Hydrogen Assisted Lignin Depolymerization with Pulp Mill Catalysts

by

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Preface

After five years of study in the Environmental Engineering program at LTH, it is inspiring to finish my education with this project that really has the potential to benefit the transition to a more sustainable society. I enjoyed performing experimental work together with Martin Sundin whom did his master thesis in parallel with mine within the development of the same process. I would like to thank my supervisors for excellent guidance. I would also like to thank everyone who have helped me with analyses and advice.

Abstract

As part of the development of a process for production of a lignin-rich oil that can serve as a renewable feedstock to existing petroleum refineries, hydrogen assisted depolymerization of lignin in filtered black liquor has been investigated. This process offers the possibility to reduce fossil emissions from transportation by utilization of the largest renewable carbon resource in Sweden, namely the forest. Compared to petroleum feedstock, lignin is richer in oxygen content and its molecular size is much larger. Challenges in the catalytic treatment is to reduce the oxygen content and shift the molecular weight distribution to lower molecular weights. Lignin is by nature resistant to degradation and hydrothermal treatment of lignin is often associated with coke formation. One approach to suppress coke formation is to use organic solvents that has high solubility for lignin fragments and hydrogen gas. However, the consumption of organic solvents in combination with expensive catalyst is not favorable from a techno-economic perspective. The approach in this work involves only the alkaline solution already present in the black liquor and catalysts that are available in the pulp and paper mill. It was found that the molecular weight distribution was shifted to molecular weights below 10 kDa, mainly around 1 kDa, during long residence time under hydrogen pressure, 20 h and 190 bar. This can be compared to the filtered black liquor, which contain compounds up to 100 kDa. More experiments with the material needs to be done in order to investigate the catalytic effect compared to blank experiments at 20 h residence time. For 15 min residence time, the catalysts did not show any visible effect on the molecular weight distribution. The presence of hydrogen gas was shown to reduce the sulfur content, which is an indication of reduction of oxygen content as well.

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Nomencalture

Abbreviation	Explanation	Unit
Ash_b	Ash measurement from external analysis, Belab	DS%
Ash_i	Ash measurement from internal analysis	DS%
Ash_{blank}	Ash content of blank experiment	wt%
$Ash_{blank\ corr}$	Ash content of blank experiment corrected for the oxygen content associated with thermal treatment during ash measurement	wt%
Ash_{cat}	Ash content of catalyst experiment	wt%
Ash_{corr}	Ash content of catalyst experiment corrected for the oxygen content associated with thermal treatment during ash measurement	wt%
Cat	The content of the ash which is assumed to be contributed by the catalyst	wt%
BCD	Base catalyzed depolymerization	
BLR	Black liquor retentate	
C_{prod}	Carbon flux in the product	mol
C_{ds}	Carbon content, weight per dry solids	DS%
DS	Dry solids	wt%
ξ	Molar absorptivity	l/(g cm)
Mill1	Pulp mill catalyst 1	
Mill2	Pulp pill catalyst 2	
MS1	Model substance 1	
MS2	Model substance 2	
m_{cat}	Mass of catalyst	g
m_{feed}	Mass of the BLR in the feed	g
m_{prod}	Mass of the product	g

M_{Na_2}	Molar mass of two sodium atoms	g/mol
$M_{Na_2O_2}$	Molar mass of sodium peroxide	g/mol
M_S	Molar mass of sulfur	g/mol
M_C	Molar mass of carbon	g/mol
org	Organic part of the dry solids	wt%
SEC	Size exclusion chromatography	
S_{cat}	Sulfur flux in catalyst addition	mol
S_{ds}	Sulfur content, weight per dry solids	DS%
S_{feed}	Sulfur in feed	mol
S_{gas}	Sulfur in the gas	mol
S_{org}	Sulfur in the organic part of the product	mol
S_{prod}	Sulfur in the product	mol
S_{wt}	Sulfur content, weight percent	wt%

1 Introduction

Levels of atmospheric carbon dioxide were higher in 2016 than ever measured before [1]. The increase of CO_2 is caused by anthropogenic emissions primarily due to use of fossil fuels and land use changes [2]. However, there are initiatives to turn the development around and reduce emissions of fossil CO_2. For example, the Paris agreement emphasizes that the global warming should be kept well below 2 °C to limit the consequences of global warming, and EU's renewable energy directive states that 20 % of the total energy requirement in EU should come from renewable energy by 2020. Based on this directive, there has been political actions to increase the production of biofuels in Sweden. For production of biofuels, lignocellulosic biomass is a suitable source since it is the most abundant and renewable resource of carbon that is available, especially in Sweden where the forest industry is large [3]. Furthermore, lignocellulosic material does not directly compete with food production as opposed to biofuels based on agricultural crops [4]. Apart from biofuel production, lignin also is a potential source of commodity chemicals due to its complex structure and aromaticity [5]-[6].

1.1 Problem Description

The distribution of energy availability in Sweden is disproportionate to the energy demand. There are large resources of hydroelectric power in the northern parts of the country, while the demand for electric energy is higher in the south. This enables more cost efficient production of hydrogen gas through electrolysis of water in the northern parts Sweden, in close proximity to the pulp and paper industry. The hydrogen gas could be used for hydrogenolysis of lignin from the pulp and paper industry to produce biofuels.

This work has been done in collaboration with the company SunCarbon. It has been part of the development of a process for production of biofuel from lignin in Kraft pulp black liquor. Black liquor is a process stream in the recovery of cooking chemicals at pulp mills. It is rich in lignin but it also contains water, cooking chemicals and non-process elements. Today, lignin is combusted in the recovery boiler in the pulp mill, which can be a bottleneck in the pulp production. If part of the lignin instead could be used to produce biofuels, the production of pulp could increase.

SunCarbon's overall process idea can be seen in Figure 1. The concentration of lignin is increased through membrane filtration and a major part of the cooking chemicals is returned to the pulp mill. The black liquor retentate, BLR, contains lignin macromolecules. These large molecules are depolymerized into lower weight fragments by hydrothermal treatment, catalysis and possibly hydrogenolysis. Water and the remainder of the cooking chemicals is then removed in a series of purification steps leaving a lignin-rich oil product. The water and cooking chemicals are returned to the pulp mill. If necessary, the lignin-rich oil could thereafter be treated again in a post treatment step where oxygen levels could be reduced further. The lignin-rich oil is then ready to enter a petroleum refinery.

This process idea offers the possibility to introduce a renewable feedstock to existing petroleum refineries. The fuel produced in the refinery would partly consist of renewable material that would decrease fossil emissions from transportation.

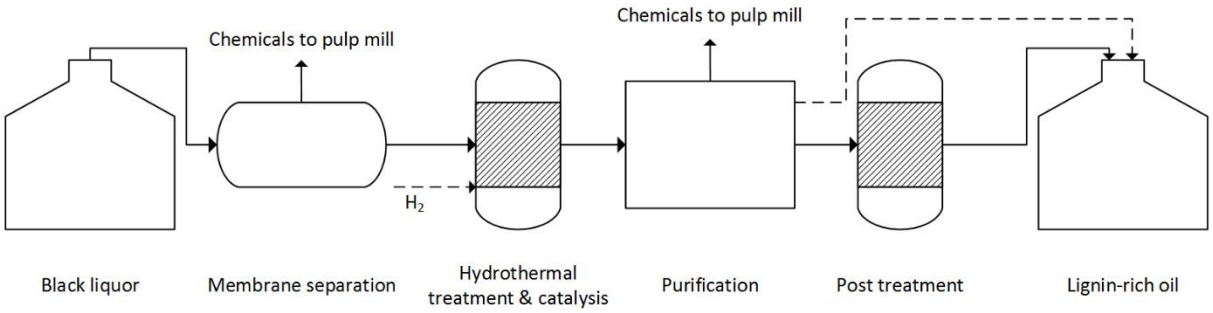

Figure 1. SunCarbon's overall process idea where black liquor is converted to a lignin-rich oil that can be introduced as feedstock to a petroleum refinery.

Lignin contains more oxygen than petroleum feedstock. Therefore, it is important to reduce the oxygen levels either in the depolymerization step or in the post treatment step; or indeed in the refinery. The water solubility of the depolymerized lignin has large impact on the purification step, where high water solubility makes isolation of lignin difficult. Thus, it is of interest to reduce the water solubility during depolymerization as well.

1.2 **Aim**

This work was focused only on the depolymerization step of the process. The aim was to investigate the catalytic effect of two pulp and paper mill available catalysts in the presence of high-pressure hydrogen. In order to investigate the effect of pure compounds, two model compounds were selected based on the composition of the pulp mill catalysts and those have been studied as well. The molecular weight distribution and oxygen content are factors that were used to determine if the depolymerization has been successful.

1.3 **Structure of the Report**

The next chapter, Theory and Background, is based on literature relevant to the subject. The structure and origin of lignin is explained as well as its way through the pulp and paper industry. The most common analysis methods and associated challenges are presented. Furthermore, the results of previous work based on literature is summarized.

In Material and Method, it is explained how experiments in this work was performed, what analyses that were made and how the data was treated as well as what assumptions that were made.

In the chapter Results and Discussion, the results from the experimental work are presented. The results are discussed continuously in the chapter since some of the analyses choices are based on previous results.

The conclusions are summarized in the chapter Conclusions and suggestions for future work is presented in the last chapter.

2 Theory and Background

It has long been of interest to produce fuel and commodity chemicals from lignocellulosic material. Yet, the reactions of lignin is not fully understood, much due to its complex structure. This chapter will try to bring clarity to what is lignin and how can it be depolymerized.

2.1 Wood Structure

The mature tree stem is composed mainly of long cells oriented in longitudinal direction. The cells provide transportation of nutrients and liquid as well as mechanical strength and storage of nutrients. The shape and function off the cells vary within the stem and also differ between softwoods and hardwoods. Hardwood cells are specialized either for support or for transport while softwood cells generally are more alike. All cells are composed of different layers or lamellae that consists of cellulose, hemicellulose, lignin and extractives in varying proportions. Between cells lies the middle lamella, which acts as glue. The outer layer of the cell is called the primary wall. Inside the primary wall is the secondary wall which is usually composed of two to three layers but in some cases even four layers. Different cell wall layers have different chemical composition and structure. In the center of the cell, there is a hollow cavity called lumen. A summary of the chemical composition in two wood-types can be seen in Table 1. [7]

Table 1 Chemical composition in some wood species, modified from [7] .

Wood constituent	Pine % (softwood)	Birch % (hardwood)
Cellulose	40	41
Hemicellulose	28	34
Lignin	28	22
Extractives	4	3

Cellulose is a linear polysaccharide that consists of glucose monomers. Cellulose is crystalline with strong intermolecular hydrogen bonds. Hemicelluloses are, just as cellulose, crystalline polysaccharides but their chemical structure differ. The monosaccharides in hemicellulose are both pentoses and hexoses and the molecular structure is branched. Their crystalline structure makes cellulose and hemicellulose suitable as material for paper production. [7]

Lignin on the other hand, has a more complex structure. It polymerized from three propylphenol monomers; p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol seen in Figure 2. From these monomers, lignin is polymerized into a three dimensional network. It has an amorphous structure, which makes it resistant to degradation and depolymerization. The propylphenol monomers are linked together with different ether-bonds and C-C bonds which seems to be randomly distributed. The most common linkage is the β-O-4 aryl ether followed by β-5 α-O-4. [7]

A suggested structure of a lignin macromolecule can be seen in Figure 3. The average molecular weight of the Kraft lignin monomer is 180 g/mol [5].

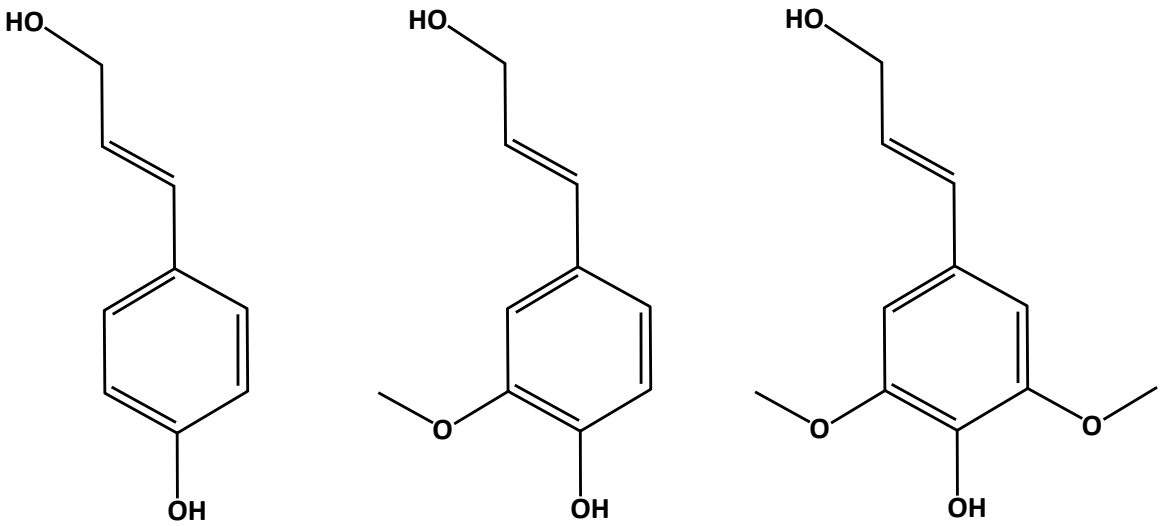

Figure 2. Three propylphenol monomers, the building blocks of lignin. From the left; p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Modified from [7].

