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LIQUEFACTION OF LIGNIN:
UNCATALYSED AND CATALYSED ETHANOLYSIS

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Biomass Refining

Master's thesis for the degree of Master of Science in Technology
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Abstract

This thesis work had three main objectives: 1) the characterisation of the bioethanol-derived lignin mass, in comparison to other varieties of technical lignin, 2) explore the thermochemical route of liquefaction by ethanolysis of the lignin mass in order to produce a 'biocrude', lignin-ethanol energy-rich mixture, and 3) finally assess the potential of the lignin mass, and determine whether the thermochemical route chosen proved a viable option for valorisation of the studied material.

The literature review offers insight into the diversity of technical lignin, the current state of lignin pretreatment processes, as well as the thermochemical processes by which depolymerisation of the lignin polymer can be achieved. The experimental work consists of two parts: the first being the characterisation of the lignin mass, and the second being the attempts at liquefaction by ethanolysis, the results and conclusions.

The lignin mass was received by St1 Biofuels Oy, in the form of a ground and dried powder. Characterisation of the lignin mass was performed in laboratory with contemporary techniques and standards. The analytical methods used were carbohydrate and lignin determination, inorganic matter determination, methoxyl group determination, molar mass distribution, GC-MS chromatography, 13C NMR analysis and Fourier-transform infrared spectroscopy (FTIR). Elemental analysis was performed out-house. These methods allowed us to determine the composition of the Lignin Mass (LM) along with its characteristics.

The aim of the ethanolysis autoclave runs was to depolymerise the Lignin Mass (LM) in ethanol, in order to achieve partial liquefaction. A total of 8 runs were included in this work, 6 of which were uncatalysed, 2 of which were catalysed by heterogeneous catalysts: 5%Ni/γ-Al_2O_3 and 5%Ru/γ-Al_2O_3 respectively. Mass balances were determined for each experimental run with further analysis of the products with above mentioned analytical methods: bio-oil, residual lignin and solid fractions.

This work provided conclusions on the suitability of the Lignin Mass as a candidate for further refinement, as well as insight into the depolymerisation mechanisms.

Keywords lignin, characterisation, bioethanol, depolymerisation, ethanolysis, bio-oil

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Espoo, 5th February 2018

Oskar Wegelius

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List of Abbreviations:

AIL: Acid insoluble lignin (Klason lignin)

ASL: Acid soluble lignin

AQ: Anthraquinone

BEDL: Bio-ethanol process-derived lignin

BO: Bio-oil fraction

$Đ_M$: Dispersity index

FTIR: Fourier-transform infrared spectroscopy

G: Guaiacyl unit

H: Hydroxyphenyl unit

H/G/S: ratio of hydroxyphenyl/guaiacyl/syringyl units

HHV: Higher heating value (Dulong's formula)

LM: Lignin Mass (study material)

M_n: Number average molar mass

M_w: Weight average molar mass

MWL: Milled wood lignin

Ni: Nickel

NMR: Nuclear magnetic resonance spectroscopy

RL: Residual lignin fraction

Ru: Ruthenium

SD: Standard deviation

S: Syringyl unit

1 Introduction

Climate change, dwindling fossil fuel reserves, and an era of increased environmental consciousness are the major driving forces behind developments of more sustainable materials, chemicals and fuels from renewable sources. In effect, there is ever-more pronounced interest in biomass as likely candidate to contribute in filling the energy needs of future generations, reducing the dependence on coal and fossil fuels. Lignocellulosic biomass, composed of carbohydrates, lignin and extractives, presents itself once again as the most appealing and sustainable feedstock for a bioeconomy. It is widely available, sustainable properly managed, and does not compete with the food industry, other than by land-use.

Valorisation of all fractions of lignocellulosic biomass is at the heart of the biorefinery concept, and a cornerstone of a bioeconomy. It is necessary in terms of economic feasibility and resource efficiency. The valorisation of the carbohydrate and extractive fractions of lignocellulose has been achieved (Demirbas, 2013), with numerous end uses for both. Methods towards to valorisation of the lignin fraction however remain limited and underdeveloped. This is mostly due to the complexity of lignin as a feedstock. Rich in energy, its most popular application remains that of a low value fuel, combusted in pulp and paper mills, and bioethanol plants worldwide. However, renewed interest in lignin as a potential natural source of phenols and aromatics for the production of higher value biofuels, biochemicals and biocomposite materials has grown over the previous decade (Demirbas, 2013; Li et al., 2009; Werpy & Petersen, 2004).

Although a major breakthrough in high value applications has yet to be seen, lignin and its possible applications have been researched across the globe at a faster speed than ever within the previous century (Kozliak et al., 2016; Xu et al., 2014).

1.1 Objectives

This thesis work has three main objectives:

1) Characterisation of the bioethanol-derived lignin mass, in comparison to other varieties of technical lignin.

2) Ethanolysis of the lignin mass: exploring the thermochemical route of liquefaction by attempting to produce a 'biocrude', lignin-ethanol energy-rich mixture. The products of which will offer insight into the reaction mechanisms as well as the reactivity of the lignin in an ethanol medium.

3) Feasibility: the final objective is to assess the quality and potential of the lignin mass, and if the thermochemical route chosen proves a viable option for valorisation of the lignin mass.

1.2 Scope and Structure

The literature review shall focus on the chemistry and diversity of technical lignin, as well as the thermochemical processes by which depolymerisation of the lignin polymer can be achieved.

In this work, lignin will be shortly introduced alongside the other major components of biomass, after which a comparison of various varieties of technical lignin, produced from both alkaline and acidic pulping processes, and their respective characteristics will be given.

The experimental work consists of two parts: the first being the characterisation of the lignin mass, and the second being the attempts at liquefaction by ethanolysis, the results and conclusions.

A full array of analytical methods were used to characterise the Lignin Mass sample, the results of which were compared to other types of technical lignin, and shed light on the reactivity and structure of the bioethanol process-derived Lignin Mass.

The aim of the ethanolysis autoclave runs was to depolymerise the Lignin Mass (LM) in ethanol, in order to achieve partial liquefaction. Eight experimental runs were included in this work, six of which were uncatalysed, two of which were catalysed by heterogeneous catalysts: 5%Ni/γ-Al_2O_3 and 5%Ru/γ-Al_2O_3 respectively. Mass balances were determined for each experimental run with further analysis of the products with analytical methods: bio-oil, residual lignin and solid fractions.

This work provided conclusions on the suitability of the Lignin Mass as a candidate for further refinement, as well as insight into the depolymerisation mechanisms.

LITERATURE REVIEW

2 Lignin vis-à-vis Biomass

Lignocellulosic biomass is composed of three primary components: cellulose, hemicellulose, and lignin. Lignin is the main non-carbohydrate polymer in plants. After cellulose, it is the most abundant natural polymer and renewable carbon source on earth, representing 15% to 30% of woody biomass, but up to 40% of the energy content (Perlack et al., 2005; Holladay et al., 2007). In contrast to carbohydrate-based cellulose and hemicellulose, Lignin is a complex phenolic highly cross-linked polymer formed by coupling reactions of mainly three hydroxy-cinnamyl alcohols, or monolignols (H. Sixta, 2006), portrayed in Figure 1:

- p-coumaryl alcohol (4-hydroxy-cinnamyl alcohol)
- coniferyl alcohol (3-methoxy-4-hydroxy-cinnamyl alcohol)
- sinapyl alcohol (3,5-dimethoxy-4-hydroxy-cinnamyl alcohol)

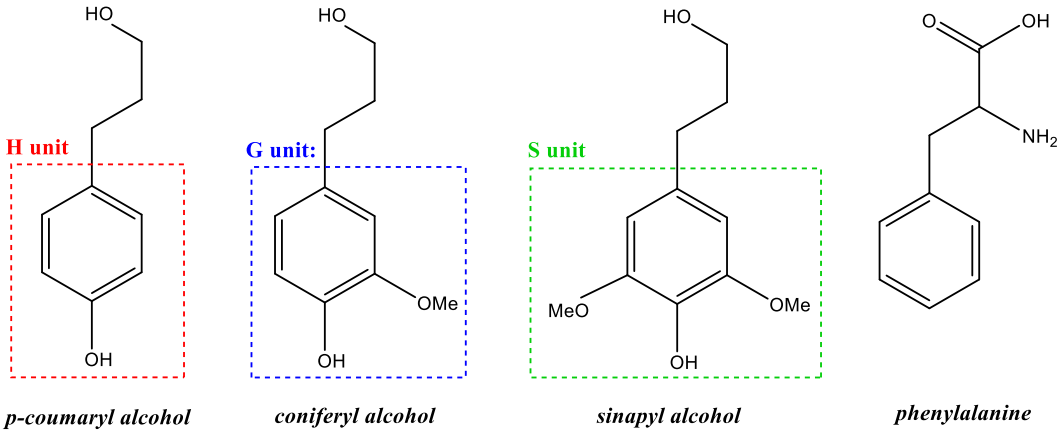

Figure 1: Representative chemical Structures of the monolignols, the respective G/H/S Units, & phenylalanine

The exact structure of native lignin, also known as protolignin, remains unknown to this date, but the more is known of the three precursor units, the synthesis of which begins with the amino acid Phenylalanine. The full reaction pathway to the precursors includes numerous steps and several enzymes, although most remains yet to be elucidated. The same enzymes most likely initiate the radical polymerisation of the monolignols into a lignin polymer (Xu et al., 2014). The three precursors are integrated into the lignin aromatic cores as phenyl propanoids, namely p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, the proportions of which vary among woody and herbaceous species.

A natural resin, lignin provides strength and plays a major role in the transportation of water and ions from the soil. Highly aromatic, it also acts as the binding medium in the plant cell wall lattice shielding cells from enzymatic and chemical degradation (J.H. Clark, F.E.I. Deswarte, 2008). The chemical reactivity of lignin could be related to the proportions of the three precursor structural units: guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H). Gymnosperm (softwood) species contain primarily G-lignin (95%). Angiosperm dicotyledons (hardwood) species contain GS-lignin (49%/49%), whilst graminoids (Grasses) contain HGS-lignin complexes (5%/70%/25%). In the case of compression wood sections, rich in lignin, GH lignin complexes (70%/30%) are predominant (Heitner et al., 2010). The ratio 'G:S:H' is generally species-specific, although this ratio can be affected by numerous factors, e.g. geographic location, quality of environment, and can even vary slightly within a species (Akash, 2016; Ragauskas et al., 2014). Figure 2 offers a good visualisation of a segment of the complex and randomised structure of a lignin polymer. The precursor units can be clearly identified.

In this work, we shall focus on the distinct differences between hardwood and softwood, the feedstock for the bioethanol process, and its lignin by-product. Lignin derived from herbaceous species will not be discussed or compared in detail.

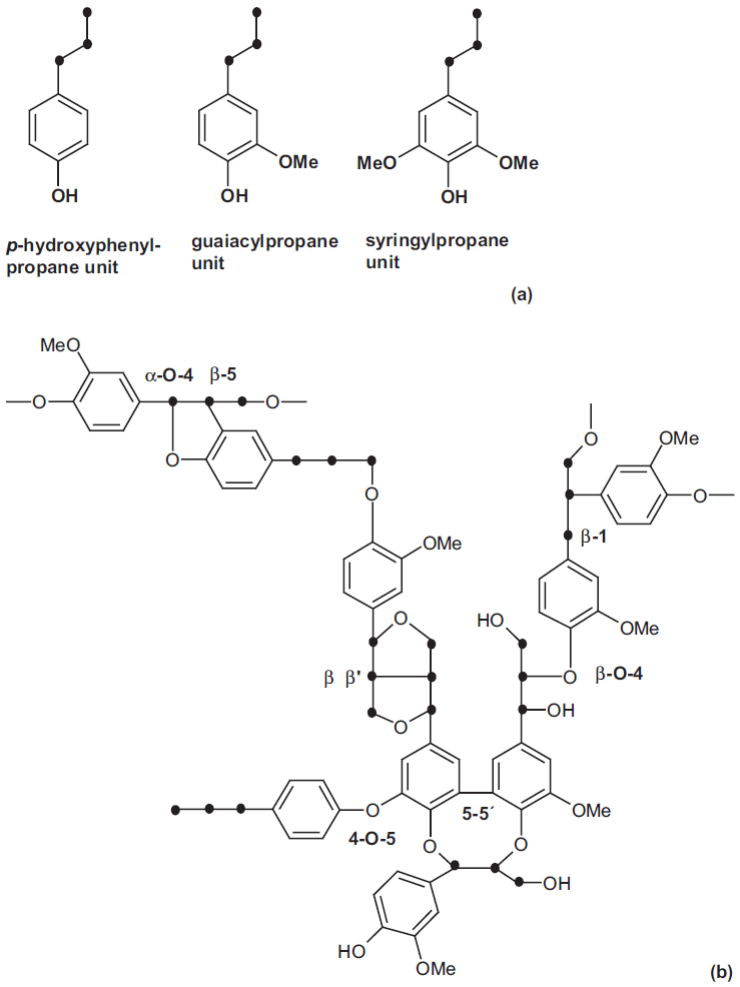

Figure 2: Example schematic of the chemical structure of lignin: (a) molecular structure of the basic phenylpropane building blocks of lignin, (b) model of important lignin linkages (H. Sixta, 2006)

As mentioned previously, the major difference in softwood and hardwood lignin is the ratio of phenyl propanoid units (G:H:S). As portrayed in Figure 2, the syringyl unit contains two methoxyl groups attached to the core aromatic ring, in contrast to one for the guaiacyl (G), and one for the p-hydroxypheyl (H). This may to a greater or lesser extent affect the linkages in the lignin polymer, as the methoxyl groups saturate the aromatic ring, preventing the formation of further linkages with the core carbon ring. However, once these methoxyl groups are cleaved, the sites could become reactive and ether bonds be formed. In contrast, guaiacyl units, due to the absence of one methoxyl

group, are more prone to carbon-carbon bonds, which are more troublesome to disrupt. It has been suggested that for this reason, a majority of guaiacyl units in softwood lignin leads to a more branched out polymer structure, in contrast to hardwood lignin.

3 Driving Forces towards the Valorisation of Lignin

The 21st century has witnessed a renewed interest in biomass conversion. The decline of the availability of petroleum, in conjunction with global consciousness of its carbon footprint, have inspired the industry and researchers alike to find alternative energy sources. Biomass already contributes considerably to the energy pool of Nordic and less developed countries, but could play a more pronounce role in the future energy pool on a global scale (Demirbas, 2013; Holladay et al., 2007; Kumar et al., 2011; Patil et al., 2011; Werpy & Peterson, 2004; Xu et al., 2014).

Lignin is produced annually in quantities of up to 50 million tons, although only 2% of it is commercially available (Zakzeski et al., 2010), as a by-product of the pulping industry and biorefining processes. Commonly combusted as a fuel, in order to recycle inorganic contents (notably Na and S) whilst producing power and heat for pulp mills and biorefineries, lignin could prove a viable source of aromatics and phenols to replace the petroleum industry-derived phenols. In average, only 40% of the lignin side stream would need to be incinerated to satisfy the energy demand of pulp mills and biorefineries, the rest being combusted to a low or no value (Galkin & Samec, 2016). In effect, the remaining 60% could potentially produce a feedstock for further refining. However, as of yet few cost-effective processes have been developed to produce specialty chemicals from lignin (Akash, 2016; Demirbas, 2013; Holladay et al., 2007; Werpy & Petersen, 2004; Zakzeski et al., 2010), due to its complex structure and the high costs of processing necessary.

Lignin has been perceived as a good candidate for the production of biofuels, specialty chemicals, aromatics and monomers (Patil et al., 2011). Furthermore, lignin is thermoplastic and can be used in a full spectrum of every-day products, from phone casings to applications in the furniture and fashion industry (Patil et al., 2011). There have been attempts at producing resins derived from lignin to partially substitute toxic

phenolic glues used in the manufacturing of plywood, and similar products (UPM, 2015). The anti-microbial, antibiotic and hydrophobic properties of lignin have and continue to be explored (Zemek et al., 1979; Dong et al., 2011).

3.1 Lignin Model Compounds and Chemistry

Figure 3 portrays a monolignol, where the carbon position numbers are displayed. As mentioned previously, native lignin is polymerised via an oxidative coupling of the three precursor alcohols with each other, and most importantly a growing polymer end. In effect, the oxidation reaction produces a phenolic radical with an unpaired electron delocalised to positions 0_4, C_1, C_3, C_5 and C_β. It has been noted that out of all the latter, the phenoxy- C_β position does appear to be the most reactive, creating β-O-4, β-5, and β-β bonds (Heitner et al., 2010), which will be discussed shortly. In order to avoid confusion, it is important to note that the numbering of the carbon atoms, when depicting lignin precursors and polymers, does not reflect the conventional numbering method; i.e. this nomenclature helps emphasise the reactive sites, and allow facilitated labelling of the various linkages.

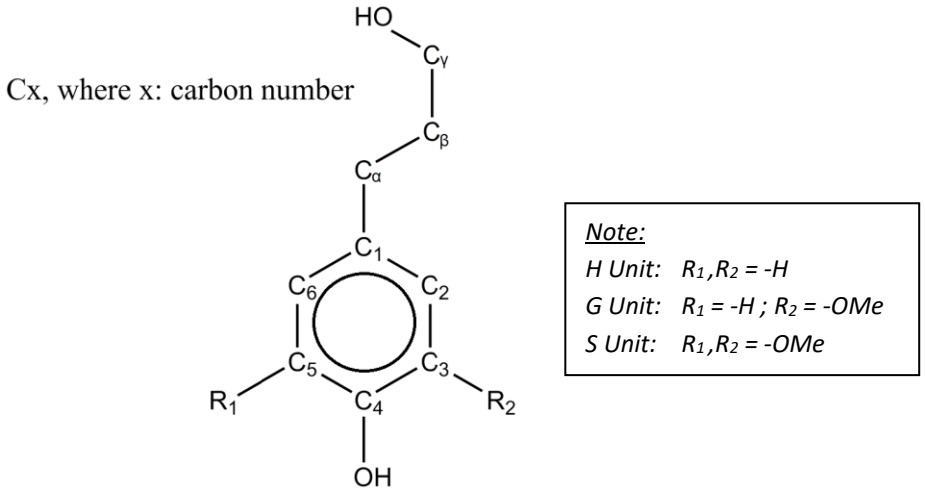

Figure 3: Schematic representation of a monolignol, where the position numbers/letters are shown

A full plethora of functional groups can be found in lignin, the most common ones being hydroxyl, methoxyl, carbonyl and carboxyl groups. However, the carbonyl groups do not occur in the monolignol precursors but randomly in the lignin polymer. Alcoholic and phenolic hydroxyl groups are also found, alongside methoxyl groups in the aromatic ring, attached in the *ortho* position with respect to the phenolic hydroxyl group (Phillips, 1983).

Generally, lignin molecules are negatively charged in aqueous environments of slightly acidic to alkaline pH. In effect, the pKa of a phenolic hydroxyl group varies between 7 and 10, depending on neighbouring substituents. In contrast, carboxylic groups usually have a pKa lower than 4. The solubility of lignin is an essential factor for industrial use and analytical work. The solubility of technical lignin is highly dependent on the manufacturing process, but most lignin is generally soluble in alkaline water, polar solvents and ionic liquids, e.g. methanol, ethanol, formic acid, ethylene glycol, ɣ-valerolactone, tetrahydrofuran, among others (Holladay et al., 2007; Li et al., 2009; Zakzeski et al., 2010).

3.2 Linkages in the Lignin Polymer

As the monolignol radicals couple with each other, numerous bonds are created, the most prominent of which is the β-O-4 bond (or β-aryl ether), which accounts for up to 60% of lignin inter-unit bonds in softwood species, and 50% in hardwood species (Zakzeski et al., 2010; Chakar et al., 2004). The other bonds include the α-O-4, 5-O-4, β-5, 5-5, β-1 and β-β bonds, of various strengths. The radicals will effectively react with the end of the growing polymer that results in a complex and randomised structure as portrayed in Figure 4.

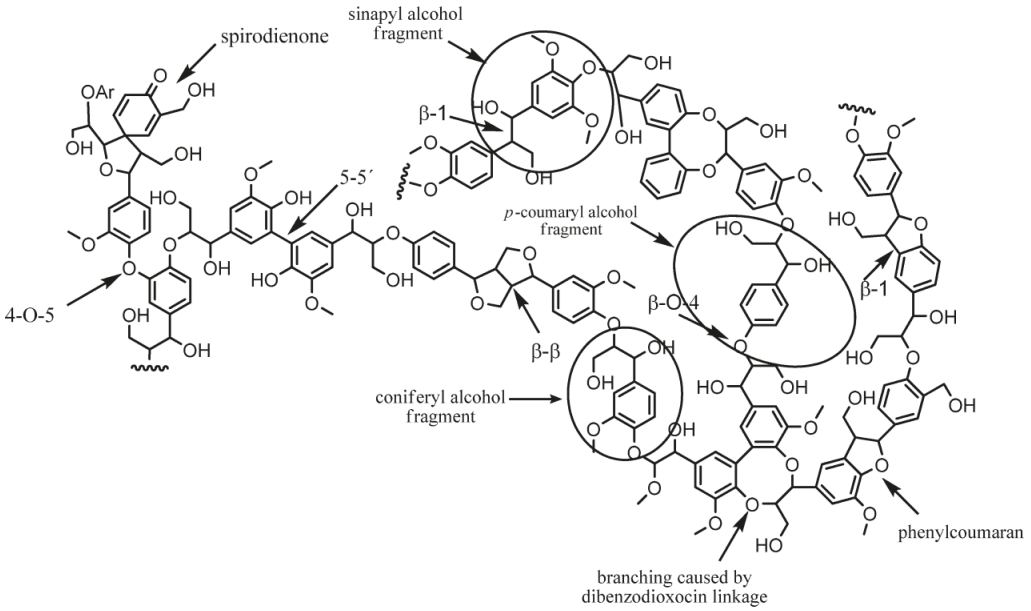

Figure 4: Schematic representation of structure of the lignin polymer, portraying the major units and bonds involved (Patil et al., 2011)

The dominant β-O-4 linkage is easily cleaved during pretreatment, and is the primary pathway via which native lignin is depolymerised. This leads to the generation of water-soluble compounds containing phenolic hydroxyl groups (Mansouri & Salvadó, 2006), as well as the formation of compounds resembling p-coumaryl, coniferyl, and sinapyl alcohols. Secondary products include 3-hydroxypropaldehyde, and arenes with various aldehyde or alkane side chains. The aromatic ring of coniferyl alcohol can be further oxidised to produce vanillin, whilst the aromatic rings once oxidised produce quinones (Zakzeski et al., 2010). However, these reactions and their respective selectivities are all subject to operating conditions.

