Valorization of lignin from biorefineries for fuels and chemicals

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VALORIZATION OF LIGNIN FROM BIOREFINERIES FOR FUELS AND CHEMICALS

DISSERTATION

FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

AT

THE TECHNICAL UNIVERSITY OF DENMARK
DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING

WRITTEN

BY

JOACHIM BACHMANN NIELSEN

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Abstract

Direct lignin liquefaction is a promising process for lignin valorization in which lignin is treated in a solvent at elevated temperature and pressure. Liquefaction of sulfur free lignin obtained as a waste product from 2nd generation bio-ethanol production can provide a sulfur free bio-oil which may substitute fossil fuel.

In this Ph.D. study the direct liquefaction of a biorefinery lignin (hydrothermally pretreated enzymatic hydrolysis lignin) is explored. The goal is to provide a bio-crude which can substitute marine diesel as the engines found aboard large ships are adapted to more crude fuels. A novel process, which easily integrates with existing biorefinery infrastructure, is presented. The process yields a lignin-diesel oil (LDO) by non-catalytic solvolysis in ethanol without hydrogen addition. The LDO is superior to pyrolysis oil as it is non-acidic, stable and readily blends with fossil diesel without the need for exhaustive deoxygenation.

Batch autoclave experiments on lignin supercritical solvolysis in ethanol revealed the effects of different reaction temperatures, reaction times and degrees of lignin loading on product yields and bio-oil quality. The highest oil yield of 50 $\text{wt\%}_{\text{d.a.f.}}$ was obtained for solvolysis of 10 g lignin for 8 h at 400 °C but 47 wt% of the solvent was also disadvantageously consumed. A lower reaction temperature and short reaction time (<1 h) yielded an improved tradeoff between oil yield and solvent consumption. In particular a high lignin:solvent ratio of up 1:2 (w:w), which is a previously unexplored domain of lignin solvolysis, provided a deoxygenated bio-oil with a low oxygen content of 9.7 wt% and an increasingly narrowed molecular size distribution dominated by species <300 g/mol (lignin monomers and dimers). Decarboxylation is the main contributor to deoxygenation as the majority of CO_2 comes from the lignin.

Solvent reaction routes were investigated in a separate study where different primary alcohols (methanol, ethanol, 1-propanol and 1-butanol) were used. Primary reactions responsible for solvent loss were direct decomposition to gas through decarbonylation, formation of light condensation products and incorporation of the alcohol into the bio-oil through covalent bonding. The latter may advantageously inhibit repolymerization and improve oil yield.

An economic study complemented the results of the parameter study and highlighted that optimum profitability is obtained with short reaction time, high lignin loading and lower reaction temperature such as 350 °C instead of 400 °C. The key challenges of lignin solvolysis in alcohols are optimizing liquefaction faction yield relative to solvent consumption and continuous processing may provide an improvement.

Resumé (Danish)

Direkte forvæskning af lignin er en lovende teknologi, hvor lignin bliver valoriseret ved behandling i et solvent ved forhøjet temperatur og tryk. Forvæskning af svovlfrit lignin, der kan fås som et restprodukt ved 2. generations bioethanolproduktion, kan give en svovlfri bio-olie, som kan substituere fossilt brændstof.

I dette Ph.D. studie bliver direkte forvæskning af bioraffinaderilignin (hydrotermisk forbehandlet enzymatisk hydrolyse lignin) udforsket. Målet er at lave en bioråolie, som kan substituere marinediesel, eftersom motorerne ombord på store skibe er tilpasset forbrænding af mere rå olier. En ny proces bliver præsenteret, som let kan integreres med eksisterende bioraffinaderiers infrastruktur. Processen giver en lignin-diesel olie (LDO) ved solvolyse i ethanol uden brug af katalysator og brint. LDO'en er af bedre kvalitet end pyrolyseolie da den ikke indeholder syre, er stabil og blandes let med fossil diesel uden at fuldstændig deoxygenering er nødvendig.

Batchautoklaveeksperimenter med ligninsolvolyse i superkritisk ethanol blev gjort ved forskellige reaktionstemperaturer, reaktionstider og mængder af lignin. Effekten på produktudbytter og oliekvalitet blev analyseret. Det højeste olieudbytte på 50 vægt% (tør askefri basis) blev opnået ved solvolyse af 10 g lignin i 8 timer ved 400 °C, men 47 vægt% af solventet blev også forbrugt. En lavere reaktionstemperatur og kort reaktionstid (<1 time) gav et forbedret tradeoff mellem olieudbytte og solventforbrug. Specielt et højt lignin:solvent forhold op til 1:2 (vægtforhold), som er et tidligere uudforsket domæne for ligninsolvolyse, gav en deoxygeneret bioolie med et lavt iltindhold på 9.7 vægt% og en indsnævret molekylstørrelsesfordeling bestående af lignin mono- og dimere (<300 g/mol). Deoxygenering sker fortrinsvis ved decarboxylering da størstedelen af CO_2 dannet kommer fra ligninen.

Solventets reaktionsveje blev undersøgt i et separat studie, hvor forskellige primære alkoholer (metanol, ethanol, 1-propanol og 1-butanol) blev benyttet. De primære reaktionsveje, hvorved solventet blev forbrugt, var ved direkte dekomponering til gas via decarbonylering, dannelse af lette kondensationsprodukter og inkorporering af alkoholen i bio-olien ved kovalent binding. Sidstnævnte kan fordelagtigt inhibere repolymerisering og forøge olieudbyttet.

Et økonomisk studie komplementerede resultaterne af parameterstudiet og understregede at optimum profitabilitet opnås ved kort reaktionstid, høj tilførsel af lignin og en lavere reaktionstemperatur såsom 350 °C i stedet for 400 °C. Hovedudfordringen ved ligninsolvolyse i alkoholer er at optimere olieudbyttet relativt til solventforbruget, og en kontinuert proces forventes at kunne forbedre dette.

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Preface and Acknowledgements

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Technical University of Denmark
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List of Publications & Conference Contributions

Articles in Peer-Reviewed Journals

Joachim B. Nielsen, Anders Jensen, Anker D. Jensen, *"Review on Reductive Direct Lignin Liquefaction Technologies and Mechanisms of Depolymerization"*, to be submitted, 2016

Joachim B. Nielsen, Anders Jensen, Line R. Madsen, Flemming H. Larsen, Claus Felby, Anker D. Jensen, *"Non-Catalytic Direct Liquefaction of Biorefinery Lignin by Ethanol: Bio Oil Yield and Quality"*, submitted, 2016

Joachim B. Nielsen, Anders Jensen, Christian B. Schandel, Claus Felby, Anker D. Jensen, *"Non-Catalytic Supercritical Alcohol Solvolysis of Biorefinery Lignin: Investigation of Solvent Consumption"*, to be submitted, 2016

Patents

Joachim B. Nielsen, Anders Jensen, Anker D. Jensen, *"Diesel–soluble lignin oils and methods of their production"*, WO2016113280 (A1), published 21 July 2016, (priority data: EP3045513 (A1), 13 January 2015)

Joachim B. Nielsen, Anders Jensen, Anker D. Jensen, *"Methods for continuous processing of lignin in supercritical alcohols"*, PA201600018, filing date: 12 January 2016

Non-Peer-Reviewed Articles

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Conference, Symposium and Workshop Presentations

*Presenter is marked by **

Joachim B. Nielsen*, Anker D. Jensen, Peter A. Jensen, Niels O. Knudsen, John Nielsen, Matthias J. Beier, *"Liquid fuel production through direct liquefaction and catalytic hydrodeoxygenation of lignin",* oral presentation at: Catalysis for Sustainability, 2013, Kerkrade, The Netherlands

Joachim B. Nielsen*, Anker D. Jensen, Niels O. Knudsen, *"Liquefaction of Biorefinery Lignin"*, oral presentation at: 2nd Brazilian-Danish Workshop on Biorefineries, 2014, Copenhagen, Denmark

Joachim B. Nielsen*, Niels O. Knudsen, Anker D. Jensen, *"Liquid Fuel Production from Lignin Solvolysis by 2-Propanol"*, poster presentation at: Renewable Chemicals from Lignin, 2014, London, England

Joachim B. Nielsen*, Anders Jensen, Claus Felby, John Nielsen, Anker D. Jensen, *"Liquid fuel production through direct liquefaction of lignin"*, poster presentation at: 4th International Congress on Green Process Engineering, 2014, Seville, Spain

Joachim B. Nielsen*, Anker D. Jensen, Niels O. Knudsen, *"Liquid fuel production from lignin solvolysis by 2-propanol"*, poster presentation at: 3rd International Symposium on Green Chemistry, 2015, La Rochelle, France

Joachim B. Nielsen*, Anders Jensen, Anker D. Jensen, *"Lignin Ethanolysis, A non-catalytic route to a green diesel"*, oral presentation at: Workshop on the use of lignocellulosic biomass, 2016, Odense, Denmark

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Anders Jensen, Joachim B. Nielsen, Anker D. Jensen, John Nielsen, Claus Felby*, *"The influence of pre-treatment methods upon the molecular weight and structure of lignin"*, poster presentation at: 36th Symposium on Biotechnology for Fuels and Chemicals, 2014, Clearwater FL, USA

Claus Felby*, Joachim B. Nielsen, Yohanna Cabrera, Anker D. Jensen, Anders Jensen, *"Lignins from biochemical processing of lignocellulose – structure and potential applications"*, oral presentation: 37th Symposium on Biotechnology for Fuels and Chemicals, 2015, San Diego CA, USA

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Abbreviations

AnH2	9,10-dihydroanthracene
APR	Aqueous phase reforming
ASTM	American standard test method
BCD	Base catalyzed depolymerization
BDE	Bond dissociation energy
CP	Cross polarization
CSTR	Continuously stirred tank reactor
d.a.f.	Dry and ash free
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
ECA	Emission control area
FID	Flame ionization detector
FT-ICR	Fourier transform ion cyclotron resonance
G	Guaiacyl
GC	Gas chromatography
H	*p*-hydroxyphenyl
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HHV	Higher heating value
HMBC	Heteronuclear multiple-bond correlation spectroscopy
HRI	Hydrocarbon Research Institute
HSQC	Heteronuclear single-quantum correlation spectroscopy
HTL	Hydrothermal liquefaction
IL	Ionic liquid
LDO	Lignin-Diesel oil
LHV	Lower heating value
MARPOL	International Convention for Prevention of Pollution From Ships
MAS	Magic angle spinning
MEC	Maabjerg Energy Center
MS	Mass spectrometry
NIST	National Institute of Standards and Technology
NMR	Nuclear magnetic resonance
NREL	National Renewable Energy Laboratory
o.d.	Outer diameter
PAH	Polyaromatic hydrocarbons
PCT	Patent Cooperation Treaty
S	Syringyl
SCF	Supercritical fluid
SD	Standard deviation
SEC	Size exclusion chromatography
SP	Single pulse
TCD	Thermal conductivity detector
THF	Tetrahydrofuran

TOCSY	Total correlation spectroscopy
TPPM	Two pulse phase modulation
ULSD	Ultra Low Sulfur Diesel
USD	U.S. Dollar
UV	Ultraviolet
WGS	Water gas shift

CHAPTER 1

Introduction

Climate change is a major challenge and biofuels are part of the solution to reduce CO_2 emissions from trucks, shipping and aviation as there are no other realistic alternative fuel technologies. The production of 2nd generation bioethanol converts non-edible plant biomass to a sustainable liquid fuel. The lignin, comprising up to 30 % of the plant biomass, is the biggest by-product from this process. Currently lignin is just burned as a low value solid fuel.[1]

A lot of lignin valorization research targets fine chemical production;[2,3] however, such processes often have low yields of specific compounds and require difficult and expensive separation. Another approach may be to use the heterogeneous nature of the lignin polymer in a reductive depolymerization as a path towards fuels. This often involves expensive catalysts and hydrogen for exhaustive deoxygenation.[4] Therefore a simple non-catalytic process for lignin liquefaction, that yields a bio-crude that blends well with fossil fuel, is needed. This is particularly relevant for combustion in large two stroke engines, such as those found aboard large ships, as these are adapted to crude fuels. In this context, it is highly relevant that biorefinery lignin in particular provides a substrate for production of sulfur-free biofuels as environmental demands for low sulfur emissions from ships in coastal areas are increasing. Commercial lignins such as Kraft lignin contain sulfur and are less suitable for fuel production.

Use of lignin rich feedstocks instead of whole biomass is a challenge in pyrolysis technologies as it typically results in lower oil yields and increased charring.[5] Solvolysis is a direct liquefaction process in which lignin rich biomass is treated in a solvent at elevated temperature and pressure. Solvolysis of lignin is of growing interest and provides improved yields and oil quality relative to pyrolysis.[4,6] Solvent consumption is however an often overlooked parameter. In particular for non-catalytic solvolysis the cost of solvent may exceed the value of the depolymerized lignin product and therefore undesired solvent consumption can hinder commercial viability.

The goal of this Ph.D. study is to valorize lignin from biorefineries for chemicals and fuels. A process was designed in which enzymatic hydrolysis lignin (biorefinery lignin) is solvolytically treated in ethanol resulting in a depolymerized and deoxygenated liquid fuel. This process allows for easy integration into existing biorefineries, as both lignin and ethanol are product streams (see Figure 1.1). The lignin-diesel oil (LDO) process does not require catalyst or added hydrogen.

In this thesis direct lignin liquefaction technologies and depolymerization reactions in solvent media are reviewed. A series of experiments were designed to investigate the effects of ethanol solvolysis of lignin. The effect of various reaction parameters on product yields and oil quality are discussed. The mechanisms of solvent consumption are highlighted and discussed in a study where different primary alcohols are used as solvent (methanol, ethanol, 1-propanol and 1-butanol). Finally the LDO process is evaluated for commercial viability with a simple economic assessment on value gain from outputs minus inputs. The thesis is concluded with suggestions for future work.

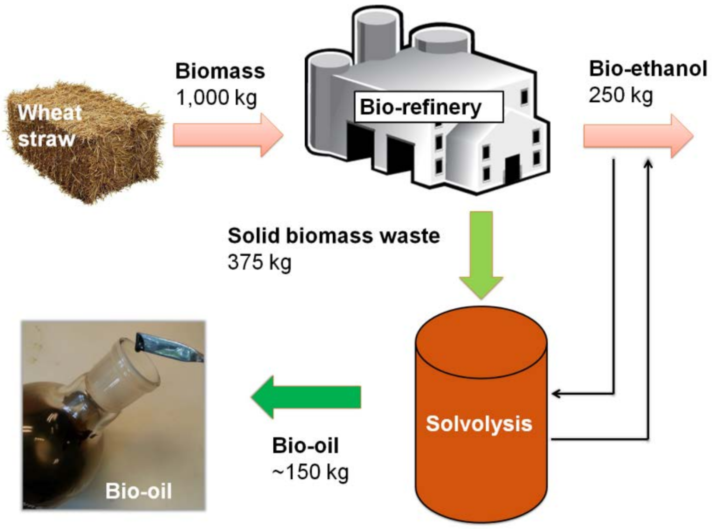


Figure 1.1 Integration of the ethanol solvolysis process in a biorefinery concept with typical yields from processing 1,000 kg wheat straw. Waste streams such as water, gas and biochar have been omitted for simplicity. The bio-oil product depicted is the actual product of this study.

1.1 Outline of Thesis

The thesis is written as a monograph. Journal articles as described on page xv comprise the majority of the thesis and have been included as individual chapters with only minor modifications. Abstracts and partially introductions have been omitted to avoid redundancy. An outline of the contents of each chapter is given below:

CHAPTER 2 is a review on state of the art direct lignin liquefaction technologies and reactions involved in lignin depolymerization in solvent media. The chapter comprises the article *"Review on Reductive Direct Lignin Liquefaction Technologies and Mechanisms of Depolymerization"*. The chapter provides the theoretical background for the thesis.

CHAPTER 3 describes the experimental setup and procedures used in this study. Analytical methods and definitions of product yields and quantification methods are described.

CHAPTER 4 is a parameter study on lignin solvolysis by supercritical ethanol. The chapter comprises the results and discussion from the article *"Non-Catalytic Direct Liquefaction of Biorefinery Lignin by Ethanol: Bio Oil Yield and Quality"*. The effect on product yields and oil quality is discussed when the lignin solvolysis is subjected to different reaction temperatures, reaction times and degrees of lignin loading.

CHAPTER 5 is a study on mechanisms of solvent consumption in lignin solvolysis by supercritical alcohols and specifically the effects of different primary alcohols. The chapter comprises the results and discussion from the article *"Non-Catalytic Supercritical Alcohol Solvolysis of Biorefinery Lignin: Investigation of Solvent Consumption"*.

CHAPTER 6 is a simple economic assessment of the non-catalytic lignin liquefaction by supercritical ethanol in order to yield a lignin-diesel oil (LDO). Profitability is evaluated based on output value minus input value for the full parameter study reported in Chapter 4. An example is given on annual profit from large scale LDO production and an energy balance is briefly discussed. The economic assessment formed the basis for patenting the LDO process[7–9] (see page xv) and has been submitted for further evaluation by Maersk Maritime Technology.

CHAPTER 7 comprises the conclusions of this Ph.D. study and suggestions for future work.

APPENDICES comprise supplementary information for Chapter 4, Chapter 5 and Chapter 6.

CHAPTER 2

Review on Direct Lignin Liquefaction

In this chapter state of the art direct lignin liquefaction technologies and reactions involved in lignin depolymerization in solvent media are described. It is desired to utilize the heterogeneous structure of lignin to produce a liquid fuel rather than high value chemical. The target is therefore to transform solid lignin to a liquid fuel or bio crude and this chapter discusses mainly non-catalytic direct liquefaction.

A short introduction to lignin as a feedstock and commonly available lignin types is given in section 2.1. Available technologies for lignin liquefaction in order to obtain a liquid fuel with an emphasis on direct liquefaction techniques employed on pilot to full scale processing are discussed in section 2.2. The chemistry involved in lignin depolymerization in different solvent media is discussed in section 2.3 where advantages and disadvantages of different solvent media are highlighted and the effects of various reaction parameters are described.

2.1 Lignin as a Feedstock

Lignin is found in quantities up to 30 % in all plant biomass. Lignin is found outside plant cell walls facilitating water transport and providing structural rigidity and first layer protection against biological attacks.[10] The latter makes lignin highly recalcitrant. The vast majority of lignin isolated worldwide is therefore burned as a low value solid fuel. The main commercial source of lignin is from the pulp and paper industry which utilizes around 95% of the recovered lignin for heat and power generation.[10–12]

Lignin is an aromatic polymer that is mainly synthesized from the three monomers paracoumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S) (see Figure 2.1). The polymerization of the monomers is a radical polymerization, initiated by laccase enzymes. As the radicals can combine in various ways the resulting polymer is unlike cellulose of a very heterogeneous nature. This complicates working with lignin in both research and technical operations.

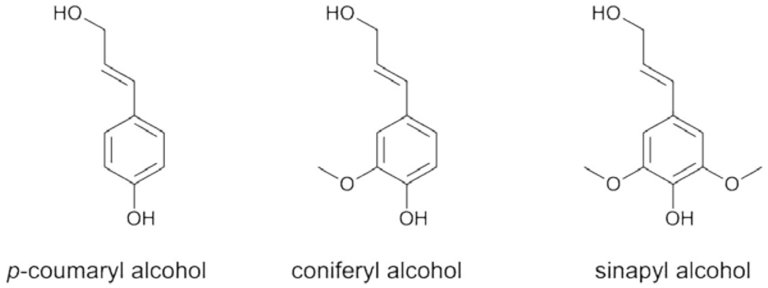


Figure 2.1 The building blocks of lignin comprising of *p*-coumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S).

The structure and composition of native lignin is described in detail in reviews by Rinaldi *et al.*[10] and Vanholme *et al.*[13] Lignins have quite different properties depending on which biomass they originate from and so lignins are often divided into softwood lignin, hardwood lignin and grass lignin. The two main differences between the three kinds of lignin is the ratio of the monomers where softwoods have no S, little H and almost exclusively G monomers. Hardwoods and grasses have about the same ratio of S:G and some H monomer; however, grasses also have tricin[14–16] and other monomers making it a quite different lignin than in hardwood. The monomers are connected through mainly ether bonds, but also carbon-carbon bonds are common. In Figure 2.2 a suggested lignin polymer with typical inter unit linkages is shown. Ether bonds are easier to cleave than C-C bonds in particular due to a lower bonds dissociation energy (BDE). The β-O-4 ether bond is the most common bond in native lignin[10,13,17] and has a BDE of 226-290 kJ/mol relative to 524-532 kJ/mol for a typical C-C bond such as β-5.[18]

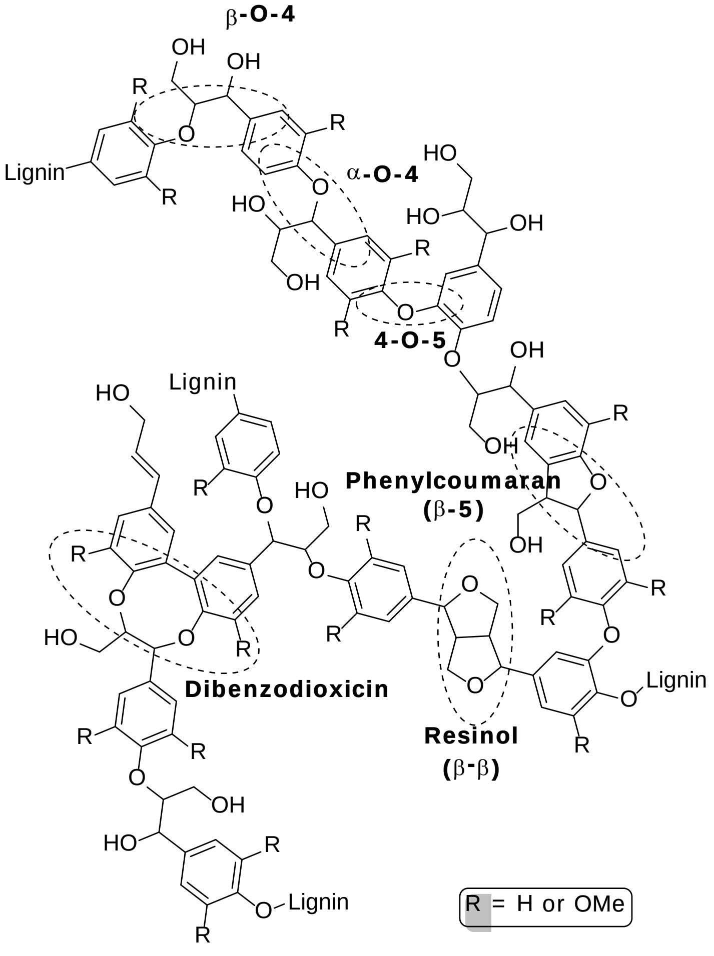


Figure 2.2 A suggested structure of a lignin polymer. Typical inter unit linkages are highlighted.

Lignins are reactive molecules which make the isolation of native lignin extremely difficult if not impossible and hence no one knows the exact structure or molecular weight of native lignin. One of the challenges of depolymerizing lignin in order to remove it is that it repolymerizes through carbon-carbon bonds that are harder to break than the original ether bonds. Nevertheless technical methods have been developed in order to produce cellulose pulp[10], but the technical lignins from these processes are often considered a waste product or low value side stream. Alternative applications of technical lignins was reviewed by Calvo-Flores and Dobado[19].

2.1.1 Kraft Lignin

Kraft lignin is the most abundant lignin produced (89-95 % of world lignin production) as the Kraft process is the most utilized in the paper and pulp industry.[20] As the process utilizes sodium hydroxide and sodium sulfide the resulting Kraft lignin contains sulfur.[21] Due to this sulfur content Kraft lignin is mainly incinerated in a recovery boiler in order to retrieve the inorganic chemicals and generate electricity.[22] The sulfur content is a challenge for further utilization of the lignin as sulfur is a known catalyst poison even though a few sulfur tolerating metal catalysts have been reported.[23,24] Kraft lignin is generally not water soluble[12] and average molecular weight is reported to be around 10,000 g/mol[25,26]; however, these values might vary some from different lignin sources.

2.1.2 Soda Lignin

The soda process is fairly simple in that only sodium hydroxide is applied for lignin removal. The process is mainly used for non-woody biomass where less severe processing is possible.[20] The paper produced from the soda process is not as strong as paper made from the Kraft process (indeed the word "kraft" is the German word for strength), however other sulfur free lignin and high value cellulose/glucose products might emerge from e.g. bagasse. Reports of molecular mass ranges from 3,200 g/mol[26] to 8,400 g/mol[25] highlighting that products can be quite different depending on biomass sources and process conditions.

2.1.3 Lignosulfonates

Lignosulfonates are products of the sulfite process where the biomass is pulped in aqueous sulfite/hydrogensulfite (ratio depends on pH) with different cations (most common is calcium or magnesium). The sulfite process only accounts for 3-4 % of the lignin produced in the world; however, alternative applications of lignosulfonates (50 % of lignosulfonates are sold for concrete production) results in a higher value lignin than Kraft lignin.[20] The process makes lignosulfonates that are water soluble and can be removed from the solid cellulose fraction. Average molecular weights are reported to be between 3,900–6,600 g/mol[25,26]. It is possible to produce vanillin from lignosulfonates and even though the process is well known and available it is only Borregaard in Norway that still does this.[10]

2.1.4 Organosolv Lignin

Organosolv lignin is a broad term for lignin that has been isolated in organic solvents or mixtures of water and organic solvents. Reaction temperature and type of solvent greatly influence properties of the lignins that are produced. Often a readily available, low boiling solvent as methanol, ethanol, 1,4-dioxane or acetone is applied as they are simple to distill from the lignin in order for the solvent to be recycled.[10] An organosolv process typically yields a sulfur free lignin that is suitable for further upgrading and hence is often used in academic research.[4] Recently the application of ionic liquids (IL) in organosolv type processes has received high attention as a sub-division of organosolv processes. The main difference of IL processing from "classical" organosolv process is the high boiling point of the IL making subsequent separation difficult. Due to the broad range of processes covering the term organosolv it is difficult to determine a specific molecular weight range for organosolv lignins. For Alcell lignin (organosolv lignin extracted using water and ethanol) specifically the molecular weight is typically around 4,000 g/mol.[26]

2.1.5 Hydrothermally Pretreated Enzymatic Hydrolysis Lignin

Most modern 2nd generation biorefineries apply either a hydrothermal or dilute acid pretreatment for the exposure of cellulose.[1,27] In a hydrothermal pretreatment the whole biomass is cooked in water or dilute acid in order to expose the cellulose to a subsequent enzymatic hydrolysis.[28] One variant of hydrothermal pretreatment is called steam explosion. During this pretreatment it is found that the abundant β–O–4 bonds are broken[29] but new carbon-carbon bonds are formed and the molecular size distribution of lignin is often reported to increase[30–32]. The pretreatment is generally thought to expose the cellulose as the temperature rises to be higher than the melting point of lignin causing the lignin to agglomerate into spherical droplets that leave part of the cellulose exposed.[33,34] Due to this agglomeration of the lignin during hydrothermal pretreatment the lignin is a very condensed lignin and high molecular weight lignin of up to 40,000 g/mol has been reported.[25,26] Further processing may require harsh reaction conditions.[35] Due to this high recalcitrance of hydrothermally pretreated lignin it holds a lower potential for upgrading to fine chemicals but uses as solid or liquid fuel might be feasible.

2.2 Technologies for the Transformation of Solid Lignin to a Liquid Fuel

In order to transform solid lignin into a liquid fuel product it is necessary to depolymerize the lignin polymer into smaller molecular weight fragments and sufficiently lower oxygen content. A depolymerization of the lignin will lead to increased solubility in solvents and decrease viscosity bringing the depolymerized fragments closer to a desirable fuel product in structure. It is advantageous to depolymerize lignin by breaking of ether linkages due to a lower bond enthalpy relative to C-C linkages. In simplified terms the steps required to convert lignin to a liquid fuel are:

1) Cleavage of ether linkages
2) Removal of oxygen

These steps may occur separately or simultaneously. Clifford and Song highlighted the five existing technologies to produce liquids from solid materials such as coal and biomass:[36] Gasification (followed by Fischer-Tropsch Synthesis), pyrolysis, thermal solvent extraction, catalytic liquefaction and synthetic crude (shale oil or oil sand) upgrading.

Gasification followed by Fischer-Tropsch synthesis brings the solid feed to a gaseous form prior to yielding a liquid product hence this processes is called indirect liquefaction. Similarly a pyrolysis without the presence of a liquid solvent is also an indirect liquefaction process as the product is cooled down in order to return to the liquid state. Solvent extraction and catalytic extraction are direct liquefaction processes in which the solid feedstock is heated in a solvent without or with the presence of a catalyst respectively. Direct liquefaction does not involve an intermediate gaseous product and hence the temperatures for direct liquefaction processes reported are lower than that of indirect liquefaction processes. Direct liquefaction is more thermally efficient (65-75 % thermal efficiency) than indirect liquefaction (40-50 %

thermal efficiency) and the amount of CO_2 produced is typically lower.[37] Indirect liquefaction such as Fischer-Tropsch synthesis utilizes air which yields partial oxidation initially and therefore a greater quantity of CO_2 produced.[36] In direct liquefaction the oxygen removal is facilitated by either dehydration or decarboxylation.[38] Removal of oxygen by dehydration requires a costly hydrogen source. Removal of oxygen in the form of CO_2 may therefore be desirable; however, this lowers the theoretical maximum liquefaction yield further as carbon is effectively removed from the product.

Hydrogenation (or hydrogenolysis) is the process of pyrolysis or solvolysis in the presence of hydrogen. It may be either gaseous hydrogen or from hydrogen donating solvents.[6] Typical temperatures range from 300-600 ˚C.[6] The presence of gaseous hydrogen and a heterogeneous catalyst has widely been reported to promote the degree of lignin fragmentation in solvents but most studies use model compounds instead of real lignin feedstocks.[4] The process of hydrogen addition to promote lignin fragmentation and subsequent oxygen removal is termed hydrodeoxygenation (HDO). The process of HDO is similar to hydrodesulfurization (HDS) when using sulfided catalysts as they follow similar reaction mechanisms by the use of hydrogen for the removal of the hetero atoms forming H_2O and H_2S respectively. In a review by Mortensen *et al.*[39] on catalytic mechanisms and processes for bio-oil upgrading it was concluded that HDO appears to have the best potential, as zeolite cracking cannot produce fuels of acceptable grade for the current infrastructure. The process of treating the solid lignin feed in a solvent helps solubilizing smaller molecular weight fragments and promotes hydrogenation and presence of catalysts improve hydrogenation[36]. Azadi *et al.*[40] argued that a semi continuous process such as a fixed bed process may advantageously allow for *in situ* removal of desirable products.

Lower operating temperatures is desirable in direct liquefaction as higher temperatures may result in increased cracking of molecules producing more gaseous and solid products at the expense of liquids. Lower pressure is desired from an ease and cost-of-operation point of view.[41] The temperature ranges in which lignin has been reported to be catalytically transformed by various means are shown in Figure 2.3 where thermal cracking without the use of a catalyst has also been indicated at temperatures above 550 °C. The figure shows that for lignin reduction with the use of heterogeneous catalyst requires temperatures higher than of oxidative routes. Homogeneous lignin reduction may be carried out at temperatures <100 °C but from an industrial point of view heterogeneous catalysis is more advantageous due to easier separation and recycling of the catalyst.

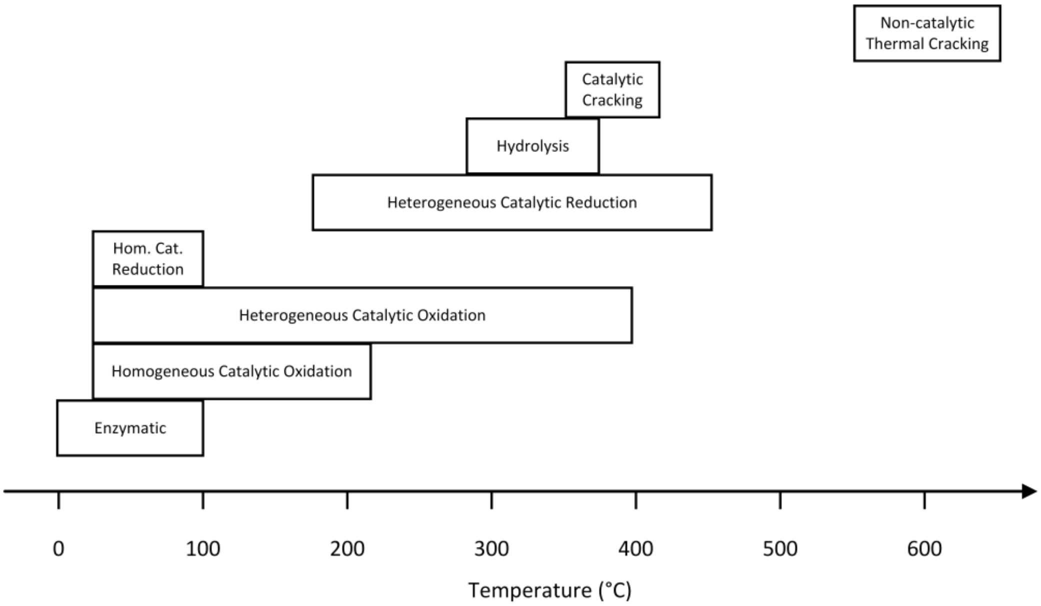


Figure 2.3 Catalyzed as well as non-catalyzed routes for lignin depolymerization represented as a function of typical reaction temperature. The plot is modified from Gasser *et al.*[42]

Both multiple step and single step processes have been demonstrated on biomass to liquid and bio-oil upgrading processes which is described in more detail in the following section 2.2.1. A single step process for lignin to liquid transformation may be desirable for an ease of operation point of view and limit the cost of plant and operation. Disadvantages of a single step process include that catalyst can be easily deactivated due to presence of heavier materials and separation of catalyst from residues becomes difficult.[36] Clifford and Song[36] recommended for a first step in a coal/biomas to liquid process the use of inexpensive catalysts for this reason as it can be disposed of. They recommended the use of iron-based catalysts for this first step such as red mud which was also used in the Bergius process (see the following section 2.2.1).[36] Hicks[43] argued a multiple step process for bio-oil upgrading is beneficial as an initial step at temperatures <250 °C and ~50 bar helps stabilize the oil by removal of thermally unstable groups (eg. carbonyl functionalities). Subsequent steps at increasing severity will be required depending on how exhaustive hydrogenation that is required.[43]

In the following section successful direct liquefaction processes on both coal and lignin are discussed. These processes have demonstrated some form of proof of concept or potentially proven industrially viable through patents and pilot scale to full scale processing.