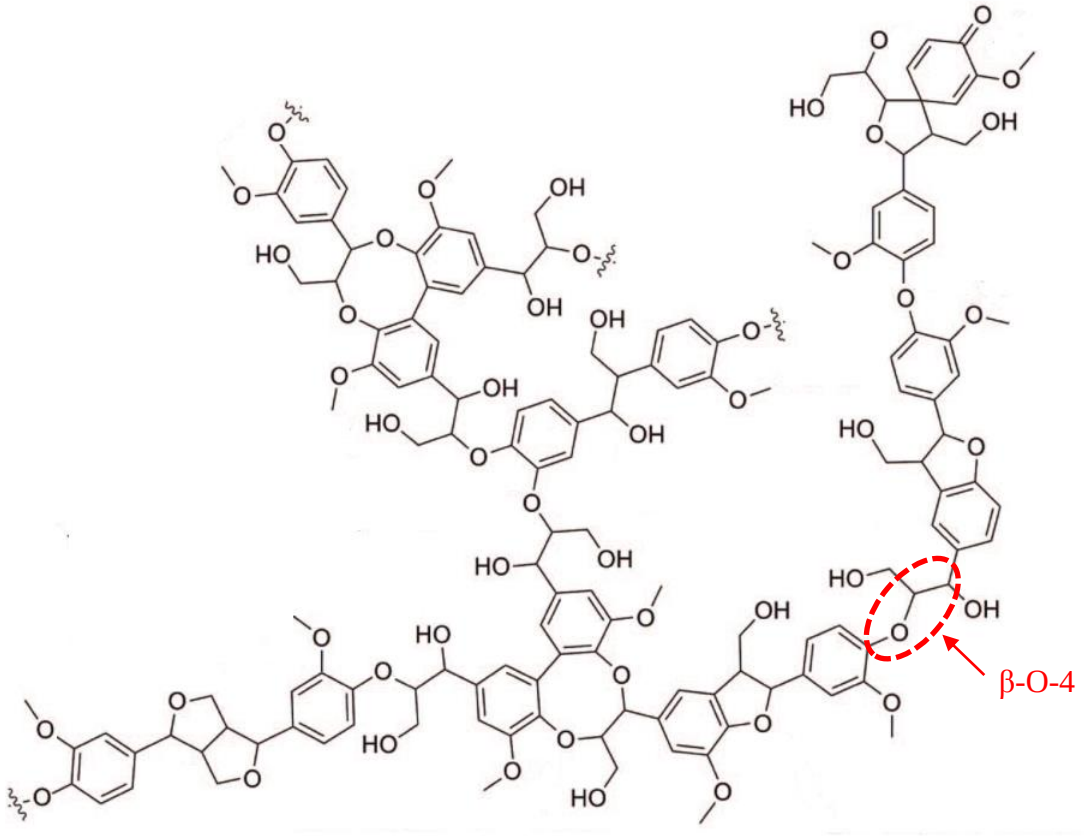

Figure 3. Suggested structure of a lignin macro molecule, modified from [5].

Extractives are mostly surface active substances that do not contribute to the mechanical strength of the wood, for example different fatty acids, terpene, resin acid and sterol [7].

2.2 Pulp and Paper Industry

Pulping can be done either chemically or mechanically. Chemical pulping includes the sulfite process and the sulfate process, also called the Kraft process, which is the most common pulping method in Sweden. The paper making process can generally be divided into two parts. First, fibrous raw material is converted into pulp where the desired materials, cellulose and hemicellulose, are separated from the lignin. The pulp is then bleached and converted into paper through pressing and drying.

The Kraft process has an alkali environment and the cooking chemicals are sodium hydroxide, NaOH, and sodium sulfide, Na_2S. Unlike the Kraft puling, in sulfite pulping there is an acid environment with pH around 4. The active cooking chemicals is usually magnesium bisulfite ($Mg(HSO_3)_2$), but sodium or calcium can also be used. In chemical pulping, lignin is removed from the wooden material by the help of chemical reactions but not all lignin can be removed without negative impact on the quality and yield of the pulp. [8]

Mechanical pulping is achieved by grinding of wooden material. Friction heat and shear stress causes the lignin to soften and bonds in the fiber walls are disrupted. There are also combined chemical and mechanical pulping where the raw material can be soaked in chemical solutions, for example sodium sulfite (Na_2SO_3). As opposed to chemical pulping (Kraft and sulfite), no lignin is removed in the mechanical process which entails high yields, up to 100 %. Because of the high lignin content in the mechanical pulp, it is used for papers that do not need much strength or whiteness, for example newsprints. The yield of the chemical pulping is lower due to removal of lignin but it produces a higher-quality pulp and paper. For chemical pulping, the yield usually varies between 45 and 60 %. [8]

2.2.1 The Kraft Process

The active cooking chemicals in the Kraft process are hydroxide ion, OH^- and hydrogen sulfide ion, HS^-[7]. After the delignification step, these chemicals are regenerated in a series of process steps and recirculated to the digester. Fresh chemicals are added in the form of sodium sulfate, Na_2SO_4, but the regeneration of cooking chemicals has become so efficient over the years that only a small amount of fresh chemicals is needed [8]. An overview of the Kraft process is depicted in Figure 4.

Wood Preparation

Wood is delivered to the mill and the bark is removed either by mechanical or hydraulic methods [10]. A common mechanical method is a rotating drum where bark is removed by friction between logs and the drum or by friction between logs themselves [8]. The bark is collected and used for steam production in the mill. The debarked wood is chopped into chips around 2 cm long. The wood chips are screened through a sieve to obtain an even size distribution which facilitates the cooking [8]. The wood chips can be stored on piles where oxidative and enzymatic degradation takes place within the wood which aids the delignification [10]. Chips are taken out by screws from the bottom of the pile so that the oldest material is being used first [8].

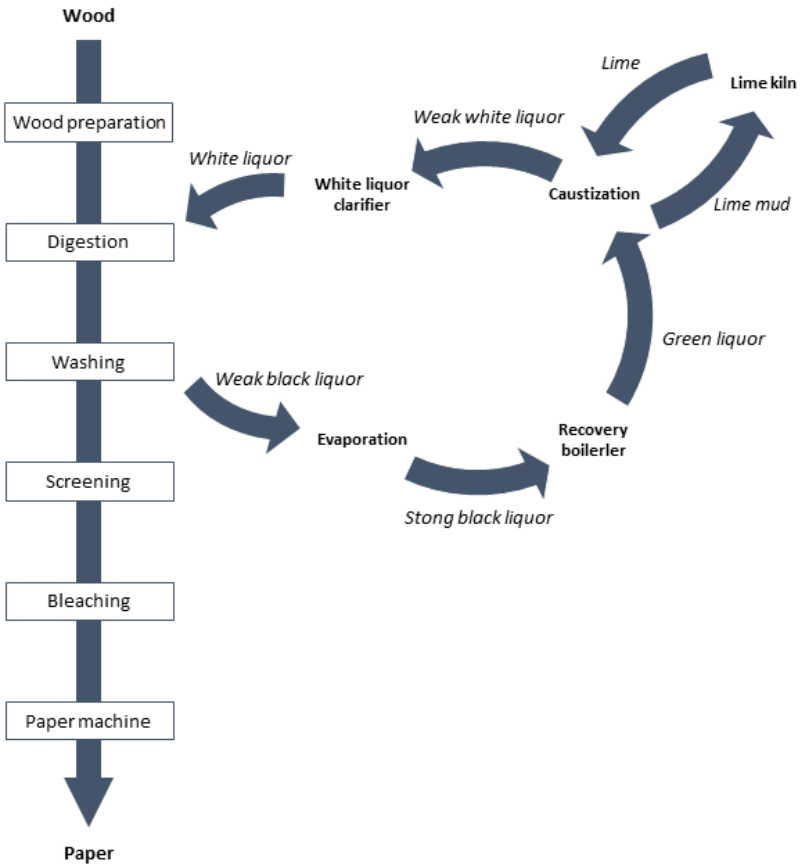

Figure 4. Simplified flow diagram of the Kraft process modified from [9].

Digestion

In the delignification step, wood chips are treated with NaOH and Na_2S, also called white liquor, at 165–175 °C for several hours [9]. The lignin is converted to smaller lignin fragments which are soluble in alkaline conditions [11]. Native lignin is, as mentioned before, rich in β-O-4 bonds which is are cleaved in the Kraft process in two major delignification reactions. In one reaction, non-phenolic β-ethers are cleaved by the hydroxyl ion, OH^-, via an epoxide mechanism [12]. This is shown in Figure 5. The other reaction is faster than the former and includes cleavage of phenolic β-ethers by the hydrosulfide anion, HS^- [7]. In this reaction, reactive quinone methide intermediates, QM, undergo addition of nucleophilic HS^- which is followed by elimination of phenolate species, shown in Figure 6 [12]. The QM can react in other routes than shown in Figure 6, which does not include cleaving of the ether bond [12].

All products formed in the reaction mechanisms depicted in Figure 5 and Figure 6 can react further. For example, in further degradation that can lead to deoxygenation of alkyl side chains, or they can take place in enol ether formation or condensation reactions. As the delignification proceed, the abundance of C-O bonds decrease whereas the abundance of C-C bonds increase. [12]

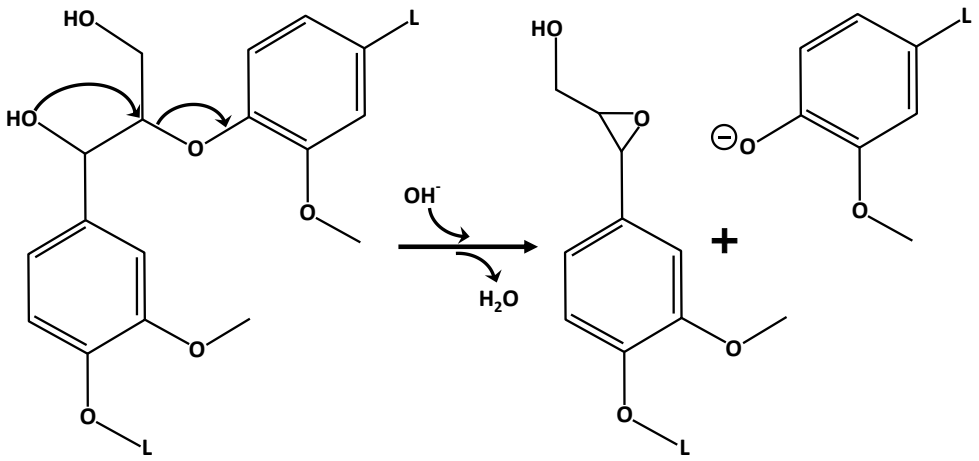

Figure 5. Cleaving of a non-phenolic β-O-4 structure in alkaline pulping, modified from [12] *and* [7]. *L denotes continuation of lignin structure*

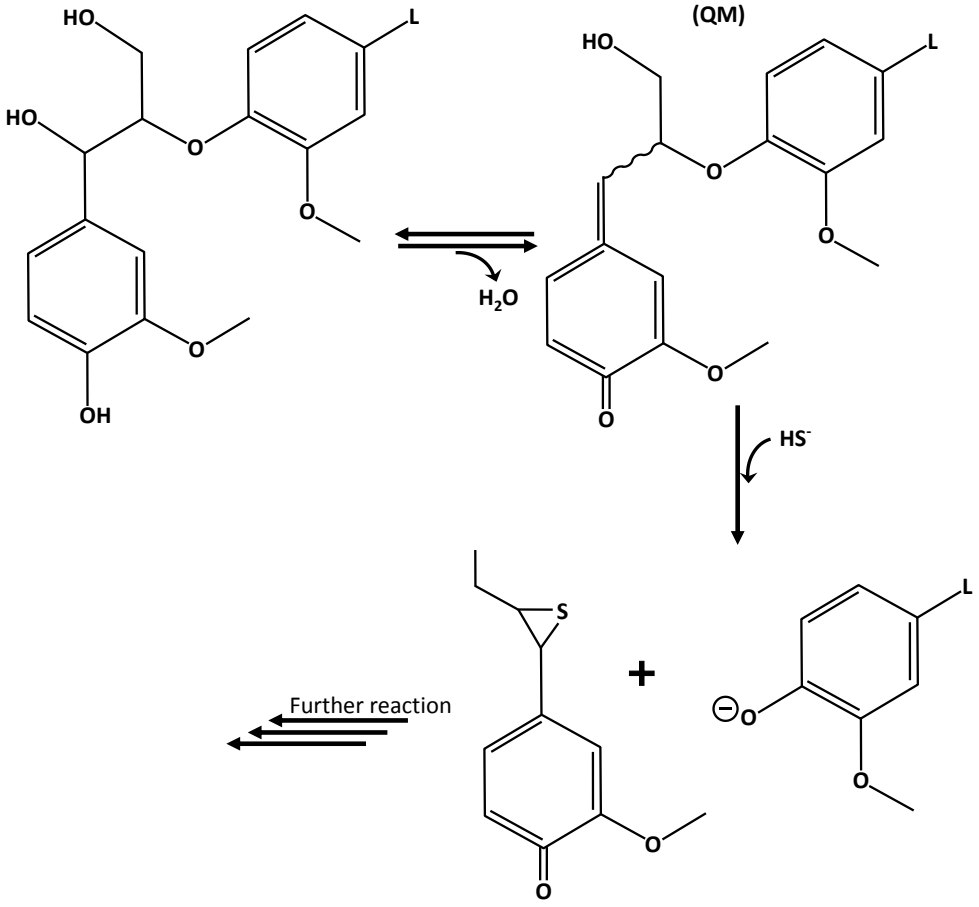

Figure 6. Cleaving of phenolic β-O-4 structure in alkaline pulping, modified from [7] *and* [12]. *L denotes continuation of lignin structure.*

Washing and Screening

After the digester, the pulp is washed and screened. In order to recover as much cooking chemicals as possible and also to reduce emissions, washing is important [9]. Washing can be performed by different techniques, usually in several steps based on diffusion or pressing [8]. Pieces of bark or uncooked wood are removed in a screening step [9]. After this, the pulp can be turned to paper. The pulp is bleached, formed into large sheets and dried.