The carbon-carbon (C-C) linkages present in lignin constitute the most challenging bonds to break, and generally survive pulping processes (Chakar & Ragauskas, 2004). Catalysts capable of disrupting these linkages have been explored but no breakthrough has been made of yet. In addition to the C-C bonds naturally occurring in the lignin polymer, additional bonds can be formed in condensation reactions in severe pretreatment

processes, which further complicate downstream processing (Demirbas, 2013; Doherty, Mousavioun, & Fellows, 2011; Galkin & Samec, 2016; Zakzeski et al., 2010).

Other linkages include the α-O-4, 5-O-4, β-5, 5-5, β-1 and β-β bonds, of various strengths. The chemistry behind the formation of each is inconclusive, and degradation pathways not fully understood. However, it is imperative to understand that these bonds will be impacted by severe operating conditions, and partake in degradation or condensation reactions, i.e. cleaved or formed. On another note, it has been suggested that the 4-O-5 aryl-aryl ether linkage present in lignin is usually a result of oligomer-oligomer couplings, which generally causes a branching of the lignin polymer (Zakzeski et al., 2010).

3.3 Lignin Model Compounds

The complex structure and variability of the polyphenolic lignin polymer has prompted the use of several simple, low molecular weight lignin model compounds in the study of lignin chemistry. In effect, these precursor building blocks, as mentioned previously, serve several primary purposes. The first and most important purpose is that these model compounds contain linkages and functional groups resembling those present in the native polymeric form, and thus their reactivities offer insight into the degradation and reaction of the polymer structure as a whole. Zakzeski and colleagues (2010) have compiled a lengthy review on a full array model compounds, their respective linkages, with reported reactions pathways. Due to the complexity of lignin, and diversity of model compounds assessed, the reader is advised to refer to the review article for more information.

Furthermore, it is important to note that many of the model molecules portrayed in Zakzeski's review (2010) are commonly found as depolymerisation products, among others, after degradation of the polymeric lignin. Indeed, the development of methods for their valorisation and further refining into higher value chemicals is essential. The model compounds present significantly less analytical challenges compared to the

complex native polymeric lignin, and the full spectrum of degradation products. The presence of usually just one type of linkage in each model compound significantly simplifies the analysis of the reaction pathways, and catalytic performance, specific to the individual model molecules.

In this work, special attention will be placed on the hydrogenolysis, alkylation and condensation reactions occurring during hydrothermal treatment of lignin with ethanol as a solvent. The former two enable depolymerisation of the lignin polymer, whilst the latter occurs once the newly produced radicals bond together to produce stronger linkages, and a more condensed structure. Other reactions have been dismissed, as they do not lay within the scope of this thesis.

3.4 Hydrogenolysis Pathway

Hydrogenolysis refers to the chemical reaction whereby a carbon-carbon, or carbon-heteroatom, bond is cleaved by the addition of hydrogen. Hydrogen can be added to the system to promote this reaction pathway, and favour the formation of hydrocarbons (Ma et al., 2014; Patil et al., 2011). In the absence of an external hydrogen source, the solvent, usually an alcohol, acts as a proton-donor to cleave the polymeric carbon-carbon and carbon-oxygen linkages, causing depolymerisation (Huang et al., 2014). These are known as transfer hydrogenolysis systems (Xu et al., 2014). Alongside the latter reactions, hydrogeoxygenation of the lignin takes place. The removal of oxygen effectively increase the energy density of the products, but in consequence may reduce their reactivity (Xu et al., 2014).

3.4.1 Alkylation Reaction

The depolymerisation of polymeric lignin via hydrogenolysis produces free radicals, notably methoxy groups. These radicals readily react with other radicals and components in the solvent medium via alkylation. In effect, this phenomenon is the most

likely cause for the vast range of products produced in the thermochemical depolymerisation of lignin. It has been reported that ethanol reacts via alkylation and esterification reactions with lignin fragments (Huang et al.,2014).

3.4.2 Condensation Reaction

Condensation refers to the repolymerisation reactions that occur when the free radicals agglomerate. In effect, as the weaker bonds are cleaved, the polymer is fragmented into shorter radicals. The latter react together and form stronger bonds, e.g. carbon-carbon linkages, which are more challenging to disrupt, the result being less reactive and agglomerated structures, i.e. condensed lignin polymeric structures. Condensation reactions are counter-productive when attempting to valorise lignin via depolymerisation. In effect, catalysts and various capping agents have been experimented with in order to repress or minimise condensation reactions (Huang et al., 2015).

4 Lignin Pretreatment Processes

Pretreatment of lignocellulosic biomass is essential in achieving efficient fractionation of lignocellulosic components, which is still as of today one of the major challenges in any biorefinery due to the complex structure of the cell wall structure and the feedstock's recalcitrance to separation (Holladay et al., 2007; Galkin & Samec, 2016; Alekhina et al., 2015).

As global interest increases in biomass as an alternative feedstock for a full spectrum of biochemicals, researchers have delved deeper into the chemistry occurring in conventional pretreatment processes. The chemical structures and properties of lignocellulosic fractions are altered as they are subject to various operating conditions and chemicals. Various processes have been developed over the last decades to improve the quality and purity of products (e.g. pulp) or increase the accessibility of enzymes to cellulose, resulting in a higher yield of fermentable sugars. The defining goal being to reduce process costs by removing structural and physico-chemical barriers with the addition of a pretreatment step. Whilst hemicelluloses and cellulose are readily processed into valuable products, lignin remains a challenging by-product.

Technical, or industrial, lignin is a co-product of the chemical pulping processes of wood and agricultural waste, and lignocellulosic ethanol production. In contrast to native lignin, it has undergone chemical and structural changes, i.e. depolymerisation and condensation reactions, cleavage of linkages and methoxyl groups, having been subject to various pretreatment processes. The production of lignin in pulping processes surpassed 50 million tons per year in 2015 (X. Ma et al., 2015), despite the potential being much higher (Fache et al., 2016). However, only a small fraction of this production is refined into higher value end products, such as biochemicals, whilst the majority is incinerated to produce heat and electricity. Among the major factors restricting the use of technical lignin in high-value applications are the non-uniform structures, unique

reactivities, as well as contaminants (Vishtal & Kraslawski, 2011). Although the properties of lignin differ between native species and geographical locations, the main differences are formed by the various pulping and chemical processes by which the lignin is extracted (Glasser, W.G., 1981).

Technical lignin can be divided into two categories: sulphur-free lignin and sulphur-containing lignin. Sulphur-containing lignin includes lignosulphonates and kraft lignin, whilst sulphur-free lignin encompasses soda lignin, ethanol process-derived lignin, organosolv lignin, ammonia-fibre expansion lignin, as well as lignin acquired from other alkaline processes, such as lime pretreatment. However, each industrial lignin offers distinct characteristics and reactivities, and hence each should be considered separately. Other forms of lignin, e.g. pyrolytic lignin and dilute acid lignin are not included in this study.

4.1 Alkaline Pulping Processes

4.1.1 Kraft Pulping

Kraft (sulphate) pulping is the most dominant chemical pulping process employed worldwide accounting for 85% of the global production of lignin (Tejado et al., 2007). The process utilises high pH, considerable amounts of aqueous sodium hydroxide (NaOH) and sodium sulphide (Na_2S), at temperature ranging between 423 and 453 K (150 and 180˚C) for approximately 2 hours to degrade lignin (up to 95%) in a stepwise process (Chakar & Ragauskas, 2004; Zakzeski et al., 2010). An advantage of this particular process is that it is the most utilised process in the pulping industry; the infrastructure is well established and technology mature. In this respect, kraft lignin, present in black liquor, is produced in the largest quantities worldwide. However, most kraft pulp mills are highly energetically integrated, relying of the energy content of the lignin side stream

for process heating (Mohan et al., 2006). Isolating the lignin side stream for a biorefinery concept can be challenging (Holladay et al., 2007).

Kraft lignin distinguishes itself from native lignin, and other technical lignin, by several unique characteristics. As it is degraded into numerous alkali-soluble lower-molecular weight fragments, an increased quantity of phenolic hydroxyl groups, produced from the cleavage of β-O-4 bonds during cooking, more biphenyl and other condensed structures can be observed (Chakar & Ragauskas, 2004). The oxidative conditions in the delignification step usually trigger the formation of quinone and catechol alongside an increase in carboxyl groups (Chakar & Ragauskas, 2004). Furthermore, kraft lignin can contain a high ash content, up to 30%, after cooking. Usually washing or treatment with diluted sulphuric acid will reduce this content to 1-5% (Mansouri & Salvadó, 2006). Figure 6 portrays the chemical structure of kraft lignin.

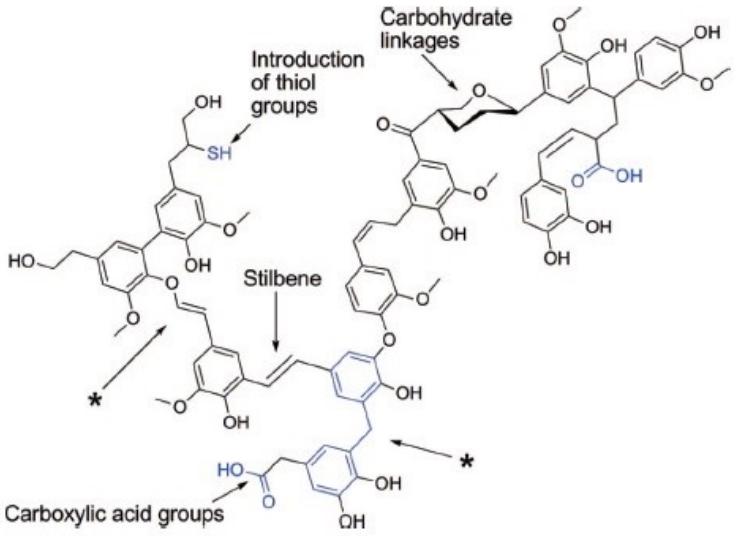

Figure 5: Schematic representation of the chemical structure of kraft lignin (Zakzeski et al., 2010)

There is a broad spectrum of possible applications for kraft lignin, as kraft pulping is the most established pulping process worldwide. This incorporates fertilizers, pesticides (Zhang, 2008), carbon fibres, thermoplastics, resins (Tejado et al., 2007) and activated

carbon, as well as specialty chemicals such as vanillin, hydroxylated aromatics, aldehydes, quinones, and aliphatic acids (Holladay et al., 2007).

4.1.2 Alkaline Pulping

Apart from kraft pulping, the most common alkaline processes are soda pulping and lime pretreatment. In these processes, NaOH or CaO, respectively, are used at medium temperatures (150-170°C) to solubilise lignin, whilst the cellulose and hemicellulose fractions remain solid, and are recovered by filtration. In this aspect, the removal of lignin allows for an improvement in the reactivity of the remaining polysaccharides (Mosier et al., 2005). In alkaline conditions, the extent of the changes in the structure of lignin is dependent on the severity of the pretreatment step, i.e. chemical charge and reaction conditions. In the case of lignin dissolution, the primary reactions responsible for lignin dissolution in an alkaline medium are reduction reactions, where for example the β-aryl bonds are severed in β-O-4 structures (Joffres et al., 2014). In addition to cleavage of acetyl groups in the lignocellulosic material, the alkaline pretreatment also allows for the removal of uronic acid substitutions on hemicelluloses, which are known to lower the accessibility of enzymes to the cellulose and hemicellulose surface (Chang et al. 2000).

Soda and soda-anthraquinone pulping accounted for 5% of the pulping industry worldwide in 2000 (R. Patt et al., 2000). The soda-based cooking process is mainly used for delignification purposes of annual crops such as flax, straw and bagasse feedstocks (Saake and Lehnen, 2007; Rodriguez et al., 2010), and less so for hardwoods. The annual crops contain less lignin in contrast to woody biomass, which allows a lower use of NaOH during pretreatment, although the high silica content can cause issues in the spent liquor. Anthraquinone (AQ) has been used as a catalyst in order to stabilise the carbohydrates and further promote dissolution of lignin (R. Patt et al., 2000). However, the use of AQ has been stopped due to it being potential carcinogen, especially when

transferred to food packaging (BfR, 2013). An advantage of the soda and Soda/AQ processes is that both processes produce sulphur-free spent liquor and products in contrast to e.g. kraft pulping (Gullichsen and Fogelholm, 2000). In effect, due to the absence of sulphur, the chemical structure of soda lignin is considerably different to those of kraft lignin and lignosulphonates. Furthermore, the low severity of the process, and inherently low lignin-containing feedstock, make soda pulping an attractive option for a biorefinery.

4.2 Acidic Pulping Processes

4.2.1 Sulphite Pulping

The sulphite pulping process yielding lignosulphonates alongside its main product, chemical pulp, is well established in the pulp and paper industry (Zakzeski et al., 2010), and produced in quantities of up to 1 million tons per annum (Belgacem & Pizzi, 2016; El Mansouri and Salvado, 2006). The process is operated in pHs ranging between 2 and 12, using sulphite with usually calcium ($CaSO_3$) or magnesium ($MgSO_3$) acting as a counter-ion (Holladay et al., 2007), during which lignin is effectively sulfonated, degraded and solubilised.

The lignosulphonates are water-soluble anionic polyelectrolytes which exhibit a large number of charged groups (Vishtal & Kraslawski, 2011). They are also soluble, highly polar, organic solvents, e.g. amines. They usually exhibit higher average molecular weight and higher monomer molecular weights in comparison to kraft lignin, a result of incorporating sulfonate groups on the arenes (Zakzeski et al., 2010). Lignosulphonates contain a full array of functional groups: phenolic hydroxyl groups, carboxylic groups, as well as sulphur containing groups (Areskogh et al., 2010). This variety of functional groups and structural features provide unique colloidal properties (Areskogh et al., 2010). The ash content of lignosulphonates is significant, and the degree of sulphonation

in the range of 0.4 to 0.5 per phenylpropanoid unit (Gellerstedt and Henriksson, 2008). Figure 6 portrays the chemical structure of lignosulphonate lignin.

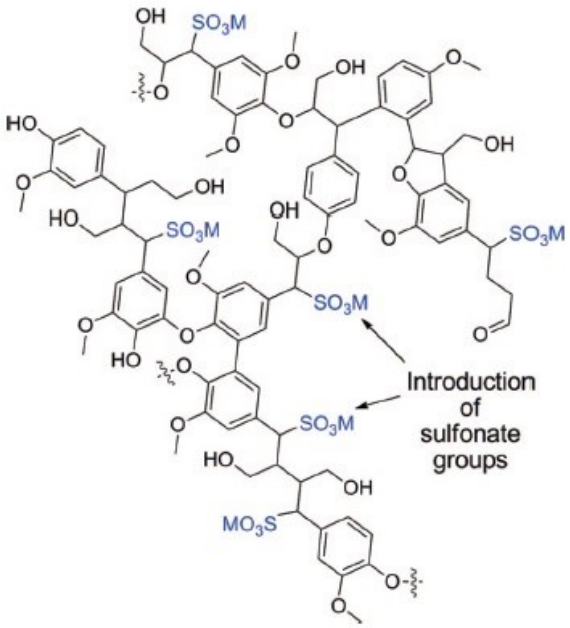

Figure 6: Schematic representation of the chemical structure of lignosulfonate lignin (Zakzeski et al., 2010)*, where M: metal*

4.2.2 Acid Pretreatment

Acid pretreatment processes aim to promote better digestibility of the cellulosic feedstock acting as a prehydrolysis step. The most common chemical in the case of a bioethanol plant is dilute sulphuric acid (H_2SO_4). However, nitric acid (Brink et al., 1994), hydrochloric acid (Goldstein et al., 1992) and phosphoric acid (Israilides et al., 1978) have also been used in experimentation. This method is often used in combination with a steam explosion step (see below), or relies on steam as a heating medium, whilst acid is sprinkled on the lignocellulosic feedstock. The sulphuric acid effectively hydrolyses hemicelluloses to xylose and other monomeric sugars, and further breaks down xylose to produce furfural (Mosier et al., 2005). Furfural, a valuable by-product, is usually recovered by distillation, purified, and sold. Furthermore, the acid also hydrolyses the

oligomers, permitting a complete hydrolysis of the carbohydrate complexes to monosaccharides but also the formation of aldehydes. However, the acid must be neutralised before the sugars proceed fermentation. In effect, the process has its limitations, including risk of corrosion and expensive recycling. Acid-resistant materials must be used, and neutralisation salts disposed of, which result in added costs (Wooley et al., 1999).

4.2.3 Steam Explosion

In the case of steam explosion, biomass is rapidly heated by high-pressure steam in order to allow a deep impregnation of the wood. The biomass/steam mixture is held for a determined period of time to promote the hydrolysis of hemicellulose, after which the contents of the reactor are abruptly transferred to another vessel at significantly lower pressure. This flash pressure drop will cause the steam within the biomass to expand; the decompression effectively explodes the cell wall lattice from within and providing access to the resulting fractions (Mosier et al., 2005).

Chemical reactions do take place during operation. Auto-hydrolysis of the woody biomass occurs and radicals and acids are formed. The latter, specifically acetic, uronic and phenolic acids, hydrolyse the hemicellulose, and further catalyse the hydrolysis, glucose and xylose degradation reactions (Mosier et al., 2005). It is notable to recognise that water also reacts as an acid in high temperatures above 150°C (Weil et al., 1997).

Steam is an effective medium in heating the feedstock to the appropriate temperatures above 150°C whilst avoiding excessive dilution (Mosier et al., 2005). In effect, the major physical and chemicals changes to lignocellulosic material during steam explosion is related to the removal of hemicellulose, which enhances the accessibility of enzymes to the cellulose. The particulate size of the biomass is significantly reduced after explosive decompression, whilst the average pore volume is increased. This does not however

enhance the digestibility of cellulose as it does not promote hydrolysis of the cellulose bulk (P. Kumar et al., 2009). This can be remedied with the addition of chemicals.

Steam explosion is often combined with dilute acid pretreatment, e.g. SO_2, in order to promote hydrolysis and prevent the formation of inhibitors and degradation products, e.g. levulinic acid and 4/5-hydroxymethylfurfural (4/5-HMF) from glucose (Torget et al., 2000), furfural from xylose (Demirbas, 2013), as well as methanol and acetic acid formed during autohydrolysis. Li and co-workers demonstrated that a SO_2 preimpregnation of hardwood allowed efficient extraction of lignin in a steam explosion pretreatment (Li et al., 2009). This was not achieved with softwood.

4.2.4 Bioethanol Process

The bioethanol process is not per se a pretreatment method, as various bioethanol plants incorporate various pretreatment technologies mentioned previously. It differs by the addition of two operations, i.e. saccharification and fermentation. Both the first, catalysed by enzymes, and the second, catalysed by yeast, do have an impact on the lignin, unless it is removed beforehand (e.g. organosolv) (Jönsson & Martín, 2016).

The pretreatment process utilised in bioethanol plant depends on various factors including feedstock, severity of pretreatment, and extent of delignification. The stability of C6 sugars, cellulosic material, and saccharification yield are paramount in that they determine the bioethanol yield. In this aspect, hemicelluloses are degraded along with lignin, in order to promote accessibility of the enzymes to the cellulose (Demirbas, 2013; L. Kumar et al., 2011; P. Kumar et al., 2009; Mosier et al., 2005).

Lignin has been proven to inhibit enzymatic activity to a minor degree, during both saccharification and fermentation operations, by reducing enzyme accessibility to cellulose and by irreversibly binding hydrolytic enzymes (Sun & Cheng, 2002). Lignin is also prone to bonding with carbohydrates. It has been suggested that lignin-carbohydrate complexes (LCCs) can be formed (Alekhina et al., 2015; Kim et al., 2016).

Although the extent of this impact is negligible, it does carry significance as to the characteristics of bioethanol process-derived lignin (BEDL): carbohydrate content will as a result usually be higher than in other technical lignin. Furthermore, the severity of the pretreatment affects the extent of depolymerisation of lignin (Akash, 2016; Rinaldi et al., 2016).

4.2.5 Organosolv Process

Organosolv lignin is extracted from the treatment of lignocellulosic material, wood or bagasse, with various organic solvents (Holladay et al., 2007). The most notable organosolv process is the Alcell process, no longer operational, demonstrated at the Repap Alcell pilot plant, where organosolv lignin was dissolved in ethanol or ethanol/water mixtures. A similar pilot-scale type of process is operational in the Fraunhofer institute in Germany. The main advantage of the organosolv process lies in the formation of three distinct product streams of cellulose, hemicellulose, and lignin, permitting valorisation of all the lignocellulosic fractions (Zakzeski et al., 2010). Furthermore, the process is considered more environmentally friendly as it avoids the harsher conditions employed in kraft and acid sulphite pulping, and does not utilise sulphur-containing chemicals.