2.2.1 Direct Liquefaction Processes on Coal and Lignin

The chemical structure of low rank coals such as peat and lignite resemble that of lignin as coal is ultimately fossilized plants. One may therefore expect the chemistry of transforming lignin into useable chemicals and fuels is reasonably comparable to the chemistry of coal transformation. The main difference is the higher oxygen content in lignin present in ether bonds and hydroxyl groups which greatly increases the polarity. For these comparative reasons it is reasonable to consider which technologies that already exist on coal to liquid fuel transformation. Compared to lignin direct liquefaction there are indeed inherent similarities with direct coal liquefaction which can be achieved with and without catalysts at pressures 200-700 bar and temperatures 425-480 °C.[37,41] The process of coal to liquid is thermally rather efficient since it is exothermic. Hydrogen reportedly accounts for an important fraction of the cost of producing liquid fuels.[37]

In 1931 Friedrich Karl Rudolf Bergius and Carl Bosch won the Nobel prize in chemistry for their work on the catalytic conversion of coal to a deoxygenated liquid product using relatively cheap iron(II,III) oxide catalyst (found in red mud) and H_2. This chemical process is now named the Bergius Process. This was the first commercially available process for coal to liquid fuel transformation and was the result of development during the First World War.[41] A schematic over the process as presented in Bergius' Nobel lecture is shown in Figure 2.4. In this process a recycled stream of liquid product served as solvent and gas splitting allowed for hydrogen recovery. The process required handling of high pressure ranging from 200–700 bar in one reactor. Temperatures in the reactor were 325–480 °C. Product streams of light and heavy fractions were separated.[41,44] 1 ton of coal would yield about 150–170 liters of gasoline, 190 liters of diesel fuel and 130 liters of fuel oil. Coal liquefaction by the Bergius Process amounted to 14 plants in Germany during World War II,[45] but after the war the process was ended due to difficulties with separation of ash and heavy oil and erosion due to cyclic pressurization.[41] The process was not profitable and could not compete with crude oil refining.

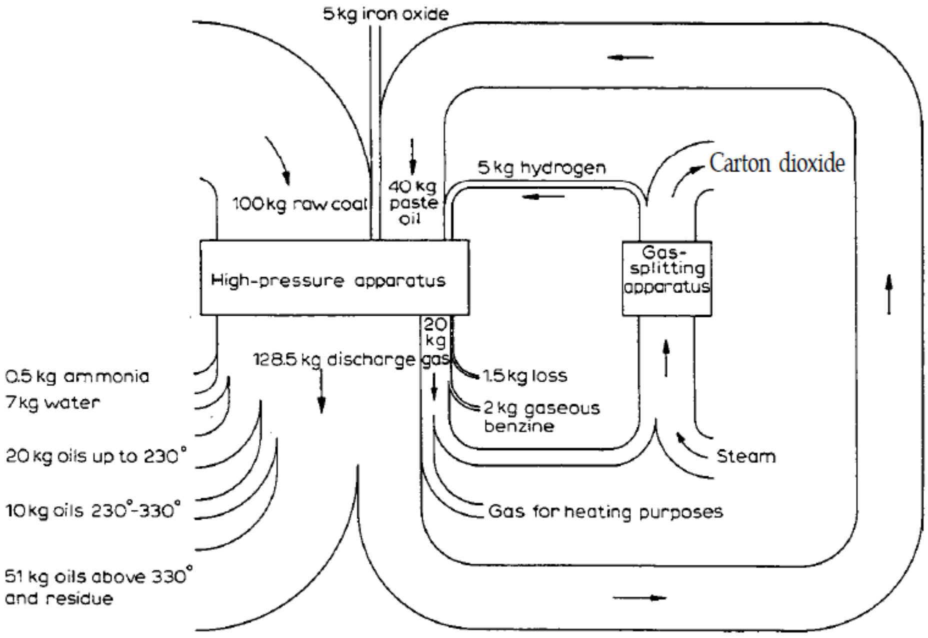


Figure 2.4 Flow diagram for continuous mode operation of coal liquefaction as proposed by Bergius in his Nobel lecture.[44]

Clifford and Song[36] reviewed pilot plant and larger industrial implementations of processes for the liquefaction of coal from the 1970s and onwards. These processes follow a generalized form much like the Bergius process but more recent designs involve a lower operating pressure of 100-200 bar and temperatures 400-450 °C.

Coal and solvent are preheated and mixed and hydrogen pressure is applied. This first step might be with or without catalyst. Subsequent steps typically involve product refinements and separation processes and solvent is recycled. Some processes implement hydrogen generation from coal and solid residues. A generalized scheme is shown in Figure 2.5. Separation of liquid product is typically by distillation and further upgrading might be necessary. Solid products may also be further valorized by gasification.[36] The solvent is nonpolar which may however limit feasibility for lignin rich feedstock with higher oxygen content than coal.

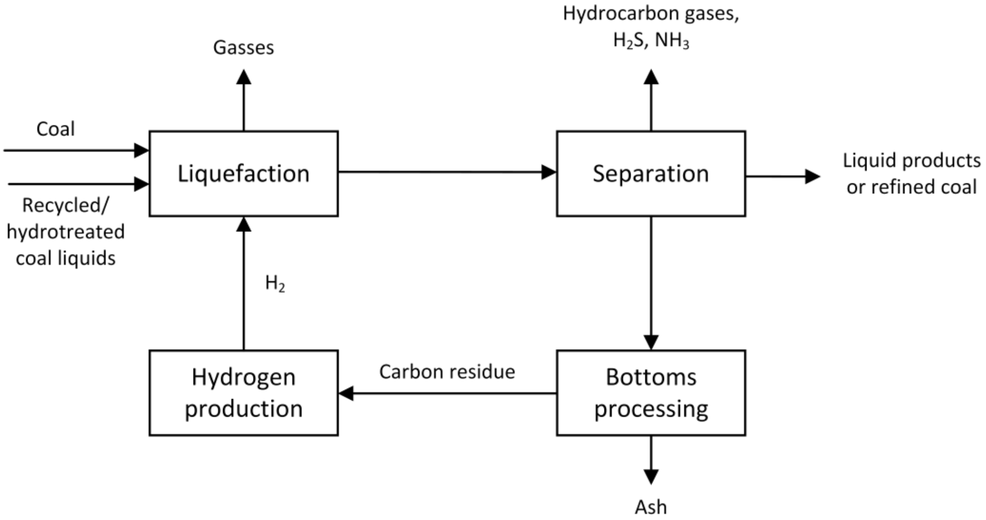


Figure 2.5 Generalized flow diagram for direct liquefaction of coal based on Bergius process. Modified from Clifford and Song[36].

Similar to coal liquefaction by using the reduced oil product as solvent attempts have been made on lignin. The Noguchi process developed in the early 1950s was a catalytic hydrotreatment of lignin dissolved in a phenolic mixture of lignin tars and phenols.[4,46] Operating conditions were 250-450 °C with an initial H_2 pressure of 152-456 bar. The catalyst was iron(II) sulfide with a co-catalyst of at least one sulfide of copper, silver, tin, cobalt, chromium, nickel, zinc or molybdenum (e.g. Fe-S-Cu-Zn in a ratio 10:12:1:1).[4,47] Inventa AG developed at process similar to the Noguchi process at a similar time using an iron sulfate catalyst.[48] Lignin liquefaction by the Noguchi process yielded C6-C9 mono phenols in yields up to 40 % but mainly due to alkylation of solvent and 21 % lignin phenol yield. This loss of phenol solvent was disadvantageous.[4] Due to expensive reactors for hydrotreatment at <400 °C and complex separation (distillation) of products it was judged non-profitable in 1965.[46]

In 1988 Universal Oil Products patented an improvement of the Noguchi Process with reported yields of up to 45 % cresols and about 65 % monophenols from Kraft lignin. The process utilized an *in situ* generated catalysts consisting of ferrous sulfide with smaller amounts of other metal sulfides as promoters.[49]

The Hydrocarbon Research Institute (HRI) developed the Lignol process which was patented in 1983.[50] The solvent was equally recycled lignin tars as lignin was hydrotreated in an ebulated catalyst bed with subsequent thermal dealkyaltion. The catalyst used was a Co- or Ni-promoted iron or molybdemum oxide on alumina and 37.5 % phenol yield was reported. The HRI process emphasizes it is important to go to atleast 400 °C.[50,51]

In recent years Shell Oil Company have had continued efforts in processes in which lignin tars resulting from hydroprocessing are recycled and used as a solvent. They reported using whole plant biomass and an initial thermal cracking at temperatures up to 400 °C in recycled product tars with or without the presence of a catalyst and hydrogen and in the presence of an acid can yield a depolymerized product that is suitable for further upgrading.[52,53]

Shabtai *et al.*[54] proposed a three step process where the first step was base catalyzed depolymerization (BCD) of lignin in supercritical methanol or ethanol at 270 °C for 1-5 min at 140 bar which yielded a 50 % decrease in oxygen content. This step was followed by HDO and partial ring hydrogenation and mild hydrocracking over sulfided CoMo/Al_2O_3 to yield a gasoline substitute of mainly alkylbenzenes. The process was also patented.[55] The authors equally patented [56] a multiple step process in which first a mild BCD did not significantly lower oxygen content of the lignin but merely allowed for solubilization in order to subsequently selectively hydrocrack C-C bonds using a superacid catalyst. The product, a high oxygen containing depolymerized lignin (mixture of alkylated phenols), was subsequently etherified with methanol and partially ring hydrogenated by acid catalysis to produce a partially oxygenated/etherified gasoline (mainly aryl methyl ethers).[54]

National Renewable Energy Laboratory (NREL) equally developed a two stage process for lignin direct liquefaction with BCD and followed by sequential two step hydroprocessing. First step of the hydroprocessing would equally utilize a hydrodeoxygenation catalyst and the second step a hydrocracking catalyst. They highlighted a disadvantage of the BCD as the potential precipitation of lignin is of great concern as base is neutralized upon reacting with formed CO_2.[57]

A recent patent by Chen[58] (Honeywell UOP) describes a process in which lignin is depolymerized in water using base or acid in hydrogen atmosphere. Depolymerized product is a mixture of depolymerized lignin structures and light C1-C3 alcohols, where the later are advantageously reformed in order to generate hydrogen stream for use in the depolymerization and hydrogenation step. Hydrogenation of depolymerized lignin yields saturated and partially saturated ring compounds using a noble metal catalyst on zeolitic support.

BASF recently patented a process in which the solvent for direct liquefaction was different organic solvents or water or a mixture of all. Specifically the process was exemplified with ethanol as solvent and a single step process at 100–205 °C and 20–200 bar H_2 would be sufficient. These are relatively mild conditions. The catalyst was supported or unsupported transition metal carbides, tungsten-carbide in particular. Reportedly the catalyst would tolerate both sulfur rich and poor streams.[59]

In recent years increasingly more research has targeted hydrothermal processing of biomass and lignin in particular.[38] Toor *et al.*[38] reviewed hydrothermal liquefaction of biomass and the reader is encouraged to consult their work for more detail. Hydrothermal treatment beneficially allows for treating wet feedstocks and the solvent (water) is readily available but a major advantage is the high energy recovery of up to 80 % reported.[38] Hydrothermal liquefaction (HTL) is a rather simple process and in particular the Catliq® process originally developed by SCF technologies operates at pressures around 300 bar and temperatures up to 400 °C where 10-15 % of the energy in the oil product can be used to drive the process.[60] It is necessary to ensure rapid heat-up and for this the Catliq® process utilizes a fairly large recycled solvent and product stream which can be seen in Figure 2.6. Typically HTL is better suited for low lignin content feedstocks such as e.g. algae as lignin rich feedstocks result in increased charring and reduced oil yield.[4,61,62] Nguyen *et al.*[63] demonstrated a similar process on a small high pressure pilot plant using LignoBoost Kraft lignin as feedstock where the highest oil yield recovered was 49.8 wt% with only 20.6 wt% char formed at conditions where the feed consisted of 0.4 wt% K_2CO_3, 5.6 wt% dry lignin and 4.1 wt% phenol with a pH of 7.9. The water solvent was subcritical (350 °C, 250 bar) and the process was carried out in a fixed bed catalytic reactor (0.5 l) filled with zirconia pellets. Feed flow rate was 1 kg/h with a residence time of 11 min and the reaction mixture is recirculated at approximately a rate of 10 kg/h. The resulting oil product had an oxygen content of 17 %.

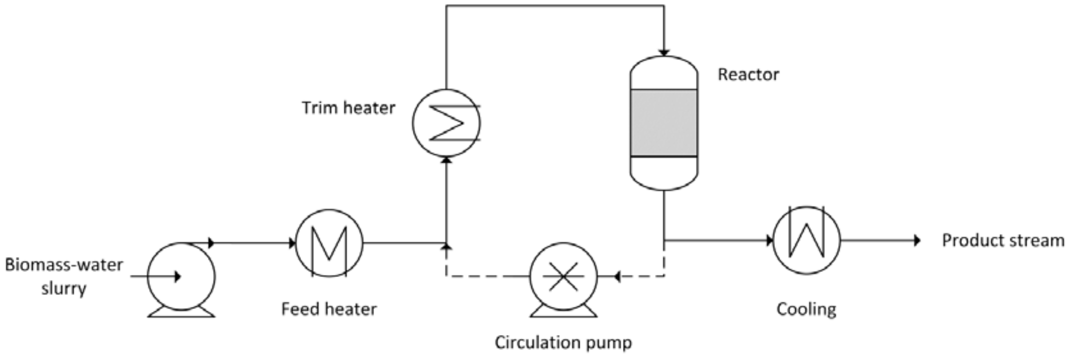


Figure 2.6 Simplified P&I diagram for the Catliq® process. The product stream comprises of liquid, gas and solid requiring separation and pressure relief. Modified from Toor *et al.*[64]

A solvent based approach to industrial biorefineries necessitates finding a solvent that shows high recyclability and allows for high biomass to solvent ratio in order to be competitive. Furthermore an often overlooked feature is the sustainability of the solvent and in particular toxicology is something that will play a major role when handling the solvent on a large scale.[65]

2.2.2 Summary of Lignin to Liquid Processes

In order to transform solid lignin to a liquid fuel a simplified approach involves cleavage of ether linkages and deoxygenation. Ether linkages are more readily cleaved due to a lower bond enthalpy compared to C-C linkages and cleavage of lignin inter unit linkages facilitates depolymerization. Different techniques exist for reductive liquefaction of biomass and main strategies comprise of catalytic as well as non-catalytic pyrolysis and gasification techniques which results in an indirect liquefaction. Direct liquefaction of biomass in a solvent is advantageous as it is thermally more efficient and compared to gasification followed by Fischer-Tropsch synthesis in particular CO_2 yields are lower. Direct liquefaction often occurs at elevated pressure due to the pressure exerted by the heated solvent when keeping it in liquid form; however, the temperature requirements are lower than for pyrolysis technologies (<450 °C).

Research on coal liquefaction in the early 1900s in Germany ultimately resulted in the Bergius process which has paved the way for attempts at recreating a process that works similarly on lignin. The Bergius process utilized recycled heavy product tars of the process as a solvent for coal liquefaction and a heterogeneous iron(II,III) oxide catalyst was added. Different more recent process proposals on coal liquefaction often involve a generalized approach in which solid carbon rich residue is processed further to provide a hydrogen that ultimately may be added to enhance the liquefaction. Lignin composition is similar to coal; however, a higher oxygen content of the former may require a more polar solvent. Similar to the Bergius process for coal liquefaction the Noguchi process for lignin liquefaction was invented in the 1950s which utilized cooking lignin in lignin tars and with the addition of a heterogeneous catalyst. Many attempts at improvement have been made. Shell in particular pursues a similar strategy in order to liquefy lignin in lignin tars but the aim is simplified to target production of a bio-crude which may then be subsequently further upgraded.

Other recent strategies for direct lignin liquefaction involve multiple step processes in which the lignin is first depolymerized using base catalyzed depolymerization and followed by catalytic upgrading by hydrodeoxygenation.

Special interest is also given to the topic of hydrothermal liquefaction in which whole biomass is treated in near supercritical water; however, high lignin content feedstocks typically results in increased charring. An important factor to achieve high liquid yields for hydrothermal processing of biomass is a fast heating rate comparable to that of fast pyrolysis.

A simple approach is necessary when transforming a relatively low value feedstock such as lignin to a bulk product like a fuel or a bio-crude. In particular for direct liquefaction a high solvent recyclability is necessary as well as tolerance for high solid to solvent loadings in order to yield an economically feasible process. An often overlooked feature is also solvent sustainability and toxicology which are factors that are important to limit when handling a solvent based process on a large scale.

2.3 Chemistry of Lignin Depolymerization and Solvent Effects

Lignin depolymerization can take place in a solvent (typically aqueous or organic) and dry form. In lignin depolymerization the bonds that are more favorably cleaved are broken. This may occur due to simple thermal cracking but in the presence of a solvent the latter may contribute by cleaving lignin polymer bonds by solvolysis. When lignin is subjected to elevated temperatures in the presence of a solvent some degree of thermal cracking always occurs due to bond dissociation energies.

A lignin feed may not necessarily be pure lignin and is often part of plant biomass containing other organics such as hemicellulose and cellulose which can affect the mechanisms of decomposition. Hemicellulose and cellulose decompose below 250 °C while the degradation of lignin mainly occurs at higher temperatures with no solvent.[66] Lignin decomposes slower over a broader temperature range (200–500 °C) than cellulose and hemicellulose (<250 °C) due to a larger variety of oxygen functional groups in the structure that have different thermal stability meaning scissions will occur at different temperatures.[67] This emphasizes the recalcitrance of lignin depolymerization relative to cellulose and hemicellulose.

Treatment of lignin in a solvent contrary to a solvent free pyrolysis allows for even more types of reactions than just thermal cracking. When treating lignin in a solvent at elevated temperatures one or more of the following effects may occur:

1) Simple dissolution
2) Homolytic cleavage
3) Heterolytic cleavage
4) Alkylation and rearrangements

The four types of overall reactions do not occur exclusively but at the same time at varying degrees depending on the type of lignin liquefaction process applied.

Simple dissolution of lignin in a solvent may not necessarily involve depolymerization of the lignin polymer.

Homolytic cleavage is the result of thermal cracking. Thermal cleavage of aryl-ether linkages results in formation of unstable free radicals that may cause repolymerization, rearrangement, electron abstraction or radical-radical interactions.[67] With the ether linkages having lower bond-enthalpy than C-C bonds[18] they are broken to a greater degree and thermal cracking of the ether bonds is believed to follow two routes in a simplified scheme depending on what side of the ether bond is (homolytically) broken.[68] The two scenarios of homolytic cleavage in guaiacol can be seen in Figure 2.7.

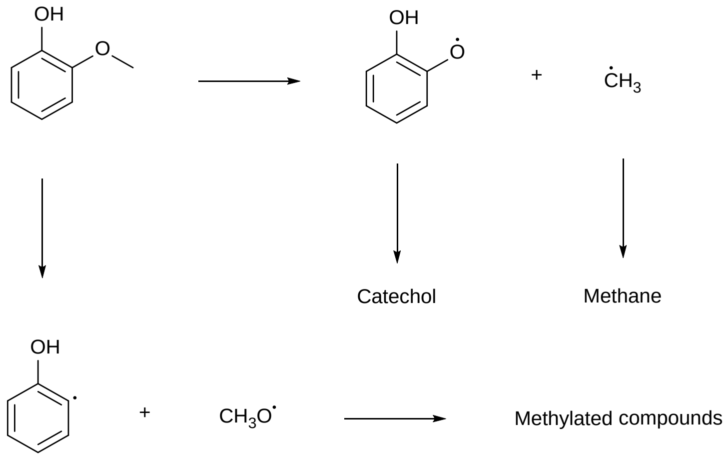


Figure 2.7 Thermal cracking of guaiacol resulting in homolytic cleavage of either side of the ether bond. Modified from Demirbas and Demicioglu[68].

Heterolytic cleavage of the ether bonds in lignin will typically be due to a nucleophilic attack on the C-atoms in the ether bond. The nucleophilic agent has been reported from treatment in alkaline solutions as OH^- and even deprotonated hydroxyl groups in the lignin molecule are believed to be responsible for nucleophilic attacks on neighboring C-atoms .[69–74]

Alkylation and rearrangements may be a result of either radical mechanisms or electron transfer mechanisms. In the case of using alcohols as solvent some degree of alkoxylation may occur.[75–78] Alkylations and rearrangements can greatly alter the structure of depolymerized lignin species and affect factors such as reactivity and solubility.

Cleavage of the primary forms of lignin linkages may yield highly functionalized aromatics with alcohol, aldehyde or acid substituents.[4] Often beneficial effects with regard to greater depolymerized yield have been reported in the use of supercritical solvents (see section 2.3.3).

Azadi *et al.*[40] divided lignin depolymerization into the five general processes: pyrolysis, catalytic hydrogenolysis, alkaline hydrolysis, supercritical water and solvent depolymerization. The alkaline hydrolysis and solvent depolymerization may have similarities and the process of hydrogenolysis can occur both in the presence of solvent and without. In the following the processes of lignin depolymerization have been divided into four categories in a generalized diagram shown in Figure 2.8.

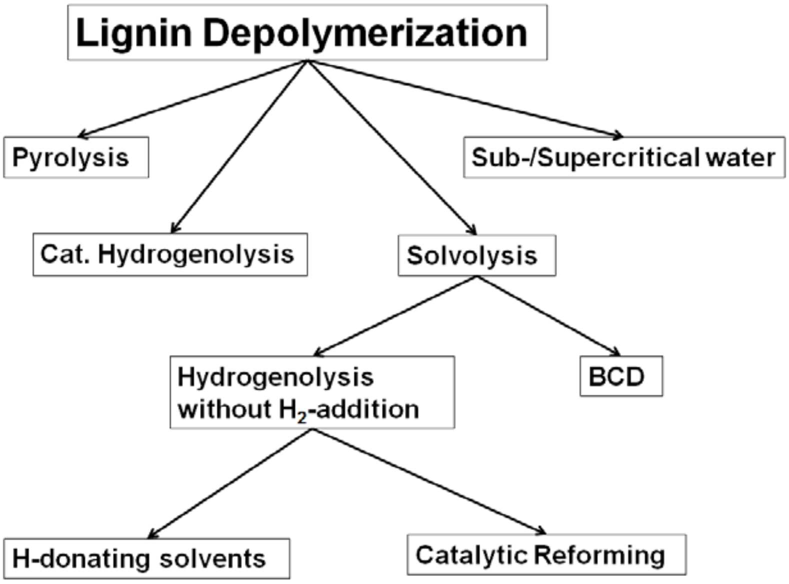


Figure 2.8 Generalized diagram showing the different routes for lignin depolymerization.

Pyrolysis can be used to describe the heating up of lignin in an inert atmosphere both with and without solvent. Pyrolysis is typically mentioned in the case of solvent free operation and in the following the term pyrolysis will only be used to describe the indirect liquefaction (i.e. producing a gas that is subsequently condensed to a liquid) method at around atmospheric pressure which is solvent free. In lignin pyrolysis lignin is depolymerized by homolytic cleavage followed by recombination reactions. Fast pyrolysis, i.e. quickly heating to temperatures above 550 °C, favors low char yield and maximizes liquid yield. Char yields of lignin pyrolysis are typically relatively high corresponding to up to half of the biomass feed and high lignin content feedstocks result in increased charring.[79]

Catalytic hydrogenolysis can be carried out with or without solvent in the presence of gaseous hydrogen at high partial pressure. Reactions may involve homolytic cleavage through radical mechanism but reactions on catalyst surfaces play an important role.[4]

Sub- and supercritical water treatment also called hydrothermal liquefaction facilitate cleavage of ether linkages and cross linking forming larger molecules predominately through Friedel-Craft mechanisms.[40,80–82] It may be argued that some degree of hydrolysis may take place but generally depolymerization in sub-/supercritical water is not a solvolysis. This is described in more detail in section 2.3.2.

Lignin solvolysis describes the processes in which solvent molecules actively facilitates the cleavage of the lignin polymer typically through nucleophilic attacks. Lignin solvolysis can be divided into two general groups listed below:[40]

1) Base Catalyzed Depolymerization (BCD)
2) Treatment with hydrogen donating solvents (hydrogenolysis without the addition of gaseous hydrogen)

Radical induced as well as ionic reactions that do not strictly fall into the categories of solvolysis may also occur but are merely a result of solvent interaction at pyrolysis conditions. An example which is not strictly solvolysis is thermal solvent extraction and cracking in different organic solvents that do not facilitate hydrogenolysis such as e.g. acetone. This emphasizes the difficulties in generalizing depolymerization.

BCD includes both alkaline hydrolysis and alkaline alcohol treatment and is described in more detail in section 2.3.1.

Hydrogenolysis when lignin is solvolytically treated without the addition of gaseous hydrogen typically requires supercritical conditions. Two general groups of processes can be used to describe this hydrogenolysis:

1) Fragmentation with *in situ* formed hydrogen from a hydrogen donating solvent
2) Fragmentation with hydrogen formed from partial reforming of the solvent in the presence of a catalyst (e.g. aqueous phase reforming (APR))

Alcohols are often considered hydrogen donating solvents and the effects of lignin solvolysis in organic polar solvents including mainly alcohols is described in detail in section 2.3.3. Fragmentation of lignin by the use of the hydrogen donating solvents such as polycyclic aromatics and formic acid is described in more detail in sections 2.3.4 and 2.3.5 respectively. The hydrogen donating solvent may reversibly donate hydrogen e.g. tetralin or irreversibly due to decomposition of the solvent molecule e.g. formic acid. Lignin depolymerization facilitated by the process of reforming of the solvent is also an irreversible process of hydrogen donation reported to occur catalyzed in aqueous phase as aqueous phase reforming (APR) described in more detail in section 2.3.2 and catalytic reforming of alcohols is equally covered in section 2.3.3. Lignin itself has even been reported to be a hydrogen-donating substance capable of cleaving aromatic ketones such as alpha-phenoxyacetophenone.[83]

For lignin solvolysis a lowering of the oxygen content of isolated liquid yields is often observed.[6] This reduction by hydrogenolysis leads to oxygen removal as water but also demethoxylation reactions, particularly observed in formic acid will effectively contribute to a reduction of oxygen.[6,76,77,84] In the case of alkaline treatment demethoxylation may be the dominant route for oxygen removal as CO_2 has been reported as the main gas specie formed.[85,86] Alternatively alkylation by solvents such as alcohols will also lead to a reduced oxygen content of the liquid yield but not necessarily a removal of oxygen atoms relative to the lignin feedstock.

A solvent based approach to lignin depolymerization can be categorized as shown in Table 2.1. The table summarizes and compares advantages and disadvantages of treatment in lignin in different solvent media reported in the literature. Depolymerization of lignin in ionic liquids has recently seen a surge in research activity but high solvent cost and difficulty in extraction of products with aromatic moieties limits commercial application.[4]

Table 2.1 Advantages and disadvantages of using different solvents for direct liquefaction of lignin.

Solvent	Advantages	Disadvantages
Alkaline	• Fast reaction within few minutes[71,73,87–89] • Both alkaline water and alcohols can be used[71,87,90–94] • Lower temperature and less severe conditions than alternative technologies[73,74,85,88,94,95] • Lignin is also deoxygenated[71,85,86,96]	• Product recovery requires several steps including neutralization and acidification[57,86,88,97,98] • Base is consumed[57,86,88,97,98]
Water	• Water is readily available • Reaction typically fast within few minutes[99–103] • Easy organic product isolation[4] • No need to dry feedstock[4,64] • Sub-/supercritical water readily dissolves and reacts with a range of different organic molecules[4,61,104–106]	• Dissolution more difficult with high lignin content feedstocks and typically high char yields reported[4,61,62] • Supercritical conditions require higher temperature and pressure[4,38] • Harsh conditions at sub-/supercritical conditions may wear equipment[38] • May require catalysts such as base or ZrO_2 to be efficient[64,107–109]
Polar organics (mostly alcohols)	• Good lignin dissolution at even lower temperatures[110–112] • Ethanol is already a product stream from bioethanol plants producing lignin as waste product • High degree of depolymerization without use of catalyst[75,113–118] • Retards repolymerization[119–123] • Hydrogen donating ability[124–127]	• Alkylation and decomposition may cause solvent loss[75,124–127] • Longer reaction times of up to several hours are typically required[116,118,121,128]
Formic acid	• Hydrogen donation by *in situ* formed hydrogen[6,129] • Low yields of char[76] • Lignin deoxygenation[6,76,77,84,129–132] • Inhibits repolymerization[110,133]	• Formic acid cannot be recycled due to decomposition[6,129]
Polycyclic aromatics (e.g. Tetralin)	• Hydrogen donation[36,62,134–136] • Solvent can be regenerated to some extend[36] • Low yields of char[62] • Lignin deoxygenation[36,62,136] • Inhibits repolymerization[62,110,133,135,137]	• More expensive than other H-donating solvents • Solvent consumption may occur[36]

In the following sections the effects from treating lignin in different solvent media are described including treatment in alkaline media, water, alcohols and other polar organic solvents and H-donating solvents such as formic acid and polycyclic aromatics. The advantages and disadvantages as highlighted in Table 2.1 are discussed and mechanisms by which lignin depolymerizes and potentially repolymerizes in the different media are discussed. The effects of different process parameters are presented with an emphasis on experiments carried out on real lignin feedstocks. It is difficult to directly compare results based on yield of oil as different authors may define the fraction differently. The effect of parameters typically requires investigation by authors independently and not comparison between data from different authors as widely different conditions makes comparison difficult.

2.3.1 Alkaline Media

In this section the solvent effects of direct lignin liquefaction in alkaline media are described. The mechanisms involved in the depolymerization and repolymerization of the lignin polymers as well as studies on individual parameter effects are discussed. Solvents typically involve alkaline alcohols or alkaline water. The process of treating lignin in an alkaline solvent is typically called Base Catalyzed Depolymerization (BCD) implying that the base is a homogeneous catalyst for the breaking of lignin unit interlinkages. A substantial amount of base may however be consumed in the BCD process and extraction procedures following alkaline treatment will involve a neutralization of the product mixture which results in loss of the base. For a process utilizing many steps means that production of high value products from lignin may be more desired than fuel production; however, BCD does provide well established deoxygenation of the lignin as significant amounts of CO_2 have been reported.[85,86] The operating conditions of BCD typically advantageously involve less severe conditions (lower temperature and pressure) relative to other means of solvent assisted lignin depolymerization.

2.3.1.1 Mechanisms

The mechanisms of lignin depolymerization by alkaline treatment are described in a review by Gierer *et al.*[71] and the reader should consult their review for a more in depth description. They described the mechanisms of both pulping and bleaching but only pulping is of relevance as this process involves strong bases and thermal treatment of lignin with the main purpose of breaking ether linkages. In the following the mechanisms of both lignin depolymerization and repolymerization are reviewed.

The principal route for alkaline depolymerization of lignin is through solvolysis of ether linkages and the reaction products of BCD can typically be divided into four fractions comprising gas, small organic compounds, aromatic monomers and aromatic oligomers.[87] Beauchet *et al.*[85] reported for aqueous BCD of Kraft lignin a gaseous fraction comprising mainly of CO_2, small organic compounds were methanol, formic acid and acetic acid totaling 10 wt%, aromatic monomers accounted for up to 19.1 wt% of lignin added and oligomers were polyaromatic molecules at 45-70 wt%. Johnson *et al.*[96] highlighted the average reaction chemistry for aqueous BCD on Alcell lignin where removal of ether linkages interlinking the lignin monomeric structures and removal of methoxy groups were dominant contributors to depolymerization yielding a reduction from initially 2-mer to 9-mer structures down to depolymerized structures of 1-mer to 3-mers. Oxygen removal was seen as a decrease from 27 wt% oxygen to 23.5 wt%.

Repolymerization occurs and Roberts *et al.*[73] argued that monomers of phenolic derivatives are the only primary products of base-catalyzed hydrolysis and oligomers are formed as secondary products of repolymerization. Limiting the degree of repolymerization increases the yield of lower molecular weight (depolymerized) compounds.

Model compound studies by Miller *et al.*[86] showed two types of reactions involving methoxy groups on aromatic rings:

1) Methyl group migration between phenolic groups
2) Loss of methyl/methoxy groups from the aromatic ring

Migration reactions are significantly faster than demethylation but ultimately the latter predominates at longer reaction times. Miller *et al.*[86] reported that demethylation/demethoxylation mainly yields methanol. They reported that the more substituted model compound syringol was more reactive than the lesser substituted compound anisole. Roberts *et al.*[73,138] equally reported that depolymerization of model compounds with only one methoxy group reacted kinetically slower than syringyl derivatives arguing that ortho positioned methoxy groups helps stabilizing formed transition states facilitating reaction.

Pulping in the paper industry bears great resemblance to the process of BCD on lignin. Pulping is generally the result of external nucleophilic attack on electron deficient centers in carbonyl and conjugated carbonyl structures and the presence of neighboring nucleophilic groups attacking β-carbon atom of side chains.[71] Whether splitting of aryl ether bonds in lignin is possible by alkaline treatment depends on factors such as hydroxyl group positioning on both the aromatic as well as the aliphatic neighboring chains.[69–72]

Cleavage of ether linkages facilitated by neighboring group nucleophilic attack is of significant importance for understanding the reaction chemistry of BCD.[71] β-ethers contribute to the majority of ether linkages interlinking the lignin monomeric structures (see section 2.1). The mechanism for β-ether cleavage may occur when in alkaline media a hydroxyl group in the α-carbon is deprotonated. The deprotonated hydroxyl group may attack the β-carbon by an intramolecular nucleophilic attack as shown in Figure 2.9.[71] The result is cleavage of the β-aryl ether bond yielding an oxirane intermediate which by nucleophilic addition of OH^- yields the product structure shown in Figure 2.9 to the far right. Gierer and Norén[69] highlighted that splitting of β-aryl ethers would only take place if they contain an etherified hydroxyl group in the para-position together with a free hydroxyl group on either the α- or γ-position of the propane side chain.