Chemical Recovery Cycle

The used cooking liquid that is recovered from washing is called week black liquor. It contains used cooking chemicals, lignin and non-process elements such as Al, Cu, Fe, Pb, Mg, K and P. Water is removed in a series of evaporation steps where dry solids are increased from 15% to at least 60% in order to combust the organic material [9]. Tall oil can be separated from the black liquor when the dry solids are above 25 %. In between evaporators, tall oil is skimmed off the surface collected in its sodium form. The concentrated black liquor is called strong black liquor or heavy black liquor. The strong black liquor is combusted in the recovery boiler where oxygen is limited and the temperature high (about 1,100 °C) [9]. Sodium sulfate is reduced to sodium sulfide in an endothermic reaction where carbon acts as reducing agent [9].

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

The cooking chemical sodium sulfide Na_2S is recovered by this reaction. The recovery boiler also produces process steam that is much needed, for example in the evaporators and in the paper dryers.

The flue gases from the recovery boiler are cleaned through an electrostatic precipitator, ESP, and a scrubber with alkali solution. The collected ESP-dust that contains sodium sulfate, Na_2SO_4, and sodium carbonate, Na_2CO_3, is mixed to the strong black liquor and returned to the process to prevent losses of cooking chemicals. [9]

In the bottom of the recovery boiler, a smelt forms that mainly consists of sodium sulfide, Na_2S, and sodium carbonate, Na_2CO_3, and small amounts of other salts such as sodium sulfate, Na_2SO_4 [9]. The smelt is dissolved in weak white liquor, which is a downstream process liquid, Figure 4. Together they form green liquor.

Insoluble materials in the green liquor are separated through precipitation and filtration. The solid material, called green liquor dreg, is where non process elements are allowed to leave the system and thus avoid build-up. Non-process elements found in green liquor dreg are for example Al, Cu, Fe, Pb, Mg, K and P. It is important that build-up is avoided since they can cause problems with bleaching, corrosion and clogging. [13]

The next step in the recovery of cooking chemicals is to convert sodium carbonate, Na_2CO_3, to sodium hydroxide, NaOH, trough addition of calcium oxide, CaO [9]. The reactions are described below.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Na_2CO_3 + Ca(OH)_2 \rightleftarrows 2NaOH + CaCO_3$$

Calcium carbonate, $CaCO_3$, forms a precipitate which is separated and treated with heat, 1,100-1,250 °C, in the lime kiln to regain calcium oxide, CaO [9].

$$CaCO_3 \rightarrow CaO + CO_2$$

At this stage, all cooking chemicals have been regenerated. The liquor is called white liquor and it is ready to be returned to the digestion step.

2.3 Analysis of Lignin

Due to its complex structure, lignin is difficult to analyze both quantitatively and structurally [7]. For example, as lignin is isolated from the wooden cell structure, some of the chemical bonds are disrupted and only fragments can be studied. This is why the exact structure of lignin is unknown.

2.3.1 Klason-Lignin and Kappa Number

Klason-lignin and kappa number are two methods for lignin quantification frequently used in pulp and paper industry. The kappa number is based on the difference between lignin and other carbohydrates in their consumption rate of permanganate. The Klason-lignin method is a gravimetrical method based on isolation of lignin through acidification. [7]

2.3.2 Solubility and pH

In cleaving of a non-phenolic β-O-4 bonds, OH^- is consumed as mentioned earlier. This leads to a decrease of pH. Thus, the pH can give an indication of the degree of the depolymerization.

The solubility of lignin in water decreases with decreasing pH as carboxylic acids are protonated and the polarity of the lignin is decreased. Generally, large molecules tend to have lower solubility than small molecules. But according to the work by Evstigneev, the solubility is better determined by the number of phenolic hydroxyls per 100 phenylpropane units in the macromolecule rather than molecular weight [14]. The number of phenolic hydroxyls can be determined by ^{31}P-NMR.

2.3.3 NMR

In ^{31}P-NMR, depolymerized lignin compounds are treated with a phosphitylation reagent such as TMDP (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane). Hydroxyl groups react with TMDP in the presence of an organic base. Aliphatic hydroxyl groups, phenolic hydroxyl groups, and carboxylic acids have different chemical shifts in the ^{31}P-NMR spectra which enables quantification of each type through internal standards. ^{31}P-NMR is useful in the analysis of catalytic hydrogenolysis. Hydrogenolytic cleavage of inter-unit linkages, such as the β-O-4 bond, increases the total concentration of hydroxyl groups. Furthermore, saturation of aromatic structures decreases the concentration of phenolic hydroxyls while it increases the concentration of aliphatic hydroxyls. [15]

^{1}H-NMR provides information of the ratio between hydrogen atoms bound to aliphatic carbons and aromatic carbons. Saturation of aromatic structures can be detected with this method.

2.3.4 Size Exclusion Chromatography

Size exclusion chromatography, SEC, is a method for analyzing the molecular weight distribution. It consists of a column with one permeable solid phase and one mobile liquid phase that moves through the column. Large molecules have shorter retention time than small molecules since the small molecules can access the total porous volume. Large molecules

cannot penetrate small pores and thereby makes their average flow path distance shorter than that for small molecules. The retention time can be translated to molecular weight through calibration, usually with polystyrene standards with known molecular weight [16]. In order to detect substances in the eluent, the column needs to be coupled with some sort of detector for example, interferometric refractometry or UV-spectroscopy [16]-[17]. The interferometric refractometry or the refractive index, RI, measure differences in the light scattering ability of different substances while the UV-spectroscopy measures absorbance.

2.3.5 UV-Spectroscopy

UV-spectroscopy or UV/vis-spectroscopy measure the absorbance of UV-visible light. UV-spectroscopy has high sensitivity to aromatic compounds and compounds with conjugated double bonds in the wavelength region 168-330 nm [17]. The absorbance varies over the interval but is relatively stable around 280 nm which makes this wavelength a suitable reference point. When coupled with SEC, the UV-absorbance is measured at 280 nm.

One drawback with UV-spectroscopy is that the sensitivity varies between groups of compounds which makes quantification by this method uncertain [17]. This means that the absorption of each depolymerized lignin molecule can be either greater or smaller than the original macromolecule. Since the depolymerized product is a mixture of thousands of unidentified species, quantification becomes imprecise. However, in the pulp and paper industry quantification of lignin through UV-spectroscopy is commonly used and there the precision is increased due to consistency in the composition of the mixture. The molar absorptivity, ξ, has been empirically derived for different types of wood, pulping methods and solvents. For example, the molar absorptivity for pine Kraft lignin in water is 24.6 l/(g cm) [7]. This allows for quantification of the lignin concentration through measurement of the UV-absorbance.

2.3.6 Mass Balance

Mass balances can be useful in lignin depolymerization. After depolymerization, there is basically three categories of lignin components; depolymerized lignin, unconverted lignin/coke and gas phase products. Of the depolymerized lignin, it is often distinguished between acid soluble and acid insoluble components. There are examples of studies that refer to a product called “lignin-oil”. It is not always clear what that includes, but often it refers to the fraction of depolymerized products extracted to an organic phase after acidification. However, it could also refer to a viscous liquid containing depolymerized lignin and water. Since the definition of products varies, it can be confusing to compare yield between studies. The gas produced during depolymerization can be analyzed with gas chromatography and mass spectroscopy, GC-MS. This method allows for both components identification and quantification.

2.3.7 Oxygen Content

For solid-state biofuels, it is common to analyze the chemical composition through elemental analysis. The content of carbon, hydrogen, nitrogen, sulfur, chlorine and ash can be measured directly as weight percent of the dry solids, DS%. Based on the assumption that the only additional significant contribution to the weight comes from oxygen, the oxygen content can be calculated according to below where all species are expressed as weight percent per dry solids (DS%).

$$O = 100 - C - H - N - S - Cl - Ash$$

For liquid samples, much water needs to be removed in order to find the amount of dry solids in the sample. Furthermore, samples with high contents of salts, such as NaOH in black liquor, also have high contents of ash. This is not preferable in the calculation of oxygen content. The accuracy of the ash content is generally poor, and high contents of ash affects the calculation of oxygen very much. Thus, this method for analysis of the oxygen content can be associated with large uncertainties.

2.4 Reactions of Lignin

There are many approaches to lignin depolymerization. In this section, base catalyzed depolymerization and catalytic hydrogenolysis will be explained as well as the coke formation phenomenon.

2.4.1 Coke Formation

Lignin has a tendency to form coke under certain circumstances, generally at high temperatures. Coke formation is the phenomenon when reactive fragments re-polymerizes via C-C bonds into large molecules that forms solid material. This is well known in the petroleum industry. Coke is different from acid insoluble lignin since it is neither soluble in alkaline solutions nor in organic solvents such as tetrahydrofuran, THF.

Coke can cause problems such as catalyst deactivation and fouling of equipment. Furthermore, organic material that could have been transformed to useful products is lost in coke formation, thus, leading to reduced yield.

However, there are methods to reduce coke formation. Hydro processing of pyrolysis oils has shown that presence of hydrogen and low temperatures are factors that can reduce coke formation [3]. Furthermore, coke formation can be suppressed in base catalyzed depolymerization by adding a capping agent such as boric acid or phenol [18]-[19].

2.4.2 Base Catalyzed Depolymerization

In base catalyzed depolymerization, BCD, a strong base (e.g. NaOH or KOH) is involved in the cleavage of lignin compounds. The slow reaction described in Figure 5, section 2.2.1 The Kraft Process, is an example of BCD. In the pulp digester the objective is only to separate lignin from the rest of the wooden material, not to maximize depolymerization. Thus, at more severe reactions conditions such as higher temperatures and pressures, depolymerization of lignin can be increased which is the idea of BCD. Even if it is called base catalyzed depolymerization, it is not really a catalytic process unless the base is regenerated, as it is in the pulp mill.

Generally, BCD is associated with coke formation. The work of Karag et al. have shown that NaOH reduces the formation of solid residue from 41 % to 14 % compared to experiments with only water [20]. They also claim that the yield of oil-products increases from 9 % to 22 % [20]. The yield varies greatly between studies, which can be seen in Table 2. This can be due to different definitions of what is considered a product or differences in the behavior of lignin with varying origin. BCD of Alcell lignin have shown 30 % yield [21]. Others have claimed to achieve yields of 45-78 % of water soluble, low molecular weight compounds [22]. Even if all Kraft lignin originates from the same type of treatment, the Kraft process, their characteristics can vary greatly. The kappa number, the wood species in the pulp and even the season are factors that affects the characteristics of Kraft lignin. This should be kept in mind when comparing the results of different studies with Kraft lignin as starting material.

During BCD, the molecular weight distribution is shifted to lower molecular weights. Experiments with Kraft lignin have shown the mean molecular weight can be reduced from 5,100 Da to 1,200 Da for the pH 7 insoluble lignin [22]. In that work, the water-soluble fraction at pH 7 had a lower molecular weight distribution than the insoluble fraction, but it still contained compounds in the range 500-2,000 Da [22].