The produced lignin is inherently sulphur-free, and of higher purity, which offer significantly advantages vis-à-vis further refining options to higher value products. Structurally, organosolv lignin contains a higher proportion of phenolic hydroxyl groups, a more oxidised structure (in contrast to other technical lignin), and is thermally processed with more ease. As a result, organosolv has many advantages over other technical lignin when considering composite-material applications (Gordobil et al., 2016). The main drawback is the high cost of solvent recovery (Zakzeski et al., 2010).

4.2.6 Ammonia Fibre Explosion

Ammonia fibre/freeze explosion (AFEX) delivered good hydrolysis yields for pretreated lignocellulosics (Holtzapple et al., 1991). It is best suited for herbaceous and agricultural residues, moderately so for hardwood, but not attractive for softwoods (McMillan et al., 1994). Biomass is effectively subject to a flow of aqueous ammonia in a packed column at moderate temperature (160-180°C), with a residency time of 14 minutes. The ammonia is then separated and recycled. In these conditions, the aqueous ammonia reacts with lignin to break lignin-carbohydrate bonds, whilst partially removing hemicelluloses and decrystallising cellulose. The latter occurs as a phase change in the structure of cellulose: a swelling caused by ammonia (Mosier et al., 2005). However, the cost of ammonia drives up the cost of this pretreatment process (Mosier et al., 2005), despite low temperature (90 °C) and less intensive operating conditions (P. Kumar et al., 2009).

4.2.7 Comparative Table of Technical Lignin

In order to portray the significant differences between the various varieties of technical lignin, the lignin, carbohydrate and inorganic ash contents of several lignin types are presented in Table 1. The lignin content has been further divided between the acid-soluble (ASL) and the acid-insoluble (Klason) fractions.

Table 1: Lignin, carbohydrate and inorganic content of technical lignin

Lignin	Klason Lignin	ASL (%)	Ash (%)	Total Sugars (%)
Kraft Spruce (Gordobil et al., 2016)	88.5	2.3	2.5	1.0
Indulin Kraft (Softwood) (Constant et al., 2016)	90.3	1.9	2.6	2.6
Soda Lignin (P1000) (Constant et al., 2016)	85.1	5.4	2.5	2.4
Organosolv (Alcell) (Constant et al., 2016)	94.3	1.9	0.1	0.2
Organosolv (Spruce) (Constant et al., 2016)	95.5	0.8	0.1	1.1

Further reinforcing the disparities between the various technical lignin, the elemental composition of several types have been compiled in Table 2. In effect, these values depend highly on the fractionation pretreatment process, and can differ significantly even within a type of lignin. Noticeable is how the sulphur content varies significantly between the various types of technical lignin. Lignosulphonates aside, kraft lignin and varieties of P1000 soda lignin contain significant amounts of sulphur (>1%). Indeed, the toxicity of sulphur has to be taken into account when considering refining opportunities for lignin. The advantage of organosolv lignin and bio-ethanol process-derived lignin lies in them being sulphur-free, which allows for numerous refining possibilities, from applications in the food industry, to specialty pharmaceuticals.

Table 2: Elemental composition of technical lignin

	wt%					molar ratio	
Lignin type	**C**	**H**	**N**	**S**	**O**	**O/C**	**H/C**
Kraft Spruce (Gordobil et al., 2016)	63.7	6.1	0.1	1.5	*28.7*	0.34	1.14
Alkali Lignin (Kleinert et al., 2008)	48.2	3.4	0.0	1.1	47.3	0.74	0.84
Soda Lignin (P1000) (J. Kim et al., 2015)	61.3	7.3	0.7	1.1	29.6	0.36	1.42
Soda Lignin (P1000) (Joffres et al.,2014)	59.4	5.6	1.1	0.1	25.7	0.32	1.12
Lignosulphonate (Kleinert et al., 2008)	42.0	4.6	0.0	6.3	47.1	0.84	1.30
Organosolv Eucalyptus (Gordobil et al., 2016)	61.4	6.0	0.1	0.1	*32.4*	0.40	1.16
Organosolv Spruce (Gordobil et al., 2016)	68.8	6.3	0.1	0.2	*24.6*	0.27	1.09
SE Lignin (MWL Spruce) (Kleinert et al., 2008)	59.2	6.0	0.1	0.1	34.6	0.44	1.21
Hydrolysis (Kleinert et al., 2008)	47.6	4.3	0.0	0.4	47.7	0.75	1.08
BEDL1 (Kleinert et al., 2008)	55.2	6.0	0.1	0.1	38.6	0.52	1.29
BEDL2 (Kleinert et al., 2008)	63.3	4.7	0.0	0.6	31.3	0.37	0.88

Where; SE: Steam Explosion; MWL: Milled Wood Lignin; BEDL: Bioethanol Process-Derived Lignin; LM: Lignin Mass

5 Lignin Dissolution

The dissolution of lignin and other lignocellulosic fractions is a critical factor in the valorisation process of biomass. This has proved challenging over the years due to the intricate structure and properties of cellulose, hemicellulose, and lignin. In effect, the insolubility of woody biomass, and products therein, has been recognised as a major factor hampering the valorisation of lignocellulosic biomass (Kilpeläinen et al., 2007).

In the case of lignin, the difficulty arises from its complicated network within the wood lattice, interlinked with the various other lignocellulosic components, binding the whole architecture together (Heitner et al., 2010). Indeed, the complex structure provides protection from microbial attack and external factors, whilst providing strength, and recalcitrance to chemical reactions (H. Sixta, 2006). The regulation of water in the wood lattice is managed by a balance between lignin and hemicellulose fractions: the first being hydrophobic, the second hydrophilic.

Crystalline cellulose itself has a low accessibility to enzymatic hydrolysis, which is further reduced by the presence of lignin and hemicelluloses that protect the cellulosic material from bacterial and enzymatic attacks. Further complicating the issue is the fact that lignocellulosic structure and composition varies significantly between species and may even vary within a species, depending of plant part, growth conditions, and geographical location (Akash, 2016; Ragauskas et al., 2014). Non-covalent hydrophobic interactions between lignin, noticeably its aromatic rings, may also hinder reactions between the lignin polymer and reactants. These non-covalent interactions are more commonly found in softwood species, less so in hardwood, and absent in straw lignin (Mattinen et al., 2008; Guerra et al., 2007).

Fractionating the lignocellulosic lattice by dissolution, physico-chemical pretreatment or other processes reduces the resistance of the biomass to chemical reaction. In effect,

the fractionation of biomass into its three components, cellulose, hemicellulose, and lignin, is an essential step in any biorefinery operation (Delmas, 2008). Much research has been produced in the identification and development of cheaper, environmentally benign, and recyclable solvents for the fractionation of biomass (Zakzeski et al., 2010).

Ionic liquids have recently become popular solvents for the dissolution of biomass. Ionic liquids are salts with melting points below an arbitrary melting point of 373 K (Zakzeski et al., 2010). They offer interesting properties, depending on the choice of cation and anion pair, such as tuneable physical properties, a very low vapour pressure and decent thermal stability (Fort et al., 2007). Interesting development in the use of ionic liquid for lignocellulosic fractionation, analysis and impurity removal has been witnessed. However, optimal ionic liquids have yet to be discovered for the dissolution of lignocellulosic biomass, and more research is expected vis-à-vis the reactions with lignocellulosic fractions, the recyclability of ionic liquids, and toxicity of the solutions. The prices for ionic liquid components are considerably high, which makes it necessary to recycle them. The separation of products from substrate poses another difficulty, notably with lignin-derived compounds, as they are more soluble in ionic liquids than the solvents by which they are extracted (Cocalia et al., 2008). However, ionic liquids will not be discussed further in this work, as it lies beyond the scope of the thesis.

6 Lignin Depolymerisation

Depolymerisation of the complex lignin polymer is an essential step for valorisation of lignin. The smaller molecules produced via depolymerisation begin to resemble the lignin model compounds depicted previously in this work, and expose the functional groups on the aromatic rings to catalytic transformation (Zakzeski et al., 2010). Among the catalytic pathways explored are thermochemical routes, cracking, pyrolysis, sub- and supercritical solvolysis. Solvolysis is a broad term to denote the fractionation of biomass in various solvents, including water. It is seen as a promising process by which to isolate biomass fractions. The use of heterogeneous catalysts can further promote depolymerisation reactions, and significantly increase yields (Azadi et al., 2013; Demirbas, 2013; Ma et al., 2014; Patil et al., 2011; Zakzeski et al., 2010).

6.1 Heterogeneous Catalysts

In recent years, increased research has focused on catalytic pathways by which some depolymerisation reaction barriers may be overcome. The tendency has been to look to the petrochemical industry for heterogeneous catalysts (Zakzeski et al., 2010). Attractive candidates have been bifunctional catalysts such as noble metals on acidic supports, for example Ru/TiO_2, or Ru/H-Beta (Patil et al., 2011), or even zeolites (Kozliak et al., 2016). Despite noble metals offering excellent results, they would ultimately prove too costly for large-scale applications, shifting research to less expensive catalysts such as nickel-based catalysts, e.g. Ni/Al_2O_3, metal oxides, and molybdenum catalysts, e.g. $CoMo/Al_2O_3$ (Kozliak et al., 2016; Patil et al., 2011).

6.2 Catalytic Pathways to Depolymerisation

Among the numerous catalytic pathways applicable to lignin, the most interesting routes discussed in this work are catalytic hydrocracking and catalytic hydropyrolysis. The significance of the solvent in the case of hydrocracking is discussed, whether in sub- or super-critical phase.

6.2.1 Catalytic Cracking & Hydro-cracking

Catalytic cracking processes are commonly found in the petrochemical industry, by means of which heavier hydrocarbons are converted into high-value products. Fluid catalytic cracking is among the most utilised process, contributing up to 50% of the gasoline pool of a refinery (Zakzeski et al., 2010). It uses tailored zeolite catalyst to disrupt the C-C bonds in an acid-catalysed reaction held between 613 and 683 K in a fixed bed reactor (Zakzeski et al., 2010), which effectively produces lighter compounds. For heavier oil fractions, a hydro-cracking process is utilised, in which catalysis occurs in a pressurised hydrogen environment (Thring & Breau, 1996). The bifunctional catalyst combining an acidic support for cracking and a metal for hydrogenation reactions (Zakzeski et al., 2010) has proved widely popular. Use of these hydrocracking catalysts have also been explored for lignin (Thring & Breau, 1996; Patil et al., 2011), often resulting in the disruption of β-O-4 linkages, and relatively unstable C-C bonds (Zakzeski et al., 2010).

6.2.2 Pyrolysis and Catalytic Hydropyrolysis

The pyrolysis of isolated lignin is considerably different from the pyrolysis of woody and other lignocellulosic biomass. This becomes evident in the composition and product distribution of the pyrolysis products: bio-oil, char and gas (Azadi et al., 2013). In this respect, the operating conditions have also been tailored for the varying technical lignin feedstock. In effect, the temperature range extends from 160°C and 900°C, in contrast

to 220 to 400°C for carbohydrates (Yang et al., 2007). The pyrolysis of lignin produces significantly more char than that of wood, and a bio-oil rich in a full plethora of aromatic and non-aromatic compounds, from lighter hydrocarbons to heavier oligomers (Azadi et al., 2013). The surface area of the char has been determined as very low (< 5 m^2/g).

Hydro-pyrolysis, also known as hydrocracking (see above), can transform dry lignin into a liquid at lower temperatures than fast pyrolysis, with the help of hydrogen and a bifunctional catalyst. The lower oxygen content of the bio-oil renders the product relatively more stable than the pyrolysis bio-oil, but the composition remains somewhat similar (Azadi et al., 2013).

6.2.3 Sub- and Supercritical Water Treatment

Sub- and supercritical solvolysis of lignin can produce smaller compounds (e.g. monomers) through the disruption of ether linkages, and larger condensed compounds through cross-linking of the reactive fragments (Karagoz et al., 2005; Zhang et al., 2008). The hydrothermal medium also permits dealkylation and demethoxylation reactions to take place. The formation of higher molecular weight residue can be minimised by optimisation of the reaction conditions, i.e. temperature, pressure and water density. Condensation reaction are minimal due to the low concentration of lignin, in comparison to dry lignin depolymerisation processes (Azadi et al., 2013). Furthermore, addition of alkali salts, phenolics, and other organic solvents can greatly facilitate the depolymerisation of lignin (Azadi et al., 2013).

Ehara (2002) and her colleagues were able to fractionate woody biomass with supercritical water into water-soluble and water insoluble components via cleavage of the β-O-4 bond, i.e. autohydrolysis. The water-insoluble fraction appeared to contain primarily of lignin-derived products, where the quantity of phenolic hydroxyl groups were superior to that of lignin in the original wood (Ehara, Saka, & Kawamoto, 2002).

6.2.4 Supercritical Solvents

Isolated organosolv and kraft lignin has successfully been depolymerised into soluble fractions in supercritical solvents with high yields (Huang et al., 2014; R. Ma et al., 2014; X. Ma et al., 2015; Patil et al., 2011; Riaz et al., 2016). The most common solvents have proved to be methanol (Xu et al., 2014; Van den Bosch et al., 2015), and ethanol (R. Ma et al., 2014; X. Ma et al., 2015; Huang et al., 2014), but other solvents and mixtures have also been experimented with (Toledano et al., 2014; Patil et al., 2011).

Lignin solvolysis can be categorised into two groups: base-catalysed depolymerisation (BCD), relying on sodium hydroxide or another basic medium, and acid-catalysed hydrogenolysis, in an acidic media. These two can be divided into three subsets: the first where the system is pressurised with hydrogen (Patil et al., 2011), the second where the solvent acts as a proton donor (Huang et al., 2015), and the third where hydrogen is synthesised via a reformation reaction catalysed by a metal catalyst (Patil et al., 2011; R. Ma et al., 2014).

The molecular weight of lignin-derived products ranges from 100 to 2500 g/mol, which entails that both liquid and solid products are present in the solvent. Despite good results in terms of the extent of depolymerisation and yield of depolymerisation products, the percentage of monomers has not exceeded 5% (Azadi et al., 2013). Decrease in the size of the lignin-derived product compounds via hydrogenolysis leads to a decrease in the boiling point of the respective fragments, followed by hydrogenation/de-oxidation steps to produce saturated hydrocarbons, i.e. C_6 to C_{11}. The decrease in boiling point allows for an easier product separation and recovery at lower temperatures and conditions. Furthermore, this decreases the chance of repolymerisation (condensation) reactions occurring, as they are more likely to occur at higher temperatures (Azadi et al., 2013).

7 Valorisation Pathways for Lignin

Conversion of renewable bioresources into higher value products, e.g. biofuels, biochemicals and specialty chemicals, has become a topic of great interest from the chemical industry in the last decade (Azadi et al., 2013; Holladay et al., 2007; Mosier et al., 2005; Zakzeski et al., 2010). Following the dwindling petroleum reserves worldwide, and conscious shift towards sustainable and renewable raw materials, researchers and industries alike are looking at alternative feedstock for the refining of indispensable chemicals. Although lignin has great potential as a renewable and sustainable source of aromatics, phenols and chemicals, the technologies for its valorisation are substantially less developed and mature as for polysaccharides (Azadi et al., 2013). However, technology has matured considerably since previous efforts in valorising biomass in the early 20th century. Lignin appears once again attractive source of aromatics and phenols, among others.

7.1 Phenols & Aromatics

Lignin has long been considered as the only renewable source for aromatics due to the inherently aromatic structure of the polymer (Kang et al., 2013). The difficulty lays in the depolymerisation and selectivity of the fractionation process.

Lignin is effectively a natural polymer, composed of alkylphenol units. In this respect, it does appear an ideal source of phenolic compounds. However, as explained in this literature review, fragmentation of the polymer into phenols has proved challenging. Neither has an efficient and selective pathway to phenols discovered. Furthermore, the presence of sulphur and other inorganic components may restrict refining options for certain varieties and grades of technical lignin (Galkin & Samec, 2016; Zakzeski et al., 2010).

Conversion of lignin to higher hydrocarbon fuels is a topic of patent literature and great interest. Numerous catalytic transformation pathways have been explored with some success. Multi-step conversion of lignin into energy rich, gasoline-range, products, such as C_7-C_9 alkybenzenes, C_5-C_{10} branched paraffins, polyalkyl cyclohexanes, alkylated naphtalenes etc., was reported by Shabtai et al. and Zmierczak et al. in their respective publications (Patil et al., 2011). In effect, the market for jet fuel is set to increase in the near future, and a conversion route from lignin to higher-grade hydrocarbons would lessen the dependence on petroleum for such fuels (Demirbas, 2013; Beauchet et al., 2012; Kim et al., 2016). Denmark has shown an interest in developing marine fuel from lignin (McMillan et al., 2014).

7.2 Others

The variety of technical lignin allows for a vast list of possible applications. From biocomposites materials to adsorbents, specialty chemicals to specialty carbon, lignin could partially, if not entirely, replace compounds produced from the petrochemical industry (Demirbas, 2013; Holladay et al., 2007; Werpy & Petersen, 2004). It has also been considered for its polymeric properties, for uses as polyurethane foams, epoxy or phenolic powder resins (Doherty et al., 2011; Zhang, 2008) – polymers are often challenging to produce, the reason why lignin would prove attractive (Doherty et al., 2011). However, more information about these possible applications lie beyond the scope of this work, and therefore not included.

EXPERIMENTAL WORK

8 Materials and Methods

8.1 Materials

All ethanolysis experiments of this study were performed with bioethanol process-derived lignin powder, effectively named '*Lignin Mass*' (LM) in this work, supplied by St1 Biofuels, Finland. The lignin batch received was partially dried, and milled purposely for this project. However, the lignin powder was sieved beforehand for homogeneity, and each batch dried in a vacuum-oven at 50°C overnight before each experiment to ensure fully dried samples. The only exception being the moisture determination of the initial mass.

96.1%, ethanol (Altia Oyj) was used in the ethanolysis reactions, whilst 99.5% ethanol (Altia Oyj) was used for the acetylation and purification of the Lignin Mass. Sodium hydroxide (99.2%, VWR chemicals BDH Prolabo) was used for separating non-degraded lignin from char. Sulphuric acid (95.0 – 97.0%, Sigma Aldrich) was used for acidification. Lichrosolv tetrahydrofuran (THF) (99.9%) and pyridine (99%) were acquired from Sigma-Aldrich as well. All chemicals were used as received except sodium hydroxide and sulphuric acid, which were diluted to required concentrations in distilled water.

The catalysts (5% Ni/ γ-Al_2O_3, Pellets 2-5 mm, 200m^2/g surface area; 5% Ru/γ-Al_2O_3, Pellets 2-5 mm, 200m^2/g surface area) were purchased from Riogen Inc., United States of America.

The ethanolysis experiments were performed in a 'PARR 4575 A' batch reactor (see Appendix 4 for additional information on the reactor specifications) with a 4848 reactor controller. The reactor has an inner volume of 500 mL with a capability of reaching temperature up to 500°C and pressures up to 34.5 MPa.

8.2 Apparatus, Procedure and Experimental Methods

A total of twelve experimental ethanolysis runs were performed with the autoclave reactor pictured in Image 1. Eight of the experiments are considered in this work: six uncatalysed runs with reaction times varying between 0 to 360 minutes, and two additional 120 min catalysed runs. The latter two followed the identical procedure as the uncatalysed runs, with the difference that a small cage was attached to the stirrer, portrayed in Image 2, containing the catalyst. The products of the ethanolysis reaction were then isolated and measured on a weight basis. However, the gaseous components were not studied, and were discarded. The ethanol was not collected, nor analysed or included in the mass balances.

Image 1: Autoclave reactor and apparatus used for the ethanolysis runs

Image 2: Catalyst Cage

Please refer to the 'Risk Analysis Report' produced for the Experimental Ethanolysis Runs in *Appendix 4* for additional information concerning the apparatus, valves, procedure and detailed safety information. The separation procedure is schematically presented in Figure 7.

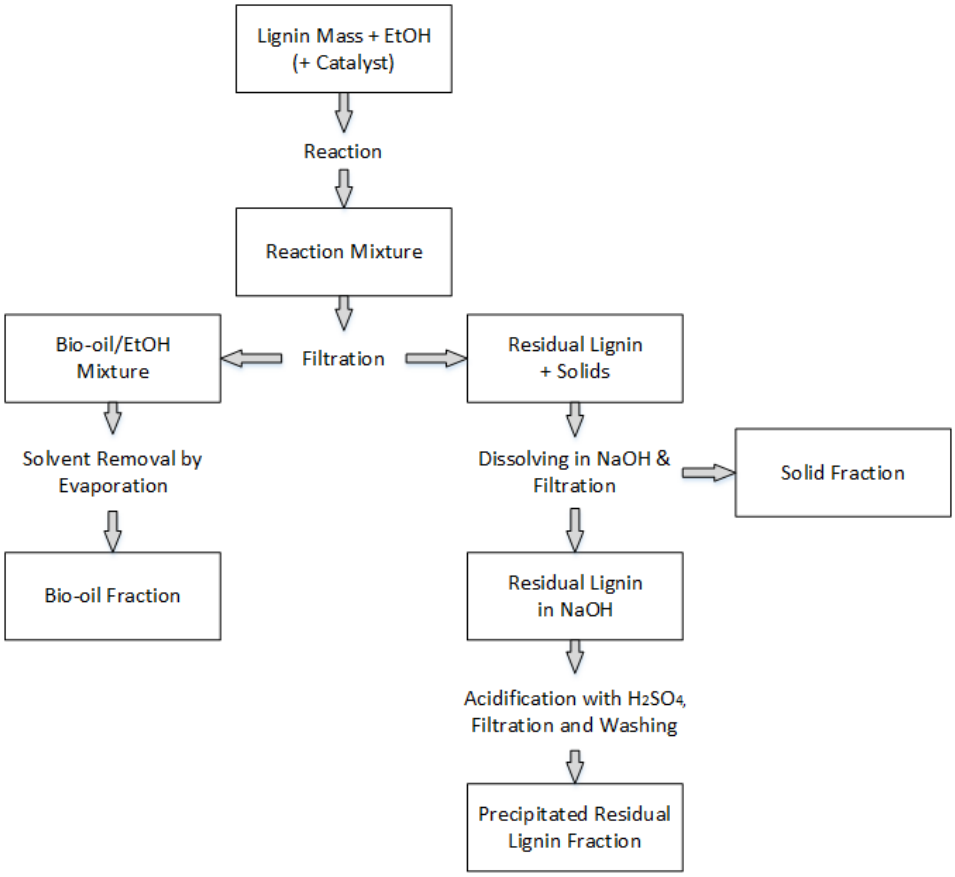

Figure 7: Separation procedure of ethanolysis products

8.2.1 Bio-oil Extraction

The contents of the reactor were emptied and filtered to remove solids from the liquid phase. Ethanol was removed from the liquid EtOH/Bio-oil mixture with a rotary evaporator and the bio-oil was recovered as a viscous liquid.