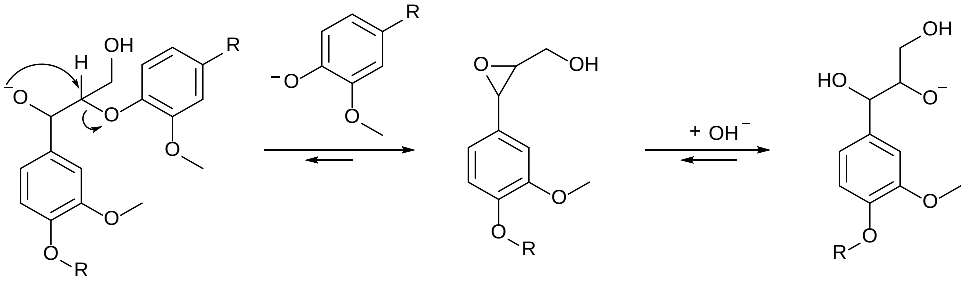


Figure 2.9 Alkaline β-aryl ether cleavage by neighboring group participation and subsequent alkaline oxirane cleavage. Modified from Gierer[71].

Roberts *et al.*[73] proposed a mechanism by which sodium ions aid in destabilizing β-ether bonds during BCD with aqueous NaOH. The sodium ion attacks the O in the ether bond forming a cation adduct thereby polarizing the ether bond which is then heterolytically cleaved due to lower energy requirement (see Figure 2.10). A proton is abstracted at the α-carbon by OH^- upon cleavage. Ortho positioned methoxy groups help stabilizing the transition state and for that reason guaiacyl species with only one methoxy group react kinetically slower than syringyl derivatives. Rearrangement of the charge on the formed phenolate will yield a carbanion which by reaction with the formed ketone may readily form stable C-C bond (see Figure 2.11).

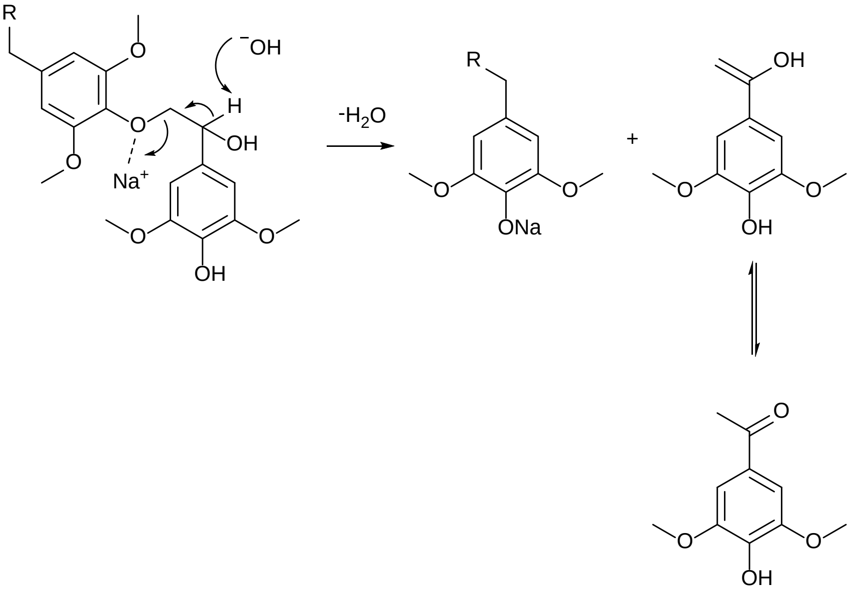


Figure 2.10 Mechanism by which proton-extraction occurs at the α-carbon and how Na^+ aids in destabilizing the ether bond. Modified from Roberts *et al.*[73]

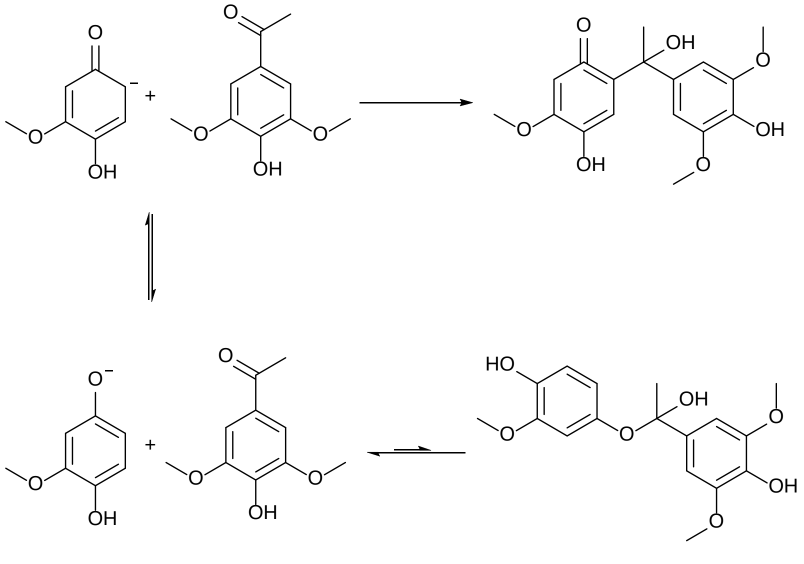


Figure 2.11 Oligomerization reaction between phenolate and ketone. The right hand side is protonated. Modified from Roberts *et al.*[73]

The mechanism for α-ether cleavage occurs through a quinone methide ion if free phenolic hydroxyl groups exist.[74] This is contrary to β-ethers which can be cleaved regardless of the presence of free phenolic hydroxyl groups or etherified hydroxyl groups.[72] Ionization of free phenolic hydroxyl groups yields a conversion to a quinone methide in alkaline medium (see Figure 2.12).[74] If only etherified phenolic hydroxyl groups exist α-ether cleavage is not possible as no conversion to quinone methide can take place.[72] Gierer and Norén[69] showed in a review that α-aryl ether bonds would only split if they contained phenolic hydroxyl group in the para-position or a free hydroxyl group on the β-carbon. This together with the fact that β-ether cleavage by neighboring hydroxyl groups plays an important role in lignin depolymerization shows that the presence of free hydroxyl groups is important for the ease of depolymerization.

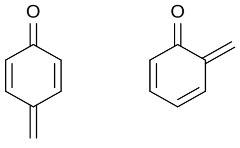


Figure 2.12 An example of simple quinone methides. Left: para quinone methide; right: ortho quinone methide.

Zhu *et al.*[139] suggested based on alkaline hydrolysis of black liquor that oxygen transfer occurs from lignin to light carbohydrate fragments through an oxygen carrier present in the reaction medium. This carrier oxidizes sulfides into sulfates and carbohydrates into organic acids. This is believed to be the pathway as no over reduction products such as cyclohexanols nor over oxidation products such as CO_2 were observed which is typical for reactions via free transfer of hydrogen and oxygen atoms.

Alkali during hydrothermal treatment accelerates the water gas shift (WGS) reaction. This may be relevant as formed hydrogen can act as a reducing agent improving the fuel quality of the obtained liquid. As an example with K_2CO_3 as catalyst the mechanism is believed to occur as follows where the alkali salt reacts with CO from a gasification reaction forming a formate salt ($HCOO^-K^+$):[38]

(2.1) $K_2CO_3 + H_2O \rightarrow KHCO_3 + KOH$

(2.2) $KOH + CO \rightarrow HCOOK$

Reaction of formate with water yields hydrogen and CO_2 is produced from $KHCO_3$:

(2.3) $HCOOK + H_2O \rightarrow KHCO_3 + H_2$

(2.4) $2KHCO_3 \rightarrow H_2O + K_2CO_3 + CO_2$

This yields the overall reaction by which K_2CO_3 catalyzes the WGS reaction:

(2.5) $CO + H_2O \rightleftarrows HCOOH \rightleftarrows CO_2 + H_2$

2.3.1.2 *Effect of Parameters*

BCD of lignin is typically highly dependent on factors such as temperature, reaction time and type of lignin, base and solvent. Experiments by Demirbas[90] with treatment of dried biomass in anhydrous glycerin in the presence of Na_2CO_3 or KOH showed that the most important variables with respect to maximize liquid yield are temperature, alkali concentration and the nominal reaction time. A large parametric study by Roberts *et al.*[73] using a continuous flow reactor indicated the relative importance of these parameters as well as the effect of varying pressures (by using a backpressure regulator) on the extracted oil yield and degree of depolymerization. The results provide an easily comparable parameter study and are illustrated in Figure 2.13 to Figure 2.16. The effects of individual process parameters reported in the literature are reviewed and discussed in the following.

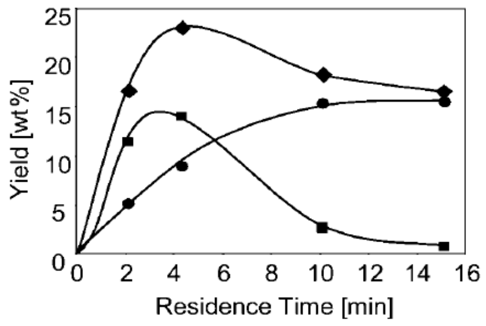


Figure 2.13 Effect of residence time on yields at 300 °C and 250 bar for a 10 wt% lignin and 4 wt% NaOH solution (diamond: oil, circle: oligomers, square: monomers)[73]

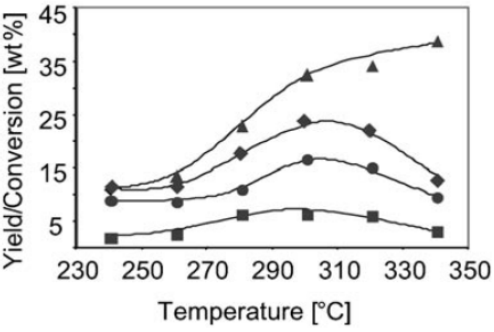


Figure 2.14 Temperature effect on oil yield and lignin conversion at 250 bar a residence time of 8 min for a 10 wt% lignin and 4 wt% NaOH solution (triangle: lignin conversion, diamond: oil, circle: oligomers, square: monomers)[73]

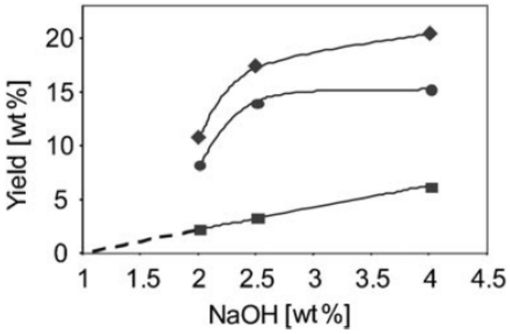


Figure 2.15 Influence of NaOH concentration on product yield with 10 wt% lignin at 320 °C, 250 bar, and a residence time of 8 min (diamond: oil, circle: oligomers, square: monomers)[73]

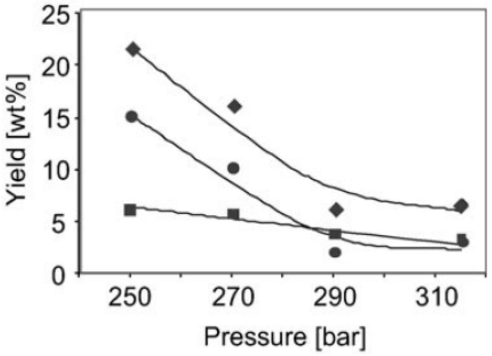


Figure 2.16 Influence of pressure on product yields at 320 °C, 8 min residence time, lignin/NaOH weight ratio 2.5 and 10 wt% lignin (diamond: oil, circle: oligomers, square: monomers)[73]

Temperature

The depolymerization of lignin greatly depends on temperature which may affect both depolymerized yield and composition. Schmiedl *et al.*[88] reported that maximum oil yield was obtained from aqueous BCD on organosolv and a sulfur containing technical lignin at 300 °C and 340 °C respectively. Beauchet *et al.*[85] reported a maximum lignin monomer yield of 8.4 wt% at aqueous NaOH treatment of Kraft lignin at 315 °C and 1.4 h^{-1} space velocity for a continuous BCD reaction. Roberts *et al.*[73] reported from experiments on aqueous BCD with temperatures varying between 240 °C to 340 °C an optimum oil yield as well as monomeric yield at 300 °C (see Figure 2.14). Mahmood *et al.*[89] concluded that higher temperatures of 350 °C for the depolymerization of Kraft lignin for 45-90 min in aqueous NaOH favored reduced molecular weight of polyols but also a significant reduction in depolymerized liquid yield of 27-28 wt% relative to ~85 wt% yield at 250 °C and 300 °C. These results indicate that in order to satisfy the highest depolymerized yield of small molecular fragments (monomers) temperatures of around 300 °C are typically required.

BCD can be compared to delignification of woody biomass. Alkaline treatment of different types of wood in the temperature range 127-227 °C have shown a linear relation between yield of delignification and temperature.[74,94,95] This emphasizes the importance of controlling the temperature even at temperatures <300 °C.

Reaction Time

The reaction time is of significant importance. Repolymerization reactions are favored at longer reaction times which indicate a competition between depolymerization and irreversible repolymerization.

Miller *et al.*[87] conducted BCD with 10 % KOH in ethanol or methanol at 290 °C for times up to 1 h. Only 7 % ether insoluble material was obtained after reaction and the maximum conversion was reached after 10-15 min. Schmiedl *et al.*[88] reported a maximum oil yield from aqueous BCD with NaOH on both technical lignin and an organosolv lignin after 10 min at 250-350 °C. Roberts *et al.*[73] reported from experiments on aqueous BCD with varying reaction times between 2 min to 15 min both an optimum monomer and optimum total oil yield after around 4 min. The monomer yield was 15 wt% but would decrease to near zero as reaction time was increased to 15 minutes (see Figure 2.13) indicating repolymerization. Mahmood *et al.*[89] argued that longer reaction times promoted dehydration/condensation reactions based on experiments with depolymerization of Kraft lignin at 250 °C / 300 °C for 45-90 min. A 6 h (5 wt% NaOH in water) depolymerization of technical hydrolysis lignin at 180°C gave a higher yield of low molecular weight phenolics compounds than with 4 h treatment by Nenkova *et al.*[140] but the reaction temperature was also lower than for typical BCD.

Base Concentration

The quantity of base added for lignin depolymerization has been reported many times in the literature to be of great importance and typically higher quantities of base are favored.[38,73,86–88] Roberts *et al.*[73] reported a linear relation between monomer formation and NaOH concentration (2-4 wt%) for aqueous BCD at 320 °C, 8 min residence time and 10 wt% lignin (see Figure 2.15). Schmiedl *et al.*[88] reported the use of up to 16 wt% NaOH in aqueous BCD for maximum oil yield. Miller *et al.*[87] reported that for treatment in KOH/ethanol the ethanol is partially converted to acetate, higher alcohols and other products in addition to alkylating phenolic rings. The formation of acidic products may account for excess base requirements.

Equally in aqueous medium Miller *et al.*[86] argued that the base:lignin ratio when using NaOH is more important than base concentration. Maximum lignin conversion was reported for a 1.5-2 NaOH:lignin mole ratio as acidic compounds in depolymerized lignin neutralized the base. Furthermore the formation of CO_2 also accounted for loss of base as Na_2CO_3 in basic medium will precipitate. The formation of insoluble Na_2CO_3 can be seen in the scheme below:

$$H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + H_2O \tag{2.6}$$

Experiments by Miller *et al.*[86] indicated that addition of CaO and NaOH improves kinetics but not lignin conversion. CaO is believed to be a scavenger for CO_2 formed and therefore beneficial in counteracting the base consumption through Na_2CO_3 formation.

Alcohols in alkaline environments will deprotonate readily and Roberts *et al.*[73] argued that excess NaOH helps converting hydroxyl groups to alcoholates of phenolic (and catecholic) compounds which increases solubility and thereby accessibility to ether bonds due to a reduction of internal hydrogen bonding between hydroxyl groups.

Another advantage of ensuring high pH is that it inhibits dehydration of monomers (alcohols). Increased dehydration yields unsaturated products which may more easily polymerize to char and tar.[38]

Type of Base

As the effect of lignin depolymerization in alkaline media is highly dependent on base concentration it is difficult to compare effects of different bases from individual studies. Based on treatment of wood biomass for 15 min at 280 °C Karagöz *et al.*[141] ranked the catalytic activity with respect to yield of oil products of different alkali as follows: K_2CO_3 > KOH > Na_2CO_3 > NaOH. Studies on KOH, NaOH, CsOH, LiOH, $Ca(OH)_2$ and Na_2CO_3 by Miller *et al.*[87] indicated that strong bases give superior conversion and a combination of bases can yield both positive as well as negative synergistic effects. Excess base relative to lignin monomer units was required for maximum conversion. The dominant depolymerization route is solvolysis of ether linkages independent of type of base. Ogi *et al.*[142] argued that carbonates and hydrogen carbonates of potassium, sodium and calcium all showed strong catalytic effects

Pressure

Limited studies are reported on the specific effect of pressurizing the vessel in which BCD on lignin are conducted. Higher pressures are obtained as a result of conducting BCD in an autoclave at autogenous pressure when higher temperatures than the normal boiling point are used which complicates comparison of BCD experiments by different authors. Roberts *et al.*[73] investigated the effect of pressure on oil yield for aqueous BCD in a continuous flow reactor at 320 °C, 8 min residence, lignin/NaOH weight ratio 2.5 and 10 wt% organosolv lignin. Pressure was regulated by adjusting a backpressure regulator. The highest oil yield of 22 wt% was found at the lowest pressure of 250 bar and the lowest oil yield of 7wt% was obtained at the highest pressure of 315 bar. As pressure was lowered the yield of oligomeric products in the oil yield increased more significantly than the yield of monomers (see Figure 2.16). The results indicated that lower pressures were favorable but pressures below 250 bar were not tested due to inherent difficulties in operating below the vapor pressure of the solvent.

Acidification and Extraction

In order to industrially make BCD viable, several steps are needed including neutralization/acidification followed by several extraction steps.[97] BCD yields dissolution of depolymerized lignin species. Following BCD the product mixture needs to be neutralized typically to an acidic pH in order to extract the pure depolymerized lignin free from alkali salts in the water phase. Acidification by addition of for example HCl or H_2SO_4 will reprotonate deprotonated species such as alcohol groups in the depolymerized lignin. The acidification may cause precipitation. Water is typically added to the acidic product mixture, if non-aqueous BCD has been performed, followed by extraction with an organic solvent. The latter may subsequently be removed industrially by flash distillation or in lab scale using rotary evaporation to yield the pure depolymerized lignin free from salts as the aqueous phase should ideally contain these. Miller *et al.*[86] suggested that neutralization of the product solution with CO_2 advantageously would yield Na_2CO_3 or $NaHCO_3$ from which Na is recoverable as an alternative to adding an acid.

García *et al.*[98] selectively precipitated lignin from a black liquor at pH values ranging from 0.7–12.6. They concluded that the pH at which lignin is precipitated greatly effects composition and properties of the lignin. This emphasizes the importance of controlling pH when neutralizing.

Schmiedl *et al.*[88] investigated the effect on oil yield and product composition when different extraction solvents were used. The effect of using different extraction solvents greatly affects the composition and in particular oil yields as the highest oil yield of 28 wt% of lignin was obtained from using ethyl acetate compared to 23 wt%, 12 wt% and 9 wt% oil yield for dichloromethane, methyl isobutyl ketone and toluene respectively.

Solvent

The solvent used in alkaline lignin depolymerization is typically aqueous or an alcohol. In particular alkaline glycerol is also used as method for delignification of biomass. Advantages of using glycerol for BCD liquefaction are higher boiling point, higher thermal degradation temperature, polarity and a dehydration effect. Furthermore glycerol is a by-product from biodiesel and soap productions making it readily available.[91] Kücük[92] argued that the main advantage of alkaline-glycerol treatment is removal of lignin at atmospheric pressure due to the high boiling point. Inevitably some glycerol may however be lost due to decomposition at elevated temperatures.[74]

Wood liquefaction in a polar solvent such as glycerol initially results in a swelling due to an attraction to the dry solid matrix by hydrogen bonding forces. Adjacent polar groups cause the swelling by repulsion. This swelling and reduced surface tension at higher temperatures is believed to allow for easier penetration of alkali into pores of wood and the diffusion of breakdown products of lignin from the wood into the solvent.[91,94]

Gan *et al.*[93] added glycerol to a BCD process on corncobs. Higher bio-oil yields were observed as more crude glycerol was added (glycerol to biomass ratio ranging from 0 to 5) together with a product having lower viscosity and density; however, the oxygen content slightly increased from 13.8 to 19.9 mole% O.

A comparison between ethanol and methanol in BCD on Kraft and organosolv lignin at 290 °C by Miller *et al.*[87] showed that ethanol had better performance. Ethanol was reported to form phenols and ethyl ethers by reaction with phenyl ethers. Equally some alkylation of phenols and catechols were believed to be due to ethanol.

Results have indicated that base in excess is favored for depolymerization of lignin, but Kuznetsov *et al.*[126] demonstrated that without the addition of a solvent they obtained only a low maximum yield of bio-liquid of 14-15 wt% at 400-450 °C from hydrolytic lignin liquefaction at low pressure (1 bar) by melted mixtures of sodium and potassium formates with NaOH and KOH. This emphasizes that solvent effects play an important role in BCD of lignin.

Lignin and Feedstock Type

The lignin type and biomass feedstock may greatly affect factors such as ease and degree of depolymerization. Miller *et al.*[87] saw that organosolv had higher conversion relative to a Kraft lignin at 290 °C for BCD with KOH in both methanol and ethanol. Using organosolv lignin the amount of residual insolubles was only 7 wt% after 60 min ethanolic BCD relative to 20 wt% when using Kraft lignin. Schmiedl *et al.*[88] similarly reported that an organosolv lignin treated by aqueous BCD required only 300 °C for maximum oil yield of 23 wt% relative to a technical lignin requiring 340 °C which yielded 15-16 wt% indicating that the organosolv lignin was more easily depolymerized.

Demirbas[143] found that both the heavy oil yield and amount of solid residue increases with increasing lignin content of treated biomass by thermal degradation in alkaline glycerol. Ramsurn *et al.*[144] reported a 40 % bio crude yield from a two-step process for switchgrass liquefaction imposing a subcritical acidic water treatment at 200 °C prior to supercritical aqueous alkaline treatment at 380 °C with $Ca(OH)_2$. The effect of the first step was to remove hemicellulose in order to allow better accessibility to cellulose and lignin and extraction of biocrude formed already after the first step should limit the extend of repolymerization between sugar degradation products and lignin. The second step was believed to be particularly beneficial due to alkali promoted swelling of the biomass. The swelling increases the internal surface area separating structural linkages between the cellulose, hemicellulose and lignin [91,94,144].

Additives for Inhibition of Repolymerization

Inhibition of repolymerization is crucial for maximizing liquefaction yield and several studies have shown beneficial effects of adding smaller amounts of additives to the alkaline depolymerization. Ogi *et al.*[142] conducted woody biomass liquefaction by aqueous BCD with potassium carbonate and addition of primary alcohols to the reaction medium. They pressured the autoclave prior to heat up with nitrogen (20-41 bar) and reaction occurred at 300 °C for 0-30 min leading to oil yields of 45-50 %. They reported that adding alcohols 1-propanol, 2-propanol or 1-butanol to the reaction mixture yielded a lower viscosity oil with yields of 50-70 %. Low viscosity oil is advantageous for transport operations. They concluded that added alcohol was not consumed nor reacting as a hydrogen donor but merely stabilizing unstable wood products. This allowed for recycling of the solvent.

The effect of stabilizing cleaved lignin species was investigated by Roberts *et al.*[73] by adding boric acid. They added boric acid to a BCD with NaOH and achieved up to 85 wt% depolymerized lignin yield. Boric acid worked as a capping or protecting agent forming esters with phenolic hydroxyl groups thereby reducing the potential for repolymerization.

Schmiedl *et al.*[88] conducted aqueous BCD (NaOH) on an organosolv lignin (beech) by adding sodium formate which would decompose under the applied conditions and generate H_2 *in situ* (see also section 2.3.1.1 for the mechanism of water gas shift acceleration by formate). Adding formate at 300 °C lowered oil yield to 17-19 wt% relative to 23 wt% in the case of NaOH only but altered the monomer composition as aryl-methyl ether bond cleavage was favored. Adding formate the BCD would favor formation of higher amounts of catechol type monomerics and oligomerics and reduce the amount of guaiacyl and syringyl monomerics.

Sulphide containing sodium hydroxide is more favorable than pure sodium hydroxide for wood digestion as suggested by Hägglund[145] which is believed to be due to the formation of thio-lignin which has greater solubility mainly due to the fact that the addition of sulfur to reactive groups in lignin results in loss of condensation propensity. This is a parameter used in sulfite pulping of lignin also (see section 2.1.3).

2.3.1.3 Summary of Lignin Depolymerization in Alkaline Media

The mechanisms of base catalyzed depolymerization (BCD) of lignin are well established and similar to those in pulping in the paper industry. The solvent in BCD is typically water but alcohols may also be used. A reaction temperature of around 300 °C is typically favored in order to maximize monomer yield and short reaction times of no longer than 10 minutes have equally been reported to be favorable. The use of different bases may not be as important as simply ensuring a relatively high base to lignin ratio or high alkalinity of the solvent. Adding different bases have even shown beneficial synergistic effects on lignin depolymerization as reported by several authors.

The principal route for lignin depolymerization is through solvolysis of ether linkages. In particular nucleophilic attack by deprotonated neighboring hydroxyl groups facilitate β-ether cleavage. In general the presence of free hydroxyls on the lignin polymer is key to provide depolymerization. A deoxygenation is typically observed in the depolymerized lignin mainly due to demethoxylation. A disadvantage of BCD is that base is typically consumed during the reaction. Neutralization/acidification is required after BCD in order to extract the liquefied lignin yield which fully eliminates residual base and different methods of extraction may greatly affect yield and composition.

2.3.2 Aqueous Media

In this section the solvent effects of direct lignin liquefaction in water are discussed. Conversion of lignin in aqueous media was reviewed by Kang *et al.*[146] who discussed three main categories comprising wet oxidation (100 - 200°C), hydrothermal liquefaction (250 - 450°C) and catalytic as well as non-catalytic gasification (350 - 500°C and 400 - 700°C respectively). They argued that oxidative means of hydrothermal conversion were advantageous due to the lower temperatures and the fact that such routes are already utilized in industry. Gasification technologies are disadvantageous due to the high temperatures and low efficiencies. They argued that hydrothermal liquefaction is a promising means of lignin valorization.[146] This section describes the mechanisms and effect of parameters on hydrothermal liquefaction only. Some overlap exists with other direct liquefaction techniques involving BCD and solvolysis in alcohols as solvent mixtures and addition of alkali have been reported to enhance liquefaction.

Understanding the effects of hydrothermal treatment on lignin alone is complicated as studies on whole biomass are more common.[38] Hydrothermal treatment of biomass holds several advantages and the main one being that water is a readily available solvent. Reactions with wet biomass are possible without drying of the feedstock prior to treatment and organic product separation from water is relatively easy which reduces cost of operation.[4] A waste stream containing organic material from hydrothermal processing may also advantageously be utilized as is be simply feeding it to a bio gas plant facilitating recovery of biogas.[1] The different properties of both sub- and supercritical water may have advantageous effects on solubility of different organic compounds and gasses which are described in more detail in section 2.3.2.1. Furthermore several organic decomposition reactions have been reported to occur without catalyst in sub-/supercritical water which is described in more detail in section 2.3.2.2. Sub-/supercritical water can however also be disadvantageous due to the harsh reaction conditions and char formation can be problematic especially on high lignin content feedstocks.[4] Typically also lower yields have been reported on high lignin content feedstocks and often the addition of a catalyst or base have shown to improve liquefaction yield.[64,107–109]

2.3.2.1 Properties of Sub- and Supercritical Water

The critical point for water is 374 °C and 221 bar. The subcritical region is defined as the temperature range between the normal boiling point and the supercritical temperature. The properties of water greatly change dependent on normal, subcritical or supercritical conditions. Supercritical water has for instance low viscosity, high diffusivity, a dielectric constant similar to many organic solvents but the advantage of thermal stability.[4,38] Relevant properties at normal, subcritical and supercritical conditions for water are shown in Table 2.2.

Table 2.2 Properties of water at conditions below and above critical conditions.[38]

	Normal water	**Subcritical water**		**Supercritical water**	
Temperature (°C)	25	250	350	400	400
Pressure (bar)	1	50	250	250	500
Density (g cm^{-3})	1	0.80	0.6	0.17	0.58
Dielectric constant (F m^{-1})	78.5	27.1	14.07	5.9	10.5
Ionic product	14.0	11.2	12	19.4	11.9
Heat capacity (kJ kg^{-1} K^{-1})	4.22	4.86	10.1	13.0	6.8
Dynamic viscosity (mPa s)	0.89	0.11	0.064	0.03	0.07

The dielectric constant of water decreases from 78 F/m at normal conditions to 14 F/m at 350 °C and 250 bar at subcritical conditions. This gives increased solubility of hydrophobic organic compounds (eg. fatty acids) as near supercritical conditions are approached but the solubility of salts is significantly decreased. Some salts though have relatively high solubility at subcritical conditions such as NaCl.[147] Supercritical water has an even lower solubility of salts due to an even lower dielectric constant. Supercritical water is however completely miscible with light gases, hydrocarbons and aromatic compounds[4] and has been reported to fully dissolve cellulose[61].

The ionic product of water is 100 times greater at near supercritical conditions ($pK_w = 12$) compared to normal conditions ($pK_w = 14$). This means a higher level of OH^- and H^+ is present due to increased dissociation of water molecules at subcritical conditions which accelerates many acid or base catalyzed reactions.[38] Supercritical water has a high ionic product but an equally lower density affects dissolution. At subcritical conditions the density of water is between that at normal conditions and supercritical and this combined with high degree of dissociation of water molecules means that ionic reactions are favored such as dehydration of carbohydrates and alcohols and aldol splitting.[104,105] At supercritical conditions radical reactions dominate causing increased degree of gasification.[38]

Near super- and supercritical water is highly corrosive. Near supercritical water is even more corrosive due to higher density.[38] The high corrosivity may be disadvantageous as process equipment may be damaged or expensive alloys are needed.

2.3.2.2 Mechanisms

The mechanisms for lignin depolymerization by water greatly depend on the properties of the water at the specific conditions. Mechanisms reported involve water acting as both a catalyst and a reactant.[38]

Hydrothermal treatment of beech, poplar, spruce and wheat straw by Wild *et al.*[148] at milder conditions at 160-230 °C for 15-120 min showed that lignin ether bonds are broken but the remaining structure is hardly affected. A study on lignin model compounds by Ehara and Saka[149] indicated that β-O-4 bonds were easily cleaved in supercritical water whereas biphenyl compounds (5-5 linkages) are stable.

Barbier *et al.*[150] conducted batch autoclave experiments for hydrothermal treatment of alkali lignin and lignin model compounds at 370 °C and 390 °C at 250 bar and reaction time between 5 and 40 min. The starting material was injected to the hot reaction medium and through a comparison of the resulting depolymerized products obtained using GC, FT-ICR/MS and NMR they proposed a reaction pathway in which lignin is depolymerized involving competitive fragmentation mainly by hydrolysis of ether bonds and condensation mainly by alkylation of aromatic rings of intermediate products.

Depending on the water properties at different reaction conditions the formation of catechol from guaiacol is believed to follow different reaction mechanisms. Guaiacol is a model compound for a phenyl ether and the mechanisms of reactions between water and guaiacol might give an insight into real lignin reactions. At subcritical conditions and near supercritical conditions of water the dielectric constant and ionic product are high and hydrolysis provides H^+ and OH^- ions which redirect selectivity of guaiacol to catechol formation (see Figure 2.17).[103]

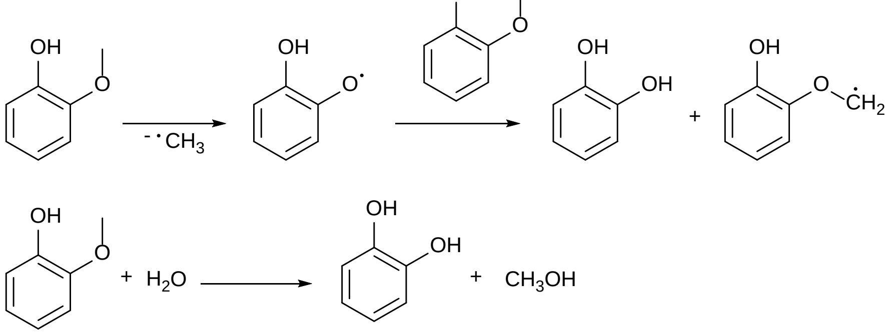


Figure 2.17 Catechol formation from guaiacol through pyrolysis (top) and through hydrolysis (bottom) at hydrothermal conditions. Modified from Yong and Yukihiko[103].

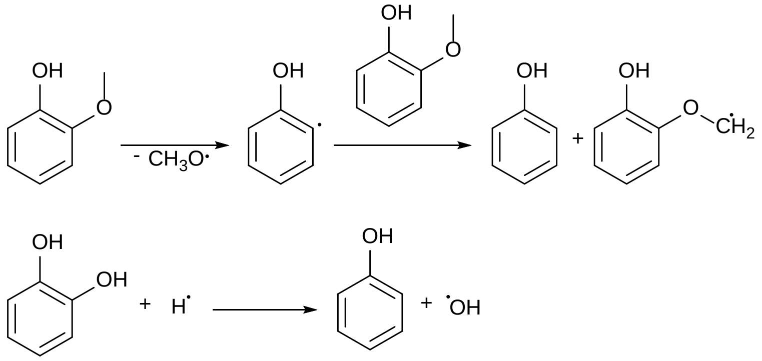


Figure 2.18 Phenol formation from guaiacol and catechol under hydrothermal conditions. Modified from Yong and Yukihiko[103].

An increase in temperature up to 370 °C indicated increased catechol yield by Yong and Yukihiko [103]. At supercritical conditions the catechol yield was considerably increased, however, it was believed to be attributed to a radical mechanism (pyrolysis) where homolytic cleavage yields catechol and a methyl radical. The catechol radicals can further abstract hydrogen from another guaiacol molecule thus forming catechol [103]. Similarly phenol formation from guaiacol is believed to occur through a radical mechanism where phenol radicals formed abstract hydrogen from a guaiacol molecule thus forming phenol (see Figure 2.18). Similarly proton abstraction from catechol is believed to potentially form phenol through reaction with another catechol molecule. Yong and Yukihiko[103] saw a decrease in phenol formation from hydrothermal treatment of guaiacol under supercritical conditions. The radical mechanism should not be affected by water properties as an increase in temperature should ideally cause an increase in the rate of phenol formation. However, since the opposite trend was observed, this may indicate that the reaction pathway is in fact not through a radical mechanism but through hydrolysis by the supply of H^+ and OH^- ions from water.