*Table 2. Summary of reaction conditions and yields of selected studies. * includes both BCD insoluble products and coke.*

Lignin	Lignin conc. wt%	Reaction temp °C	Reaction time min	NaOH wt%	Yield wt%	Solids/coke wt%	ref
Alcell	6	200-320	30 min	4	20	40	[21]
Organosolv	2.5-10	240-340	8 min	2.5-4	2-25	Not stated	[19]
Kraft	17	280	15 min	4	22	14	[20]
Kraft	10	270-330	40 min	2-4	18-31	52-71*	[22]

2.4.3 Catalytic Hydrogenolysis

In petroleum refining hydrogen is extensively used, for example in hydrotreating and hydrocracking. In hydrotreating, hetero-atoms such as sulfur, oxygen and nitrogen are removed producing hydrogen sulfide, water and ammonia. This process is also known as hydrodesulfurization, hydrodeoxygenation and hydrodenitrifaction, respectively. Hydrogen is also used in hydrocracking which seeks to reduce molecular weight of heavy petroleum components into lower-weight products. Iron-based catalysts have been used since 1911 in the Bergius process where solid charcoal is processed into a liquid oil-product through hydrogenation under harsh conditions, up to 700 bar and 380 °C. [23]

Even though petroleum and lignin feedstock differ, there are similarities in their reactions with hydrogen. Hydrogenolysis is the reaction of an organic compound with hydrogen where C-C bonds or C-heteroatom bonds are cleaved. Another possible reaction is saturation of double bonds with hydrogen. Hydrogen in combination with a catalyst can therefore increase lignin depolymerization and reduce the oxygen content. Many different catalysts have been examined for this purpose. For example, various noble-metal catalysts and H-ZSM-5 has been shown to have good selectivity for cleavage of ether linkages which yields monomers such as guaiacylpropane, syringylpropane, guaiacylpropanol, syringylpropanol [24]. Another type of catalyst that has been studied is different Ni-based catalysts. It can be seen below, Figure 7, how lignin model compounds with α-O-4 , β-O-4 or 4-O-5 bonds can be cleaved into monomers over a Ni-based catalyst [24].

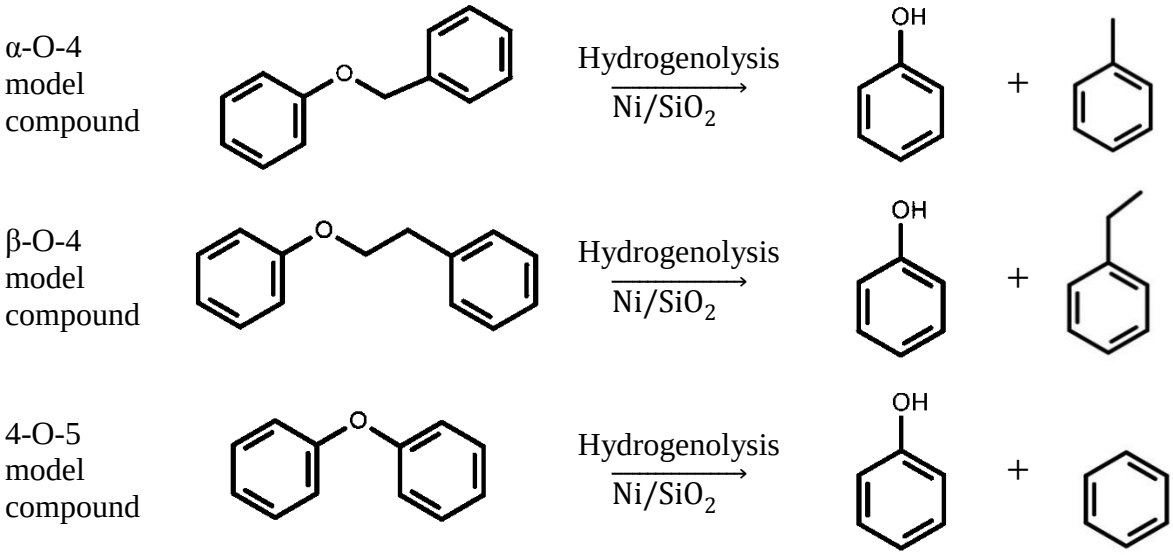

Figure 7. Hydrogenolysis of lignin model compounds over Ni-based catalyst. Modified from [24].

Various reaction conditions and yields of experiments with hydrogen are displayed in Table 3. Compared to BCD, the reaction time of experiments with hydrogen is considerably longer ranging from three to 20 hours in order to give the hydrogen gas time to dissolve in the solvent. Whereas the reaction time for BCD is normally below one hour. In the study of pyrolysis oil, it was shown that increasing hydrogen partial pressure increased the thermal stability of the products and reduced coke formation [3]. High partial pressure of hydrogen also increased hydrodeoxygenation and decreased production of light alkanes, C_1-C_4 [3].

*Table 3. Summary of reaction conditions and yield for selected studies. * Depolymerization in MeOH.*

Lignin	Catalyst	P_{H_2} bar	Reaction temp °C	Reaction time h	Yield wt%	Solids/coke wt%	ref
Pyrolysis oil	Ru/C, Pt/C, zeolite	52-100	116-250	3	20-60	13-50	[3]
Enzymolysis lignin	Raney Ni, NaOH	2	160	3,5	44	Not stated	[25]
Organosolv lignin (nutshells)*	Cu-PMO	3-6	140-220	8-20	32-64	10-77	[26]

The solubility of hydrogen is an important factor regarding hydrogenolysis. Unfortunately, the solubility of molecular hydrogen is poor in polar media such as water. Hydrogen has high solubility in organic solvents and it is approximately one order of magnitude lower in water than in methanol [27]. The Henry's constant for hydrogen in water is 0.78 mmol/(bar kg) [28]. The presence of salts such as sodium hydroxide lowers the solubility of hydrogen while carbohydrates has been shown to increase the hydrogen solubility [27].

3 Material and Method

The raw material was black liquor retentate, BLR, produced at a Kraft pulp & paper mill in Northern Sweden. According to their analyses, the lignin concentration was 23.1 wt% and dry solids were 32.0 wt%. The composition of the two pulp mill catalysts, Mill1 and Mill2, was analyzed by ALS Luleå. Based on the analysis, two model substances were selected. The catalysts investigated were;

- Model substance 1 –MS1
- Model substance 2 – MS2
- Internal pulp mill catalyst 1 – Mill1
- Internal pulp mill catalyst 2 – Mill2

3.1 Experimental Setup and Procedure

Experiments were performed in a 500 ml Parr autoclave equipped with stirrer and heating jacket. The temperature was controlled with a Parr PID-controller and a fan was used for cooling. The gas vent and the safety valve were connected to an expansion vessel of 200 L, which is 800 times the head space of the autoclave. A picture of the experimental setup can be seen in Figure 8.

Figure 8. Picture of the experimental setup.

In a typical procedure 250 ml of retentate was added to the autoclave and the weight of the retentate was noted. The amount of catalyst was 5 wt % of the lignin content. The water content of the catalyst Mill1 was compensated for. The retentate and catalyst was manually stirred with spatula for five minutes before the autoclave was sealed. In the experiments

where hydrogen gas was used, the autoclave and the expansion vessel was inerted with nitrogen gas four times the volume.

The autoclave was heated to desired temperature and held there for 15 minutes. Different PID-parameters was used for experiments with and without hydrogen. The PID-parameters were optimized for each material in order to achieve consistent heating time, approximately 60 minutes. After 15 minutes at the desired temperature, the autoclave was air-cooled by fan. The gas was vented when the temperature reached 40-45 °C. The products were stored below 4 °C.

3.2 **Method Development**

Only the reaction conditions that gave products that could be pumped were accepted when deciding the temperature for depolymerization. After initial tests, 220 °C was selected as the temperature for comparison between catalysts.

All catalysts were tested in combination with hydrogen as well as without. Blank tests, i.e. base catalysis without any additional catalyst were also performed with and without hydrogen. Moreover, there was one experiment performed with MS1 at 190 bar hydrogen pressure and long residence time, 20 hours. This experiment was performed after all catalysts had been tested with 15 min residence time and the choice of reaction conditions were made based on the results of the previous experiments. Even though the product could not be pumped, it was analyzed to evaluate the effect of longer residence time. A summary of the reaction conditions of all experiments can be seen in Table 4. Green circle indicates product that can be pumped and red cross indicates solid material which cannot be pumped.

Table 4. Summary of reaction conditions, circle indicates product that could be pumped and cross indicates solid material.

Temp [°C] 15 min		220	230	240	250	260	220 (20h)
Blank		O	O	O	X	X	
H_2-pressure [bar]	50	O					
	100			O		X	
	190	O					
MS1		O					
H_2-pressure [bar]	190	O		X			X
MS2		O					
H_2-pressure [bar]	190	O	O				
Mill1		O					
H_2-pressure [bar]	190	O					
Mill2		O					
H_2-pressure [bar]	190	O					

3.3 **Analysis and Assumptions**

Since some advanced analyses was required and the analysis equipment was not available at LTH or at SunCarbon, samples were sent to external laboratories. Other analyses were made at the experimental site at SunCarbon and some were made at LTH. This section will explain

which analyses that were made and by whom. Assumptions regarding calculations are also stated.

3.3.1 External Analysis

As mentioned before, an elemental analysis of the two pulp mill catalysts was performed by ALS Luleå and the analysis was the basis for selection of model substances. It was also used in sulfur molar balance calculations.

Analysis of hydroxyl groups and aliphatic to aromatic hydrogen was performed by Rise PPD through ^{31}P-NMR and ^{1}H-NMR respectively. Only the portion of compounds soluble in mesityl oxide was analyzed.

Analysis of the chemical composition of C, H, N, S and Cl was performed by Belab Norrköping and the results were presented as weight percent per dry solids, DS%. Since the products contain much salt such as sodium hydroxide as well as catalysts, the ash contents are high. Therefore, the chemical composition was recalculated on the basis of organic content instead of dry solids, presented in Appendix I. The organic content was defined as dry solids minus ash, which is described in section 3.3.2 Internal Analysis.

The oxygen content was calculated from the content of C, H, N, S, Cl and ash as described in section 2.3.7 Oxygen Content.

Sulfur Balance

A sulfur balance was constructed from the analyses of chemical composition. A schematic picture of the sulfur balance is shown in Figure 9 where the only unknown was the amount of sulfur the gas phase, S_{gas}. Calculations were performed on molar basis and they can be seen in Appendix II**.**

The amount of sulfur in the feed, S_{feed} (mol), was calculated from the sulfur per dry solids, S_{ds}(DS%), the dry solids of the BLR, DS (wt%), the sample weight, m_{feed} (g), and the molar mass of sulfur, M_S (g/mol).

$$S_{feed} = S_{ds} \cdot DS \cdot m_{feed}/M_S$$

The amount of sulfur in the catalyst, S_{cat} (mol), was calculated from the added mass of catalyst, m_{cat}(g), the sulfur content, S_{wt} (wt%), and molar mass of sulfur.

$$S_{cat} = m_{cat} \cdot S_{wt}/M_s$$

The amount of sulfur in the product, S_{prod} (mol), was calculated from the sulfur per dry solids in the product, S_{ds}(DS%), the dry solids of the product, DS (wt%), the product weight, m_{prod} (g), and the molar mass of sulfur, M_S (g/mol). Since there was no measurable weight difference before and after depolymerization, it was assumed that the weight of the product was the same as the added BLR and catalyst.

$$m_{prod} = m_{feed} + m_{cat}$$
$$S_{prod} = S_{ds} \cdot DS \cdot m_{prod}/M_S$$

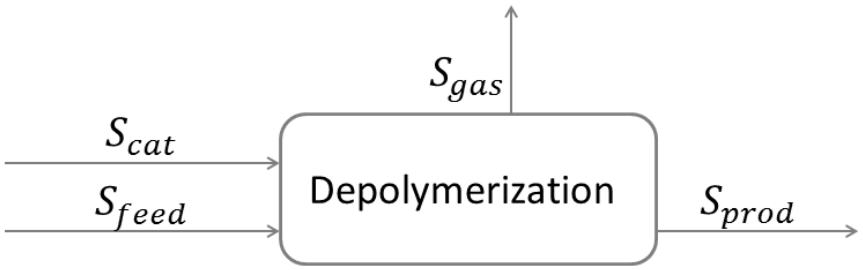

Figure 9. Sulfur balance. S_{cat} is the amount of sulfur in the catalyst, S_{feed} is the amount of sulfur in the retentate, S_{gas} is the amount of sulfur in the gas phase after depolymerization and S_{prod} is the amount of sulfur in the liquid product.

The amount of sulfur in the gas, S_{gas} (mol), was calculated from the following relation;

$$S_{gas} = S_{cat} + S_{feed} - S_{prod}$$

Since the sulfur analysis detects all sulfur present in the sample, both inorganic sulfur (ash) and organic sulfur, it gives a more accurate description of the organic material if the contribution from the catalyst is removed. Based on the assumption that all sulfur in the catalyst ends up in the ash, the sulfur content of the organic part of the product, S_{org} (mol), was calculated as follows;

$$S_{org} = S_{prod} - S_{cat}$$

The molar ratio between sulfur and carbon, S/C, was calculated from S_{org} and the amount of carbon in the product, C_{prod}. The amount of carbon in the product, C_{prod} (mol), was calculated from the carbon per dry solids, C_{ds} (DS%), the dry solids of the product, DS (wt%), the weight of the product, m_{prod} (g), and molar mass of carbon, M_C (g/mol).

$$C_{prod} = C_{ds} \cdot DS \cdot m_{prod}/M_C$$

3.3.2 Internal Analysis

Internal analysis were performed by the author, except the GC-analysis, which were performed by SunCarbon-personnel at the experimental site. SEC-analysis was performed at LTH.

pH

The pH of the product and the retentate was measured with pH-probe. At each experiment, the pH-probe was calibrated with three standards; pH 7, 10 and 13. pH measurements of the retentate just after calibration showed a decline of the measured value. Thus, a routine for pH measurements was developed. After calibration, the pH-probe was submerged in a sample of BLR and kept there for approximately three hours. During this time, the depolymerization experiment was performed so that when the autoclave was emptied, the pH-probe could be rinsed and transferred from the BLR to the product. The pH of the product was then measured for approximately 30 min. The decrease of pH from the retentate to the product for each experiment provides a value that can be compared between experiments even though there were variations of the absolute value from day to day.