8.2.2 Solids Separation

The reactor was filled with 200 mL of 1 M NaOH and agitated under high speed (700 rpm) for 30 minutes to clean the reactor from char and residual lignin remaining on the reactor walls and the stirrer. The caustic solution from the reactor was mixed with the

filtered solids. Subsequently, the solution was filtered, separating the solid char from the dissolved lignin residue. 5 M H_2SO_4 was added to acidify the filtered caustic solution to a pH of 1.5 at which the residual lignin was precipitated and the solution was filtered to recover the residual lignin. After a thorough wash with distilled water, the precipitated lignin was left for drying at room temperature overnight.

8.3 Analytical Methods

8.3.1 Elemental Analysis

All elemental analyses were performed at the Microanalytical Laboratory of the Faculty of Chemistry, University of Vienna. CHNS- triple determination and O- triple determination were performed for the lignin sample (LM), whilst CHNS- double determination was performed for the bio-oil and solid fractions. In the latter case, the oxygen content was estimated as 100 minus the sum of the other fractions.

8.3.2 Carbohydrate and Lignin Determination

The Standard NREL/TP-510-42618 'Determination of Structural Carbohydrates and Lignin in Biomass' was followed to determine the carbohydrate and lignin content of the Lignin Mass (LM).

8.3.3 Inorganic Matter Determination

The Standard NREL/TP-510-42622 'Determination of Ash in Biomass' was followed to determine the ash content of the Lignin Mass (LM).

8.3.4 Methoxyl Group Determination

The methoxyl groups in the Lignin Mass (LM) were quantified according to the Zeisel-Vieböck-Schwappach method. The experimental procedure is attached in Appendix 1. Image 3 portrays the apparatus set-up used for the determination of the methoxyl group determination.

Image 3: Photo of the apparatus used for the methoxyl group determination

8.3.5 Molar Mass Distribution

The molecular weight averages of the substrate Lignin Mass (LM), and the ethanolysis products (with the exemption of the residual lignin fractions) were determined with an Agilient HPLC-system, by means of Phenogel (5µm – 5nm and 100nm) columns and UV detector at 280 nm. THF was used as eluent at a rate of 1.0 mL/min and analysis was

performed at room temperature. The Lignin Mass (LM) sample was acetylated prior to analysis to make it fully soluble in THF by a published method (Gellerstedt, 1992) with a slight modification: Ethanol was used instead of methanol, and was added and removed seven times to remove unreacted acetylation chemicals. The acetylated sample was then dried in a vacuum drier at 40°C for a period of 48 hours. The bio-oil samples, not requiring an acetylation step, were dissolved directly in the THF solvent.

8.3.6 GC-MS Chromatography

Phenolic products present in the bio-oil fractions of the 120 minute runs were characterised using GC-MS (Thermofischer scientific TG-200 MS capillary column with dimensions: 30 m, 0.25 m, 0.25 µm). 10 mg of bio-oil was dissolved in 1 mL of pyridine. The sample was injected at 280°C into the column using splitless mode. Helium was utilised as a carrier gas at a rate of 1 mL/min. The temperature program for the analysis was performed as follows: after a 2 min hold at 40°C, the oven was heated to 280°C at a rate of 6°C/min and held for 2 min. MS detector was operated in an electron ionisation mode at 70 eV at an ion source temperature of 280°C.

8.3.7 ^{13}C NMR Analysis

NMR analysis of the Lignin Mass (LM) sample was performed with a Bruker 400 MHz UltraShield NMR. The acetylated sample was dissolved in Chloroform-D ($CDCl_3$) with 0.03 % tetramethylsilane (TMS), with a concentration of 250 mg/mL, and then transferred to a 5 mm NMR-tube. The number of scans was 60 000.

8.3.8 The Higher Heating Value

The Higher Heating Value (HHV) for each sample was estimated with the use of the Dulong's formula (Demirbas, 2013):

(1) $$HHV = 0.335(CC) + 1.423(HC) - 0.154(OC) - 0.145(NC)$$

Where: CC: carbon content; HC: hydrogen content; OC: oxygen content; NC: nitrogen content of sample (wt%)

The values from the elemental analyses of the Lignin Mass (LM) samples, and the ethanolysis products (with the exemption of the residual lignin fractions), were used in the calculations.

8.3.9 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was used to assess changes between the chemical structure of the 'Lignin Mass' and that of the ethanolysis solid fractions. 0.2 g of sample were mixed in with 2.0 g of KBr. The mixture was thoroughly milled to ensure uniform particulate size. The mixture was then subject to high pressure, with the help of a hydraulic press, to form a pellet. This pellet was transferred to the 'PerkinElmer Spectrum One' FTIR apparatus, and locked with clamps within the chamber. The absorbance of the sample was analysed using a background KBr spectrum. Special care was taken to ensure dryness of the sample, working under an infrared light, as the IR signal of water is strong which would result in overlapping peaks unless the sample is completely dry.

9 Results and Discussion

9.1 Lignin Characterisation

The first step of this thesis work was the characterisation of the lignin powder provided by St1 Biofuels Oy. It allowed for a comprehensive understanding of the feedstock before the ethanolysis reactions.

9.1.1 Mass Balance

A minimum of two sets of duplicates samples, i.e. 4 in total, were used to determine the following mass balances of the Lignin Mass to ensure accurate results. The mass balance consists of the moisture, acid-insoluble lignin (Klason), acid-soluble lignin, carbohydrates, and inorganic ash contents. The average results of which are summarised in Table 3.

Table 3: Mass balances of Lignin Mass (LM)

Sample	Moisture (%)	AIL (%)	ASL (%)	Carbohydrates (%)	Ash (%)	Σ (%)
LM (average)	4.05	85.37	1.04	7.67	0.24	98.37
SD	0.11	0.13	0.06	0.12	0.02	0.05

where: AIL: Acid Insoluble Lignin (Klason Lignin), ASL: Acid Soluble Lignin, SD: Standard Deviation

9.1.2 Lignin Content

The lignin content of the lignin mass proved quite high ~86%. It is a good indicator of lignin purity, as well as the efficiency of the fractionation process and isolation method. A higher content is desired, naturally, especially if no isolation step is required. The value is less than industrial kraft lignin (see Table 1), without subtracting the carbohydrate content. No complications arose from the standard procedure, and the duplicate results proved accurate.

9.1.3 Carbohydrate Content

As a by-product of a bioethanol process, a higher carbohydrate content was expected than in other types of technical lignin. However, the value does not stretch beyond 8% of dry matter, as portrayed in Table 4. The absence of C5-sugars infers to an efficient prehydrolysis step, in which the hemicelluloses fractions are rapidly hydrolysed and processed. In effect, the carbohydrate content consisted near-entirely of C6-sugars, notably glucose from unhydrolysed carbohydrates. This was expected, as the lignin mass was effectively collected as a solid residue after the hydrolysis/saccharification step in the bioethanol process, which accounts for the residual carbohydrates.

Table 4: Carbohydrate determination of Lignin Mass (LM)

C (anhydro; %)	**average**
*Arabinose**	0.18 %
Rhamnose	0.03 %
Galactose	0.06 %
Glucose	6.89 %
*Xylose**	0.06 %
Mannose	0.45 %
Σ:	7.67 %

*(*C5 sugars)*

9.1.4 Ash Content

The ash content was very low, which bears witness to the quality of the feedstock. The ash was of a light brown colour, if slightly orange, which could be indicative of the specific inorganic compounds present, as portrayed in Image 4. The results from the duplicate sets were very similar, and hence no further analysis was performed.

Image 4: Ash residue in Crucibles

9.1.5 Elemental Analysis

The average results from the elemental CHNSO-analyses are summarised in Table 5. The results of which can be compared to other types of lignin in Table 2. The Oxygen/Carbon (O/C) and Hydrogen/Carbon (H/C) ratios were calculated using the molecular mass of each compound and the values from the analyses. In effect, a total mass content of 98-99% was achieved for the sample. The second row of 'corrected' values were calculated by subtracting the carbohydrate content in order to better estimate the elemental composition of the lignin, and hence determine a C9-formula (equation 2). The C9-formula (equation 3) of spruce milled wood lignin (Calvo-Flores et al., 2015) is added for comparison.

The carbon, hydrogen, and oxygen contents give insight into the different phenylpropane units present in the lignin mass. A high carbon content paired with a low oxygen content refer to a higher proportion of guaiacyl units, which is expected in

softwood. The contrary would prove an indication of more syringyl units, which would further indicate a higher methoxyl content.

*Table 5: Elemental analysis of Lignin Mass (LM) and LM **sugar-free** (corrected values once the carbohydrate content is subtracted)*

Sample:	*wt%C*	*wt%H*	*wt%N*	*wt%S*	*wt%O*	*O/C*	*H/C*	*OCH_3*	*∑ %*	HHV
LM	63.75	5.85	0.78	0.05	28.52	*0.34*	*1.09*	0.11	98.95	25.18
$LM_{sugar\text{-}free}$	65.34	5.82	*N.A.*	*N.A.*	26.80	*0.31*	*1.06*	0.11	97.97	25.93

(2) C_9 Formula ($LM_{sugar\text{-}free}$) = $C_9H_{8.34}O_{2.34}(OCH_3)_{0.63}$

(3) C_9 Formula (MWL_{spruce}) = $C_9H_{8.83}O_{2.37}(OCH_3)_{0.96}$ (Calvo-Flores et al., 2015)

A major advantage of the bioethanol process vis-à-vis lignin is the absence of sulphur, which is made evident in the results. The 0.05% is likely inherently present in the native wood. This absence allows for more refining opportunities in contrast to sulphur-containing/sulphonated lignin. The nitrogen content could account for protein contamination during the fermentation stage of the process (Mansouri & Salvadó, 2006). However, the determined value is very low, and hence contamination, if any, insignificant.

9.1.6 Methoxyl Group Determination

The proportion of methoxyl groups in lignin is relative to the H:G:S unit ratio. As a by-product of softwood, naturally richer in guaiacyl units in contrast to hardwood, a lower proportion of methoxyl groups was expected than in hardwood lignin, e.g. organosolv. However, a lower value (lower than that of MWL_{spruce}) is also indicative of a more severe pretreatment step in which a greater extent of bond cleavage occurs, which does indeed correlate with our results. In this case, both statements appear to be valid. It is

noticeable when comparing both C9-formulae: the formulae are similar in all parts, except for the methoxyl content.

9.1.7 Higher Heating Value

The HHV of the Lignin Mass (LM) sample was estimated to be around 25-26 kJ/g, which is similar to that of lower grade bituminous coal (~25 kJ/g), and superior to that of wood (~21 kJ/g). Lignin has always proved an attractive and cheap fuel and the higher the lignin content, the higher the HHV. Considering Dulong's formula, the oxygen content slightly reduces the overall HHV. Indeed, the LM is already at this stage a fuel of decent grade. However, it should be taken into consideration that it was dried and ground for the purpose of this work, which results in a higher HHV in contrast to that of the moist lignin slurry as initially discharged from the process.

9.1.8 Molecular Weight Distribution

As the lignin mass was not entirely soluble in THF, an acetylation step was performed, after which the lignin was dissolved in THF with no complication. In effect, the insolubility of woody biomass components has proven the greatest challenge to attempts at its valorisation (Holladay et al., 2007; Kilpeläinen et al., 2007; Zakzeski et al., 2010). Due to its complex three-dimensional structure and hydrophobicity, it requires fragmentation by means of chemical reactions to better dissolve in standard solvents. The high molecular mass can also prove a considerable factor vis-à-vis solubility; the higher the molecular mass, the more condensed the structure is, and hence the less soluble it is. The solubility of the lignin mass was assessed in ethanol and sodium hydroxide, as portrayed in Image 5. Partial solubility was observed, although most of the mass persisted as a solid deposit. Furthermore, full solubility was not achieved with pure THF and acetone.

Image 5: LM/EtOH and LM/NaOH mixtures

The results are expressed as the number average molar mass (M_n) and the mass average molar mass (M_w), from which the dispersity value ($Đ_M$) was calculated. M_n represents the arithmetic mean or average of the molecular masses of the individual molecules. As some polymer properties are dependent of molecular size, a larger molecule will contribute more than a smaller molecule: M_w takes this into account, representing a weighted mass average in contrast to M_n. The dispersity index $Đ_M$, the ratio of Mw/Mn, refers to the homogeneity, or effectively heterogeneity, of the size of particles within a solution/sample. In this case, a value circa 1 is indicative of a uniform distribution of molecular masses. A higher value (>1) would infer to a non-uniform lignin polymer, in which the polymer chains vary over a wide range of molecular masses. Indeed, the lignin polymer has undergone many chemical changes during pretreatment, such a bond cleavage and condensation reactions, which have significantly altered the structure of the polymer. The results are summarised in Table 6, and compared to other softwood lignin presented in Balakshin's (2015) results.

Table 6: Molecular weight distributions of Lignin Mass samples

Sample	Mn (g/mol)	Mw (g/mol)	$Đ_M$ (Mw/Mn)
Indulin-1 (SW Kraft)[1]	1030	4443	4.31
Indulin-2 (SW Kraft)[1]	1177	5539	4.71
Curan (SW Kraft)[1]	1358	6839	5.04
Pine WML[1]	1139	3708	3.26
LM (average):	**516.1**	**1863**	**3.61**
SD (LM)	4.67	34.65	0.03

[1]*Balakshin et al. 2015*

The low molar mass value of the Lignin Mass (LM) indicate that it has undergone severe pretreatment and significant depolymerisation in contrast to the other softwood lignin grades, which exhibit twice as large molecular mass.

9.1.9 ^{13}C NMR Spectrum

The lignin sample was first acetylated before dissolved in Chloroform-D (CDCl). However, the ^{13}C NMR analysis proved challenging to perform due to the viscosity of the sample. Too low a concentration would result in signals indistinguishable from the noise, caused by the particles in suspension. A higher concentration would result in too viscous a sample, and difficulties for the solvent lock procedure: a procedure by which the apparatus can "lock" onto a specific solvent, which allows for the removal of interfering solvent signals. A suitable concentration was discovered around ~250 mg/mL, once the solution was accordingly warmed up to 37°C. The results of the ^{13}C NMR analysis of LM is observable in Figure 8.

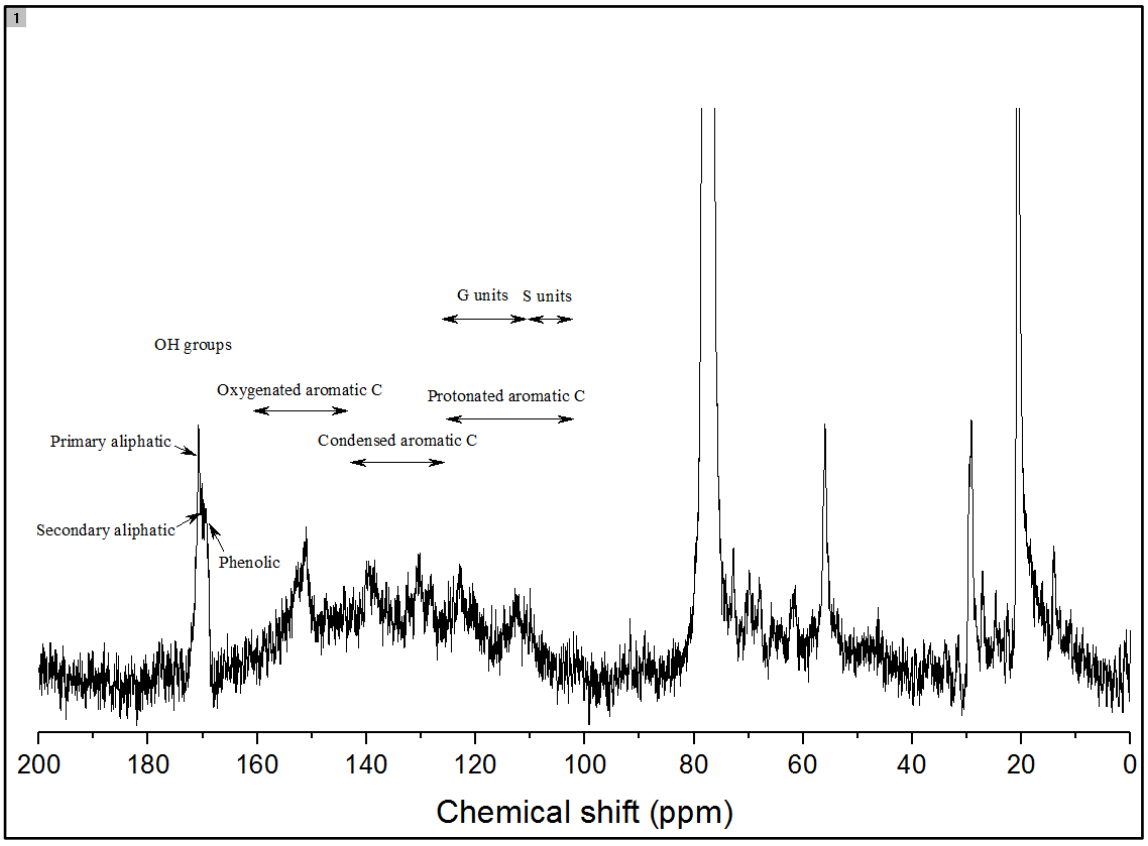

Figure 8: ^{13}C NMR spectrum of Lignin Mass

Despite a significant amount of noise, distinct signals were achieved. An attempt at quantitative analysis delivered the results compiled in Table 7, and compared to the published results of other types of technical lignin (Balakshin et al., 2015; Lê et al., 2016) in Table 8. The reader is reminded that these results are suggestive, and further research and work with the sample would be required to confirm these ratios.

The aliphatic and phenolic hydroxyl groups were however recognisable, alongside the aromatic ring substitutions. Guaiacyl and syringyl units were detected in a ratio that would appear to correlate with a mixture of hardwood and softwood, which renders it difficult to make assumptions on the structure of the polymer.

Table 7: Quantitative Lignin Mass (LM) analysis by ^{13}C NMR

Structural element	from (ppm)	to (ppm)	Integral area	per Ar
Aromatic			28.66	6.00
Primary aliphatic OH*	171.0	169.8	0.98	0.11
Secondary aliphatic OH*	169.8	168.8	0.92	0.10
Phenolic OH*	168.8	167.5	0.82	0.09
O substituted aromatic C**	158.0	140.5	8.24	0.91
C substituted aromatic C***	141.0	126.3	8.60	0.95
H substituted aromatic C	126.3	101.5	11.82	1.30
Guaiacyl, G2,5,6 :3	126.3	109.5	8.55	0.60
Syringyl, S2,6 :2	109.5	101.5	3.29	0.34
ß-ß	87.0	85.2	1.21	0.13
ß-O-4	82.7	80.0	1.48	0.16
Methoxyl	57.0	54.5	1.11	0.12
ß-ß, ß-5, ß-1, tert.aliph.C-C	54.5	49.0	1.83	0.20
		6 aromatic Cs	**40.50**	**4.46**

**acetylated, **plus non-etherified phenolic C-O-Ac, ***minus non-etherified phenolic C-O-Ac*

Table 8: Comparative ^{13}C NMR results of various types of technical lignin samples

Structural element (per 100 Ar)	LM	Indulin (SW Kraft)[1]	Curan (SW Kraft)[1]	Pine MWL[1]	Organosolv Beech Lignin[2]
Primary aliphatic OH*	11	31	35	67	50
Secondary aliphatic OH*	10	18	16	40	32
Phenolic OH*	9	66	69	33	43
Guaiacyl, G2,5,6 :3	60	92	86	99	43
ß-ß	13	4	3	4	N.A.
ß-O-4	16	7	5	42	26
Methoxyl	12	81	82	97	24

**acetylated; [1]Balakshin et al. 2015; [2]Lê et al. 2016*

Indeed, in contrast to the Pine MWL and the organosolv lignin, the methoxyl and ß-O-4 bond content are considerably low: this is indicative of a harsh pretreatment step in which the majority of methoxyl groups and ß-O-4 bonds have been disrupted or cleaved. The higher ß-ß bond value correlate with condensation reactions, in which lignin-derived radicals bond to form stronger carbon-carbon bonds. The low OH content of the Lignin

Mass confirms the low reactivity of the sample. Table 9 offers summarised results vis-à-vis aromatic ring constituents, and percentages of the G:S units. These values may prove worthwhile in further attempts to characterise the Lignin Mass or similar lignin.