Lu *et al.*[151] investigated the deoxygenation of several aquatic plants obtained relatively low yields of liquid oil (11.23 - 16.70 %) at 80-100 bar and temperatures of 350-400 °C with a heat up time of 80 °C/min and short treatment time of 15 mins. They did however propose radical mechanisms for a range of reactions potentially taking place which are shown in Figure 2.19. Since they observed high amounts of CO_2 it was suggested that the formation of this specie resulted from mainly CO removal from terminal aldehydes (1) which at the high temperature and high pressure conditions would react with HO* or RO* radicals (produced from thermal cracking in reaction(4)) in order to form the more stable CO_2 (reactions (5) and (6)). Reaction (6) was found to be the most dominant reaction for deoxygenation. Another dominant deoxygenation pathway was believed to be through dehydration as water constituted a great portion of the products (see reactions (3) and (8)). H* radicals from (5) may react and terminate alkyl group radicals (9) and similar termination could also be obtained by alkyl group radicals reacting with each other (7). At 400 °C and 80–100 bar phenolic side chain alkylation and deoxygenation was believed to occur through a radical mechanism. Here CH_3* radicals formed, as a result of methoxy bond cleavage at the applied conditions, react to yield 1-3 methyl substituted phenolics. Furthermore, CO removes oxygen at the PhO* radical in the form of CO_2.

$$\mathrm{R{-}CHO} \longrightarrow \mathrm{CO} \qquad (1)$$

$$\mathrm{R{-}OH} \longrightarrow \mathrm{R}^{\bullet} + {}^{\bullet}\mathrm{OH} \qquad (2)$$

$$\mathrm{R{-}OH} + \mathrm{R'{-}OH} \longrightarrow \mathrm{R{-}O{-}R'} + \mathrm{H_2O} \qquad (3)$$

$$\mathrm{R{-}O{-}R'} \longrightarrow \mathrm{R{-}O}^{\bullet} + {}^{\bullet}\mathrm{R'} \qquad (4)$$

$$\mathrm{CO} + {}^{\bullet}\mathrm{OH} \longrightarrow \mathrm{CO_2} + \mathrm{H}^{\bullet} \qquad (5)$$

$$\mathrm{CO} + \mathrm{R{-}O}^{\bullet} \longrightarrow \mathrm{CO_2} + {}^{\bullet}\mathrm{R} \qquad (6)$$

$$\mathrm{R}^{\bullet} + {}^{\bullet}\mathrm{R'} \longrightarrow \mathrm{R{-}R'} \qquad (7)$$

$$\mathrm{H}^{\bullet} + {}^{\bullet}\mathrm{OH} \longrightarrow \mathrm{H_2O} \qquad (8)$$

$$\mathrm{H}^{\bullet} + \mathrm{R}^{\bullet} \longrightarrow \mathrm{RH} \qquad (9)$$

Figure 2.19 Proposed radical induced pathway for the formation of benzenes and phenols. Modified from Lu *et al.*[151]

Matsumura *et al.*[61] suggested that other alkylated phenols with vacant ortho or para positions of hydroxyl groups can also be used as capping agents. Since these agents can be obtained from lignin they proposed a possible process for lignin conversion as the following:

1. Conversion of lignin in water-phenol mixtures and obtain low molecular products
2. Decomposition of phenolic products in the reforming such as partial oxidation or gasification in supercritical water to recover monomeric alkyl phenols and phenol
3. A part of monomeric alkyl phenols and phenol is recycled to feed

This proposed process bears similarity to the Bergius process[44] and the Noguchi process[4,46] where the solvent/product mixture is recycled (see section 2.2.1).

Zhang *et al.*[152] did a kinetic study on hydrothermal treatment of high-diversity grassland perennials and the highest liquid yield obtained was 82 % at 374 °C, 221 bar and 1 min reaction time. They applied different simple kinetic models to the biomass decomposition from two data sets (300 and 374 °C at 100 and 221 bar respectively for 1 min) and found the best fit for a model, where biomass is first decomposed to tars (liquid products or bio-oil), gaseous products and chars via three parallel reactions. Subsequently tars are subjected to a second cracking step producing gases. This model is typically used to describe solvent free pyrolysis and hence this indicates that there is no effect of the solvent. The reaction scheme can be seen in Figure 2.20.

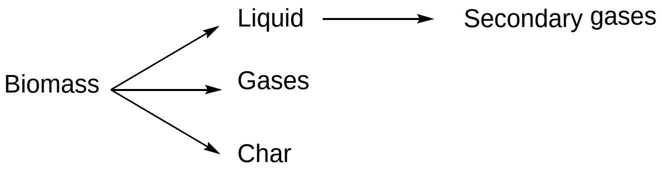


Figure 2.20 Proposed route for the hydrothermal decomposition of high-diversity grassland perennials. Modified from Zhang *et al.*[152]

Forchheim *et al.*[153] also kinetically modelled hydrothermal lignin depolymerization but used data sets using a wide range of different lignins and conditions. They concluded that at <400 °C the rate constants for hydrolysis (cleavage of C-O bonds) are higher and the activation energies lower compared to more severe conditions.

Aida *et al.*[154] reported that retro-Friedel-Craft reactions break C-C bonds for phenolic compounds and alcohol or aldehyde in supercritical water. However, because of the extremely high reactivity for phenol to react with aldehydes (Friedel-Craft reaction), cross-linkage formation takes place for phenolic structures which makes complete dissolution of lignin in supercritical water difficult.[61,62] Intermediate carbonium species may react by cleavage of β-O-4 ether bonds, however, adjacent aromatic electron rich carbon atoms may compete for the carbonium ion forming stable C-C linkages resulting in repolymerization.[30] Cross linking of formed species in hydrothermal lignin treatment react predominately through Friedel Craft mechanism.[40,80–82] During steam explosion of 4 g aspen wood by Li *et al.*[30] repolymerization was inhibited by addition of 160 mg 2-naphthol. They argued that 2-Naphthol may have acted as a scavenger for formed carbonium ions.[30]

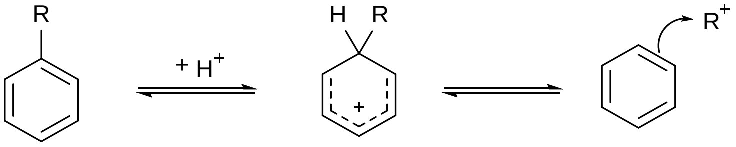


Figure 2.21 Friedel craft reaction (electrophillic alkylation).

Aqueous Phase Reforming (APR)

Reforming of alcohols may contribute to hydrogen that can facilitate lignin ether bond cleavage as well as lower oxygen content by hydrogenolysis (see also section 2.3.3 for effects of alcohol reforming). The presence of sugars in the lignin or biomass feed may also readily contribute to hydrogen formation through APR *in situ.* This reaction is typically catalyzed. Several reactions are believed to take place in the aqueous reforming of alcohols. Peppley *et al.*[155] listed the three overall reactions for the steam reforming of methanol on $Cu/ZnO/Al_2O_3$ yielding H_2 and CO/CO_2 formation:

(2.7) $CH_3OH + H_2O \rightleftarrows CO_2 + 3H_2$

(2.8) $CO + H_2O \rightleftarrows CO_2 + H_2$

(2.9) $CH_3OH \rightleftarrows CO + 2H_2$

Zakzeski and Weckhuysen[156] reported on the aqueous reforming of a range of different lignin types and model compounds at temperatures ≤225 °C and pressures ≤ 29 bar (reaction time 1.5 h). Optimum product yields were found with the addition of H_2SO_4 and Pt/Al_2O_3. The process of lignin depolymerization was believed to involve disruption of β-O-4 linkages mainly to form monomeric aromatic compounds. Of the monomeric compounds the alkyl chains were reformed to produce hydrogen and simple aromatics particularly guaiacol and syringol depending on lignin source. Methoxy groups present on the aromatics were hydrolyzed to form methanol which in turn was also reformed to produce hydrogen.

Zakzeski *et al.*[157] dissolved Kraft lignin in a 1:1 (v:v) water-ethanol mixture and in a one pot experiment compared results from aqueous phase reforming over Pt/Al_2O_3 in both basic and acidic conditions with a reduction using noble metals and nickel on different supports where gaseous hydrogen was added. At 225 °C and 58 bar the aqueous phase reforming yielded 17.6 wt% isolated aromatic yield using H_2SO_4 as co catalyst. The highest isolated aromatic yield from the reductions with gaseous hydrogen was 6.2 wt% using Pt/Al_2O_3.

2.3.2.3 Effect of Parameters

Sub- and supercritical water treatment of lignin containing feedstock depend on many factors such as type of feedstock, severity of the process conditions and reaction time. Furthermore, research has shown that water-alcohol mixtures (phenolics in particular) give higher yields of lignin-oil than water alone.[63,80,123,154,158–160]

Hydrothermal treatment at subcritical conditions is comparable to BCD when the medium is alkaline. The alkaline conditions in BCD have widely been reported to benefit lignin depolymerization (see section 2.3.1). Even the addition of small quantities of base (1.0 wt% Na_2CO_3) to semi continuous hydrolysis experiments on cornstalk lignin by Song *et al.*[107] provided an increase in biocrude yield from 33.4 to 47.2 %. The Catliq© process utilizes a similar catalytic system to improve yield and product quality of hydrothermal treatment where a continuous plant experiment (30 dm^3/h wet biomass) on wet distillers grain at 280-370 °C and 250 bar in the presence of alkali (2.5 wt% K_2CO_3) and a heterogeneous ZrO_2 catalyst would give an oil yield on dry biomass of 33.9±1.8 %. The LHV of the oil was 35.8±0.2 MJ/kg and elemental composition revealed a significantly decreased O-content of 5.6±0.4 wt%.[64]

Acidic conditions have also shown an increase in oil yield from hydrothermal treatment by Funazukuri *et al.*[161] who treated lignin sulphonate with water at a density of 375 kg/m3 at 350 °C for 5 min. Adding HCl (0.009M aqueous solution) gave a slight increase in obtained oil yield from 24.8 to 27.9 wt%.

The effects of individual process parameters on hydrothermal lignin liquefaction are reviewed in the following subsections.

Reaction Time

The effects of hydrothermal treatment of biomass is highly dependent on reaction time.[99–103] Hydrothermal liquefaction of Cunninghamia Lanceolata (China fir) by Qu *et al.*[100] in an autoclave for 10-30 min indicated that the lowest reaction time of 10 min yielded the highest maximum heavy oil yield at all temperatures in the range 280-360 °C. Maximum heavy oil yield was 24 % with 8 g biomass in 100 ml water at 320 °C. A much higher liquid yield of 90.2±2.2 wt% was obtained from hydrothermal treatment of aspen lignin for 10 min after rapid heat up (140 °C/min) by Zhang *et al.*[101] Air drying of the liquid yield did however lower the yield to 78 wt% liquid which emphasizes the difficulty in comparing results from different authors as the post treatment liquid separation/extraction processes may differ and impose significant differences in how the liquid yield is defined. It was argued that the breakdown into lignin monomers is fast whereas the repolymerization is slow hence short reaction times with rapid heat up and fast cool down is desired. Brand *et al.*[102] equally observed an increased liquefaction yield of pine saw dust in sub critical water (350 °C) with both increased heating and cooling rate and they argued for similarity to fast pyrolysis.

For even shorter residence times (<1 min) Yong *et al.*[103] conducted experiments on guaiacol conversion in both sub- and supercritical water (300-450 °C, 250 bar) with varying residence times 0.5-40 s in a continuous flow reactor. Longer reaction times favored char and gas formation.

Subcritical vs. Supercritical Water (Temperature and Pressure)

Many studies show significant differences in yield and product composition depending on the water properties as a direct result of varying reaction temperature which affects reaction pressure[99,103,106,108,109,162]

Kumar *et al.*[108] conducted semi continuous subcritical water treatment of switchgrass in the temperature range 235-260 °C which are temperatures lower than traditional subcritical treatment temperatures. More than 50 wt% of organic carbon was converted to a biocrude after 20 min at 235 °C in the presence of only 0.15 wt% K_2CO_3 as catalyst. This catalyst was believed to lower the severity of the required reaction conditions. At 260 °C dehydration reactions were favored over hydrolysis reactions ultimate leading to increased char formation by condensation.

González and Montané[163] investigated in the presence of NaCl on the kinetics of dibenzylether cleavageat 325 to 390 °C and 225 to 362 bar. Under supercritical conditions Na^+ ions may act as a Lewis acid by charge transfer to water molecules which were believed to catalyze the hydrolysis of dibenzylether.

Guaiacol conversion in sub-/supercritical water at 300-450 °C at a pressure of 250 bar in a continuous flow reactor by Yong and Yukihiko[103] indicated that supercritical conditions would favor increased char and gas formation. Favorably higher liquefaction yields observed in the subcritical regime[100,103] may be due to increased solvent density as Funazukuri *et al.*[162] treated lignosulphonate by sub-/supercritical water and showed almost independent of reaction time (2-5 min) at 400 °C an increase in oil yield for increasing water density up to ~300 kg/m^3 near the critical point. For higher water densities up to 600 kg/m^3 the oil yield was almost constant at 22-28 wt%.

Pínkowska *et al.*[106] conducted a three step process for subcritical conversion of rapeseed straw with increasing severities (temperature) at each step. The first two steps depolymerized/decomposed hemicellulose and cellulose, whereas the third and final step yielded up to 89.82 % insolubles (determined as sulfuric acid insoluble) consisting mainly of phenolic biochar. It leads to believe the first two steps may have caused increased polymerization of lignin which ultimately makes it harder to depolymerize.

Nguyen *et al.*[109] conducted continuous LignoBoost Kraft lignin conversion in near-supercritical water (290-370 °C) using ZrO_2/K_2CO_3 as catalyst. The effect of increased reaction temperature resulted in a char increase from 16 to 22 wt% and an oil yield decrease from 87 to 69 wt%; however, the yield of monomeric aromatics was increased.

Solvent Mixtures

Okuda *et al.*[158] treated organosolv lignin for 1 hour in water, phenol and a water-phenol mixture (1.8 g : 2.5 g) at 400 °C and showed that a mixture of water and phenol has synergistic effects on lignin depolymerization. No char formation was observed for the mixture and 99 wt% of the products of depolymerization in phenol-water mixture was soluble in tetrahydrofuran (see Figure 2.23). The THF soluble yield from reaction in water or phenol was only 82 wt% and 87 wt% respectively at similar conditions. The synergistic effects of phenol and water effect was also verified by Fang *et al.*[159] and Aida *et al.*[154].

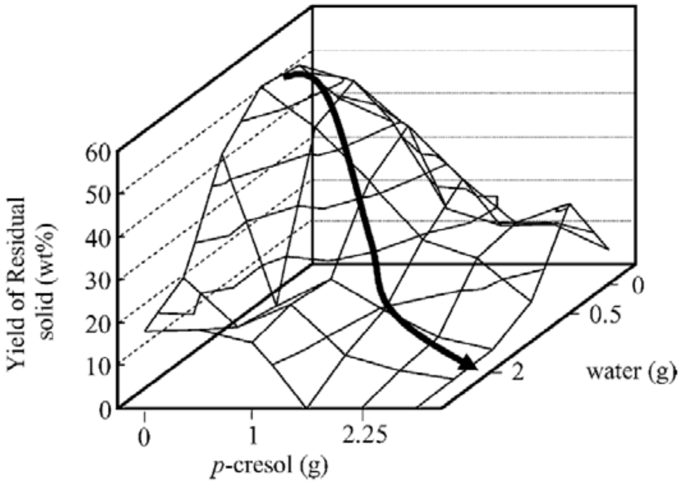


Figure 2.22 The yield of THF insoluble products over a wide range of compositions of water-*p*-cresol solvent mixtures by Okuda *et al.* [160] Modified by Dorrestijn *et al.*[61]

Okuda *et al.*[160] also investigated the optimum lignin solubility in a mixture of water and *p*-cresol. Complete dissolution of 0.1 g organosolv lignin was found in 4.3 g solvent with a water:*p*-cresol ratio of 1.8:2.5 (w:w) for 60 min treatment at 400 °C. The yield of THF insolubles for different water and *p*-cresols mixtures is shown in Figure 2.22.

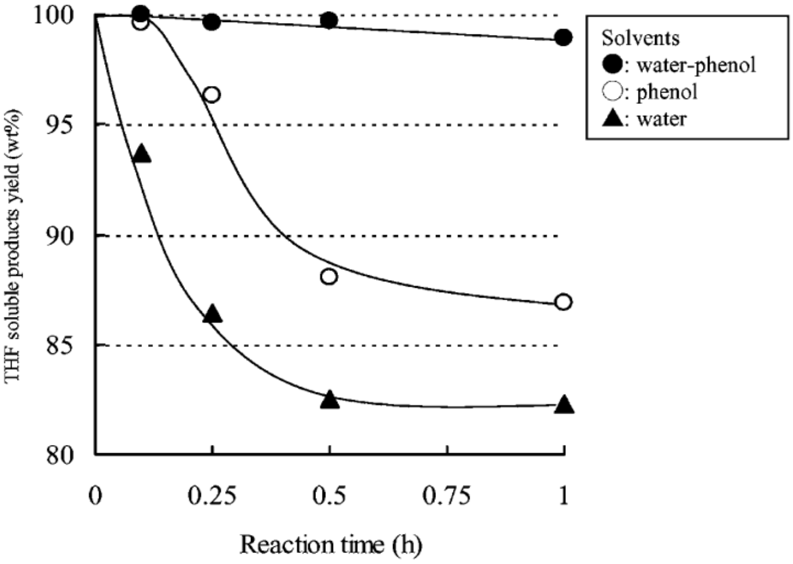


Figure 2.23 The effect of reaction time on the yield of THF soluble products by reactions at 350 °C in three different solvents (closed circles: water-phenol (1.8g:2.5g), open circles: phenol (2.5g), closed triangles: water (2.5g))[158]

Okuda *et al.*[158] proposed a mechanism involving initial cleavage by hydrolysis at ether and hydroxyl group sites in the lignin molecule. Decomposition of lignin by hydrolysis and dealkylation occurs in supercritical water without phenol forming reactive low molecular weight fragments, formaldehyde etc. and compounds such as syringols, guaiacols and catechols.[80] Cross-linking between these fragments and residual lignin yields heavier molecules corresponding to residual solids. Saisu *et al.*[80] argued that in the presence of phenol or *p*-cresol these react with the reactive fragments suppressing formation of heavier components. Okuda *et al.*[158] similarly argued in their study that phenol helps by trapping active sites as a result of the cleavage thereby inhibiting repolymerization between larger molecular fragments. Furthermore formed components of formaldehyde were also believed to facilitate re-polymerization of lignin fragments and the formaldehyde was also believed to be effectively trapped by reacting with excess phenol forming dimers instead.

Belkheiri *et al.*[63] highlighted the synergistic effect of adding both phenol (<5 wt%) and methanol (up to 61 wt%) to near critical (280–350 ˚C and 250 bar) hydrothermal depolymerization of Kraft lignin in a continuous fixed bed reactor with ZrO_2 as catalyst and K_2CO_3 as co-catalyst. Methanol seemed to inhibit char formation but negatively impact oil yield, but the latter was enhanced by the phenol addition. The highest oil yield of 72.2 wt% was however obtained in the case of zero methanol addition and only 4.1 wt% added phenol.

Depolymerization of an organosolv lignin and Klason lignin by Yoshikawa *et al.*[123] was performed in a 1-butanol/water mixture in the presence of a silica-alumina catalyst. Only ~15 % char was formed with a molar H_2O:BuOH ratio of 4 by treatment at 300-350 ˚C for 2-4 h. A reaction mechanism was proposed whereby hydrolysis occurs in the aqueous phase and the BuOH phase facilitates the process by removal of formed species and potentially esterification of formed acids. The authors proposed that a second step involving treating the products of the first step in a fixed-bed flow reactor over an iron oxide catalyst as a route to phenol production.

Gasses

A few studies have addressed the effects on hydrothermal processing by pressurization with individual gasses. Bembenic and Clifford[164] investigated the effect of adding gases (N_2, H_2, CO, CO_2 at initial pressure of 34.5 bar) to organosolv subcritical depolymerization in a tubular reactor at 365 °C for 30 min. The highest yield of dichloromethane (DCM) solubles (oil yield) was 60.8 wt% for the addition of N_2 and the lowest yield was 23.4 wt% with no pressurization prior to heat up. Liquid products analyzed by GC/MS from the addition of CO showed the widest variety of products of mainly methoxy substituted products. It was argued that CO_2 may have been poorly dissolved in water at the applied conditions and hence the reason for having the smallest effect on depolymerization.

Funazukuri *et al.*[161] treated lignin sulphonate with water at a density of 375 kg/m3 at 350 ˚C for 5 min. Adding both Na_2CO_3 (5 wt% aqueous solution) and CO (20 bar initial pressure) gave an oil yield of 25.5 wt% but for a similar experiment with no CO added the oil yield was lowered to only 15.6 wt%.

Lignin and Feedstock Type

The type of biomass/lignin may greatly influence the oil yields obtained by hydrothermal treatment. A comparative investigation by Karagöz *et al.*[165] on woody biomass (pine wood sawdust), nonwoody biomass (rice husk), cellulose and lignin with hydrothermal treatment at 280 °C for 15 min showed the following order of conversion: cellulose > sawdust > rice husk > lignin. The type of lignin was a commercial one but no further details were given. The recovered oil yield from lignin was only

3.9 %. Subcritical aqueous treatment of nine species of biomass by Demirbas[166,167] equally indicated that oil yield decreased and char increased with increasing lignin content. Adding KOH would increase oil yields as one might expect as the process would resemble BCD (see section 2.3.1). Hydrothermal liquefaction of a Kraft lignin, organosolv lignin, aspen lignin and hardwood and switchgrass residues by Zhang *et al.*[101] gave different oil yields depending on lignin type. The highest air dried liquid yield of 78 wt% was obtained by 10 min treatment of alkaline extracted Aspen lignin at 350 °C. Only the Aspen lignin was treated at 350 °C and the other lignins were treated at 374 °C. At these more severe conditions a Kraft pine lignin yielded the highest air dried liquid yield of 58.8 wt% due to a higher content of Klason lignin and the lowest yield of 15.2 wt% was obtained from switchgrass residue.

Demirbas[168] subjected a range of agricultural wastes to supercritical fluid extraction using acetone, methanol or water as a solvent. The highest dissolution/depolymerization was obtained from olive waste at 405 °C using water giving a yield of 59.3 % despite the relatively high lignin content of 45.6 wt% (d.a.f.). Liu and Liu[169] equally compared whole biomass liquefaction in water to liquefaction in alcohol solvents (ethanol and methanol). For batch autoclave experiments with Cypress liquefaction at temperatures up to 300 °C they achieved the highest bio-oil yield using water but the oil consisted of four to six times as much carbohydrate breakdown products compared to solvolysis in alcohols and the maximum oil yield was 32 wt% which was twice as great as when using alcohols.

A 46 wt% bio-crude yield from Nannochloropsis Salina (algae) at 350 °C and 175 bar hydrothermal treatment was reported by Toor *et al.*[170] Algae typically have a low or no lignin content which may explain the higher oil yield relative to pure lignin feedstocks. A range of plant biomasses were pyrolytically treated by Wang *et al.*[171] in a closed vessel with only 15 % water at 350 °C for 2-3 h reaching pressures 120-130 bar. The heating rate was low at 10 °C/min. The highest oil yield obtained was 10.5 % from legume straw and gas production was significant for all feedstocks ranging from 38-52 %. CO_2 was the dominant gaseous specie ranging from 82-86 % for all feedstocks. The oil did however mainly consist of aromatic compounds.

2.3.2.4 Summary of Lignin Depolymerization in Aqueous Media

Near supercritical water is desired for hydrothermal processing of biomass as subcritical water has a higher density than supercritical water and the high dissociation constant of water at these conditions favors hydrolysis. At the elevated temperatures (<374 °C) cleavage of lignin inter unit linkages is however dominated by thermally induced radical mechanisms and through retro Friedel craft reactions. It is required to keep residence times short and a fast heat-up time is required similarly to the process of fast pyrolysis in order to limit repolymerization. High lignin content feedstocks typically results in increased charring and whole biomass is often a preferred feedstock over use of pure lignin. Addition of catalyst such as base has shown increased liquefaction yields and at high base concentrations the process resembles increasingly base catalyzed depolymerization as described in section 2.3.1. Typically addition of a solid catalyst such as ZrO_2 addition has also shown increased yield. A water-phenolic mixture equally improves liquid yields possibly attributed to inhibition of reactive fragments formed limiting repolymerization.

2.3.3 Polar Organic Media

In this section the solvent effects of direct lignin liquefaction in polar organic solvents are described. Most of these solvents reported in the literature are alcohols. The organosolv process for lignin separation from lignocellulosic biomass may to some extent resemble direct liquefaction of lignin in alcohols where near complete lignin dissolution has been reported. Less severe conditions are applied in the organosolv process (see section 2.1.4) limiting the degree of depolymerization. Some alcohols have been reported to work as hydrogen donors and are often applied in systems with solvent mixtures.[124–127] Supercritical conditions have been reported to be advantageous for increased degree of depolymerization and the short chain alcohols require less severe conditions in order to obtain supercritical conditions relative to water which is advantageous. Lignin stemming from the unutilized lignin waste stream that is obtained by bioethanol production may advantageously be treated by direct liquefaction on the plant site. This improves transport logistics as ethanol is already a product stream that can be used for the lignin liquefaction. A disadvantage of using alcohols is the potential for solvent loss in the form of alkylation or decomposition which may impose an added cost relative to liquefaction in water for example. Produced lignin oil from treatment in polar organic solvents may be more difficult to separate from the product stream requiring a large scale flash evaporation operation and lower boiling point alcohols are thus more desired solvents.

An alternative to solvent recovery includes using the resulting liquefied lignin and solvent mixture as a fuel mix. Alcohols are already used in liquid fuel blends and an alternative implementation of using alcohol in fuels by Jiang *et al.*[172] involved making an emulsion of an ether soluble fraction of pine pyrolysis oil with a biodiesel (4:6 by volume) using 3 % octanol as surfactant. This highlights another potential use of an alcohol in the production of liquid fuel from lignin.

2.3.3.1 Mechanisms

Delignification of wood by different alcohols is not fully understood.[92] The presence of alcohols in different lignin depolymerization processes have been reported to retard polymerization reactions (see also section 2.3.2.3).[119–123] Alcohols may contribute to direct cleavage of lignin ether linkages but also hydrogen donating effects of alcohols have been reported to be of importance. In catalytic systems the reforming of alcohols can yield *in situ* formed hydrogen which may explain one way by which alcohols can work as hydrogen donors. An example of reversible hydrogen donation from an alcohol is in the case of using 2-propanol, where hydrogenation of the lignin by the use of an appropriate catalyst for example Raney Nickel yields acetone.[124] The latter can potentially be regenerated to 2-propanol by hydrogenation.

Zhao *et al.*[75] proposed a mechanism by which supercritical ethanol depolymerizes guaiacyl groups of lignin (see Figure 2.24). They proposed that supercritical conditions result in cleavage of the C-O bond in ethanol yielding ethyl and hydroxyl radicals which are believed to actively participate in both ether and C-C bond cleavage. Initially a hydroxyl radical is believed to attack the β-carbon and subsequent dehydration reaction contributes to removal of oxygen. Ethyl radicals were believed to attack on either side of the beta carbon. The mechanism proposed includes several homolytic cleavages and the presence of hydrogen radicals would ultimately form more stable non-radical species.[75] The hydrogen donating capability of ethanol may also yield stabilization of the free radicals formed.[121]

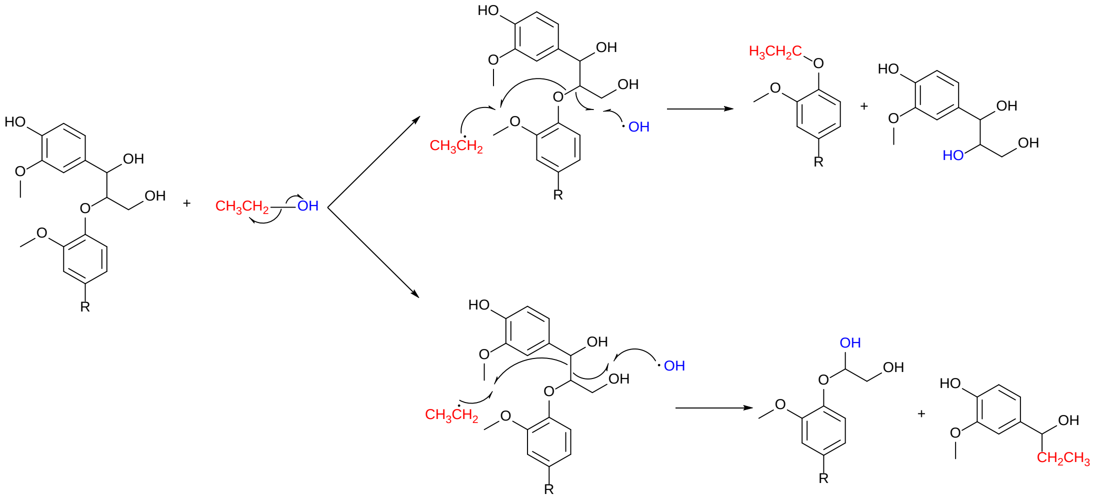


Figure 2.24 Proposed pathway for the formation of phenol derivatives from supercritical ethanolysis of guaiacyl groups in lignin and wheat stalk powder. Ethyl and hydroxyl radicals facilitate ether bond cleavage and are colored for reference. The radical mechanism may continue by dehydration reactions and thermally induced bond cleavage yielding more radicals. Presence of H* may terminated formed radicals. Modified from Zhao *et al.*[75]

Reforming of alcohols typically over a solid catalyst is one way of providing gaseous hydrogen. Reforming without the presence of water typically occurs over a metal catalyst[125,126] and in the presence of water through APR (see section 2.3.2.2). 2-propanol and ethanol have been reported to have a higher H-donating capability than methanol.[126] Experiments by Song *et al.*[127] on birch wood sawdust depolymerization at subcritical conditions (200 °C for 6 h) with Ni/C in the alcohols methanol, ethanol and ethylene glycol indicated that hydrogen from the alcohols provide the active hydrogen species as further addition of gaseous hydrogen did not improve conversion. Similarly the presence of gaseous hydrogen together with hydrogen donating solvents has also been reported to have negligible influence on the degree of depolymerization by Schurchardt *et al.*[133] Kim *et al.*[110] observed however increased depolymerization of organosolv lignin in supercritical ethanol with hydrogen added without the presence of a catalyst and hydrogen was believed to suppress recondensation. Results of different studies where hydrogen was added is discussed further in section 2.3.3.2. Results of isotopic deuterium labeling of ethanol by Song *et al.*[127] showed that alcohol molecules act as a nucleophilic reagent for C-O-C cleavage in an alcoholysis reaction. Conversion of smaller lignin fragments into monomeric phenols by labelling experiments was shown to undergo elimination by dehydration at the β- and α-carbon followed by hydrogenation. The gamma carbon was believed to be reduced by direct cleaving of the -OH bond by hydrogenolysis. Song *et al.* [127] did not describe to what degree ethanol would be consumed in the reaction or what would happen with ethanol species that have contributed with hydrogen donation following donation. Huang *et al.*[173] equally investigated catalytic lignin depolymerization in ethanol without the addition of hydrogen. The catalyst was solid $CuMgAlO_x$ and a range of lignins were tested at 380 °C reaction temperature and 8 h reaction time. Kraft lignin liquefaction gave the highest monomeric product yield of 86 wt% but a mass balance closure of 146 wt% indicated a significant proportion of solvent polymerization products. In addition to facilitate lignin polymer cleavage the alcohol was believed to effectively inhibit repolymerization due to a formaldehyde scavenging effect as formaldehyde formed as a product of lignin depolymerization may readily react in a polymerization reaction with phenolic hydroxyl groups. These effects have equally been attributed to hydrothermal liquefaction in water-alcohol mixtures (see section 2.3.2).

2.3.3.2 Effect of Parameters

Treatment of lignin in polar organic solvents depend on many factors such as reaction time, temperature, lignin feedstock and lignin:solvent ratio. The types of solvent also greatly affects yields and quality of the obtained oil products and even different solvent mixtures have been reported to have beneficial effects on depolymerization. The effects of individual process parameters reported in the literature are reviewed in the following.

Reaction Time

The reaction time applied greatly differs in many studies from minutes up to several hours. Typically, the greater the severity of the conditions applied the shorter the reaction time required for maximum depolymerization/conversion.[75,110] The effect of heating rate on lignin liquefaction rate has not been widely studied in supercritical solvents but pine wood liquefaction in supercritical ethanol (350 °C) by Brand *et al.*[102] suggests that only marginal improvement of the oil yield was seen when the heating rate was increased from 2 °C/min to 20 °C/min and a significantly more pronounced effect was seen when using water as solvent instead. For processes at lower temperatures (<250 °C) and conditions resembling organosolv process conditions longer reaction times of up to several hours have been reported.[121,128] Singh *et al.*[174] conducted rice straw liquefaction in ethanol and methanol at reaction temperatures between 250 °C and 300 °C and no clear change on oil yield was seen for residence times 15, 30 and 60 min. Lee and Lee [116] varied the reaction time in conversion of Kraft lignin in both acetone and butanol at 250-450 °C up to 70 min, and found a maximum yield of hexane extractable products after 50 min after which the yield leveled off. Sub- and supercritical ethanol depolymerization of organosolv lignin by Kim *et al.*[110] yielded a maximum oil yield of 94.9 wt% at 200 °C after 20 min reaction time relative to 40 min and 60 min treatments. No gasses were formed possibly due to the low temperature. At 350 °C the effect of shorter reaction times was even more pronounced. Zhao *et al.*[75] reported that an even shorter reaction time of 10 min for wheat stalk lignin depolymerization in ethanol at 300 °C would yield the highest liquid yield at 52.5 % relative to higher reaction times up to 60 min.

Temperature

It has been well reported that for treatment at conditions near the conditions of organosolv extraction high degrees of lignin solubility occur but the dissolution of lignin does not necessarily indicate a substantial degree of depolymerization. The quality of the depolymerized liquid yield reported by different authors therefore becomes just as important as the actual amount of isolated yield.