Dry Solids and Ash

The amount of dry solids, DS (wt%), was found through evaporation for 28 hours at 105 °C. The ash content (wt%) was determined after thermal treatment at 900 °C for 3 hours.

Since it was oxygen present during ash treatment, it is likely that oxygen reacted with sodium, which was probably in the form of sodium carbonate, $NaCO_3$, after depolymerization. Formation of sodium peroxide, Na_2O_2, was assumed to occur during thermal treatment of ash measurement according to the following reaction.

$$NaCO_3(s) + \frac{1}{2}O_2(g) \rightarrow Na_2O_2(s) + CO_2(g)$$

Based on this, it is likely that the ash contained a considerable amount of oxygen that affected the weight of the ash. The ash of the blank experiments was assumed to contain mainly sodium peroxide, Na_2O_2, based on thermodynamic calculations, whereas the ash of the other experiments was assumed to also contain the catalyst. In order to compensate for the extra weight from the oxygen, a corrected value of the ash was calculated. The calculation are explained below.

Since the blank experiment and the catalyst experiment was assumed to have different compositions of the ash, they were calculated in different ways. The corrected value of the ash in blank experiments, $Ash_{blank\ corr}$ (wt%), was found through the relation between sodium and sodium peroxide. The measured ash of the blank experiments, Ash_{blank} (wt%), was multiplied by the ratio between the molar mass of Na_2, M_{Na_2}(g/mol), and the molar mass of Na_2O_2, $M_{Na_2O_2}$(g/mol).

$$Ash_{blank\ corr} = Ash_{blank} \cdot \frac{M_{Na_2}}{M_{Na_2O_2}}$$

The catalyst contribution to the ash, Cat (wt%), was assumed to be represented by the difference between ash in catalyst experiment, Ash_{cat} (wt%), and ash in blank experiment, Ash_{blank} (wt%). Experiments with hydrogen were compared to the blank experiment with hydrogen, and experiments without hydrogen was compared to the blank experiment without hydrogen.

$$Cat = Ash_{cat} - Ash_{blank}$$

For experiments with catalyst, they were assumed to contain the same amount of sodium as the corresponding blank experiment. The corrected ash content of the catalyst experiments, Ash_{corr} (wt%), could then be calculated from the corrected ash in blank experiment, $Ash_{blank\ corr}$ (wt%), and the catalyst contribution, Cat (wt%).

$$Ash_{corr} = Ash_{blank\ corr} + Cat$$

The corrected ash values, Ash_{corr} (wt%), were used to recalculate the chemical composition on the basis of organic material, as mentioned before. The organic material, org (wt%), was defined as the difference between dry solids, DS (wt%), and the corrected ash values, Ash_{corr} (wt%).

$$org = DS - Ash_{corr}$$

Molecular Weight Distribution

The molecular weight distribution was analyzed with size exclusion chromatography together with a UV-spectrophotometer. Polyethylene glycol standards were used for calibration of molecular mass where the detection method was RI. The eluent was NaOH 5 g/l and the flow rate was 1 ml/min. The samples were diluted 100 times in NaOH 5g/l, except for the liquid sample from experiment with long residence time. Due to lower concentration of lignin associated with formation of solid material, the sample was diluted 25 times.

Since it was shown that samples were not stable at 3 °C after dilution, analysis was performed just after dilution. Each SEC-analysis took three hours.

GC-Analysis

Analysis of sulphuric compounds in the gas was performed using a Scion 456-GC Gas Chromatograph equipped with a 500 µl inert steel sample loop 1/16" for Valco injection valve, a Rtx-DHA-50 Cap. Column 50m, 0.20mm ID, 0.5µm and a PFP-detector with Electrometer (S and P Modes), with 30 min intervals. Calibration was done using 0.5, 1 and 2 ppm in the lower region (up to 3 ppm) and for the higher region a calibration using 5 and 10 ppm. The injector was set to 280 °C, the split ratio was 20, the oven was set at 120 °C for 8 min and then increased to 180 °C using 20 °C/min increase and was held at this temperature for 3 min.

Analysis of hydrocarbons in the gas was performed using a Varian CP-4900 2-Channel Micro Gas Chromatograph (one mol-sieve 5A PLOT column and one PoraPlot column, with double TCD detectors).

The gas sample analyzed was collected at room temperature after depolymerization at 220 °C, 190 bar initial hydrogen partial pressure and 20 h residence time at the temperature. The gas tube was first flushed with nitrogen gas and then flushed 3 times with the gas in the reactor.

Hydrogen Solubility

As mentioned before, the Henry's constant for hydrogen in water is 0.78 mmol/(bar kg). This can provide a rough estimate of how much hydrogen that is dissolved in the experiments in this work. For 190 bar and 250 ml water, there should be 0.04 mol hydrogen in solution. However, the BLR contains NaOH, which could lower the solubility of hydrogen. On the other hand, the presence of carbohydrates has been shown to increase the hydrogen solubility [27]. Thus, it is not certain how much hydrogen that is dissolved in the experiments.

4 Results and Discussion

After depolymerization the visual appearance differed between the experiments. There were three different categories of consistence; low viscosity and homogeneous (A), high viscosity and homogeneous (B) or low viscosity with suspended particles (C). Pictures of each category can be seen in Figure 10. A summary of the visual appearance of each experiment can be seen in Table 5.

A: Low viscosity, homogeneous

B: High viscosity, homogeneous

C: Low viscosity, suspended particles

Figure 10. Categories of visual appearance after depolymerization.

4.1 pH and Chemical Composition

The average pH of the retentate was 13.1 ($\pm$0.05) based on measurements on each experimental occasion. The pH decrease after depolymerization varied between 1.9 and 2.5 units and is summarized in Table 5. Generally, for each catalyst the pH decrease was larger for experiments with hydrogen gas than without. The largest decrease was seen for MS2 and MS1 with hydrogen gas and the smallest decrease was seen for the blank base catalysis without hydrogen gas. This could be an indication of further depolymerization in the experiment with larger pH decrease since OH^- is consumed in base catalysis.

The dry solids and ash content varied slightly between experiments while the organic content was the roughly same for all experiments, 27 wt%. The organic content of the BLR was higher, 29 wt%. The difference can be explained by loss of organic material during depolymerization due to gas formation.

The chemical composition as weight per dry solids are presented in

Table 6. Since the oxygen content is calculated from the other components, it is associated with some uncertainties. In

Table 6, the oxygen is calculated both from the internal ash measurements, Ash_i, and from Belab's measurements of the ash, Ash_b. The difference in ash measurements severely affects the calculation of oxygen content. Thus, it was concluded that this method for determination of the oxygen content is not reliable.

Table 5. Results from experiments at 220 °C with residence time 15 min. The pH decrease was calculated from the measurement of the BLR the same day. Ash_{corr} is the corrected value of the ash where it has been compensated for the oxygen content of the ash associated with thermal treatment. Org is the organic content of the samples calculated as DS (dry solids) minus Ash_{corr}.

	Visual appearance category	pH	pH decrease	DS (wt%)	Ash (wt%)	Ash_{corr} (wt%)	Org (wt%)
BLR	A	13.1	-	33.1	7.6	4.5	28.6
Blank	A	11.1	1.89	31.8	7.5	4.4	27.4
with H_2	A	10.7	2.12	32.2	8.2	5.1	27.1
MS1	C	10.9	2.15	32.5	8.9	5.9	26.7
with H_2	C	10.7	2.45	32.1	7.9	4.8	27.3
MS2	B	10.9	2.16	32.8	8.5	5.4	27.4
with H_2	C	10.6	2.46	31.4	7.4	4.4	27.1
Mill1	A	11.2	2.00	32.0	8.1	5.1	26.9
with H_2	B	10.9	2.16	31.8	8.3	5.2	26.6
Mill2	A	11.2	1.84	31.8	7.9	4.9	26.9
with H_2	A	11.0	2.01	32.0	8.3	5.3	26.8

Table 6. Chemical composition as weight per dry solids performed by Belab. The samples analyzed were products from experiments were performed at 220 °C with 15 min residence time as well as BLR. Empty cells indicates values below detectable amounts and were assumed to be zero. O_b is the oxygen content based on Belab's measurement of the ash, Ash_b. O_i is the oxygen content calculated from the internal measurement of the ash, Ash_i.

DS%	Ash_i	Ash_b	C	H	S	N	Cl	O_i	O_b
BLR	23.1	24.9	45.5	4.4	2.2	-	-	24.9	22.9
Blank	23.6	27.2	46.9	4.2	2.1	-	-	23.2	19.4
with H_2	25.3	25.8	49.1	4.4	1.8	-	0.06	19.3	18.8
MS1	27.5	30.8	46.4	4.1	2.4	-	-	19.6	16.2
with H_2	24.5	30.4	44.4	4.0	2.6	-	0.04	24.5	18.5
MS2	25.8	31.3	46.0	4.1	3.4	-	-	20.7	15.1
with H_2	23.6	29.2	46.7	4.2	2.1	-	-	23.4	17.7
Mill1	25.4	30.1	46.1	4.1	2.0	-	-	22.4	17.6
with H_2	26.0	29.1	47.3	4.2	1.8	-	-	20.7	17.6
Mill2	24.8	30.1	44.9	4.1	2.7	-	-	23.4	18.1
with H_2	25.9	30.2	46.4	4.2	2.3	-	-	21.2	16.8

For all catalysts except MS1, there was a trend in the hydrogen experiments, which can be seen in

Table 6. The hydrogen gas appears to have increased the content of carbon and hydrogen and reduced the content of sulfur. Compared to the BLR, some of the experiments showed increased levels of sulfur. This can be explained by the fact that the analysis method detects all sulfur present in the sample, both organic and inorganic. Since the catalysts contain sulfur,

they contribute to the sulfur content. Therefore, it is interesting to subtract the amount of sulfur in the catalyst from the product, which is presented in the next section, Sulfur Balance.

The chemical composition was also expressed on the basis of organic content and the results can be seen in Appendix I.

4.2 Sulfur Balance

Since sulfur and oxygen are considered analogues in reactions with lignin, the sulfur content can provide information on how the oxygen content changed during reaction as well. The results of the sulfur balance calculations are displayed in Table 7. Calculation were made according to the description in section 3.3.1 External Analysis. The amount of sulfur in the BLR, S_{feed}, the catalyst added, S_{cat}, and the liquid product, S_{prod}, were known from analysis of the chemical composition, from which the amount of sulfur in the gas, S_{gas}, and the organic part of the liquid product, S_{org}, were calculated.

For the MS1 experiment with hydrogen gas, it can be seen in Table 7 that the amount of sulfur in the product was slightly higher than the sum of the feed (BLR) and catalyst. The difference was small, within the error of measurements, but it caused the calculation of the sulfur amount in the gas to be negative. It seems unreasonable that the hydrogen gas would affect the reaction so that no sulfur would be eliminated, especially since the MS1 experiment without hydrogen gas reduced the amount of sulfur in the product. Thus, the sulfur measurement of the experiment with MS1 with hydrogen is not considered reliable. It is disregarded in further analyses of the results. According to Belab, the sample of MS1 with hydrogen behaved somewhat different from the other samples in determination of the dry solids and ash. If the determination of dry solids were incorrect, this would affect the sulfur content since it is based on the weight of the dry solids. Furthermore, since the consistence varied between the samples, it is possible that not all samples were representative of the experiment. For example, the product from MS1 and hydrogen gas had low viscosity with suspended particles. It is possible that the particles congregated over time and separated through sedimentation.

The sulfur to carbon ratio, S/C (mol/mol), was calculated from the organic sulfur amount S_{org} and the carbon content, and the results can be seen in Table 7. The S/C in the BLR was 0.018. This ratio was decreased for all experiments except MS1 with hydrogen gas. Generally, the presence of hydrogen gas reduced sulfur content compared to experiments without hydrogen gas for the same catalyst. The lowest S/C ratio was seen for MS2 with hydrogen gas, 0.006. This is 1/3 of the sulfur content of the BLR, which is a significant decrease. Since sulfur and oxygen are considered analogues in reactions with lignin, it is reasonable to suspect that the oxygen content would have decreased by the same magnitude.