Table 9: Derived ratios for Lignin Mass (LM) (calculated from the 'per Ar' values above)

Important values	
S/G ratio	0.58
Ar-O-R / Ar	0.91
Ar-C-R / Ar	0.95
Ar-H-R / Ar	1.30
Ar-H / (Ar-C + Ar-O)	0.70
Syringyl %	36.60
Guaiacyl %	63.40
Methoxyl / Ar	0.12
Acetyl phenol. / Ar	0.09
Acetyl prim. Alcohol / Ar	0.11
Acetyl sec. Alcohol / Ar	0.10
ß-O-4 / Ar	0.16
ß-ß / Ar	0.13

Where: S/G: syringyl/guaiacyl ratio; Ar: Aryl

9.2 Catalysed and Uncatalysed Ethanolysis

At any reaction condition, lignin degradation products were classified in three categories: bio-oil (EtOH-soluble fraction), residual lignin (soluble in NaOH), and a solid fraction. It is important to mention that the monoaromatic, including phenolic, compounds were recovered in the bio-oil fraction. The solid fraction accounts for all mass unreacted, and formed during the process, acquired by filtration. Apart from these three major fractions, gaseous components were most assuredly formed. However, the gaseous phase was neither recovered nor analysed, but instead discharged through the reactor's relief valve into the atmosphere. It is however possible to estimate the quantity of gaseous products formed from the pressure difference in the reactor, i.e. before heating, and once cooled down. Each experimental run was performed but once, due to a strenuous time schedule – the greater quantity of runs offered more insight into the depolymerisation mechanisms.

Table 10 compiles the important data concerning the experimental runs, including reactor load and reactor conditions. The temperature of 280°C was determined from literature (Patil et al., 2011; Ma et al., 2014; Ma et al., 2015) as sufficient in order to achieve ethanol in a supercritical phase. The volume of ethanol was determined by calculating the volume occupied by supercritical ethanol at 280°C within the autoclave reactor - detailed calculations can be found in the Risk Analysis Report (Appendix 4). The initial pressure of 10 bar was determined by trials runs in order to achieve a pressure at 280°C superior to 80 bar. The longer runs (120 to 360 min) were determined from literature, whilst shorter runs (0 to 60 min) explored in order to attain more insight into the depolymerisation reactions occurring.

The catalysts, 5%Ni/γ-Al_2O_3 and 5%Ru/γ-Al_2O_3, had been selected from literature as suitable candidates to promote the depolymerisation of lignin in ethanol (Patil et al., 2011), whilst inhibiting condensation reactions (Huang et al., 2015). Furthermore, a comparison between the influences of a noble metal catalyst versus a nickel catalyst

upon the reaction was considered. However, their influences did not prove significant enough to produce conclusions.

Table 10: Experimental data from catalysed and uncatalysed ethanolysis runs

	Uncatalysed Runs						Nickel	Ruthenium
Run #	1	2	3	4	5	6	7	8
Reaction Time (min):	0	30	60	120	240	360	120	120
Load:								
Ethanol (mL):	100	100	100	100	100	100	100	100
Lignin (g):	10.002	10.000	10.001	10.003	10.009	10.003	10.001	10.002
Catalyst (g):	0	0	0	0	0	0	1	1
N2 Load (bar):	10	10	10	10	10	10	10	10
Reactor Conditions:								
Set Temperature:	280	280	280	280	280	280	280	280
Pressure @280°C (bar):	81.2	82.0	81.0	82.5	82.4	82.0	81.7	89.0
Pressure Difference (bar):	0.2	0.1	0.2	0.1	-0.2	-0.3	-0.3	4.2

The only exception being the case of the large pressure difference in the ruthenium-catalysed run, i.e. 4.2 bar. This is indicative of a high quantity of gaseous products formed. As this was not observed in other experimental runs, one could assume that the catalyst may have had some influence in producing gaseous depolymerisation products: e.g. lighter hydrocarbons, carbon monoxide and dioxide, acetylene, formic acid etc. Unfortunately, the gaseous phase was not analysed, nor was the available GPC apparatus calibrated for such samples. However, this pressure difference does suggest that the production of lighter compounds was catalysed or promoted by the presence of the ruthenium catalyst.

Figure 9 portrays the experimental run as it proceeded. Noticeable are the heating phase, the reaction time (plateau), and cooling phase. The Parr autoclave reactor has a full proportional, integral and derivative (PID) reactor control regulating the heating with the temperature of 280°C, set for these experimental runs. The heating would usually take approximately 30 minutes, after which the PID worked to stabilise the temperature.

Cooling of the reactor chamber was performed by running cold water through the integrated cooling coil. Notable was how rapidly the system reacts to this cooling water flow. The pressure dropped rapidly and significantly once the cooling line was opened. Stirring was maintained at 600 rpm throughout the reaction time, and beyond, to ensure full mixing of the reactor mixture.

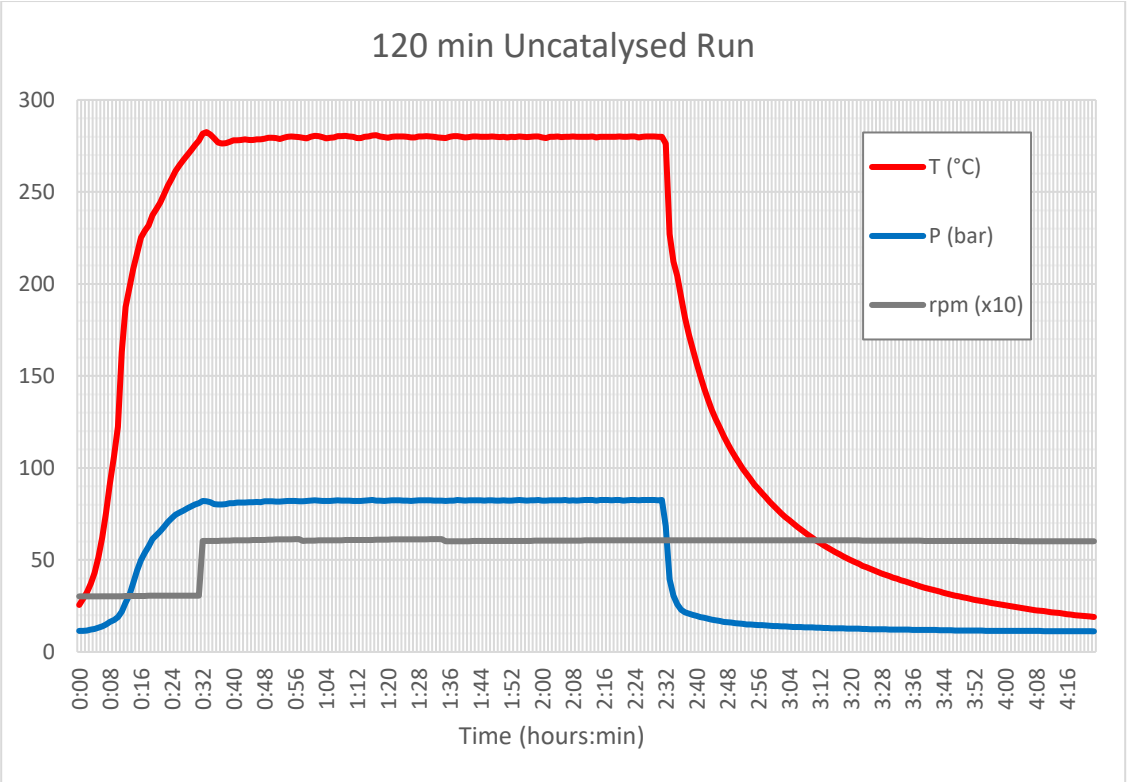

Figure 9: 120 min run, including heating and cooling phases

9.2.1 Mass Balances

The results of the uncatalysed and catalysed experimental runs are compiled in Figure 10, 11 and 12 respectively. Detailed tables of the product distributions are attached in Appendix 2.

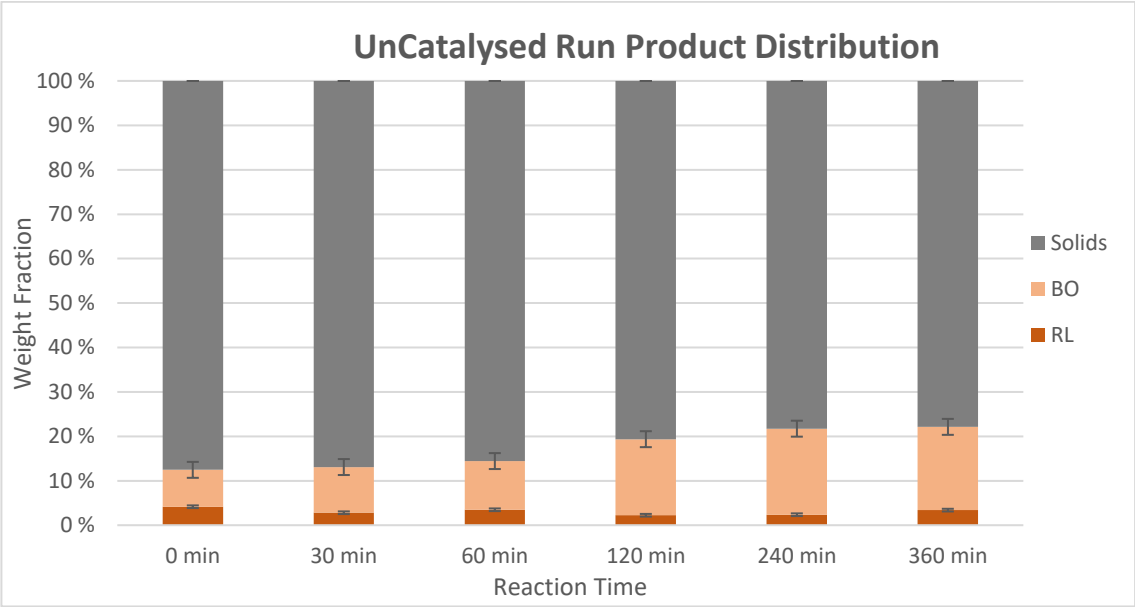

Figure 10: Mass balances of uncatalysed runs, where, BO: bio-oil fraction; RL: residual lignin fraction; Solids: solid fractions

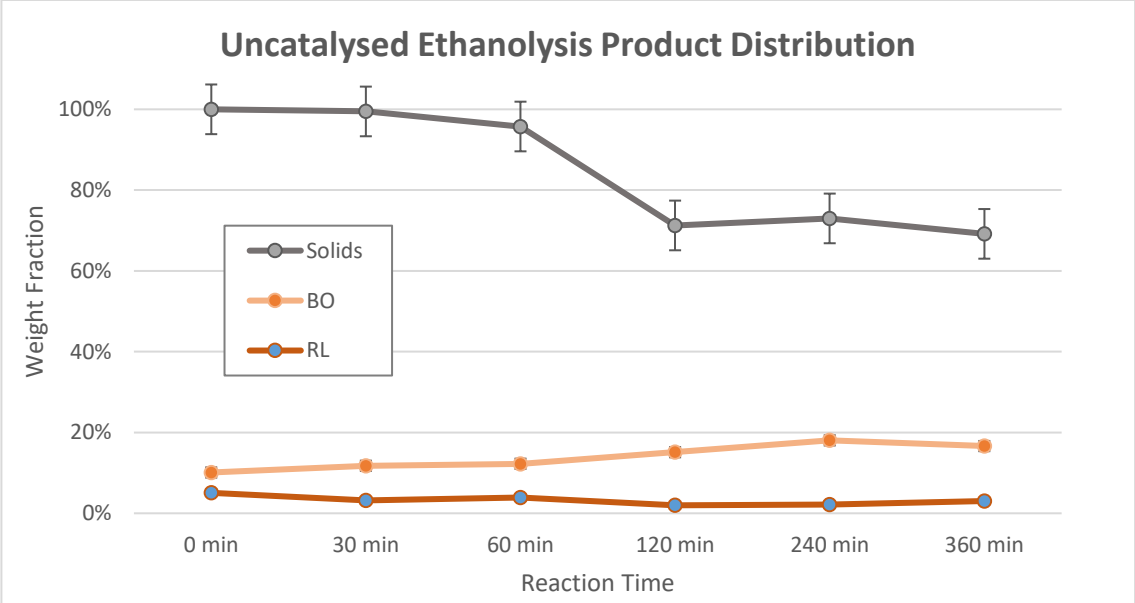

Figure 11: Product distribution over time, where, BO: bio-oil fraction; RL: residual lignin fraction; Solids: solid fractions

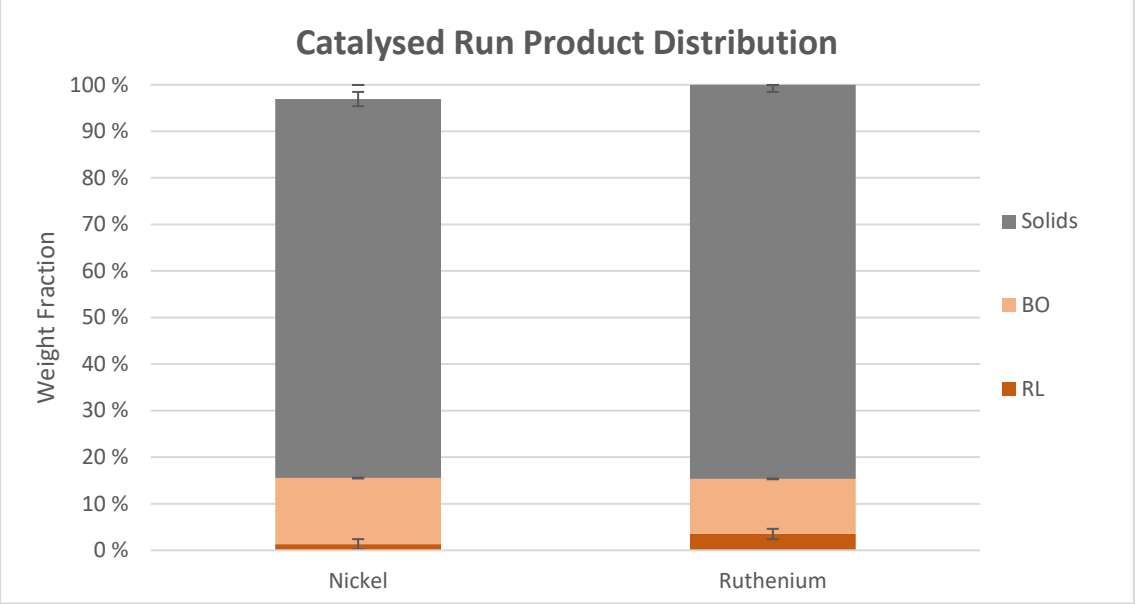

Figure 12: Mass balances of catalysed runs, where, BO: bio-oil fraction; RL: residual lignin fraction; Solids: solid fractions

In effect, under reaction conditions, ethanol proved an aggressively reactive solvent, acting as a both a minor acid and a proton donor in the absence of hydrogen. It should be noted that the quantity of ethanol collected post-reaction, via vacuum evaporation, was each time less than the 100 mL introduced to the autoclave reactor, by 10-15 mL. This difference accounts for discarded gaseous components, and reacted ethanol.

The high amount of solids obtained throughout all experimental runs was surprising. After a troubleshooting phase, in which organosolv lignin was used instead of Lignin Mass during the same procedure, it became apparent that the high solids content was due to the low reactivity of the Lignin Mass and not the experimental conditions and procedure. Indeed, perhaps the unreactive lignin reacts strongly with the ethanol solvent to produce blackened condensed structures and/or proceeds to burn within the autoclave. The FTIR spectra confirm a similar structure between the solid fraction and Lignin Mass, which correlates with the assumption that the low reactivity and already condensed structure of the Lignin Mass (post-pretreatment) are to blame for higher

solids content. It may be that the supercritical ethanol/nitrogen pressurised environment is not optimal to achieve larger extents of depolymerisation: pressurising the autoclave with hydrogen would increase the quantity of protons in the autoclave and perhaps promote, or at best increase, the reactivity of the Lignin Mass.

9.2.2 Elemental Analysis

The elemental analyses of the ethanolysis products was necessary in order to understand which reactions occurred during the reaction time. The oxygen content was estimated as 100 minus the sum of other weight fractions. The average results of the bio-oil fractions and solid fractions are summarised in Table 11 and 12 respectively.

Table 11: Elemental analysis of bio-oil samples (2h Reaction Time)

Sample	wt%C	wt%H	wt%N	wt%S	*wt%O*	*O/C**	*H/C**	Total %	**HHV***
UnCat	69.27	7.96	0.69	0.07	*22.02*	*0.24*	*1.37*	77.98	**31.03**
Ni	69.28	8.10	0.79	<0.02	*21.81*	*0.24*	*1.39*	78.19	**31.26**
Ru	70.89	8.19	0.76	<0.02	*20.14*	*0.21*	*1.38*	79.86	**32.18**

In comparison to the elemental data of the lignin mass, a significant decrease in oxygen content is observed in both uncatalysed and catalysed bio-oil fractions. This resulted in an increase in carbon and hydrogen content, which effectively produce considerably higher HHVs than the initial LM HHVs. The slight increase in nitrogen content is because the very same gas was used to pressurise the autoclave reactor to 10 bar.

Producing an energy-richer bio-oil fraction, in contrast to the initial Lignin Mass (LM), was within the scope of the project, and these results satisfy the assumption that a hydrogenolysis pathway took place, in which deoxygenation occurs.

Table 12: Elemental analysis of solid fractions (120 min reaction time)

Sample	wt%C	wt%H	wt%N	wt%S	*wt%O*	*O/C**	*H/C**	Total %	HHV*
UnCat	59.39	5.06	0.92	< 0.02	*34.61*	*0.44*	*1.02*	65.39	**21.64**
Ni	54.22	4.80	0.79	< 0.02	*40.17*	*0.56*	*1.05*	59.83	**18.69**
Ru	51.58	4.76	0.68	< 0.02	*42.97*	*0.62*	*1.10*	57.04	**17.34**

In the case of the solid fractions, the contrary phenomena occurred in contrast to the bio-oil fraction. The oxygen content increased, and hence oxygen to carbon ratio, reducing the carbon and hydrogen content overall, and consequentially the HHV. Furthermore, it seems that these differences are more significant with the catalysed samples, which would infer that the catalysts did have an influence during the reaction.

9.2.3 Molar Mass Distribution

The uncatalysed and catalysed ethanolysis bio-oil samples were dissolved directly in THF, not requiring acetylation. The results of which are summarised in table 13 and 14 respectively. For more information, graphs of the MMD are attached in Appendix 3.

Table 13: Molecular weight distributions of uncatalysed bio-oil samples

Reaction Time	Mn (g/mol)	Mw (g/mol)	$Đ_M$ (M_w/M_n)
0	328.8	670	2.04
30	374.9	822	2.19
60	353.3	773	2.19
120	326.1	606	1.86
240	344.7	748	2.17
360	380.1	934	2.46

In contrast to the molar mass distribution of the lignin mass (see Table 6), a decrease in overall size is obvious, alongside a reduction in dispersity. The lignin polymer has undergone evident depolymerisation during the ethanolysis reaction, the results of which are present in the bio-oil fraction. Data from the zero-minute run proves that

depolymerisation reactions occurred already during the heating phase of the reaction, prior to achieving the set temperature, producing a bio-oil fraction rapidly. This was followed by a significant increase in average molecular weight within the first thirty minutes. The average molecular weight then proceeded to decrease between 30 and 120 minutes. If this is due to the formation of smaller products or further depolymerisation of larger compounds is difficult to say, and would require efforts into the product distribution at each reaction time. However, the trend is reversed beyond 120 minutes, and the average molecular weight steadily increases until 360 minutes. Furthermore, the graphs in Appendix 3 clearly portray how peaks are consumed and formed over time, indicative of the consumption of smaller molecules during the formation of larger molecules.

An interesting observation lies in the changes in dispersity ratio as the reaction proceeds. As the average molecular weight increased, so does the dispersity, which is indicative of a non-uniform distribution. In effect, the greater the average molecular weight, the larger the range of distribution. This infers that as the reaction proceeds, more compounds of random molecular weights are formed within the solvent medium.

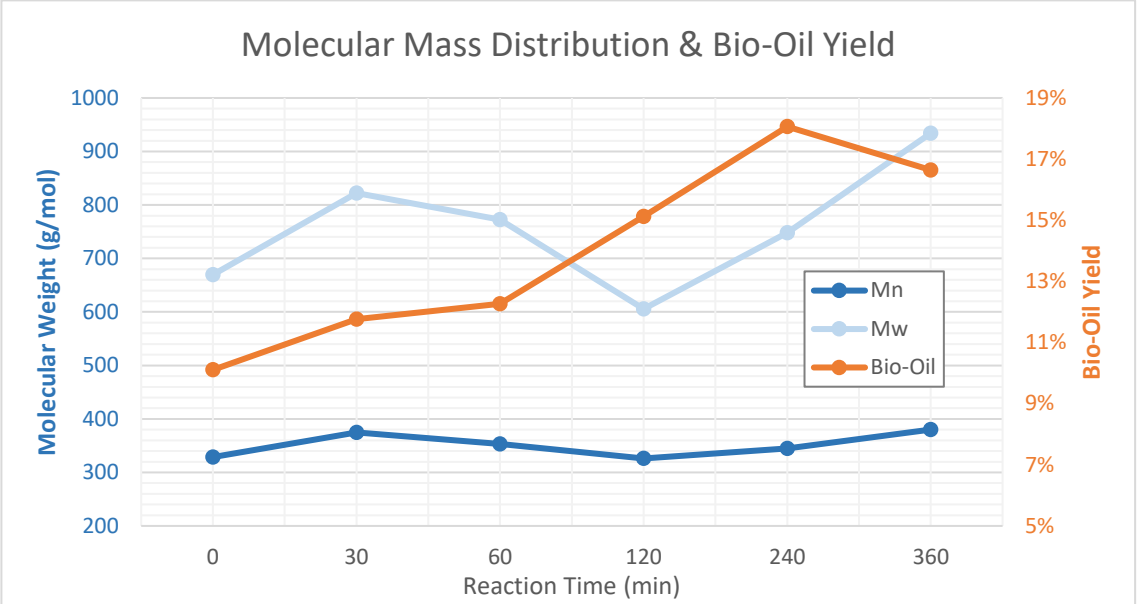

Figure 13: Correlation between bio-oil yield and molecular mass distribution

Figure 13 compiles the bio-oil yields from the uncatalysed runs alongside the molecular mass distribution of the uncatalysed bio-oil samples. Although the higher bio-oil yield was achieved at t = 240 min, if lower molecular masses are the target of depolymerisation, then it would seem that t = 120 min proved the most successful run.