Soria *et al.*[113,114] argued that super critical methanol treatment of pine wood was dependent on density of the methanol. They varied density by different loading ratios of the vessel. The main gas formed were CO and CO_2 comprising around 90 wt% of all gasses formed[113]. They achieved a maximum wood liquefaction of 48 % (w/w) with subcritical methanol at 235 °C. At supercritical conditions for methanol a maximum of 90 % liquefaction was achieved at 367 °C. When even more severe conditions were applied by treating 2 g of lignin in 35 ml methanol at 500 °C a 98 % liquefaction was achieved with a volume ratio of methanol/vessel of 0.46 (resulting in a MeOH density of 0.325 g/ml). Char formed was mainly composed of crystalline polysaccharides mixed with some condensed residual lignin.

Minami and Saka[115] also emphasized the need for high severity for supercritical methanol depolymerization of beech and cedar wood as treatment for 30 min at 350 °C / 430 bar would yield more than 90 % liquefaction. At 270 °C and 270 bar the yield was lowered to 53 wt% for cedar wood but nearly unchanged at 89 wt% for beech wood. Treatment of wheat stalk by supercritical ethanol by Zhao *et al.*[75] at temperatures of 240-300 °C equally indicated an optimum oil yield at increased severity at the temperature 300 °C. For solvolysis temperatures 250–300 ˚C for rice straw liquefaction in ethanol by Singh *et al.*[174] the highest liquefaction yield of 48 wt% was equally observed at 300 ˚C and an almost proportional dependence on reaction temperature for different reaction times tested (15, 30 and 60 min). When using methanol as solvent the yield was however nearly unchanged at around 20 to 25 wt%.

Lee and Lee[116] investigated the effect of varying the temperature between 250-450 °C for Kraft lignin in both acetone and butanol. They experienced an increase in conversion (determined by the amount of residual solid) up to 60 % when the temperature was increased to 400 °C but hereafter the conversion leveled off. Despite the high conversion the maximum yield of recovered product through hexane extraction was only about 13 % as a considerable amount gaseous products were formed.

Solvent

Yamazaki *et al.*[117] compared liquefaction of beech wood in a range of supercritical primary alcohol solvents at 350 °C (see Figure 2.25). Alcohols with long alkyl chains showed the trend of exhibiting faster wood conversion. After 3 minutes 1-octanol yielded 95 % liquefaction of the entire wood. Liu and Liu[169] equally observed both similar oil yields and solid residues after liquefaction of Cypress in ether methanol or ethanol at temperatures 180–300 °C. Significant differences between supercritical methanol and ethanol liquefaction of rice straw was reported by Singh *et al.*[174]. At temperatures 250-300 °C the oil yield obtained when using methanol was almost unchanged between 20-25 wt% whereas as the oil yield increased to up to around 45 wt% when using ethanol showing a significant disadvantage of using methanol as solvent.

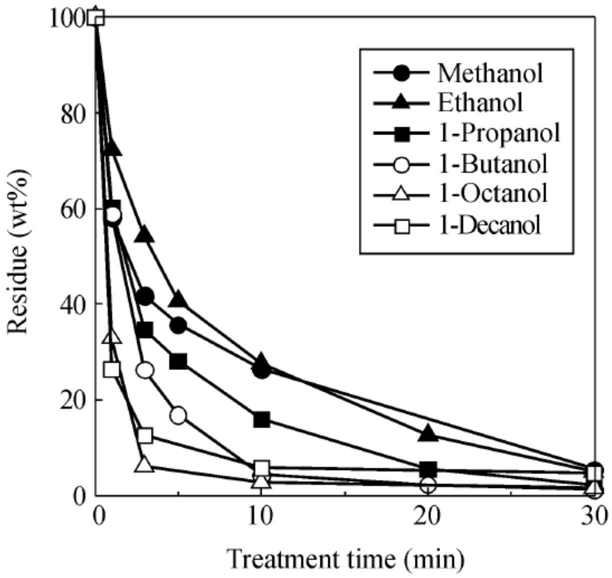


Figure 2.25 Changes in the solid residue of beech wood in supercritical primary alcohols at 350°C.[117]

Thermal cracking of Kraft lignin by Lee and Lee[116] in acetone and butanol for comparison indicated similar conversions at varying temperatures and reaction times determined by amount of residual solids. GC-MS indicated great differences in product distribution for the two solvents in mainly aliphatic esters and ethers from treatment in butanol. Products of solvent decomposition may however be responsible for this. Torre *et al.*[175] reported that for organosolv extraction of lignin ethanol and acetone are equally efficient at lower temperatures but ethanol acts faster. The opposite with respect to conversion rate was experienced by Liu *et al.*[176] as acetone would yield the highest rate of conversion relative to ethanol and water for pinewood liquefaction. They investigated the liquefaction of pinewood by solvolysis in water, acetone or ethanol but not a mixture. Maximum oil yield of 26.5 % was achieved in ethanol at only 200 °C. The use of water significantly narrowed the product distribution. The results make it difficult to predict exact results on pure lignin due to the cellulosic and hemicellulosic content of the wood used and low lignin content of 22 wt%. Erdocia *et al.*[177] conducted solvolysis in a batch reactor of different organosolv lignins form olive tree pruning in pure acetone, methanol and ethanol at 300 °C for 40 min. Lignin to solvent ratio was kept constant at 1:20 (w:w) and they concluded that acetone performed the best with respect to depolymerization to monomeric phenols as the highest oil yield of 38.04 wt% was observed. In order of depolymerization efficiency the solvents were ranked acetone > ethanol > methanol. Acetone was believed to facilitate increased demethoxylation, dealkylation and demethylation consequently leading to formation of more cresols and catechols.

At relatively mild conditions Yip *et al.*[118] experienced the highest liquefaction yield of 99 % for bamboo liquefaction in phenol at 180 oC after 18 hours relative to a maximum liquefaction of 80 % in ethylene carbonate and 69% in ethylene glycol. Lignin liquefaction in polyhydric alcohols such as polyethylene glycol and glycerol have shown promising as means of obtaining a depolymerized product suitable as precursor for polyurethane production.[111,178,179] Higher boiling alcohols may result in difficulties in recycling; however, advantageously a liquefaction process may be carried out at ambient pressure. Li *et al.*[112] conducted liquefaction of lignin from bioethanol production (cornstalk residue with a lignin content of 62.18 wt%) in furfuryl alcohol at temperatures up to the boiling point of 170 °C. At the highest temperature, 15 min reaction time and a solvent to feedstock ratio of 5:1 (w:w) the highest liquefaction yield of 80.23 wt% (dry ash free lignin basis) was achieved. The use of furfuryl alcohol as solvent compared to a mixture of poly ethylene glycol and glycerol (80:20 on a weight basis) resulted in slightly lower solid residue after reaction; however, liquefaction yields in the latter solvent mixture were not reported.

Water Mixtures

Alcohols and water have shown synergistic effects with respect to lignin liquefaction.[120–123] The majority of studies comprise whole biomass which may explain improved yields due to improved liquefaction of cellulose and hemicellulose in aqueous medium (see section 2.3.2). The alcohols ethanol or methanol showed synergistic effects with water for biomass liquefaction by Cheng *et al.*[120] as higher solubility in a mixture was observed than in pure alcohol or water. For ethanol-water or methanol-water at 50 wt% mixture optimum pine sawdust to oil conversion of 65 wt% was observed at 300 °C. Rice husk liquefaction in 1.1 (v:v) ethanol-water solvent also yielded a higher oil yield than either of the solvent alone in studies by Liu *et al.*[180] Increasing the solvent density by increasing the solvent to vessel volume ratio had a positive impact on oil yield. Reaction temperatures tested were 260-340 °C and with the water-ethanol mixed solvent the highest oil yield was 21.15 wt% at 260 °C.

For a hydrothermal depolymerization of enzymatic hydrolysis cornstalk lignin in an ethanol-water mixture (0-95 vol%) at residence times 30-180 min, and reaction temperatures 225-300 °C Ye *et al.*[121] determined optimal conditions of 250 °C, 90 min and 65 vol% ethanol-water with a yield of liquid products of 70 wt%. A solvent mixture of 65 vol% ethanol in water showed synergistic effects as the liquid yield was highest and solid yield lowest which indicated an inhibition of condensation, dehydration and gasification of lignin. Product distribution greatly depended on water to ethanol ratio. They suggested that the hydrogen-donating capability of ethanol yielded a stabilization of free radicals generated from the depolymerization of lignin. In another study by Ye *et al.*[122] Klason lignin was treated at similar conditions where 3 wt% lignin in a solution of 65 vol% ethanol in water yielded 65.5 % recoverable liquid products and only 17 % solid residue. ~30 % of identified compounds were value adding phenolics including 4-ethylphenol, 4-vinylphenol, guaiacol, 4-ethylguaiacol and 4-vinylguaiacol. Kraft lignin depolymerization in water-ethanol mixtures was also investigated at 300 °C by Lee *et al.*[181] who observed the highest yield (35 wt%) of monomeric aromatics in the oil product when using pure ethanol. When the concentration of water was increased (up to 100 %) the formation of phenol, guaiacol and alkyl guaiacols was reduced but catechol formation increased.

Yan *et al.*[182] observed synergistic effects of using a water-methanol mixture as solvent for Poplar liquefaction compared to water or methanol alone at reaction temperatures 240-320 °C for 0-90 min. The highest liquefaction yield of 44.2 wt% was obtained at 270 °C for 15 min in a solvent with 70 vol% water and 30 vol% methanol. Methanol was believed to facilitate esterification which would not occur in water alone. The positive synergy between methanol and water was mainly seen on cellulose and hemicellulose liquefaction; however, oil products stemming from the lignin were still increased. Similar results were also observed for cornstalk liquefaction in a methanol-mixture by Zhu *et al.*[183] where the solvent mixture performed better than pure alcohol or water. Optimum conditions with respect to maximizing methanol and carbon disulfide/acetone extractables were 300 ˚C and 30 min.

Hydrogen

Kim *et al.*[110] investigated the effect of adding gaseous H_2 to supercritical ethanol depolymerization of an organosolv lignin. The effect of increasing hydrogen pressure was investigated at 350 °C and an increase from 0 to 30 bar initial H_2 pressure increased the oil yield from 36.3 to 54.3 wt%. Increasing the hydrogen pressure and increasing the temperature increased the amount of alkylated phenols found in the oil. Hydrogen gas was believed to suppress the recondensation of monomeric fragments.

Hydrolytic eucalyptus lignin was hydrogenated in hydrogen donor (tetralin, isopropanol, cyclohexanol) as well as non-donor solvents (xylene, pyridine) by Schuchardt *et al.*[133]. At all conditions the solvents were supercritical with the exception of experiments with tetralin. The heavy oil yields increased more with hydrogen pressure for the non-donor solvents than for donor solvents. At very high hydrogen pressure (<360 bar) the effect of the hydrogen donating solvent was annulled. Adding a ferrocene catalyst had only small influence on the oil yields in hydrogen donating solvents but a much larger influence in the non-donor solvents. This led to the conclusion that hydrogen is mainly transferred from the solvent itself in the donor solvents. For all solvents studied the heavy oil yield increased with increased density of the solvent up to a maximum of 0.30 g/ml above which the effect of increased solubility is negligible. The highest oil yield was 94.0 % from treatment at 330 bar at 400 °C in cyclohexanol with the presence of the Fc/S catalyst. The lignin conversion was actually lower at 78.3 % due to decomposition of the solvent which reacted by condensation and was recovered in the heavy oil fraction.

Barta *et al.*[125] reported complete conversion of an organosolv lignin with no char formation by using supercritical methanol and a 20 % Cu-doped porous metal oxide (hydrotalcit). The quantity of gas formed was not reported. The catalyst acted by *in situ* generation of hydrogen by reforming methanol which in a one step process yielded complete hydrogenolysis of phenyl-ether bonds and almost complete hydrogenation of aromatics yielding a mixture of monomeric substituted cyclohexyl derivatives with reduced oxygen content. The oxygen content was not reported though.

Kuznetsov *et al.*[126] achieved a yield of bio-liquids of 80-90 wt% from hydrolytic lignin liquefaction in methanol attributed to H-donation at 410 °C and 200 bar using a Fe-Zn-Cr catalyst. The presence of the catalyst increased liquid yields up to 5-10 times and the obtained liquids had a low oxygen content of 6-10%.

Acidic Conditions

Acid-catalyzed liquefaction of lignocellulosic biomass in ethanol mainly leads to the formation of ethyl esters.[78,123] Combining ethanol with hydrochloric acid has also been reported to increase the extraction efficiency of lignin from biomass.[175]

Taner *et al.*[184] compared the yields from acetic acid and sodium hydroxide treatment respectively of cotton stalk at 250 ºC, 300 ºC and 350 ºC with initial nitrogen pressure of 50 bar. In acetic acid treatment it was argues that high molecular compounds would degrade to low molecular weight water soluble compounds at a temperature increase from 300 to 350 °C explaining a drop in oil yield and increase in the water soluble fraction. The highest amount of water solubles in sodium hydroxide was at 300 °C. It is however difficult to interpret the obtained data due to overlapping fractions of solid tar, oil and water solubles. Different reaction mechanisms are expected for acidic treatment relative to alkaline treatment where the mechanisms of the latter are described in more detail in section 2.3.1.

Jin *et al.*[111] liquefied an enzymatic hydrolysis lignin in a mixture of polyethyleneglycol, glycerol and sulfuric acid at temperatures 130-170 °C and the undissolved residue amounted to only 1.6-9.0 wt%. The liquefaction product was polyether polyols and they proposed that these products could be used in manufacturing polyurethane. Similar experiments were conducted by Zhang *et al.*[179] using Bagasse indicated that the most important parameter was the concentration of sulfuric acid.

Lignin Type and Loading

As previously mentioned Minami and Saka[115] reported differences in depolymerization yield on beech (89 wt% yield) and cedar wood (53 wt% yield) treated at 270 °C / 270 bar in supercritical methanol. This originated from differences in intrinsic properties of lignin structures of hardwood and softwood. 1-3 wt% of the supplied biomass was found to be methanol-insoluble condensed lignin. At 350 °C similar yields of 90 wt% were obtained from both woods.

Erdocia *et al.*[177] argued that the molecular weight of the lignin starting material has an influence on the maximum oil yield obtained when they conducted solvolysis of different types of organosolv lignins in acetone, methanol or ethanol. They observed that the lower the molecular weight of the lignin the lower the maximum oil yield becomes.

The lignin:solvent ratio may greatly influence the quantity of obtained lignin-oils. The effects of different lignin to solvent ratios can be difficult to compare between different authors as an increased liquid loading of a batch reactor may affect the solvent density which also affects the yield of depolymerized product[113]. Zhao *et al.*[75] conducted wheat stalk solvolysis in ethanol at 240-300 °C for 10 – 60 min at varying solid to ethanol ratios (1:8, 1:12 and 1:24). They argued that the optimum conditions were a wheat stalk:ethanol ratio of 1:24 at a reaction temperature of 300 °C for 10 min yielding the highest oil yield of 52 wt%. At the lowest wheat stalk to ethanol ratio (1:24) the highest oil yields were equally observed at the lower reaction temperatures tested; however, reaction times were also different making a direct comparison between the results difficult. Kim *et al.*[110] depolymerized organosolv lignin in ethanol with solvent-to-lignin ratios 50, 100 and 150 ml/g. The maximum oil yield was obtained as 94.9 wt% at 200 °C with 100 mL/g solvent ratio and 20 min reaction time with no hydrogen added. Yip *et al.*[118] varied the solvent-feedstock ratio for bamboo in phenol, ethylene glycol and ethylene carbonate from 2:1 to 10:1. Maximum liquefaction yield was obtained for phenol and ethylene carbonate liquefaction at 180 °C for 18 h at a solvent ratio of 10:1. In ethylene glycol however a solvent ratio of 5:1 would yield the maximum liquefaction yield of 69 % which was significantly higher than the yield of 52 % obtained for a solvent ratio of 10:1. Results of liquefaction of cornstalk biorefinery lignin in furfuryl alcohol at 170 °C for 15 min by Li *et al.*[112] showed that an increase from a solvent to lignin ratio of 3:1 to 5:1 (w:w) equally resulted in an increased liquefaction yield of 72 wt% to 80 wt%.

2.3.3.3 Summary of Lignin Depolymerization in Polar Organic Media

Direct lignin liquefaction by polar organic solvents has typically been reported using alcohols as suitable solvents. Supercritical solvent conditions are often reported as a necessity for effective lignin depolymerization resulting in typical temperatures between 300-400 °C. An increased reaction temperature typically increases liquid yield and when the reaction severity is increased a shorter reaction time is required. Reaction times of up to several hours are however often reported in order to maximize liquid yield. An increased lignin to solvent ratio has also been investigated to some extend and typically results in a decreased oil yield and no beneficial effects have been reported. Alcohol solvents facilitate reductive depolymerization through cleavage of ether linkages in the lignin and hydrogen donating effects of the solvent have also been reported. Cleavage has been reported to follow both radical mechanisms as well as reactions in which for example ethanol facilitates heterolytic cleavage by nucleophilic attack. It is widely established that alcohols inhibit repolymerization reactions and in particular mechanisms of direct alkylation of alcohols reacting with depolymerized lignin species have been reported.

2.3.4 Formic Acid

In this section the solvent effects of direct lignin liquefaction in formic acid are described. The reactivity and reaction between aryl ether linkages and H-donating solvents is described in more detail in a review by Dorrestijn *et al.*[62] Typically solvent mixtures and not pure formic acid is reported in the literature. An advantage of using formic acid for the depolymerization of lignin is the generation and donation of hydrogen *in situ* during depolymerization and typically char yields reported are low for H-donating solvents. The H-donating ability of formic acid is however irreversible due to decomposition of the molecule which can be disadvantageous as the solvent cannot be recycled.

2.3.4.1 Mechanisms

Formic acid works as a hydrogen donor by irreversibly decomposing to form H_2. At high pressure and temperature yields of CO_2 and H_2 are major products from formic acid decomposition, so decarboxylation is the preferred pathway. The mechanisms of formic acid decomposition at high temperatures in aqueous medium are illustrated in Figure 2.26 where the formation of H_2 and CO_2 is the preferred pathway.[129]

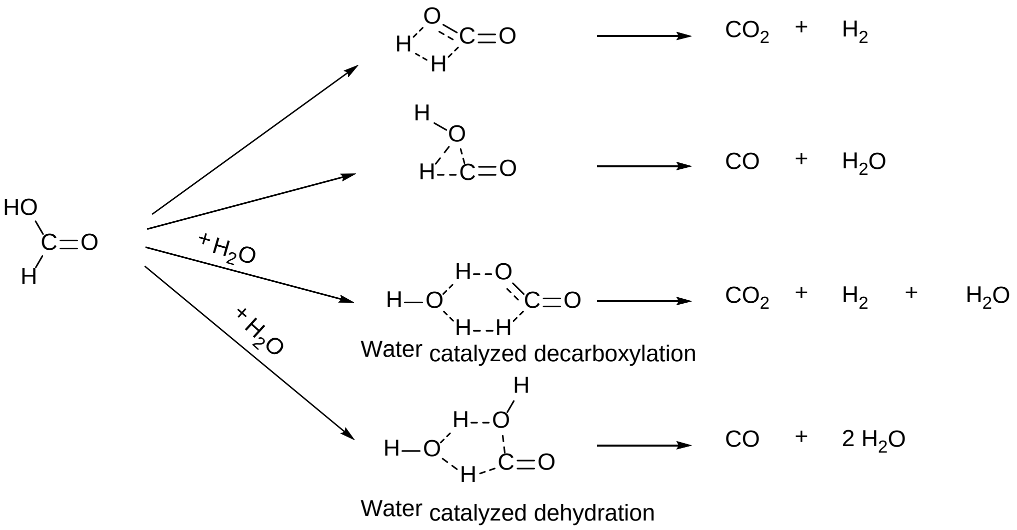


Figure 2.26 Different decomposition reactions for formic acid at high temperatures in aqueous medium. The preferred pathway is highlighted in the top. Modified from Yu and Savage[129].

The reactions with *in situ* formed H_2 from decomposition of formic acid favors hydrodeoxygenation through demethoxylation of the lignin yielding reduced monomers.[6] Depolymerization experiments of model compounds in formic acid and ethanol (1:2 v/v) by Holmelid *et al.*[84] indicated that demethoxylation was first initiated by a homolytic cleavage of the inter unit linkages producing radical pairs which may participate in fragment recombinations or further reaction. Such reaction is shown in Figure 2.27 where a methoxy group is eliminated from an *o*-methoxy phenoxy radical. Lignin depolymerization by formic acid is often conducted in a mixture of solvents so many mechanisms facilitating cleavage described in section 2.3.3 may also contribute to the mechanism of cleavage here. Studies have indicated that increasing hydrogen partial pressure alone using alcohols would yield more depolymerized species showing that hydrogen availability from the solvents limits the depolymerization (see section 2.3.3.2).[110,133] Formic acid in alcohol will lower the pH and organosolv processes have also been reported to benefit from the addition of acids with respect to the degree of lignin dissolution.[111,175,184]

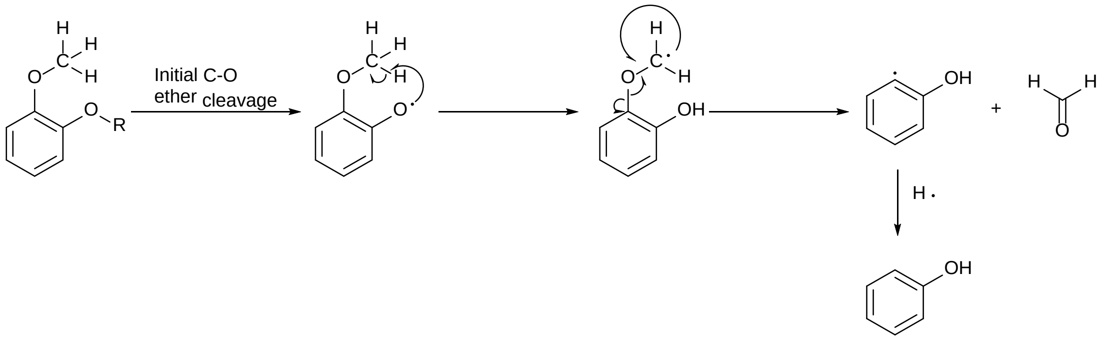


Figure 2.27 Radical initiated elimination of the methoxy group from *o*-methoxy phenoxy radical. Modified from Holmelid *et al.* [84]

2.3.4.2 Effect of Parameters

The addition of alcohol as co-solvent to formic acid depolymerization of lignin is widely reported to improve both yield and H/C ratio.[76,77,130,131] Kleinert and Barth[76] and Kleinert *et al.*[77] obtained near similar O/C and H/C ratios of oils from solvolytic treatment of different wood lignins, hydrolysis lignin and lignosulphonate in formic acid and alcohols (MeOH, EtOH and isoPrOH). Optimization experiments on the conversion of lignin treated at 350-400 °C indicated that low loading of lignin with moderate or low concentration of formic acid gave the highest oil yields and the highest H/C molar ratio of 1.8.[76,77] Liquid yields of 82-99 % were obtained after 8-54 h treatments at 380 °C.[76] Solvent polymerization did however contribute significantly to the obtained organic yields as Kleinert *et al.*[77] reported the extracted organic fraction higher than the amount of initially added lignin. Alkylating effects of using ethanol as solvent in formic acid depolymerization of a range of differently pretretead lignins from Birch and Norway Spruce were also highlighted recently in a similar study by Løhre *et al.*[185] when compared to using water as an alternative solvent. They equally argued that the main difference between different lignin rich feedstocks was an inverse relationship between oil yield and oxygen content in the feedstock as carbohydrate rich feedstock with higher oxygen content would undergo increased deoxygenation effectively lowering the yield. Riaz *et al.*[131] similarly used formic acid in ethanol for reductive depolymerization of a sulfuric acid hydrolysis lignin (oak wood) and Kraft lignin and oil yields of 85 wt% and 90 wt% respectively were obtained after 30 min at 350 °C with a formic acid to lignin ratio of 3:2 (w:w) and ethanol to lignin ratio of 10:1 (w:w) . The lower oil yield from the acid hydrolysis lignin compared to the yield from Kraft lignin was attributed to the higher recalcitrance of the former lignin. An oxygen reduction of up to 44 tw% was achieved resulting in an oil mixture of mainly phenols, esters, furans, alcohols and small amounts of aliphatics hydrocarbons.

Organosolv hardwood and wheat straw lignins were by Gosselink *et al.*[186] converted in a supercritical fluid of CO_2/acetone/water at 300-370 °C and 100 bar for 3.5 h to a phenolic oil (oligomeric and monomeric aromatics) with a yield of 10-12 wt% (based on lignin). The effect of formic acid addition was an increased yield of monomeric aromatics attributed to a stabilization of aromatic radicals. A substantial amount of char was however formed in all experiments (40-55 %).

One step hydrogenation of wheat straw lignin in ethanol and formic acid by Forchheim *et al.*[187] showed that higher heating rates and continuous feeding of formic acid aids in suppressing gas and char formation. The conclusion was that continuously stirred tank reactor (CSTR) operation is superior to a batch process. A temperature increase gave an increase of the rate coefficients of the deoxygenation reactions which decreased the yield of intermediate phenolics which by recombination may form insolubles. An increase in gaseous yield at higher temperatures was believed to be attributed to ethanol gasification and not from lignin derived components.

Gasson *et al.*[188] developed a lump kinetic model for the degradation of wheat straw lignin (0.33 g) in formic acid (0.27 g) and ethanol (2.0 g). Experiments involved rapid heat up at 40 °C/min to 360 °C at which the process was conducted at different durations. Repolymerization was slow compared to the depolymerization. The charring vulnerability was lower for deoxygenated phenols than for catechols hence it was suggested that catalysis of deoxygenation reaction steps would be beneficial.

Xu *et al.*[132] depolymerized and hydrodeoxygenated organosolv switch grass lignin using formic acid as H-donor together with a 20 wt% Pt/C catalyst and ethanol solvent at 350 °C. After 20 h of reaction a 50 % reduction in O/C and 10 % increase in H/C molar ratios were observed. No solid residual lignin was present after reaction. The combined presence of formic acid and catalyst yielded the highest fraction of lower molecular weight liquid products observed from size exclusion chromatography [132].

Toledano *et al.*[189] investigated the effect of first fractionating organosolv dissolved lignin by ultrafiltration into different molecular sizes prior to catalytic depolymerization/upgrading in formic acid. An increase in oil yield and phenolic monomers was observed for smaller membrane cut offs; however, low oil yields were generally observed (<40%). The molecular sizes were in the range <5 kDa to >300 kDa. Surprisingly however the fraction comprising a molecular size of 50-150 kDa provided the lowest oil yield of only 15 wt% which could not be explained by the authors. These results clearly demonstrate the difficulties in comparing experimental data in which different lignin feedstocks have been sued as even fractionation of the lignin has a dramatic influence on degree of depolymerization.

2.3.4.3 Summary of Lignin Depolymerization in Formic Acid

Formic acid provides and effective means of hydrogen donation through *in situ* hydrogen formation; however, formic acid is irreversibly decomposed in the process. Typically solvent mixtures involving alcohols improve lignin liquefaction and addition of heterogeneous catalysts has equally been reported to improve yields. The process of lignin liquefaction by formic acid typically results in low char yields but also liquid yields greater than the starting biomass feedstock which indicates some degree of solvent incorporation into the liquefied product. Product yields are typically deoxygenated and the principal route is through demethoxylation.

2.3.5 Polycyclic Aromatics

In this section the solvent effects of direct lignin liquefaction in polycyclic aromatics such as tetralin and 9,10-dihydroanthracene (AnH2) are described. The reactivity and reaction between aryl ether linkages and H-donating solvents such as polycyclic aromatics is described in more detail in a review by Dorrestijn *et al.*[62] Processes that use polycyclic aromatics as H-donating solvents have mainly been reported for coal liquefaction and only limited studies on lignin exist. The process of hydrogenation of lignin by polycyclic aromatics often results in low or nonexistent char formation[6] and the solvent can be regenerated allowing for recycling which are advantageous abilities. Reactions between the solvent and lignin fragments however often cause that solvent can only be partly recovered which is disadvantageous as large quantities of a solvent are needed and tetralin for example is more expensive than other H-donating solvents such as formic acids or alcohols.[135]

2.3.5.1 Mechanisms

Polycyclic aromatics such as naphthalene and anthracene (reduced forms of tetralin and AnH2) are called hydrogen shuttlers as they can act as an agent for hydrogen transfer to coal or biomass from the gas phase or from other organic compounds.[36] As an example tetralin donates hydrogen in a process which is reversible whereby it can be regenerated shown in Figure 2.28. Afifi *et al.*[134] investigated the decomposition of lignin model compound anisole in tetralin at temperatures 400-500 °C and suggested a radical reaction mechanism involving methyl, phenoxyl, phenoxymethyl and phenyl radicals mainly. AnH2 is a stronger hydrogen donor compared to tetralin and also serves as radical scavenger.[135] The radical scavenging effect may be of benefit in order to inhibit possible repolymerization reactions forming stable C-C bonds.

It has been suggested that the process of hydrogen transfer from tetralin is through a radical mechanism where tetralin reacts with naphthalene yielding the intermediate radical cyclohexadienyl which facilitates hydrogenolysis by hydrogen radical transfer (see Figure 2.29).[36]

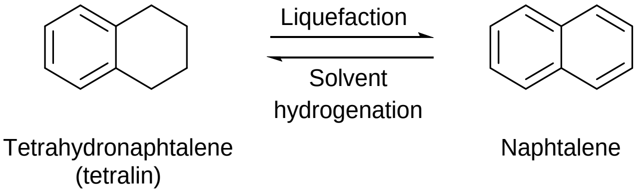


Figure 2.28 Equilibrium of tetralin and naphtalene. Naphtalene is formed as a result of H-donation and tetralin can be regenerated by hydrogenation. Modified from Clifford and Song[36].

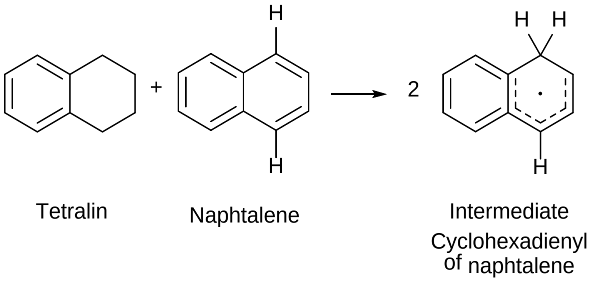


Figure 2.29 Reaction of tetralin and naphthalene to form reactive cyclohexadienyl intermediate. Modified from Clifford and Song[36].

The regeneration of tetralin may be facilitated by the presence of a catalyst and H-spillover describes the mechanism by which a heterogeneous catalyst may facilitate the hydrogen transfer on the catalyst surface regenerating tetralin. A heterogeneous catalyst regenerates tetralin which is said to act by H-shuttling as hydrogen is subsequently donated to terminate biomass radicals from the thermal conditions and thereby yielding depolymerized smaller molecular weight fragments in the form of a liquid product.[36]

Dorrestijn *et al.*[62] reviewed different mechanisms for ether bond breakage by H-donating solvents in a range of aromatics similar to lignin. In Figure 2.30 a proposed mechanism by which guaiacol thermally degrades by homolytic cleavage is presented. Catechol is formed after homolysis of the O-CH_3 bond and reaction with hydrogen from a H-donor. Similarly radical induced pathways also yield *o*-hydroxybenzaldehyde, *o*-cresol and phenol originating from an *o*-methoxyphenoxyl radical. The formed intermediate *o*-hydroxybenzylalcohol was also reported at temperatures 281 °C to yield an *o*-hydroxybenzylic cation which by hydride transfer from a hydrogen donor yields *o*-cresol through an ionic reaction rather than a radical mechanism (see Figure 2.31).[62,83] This highlights the importance of considering both ionic as well as radical reactions that can take place simultaneously in lignin liquefaction by hydrogen donors. The *o*-hydroxybenzylic cation is however at lower temperatures prone to facilitate polymerization by an electrophilic aromatic substitution.[62]

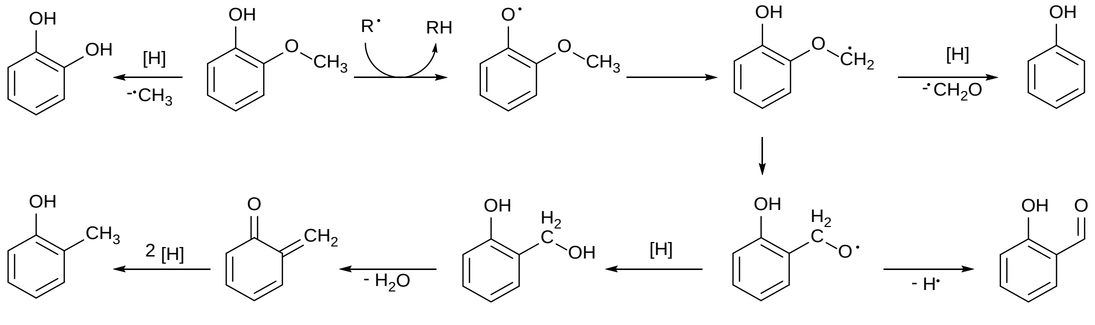


Figure 2.30 Radical induced pathway for the degradation of guaiacol at harsh conditions in a H-donating solvent. Modified from Dorrestijn *et al.*[62]

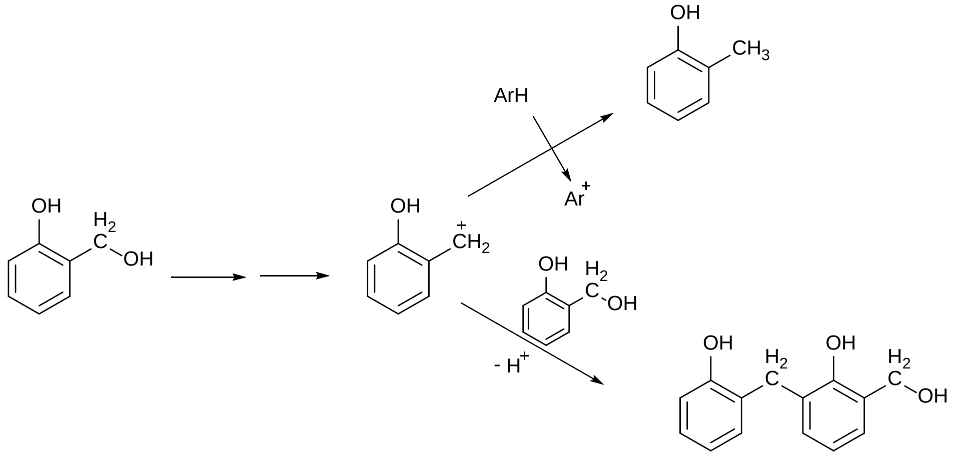


Figure 2.31 The ionic reactions of an *o*-hydroxybenzylic cation to either polymerize or form *o*-cresol through a hydride transfer for an H-donating solvent. Modified from Dorrestijn *et al.* [62]

2.3.5.2 Effect of Parameters

Kim *et al.*[137] observed a decrease in molecular mass of liquefied organosolv lignin (corn-stover) using tetralin when the reaction time was increased from 5 to 10 min at reaction temperatures 300-400 °C. The same effect was equally observed using isopropanol as hydrogen donor solvent. The opposite effect was observed when a non-donor solvent naphthalene was used. The presence of a hydrogen donor was believed to suppress repolymerization and promoting demethoxylation.