Table 7. Sulfur balance of experiments with 15 min residence time at 220 °C . The S/C ratio in the BLR was calculated per gram sample. For the other samples, S/C is calculated from S_{org} and the carbon content. ($S_{gas} = S_{cat} + S_{feed} - S_{prod}$);($S_{org} = S_{prod} - S_{cat}$)

mol	S_{feed}	S_{cat}	S_{prod}	S_{gas}	S_{org}	S/C
BLR	-	-	-	-	-	0.018
Blank	0.063	-	0.060	0.004	0.060	0.017
with H_2	0.064	-	0.049	0.014	0.049	0.014
MS1	0.064	0.012	0.070	0.006	0.059	0.016
with H_2	0.065	0.012	0.077	-0.0001	0.065	0.019
MS2	0.064	0.038	0.100	0.003	0.062	0.017
with H_2	0.064	0.038	0.061	0.041	0.023	0.006
Mill1	0.064	0.004	0.059	0.009	0.055	0.015
with H_2	0.064	0.004	0.052	0.016	0.048	0.013
Mill2	0.064	0.022	0.082	0.004	0.060	0.017
with H_2	0.064	0.022	0.066	0.020	0.045	0.012

4.3 **NMR**

From NMR-analysis, the concentration of hydroxyl groups and the ratio of aliphatic to aromatic hydrogen is shown in Table 8. The concentration of each type of hydroxyl groups as well as the total concentration of hydroxyl groups decreased in all of the experiments compared to the BLR. Out of all the depolymerized products analyzed, the concentration of phenolic hydroxyl groups decreased the least for MS1 with hydrogen gas. Whereas the largest decrease was found for MS2 with hydrogen gas. The concentration of aliphatic hydroxyl groups was lower for all experiments with hydrogen gas compared to the blank (base catalysis without hydrogen gas). For MS1, the combination of moderate decrease in phenolic hydroxyls and no increase of aliphatic hydroxyls speaks for that saturation of aromatic structures does not occur. If saturation had occurred, it would have been likely to see an increase of aliphatic hydroxyls in combination with a decrease of phenolic hydroxyls.

On the other hand, the ratio of aliphatic hydrogen to aromatic hydrogen is larger for experiments with hydrogen, which is in indication of saturation of aromatic structures. It should be noted that the accuracy of the analysis of aliphatic to aromatic hydrogen is reduced due to the large molecular weight of the analyzed products. The largest increase of aliphatic to aromatic hydrogen was observed for MS2 with hydrogen, 4.1, which could indicate saturation of aromatic structures.

Even though the hydroxyl groups in carboxylic acids decreased compared to the BLR for all experiments, it decreased the least for MS1 with hydrogen gas. Since formation of COOH is associated with depolymerization, it could be an indication of further depolymerization in the mentioned experiment compared to the others.

To conclude, experiment with MS1 and hydrogen gas showed the most promising results from the NMR analysis. The saturation of aromatic structures seemed to be low and depolymerization more complete compared to the other samples analyzed.

Table 8. Concentration of aliphatic, phenolic and carboxylic acid hydroxyl groups as well as aliphatic hydrogen to aromatic hydrogen of selected experiments. Only the portion of the samples that were soluble in mesityl oxide was analyzed.

mmol/g	Aliphatic OH	Phenolic OH	COOH	Tot OH	Aliphatic H : Aromatic H
BLR	1.51	5.54	1.1	8.15	1.5
Blank	0.94	4.74	0.79	6.47	2.5
Blank with H_2	0.73	4.81	0.74	6.28	2.9
MS1 with H_2	0.83	4.98	1.03	6.84	2.7
MS2 with H_2	0.80	4.62	0.93	6.35	4.1

4.4 Molecular Weight Distribution

It was shown that the molecular weight distribution was not stable over time at 3 °C after dilution as can be seen in Figure 11. The UV-response has been corrected with the dilution factor. Analysis was made for the blank experiment (base catalysis) with hydrogen gas. One sample was analyzed directly after dilution. Another sample was diluted, stored at 3 °C for 24 h and then analyzed. The shape of the molecular weight distribution as well as the integral differed between the two samples. The sample stored for 24 h had a higher maximum response, which was slightly shifted to the right compared to the freshly diluted sample. The absorption at small molecular weights in the range 0.1-1 kDa was larger for the freshly diluted sample than for the stored sample. In total, it seems likely that some repolymerization occurred during storage. For the BLR, the molecular weight distribution was not affected by storage after dilution.

The same result was achieved when the procedure was repeated. It was concluded that the diluted samples were not stable at 3 °C, but the original, undiluted sample was stable. Hence, all analyses were preformed directly after dilution.

The total amount of material was the same for both samples in Figure 11 since they originate from the same staring material. However, it appears as if there were less material in the freshly diluted sample since its integral was considerably smaller. This can be explained be the fact that UV-absorbance differs between compounds, which is why UV-absorbance is not suitable for quantification. In order to facilitate comparison of different experiments, the UV-response has been normalized to the maximum response of the BLR for some of the SEC results. As seen in Table 5, the organic mterial of all experiments was roughly the same, which speaks for the correction.

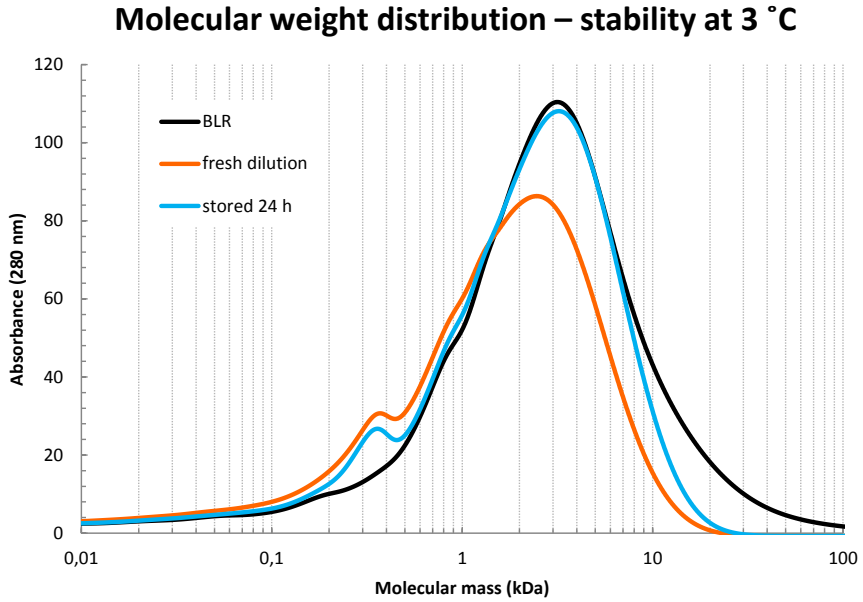

Figure 11. Molecular weight distribution of blank experiment with 190 bar hydrogen gas and 15 min residence time at 220 ˚C. One sample was analyzed directly after dilution and the other was stored at 3 ˚C for 24 h after dilution before it was analyzed. The absorbance has been corrected with the dilution factor.

All experiments without hydrogen gas were compared in Figure 12. The blank experiment (base catalysis) without hydrogen gas removed the content of large molecules in the range 20-100 kDa that were present in the BLR. The peak of the molecular weight distribution of the BLR was around 3 kDa. This can be seen in Figure 12, where the UV-response has been noramlized to the maximum response of BLR. The majority of the material in the blank experiment appeared to be in the range 2-3 kDa. Similar results were shown for all catalysts, which means that they had no significant effect on the degree of depolymerization compared to the blank experiment.

Only small differences between the catalysts can be distinguished, for example, experiments with MS2 and MS1 showed some material in the range 20-30 kDa while the other experiments had no material larger than 20 kDa. For MS2, the absorbance in the interval 0-2 kDa was slightly higher compared to the other catalysts.

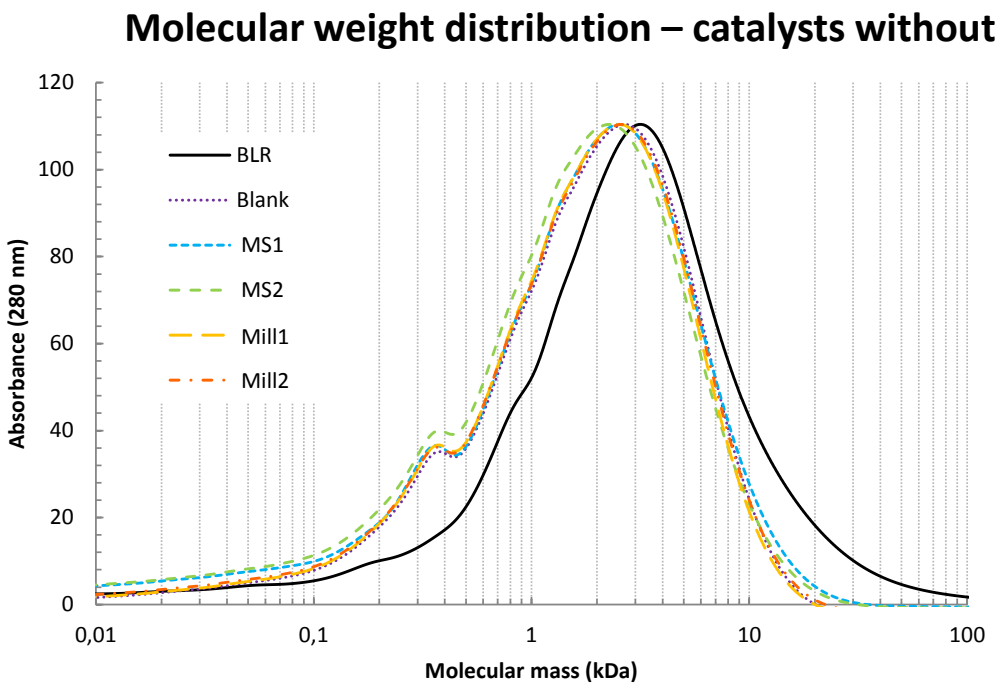

Figure 12. Molecular weight distribution of experiments with 15 min residence time at 220 ˚C for different catalysts. The UV-response has been normalized to the maximum response of the BLR.

The molecular weight distribution of expeiments with hydrogen gas was compared to experiments without hydrogen gas for the same catalyst. In Figure 13, it can be seen that the hydrogen had no significant effect for any of the catalysts at given reaction conditions; 190 bar initial pressure of hydrogen gas and 15 min recidense time at 220 °C. The UV-response in Figure 13 has been normalized to the maimum response of the BLR. The UV-response which has only been corrected with the dilution factor can be seen in Appendix II**.**

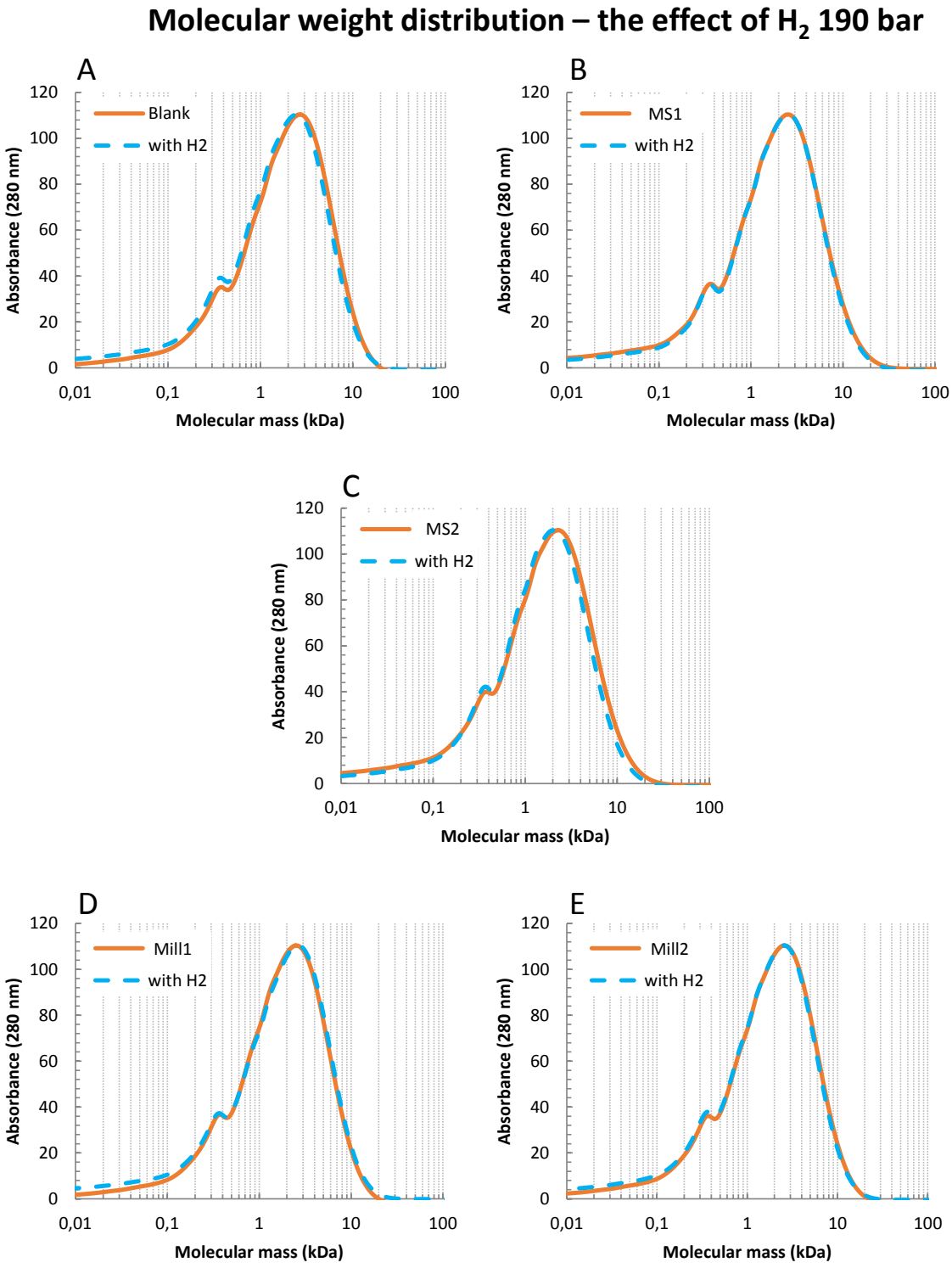

Figure 13. Molecular weight distribution of experiments with and without hydrogen gas (initial pressure 190 bar) for different catalysts. Residence time 15 min at 220 ˚C.
A: Blank (base catalysis), B: MS1, C: MS2, D: Mill1, E: Mill2. The residence time of each experiment was 15 min at 220 ˚C. The UV-absorbance has been normalized to the maximum response of the BLR.