Table 14: Molecular weight distributions of nickel- and ruthenium-catalysed bio-oil samples (120 min reaction time)

Sample	Mn (g/mol)	Mw (g/mol)	$Đ_M$ (M_w/M_n)
Ni Average:	401.8	995	2.48
SD:	*0,1*	*7*	*0,02*
Ru Average:	380.5	814	2.14
SD:	*0,4*	*1*	*0,00*

Based on Table 12, at first glance it is evident that the average molecular weights of both catalysed bio-oil fractions are superior to that of the 120-minute uncatalysed experimental run. It would seem that the catalysts have had an influence upon

depolymerisation reactions in the autoclave reactor. Both catalysts promoted the formation of larger products, as observed by the graphs in Appendix 3, although neither catalyst proved more selective. The dispersity ratio for the nickel-catalysed bio-oil sample shows a larger distribution of product molecular weight, in contrast to that of the ruthenium-catalysed bio-oil, and most particularly that of the uncatalysed bio-oil. The ruthenium appears more selective in producing a smaller distribution of product molecular weights compared to the nickel catalyst.

9.2.4 GC-MS Results

The bio-oil fractions were dissolved in pyridine for the GC-MS analyses. The pyridine solvent provided significantly more accurate results in contrast to ethanol as solvent, which caused duplicate peaks to appear. The results of the 120 min uncatalysed, nickel-catalysed and ruthenium-catalysed bio-oil fractions are portrayed in Figures 14, 15 and 16 respectively.

The GC chromatograms are quite similar with the exception of the heavier components detected beyond a retention time (RT) of 26 minutes. This is most likely due to the catalysts promoting the formation of heavier compounds. A brief approach at identifying the most prominent compounds is compiled in Table 15.

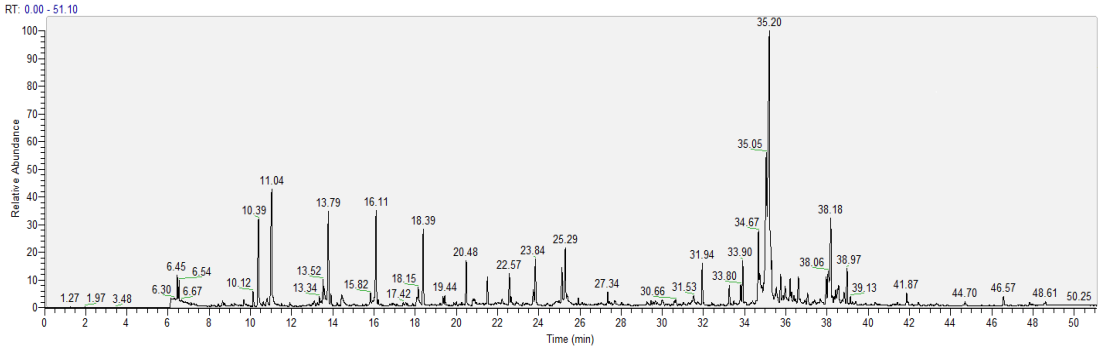

Figure 14: GC-MS chromatogram of uncatalysed bio-oil fraction

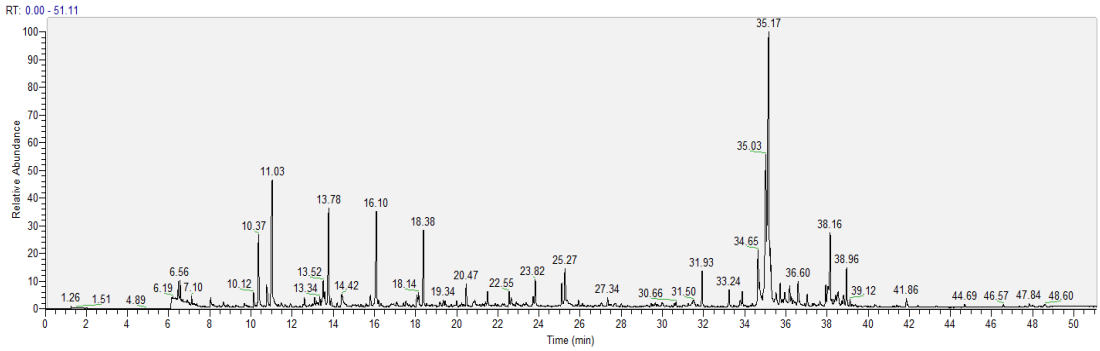

Figure 15: GC-MS chromatogram of nickel-catalysed bio-oil fraction

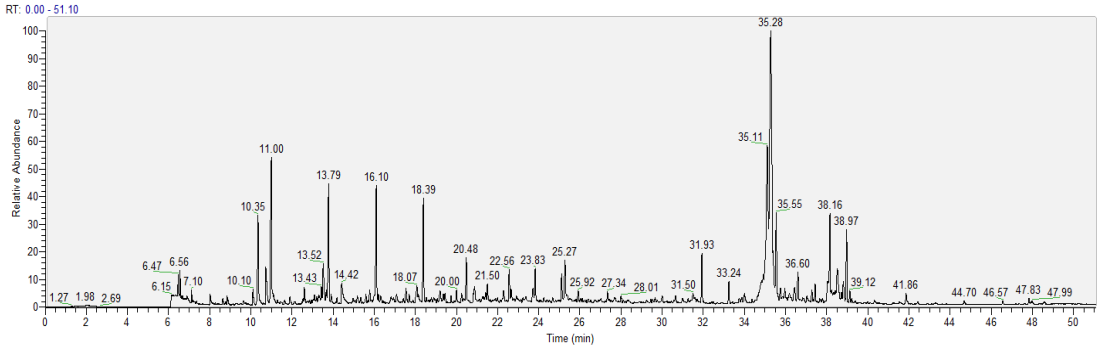

Figure 16: GC-MS chromatogram of ruthenium-catalysed bio-oil fraction

Table 15: Possible compounds identified from GC-MS chromatograms

RT (min)	Main Fragments	Compounds*:
6.45 ; 6.50	91, 79, 106	x-Xylene
8.66	94, 66, 65	Phenol
10.40	99, 129, 101	Levulinic Acid
11.05	109, 124, 81	Guaiacol
13.55	101, 129	Succinic Acid
13.80	138, 123, 95	4-Methylguaiacol
14.44	110, 64	Catechol
15.82 ; 16.10	137, 152	p-Ethylguaiacol
16.82	124, 123, 78	4-methyl-pyrocatechol
18.08 ; 18.40	137, 166	2-methoxy-4-propyl-phenol
18.15	164, 137	Eugenol
19.35	151, 152	Vanillin
20.48	164, 149	2-methoxy-4-(1-propenyl)-(Z)-phenol
21.52	151, 166, 123	Apocynin
22.57	137, 180, 122	Guaiacylacetone
23.84	151, 196	Vanillic Acid
25.29	137, 182, 138	4-hydroxy-3-methoxy benzenepropanol
35.20	55, 69, 83 ,97	Ethyl Oleate

**Compounds identified using Thermo Fischer Xcalibur Library, and published work of Farhan Hashmi (2017).*

The compounds recognised, in all three chromatograms, correlate with findings in literature (Holladay et al., 2007; Huang et al., 2014; Ma et al., 2014). These are common depolymerisation products from the thermochemical processing of lignin. Phenolic products such as guaiacol, catechol, their derivatives, vanillin and vanillic acid are clearly present. Levulinic acid is a by-product of the heating of C6 sugars, notably glucose and fructose, and formed from the residual carbohydrate present in the lignin mass. These results most likely confirm the presence of the listed compounds but quantifying them would have required a significant amount of further analytical work, which was not possible within the timeframe of this work.

9.2.5 Fourier-Transform Infrared Spectroscopy

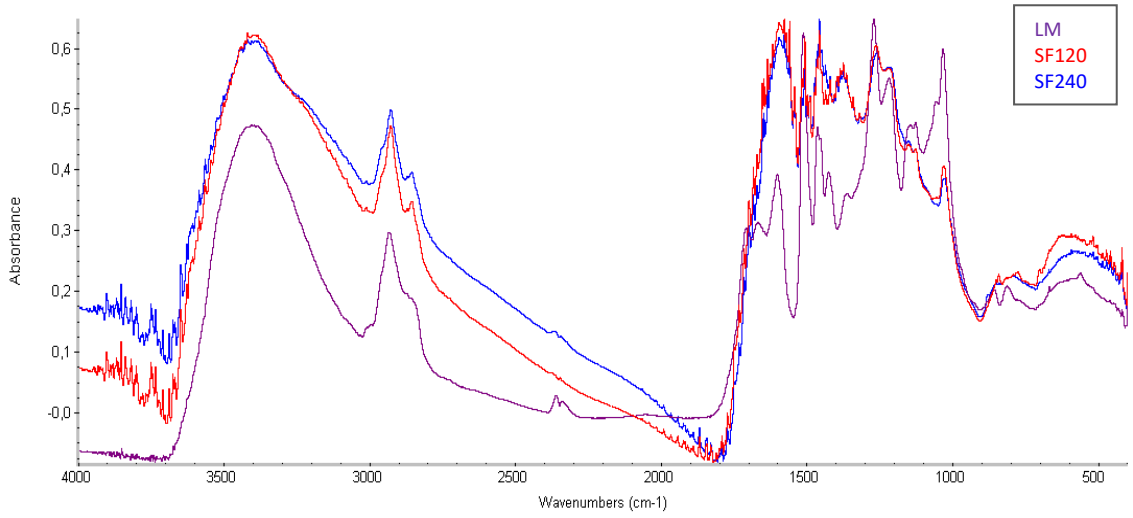

Figure 17: FTIR spectrum of Lignin Mass, 120 min and 240 min uncatalysed solid fractions (SF120 and SF240 respectively)

FTIR analysis was attempted in order to determine the chemical structure of the solid fraction of the ethanolysis runs, the results of which are portrayed in Figure 17. The question arose is the solid fraction contained primarily unreacted lignin mass, or condensation products, i.e. depolymerisation products which have condensed into agglomerate compounds. Indeed, was the change in colour, from brown to black, due to chemical changes within the material or simply a morphological change? In answer to this, the FTIR spectra clearly reveal similarities between the lignin mass and the 120-, 240-minute solid fractions. Indeed, the solid fractions both reveal similar absorbance, and notably peaks, to the lignin mass spectrum. This concludes that the solid fractions contain primarily unreacted/unreactive lignin mass. The variances further down the spectra infer to some minor chemical changes within the respective structures.

10 Conclusion

The ultimate goal of this thesis was to successfully characterise the lignin mass, compare it with other varieties of technical lignin, and gain insight into its depolymerisation mechanism in thermochemical ethanolysis. This was achieved by combining the information from the literature review, and experimental work.

Characterisation of the lignin mass was successful and thorough, yielding plenty of information about its structure, elemental composition, purity, as well as reactivity. Comparing these results with the technical lignin presented in the literature review provided valuable information about its differences and properties, as well as its advantages in term of refining options. The lignin proved of decent purity (>84 wt%). Combining these results with the absence of sulphur (<0.05%w) make this lignin mass an attractive candidate for further refining, despite a significant carbohydrate content (7.68 wt%). However, it would appear that the reactivity of the lignin mass suffered during the pretreatment step of the bioethanol process. In effect, the low methoxyl (<12%w) and ß-O-4 linkage content affirm that an extent of polymerisation took place during the pretreatment and saccharification steps of the process, the result being that the lignin mass is a combination of condensed lignin mass structures, and less reactive polymer chains. This correlates with data from the ethanolysis runs, in which the solid fraction contains primarily unreacted lignin mass.

The ethanolysis runs were successful, and the desired product fractions were produced: reflected in a decrease of molecular weight (Mw) from 1863 (LM) to 606-995 (bio-oil fractions). An energy-richer bio-oil fraction was produced with yields up to 18%, containing a full array of depolymerisation products, including phenolic compounds, detected in GC-MS analyses. The solid fraction remained significant throughout all experimental runs (>69%w), a consequence of the low reactivity of the lignin mass. Its energy content was significantly reduced (HHV of 17-22 kJ/g) in contrast to the initial

lignin mass (HHV of 25-26 kJ/g), a logical consequence of enriching the bio-oil/EtOH fraction (HHV of 31-32 kJ/g). Although the bio-oil yields were significantly less than found in articles of similar experiments (<20%), valuable information was nonetheless gathered.

A minor influence of the catalysts, 5%Ni/γ-Al_2O_3 and 5%Ru/γ-Al_2O_3 respectively, on the reactions was observed in the catalysed runs, but not to such an extent as to bear significance, except in the case of the resulting pressure in the autoclave after the ruthenium run. This is indicative that the formation of gaseous and lighter compounds was either catalysed or promoted by the presence of the catalyst. Analysis of the gaseous components would have offered more insight into this particular case.

From an economic perspective, the bio-oil and "biocrude" (bio-oil/EtOH mixture) are effectively higher value products in contrast to the lignin mass, in terms of energy content and as a fuel source. The solid fraction, although poor in energy content, displayed interesting features. It was formed as a fine black powder, inert and odourless. These characteristics, in combination with its significant carbon content, could make it a potential candidate for filtration purposes or as an additive to construction material, e.g. bitumen asphalt. As a candidate for specialty carbon or carbon fibre, the solid fraction is neither rich enough in carbon nor of high enough quality to be of any interest. The economic feasibility of this refining route depends entirely on the valorisation of all product fractions, due to the cost of energy required to partially thermochemically liquefy the lignin mass.

The lignin mass itself may prove of sufficient quality to utilise as such. The main advantage being that it is sulphur-free, and can possibly be utilised for its inherent antibacterial and hydrophobic properties. Naturally rich in phenolics, it could be considered for paints and resins. More research would be required to determine which properties are required for this application.

11 Recommendation for further studies

In the future, an interesting approach would be to explore if the reactivity of the lignin mass could be increased with a milder pretreatment step within the bioethanol hydrolysis process. In effect, a sweet spot in the operating conditions of the bioethanol process could be researched, in order to yield sufficient sugars for fermentation, as well as a reactive sulphur-free lignin. The latter could then be refined into higher value products, generating a second profit stream.

Considerable insight into the depolymerisation mechanisms presented in this work could be achieved by substituting the Lignin Mass by other types of reactive lignin, e.g. feedstock MWL (that has not yet undergone pretreatment), and other softwood MWL. This would shed more light on the relationship between the reactivity and structure of the Lignin Mass and the bio-oil yield. Such results could be compared to those presented in this work in hope of acquiring additional insight into the reaction pathways at hand, and how such a liquefaction process may be optimised.

This work focused on the thermochemical ethanolysis route as a candidate for lignin depolymerisation. Research into other thermochemical routes may prove worthwhile, although the reactivity, and condensed structure, of the lignin mass will most assuredly prove troublesome in other reaction pathways. As mentioned previously, possible direct applications of the Lignin Mass as a phenol-rich feedstock or source of natural polymers could be explored.

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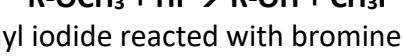
Appendices

Appendix 1: Methoxyl group determination

1. **Principle:**

In this instruction, the methoxyl group in lignin is quantified according to the Zeisel-Vieböck-Schwappach method, which is based on the quantitative reactions:

a. Methoxyl group is converted to Methyl iodide

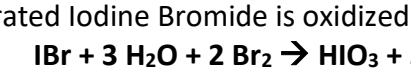


$R\text{-}OCH_3 + HI \rightarrow R\text{-}OH + CH_3I$

b. Methyl iodide reacted with bromine to methyl bromine

$CH_3I + Br_2 \rightarrow CH_3Br + IBr$

c. Liberated Iodine Bromide is oxidized to iodic acid

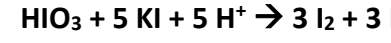


$IBr + 3\ H_2O + 2\ Br_2 \rightarrow HIO_3 + 5\ HBr$

d. Iodine is liberated from iodic acid

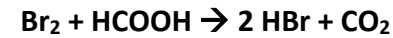
$HIO_3 + 5\ KI + 5\ H^+ \rightarrow 3\ I_2 + 3\ H_2O + 5K^+$

e. Liberated I_2 is titrated by sodium thiosulfate with starch as indicator



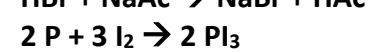
$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$

Other reactions occurring in the system:

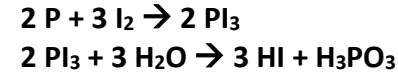


$Br_2 + HCOOH \rightarrow 2\ HBr + CO_2$

$HBr + NaAc \rightarrow NaBr + HAc$



$2\ P + 3\ I_2 \rightarrow 2\ PI_3$



$2\ PI_3 + 3\ H_2O \rightarrow 3\ HI + H_3PO_3$

2. **Glassware and chemicals**

2.1 Glassware:

- 3-necked flask, 100 mL
- Special condenser, exhaust pipe, stopper
- Nitrogen flow connection
- Oil bath (paraffin oil) with magnetic bar
- Heating plate (with temperature controller) + magnetic stirrer
- Lifters x3
- Laboratory grease (high vacuum quality, operable at -40 – 320°C)
- Single washing vessel
- Double washing vessel
- Tiny sample cups

2.2 Chemicals:

1. Titration indicator: Starch – $NaHCO_3$ (1:1 – v:v):
   1g starch + 100 ml distilled water. Boil then filtrate
   Saturated $NaHCO_3$ (ca. 9.5 g to 100 mL)
2. CH_3COONa / CH_3COOH:
   165.85 g $CH_3COONa.3H_2O$ + 834.1 CH_3COOH (>96%), heating 50 – 60°C
3. $Na_2S_2O_3$ 0.05N titrant:
   12.5 g $Na_2S_2O_3$ to 1L water (check exact normality)
4. Br_2 (handle with extreme caution)
5. KIO_3: 891.76 mg (99.7%) in 500 mL H_2O
6. CH_3COONa, dry (Oven 40°C)
7. HCOOH 5%
8. KI
9. HI
10. Phenol
11. P (red)
12. Acetic Anhydride
13. Vanillic acid
14. $NaHCO_3$ saturated (100 mL)

3. Procedure

Lignin sample is dried in the vacuum oven at 40°C overnight.

3.1 Blank

a. Prepare blank sample in an Erlenmeyer flask (addition exactly in the following order + well mixing):

- mL CH_3COONa/ CH_3COOH
- 0.5 mL Br_2
- 20 mL KIO_3
- ~150 mL water (increasing mixture volume for titration)
- 2 spatulas of dry CH_3COONa (< 0.5 g)
- 20 mL HCOOH (slow addition to the mixture)
- ~1 g KI

b. The blank sample flask is covered with glass disk and kept in dark place for exactly 10 minutes.

c. Blank sample is titrated by $Na_2S_2O_3$, with starch as indicator. The thiosulfate consumption should be about 20 mL (Colour change pattern: Brown → Yellow, indicator added → Blue → colourless).