Studies by Thring and Chornet[190] indicated that for a ratio of lignin to tetralin (w/w) up to 0.16 the conversion of an organosolv lignin remained constant around 60 %. The lignin was treated at 400 °C for 30 minutes. At higher mass ratios the conversion decreased.

Addition of co-solvents has widely been reported to be beneficial in lignin depolymerization processes. Afifi *et al.*[134] added the homogeneous Lewis acid catalyst $FeCl_3$ to supercritical tetralin and argued that this may destabilize the oxygen linkage of methoxy groups at temperatures <455 °C as selectivity towards phenols and cresols from anisole conversion were enhanced. Dorrestijn *et al.*[83] argued that the application of a polar co-solvent (1,4-dioxane) to lignin hydrogenation is beneficial for the yield of phenolic compounds when using 9,10-dihydroanthracene and 7H-benz[de]anthracene as H-donor solvents.

Vuori and Bredenberg[136] obtained a maximum yield (20.3 wt%) of ether soluble phenols and acids from Kraft lignin liquefaction in a mixture of tetralin and *m*-cresol as reaction solvent at 345 °C. Reportedly the main reactions were demethylation of methoxyl groups, as high yields of methane were observed, and also char formation through condensations. Adding hydrogen and a conventional CoMo catalyst did not improve liquid yield but only gaseous and char yield indicating that at the applied conditions condensations could not be prevented.

Li *et al.*[191] conducted tetralin liquefaction of mild alkaline aqueous pretreated (1 wt% NaOH) Eucalyptus woodchips. For temperatures 220- 330 °C and using either pure water, pure tetralin or 1:1 (w:w) tetralin-water mixture they observed both the highest conversion of 97.3 wt% and highest heavy oil yield of 57.3 wt% for liquefaction using the water-tetralin mixture. They argued that the presence of water improved the liquefaction due to a solvent density increase arising from the increased reaction pressure.

2.3.5.3 Summary of Lignin Depolymerization in Polycyclic Aromatics

Polycyclic aromatics provide excellent hydrogen donors that can be regenerated. A widely reported donor solvent is tetralin which after H-donation yields naphthalene. The effect of H-donation is often described by a spill over effect in which a heterogeneous catalyst in the presence of hydrogen allows for transfer of surface bound hydrogen to for example naphtalene which yields tetralin. The H-donor is thus said to behave by hydrogen shuttling facilitating hydrogen transfer which induces ether bond cleavage and both deoxygenates the lignin and inhibits repolymerization. Only limited studies exist on lignin depolymerization by polycyclic aromatics as the majority of research is focused on coal liquefaction. Use of polycyclic aromatics have shown like most donor solvents to limit char formation. Both ionic reactions as well as thermally induced radical reactions are responsible for lignin depolymerization.

2.4 Conclusions

In order to transform solid lignin to a liquid fuel a simplified approach involves cleavage of ether linkages and deoxygenation. Ether linkages are more readily cleaved due to a lower bond enthalpy compared to C-C linkages and cleave of lignin inter unit linkages facilitates depolymerization. Different techniques exist for reductive liquefaction of biomass and main strategies comprise of catalytic as well as non-catalytic pyrolysis and gasification techniques which results in an indirect liquefaction. Direct liquefaction of biomass in a solvent is advantageous as it is thermally more efficient and compared to gasification followed by Fischer-Tropsch synthesis in particular CO_2 yields are lower. Direct liquefaction often occurs at elevated pressure due to the pressure exerted by the heated solvent when keeping it in liquid form; however, the temperature requirements are lower than for pyrolysis technologies (<450 °C).

A simple approach is necessary when transforming a relatively low value feedstock such as lignin to a bulk product like a fuel or a bio-crude. In particular for direct liquefaction a high solvent recyclability is necessary as well as tolerance for high solid to solvent loadings in order to yield an economically feasible process. An often overlooked feature is also solvent sustainability and toxicology which are factors that are important to limit when handling a solvent based process on a large scale.

Depolymerization of biomass is found to involve effects of dissolution, homolytic cleavage, heterolytic cleavage and alkylation and rearrangement reactions. The competition between the kinetics of depolymerization and irreversible repolymerization dictates the depolymerized lignin yields. At elevated temperatures radical mechanisms (homolytic cleavage) are favored but electron transfer mechanisms may also play a significant role. The latter is particular important for alkaline treatment (BCD) for lignin depolymerization where solvolysis of ether linkages interlinking lignin monomers and decarboxylation are dominant pathways. In hydrothermal lignin depolymerization radical mechanisms are believed to dominate but ionic reactions at subcritical conditions are also believed to play a key role due to the high dissociation constant of water at these conditions which may favor hydrolysis. Polar organic compounds and specifically alcohols are efficient solvents/reactant as they both facilitate aryl ether cleavage but also stabilize depolymerized radical species. For this reason solvent mixtures are typically beneficial in the process of lignin depolymerization. Hydrogen donating solvents include the reversible H-donors such as polycyclic aromatics but also irreversible H-donors such as formic acid which decomposes to form H_2 at elevated temperatures and alcohols which can form hydrogen *in situ* by reforming. The main role of hydrogen donating solvents other than facilitating aryl ether cleavage is stabilization of formed radicals which limit the potential for repolymerization. Both mechanisms involving *in situ* formation of hydrogen and direct hydrogen transfer from the solvent are believed to occur.

For lignin depolymerization in alkaline media the optimal process conditions are well defined at temperatures around 300 °C with strong base in excess. Short reaction times are favored particularly at increasing temperature. Hydrothermal treatment and BCD typically benefit from reaction times of a few minutes whereas high yields in H-donor solvents and alcohols have been reported after treatments of up to several hours. For lignin depolymerization in polar organic solvents supercritical conditions are often favored but more severe conditions at temperatures exceeding 400 °C may enhance char and gas formation. The liquid density is believed to play a key role in especially lignin depolymerization in alcohols and an increased density may improve liquefaction yield.

CHAPTER 3

Experimental Work

At the CHEC research center at DTU direct lignin liquefaction experiments were carried out in a single high pressure batch autoclave. A description of the experimental setup and procedure is described in section 3.1. Product fractions were all analyzed at DTU while additional analyses on the oil fractions were conducted at the University of Copenhagen. Analysis methods are described in section 3.2.

3.1 Batch Reactor Experiments

The experimental setup is described in section 3.1.1. The lignin rich feedstock used for all of the experiments is described in section 3.1.2. The experimental procedure is described in section 3.1.3 together with definition of product yields. In section 3.1.4 the mass losses from a typical experiment are described together with how solvent consumption is defined.

3.1.1 Setup Description

A 500 ml stirred HT 4575 Parr batch autoclave (T316 stainless steel) with a fixed head was used for all of the experiments conducted in this study. A Parr 4848 control unit provides digital temperature readouts and control and a manual adjustment of stirrer speed. Figure 3.1 shows the experimental setup used and the internals of the reaction vessel.

Figure 3.1 The experimental setup used for all of the experiments. Left: The assembled batch reactor with the heating jacket mounted. Right: The internals of the reaction vessel comprising of sampling tube, stirrer, cooling coil and thermowell seen from left to right.

A cylindrical stainless steel liner is fitted inside the vessel for easier product removal after reaction. The liner is fitted with a 1-2 mm gap between the liner wall and the internal reaction vessel wall. The internals of the reaction vessel comprise of a protruding internal cooling coil, stirrer, thermowell and a sampling tube. A P&I diagram of the reaction vessel is shown in Figure 3.2 and all tubing is made of ¼” stainless steel and connections and valves are Swagelok™.

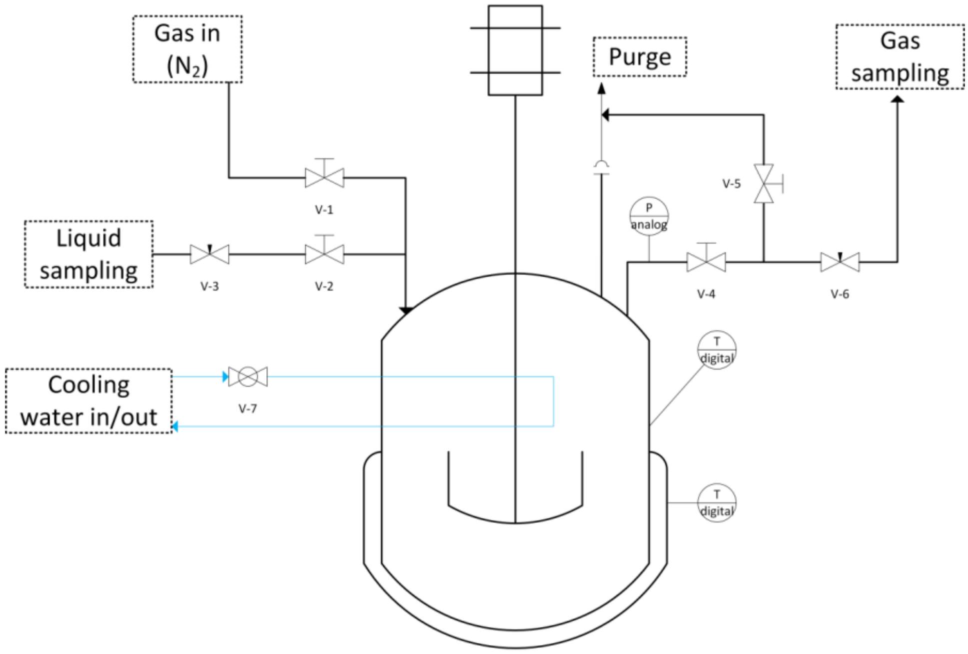


Figure 3.2 P&I diagram of the high pressure and high temperature Parr batch autoclave setup used for the experiments

The internal cooling coil is connected to a VWR RC-10 Basic chiller and a manually adjusted valve regulates the flow of cooling water (water-ethylen glycol mixture at 0-5 °C). The internal cooling was only used to assist in cooling down the reaction mixture after reaction and therefore the valve regulating the flow of cooling water is never opened when heat issupplied to the vessel. Cooling is however continuously supplied at all times to the magnetic stirring unit located above the heated reaction vessel in order to protect the magnetic drive from high temperatures (<100°C).

The stirrer reaches the bottom of the closed reaction vessel with gap less than 1 cm. The speed is manually adjusted by turning a knob (0-700 rpm).

The setup is connected to a gas supply of 6 bar nitrogen from a central storage. The gas inlet is connected through a sampling tube. Sampling of liquid during experiments was never conducted. Gas can be evacuated from the reaction vessel to a gas bag or purged to the ventilation.

The reaction vessel is sealed with a graphite gasket and 8 screws tightened in a criss-cross pattern (54 Nm torque). A rupture disc protects against pressure buildup above the safe limit rated at 345 barg at 500 °C. The operating pressure is read on an analog pressure gauge (0-344 bar) and the internal temperature is measured digitally in the thermowell using a J type thermocouple. This temperature measurement controls the heating of a heating jacket through PID control. The heating jacket can supply up to 2 kW and an additional thermocouple is located in the jacket. This measurement is also digitally measured and provides functionality to turn off the heating temporarily if a lower alarm limit has been reached or turn of the heating requiring manual intervention if an upper alarm limit has been reached.

3.1.2 Lignin Rich Feedstock

The biomass feedstock used for the solvolysis experiments is a lignin rich solid residual obtained from enzymatically hydrolyzed, hydrothermally pretreated wheat straw. The conditions of the hydrothermal pretreatment were 190°C for 10 min. The biomass feedstock is denoted lignin in this study as it is comprised mainly of acid insoluble lignin (65 wt%). A detailed compositional analysis by the NREL protocol[192] is shown in Table 3.1 where residual sugars mainly comprise of glucan. The lignin is a fine dry powder with an ash content of 13–15 wt% and a moisture content of 2 wt%. For calculation of yields on a dry ash free basis an organic content of 85 wt% is assumed for the lignin rich feedstock. Elemental composition is shown in Table 3.2 using the analysis method described in section 3.2.2.

Table 3.1 Compositional analysis data of the lignin rich residual. The NREL protocol[192] was used for the analysis.

	Glucan	**Xylan**	**Mannan**	**Arabinan**	**Galactan**	**Acid insoluble lignin**	**Ash**	**Total**
wt%	12.43	3.04	3.05	1.39	1.55	65.39	14.65	101.51
SD	0.28	0.14	0.083	0.045	0.050	0.53	0.066	

Table 3.2 Elemental composition of the dry ash free lignin as determined in section 3.2.2 where oxygen is determined by difference. The results are correlated for a 13 wt% ash content and 2 wt% moisture content.

	C	**H**	**N**	**S**	**O**
wt%	62.0	6.29	1.40	-	30.3
SD	2.23	0.183	0.662	-	2.41

3.1.3 Experimental Procedure

A pre-weighed amount of lignin (0–40 g) and 100 ml of methanol, ethanol, 1-propanol or 1-butanol (99.9%, Sigma-Aldrich) were added to the reaction vessel prior to sealing. The atmosphere inside the vessel was flushed three times with Nitrogen to leave a non-pressurized inert atmosphere prior to heat-up. Heating was applied through a jacket with a rate of 5–10 °C/min. Stirring was applied (~400 rpm) during heat-up and maintained throughout the experiment. When the desired set point for the internal temperature of the vessel was reached the reaction period was defined to begin. At supercritical solvent conditions there is no distinct vapor and liquid phase so the solvent occupies the entire internal volume of the reaction vessel yielding a constant solvent density of e.g. 0.16 g/ml when using ethanol as solvent (500 ml vessel). After a reaction period of 0 to 8 h the vessel was rapidly cooled (10–30 °C/min) with ice and opening of the valve regulating the flow of cooling water to the internal cooling coil and the reaction period was defined to end when cooling was commenced. The final gas pressure was noted at ambient temperature after which gas was evacuated to a gas bag for further analysis. The contents of the batch autoclave were transferred to a beaker, weighed and suction filtered on a pre-weighed filter. The filter cake comprising of the solid residual product of the solvolysis reaction was washed with an additional 25-100 ml of fresh solvent and subsequently dried at 70 °C for 72 h or until stable weight. The filtrate was rotary evaporated (45

°C, 5 mbar) for 45 min or until stable weight of the heavy liquid fraction. The heavy fraction is denoted the oil product in this study and is assumed water free due to the severity of the evaporation. Both the oil and the light product obtained were subjected to further analyses.

3.1.3.1 Solid Yield

The yield of solid residual product was determined as the weight of dried isolated solid product relative to the weight of added lignin feedstock.

3.1.3.2 Oil Yield

The yield of oil product was determined as the weight of isolated heavy liquid product relative to the weight of added lignin feedstock. Yields can also be expressed on a dry ash free basis (d.a.f.) relative to the mass of organic content in the lignin rich feedstock processed:

$$\text{Oilyield(d.a.f.)} = \frac{\textit{oil product isolated}}{\textit{organics in feedstock}(\textit{lignin})} 100wt\% = \frac{m_{oil}}{0.85 \cdot m_{lignin}} 100wt\% \ (wt\%_{d.a.f.}) \tag{3.1}$$

3.1.3.3 Gas Yield

The gas yield was determined as the gauge pressure read after cooling of the reaction vessel to room temperature. For experiments in which reliable gas compositional data existed the mass of gas produced was calculated assuming ideal gas behavior, neglecting dissolution of gas in liquid and assuming a gas volume of 400 ml inside the reaction vessel.

3.1.4 Mass Losses and Solvent Consumption

A mass balance closure better than 90 wt% was not achievable for all of the experiments conducted. The mass balance for one experiment is shown as an example in Figure 3.3. The distribution of different fractions comprising liquids, solids and gas immediately after the experiment, after subsequent filtering and after evaporation is shown and a substantial mass loss due to handling can be seen. A typical mass loss of around 10 wt% was observed for all experiments after weighing the extracted cooled contents of the reaction vessel. The majority of this mass loss is most likely due to evaporation of solvent and light reaction products after opening the vessel as similar mass losses were observed in solvent blank experiments. Filtering of the product slurry also yielded a further mass loss. This mass loss was increased if there was a high amount of solids present as an increased amount of light solvent fraction was retained in the filter cake. Further evaporation due to the vacuum applied during filtration is most likely responsible for increased loss of light liquid products. Rotary evaporation would also yield a mass loss which is most likely due to lighter products condensed in the connecting tube before the condenser as droplets were sometimes visible.

Based on the above it is assumed that the mass losses observed immediately after the experiment and during handling is solely due to loss of the light liquid fraction comprising of water, unreacted solvent alcohol and other light organic species. GC-FID and Karl Fischer titration was used for the quantification of alcohol solvent, other light organics and water in the light fraction obtained after rotary evaporation (see section 3.2.1 and 3.2.3 for analysis methods). In this study the solvent consumption is addressed in particular and different assumptions and methods for determining this is discussed in the following.

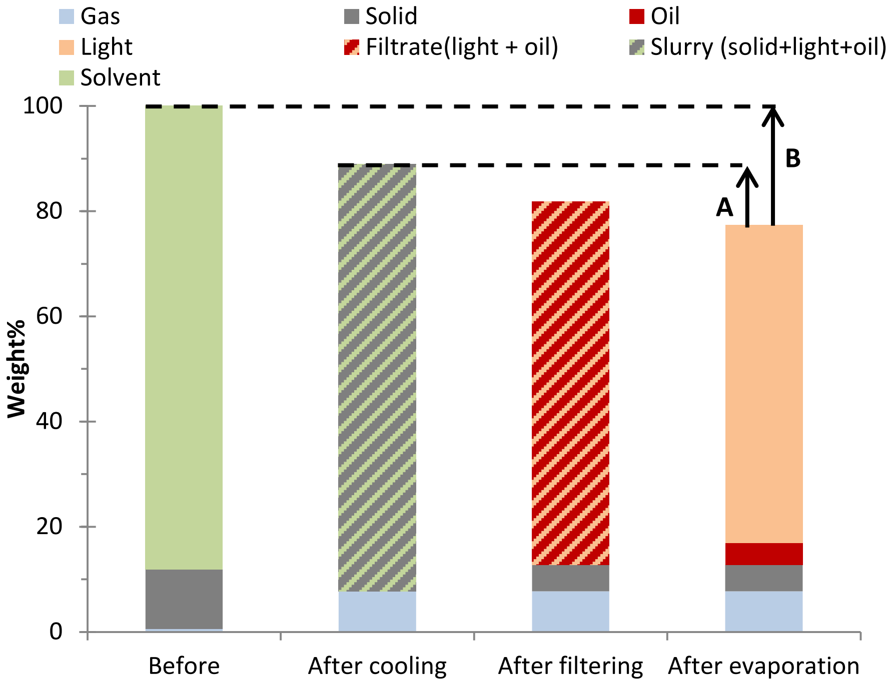


Figure 3.3 Mass balance shown for an experiment in which 10 g lignin and 100 ml ethanol was heated at 400 °C for 4 h in a non-pressurized N_2 atmosphere prior to heat up. Light fraction is comprised of unreacted solvent (ethanol), other light liquid organics and water. "Before" indicates the mass of individual fractions measured prior to the experiment. "After cooling" indicates the mass of individual fractions as determined immediately after cooling and upon opening the reaction vessel. "After filtering" indicates the mass of individual fractions as determined immediately after filtering and drying of the filter cake and added mass from the filter wash (25 ml) is subtracted. "After evaporation" indicates the mass of individual fractions as determined immediately after rotary evaporation. Arrows A and B indicate two ways in which the light fraction is increased (while keeping relative concentration of solvent, light organics and water constant) in order to determine product recovery (specifically solvent consumption) more realistically (A) or as a best-case (B) while disregarding losses due to handling.

3.1.4.1 Solvent Consumption

The solvent consumption was determined as the difference between mass of alcohol solvent after reaction and mass of alcohol solvent added prior to reaction. The quantified mass of solvent alcohol in the isolated light fraction (water, solvent and other light organics) is however lower than the mass of solvent alcohol immediately after reaction due to mass losses from handling. This mass loss is assumed to comprise solely of water, solvent and other light organics in unchanged proportions. The light fraction immediately after reaction thus equals the sum of handling loss and mass of isolated light fraction. Of this sum the solvent consumption is calculated as.

$$\text{Solvent consumption} = m_{alcohol,added} - \left(m_{light,isolated} + m_{lost}\right) \cdot Concentration_{alcohol} \tag{3.2}$$

Different assumptions and methods for determining the solvent consumption were used for the study as described in Chapter 4 through Chapter 6.

For the study in Chapter 4 and Chapter 5 the mass loss was determined as the difference between the weight of the non-gaseous contents of the reaction vessel immediately after the reaction and the combined mass of isolated dry solid residual, heavy oil and light reaction products. This corresponds to an increase of the isolated light fraction as indicated by arrow A in Figure 3.3 where the relative concentration of water, solvent other light organics is unchanged. This increased light fraction thus provides a reasonable assumption to the quantity of solvent alcohol potentially recoverable.

For the study in Chapter 6 a complete mass balance closure was assumed in order to getbest case data for a simple economic assessment. The mass loss was determined as the difference between the combined weight of the contents of the reaction vessel prior to reaction and the combined mass of quantified gas yield and isolated dry solid residual, heavy oil and light reaction products. This corresponds to an increase of the isolated light fraction as indicated by arrow B in Figure 3.3 where the relative concentration of water, solvent and other light organics is unchanged. This method for calculating the solvent consumption is more uncertain than the one described in the above as the solvent consumption also depends on the quantified gas yield. For experiments in which reliable gas data did not exist special assumptions regarding an average gaseous weight per pressure inside the vessel was assumed (see section 6.1).

3.2 Product Analysis

The reaction products comprising of gasses, liquids (heavy and light) and solids were analyzed by different methods described in the following.

3.2.1 GC MS/FID

Analysis of the light liquid fraction obtained after rotary evaporation was analysed by a Shimadzu GCMS/FID-QP-2010UltraEi. The column was a Supelco Equity-5. Liquid samples were injected with a split ratio of 1:80 at 250 °C. The column was held at 40 °C for 3 min, heated to 100 °C (2 °C/min), heated to 250 °C (20 °C/min) and held for 2 min at 250 °C. A mass spectrometer using a scanning rate of 1666 m/z/s in the range 20–300 m/z was used for the identification of light organic reaction products. A flame ionization detector was used for quantification of ethanol solvent. The area percent of the solvent alcohol peak in the chromatogram was used to determine the solvent alcohol percentage of the organic fraction. After quantification of the water content of the light fraction by Karl Fischer titration (see section 3.2.3) the weight percent of ethanol in the light fraction was calculated as:

$$\text{wt\%}_{\text{solvent}} = \left(100 - \text{wt\%}_{\text{water}}\right) \cdot \text{area\%}_{\text{solvent}} \tag{3.3}$$

3.2.2 Elemental Analysis (CHNS-O)

Elemental analysis of solid and liquid samples was performed using a Eurovector EA-3000 calibrated for C, H, N and S. Oxygen was determined by difference. The sample size was 1.00 mg and the analysis was repeated three times.

The higher heating value (HHV) was calculated for solid and oil samples based on the elemental composition using an empirical correlation[193] shown in equation (3.4) where the weight% of the elements are denoted by respective letters and A denotes the ash content of the sample:

$$\text{HHV} = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (MJ/kg) \tag{3.4}$$

3.2.3 Karl Fischer Titration

The water content of light liquid fractions was quantified using a 701 KF Titrino auto titrator with HYDRANAL®-Composite 5 (Sigma-Aldrich). A sample size of 1-2 ml was used and titration was repeated three times.

3.2.4 Solution State NMR Spectroscopy

NMR spectra were acquired using a 600 MHz Bruker Avance III HD equipped with a cryogenically cooled 5 mm dual probe optimized for ^{13}C and ^{1}H. Samples were dissolved in 600 µL acetone-d_6 (Sigma-Aldrich, 99.9 atom % D) (acetone completely dissolved bio-oils) and analyzed at 300 K. Data processing was done in Bruker TopSpin. Calibration standard was acetone (^{13}C = 29.84 ppm, ^{1}H = 2.05). For ^{13}C-HSQC-NMR 16 scans of the Bruker pulse sequence hsqcetpg was applied with a fixed spectral width of 220 ppm for ^{13}C and 13 ppm for ^{1}H. For ^{13}C-HMBC-NMR 8 scans of the Bruker pulse sequence hmbcgpndqf was used with a fixed spectral width of 220 ppm for ^{13}C and 13 ppm for ^{1}H. Lignin peak assignment was done according to a standard procedure[17]. For ^{1}H-TOCSY NMR the Bruker pulse sequence mlevphpp was used with a fixed spectral width of 13 ppm in both dimensions. Spectra were coloured in Adobe Illustrator

3.2.5 Solid State NMR Spectroscopy

Solid-state NMR spectra were recorded at 296 K on a Bruker Avance 400 spectrometer operating at Larmor frequencies of 100.62, 105.85 and 400.13 MHz for ^{13}C, ^{23}Na and ^{1}H, respectively, using a double-tuned cross polarization (CP) magic angle spinning (MAS) probe equipped for 4 mm (o.d.) rotors. ^{13}C MAS spectra were recorded using a contact time of 1.0 ms, a spin-rate of 13 kHz, a recycle delay of 2 s, 4096 scans, and an acquisition time of 30.6 ms during which ^{1}H TPPM decoupling (80 kHz rf-field strength) was employed.[194] For the SP/MAS spectra a recycle delay of 64 s and 1024 scans were used, whereas a recycle delay of 2 s, 4096 scans and a contact time of 1 ms was employed for the CP/MAS spectra. The cross polarization was carried out using variable-amplitude CP[195] with a maximum rf-field strength of 80 kHz for both ^{1}H and ^{13}C. ^{13}C chemical shifts are referenced to an external sample of α-glycine (carbonyl group) at 176.5 ppm. Single-pulse ^{23}Na MAS NMR spectra were recorded using a 1.8 µs pulse (69.4 kHz rf-field strength), spin-rate of 13 kHz, a recycle delay of 16 s, 1024 scans, and an acquisition time of 40.9 ms. ^{23}Na chemical shifts are referenced to an external sample of 1.0 M NaCl (aq).

3.2.6 Size Exclusion Chromatography

Size exclusion chromatography was performed with a 100 Å PolarSil column (Polymer Standard Service) at a column temperature of 40 °C and flow rate of 1 mL/min. The eluent was a 0.05 M LiBr in 9:1 DMSO:H_2O solution, which was also used as solvent for the bio-oil samples. One experiment lasted 15 min. As standards, phenol (Mw = 94 g/mol) and guaiacylglycerol-beta-guaiacyl ether (Mw = 320 g/mol) were used.

3.2.7 Gas Analysis (GC-TCD)

Quantification of gas species was conducted by analysing the gas phase after solvolysis using a calibrated Agilent Technologies 7890A GC-TCD with two separate sample loops with argon and helium as carrier gasses respectively. Gas sampling from the batch reactor was done using a gas bag and injection was done using a pump with a fixed pressure. The argon loop was capable of separating H_2 with 6 psi argon on a packed Haysep Q column and a packed 5A column at 50 °C. The helium loop was capable of separating the gasses CO, CO_2, N_2, O_2, CH_4, C_2H_6, C_2H_4, C_3H_8 and C_3H_6 with 8 psi helium on a packed Haysep Q column and two packed 5A columns at 50°C. Total analysis time was 20 min.

3.2.8 Ash Quantification

Ash content of obtained oil and solid samples was determined in a method similar to a standard test method for ash in wood, ASTM D1102-84 (2013), such as to eliminate the potential for evaporation and loss of ash during combustion/heat-up. 0.1-1 g sample was placed in a preweighed ceramic crucible in a muffle furnace which was subsequently heated by 5 °C/min to a final temperature of 580°C which was held for up to 1 h. Immediately after cooling the sample was kept in a desiccator until weighing. The heating in the muffle furnace was repeated if char was not eliminated.

3.2.9 Solubility in Heptane

Oil product obtained in quantities greater than 2 g were subjected to a solubility test in heptane as a model solvent having similar properties to those of fossil diesel. 2 g or more of product oil were mixed in heptane in a 1:9 (w:w) ratio in an Eppendorf^{TM} tube in duplicates. After mixing, the tube was centrifuged and the supernatant removed and placed in a separate tube. Both supernatant and insoluble fractions were evaporated under vacuum to remove heptane and masses of the two fractions were determined. Solubility was determined as the weight of heptane solubilized oil relative to the initial weight of oil.

CHAPTER 4

Parameter Study on Lignin Solvolysis by Ethanol

As discussed in Chapter 2 the solvolysis of lignin by alcohols is not fully understood. Several studies have highlighted the reductive depolymerization of lignin due to the alcohol facilitating direct cleavage of ether linkages[75,127] and hydrogen donating effects.[121,126,127] It is also widely established that alcohols inhibit repolymerization reactions.[119–123] It is often reported in literature that the alcohol solvent should be supercritical to ensure the highest liquefaction yield.[4,6] Also an increase in reaction temperature results in increased liquid yield,[75,115,116] and when the reaction severity is increased a shorter reaction time is required.[75,110] Increased lignin:solvent ratio typically results in a decreased oil yield and no beneficial effects have been reported. The maximum reported lignin:solvent ratios include 2-15 g lignin per 100 ml primary alcohol solvent.[76,87,110,122,125,196,197] The solvent loss in lignin solvolysis is often not reported, even though a low solvent consumption and high lignin loading are crucial for a commercially viable process.

In this chapter the results of a parameter study on lignin solvolysis by supercritical ethanol are discussed. A series of batch experiments were designed to investigate parameters relevant for a commercially viable lignin solvolysis process. The lignin was subjected to solvolysis in supercritical ethanol at different reaction temperatures, reaction times and degrees of lignin loading. All of the reaction products were quantified and analyzed to understand the effects of different processing parameters and provide information on mechanistic aspects of the reaction.

4.1 Results and Discussion

The different product yields obtained as a function of the different reaction parameters are discussed in section 4.1.1. The effect on oil quality and composition is discussed in section 4.1.2 and the effect on the residual solid product composition is discussed in 4.1.3 Data from additional experimental series carried out support the main experimental series and is supplied in Appendix A.

4.1.1 Product Yields

The main products of lignin solvolysis are lignin oil, solid char residual and gases. Oil, solid and gas yields of the solvolysis are shown together with solvent consumption as a function of reaction temperature, reaction time and amount of lignin added to the reaction vessel in Figure 4.1. Compositional gas data is shown for the experimental series as a function of reaction period and degree of lignin loading in Figure 4.2.

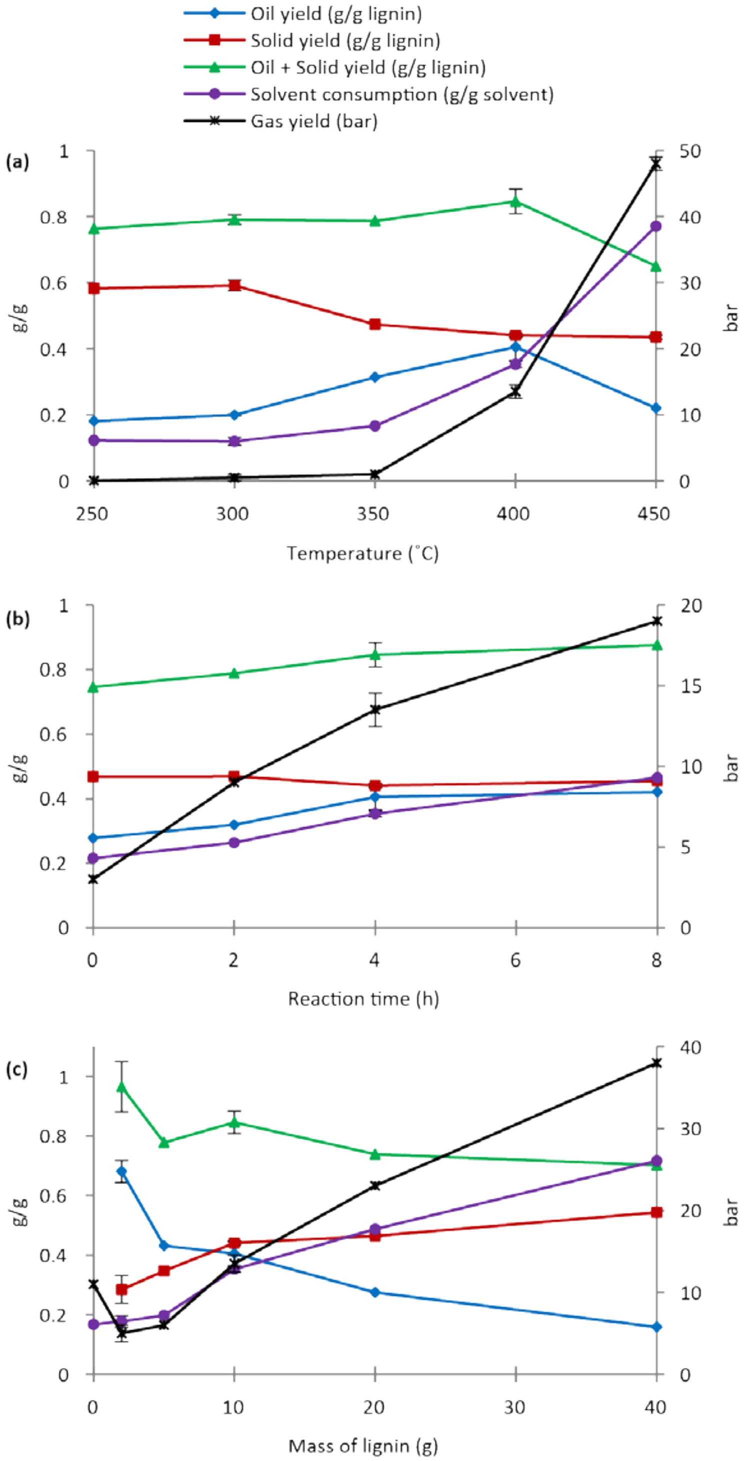


Figure 4.1 The oil yield, residual solid char yield and sum of oil and residual char yield are represented together with gas yield and amount of solvent consumed/lost as a function of reaction temperature (a), reaction time (b) and amount of lignin added (c). Oil yield, residual solid yield and sum of oil and residual solid yield are represented per lignin added (w:w) and amount of solvent consumption/loss is represented per solvent initially added (w:w). Conditions: 10 g lignin and 4 h reaction time (top); 10 g lignin and 400 °C reaction temperature (middle); 4 h reaction time and 400 °C reaction temperature (bottom). Error bars represent standard error of the mean.