In order to investigate if the hydrogen could have any effect with longer residence, one experiment was performed where the residence time was 20 h at 220 °C. MS1 was selected as catalyst due to the results from the NMR analysis where it showed low activity for saturation of aromatic structures. This experiment gave some solid material after depolymerization as well as a liquid product. The pH after depolymerization was 9.6 which corresponds to a pH decrease of 3.66 units. This can be compared to the pH dercrease of the experiments with 15 min residence time seen in Table 5, where the largest decrease was 2.46 units. On molar basis, this means that the consumption of OH^- was 60 % larger for the 20 h experiment compared to the 15 min experiment with the largest pH decrease. The extra pH decrease could indicate further depolymerization than the prevoius experiments. The solid material formed during depolymerization for 20 h was partially soluble in warm NaOH 5 g/l. Based on visual inspection, it was estimated that approximately 75 % of the solid material was soluble. The insoluble residue was assumed to be coke. The soluble fraction of the solid material as well as the liquid phase was analyzed in SEC.

From Figure 14, it is clear that the experiment with 20 h residence time shifted the molecular weight distribution to lower molecular weights compared to the experimnent with 15 min residence time. The UV-absorbance was lower for the liquid phase than for the solid phase, as can be seen in Figure 14A, where the UV-absorbance has been corrected by the dilution factor. This is probably due to lower concentration of lignin compounds in the liquid phase compared to the solid phase. The solid phase had higher UV-absorbance at small molecules than the liquid phase. This probably means that not only large molecules precipitates at the given pH, but also small ones. The summed UV-absorbance for the liquid and solid phase is denoted “tot 20 h” in Figure 14A and B.

In Figure 14 B, the UV-absobance has been normalized to the maximum response of the BLR. It apeared as the majority of the material was around 1 kDa since that is where the peak of the distribution was found, whereas it was around 3 kDa for the 15 min experiment. It can also be seen that all molecules larger than 11 kDa was removed in the 20 h experiment. This can be compared to 30 kDa for the 15 min experiment.

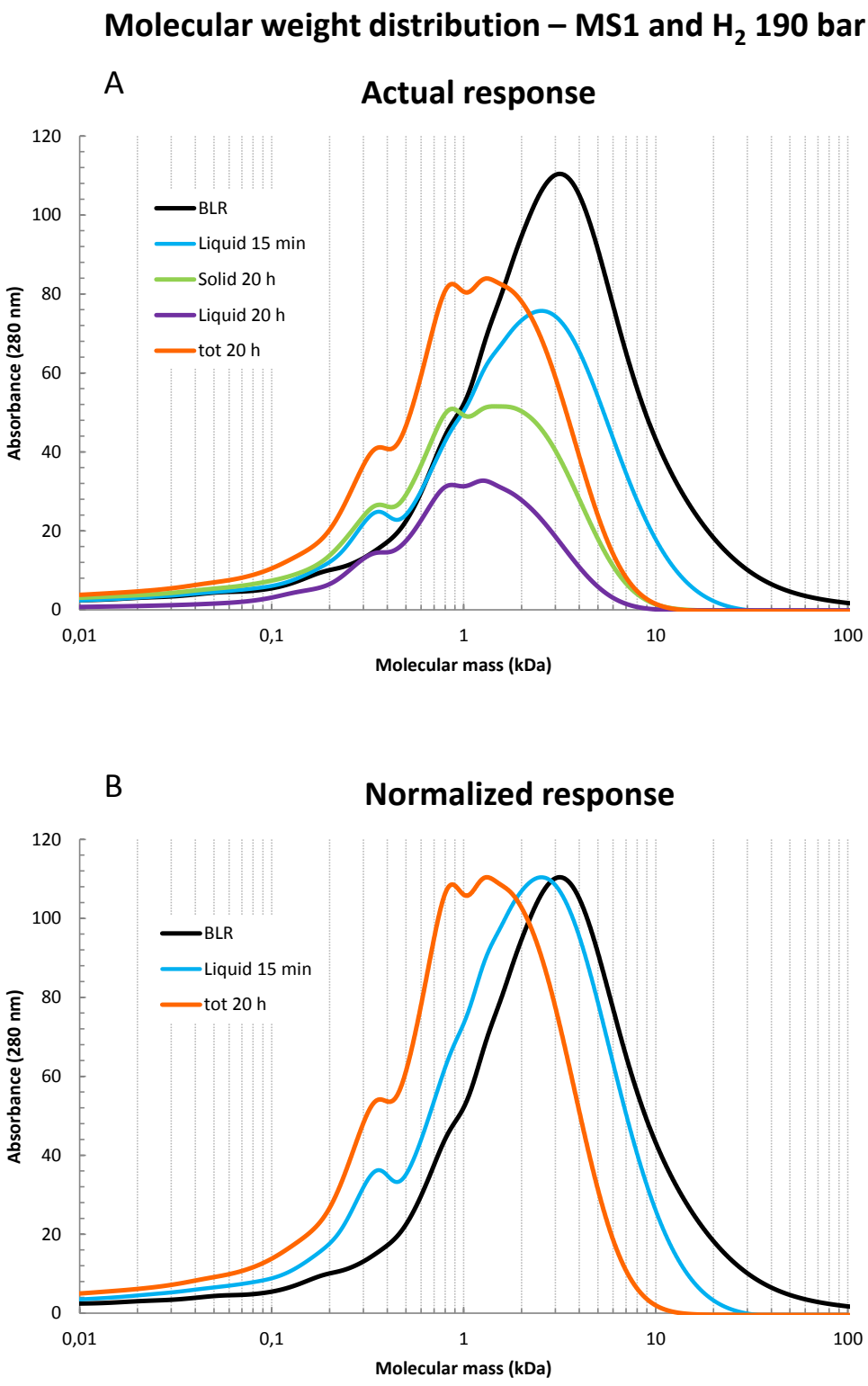

Figure 14. Molecular weight distribution of experiments with MS1 and H_2 (initial pressure 190 bar). For 15 min residence time, there was only liquid phase product. For 20 h residence time, there were both one liquid phase and one solid phase. They were analyzed individually and "tot 20 h" shows the summation of the two. A: the UV-response has been corrected by the dilution factor. B: UV-response has been normalized to the maximum response of the BLR.

4.5 **GC**

In GC-analysis of the gas from the 20 h experiment, dimethyl sulfide was identified. The content was approximately 300 ppm. Two other organic sulfuric compounds were detected but unidentified. In total, there was in the order of magnitude 0.1 % organic sulfuric compounds in the gas. This corresponds to 0.19 mol sulfuric compounds, which is more than was added in the feed (around 0.06 mol, Table 7). The difference is probably due to that the response was far above the calibration interval of the GC, which made quantification imprecise. However, the measurement indicates that there was a considerable amount of sulfuric compounds in the gas.

GC-analysis of hydrocarbons in the gas from the 20 h experiment showed that there were methane, carbon dioxide, ethane, ethane and propene present. Methane could have been formed from carbon dioxide and hydrogen gas.

The GC-chromatograms are shown in Appendix IV.

5 Conclusions

The presence of hydrogen gas reduced sulfur content, and possibly the oxygen content as well. It is possible that aromatic structures were saturated in experiments with hydrogen, where MS1 showed the least activity towards saturation.

The blank experiment (base catalysis) removed the content of large molecules in the range 30-100 kDa that were present in the BLR. The majority of the material appeared to be in the range 2-3 kDa. For 15 min residence time, none of the catalysts tested showed any significant effect on the molecular weight distribution i.e. they all showed similar results as the blank experiment. Nor did the combination of catalyst and hydrogen gas show any effect at 15 min residence time.

20 h residence time for MS1 and hydrogen gas showed a clear shift of the molecular weight distribution to lower molecular weights. The majority of the material appeared to be around 1 kDa. After depolymerization, there were no molecules larger than 11 kDa.

- H_2 generally reduced sulfur content
- MS1 and H_2 – lowest activity for saturation
- 15 min residence time – no effect on molecular weight distribution
- 20 h residence time with MS1 and H_2 – significant effect on the molecular weight distribution

6 Future Work

A method for purification of samples before analysis of the chemical composition should be developed. The analysis of the chemical composition should be performed on samples that are representative for the experiment and with low ash content. This could be achieved by extraction to an organic solvent with good solubility for lignin components and that can be evaporated completely before analysis. THF could be investigated as such a solvent.

The effect of varying residence time should be investigated further. Experiments should also be performed under inert atmosphere at the same pressure as hydrogen gas. The effect of the initial pressure should also be investigated.

- Purification before analysis
- Effect of residence time
- Inert atmosphere
- Initial pressure

7 References

[1] E. Dlugokencky and P. Tans, “Trends in Atmospheric Carbon Dioxide,” *NOAA/ESRL*, 2017. [Online]. Available: www.esrl.noaa.gov/gmd/ccgg/trends/. [Accessed: 05-Apr-2017].

[2] U.S. Environmental Protection Agency, “Inventory of U.S. greenhouse gas emissions and sinks: 1990-2014,” *Federal Register Notice*, 2016. [Online]. Available: https://www.epa.gov/sites/production/files/2017-04/documents/us-ghg-inventory-2016-main-text.pdf. [Accessed: 04-Jun-2017].

[3] T. P. Vispute, H. Zhang, A. Sanna, R. Xiao, and G. W. Huber, “Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils,” *Science (80-.).*, vol. 330, no. 6008, pp. 1222–1227, Nov. 2010.

[4] C. Li, X. Zhao, A. Wang, G. W. Huber, and T. Zhang, “Catalytic Transformation of Lignin for the Production of Chemicals and Fuels,” *Chem. Rev.*, vol. 115, no. 21, pp. 11559–11624, Nov. 2015.

[5] J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, and B. M. Weckhuysen, “The Catalytic Valorization of Lignin for the Production of Renewable Chemicals,” *Chem. Rev.*, vol. 110, no. 6, pp. 3552–3599, Jun. 2010.

[6] H. Werhan, N. Assmann, and P. Rudolf von Rohr, “Lignin oxidation studies in a continuous two-phase flow microreactor,” *Chem. Eng. Process. Process Intensif.*, vol. 73, pp. 29–37, Nov. 2013.

[7] G. Gellerstedt, H. Lennholm, G. Henriksson, and N.-O. Nilvebrant, *Wood Chemistry*. Stockholm: Kungliga Tekniska Högskolan, 2001.

[8] N. Jirvall, J. Ott Kann, M. Kassberg, S. Larsson, C. Molde, and A. Thorén, *Miljöinfo från Skogsindustrierna*. Stockholm: Media Express AB, 1995.

[9] O. Borg, *Sulfatmassatillverkning*, 4th ed. Markaryd: Sveriges Skogsförbund, 1991.

[10] P. Bajpai, “Environmentally Friendly Production of Pulp and Paper,” 2010, pp. 110–263.

[11] O. Y. Abdelaziz *et al.*, “Biological valorization of low molecular weight lignin,” *Biotechnol. Adv.*, vol. 34, no. 8, pp. 1318–1346, Dec. 2016.

[12] R. Rinaldi *et al.*, “Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis,” *Angew. Chemie Int. Ed.*, vol. 55, no. 29, pp. 8164–8215, Jul. 2016.

[13] J. Svensson, “Non - process Elements in the Green Liquor System,” 2012.

[14] E. I. Evstigneev, “Factors affecting lignin solubility,” *Russ. J. Appl. Chem.*, vol. 84, no. 6, pp. 1040–1045, 2011.

[15] Y. Pu, S. Cao, and A. J. Ragauskas, “Application of quantitative 31P NMR in biomass lignin and biofuel precursors characterization,” *Energy Environ. Sci.*, vol. 4, no. 9, p. 3154, 2011.

[16] A. V. Gidh, S. R. Decker, T. B. Vinzant, M. E. Himmel, and C. Williford, “Determination of lignin by size exclusion chromatography using multi angle laser light scattering,” *J. Chromatogr. A*, vol. 1114, no. 1, pp. 102–110, May 2006.

[17] V. Lagesson, L. Lagesson-Andrasko, J. Andrasko, and F. Baco, “Identification of compounds and specific functional groups in the wavelength region 168–330 nm using gas chromatography with UV detection,” *J. Chromatogr. A*, vol. 867, no. 1–2, pp. 187–206, Jan. 2000.

[18] A. Toledano, L. Serrano, and J. Labidi, “Improving base catalyzed lignin depolymerization by avoiding lignin repolymerization,” *Fuel*, vol. 116, pp. 617–624, Jan. 2014.