3.2 Lignin sample

1. Assemble the glassware as shown in the picture **in the end of this instruction**
2. Oilbath is heated to 160°C
3. Cooling water flow ~200 mL/min (measure by graduated cylinder)
4. In 3-necked flask, add 2 spatula of phenol, 2 spatula of P, ~2 mL of acetic anhydride (with syringe)
5. Assemble the glassware, with the help of grease to make it tight
6. **Slowly** add 20 mL HI (with glass pipette)
7. Attached nitrogen inlet
8. Connect the condenser and the exhaust pipe (on top of the condenser)
9. Nitrogen flow 15 – 20 mL/min
10. Oilbath is lifted up to the 3-necked flask
11. Holding at 160°C for 90 minutes

In the meanwhile:

12. Weigh 15 – 20 mg of sample (amount according to the methoxyl group content) into tiny sample cup. Make at least duplicate
13. Weigh 15 – 20 mg vanillic acid, used as standard
14. Add 10 mL of CH_3COONa/CH_3COOH to the double washing vessel and 5 mL to the single one
15. Add 30 drops of Br_2 (using Pasteur pipette) in double washing vessel and 20 drops in the single one, mixing with the same pipette
16. Distribute the liquid between the two chambers in the double washing vessel

After 90 minutes:

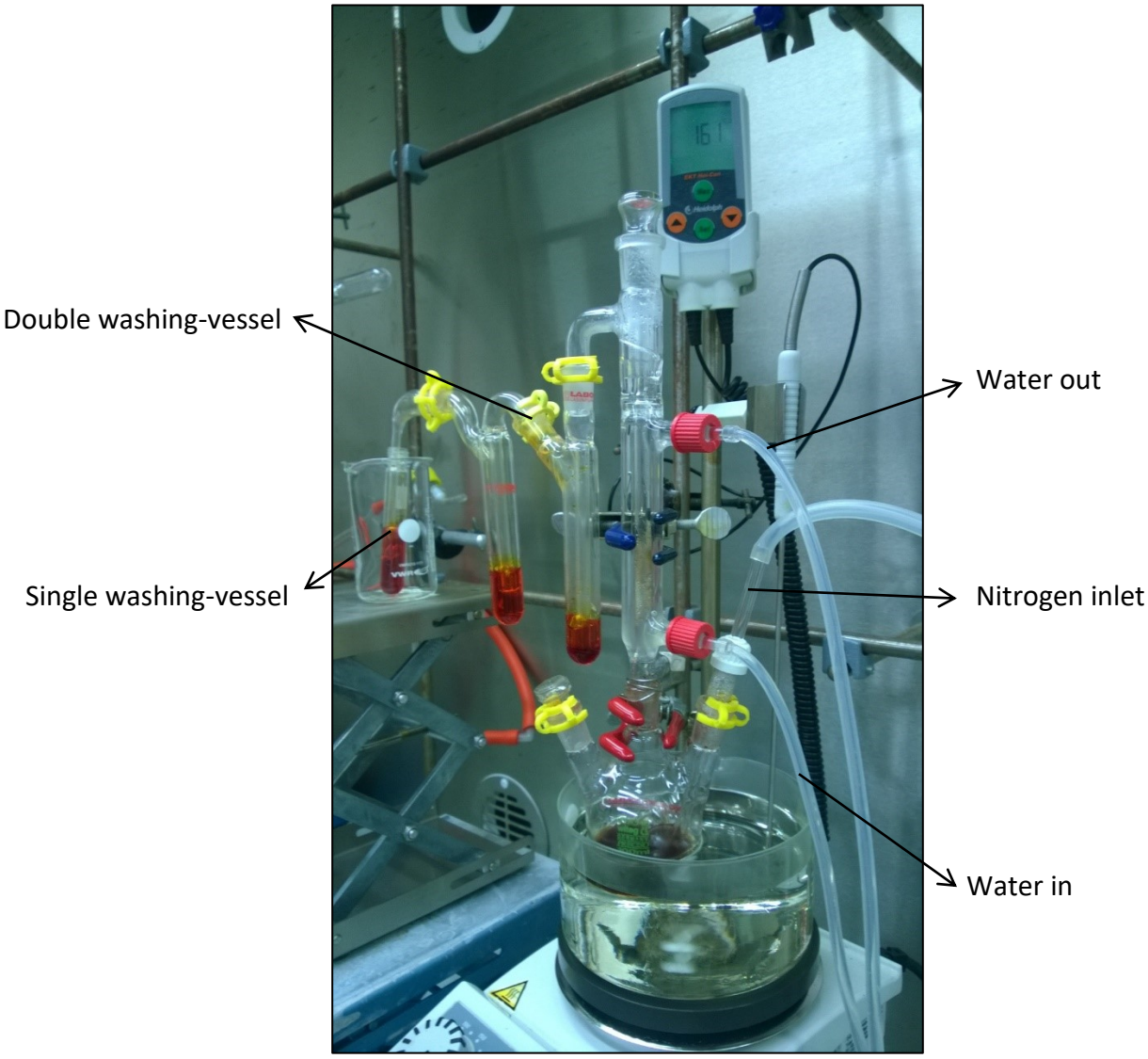
17. Washing vessels are connected together and to the condenser, supported by 2 lifters
18. Remove the exhaust pipe from the top of the condenser and fill half of the condenser with $NaHCO_3$
19. Close the condenser with stopper
20. Ensure there is N_2 bubbles in the washing vessels.
21. Rapidly slide the sample containing tiny cup with tweezers to 3-necked flask, close the neck, 45-minute reaction time
22. Transfer the liquid from both washing vessels to the Erlenmeyer flask with the help of distilled water
23. Add 2 spatula of dry CH_3COONa (< 0.5 g), 20 mL HCOOH (slow addition to the mixture) and ~1 g KI.
24. Add magnetic bar, cover the flash with the glass disk, keep in dark for exactly 10 minutes
25. Titration like with blank sample
26. Washing the excessive Br_2 with $Na_2S_2O_3$

4. **Calculation:**

$$\%MeO = \frac{0.258\left[\frac{mg}{mL}\right] \times V_{Na_2S_2O_3}[mL] \times \frac{20\ [mL]}{V_{Na_2S_2O_3(blank)}[mL]}}{m_{sample}[mg]}$$

0.258 is the correlation of the amount of methoxyl group equivalent to thiosulfate consumption

Apparatus Set-up:



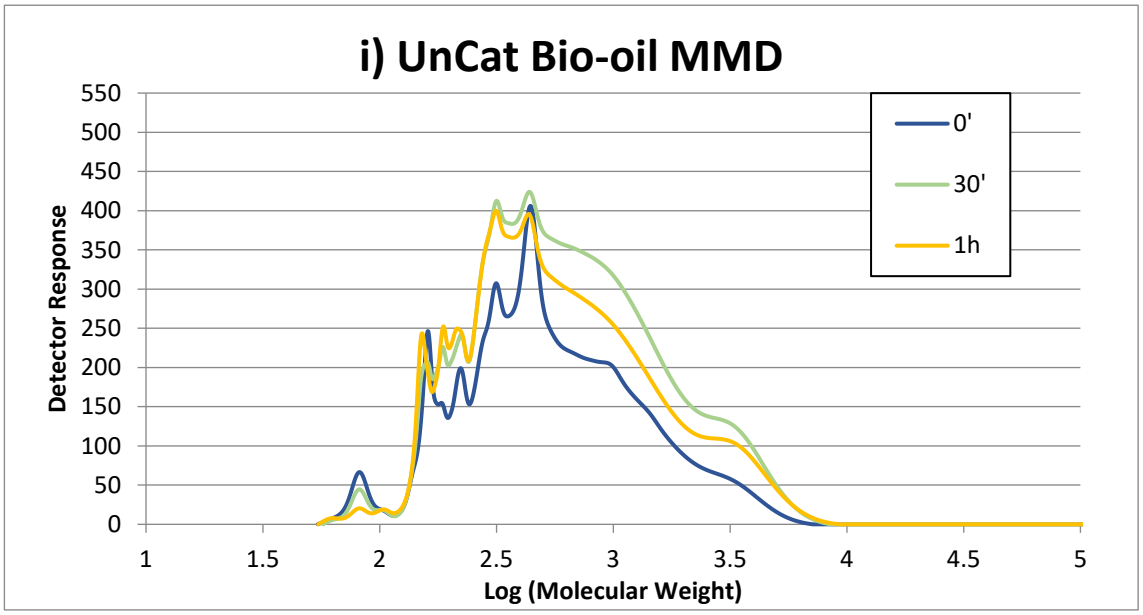
Uncatalysed runs product distribution:

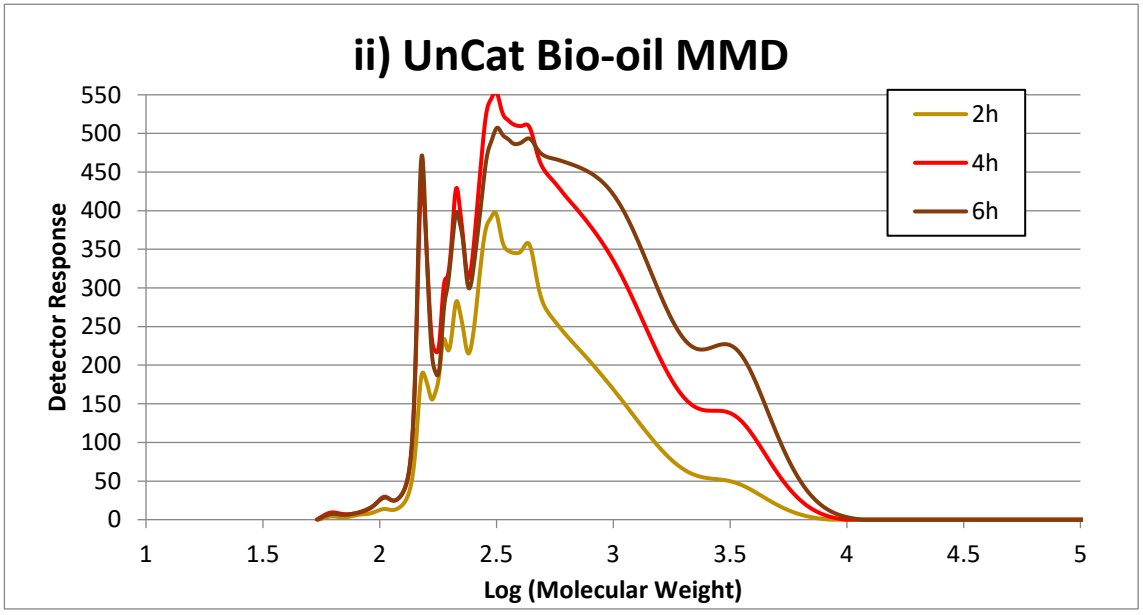
Reaction Time (min)	LM w(g)	LM w(%)	*BO* w(g)	*BO* w(%)	*RL* w(g)	*RL* w(%)	*Solids* w(g)	*Solids* w(%)	*Σweight* w(g)	*Σweight* w(%)
0	**10.002**	100.00 %	**1.011**	10.11 %	**0.507**	5.07 %	**10.666**	106.64 %	**12.184**	121.81 %
30	**10.000**	100.00 %	**1.177**	11.77 %	**0.321**	3.21 %	**9.948**	99.48 %	**11.446**	114.46 %
60	**10.001**	100.00 %	**1.227**	12.26 %	**0.389**	3.89 %	**9.575**	95.75 %	**11.191**	111.90 %
120	**10.003**	100.00 %	**1.513**	15.13 %	**0.198**	1.98 %	**7.127**	71.26 %	**8.839**	88.37 %
240	**10.009**	100.00 %	**1.808**	18.06 %	**0.220**	2.20 %	**7.306**	72.99 %	**9.334**	93.26 %
360	**10.003**	100.00 %	**1.665**	16.65 %	**0.302**	3.02 %	**6.920**	69.17 %	**8.886**	88.84 %

Catalysed runs product distribution:

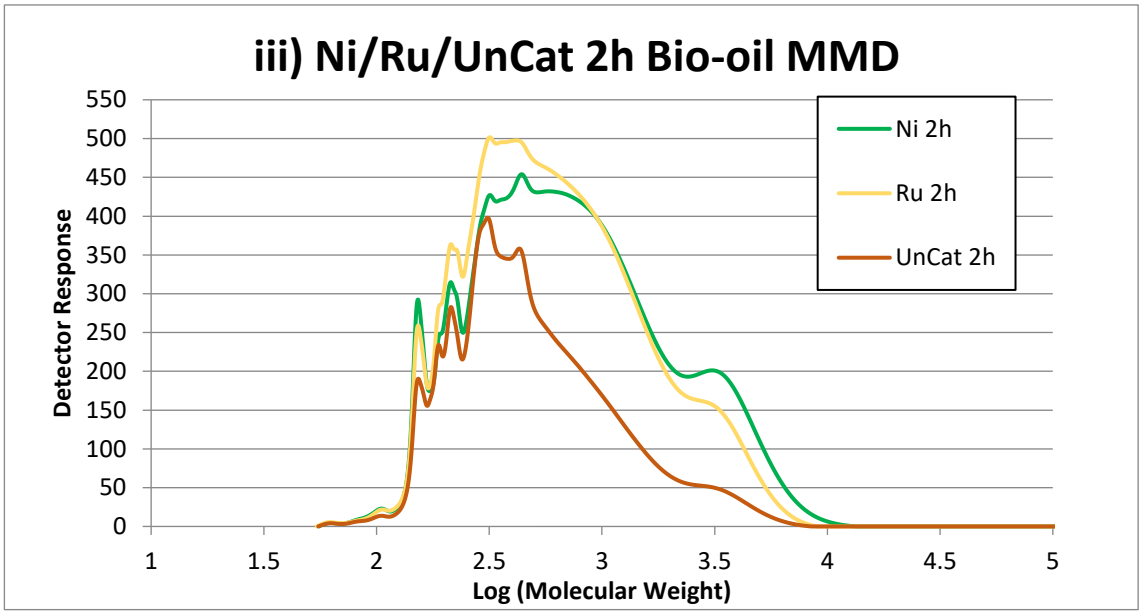
	LM w(g)	**LM w(%)**	***BO* w(g)**	***BO* w(%)**	***RL* w(g)**	***RL* w(%)**	***Solids* w(g)**	***Solids* w(%)**	***Σweight* w(g)**	***Σweight* w(%)**
Nickel	**10.001**	100.00 %	**1.422**	14.22 %	**0.130**	1.30 %	**8.140**	81.39 %	**9.693**	96.91 %
Ruthenium	**10.002**	100.00 %	**1.259**	12.59 %	**0.374**	3.74 %	**9.004**	90.02 %	**10.637**	106.35 %

Appendix 3: Molar mass distributions graphs (bio-oil fractions)





The graphs offer a visual representation of the molecular mass distribution over time. In effect, from t=0 to t=6h, significant changes occur, not only sheer quantity, but peaks disappear, e.g. Log(MW)~1.9, and new peaks appear, e.g. Log(MW)~2.25 and Log(MW)~3.5), indicative of the formation of new molecules.



This visual representation of the molecular mass distributions of the three 120-minute runs offers insight into the selectivity of the catalysts. Indeed, both catalysts appear to have promoted the formation of larger molecules, represented by the larger surface area under the curves between Log(MW)=2.5 and Log(MW)=4. However, neither catalyst proved significantly more selective in producing a certain rage of molecules, albeit a taller curve for the ruthenium catalyst.

Appendix 4: Risk Analysis Report

AALTO UNIVERSITY

School of Chemical Engineering

28.02.2017

OSKAR WEGELIUS (MASTER'S STUDENT)

LIQUEFACTION OF LIGNIN: RISK ANALYSIS

Supervisor: **Professor Herbert Sixta**

Instructor: **Lecturer Kyösti Ruuttunen**

Liquefaction of Lignin:

RISK ASSESSMENT REPORT:

1. Description of Work

1.1 Experiment

1.2 Scheduling

1.3 Operators and their training

1.4 Supervisor & Back-up

1.5 Laboratory

2. Properties of the Gases, Chemicals and Materials in Use

3. Equipment

3.1 Flowcharts, instructions and Special Safety Accessories

3.2 Emergency Shutdown Procedure

3.3 Person in Charge of Equipment

4. Working Place

5. Risk Assessment Table

Appendices:

Appendix 1: Reactor Specifications

Appendix 2: Laboratory Layout *(removed – not relevant)*

Appendix 3: Gas Alarm System *(removed – not relevant)*

Appendix 4: INERGEN Gaseous Extinguishing System *(removed – not relevant)*

Appendix 5: Additional Safety Information

Appendix 6: Materials Safety Data Sheets *(removed – not relevant)*

1. Description of Work

1.1 Experiment

Uncatalysed and Catalysed Ethanolysis of Lignin in Supercritical Ethanol

Risk Assessment Work Description:

Liquefaction experiments will be performed in a 'PARR 4575 A' batch reactor (see Appendix 1: Reactor Specifications for details) with a 4848 reactor controller. It has an inner volume of 500 mL with a capability of reaching temperature up to 500°C and pressures up to 34.5 MPa.

The reaction mixture will consist of a lignin sample and ethanol with and without a catalyst (5% Ru/γ-Al_2O_3 or 5% Ni/ γ-Al_2O_3). All of the latter will be transferred to the vessel at room temperature.

The reactor will be purged thrice with Nitrogen to remove air then pressurised to 2 MPa below the Proportional Pressure Relief Valve's limit for a minimum of 4 hours to test for leakage.

The T316SS Flexible Graphite Gaskets (see section 3 for details) will be checked for wear and tear, and be replaced if need be.

Once the seals have been verified, the contents of the reactor will be heated from room temperature to the set temperature. Once at the desired temperature, the reaction will continue until reaction time has been reached.

Once the Reaction time has been achieved, the Reactor will be allowed to cool down to room temperature by turning off the heater and running water through the cooling apparatus inside the reactor vessel. A gaseous sample can be obtained at this stage by securing a clean Gas Sampling Bomb to the inlet above the reactor. Once attached, the corresponding valve can be opened to fill the Sampler, and then closed and Sampler removed. After releasing the gas pressure through the safety relief valve and carefully flushing with Nitrogen, the reactor will be unlocked.

The reactor vessel will be covered with a cap to prevent any spill during its transfer to the fume cupboard, where, once the contents have been transferred to a suitable container, it will be filled and rinsed with a Deconex/Water solution. This same solution will be recovered and reused until dirty. NaOH can be used to clean problematic stains and deposits, if such were formed. The product mixture containing the bio-oil, liquid phenolic products (see Appendix 5) and unreacted lignin will be collected and analysed.

The effects of reaction time, pressure, temperature and loading will be tested with varying amounts of ethanol. Reactor operating condition are as follows:

Reaction Conditions:

Reaction Time	30 – 480 min
Reaction Pressure (Resulting)	4 – 10 MPa
Reaction Temperature	260 – 300°C
Ethanol	10 – 100 mL
Lignin	1 – 10 g
Heterogeneous Catalyst*	0 – 1 g

(*5% Ru/γ-Al_2O_3 or 5% Ni/γ-Al_2O_3)

1.2 Scheduling

Work in the laboratory shall take place during office hours, i.e. 8-16:00. If supervision is available, the working hours may be extended by a couple of hours. However, Experiments will not be performed overnight, nor over the weekend. Pressure testing of the reactor may be performed overnight, once it has been verified that the procedure is safe and contained. A note will be clearly exposed on the reactor chamber door, if an experiment is in progress, or if there is pressure in the reactor.

1.3 Operators and their training

Operators should have a background in chemical engineering, chemistry or previous experience with similar reactors. Time is required for the training of new operators. This is due to the complex apparatus and numerous components, not to mention safety issues. It should be performed by the person in charge of the equipment. Special training should be given to new operators handling carcinogenic or hazardous materials.

1.4 Supervisor & Back-up

Laboratory Supervisor: (to be determined)

"Back-up": When possible, the "back-up" person should be another operator of the apparatus. If not available, a supervisor from the School of Chemical Technology is suitable.

1.5 Laboratory

Equipment is located in Chemistry building, in room F309, in bunker 6. See Appendix 2.

2. Properties of the Gases, Chemicals and Materials in Use

Personal protection required consists of a laboratory coat, safety goggles, and nitrile rubber gloves. During the loading and emptying of the reactor, a protective visor, leather gloves and a disposable filter mask should be used. The filter mask will protect the operator from glass fibre dust from the insulation material, as well as chemical dust and volatiles when handling the reagents. If handling hazardous materials and catalysts, the filter mask is mandatory.

An 'Inergen' Fire Safety System is installed in the bunker (reactor chamber). The System extinguishes fire with by purging the reactor chamber with inert gas. It is initiated when both the spark and smoke alarms are triggered. Photographs with Flash and opening window blinds is strictly forbidden, as they can trigger the Inergen spark detector.

Fire extinguishers and fire blankets are available outside the reactor chamber, along with an emergency shower, a first aid kit, and an emergency button (another is located within the reactor chamber).

Chemical waste from the experiments is to be collected in an appropriate glass or plastic bottles. The pressure, temperature and contents of the bottles must be checked to ensure no side-reactions are taking place. Once verified, they must be delivered to the waste room in the Forestry Products Building "Puu", from where they are delivered to a waste treatment facility. It is imperative to label the contents of waste bottles. Samples and chemicals should be stored in a cool place. Containers should be sealed, and stored in a dry and ventilated space (i.e. fume cupboard).

The labelling on the waste bottle must have the following:

- Name
- Chemicals
- Date
- H Codes
- Transport Safety Number: UN Number (MSDS section 14.1)
- Transport Hazard Class(es): ADR/RID (MSDS section 14.3)
- Packaging Group (MSDS section 14.4)

3. Equipment

3.1 Flowcharts, instructions and Special Safety Accessories

Temperature and Pressure Limits can be set for the Batch Reactor, which, once reached, shut down the heating of the reactor vessel. As mentioned previously, H_2 and O_2 detectors are present in the reactor chamber, alongside the Inergen spark and smoke detectors. The latter will automatically set off an alarm once triggered which will shut off all feeds to the whole bunker, if H_2 levels increase considerably, or if O_2 level is dangerously low. The Autoclave is currently fitted with QTT1100P 'KLINGERgraphite' PSM (75,7/63,6x1,5) gasket seals (see photo below for specifications).

Furthermore, the batch reactor itself is equipped with a *Manual 20 MPa Pressure Relief Valve*, and a *Rupture Disc* Valve in case of drastic pressure increases. These safety valves allow discharge of excess pressure and gaseous components out of the bunker were the pressure to reach dangerous levels.

An additional *20 MPa Proportional Pressure Relief Valve* will be installed on the Reactor prior to the aforementioned experiments. In effect, the valve will open if the pressure surpasses the 15 MPa Pressure Limit, and shut when the pressure is below the threshold. This safer valve will act as a safeguard were the pressure to increase rapidly. As it is automatic, it does not require any manipulation, and does not require an operator inside the reactor chamber.