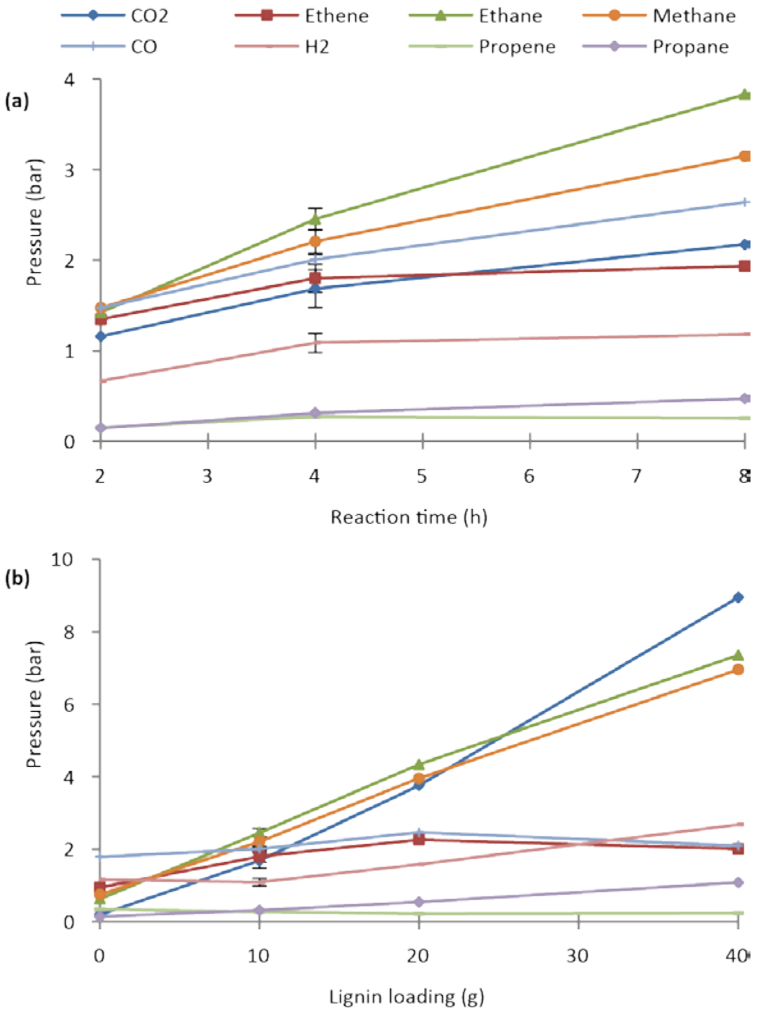


Figure 4.2 Final pressure (gauge pressure) at room temperature of different gasses formed as a function of reaction time for the solvolysis of 10 g lignin in 100 ml ethanol at 400 °C (a) and as a function of lignin loading for the lignin solvolysis in 100 ml ethanol at 400 °C for 4 h (b). Error bars represent standard error of the mean.

4.1.1.1 Effect of Reaction Temperature on Product Yields

The effect on yields of solvolysis temperatures ranging from 250–450 °C in ethanol seen in Figure 4.1a shows an optimum oil yield of 0.4 g/g lignin around 400 °C. If the temperature is increased further the final pressure after cooling of the vessel increases from 10 to 50 bar. The yield of oil and solid char product is approximately 80 % of the initial lignin feed for temperatures up to 400 °C, but at 450 °C there is a drop to approximately 60 % indicating that at least 20 % of the lignin is gasified. The sharp increase in gas formation indicates that the pathway for lignin depolymerization and decomposition is dominated by simple thermal breakage of lignin interlinkages to light species. Lee and Lee[116] conducted thermal cracking of kraft lignin in *n*-

butanol from 250 °C to 450 °C and equally found an optimum temperature of 400 °C with respect to maximizing degree of lignin conversion determined by amount of residual solid; however, at higher temperatures the conversion levelled off contrary to the observation herein. The majority of studies on lignin solvolysis by alcohols typically investigate temperatures below 400 °C.[4,6] Kim *et al.*[110] found an optimum oil yield of 95 wt% from organosolv solvolysis in ethanol at only 200 °C for temperatures up to 350 °C tested, but the oil product was substantially less depolymerised at the lower temperature (~2500 g/mol) relative to higher temperature (~800 g/mol).

Solvent consumption as a function of reaction temperature shows a minor increase from a 10 wt% at 250 °C and 300 °C to 18 wt% at 350 °C. When the temperature is increased further from 400 °C to 450 °C the solvent consumption increases more than two-fold from 35 wt% to 77 wt%. The results show that despite a higher oil yield at 400 °C it can be advantageous to conduct the process at lower temperatures to reduce solvent consumption.

4.1.1.2 Effect of Reaction Time on Product Yields

The effect of reaction time on yields of lignin solvolysis is shown only for a reaction temperature of 400 °C (Figure 4.1b). The oil yield increases from 0.28 g/g lignin after 0 h to 0.42 g/g lignin (50 $\text{wt\%}_{\text{d.a.f.}}$) after 8 h. This is an unprecedentedly high organic liquid yield considering hydrolysis lignin is used.

Gaseous reaction products were continuously formed for all experiments at 300 °C and higher. For the reaction temperature of 400 °C the gas yield increases proportionally as a function of reaction time up to 8 hours (Figure 4.1b). The yield of oil plus char equally increased as a function of reaction time. Therefore the additional amount of gas formed over time must primarily come from solvent decomposition. The solvent consumption equally exhibits a linear increase as a function of reaction time. The rate at which additional solvent is consumed at 2.6 g/hour exceeds the rate at which additional oil is produced at an average of ~0.20 g/hour by more than ten-fold (see Figure 4.3). A zeroth order reaction of solvent degradation is thus inevitable. Additional experimental data for a reaction temperature of 350 °C showed similar zeroth order behavior (see Appendix A).

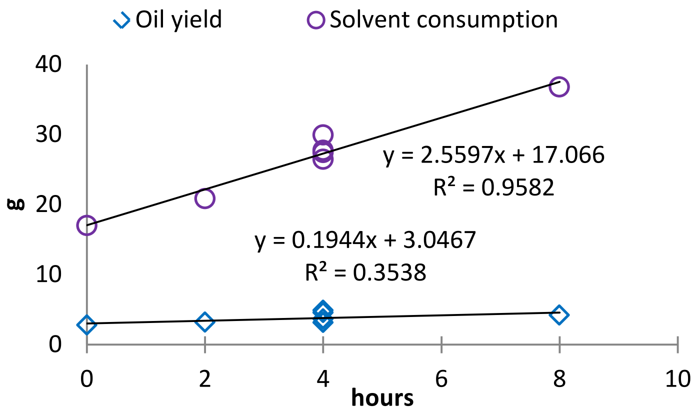


Figure 4.3 Linear fit to oil yield and solvent consumption as a function of time obtained for solvolysis of 10 g lignin in 100 ml ethanol at 400 °C.

Propene and Propane comprise the smallest percentage of gasses formed (<4 vol%) (see Figure 4.2a). The saturated hydrocarbon gas species comprising propane, ethane and methane increase faster as a function of time relative to their unsaturated counterparts (propene and ethene). The yield of ethane and methane increases faster than the yield of CO and CO_2, which shows a disadvantageous effect of longer residence time for optimizing the degree of lignin deoxygenation.

4.1.1.3 Effect of Lignin Loading on Product Yields

For what seems to be an optimum temperature in order to maximize oil yield at 400 °C, a series of experiments were conducted with varying degrees of lignin:solvent ratio (see Figure 4.1c). The high lignin to solvent loading of up to 40 g lignin in 100 ml ethanol resulted in a mixture resulting in a surprisingly low viscosity fluid that was easy to handle and this high lignin loading is substantially higher than previously reported values.[76,87,110,122,125,196,197] There are few studies that investigate the effects of different lignin to alcohol ratios,[75,110,118] and a comparison is difficult due to differences in lignin feedstock, alcohol and reaction parameters.

The oil yield decreases when the lignin loading is increased, and the yield of residual char correspondingly increases. This was equally observed for all temperatures between 250 °C and 450 °C (see Appendix A). This effect is expected due to increased repolymerisation from a 2nd order reaction as the lignin concentration is increased at high lignin loading. However, it poses other questions whether the lignin solvolysis is limited by a maximum solubility effect in ethanol and/or simply varying degrees of mixing.

The reduced mixing at higher degrees of lignin loading was visually confirmed upon opening of the vessel after cooling. For all lignin loadings tested a clear line of char was visible only on the inside wall of the liner. This was more pronounced for a loading of 20 g and 40 g lignin where char formed was harder to remove as it was condensed to the inside of the liner. These observations indicate that during reaction the repolymerization products (char) are formed and kept only within the liner hence they are insoluble in supercritical ethanol. Upon opening of the vessel condensed clear liquid, mainly comprising of solvent, was found in the space occupied between the outside of the liner wall and the reactor vessel wall. The filtrate upon isolating the solids from the liquid phase inside the liner prior to analysis is pitch black indicating that liquid condensed on the outside of the liner did not contain noticeable amounts of depolymerized lignin species/oil. This highlights a potentially important discovery that both lignin and bio-oil is not dissolved in the supercritical ethanol at reaction conditions. Instead a distinct lignin phase occupies the bottom of the vessel, and a lower relative ethanol concentration in this phase may be responsible for differences in oil and gas yields and solvent consumption when the loading of lignin is increased. Soria *et al.*[113,114] found for pine wood solvolysis in supercritical methanol that a high solvent to vessel loading (0.46 g/ml) ensures near complete liquefaction (98 %) at even the very high temperature of 500 °C. The low density of the supercritical ethanol (0.16 g/ml) herein may be responsible for the insolubility of large depolymerized lignin fragments greatly affecting the mechanism of the solvolysis. Hydrolysis lignin may also be less soluble in supercritical ethanol due to increased repolymerisation from pretreatment[30] compared to solvolysis of unprocessed woody biomass.

Strikingly more gas is formed with no lignin addition compared to adding 2-5 g lignin. This indicates an effect by which lignin inhibits ethanol to gas decomposition. At higher degrees of lignin loading the final gas pressure proportionally follows the amount of lignin added indicating that the majority of gaseous species formed comes from lignin. Lignin is increasingly decomposed to gasses as a function of lignin loading as the sum of char and oil product decreases.

Solvent consumption per solvent added increases with increased lignin loading indicating that solvent is lost due to a reaction in the presence of lignin and a 40 g lignin loading results in 60 wt% solvent consumption.

Gaseous hydrocarbons such as ethane and methane are formed even in the case of no lignin addition (see Figure 4.2b) hence these are products of solvent decomposition. The yield of all gaseous hydrocarbons is however strikingly proportional to the amount of lignin added. In particular ethane and methane yields increase at the same rate and in near identical quantities. Gaseous hydrocarbons may be formed as a direct lignin breakdown product as the methoxy functionalities in the lignin are converted to methane. Different breakdown reactions of the phenyl propane monomers may yield ethane and propane. On the other hand the presence of lignin in supercritical ethanol could also facilitate solvent decomposition to gas. Zhao *et al.*[75] proposed a mechanism in which thermally induced homolytic cleavage of supercritical ethanol forms ethyl radicals that facilitate the cleavage of the lignin polymer but is equally incorporated into the depolymerized structure (see also section 2.3.3.1). Such incorporation of the solvent ethanol into the depolymerized lignin structure and a subsequent thermally induced bond cleavage may ultimately yield ethane gas. Here we find that ethene and propene are nearly unchanged relative to the yields of ethane and propane respectively showing that the former likely are products of solvent decomposition only.

When no lignin is added the CO_2 yield is near zero, and it increases linearly with lignin addition (see Figure 4.2b). This shows that CO_2 is mainly a product of lignin deoxygenation through decarboxylation. In one experiment where 40 g lignin was solvolysed at 350 °C for 2 h the formed CO_2 comprised more than 50 vol% of all of the gasses formed (experimental data is supplied in Appendix A). This accounts for 18 wt% of the oxygen initially present in the lignin. At a reaction time of 4 h and a temperature of 400 °C the oxygen removal by CO_2 was increased to 34 wt%. The water gas shift reaction (see equation (4.1)) has a negligible influence on the high CO_2 yield as the reaction is far from equilibrium with a reaction constant that is a factor $\sim 10^2$ smaller than the equilibrium constant for the water gas shift reaction at 400 °C (data for calculation is supported in Appendix A).

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \quad (4.1)$$

The amount of water formed also increases as a function of lignin addition (see Figure 4.4); however, when lignin addition increases from 20 to 40 g the rate of water formation is slightly decreased.

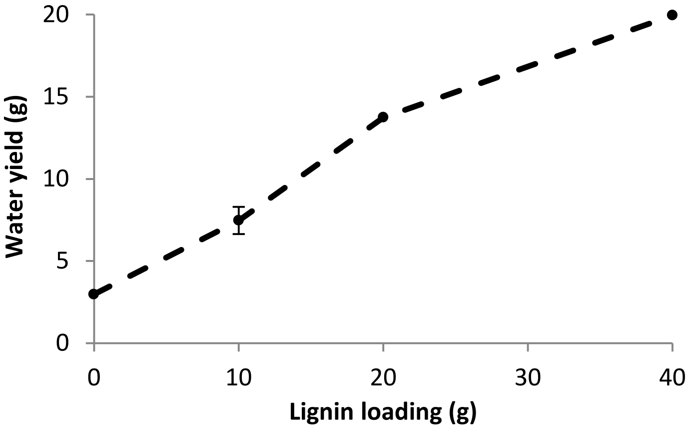


Figure 4.4 Final amount of water produced as a function of lignin loading for lignin solvolysis in 100 ml ethanol at 400 °C for 4 h. Error bars represent standard error of the mean.

The CO yield is nearly constant as a function of lignin loading showing that this gas specie is mainly a product of ethanol decomposition. CO, CH_4 and H_2 are also expected reaction products of ethanol decomposition at elevated temperatures.[198]

The hydrogen yield is low and increases from 1 bar with no lignin addition to 3 bar with 40 g lignin addition. As hydrogen is highly reactive at the experimental conditions it can only be concluded that hydrogen is a thermal breakdown product of alcohol and lignin.

4.1.2 Oil Product Analysis

It is desired to reduce the oxygen content of the product oil as much as possible as low oxygen content yields a higher heating value of the lignin-oil. For an application of the lignin oil where blending with a fossil fuel is required a lowering of the oxygen content also reduces the polarity and hence increases the miscibility. Low oxygen content in the product oil also has benefits including reduced reactivity and higher stability of the oil product. Especially carbonyl functionalities in the oil are believed to cause polymerization reactions.[199] None of the lignin oils obtained in this study had a, by NMR, detectable aldehyde or ketone content (see Figure 4.5).

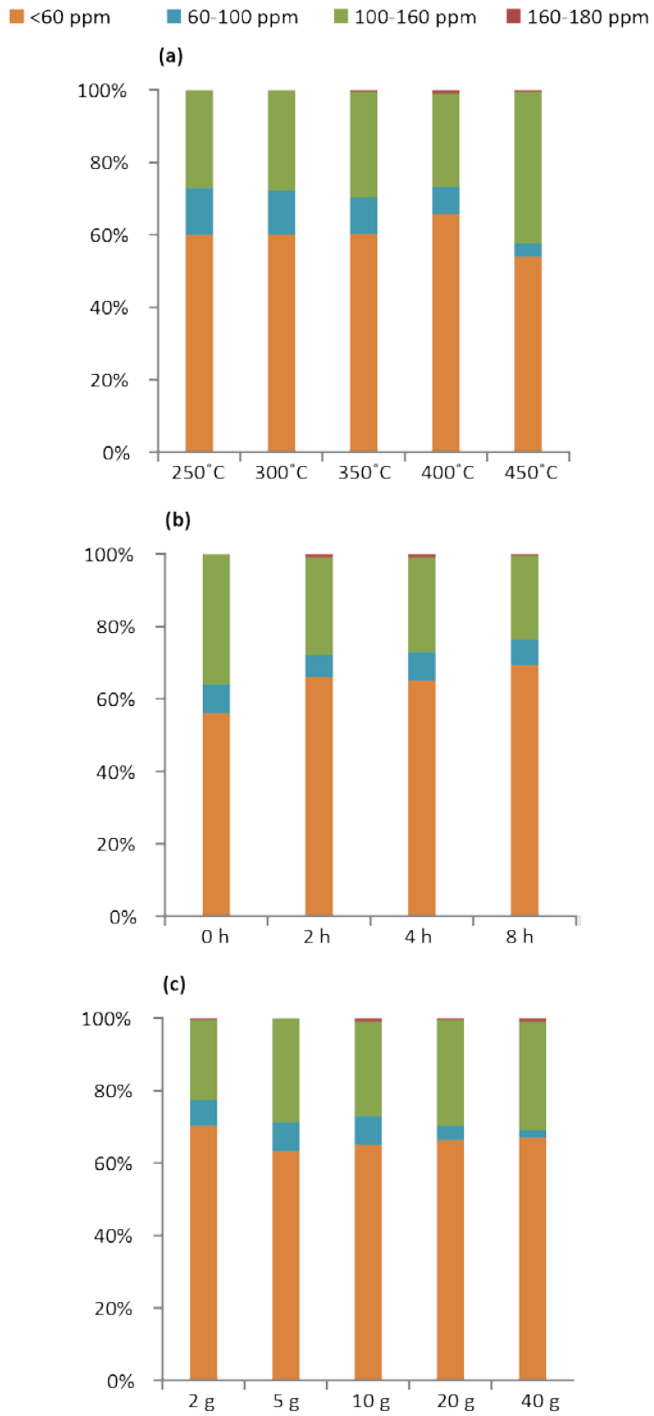


Figure 4.5 ^{13}C NMR integrals of lignin oils normalized to 100 %. The lignin oils are obtained at different reaction temperatures (a), reaction times (b), and degrees of lignin loading (c). Chemical shifts <60 ppm originate from the aliphatic fraction, 60-100 ppm from the oxygenated sp^3, 100-160 ppm from the aromatic fraction and 160-180 ppm from the carboxylic acid and ester fraction of the bio-oil. Reaction conditions for the produced oils: 10 g lignin and 4 h reaction time (a); 10 g lignin and 400°C reaction temperature (b); 4 h reaction time and 400°C reaction temperature (c).

This corresponds well with the fact that neither formation of sediments nor a change in molecular size distribution was detected in oils stored at room temperature for 11 months (see Figure 4.6). ^{13}C-HMBC NMR spectra also showed no detectable amount of both aldehydes and carboxylic acids in any of the lignin oils obtained (see Figure 4.7). This is a highly desirable property as this reduces the potential for polymerization and a low acidity is required for fuels used in internal combustion engines. The oils obtained by solvolysis are of better quality than pyrolysis oils as the latter are acidic and readily polymerize due to oxygen functionalities. Esters in the oil fraction show a way in which lack of acidity is obtained from condensation between carboxylic acids and alcohols.

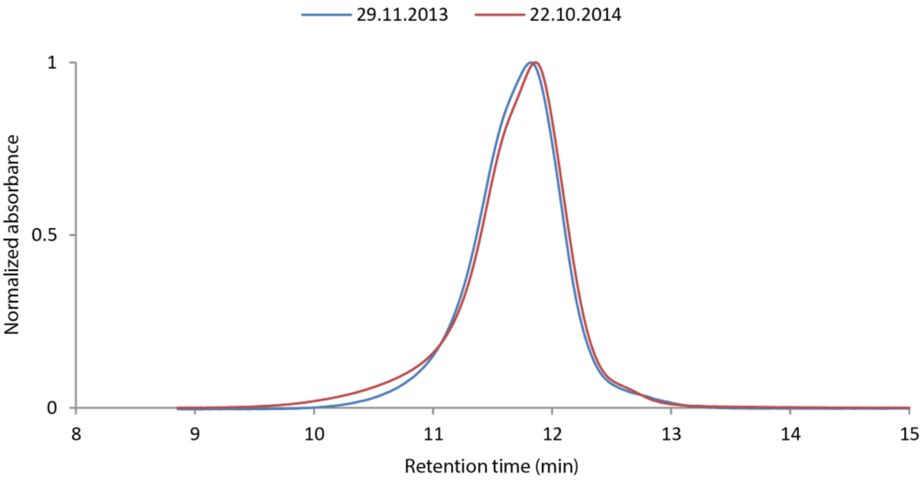


Figure 4.6 SEC of the same bio-oil at two different times with 11 months between the experiments. The bio-oil was produced at 350 °C for 4 h with 10 g of lignin in 100 ml ethanol. The oil was stored on a shelf at ambient temperature, no direct sunlight and in a closed vessel. As can be seen there is, unlike pyrolysis oil, no polymerization of the bio-oil over time

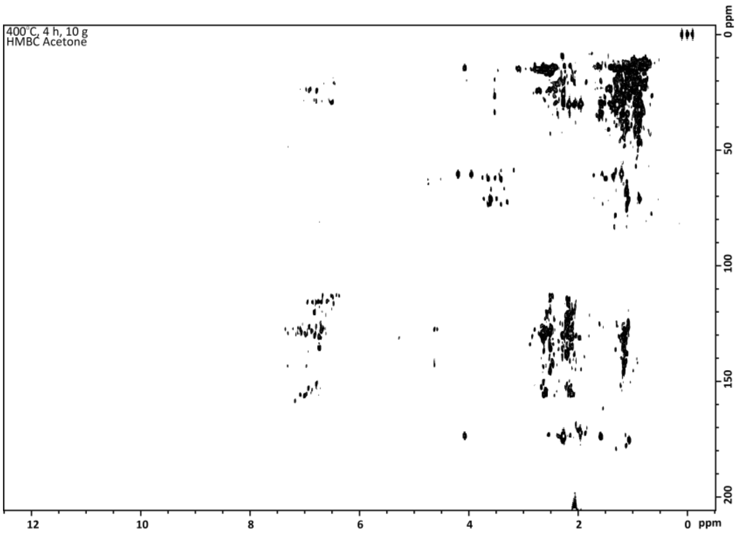


Figure 4.7 ^{13}C-HMBC NMR data on a bio-oil produced in ethanol at 400 °C, 4 h and 10 g lignin loading. As can be seen, there are no signals from aldehydes (^{1}H: 9-10 ppm, ^{13}C: 190-200 ppm) carboxylic acids (^{1}H: 10-13 ppm, ^{13}C: 160-190 ppm).

^{13}C-HSQC NMR analysis was carried out for the lignin starting material and oils obtained by solvolysis at all temperatures (full spectral data is supplied in Appendix A). The NMR data on the lignin starting material shows that it is identical to previous reports on hydrothermally pretreated wheat straw.[29] For all of the oils obtained ^{13}C-HSQC NMR spectra show a complete removal of carbohydrates that are found in the lignin feedstock. The lignin unit linkages such as β-O-4, β-5 and β-β identified in the lignin feedstock are broken at all temperatures tested in the ethanol solvolysis. The lignin feedstock is composed of syringyl (S) and guaiacyl (G) units with no noticeable amount of *p*-hydroxyphenyl (H) units. The lignin oil contains a narrow aromatic region showing a reduction in substituents on the aromatic rings and no noticeable S units.

In the following the oil product is analyzed and discussed in regards to oxygen content (Figure 4.8), molecular size distribution by SEC (Figure 4.9) and composition by ^{13}C NMR (Figure 4.5). Data from additional experimental series is supplied in Appendix A.

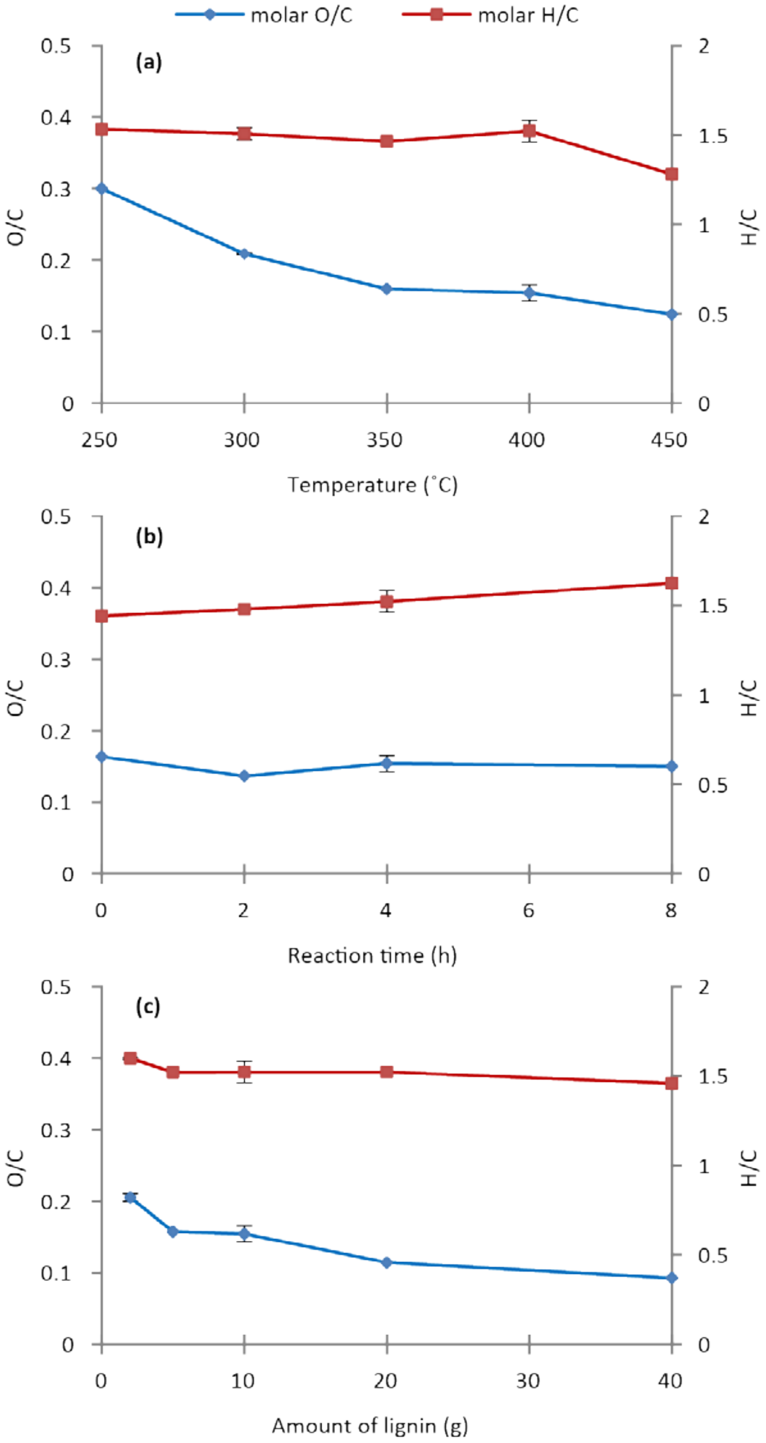


Figure 4.8 Molar O/C and H/C ratio in the oil product plotted as a function of reaction temperature (a), reaction time (b) and degree of lignin loading (c) for different reaction conditions. The lignin feedstock has an O/C of 0.4 and H/C of 1.3. Reaction conditions: 10 g lignin and 4 h reaction time (a); 10 g lignin and 400 °C reaction temperature (b); 4 h reaction time and 400 °C reaction temperature (c). Error bars represent standard error of the mean.

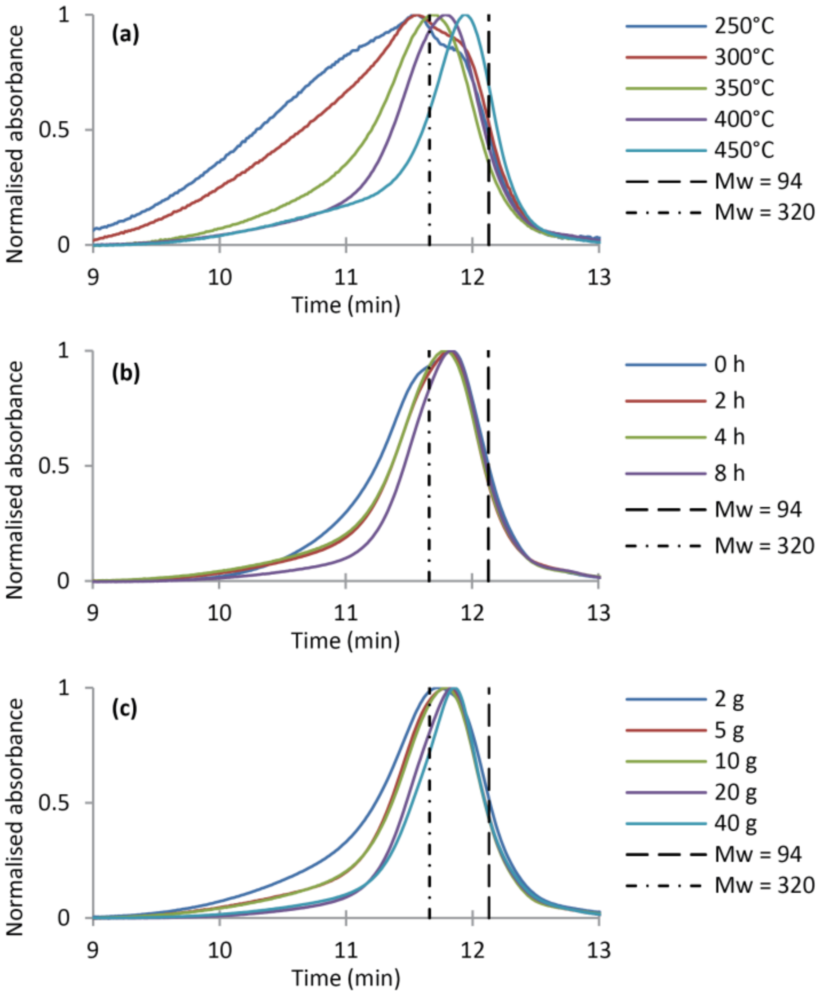


Figure 4.9 Molecular mass distribution for lignin oils obtained at different reaction temperatures (a), reaction times (b), and degrees of lignin loading (c). Size exclusion chromatography was conducted and the normalised absorbance at 280 nm wave length is shown as a function of elution time. Reaction conditions for produced oils: 10 g lignin and 4 h reaction time (a); 10 g lignin and 400 °C reaction temperature (b); 4 h reaction time and 400 °C reaction temperature (c).

4.1.2.1 Effect of Reaction Temperature on Oil Quality

The lignin feedstock has a molar O/C of 0.4 so a reduction in oxygen content for all reaction temperatures is obtained (see Figure 4.8a). An increase in temperature increases the degree of deoxygenation which corresponds well with a lower bond enthalpy for oxygen functionalities and linkages than for C-C bonds.[18] Solvolysis at 450 °C yielded an oil product with a molar O/C of 0.12.

When the reaction temperature increases the molecular size distribution in the oil product mixture narrows with species similar in size to lignin monomers (see Figure 4.9a). At 250 °C and 300 °C specifically there is a shoulder in the molecular size distribution curves indicating a very heterogeneous mixture with the majority of species having a molecular weight larger than 320 g/mol potentially representing a mixture dominated by lignin dimers and larger products. At these lower reaction temperatures the oils were also substantially more viscous than those obtained at higher temperatures. Oxygen removal at elevated temperatures corresponds well with ^{13}C NMR on the product oil (see Figure 4.5a) where the aliphatic oxygenated region (sp^3 oxygenated) is reduced as a function of reaction temperature. NMR data on the oil product further shows that the ratio between the non-oxygenated aliphatic and aromatic fractions is hardly changed when produced in the temperature range from 250 °C to 350 °C. As the temperature increases to 400 °C, the oxygen content is further reduced, and the deoxygenated aliphatic fraction increased. The aromatic fraction is nearly unchanged up to 400 °C which is also seen from the near constant molar H/C ratio (see Figure 4.8a). At a reaction temperature of 450 °C, the oxygenated fraction is almost fully reduced, and the unsaturated fraction is increased resulting in a drop in molar H/C from 1.5 to 1.3. At 450 °C there is an increased degree of gas formation directly stemming from the lignin (see Figure 4.1a) and the oil yield is reduced by around 50 % while the char yield remains unchanged. This observation together with the near doubling in relative aromatic content indicates that an increasing proportion of aliphatic functionalities in the oil fraction are transformed to gas at 450 °C.

4.1.2.2 Effect of Lignin Loading on Oil Quality

The molar O/C is reduced at increased lignin loading at 400 °C (see Figure 4.8c). A reduction in molar O/C was equally observed at increased loading for all temperatures (see Appendix A).

At the highest degree of lignin loading the molar O/C was substantially lowered to 0.09 or an oxygen content of 9.7 wt%. Such high degree of deoxygenation has not previously been reported on liquefaction of lignin by non-catalytic means and without a reducing agent such as hydrogen. The oil yield drops faster than the drop in oxygen content at increased lignin loading suggesting increased repolymerisation.

^{13}C NMR of the resulting oils clearly shows an increased oxygen removal from sp^3 carbon as a function of loading (see Figure 4.5c). The aromatic fraction of the oil increases when the lignin loading is increased from 2 g to 5 g after which the aromaticity barely changes; however, the highest degree of aromaticity is found for the highest lignin loading. The molar H/C, shown as a function of lignin loading (see Figure 4.8c), equally shows a near constant value of 1.5 going from 5 g to 40 g loading and a slightly higher value of around 1.6 at 2 g loading. This combined with the higher oil yield at the lowest lignin loading indicates that a fraction of the oil is polymerisation products of the solvent ethanol.

At 400 °C the molecular size distribution becomes narrower and shifts towards smaller molecular size species for increasing lignin loading (see Figure 4.9c). This was equally observed at 300 °C (see Appendix A). A high degree of lignin loading is thus beneficial with respect to both obtaining a deoxygenated oil product and a reduced molecular size.