[19] V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li, and J. A. Lercher, “Towards Quantitative Catalytic Lignin Depolymerization,” *Chem. - A Eur. J.*, vol. 17, no. 21, pp. 5939–5948, May 2011.

[20] S. Karagöz, T. Bhaskar, A. Muto, Y. Sakata, T. Oshiki, and T. Kishimoto, “Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products,” *Chem. Eng. J.*, vol. 108, no. 1–2, pp. 127–137, Apr. 2005.

[21] R. . Thring, “Alkaline Degradation of Alcell Lignin,” *Biomass and Bioenergy*, vol. 7, no. I-6, pp. 125–130, 1994.

[22] R. Katahira *et al.*, “Base-Catalyzed Depolymerization of Biorefinery Lignins,” *ACS Sustain. Chem. Eng.*, vol. 4, no. 3, pp. 1474–1486, Mar. 2016.

[23] L. Lloyd, “Industrial Catalysts,” Bath: Springer, 2011, pp. 53–69.

[24] N. Li, W. Wang, M. Zheng, and T. Zhang, “Chapter 2. General Reaction Mechanisms in Hydrogenation and Hydrogenolysis for Biorefining,” in *RSC Energy and Environment Series*, vol. 2015–Janua, no. 13, 2015, pp. 22–51.

[25] J. Xin, P. Zhang, M. P. Wolcott, X. Zhang, and J. Zhang, “Partial depolymerization of enzymolysis lignin via mild hydrogenolysis over Raney Nickel,” *Bioresour. Technol.*, vol. 155, pp. 422–426, Mar. 2014.

[26] K. Barta, G. R. Warner, E. S. Beach, and P. T. Anastas, “Depolymerization of organosolv lignin to aromatic compounds over Cu-doped porous metal oxides,” *Green Chem.*, vol. 16, no. 1, pp. 191–196, 2014.

[27] R. Rinaldi, “Chapter 4. Solvents and Solvent Effects in Biomass Conversion,” in *RSC Energy and Environment Series*, vol. 2015–Janua, no. 13, 2015, pp. 74–98.

[28] NIST, “Hydrogen,” 2016. [Online]. Available: http://webbook.nist.gov/cgi/cbook.cgi?ID=C1333740&Mask=10. [Accessed: 09-May-2017].

Appendix I

Table 9. Chemical composition on the basis of organic content. Experiments were performed with 15 min residence time at 220 °C.

org%	C	H	S
BLR	53	5.1	2.5
Blank	55	4.9	2.5
with H_2	57	5.1	2.1
MS1	55	4.9	2.9
with H_2	53	4.7	3.1
MS2	56	5.0	4.1
with H_2	56	5.0	2.5
Mill1	54	4.8	2.3
with H_2	56	5.0	2.1
Mill2	54	4.9	3.3
with H_2	55	5.0	2.7

Appendix II

Table 10. Sulfur balance calculations. The S/C ratio in the BLR was calculated per gram sample.

Sample	S DS%	C DS%	DS wt%	cat (g)	BLR (g)	S_{prod} mol	S_{cat} mol	S_{feed} mol	S_{gas} mol	S_{org} mol	C mol	S/C
BLR	2.2	45.5	33.1	-	-	-	-	-	-	-	-	0.0178
Blank	2.1	46.9	31.8	-	282.7	0.060	0.0000	0.0633	0.0036	0.0597	3.517	0.0170
Blank H_2	1.8	49.1	31.4	-	284.5	0.049	0.0000	0.0637	0.0144	0.0494	3.659	0.0135
MS1	2.4	46.4	32.2	3.29	286.3	0.070	0.0118	0.0641	0.0056	0.0585	3.602	0.0162
MS1 H_2	2.6	44.4	32.0	3.33	289.6	0.077	0.0120	0.0649	-0.0001	0.0649	3.466	0.0187
MS2	3.4	46.0	32.5	3.31	287.7	0.100	0.0377	0.0644	0.0026	0.0618	3.628	0.0170
MS2 H_2	2.1	46.7	31.8	3.3	286.8	0.061	0.0376	0.0642	0.0411	0.0231	3.592	0.0064
Mill1	2.0	46.1	32.1	6.89	285.9	0.059	0.0039	0.0640	0.0094	0.0547	3.607	0.0152
Mill1 H_2	1.8	47.3	31.8	6.87	285.1	0.052	0.0039	0.0639	0.0156	0.0482	3.656	0.0132
Mill2	2.7	44.9	32.8	3.29	286.5	0.082	0.0215	0.0642	0.0041	0.0601	3.561	0.0169
Mill2 H_2	2.3	46.4	32.0	3.29	286.5	0.066	0.0215	0.0642	0.0196	0.0445	3.586	0.0124

Appendix III

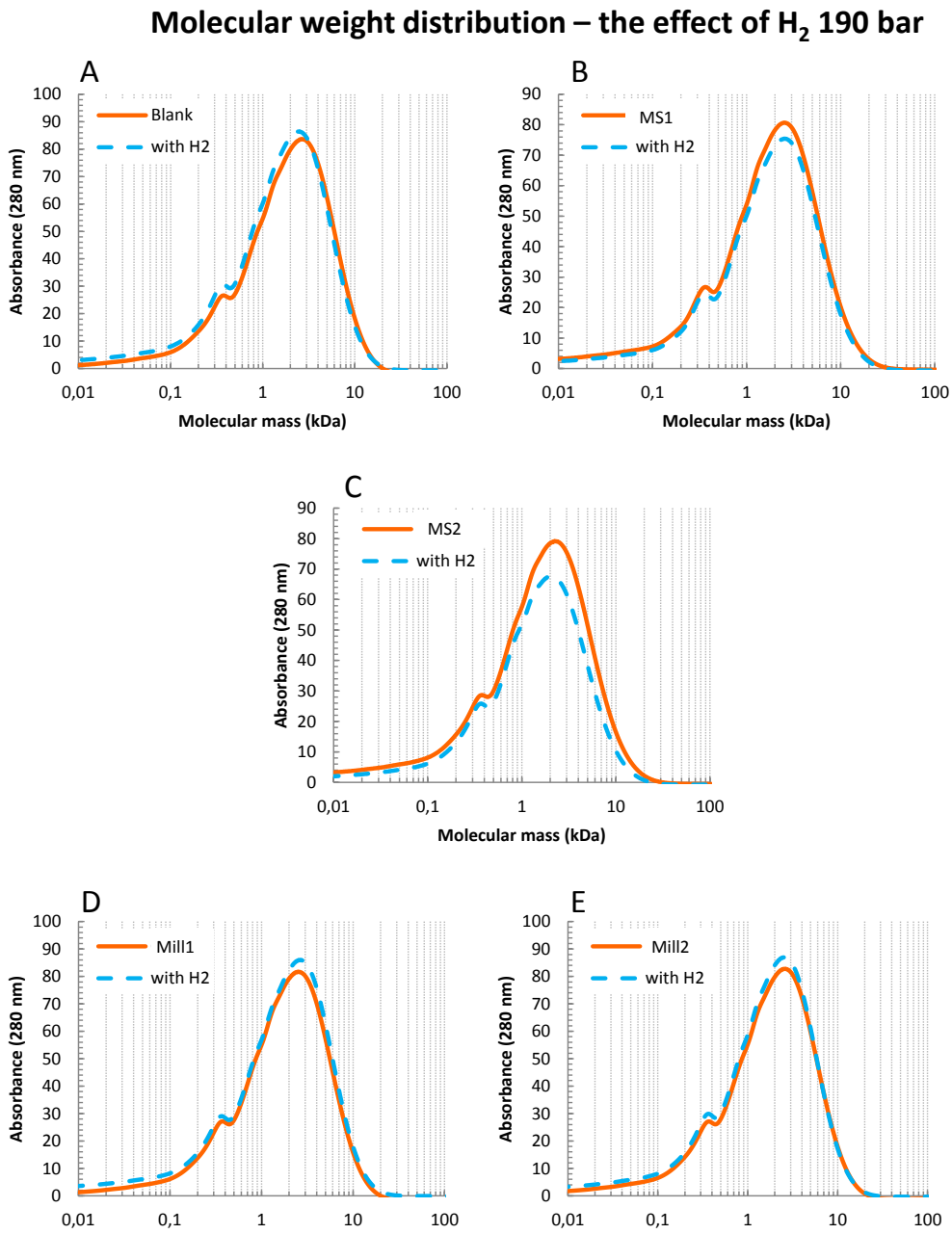

Figure 15. Molecular weight distribution where the UV-response only has been corrected with the dilution factor.

Appendix IV

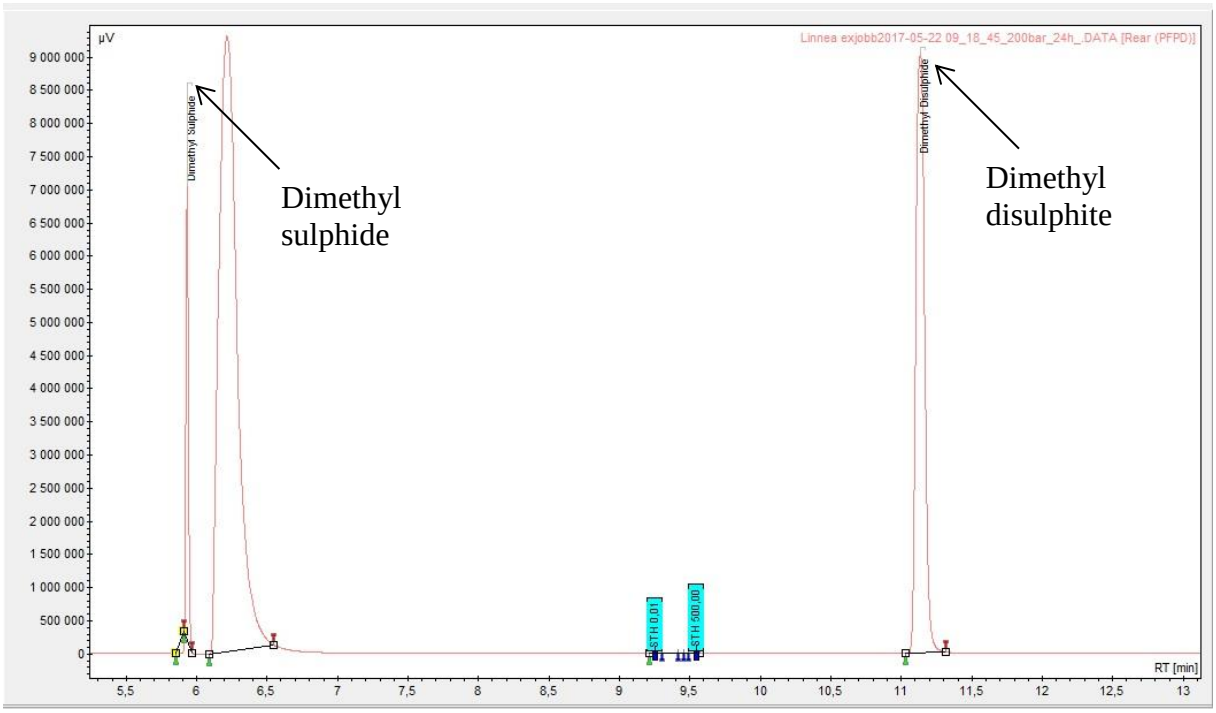

Figure 16. GC- chromatogram of sulfuric compounds

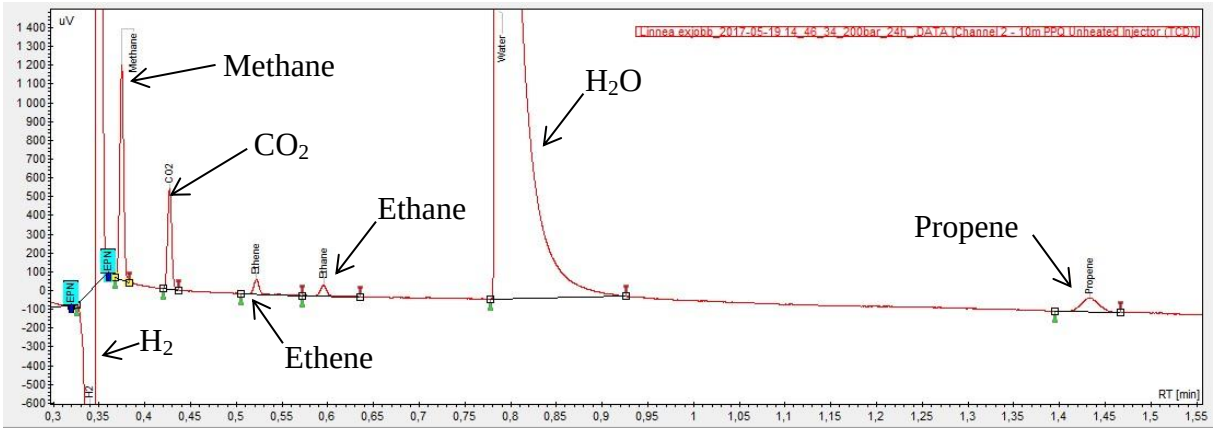

Figure 17. GC-chromatogram of hydrocarbons