Reactor Flow Diagram:

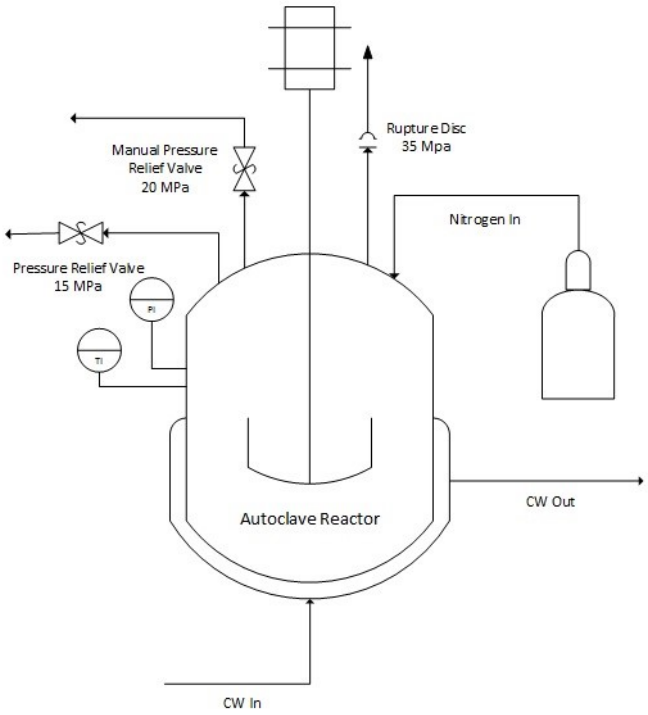


Photo of KLINGERgraphite PSM Gasket Order & Specifications:


KLINGER Ramikro

Lähetyslista 315936 14.04.2015

Sivu 1/1

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Tilaajan tilausnro	T10404-6750
Tilausnumero	TNY115 / 1145
Toimitusehto	NOL Masala FIN01
Toimitustapa	POSTI 14
Toimituspäivä	14.04.2015
Tilaajan viite	Seppo Jääskeläinen
Viitteemme	Tony Nyholm
Lähetyslistan nro	315936

Pos	Erittely		Toimitetaan	Jälkitoimitettu
10	QTT1100P 75,7/63,6x1,5 KLINGERgraphite PSM	kpl	100.00	100.00

Experiment Procedure:

- Dress fully in Protective Attire (especially in Reactor Chamber)
- Check on Reactor and components for 'Wear and Tear'
- Clean Reactor and Components if necessary
- Weigh necessary reactants (fume cupboard)
- Fill autoclave reactor (fume cupboard)
- Fix and Seal the reactor
- Flush with nitrogen no less than 3 times to check for instant leaks and to remove air
- Fill with nitrogen to 2 MPa under Proportional Pressure Relief Valve Limit (i.e. 15 MPa)
- Leave for a minimum for 4 hours (or overnight) to verify no pressure leaks: compare pressure gauge values and derive an average pressure drop per hour
- (If the Pressure leakage is significant: release the gases, check the reactor and apparatus, and re-affix and reseal – repeat pressure tests)
- Release Nitrogen to lower pressure to 1 MPa (carefully, gradually to avoid flash)
- Double-Check input values in Control Screen:
    - Temperature set to 270°C
    - Alarm Temperature at 320°C
    - Alarm Pressure at 15 MPa
    - PID active with Heat/Cool option
- Activate Reactor equipment: Reactor and Stirrer Cooling Water cycles, and finally Heater
- Monitor Reactor for the duration of the Experiment (4 to 8 hours)
- Once the experiment is complete, turn off the heater
- The cooling time is approximately 2 hours
- With drop in Temperature, the Pressure in the reactor will drop
- The cooling water for both the reactor and stirrer must still be on.
- (Once sufficiently cool, a gas sample can be taken with the help of a Gas Sampler Bomb for analysis – see 1.1)
- After Cooling, release excess pressure and discharging gaseous components
- Carefully open the seal and open the reactor
- Transport the reactor to the fume cupboard
- Transfer contents to respective beaker/decanter overnight for phase separation
- Clean Reactor and Apparatus with NaOH, Deconex or Acetone, and check for Wear and Tear. NaOH should be applied to specific stains, whilst the apparatus (i.e. stirrer) can be submerged in the vessel filled with a Deconex/Water solution.
- Turn off cooling water to reactor and Stirrer

- Contents will be stored accordingly for further analysis and characterisation.

Note: 'Wear and Tear' refers to char, deposits, dirt, corrosion or any damage to equipment

3.2 Emergency Shutdown Procedure

In emergency, shut down power from the bunker by pressing an emergency shutdown button. There is one both inside and outside of the bunker. The button on the inside is at shoulder height on the left side of the door, looking from the outside. The button on the outside is on the control box located on the left side of the door at approximately waist height. After shutdown, ensure no gas is supplied to the specific bunker chamber by closing respective gas bottles and valves.

3.3 Person in Charge of Equipment

Master's Student Oskar Wegelius
(details removed)

4. Working Place

The 'Parr 4575 A' batch reactor is located in the Chemistry building, in room F309, in bunker 6. Due to the flammable and potentially explosive chemicals and gases involved, the reactor chamber is fitted with an 'Inergen' Fire extinguishing system.

5. Risk Assessment Table

Workplace	Chemistry Building Laboratory Bunkers - School of Chemical Technology - Aalto University			
Risk Assessor(s).	Oskar Wegelius		Title: Master's Student	Assessment Date:
Title of Project:	Liquefaction of Lignin			Review Date:
Title of Procedure:	Un-/Catalysed Ethanolysis			
Frequency of Procedure:	One Experiment per day + Pressure Test + Reactor Cooling time		Duration of Procedure: 30 - 480 mins	
Complete for each chemical referring to the (Material) Safety Data Sheet (M)SDS				
Chemical (and concentration if applicable)	Hazardous Chemical / Substance?	Classification (1999/45/EC)	CAS (UN) number	Volume or Quantity (mL or g) used in Procedure
Ethanol	YES	H225 H315 + H320 H335, H401	64-17-5 (ADR/RID:1170)	10-100 mL
Lignin	NO	P261	N.A.	1-10 g
Nitrogen	YES	H280	7727-37-9 (ADR/RID:1066)	N.A.
Sodium Hydroxide	YES	H290, H314, H318, H402	1310-73-2 (ADR/RID:1823)	N.A.
Deconex® 11 Universal	YES	H290 H315 H319	1310-58-3 (ADR/RID:3266)	N.A.
Ruthenium/ Alumina Catalyst	NO	(P261)	7440-18-8	0.5-5 g
Nickel/ Alumina Catalyst	YES	H305, H316 H317, H320 H335, H350	7440-02-0	0.5-5 g

2. Exposure Controls		
Appropriate laboratory facilities provided:	YES	NO
- Fume Cupboard	X	
- Inergen System (see Appendix 4)	X	
- Gas and Spark Detectors (see Appendix 3&4)	X	
- Flammable Cabinet(s)	X	
- Reactor Chamber (Bunker) (See Appendix 2)	X	
- Fire Extinguisher	X	
Personal Protective Equipment Supplied:	YES	NO
- Laboratory Coat / Flame retardant Antistatic Protective Coat	X	
- Protective Gloves	X	
- Enclosed Footwear	X	
- Safety Eyewear Suitable to Purpose	X	
- Face Visor	X	

3. Step by Step Identification of Hazards and Required Risk Controls						
What Could Happen	**Potential Hazards**	**Consequence of Exposure**	**Likelihood of it occurring**	**Risk Rating**	**Controls Required**	**Controls Implemented**
1. Acquisition/Storage - Primary Sources and Samples						
Ethanol may Spill	Flammable	Detrimental	Unlikely	Moderate	Fume Hood, Fire Extinguisher	YES
Lignin Powder	Non Hazardous	Negligible	Unlikely	Minor	Nitrile Gloves, Safety Glasses, Lab Coat, Filter Mask	YES
NaOH solution may come in contact with the body.	Corrosive	Harmful	Unlikely	Minor	Nitrile Gloves, Safety Gloves, Lab Coat	YES
2. Preparation - Decanting and Transfer to Laboratory						
Ethanol may Spill during Decanting	Flammable	Detrimental	Unlikely	Moderate	Fume Hood, Fire Extinguisher	YES
NaOH may come in contact with the body during solution making	Corrosive	Harmful	Unlikely	Minor	Nitrile Gloves, Safety Glasses, Lab Coat	YES
Catalyst may come in contact with the body during preparation	Irritatant	Harmful	Unlikely	Minor	Nitrile Gloves, Safety Glasses, Lab Coat, Filter Mask	YES

3. Process - Use of Chemicals and Equipment						
Burn from hot reactor	Burns	Personal Harm	Unlikely	Minor	Cooling Period, Leather/Padded Gloves, Lab Coat	YES
Ethanol may spill during transfer to reactor vessel	Flammable	Detrimental	Unlikely	Moderate	Fume Hood, Fire Extinguisher	YES
NaOH may come in contact with the body	Corrosive	Harmful	Unlikely	Minor	Nitrile Gloves, Safety Gloves, Lab Coat	YES
Pressure leak may cause a release of chemicals/gases	Flammable / Corrosive / Toxic	Detrimental	Unlikely	Moderate	Pressure Test with Nitrogen at high P for min. 2 hours; Gas Detectors in Reactor Chamber; No Entry in to chamber during Reaction time	YES

Reactor may explode at high pressure	Flammable / Corrosive	Life Threatening	Unlikely	Major	Reactor placed in Bunker, No entry during Reaction, Pressure sustaining door, Safety Relief Valves, Rupture Valve, Automatic Shutdown of Reactor at High Temperature or High Pressure, Spark/Flame Detectors, Smoke Detectors, INERGEN system	YES
Explosion due to accumulation of flammable gases	Flammable	Life Threatening	Unlikely	Major	Reactor placed in Bunker, No entry during Reaction, Pressure sustaining door, Safety Relief Valves, Rupture Valve, Automatic Shutdown of Reactor at High Temperature or High Pressure, Spark/Flame Detectors, Smoke Detectors, INERGEN system, Gas Detectors (Hydrocarbons and Hydrogen)	YES

4. Waste - Handling, Storage and Disposal						
Waste solution from Reactor Washing	Flammable	Harmful	Unlikely	Moderate	Washing is performed in a Fume Cupboard and waste solutions safely collected in labelled glass bottles, which are deposited in the department's waste room for further disposal	YES
Condensate spill when emptying Vessel	Flammable, Irritating to Skin	Personal Harm	Unlikely	Minor	Nitrile Gloves, Safety Glasses, Lab Coat Fume Cupboard	YES

Appendices:

Appendix 1:

Reactor Specifications:

4575 REAKTORI PARR
4575A-FG-SS-M-230-VS.12-5000-4848B-A19254-MCM-PDM-HTM-CE/PED
MODIFIED WITH 10 MICRON FILTER INSTALLED IN DIP TUBE
Model No 4575 A High Pressure/High Temperature reaction apparatus 500 ml volume
rating MAWT 500C, MAWP 5000 psi / 345 bar
Fixed head design
Constructed of T316 stainless steel
FG Flat, graphoil head gasket
A1120HC series magnetic drive - 16 in lbs
Magnetic drive material T316 Stainless Steel
double valve with dip tube, gas release valve
Pressure gage range 345bar (5000 psi)
with 5000 psi (345 bar) pressure transducer
Inconel Rupture disc
rupture disc plain and rated at temperature
rupture disc rated 5000 psi

options listed below:
external thermocouple installed through heater
230 VAC, European
variable speed motor, 1/8 hp, 130 VDC
standard RPM pulley installed
grounded thermocouple/sensor, dual element
with optical tachometer sensor
CE compliant
Installed Mad Drive shield

4848B reactor controller
Tachometer with Motor Control DPM (MCM)
Pressure DPM (PDM)
Pressure in bar display
for use with 5000 psi (345 bar)(34,48MPa) Press Trans

Appendix 5: Additional Safety Information

Uncatalysed and Catalysed Ethanolysis of Lignin will be carried out in the Parr Autoclave Reactor. The reaction conditions require additional consideration to ensure the safety of the operator and laboratory premises. A list of key safety issue is listed below, and should be addressed before engaging in experiments and manipulation of the reactor:

1. Increase in Pressure due to Product Gases (see list of possible products at the end of this appendix)

The pressure in the reactor will increase due to the expansion and vapour pressure of the reactants: ethanol, the product gases and compounds formed by the reaction between lignin and ethanol. The experiments are expected to result in the formation of bio-oil and product gases, both of which are formed under high pressure (5-10 MPa) and high temperature (270-300°C). Furthermore, these high parameters have been set in order to allow ethanol to enter its supercritical phase. Hence, it is imperative to assess the permeability of the batch reactor thoroughly before manipulation, and test for pressure leakage in order to contain the volatile and pressurised products within the reactor.

Preventive Measure:

Based on Literature [1-10] and communication with a previous Operator, Doctoral Candidate Syed Farhan Hashmi who performed similar experiments, a *Manual Pressure Relief Valve* was installed on the reactor alongside a pressure and temperature indicator in order to prevent any complications caused by a sudden increase in pressure. The operating pressure of the Safety Valve installed is **20 MPa**.

An additional *15 MPa Proportional Pressure Relief Valve* will be installed on the Reactor prior to the aforementioned experiments. In effect, the valve will open and discharge gaseous contents out of the bunker, into the atmosphere, if the pressure surpasses the **15 MPa** (Pressure Limit, and shut when the pressure is below the threshold. This safer valve will act as a safeguard were the pressure to increase rapidly. As it is automatic, it does not require any manipulation, and does not require an operator inside the reactor chamber, in contrast to the *Manual Pressure Valve* mentioned above.

2. Flammable Material

Ethanol is a highly flammable chemical and must be handled with care, and adequate equipment, at all times. It must be stored and handled in a fume cupboard, far from heat sources, sparks, open flames, and heated surfaces. In case of an accidental spill and/or ignition, ensure adequate ventilation, remove all sources of heat/ignition and be wary of produced vapours, and the accumulation thereof that could result in an explosion.

Max volume of flammable gas, which could be produced from ethanol in case of an explosion:

Max Mass_{EtOH} = 137 g

MW_{EtOH} = 46.06844 g/mol

n_{EtOH} = 2.980 moles

The Ethanol will approach atmospheric conditions of temperature and pressure at the time of the explosion, and hence using the Ideal gas law: $V = \frac{nRT}{P}$

Where:	P =	101 kPa	= 101 000 Pa
	R =	8.314 J/(mol.K)	
	T =	25°C	= 298.15 K
	n =	2.98	
gives:	V =	0,073 m^3	= 73 L

Assuming the height of the bunker room to be 2.68m, Length 1.45m and Width 2.62m, the volume will be 10.2m^3. The volume percentage occupied by the ethanol vapour will be 0.74%.

LEL for ethanol gas (%V) = 3.3

UEP for ethanol gas (%V) = 19

Preventive Measures:

The reactor chamber is equipped with a fire alarm, smoke detector, spar detector, Inergen system, as well as gas detectors. Fire extinguishers can be found in the hallway outside the reactor chamber. Air is removed at a rate of 40L/s to avoid accumulation of gases.

3. Handling of Chemicals

5%Ru/γ-Al_2O_3 and 5%Ni/γ-Al_2O_3 Catalyst Handling and Preparation

The catalysts are not classified as hazardous, but care should be taken during handling and preparation. They should be stored in a securely sealed container in a dry and cool place, away from light. They can possibly cause mild skin inflammation depending on the severity of exposure. In case of contact with skin, remove contaminated clothing immediately and proceed to wash with soap and plenty of water. If the catalyst is in powdered form, use of a filter mask is compulsory, and extra care must be taken during handling.

Note: Nickel compounds have been classified as carcinogenic to humans.

Preventive Measures:

Adequate personal equipment must be available in the laboratory and in use when these catalysts are handled i.e. Laboratory coat, safety glasses, nitrile gloves and filter mask depending of the form (pellets or powder). One should undergo Laboratory Safety Training before conducting any experimental work including Sodium Hydroxide.

NaOH

Sodium hydroxide can be used for cleaning purposes, and is hazardous if in contact with skin. It should be stored in a securely sealed container in a dry and cool place. It can cause skin

inflammation and depending on the severity of exposure. In case of contact with skin, remove contaminated clothing immediately and proceed to wash with soap and plenty of water. If symptoms persist, immediately contact laboratory staff.

Preventive Measures:

Adequate personal equipment must be available in the laboratory and in use when this chemical is handled i.e. Laboratory Coat, Safety Glasses, Nitrile (or thicker) Gloves and Sealed Shoes depending of the concentration. One should undergo Laboratory Safety Training before conducting any experimental work including Sodium Hydroxide.

Nitrogen

Nitrogen is an inert gas, but can cause asphyxiation and suffocation in high concentrations. In effect, as a lighter gas, it will replace oxygen and effectively push other gases out of a sealed area. One can lose consciousness upon inhalation.

Preventive Measures:

The air in the reactor chamber is changed 11 times per hour to ensure an adequate supply of oxygen, and circulation of air. Moreover, Oxygen indicators are present in the bunker, and will reveal the concentration of oxygen in the room. The reactor chamber is equipped with a Blast door and seals to prevent any leakages of gases and flames.

Deconex:

Deconex 11 Universal is a mildly alkaline, liquid concentrate for the cleaning and decontamination of laboratory glassware. The product can be universally used in different sectors of the chemical industry as well as in routine analysis and medical diagnostics (Borer Chemie AG). It shall be used to clean the reactor vessel, the stirrer apparatus and glassware.

Preventive Measures:

Adequate personal equipment must be available in the laboratory and in use when this chemical is handled i.e. Laboratory Coat, Safety Glasses, Nitrile (or thicker) Gloves and Sealed Shoes depending of the concentration. One should undergo Laboratory Safety Training before conducting any experimental work including Deconex.

First Aid

First Aid supplies are available in the laboratory. No special requirements.

Emergency Reactor Shutdown

In case of an emergency shutdown, power to the reactor will be cut from outside the reactor chamber, by turning off the hardware and heater. Heating of the reactor vessel will cease, and the cooling system will be activated – cooling water will be circulated in the reactor jacket until cool.

In case of Temperature Runaway

The Reactor has three temperature sensors for handling temperature runaway. The first being a set temperature which regulated the reaction temperature. The second being a safety limit value, set beforehand, and above the set reaction temperature, beyond which power and heating to the reactor will be cut automatically. The third is a safety pressure gauge, which will do the same if the reactor pressure exceeds the set limit value.

If all the three controls above fail, the Proportional Pressure Relief Valve installed on the reactor will be triggered at 15 MPa, and discharge the gaseous contents of the reactor outside the building. Finally, yet importantly, a rupture valve has been installed during assembly of the apparatus, which will rupture at 35MPa and safely discharge the contents of the reactor into the environment.

The reactor may also be shut down manually by unplugging the electrical cable from the wall socket.

List of possible products from Catalytic Ethanolysis of Lignin:

Ethers:

- Ethyl-3-methylpentanoate $C_8H_{16}O_2$
- Ethyl hexanoate $C_8H_{16}O_2$
- Ethyl trans-3-hexenoate $C_8H_{14}O_2$
- Ethyl trans-2-hexenoate $C_8H_{14}O_2$
- Ethyl trans-2-octenoate $C_8H_{18}O_2$
- Ethyl trans-3-octenoate $C_8H_{20}O_2$

Alcohols:

- 2-ethyl-1-butanol $C_6H_{14}O$
- Trans-3-hexen-1-ol $C_6H_{12}O$
- Trans-2-methyl-2-hexen-1-ol $C_7H_{14}O$
- 1-Hexanol $C_6H_{14}O$

Arenes:

- P-Xylene C_8H_{10}
- O-Xylene C_8H_{10}
- 3-ethyltoluene C_9H_{12}
- Allyl-benzene C_9H_{10}
- 1,4-dimethyl-2-ethylbenzene $C_{10}H_{14}$
- 1-ethyl-2,4-dimethylbenzene $C_{10}H_{14}$

Benzyl Alcohols:

- Benzyl alcohol C_7H_8O
- 4-methylbenzyl alcohol $C_8H_{10}O$
- 2-methylbenzyl alcohol $C_8H_{10}O$
- 4-ethylbenzyl alcohol $C_9H_{12}O$
- 2,4,5-trimethylbenzyl alcohol $C_{10}H_{14}O$
- Hydrocinnamyl alcohol (3-phenyl-1-propanol) $C_9H_{12}O$
- 3-phenyl-1-butanol $C_{10}H_{14}O$

Monophenols:

- Guaiacol (2-methoxyphenol) $C_7H_8O_2$
- Creosol (4-methylguaiacol; 2-methoxy-4-methylphenol) $C_8H_{10}O_2$
- 4-ethylguaiacol (4-ethyl-2-methoxyphenol) $C_9H_{12}O_2$
- 4-propylguaiacol (2-methoxy-4-propylphenol) $C_{10}H_{14}O_2$

Aliphatic Ester:

- Ethyl caprylate (ethyl octanoate) $C_{10}H_{20}O_2$

Risk Analysis Report References:

[1] Hashmi, Syed Farhan, *Conversion of Lignin to Higher Value Products through Base Catalysed Depolymerization: Risk Assessment* – Aalto University, School of Chemical Technology

[2] David, F.B., Dodge, B.F., *Vapor-Liquid Equilibrium at High Pressures: The Systems Ethanol-Water and 2-Propanol-Water* – Journal of Chemical Engineering. Vol.4, No.2, APRIL 1959

[3] Ye, Y., Fan, J., Chang, J., *Effects of Reaction Conditions on Hydrothermal Degradation of Cornstalk Lignin* – Journal of Analytical and Applied Pyrolysis, 94 (2012) 190-195

[4] Mahmood, N., Yuan, Z., Schmidt, J., and Xu, C., *Production of Polyols via Direct Hydrolysis of Kraft Lignin: Effect of Process Parameters* - Bioresource Technology 139 (2013) 13-20

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[7] Ye, Y., Zhang, Y., Fan, J., Chang, J., *Selective Production of 4-Ethylphenolics from Lignin via Mild Hydrogenolysis* - Bioresource Technology 118 (2012) 648-651

[8] Zakzeski, J., Jongerius, A., Bruijnincx, P., Weckhuysen, B., *Catalytic Lignin Valorization Process for the Production of Aromatic Chemicals and Hydrogen* - ChemSusChem 5 (2012) 1602-1609

[9] Ma, R., Hao, W., Ma, X., Tian, Y., Li, Y., *Catalytic Ethanolysis of Kraft Lignin into High-Value Small-Molecular Chemicals over a Nanostructured α-Molybdenum Carbide Catalyst* – Angew. Chem. Int. Ed. 53 (2014) 7310-7315

[10] Patil, P.T., Armbruster, U., Richter, M., Martin, A., *Heterogeneously Catalyzed Hydroprocessing of Organosolv Lignin in Sub- and Supercritical Solvents* – ACS, Energy Fuels 25 (2011) 4713-4722