 10 and 15 bar experiments and at all temperatures, 110-150 °C. Its lignin content was ~55% and likewise the total solids content. The amount of heavy phase was 80-91g, excluding the compromised 110/15/H, and bearing in mind that the starting weight was 300g; the amount to process in the following stages has been greatly reduced. SEC analysis of the heavy liquid-phase shows that even the smallest monomers and dimers are found in the heavy liquid-phase. This is great if de-polymerization is improved, as the smaller lignin molecules still can be recovered. The lignin yield was high; 76-85% of the initial lignin precipitated as the heavy liquid-phase. In addition, beneficial for processing costs, a lower temperature improved yield. Ash content in the starting retentate was 23% and this was reduced to ~12% in the heavy phase while the light phase AC increased to ~35%. Taking a mean of all 10 and 15 bar experiments it could be concluded that the 72% of the original AC was removed with the light liquid-phase. This is great as two birds are killed with one stone, the amount of material to process in the ALPHA process is reduced and likewise the AC which needs to be removed. Again, a lower temperature was beneficial and resulted in lower AC in the heavy-liquid phase. The same could be seen in SEC analysis of the 15 bar experiments, a lower temperature seemed to precipitate smaller molecules as the mass distribution was shifted towards lower molecular masses. The only reason found to use a temperature higher than what is required for the heavy liquid-phase to form, would be to decrease viscosity of the heavy liquid-phase to facilitate pumping and/or decrease risk for material build-up in reactors and pipes.

The ALPHA process proved difficult to master, initial experiments with acidulation powder failed. Using the model substance, LignoBoost, worked and investigations into what caused the acidulation powder and INDULIN AT to fail was started. It was found that pH plays an important role and after pH adjustments, the process worked for INDULIN AT. The acidulation powder worked sporadically and no definite reason for this behavior was found. Two-stage purification of the model substance showed that a yield >92% is easily achieved. Performing a two-stage purification on the acidulation powder showed that AC is reduced, not in the tenfold as seen in literature, but as the heavy liquid-phase in the ALPHA process did not form properly it cannot be expected. It also showed that to achieve a high yield, the formation of the heavy liquid-phase in the ALPHA process is crucial.

5.2 Future work

Foremost the ALPHA process needs to be further investigated. The sporadic behavior that was seen when using acidulation powder needs to be resolved. Further investigations into differences between the model substance, e.g. molecular size or ionic strength, and the acidulation powder could explain the sporadic behavior.

A new method for AC analysis is needed for the ALPHA process; the method used in this work is too coarse for low ACs. An oven where an inert atmosphere can be used would also be beneficial as reactions with oxygen occur and affects the ash measurements, taking these reactions into account is very hard and impossible without knowing the composition before. It is also plausible that between two ALPHA stages the composition changes as some substances are easier to wash away, resulting in that first and second wash are not comparable as different reactions with oxygen have occurred. Atomic emission spectroscopy should be used to measure metal content when evaluating the ALPHA process; a low sodium content is important and needs to be measured.

When the processes have been sorted, their economics should be investigated. Calculations on ongoing costs such as chemicals and power consumption is of great importance to further research and can be a deal-breaker that forces the process in another direction.

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