Increased lignin loading results in locally ethanol starved regions due to reduced mixing and especially at the bottom of the reaction vessel where undissolved lignin fragments displace the ethanol. This results in reduced interaction between solvent and lignin. Still, the resulting oil product in this study is inherently different and of better quality than pyrolysis oil.

4.1.2.3 Effect of Reaction Time on Oil Quality

For up to 8 h reaction time the molar O/C in the obtained oil product is fairly uniform at around 1.5 for a reaction temperature of 400 °C and 10 g lignin loading (see Figure 4.8b). The molar H/C in the oil increases from 1.44 to 1.57 going from 0 to 8 h reaction time. This decrease in aromaticity corresponds to a reduction in relative aromatic carbon atoms by one third (see Figure 4.5b). The molecular size distribution of the oil becomes increasingly narrow and shifts towards smaller molecular size species below 320 g/mol after 8 h (see Figure 4.9b). This in conjunction with increased oil yield shows that the relative increase in aliphatics over time in the oil is not due to an increase in aliphatics attached to aromatic oil species, as the SEC data only represents aromatic molecules. This is likely arising from irreversible solvent reactions.

4.1.2.4 Miscibility with Diesel Oil

A clear advantage of low oxygen content in the oil is the increased miscibility with a non-polar fossil diesel. The target of this study is to produce a lignin-oil that will satisfy fuel standards and successfully blend with a fossil diesel. The molar O/C also serves as a benchmark for the oil quality as can be seen in Figure 4.10 where the solubility in heptane as a function of molar O/C for select oils is represented. Heptane was used as a substitute for fossil diesel possibly representing an even more non-polar substance due to the lack of aromatics. As the molar O/C is reduced to near 0.1 the solubility approaches 80% thus showing that exhaustive deoxygenation is not needed.

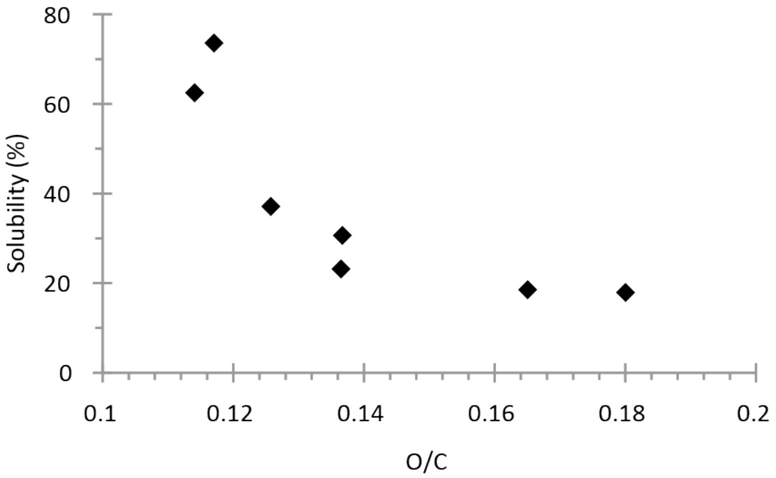


Figure 4.10 Solubility of lignin-oils in heptane as a function of molar O/C. Solubility is defined as the weight percent of heptane soluble oil with a mixing ratio of 1:9 (oil:heptane).

4.1.3 Residual Solid Product Analysis

The residual solid product of the solvolysis is a potentially valuable by-product. This biochar can be put back into the soil from where the biomass was harvested in order to improve soil quality.[200] Alternatively the biochar can be burned in a power plant as a coal substitute.

Figure 4.11 shows the ^{13}C and ^{23}Na solid-state MAS NMR spectra for residual char obtained at solvolysis temperatures of 250 °C to 450 °C. Three different types of solid-state MAS NMR spectra were recorded: ^{13}C CP/MAS, ^{13}C SP/MAS and

^{23}Na SP/MAS. In the ^{13}C CP/MAS NMR spectra the intensity of carbon sites situated in immobile regions of the sample are enhanced whereas the carbon sites are recorded in a quantitative manner by the ^{13}C SP/MAS NMR experiments. The ^{23}Na SP/MAS NMR were also quantitative. A full description of the solid state NMR data on the lignin rich starting material is supplied in Appendix A together with data on the solid residual obtained from the experimental series with varying reaction time and lignin loading.

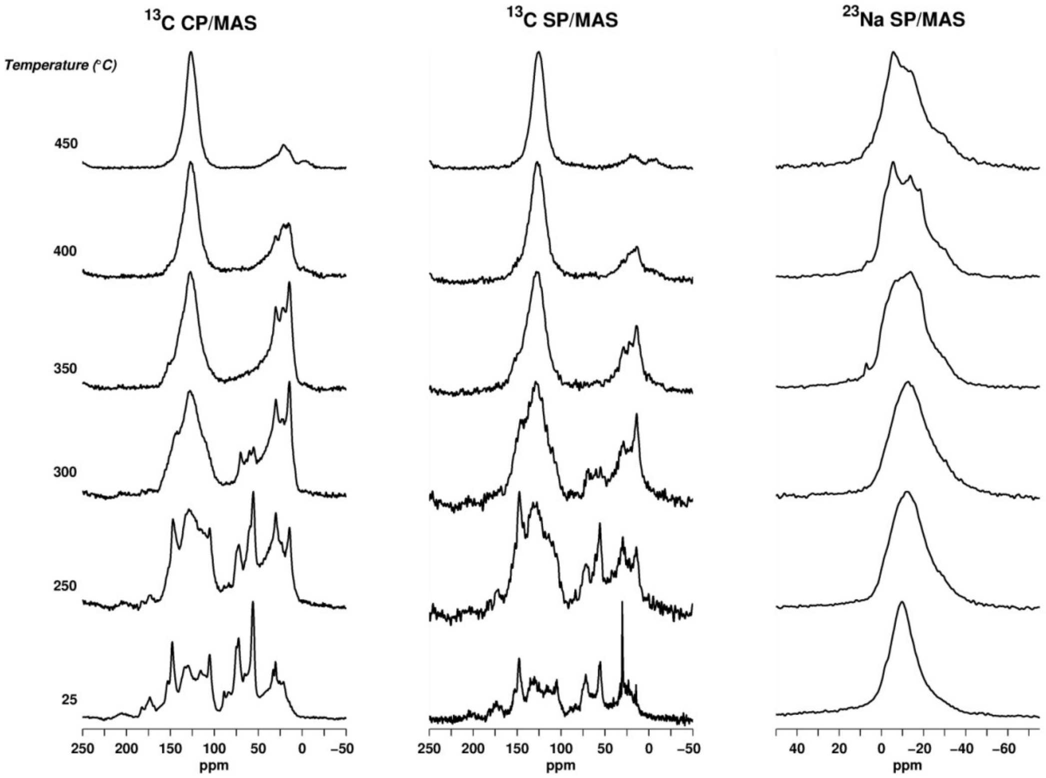


Figure 4.11 ^{13}C and ^{23}Na solid state MAS NMR of the residual solids from conducting solvolysis of 10 g lignin in 100 ml ethanol for 4 h at different reaction temperatures. The sample at 25 °C is the solid lignin rich starting material.

The ^{23}Na SP/MAS spectrum for lignin shows an almost featureless Lorentzian line shape which shows that sodium is located in a disordered environment. In the ^{13}C spectra it is seen that there is a dramatic change in the residual bio char structure when heating the biomass in ethanol. Upon heating to 250 °C, it was noted that lipids were removed and the carbohydrate content reduced. In addition the amount of etherified C3 and C5 in S units (syringyl) was significantly reduced whereas the non-etherified C3 and C5 in H units (*p*-hydroxyphenyl) as well as C1 and C4 in G units (guaiacyl) were still observable. The aliphatics were also modified as seen by the appearance of two intense resonances at 15.0 and 30.4 ppm indicating formation of saturated aliphatics. Judging by the intense resonance of the methyl groups (15.0 ppm), the aliphatics are either short or highly branched. The applied lignin has been pretreated at 190 °C (see section 3.1.2), so a lot of structural change has already taken place and treatment in ethanol at 250 °C is not severe enough to impose further structural changes to the majority of the lignin matrix. One could consider the solvolysis at 250 °C more as an organosolv process. As the reaction temperature is increased, the oxygenated part of the biomass is greatly reduced, and already at 300 °C, there is a clear reduction of carbohydrates and oxidized sp^3 carbons between 60 and 107 ppm as well as for the methoxy resonance ~56 ppm. The distinct syringyl/guaiacyl resonances ~150 ppm were also reduced in this process. At a reaction temperature of 350 °C the oxygenated fraction is completely gone and the aromatic resonances are starting to become uniformly centred at 127 ppm. As the temperature reaches 400 °C the aliphatic part of the biomass decreases dramatically, and at 450 °C it is almost completely gone, leaving only a highly uniform aromatic part of the biochar. This suggests that the char is mostly some sort of polyaromatic hydrocarbon (PAH). By the ^{23}Na SP/MAS spectra it is observed that the sodium changes from a disordered environment in the lignin via an intermediate stage having either a larger chemical shift distribution or sites with larger quadrupolar interactions at 250-300 °C to a more ordered environment at higher temperatures. This is demonstrated by the presence of a second order quadropolar line shape in the biochar produced at 350 °C and even more pronounced at 400 °C. As Na^+ is expected to be in the vicinity of oxygen, the complete lack of carbohydrate structure in the biochar produced above 300 °C, suggests that Na^+ is mostly bound to the silicates found in the biochar. This sodium-silicate interaction appear to be well ordered when produced around 400 °C, and less so when produced at 450 °C. One explanation for this could be that the silicates start to melt or rearrange and the Na^+ become trapped in more heterogeneous structures at 450 °C.

For changes in reaction time of the lignin solvolysis the char composition is seemingly unchanged even at an extended reaction time of 8 h (full solid state NMR spectral data as a function of reaction time is shown in Appendix A). This shows that a state of equilibrium is reached at or before two hours of reaction time at the reaction temperature of 400 °C. It further supports that a long reaction time is not advantageous for the liquefaction of lignin by ethanol, as a longer reaction time mostly contributes to disadvantageous solvent loss/consumption. In the ^{23}Na MAS NMR spectra substantial changes as a function of reaction time are observed. At 2 h the sodium in the ordered environment (second order line shape) dominates, whereas the sodium in less ordered (narrow line around -10 ppm) environments are more pronounced after 8 h of reaction.

For changes in lignin loading between 10 g and 40 g lignin the carbon species of the char product is almost unchanged as was also observed for the samples exposed to different reaction times at 400 °C (full solid state NMR spectral data as a function of lignin loading is shown in Appendix A). This indicates that there is a clear energy activation barrier that needs to be overcome before the biomass decomposes further. All of the biochar obtained was however subjected to a reaction time of 4 h, which means that differences in composition due to varying degrees of lignin loading at shorter reaction times may still exist. It seems as reaction temperature is the only parameter that substantially changes the composition of the organic fraction of the biochar. The ^{23}Na NMR spectra change towards a single sharp peak at increased loading. A plausible explanation for this could be that the solvent affects the Na coordination to the inorganic fraction of the biochar, since this is the only concentration we change relative to lignin and ash.

Both higher loadings and longer reaction times promote formation of the disordered (sharp peak) sodium environment, and it was observed that the spectrum of solid residual char from solvolysis of 10 g lignin for 8 h at 400 °C is similar to the spectrum of solids from solvolysis of 20 g lignin for 4 h at 400 °C even though slightly more disordered sodium was observed in the latter.

Since an increase in lignin loading yields more char with similar composition the additionally formed char must stem from a similar process/reaction as char formed at lower loadings. The majority of char is a direct result of lignin polymerization reactions, which occur to a greater extent when the "local" ethanol concentration and availability near depolymerized lignin species is lower and hence the potential for inhibiting repolymerization is lower.

4.2 Conclusions

Batch autoclave experiments have shown that simple non-catalytic solvolysis of biorefinery lignin in supercritical ethanol can produce a sulfur free and diesel soluble bio-oil without the need for addition of catalyst or reducing agent such as hydrogen.

In contrast to pyrolysis without a catalyst all of the oils obtained by ethanol solvolysis were acid free with no detectable carbonyl functionalities. This explains the high shelf stability (11 months) with neither sedimentation nor change in molecular size distribution. The char product has reduced oxygen content relative to the lignin feed making it a candidate for use as a biochar.

Decarboxylation is the main contributor to the lignin deoxygenation as the majority of CO_2 formed comes from the lignin. CO was mainly the result of ethanol decomposition. Ethanol inhibits the repolymerization of depolymerized lignin species; however, reactions in which the solvent alcohol actively facilitates cleavage and becomes incorporated into the final oil product can also be argued, and most likely both kinds of reactions take place.

The highest oil yield of 50 $wt\%_{d.a.f.}$ was obtained for solvolysis of 10 g lignin for 8 h at 400 °C but 47 wt% of the solvent was also consumed. Solvolysis of 10 g lignin at 350 °C for 4 h resulted in a lower oil yield of 37 $wt\%_{d.a.f.}$; however, the degree of solvent consumption was advantageously lower at 17 wt%.

The lignin to solvent ratio was tested at loadings higher than previously reported. In this study it was found that at a 2:1 weight ratio of ethanol:lignin the resulting oil product had a very low molar O/C ratio of 0.09 and an increasingly narrowed molecular size distribution dominated by species <300 g/mol.

The solvolysis was advantageously carried out with a low reaction time (<1 hour) in order to limit solvent consumption. This combined with a reduced solvent to lignin ratio reduces the requirements for the scale of processing equipment in a future industrial scale up.

CHAPTER 5

Investigation of Alcohol Solvent Consumption

In Chapter 4 the results of a parametric study of biorefinery lignin solvolysis by ethanol were discussed while assessing the effect of reaction time, reaction temperature and degree of lignin loading on product yields and composition. The amount of solvent consumed was substantial and exceeded the yield of depolymerized lignin by a zeroth order reaction more than tenfold faster than the rate of bio-oil production.

The mechanisms of solvent consumption in biomass solvolysis reactions are not well understood. Alcohols thermally decompose to gasses at elevated temperatures and decompose already at the supercritical temperature.[201] Even in reactions where the solvent is recognized as being a reactant, and acting as a hydrogen donor, solvent consumption is often an overlooked parameter.[4,6]

Reactions in which alcohol solvent is consumed due to reaction with lignin is seen in some studies where the yield of solids and liquid depolymerized lignin species exceed the amount of initial added lignin[77,173] hence transformation of solvent to bio-oil must occur. Direct alkylation of depolymerized lignin by ethanol can be described by a mechanism by Zhao *et al.*[75], where alcohol radicals facilitate cleavage and resulting in its incorporation in the depolymerized lignin molecule. Barnard investigated the thermal decomposition of ethanol at 576–624 °C and observed significant gas yields and in particular also a brown polymer.[198] Higher alcohol synthesis as described by Guerbet[202,203] may be responsible for formation of heavier alcohol polymerization products that will be found in the bio-oil fraction after lignin solvolysis.

In this chapter the effects of solvent consumption are investigated by using different primary alcohols (methanol, ethanol, 1-propanol and 1-butanol) as solvents for lignin solvolysis. Solvent reaction products obtained when conducting lignin solvolysis in different alcohols allow for a comparison in which products directly stemming from the alcohol can be identified and hence the mechanisms of solvent consumption are readily identified.

5.1 Results and Discussion

The differences in degree of lignin liquefaction and lignin product yields and composition are discussed in section 5.1.1. In section 5.1.2 the solvent consumption is discussed with respect to reaction paths yielding gaseous products, light solvent phase reaction products and heavy oil products where the solvent alcohol is a reactant. Additional supplementary analytical data is supplied in Appendix B.

5.1.1 Effect of Different Alcohols

Solvolysis of lignin by methanol, ethanol, 1-propanol and 1-butanol was conducted at temperatures of 300 °C, 350 °C and 400 °C at which the mentioned alcohols are supercritical. In Figure 5.1 the oil, solid residual and gas yields are shown as a function of reaction temperature for the lignin solvolysis. The different alcohol solvents behave similarly in lignin liquefaction with the exception of methanol, which results in lower oil yields. In particular at 400 °C the oil yields using ethanol, 1-propanol and

1-butanol were 0.4 g/g lignin while methanol yielded only 0.2 g/g. Yamazaki *et al.*[117] equally observed similarities between beech wood liquefaction in different primary alcohols of chain length C1 to C10 at 350 °C. Longer chain alcohols provided faster wood conversion at short reaction times; however, after 30 minutes reaction time all alcohols performed similarly. It was in Chapter 4 demonstrated that the reaction temperature is the most important parameter with regards to degree of deoxygenation and depolymerization for lignin solvolysis in ethanol. This was equally seen in this study where using ethanol, methanol, 1-propanol or 1-butanol yielded similar oil composition as revealed by NMR, SEC and elemental analysis. Full spectral NMR data and elemental composition data is supplied in Appendix B. SEC data is discussed in section 5.1.2.4.

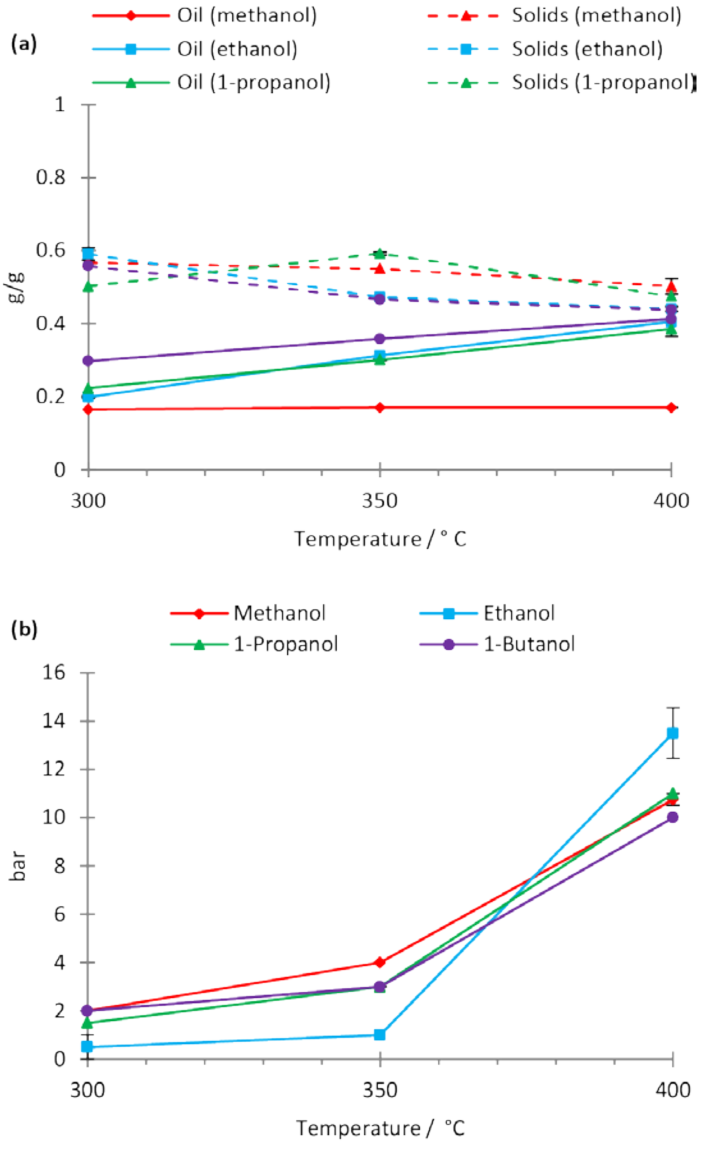


Figure 5.1 Oil and solid yields per mass of initially added lignin (a) and gas yields at room temperature (b). Reaction conditions: 10 g lignin treated for 4 h in 100 ml of alcohol solvent with a non-pressurized inert atmosphere prior to heat up. Error bars represent standard error of the mean.

5.1.2 Solvent Consumption

Due to the cost of solvent its consumption is highly undesired. Solvent decomposition products at different reaction temperatures are shown in Figure 5.2. The major products comprising around 50 wt% of solvent consumption are water and other light organics. A higher amount of both water and other light organics is formed when lignin is added to the reaction in any of the solvents. The solvent blank experiment with methanol yields almost exclusively decomposition to gas products and a higher solvent consumption than with lignin addition indicating that lignin inhibits solvent decomposition to gas. When the reaction temperature is increased the solvent consumption equally increases for all of the alcohol solvents used and the highest solvent consumption was 35 wt% for lignin solvolysis in ethanol at 400 °C.

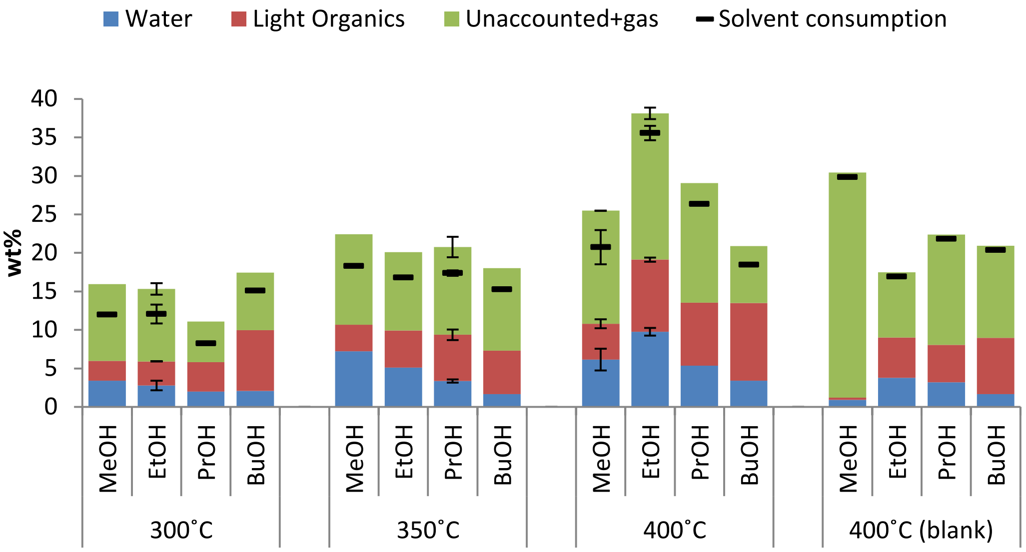


Figure 5.2 Solvent consumption and yields of water, light organics other than the solvent and unaccounted mass (gas) both in the presence of 10 g lignin and without for a 4 h reaction at different reaction temperatures using 100 ml alcohol solvent. Data is represented per mass of solvent added. Error bars represent standard error of the mean.

5.1.2.1 Solvent Reaction Paths

Main routes for solvent decomposition and breakdown product formation have been identified and are shown in Figure 5.3. The primary breakdown reactions are denoted (a), (b) and (c). The heavy bio-oil fraction and the light organic fraction are separated by evaporation at 45 °C and 5 mbar and are hence defined with boiling points higher and lower than these conditions respectively. Secondary breakdown mechanisms are the reactions of the products of the primary breakdown reactions denoted (d), (e) and (f). As can be seen, gas is the final product of solvent decomposition over time. In a previous study with lignin solvolysis in ethanol at 400 °C for up to 8 hours reaction we equally observed a linear gas formation over time (see section 4.1.1.2).

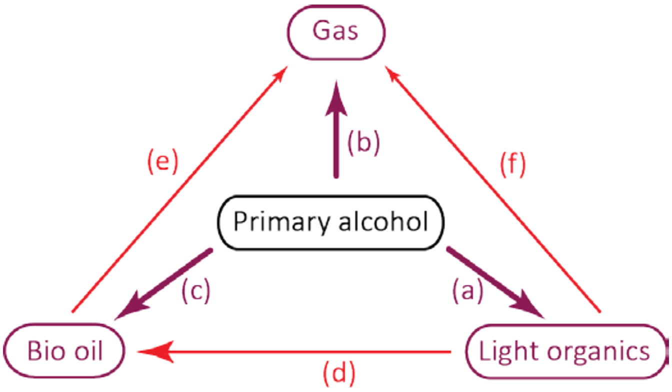


Figure 5.3 Reaction paths for solvent consumption. Primary reactions are (a), (b) and (c) and secondary reactions are (d), (e) and (f).

Direct decomposition of the alcohol to form gaseous species as described by Barnard[198] are responsible for reaction (b).

The primary alcohol reacts with itself in condensation/dehydration reactions (a) of the Cannizzaro/Tishchenko[204,205] type yielding lighter oxygenated species and water. Also longer chain alcohols are formed from Guerbet reactions.[202,203] Formed light organic products may subsequently decompose thermally to form gaseous products through the secondary reaction (f). Alternatively the formation of heavy aliphatic products from higher alcohol synthesis (d) will yield high boiling products that are left in the bio-oil fraction.

Reaction of the primary alcohol solvent with lignin (c) can yield a bio-oil product with incorporated ethers or esters of chain length similar to the alcohol solvent. Esters and ethers can be formed through alcohol condensation with carboxyl and hydroxyl groups present in depolymerized lignin. Alcohol is incorporated already at 200 °C during organosolv extraction.[206,207] Finally a radical induced pathway may equally be responsible for the incorporation of solvent into the oil product as proposed by Zhao *et al.*[75] These reactions may be responsible for inhibiting repolymerization.[119–123] Both reaction products of reaction (c) and (d) will increase the oil yield by a solvent-to-oil reaction. These reactions further reduce the aromaticity and contribute to relatively lower oxygen content. Solvent alcohol products found in the heavy oil fraction may finally yield gaseous products through subsequent decomposition (e).

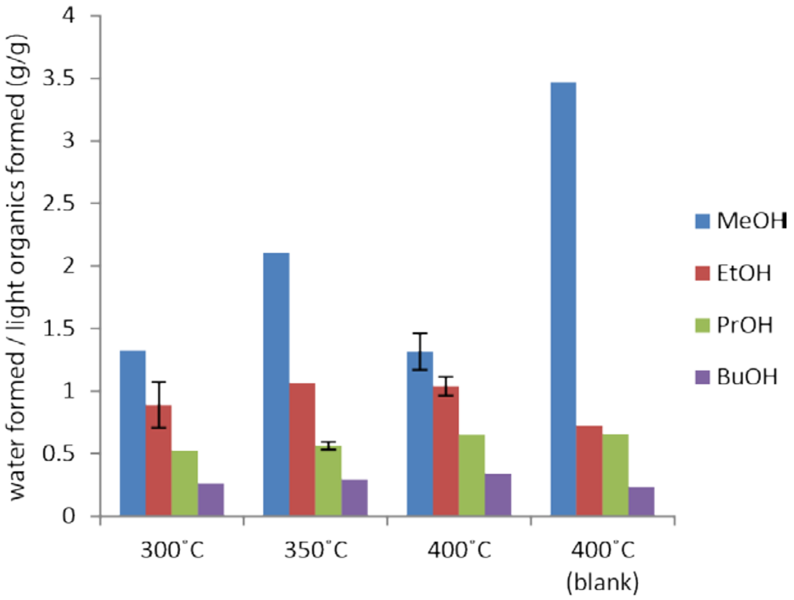
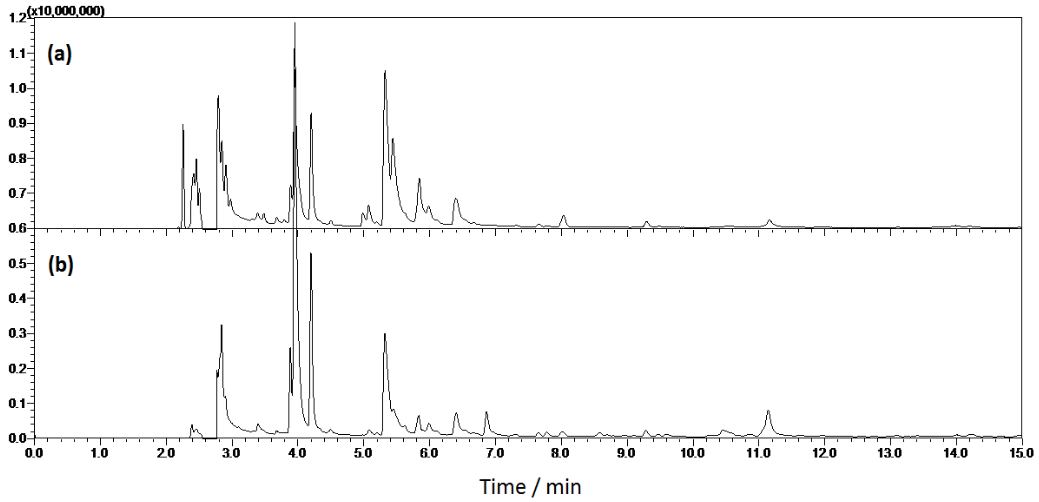


Figure 5.4 Mass of water formed per mass of light organics formed as a function of reaction temperature for a 4 h reaction with 10 g lignin in 100 ml solvent. Solvent blank shows the yields in the case of no lignin addition. Error bars represent standard error of the mean.

5.1.2.2 Solvent to Light Organics Reactions

The products of the solvent – solvent reactions (a) in Figure 5.3 are mainly water and light organics. The mass of water formed per mass of light organics in the solvent phase after solvolysis is plotted as a function of reaction temperature and alcohol in Figure 5.4. The water to light organics ratio is highest for methanol and drops as the chain length of the alcohol solvent is increased for all reaction temperatures tested even with and without lignin addition. This indicates that the majority of water and light organics formed are simply products of undesired solvent reactions as longer chain alcohol solvents will indeed yield less water and equally more organic light species on a mass basis of solvent added. As a function of reaction temperature there is a constant water to light organics ratio of 1, 0.6 and 0.3 for lignin solvolysis in ethanol, 1-propanol and 1-butanol respectively. This indicates that the solvent-solvent reaction (a) in Figure 5.3 proceeds through condensation and dehydration reactions in a similar fashion at all temperatures and the rate of reaction increases with temperature. This effect was equally seen by GC-MS analysis of the solvent fraction after reaction where species formed at 300 °C are equally formed at higher temperatures but as the temperature was increased more species were seen. In Figure 5.5 the GC-MS chromatogram of the solvent fraction is shown for the reaction at 400 °C in ethanol both with and without lignin present and GC-MS chromatograms for all reaction temperatures and solvents used are supplied in Appendix B. The species formed in the solvent blanks resemble the ones formed with lignin present during solvolysis.



Time / min	Name
2.45	acetaldehyde
2.81	acetone
2.90	diethyl ether
3.30	2-propen-1-ol
3.89	2-butanone
3.96	2-butanol
4.20	ethyl acetate
4.99	2-butenal
5.20	3-methyl-2-Butanone
5.34	1-butanol
5.99	2-pentanone
6.39	2-pentanol
6.87	propanoic acid ethyl ester
8.03	4-methyl-cyclohexene
11.15	butanoic acid ethyl ester

Figure 5.5 Chromatograms of the light fraction from (a) a blank reaction of 100 ml ethanol reacted for 4 h at 400 °C and (b) 10 g of lignin in 100 ml of ethanol reacted for 4 h at 400 °C. Major peaks identified are shown in the table with the retention times.

The chain lengths of organic species recovered in the solvent fraction are increased with increasing chain length of the alcohol solvent used (see Appendix B). The main species found in the organic light fraction include non-aromatic alcohols, aldehydes, ketones, ethers and esters i.e. not lignin degradation products. In particular no carboxylic acids were detected in any of the experiments.

Alcohols and esters are most likely formed via aldehyde intermediates, which can undergo Guerbet reactions[202,203,208] (higher alcohol synthesis) or Cannizzaro/Tishchenko type reactions[204,205] (aldehyde disproportion to form esters). These solvent-solvent reactions are shown in Figure 5.6 and contribute to reaction (a) in Figure 5.3. Ethers may readily form from thermally induced alcohol condensations.

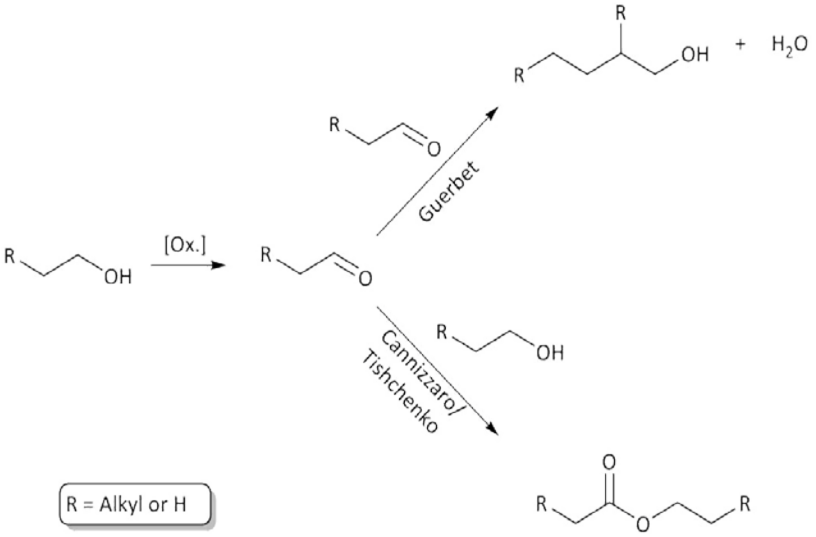


Figure 5.6 Solvent-solvent reaction paths through an aldehyde intermediate. Higher alcohol synthesis through Guerbet reaction and ester formation through Cannizzaro/Tishchenko reactions.

Some aldehydes are detected for all experiments at 400 °C; however, the relative quantity is low which is expected as the reactivity of aldehydes is high and thus becomes mainly an intermediate product. Reaction with other light species as well as depolymerized lignin species is expected to be prominent. Ketones are equally detected for all solvolysis experiments and are expected to be formed as a result of proton donation from secondary alcohols.

Alcohols recovered include primary and secondary linear as well as branched alcohols. Longer chain alcohols recovered in the light fraction are largest for the lignin solvolysis in 1-butanol where 4-octanol was identified as the heaviest alcohol at a reaction temperature of 400 °C both in the solvent blank and in the case of lignin addition (see Appendix B). In the solvent blank experiments there is a slightly increased proportion of longer chain organics recovered compared to the solvolysis with lignin present. This indicates that lignin inhibits the long chain alcohol synthesis possibly by reacting with formed solvent breakdown products e.g. aldehydes and/or unsaturated aliphatics. The latter species are also predominantly observed in the solvent blank experiments.

Some ethers are formed for all solvolysis experiments. In particular symmetric ethers resulting from the condensation of two solvent molecules are identified as diethyl ether, dipropyl ether and dibutyl ether from solvolysis in ethanol, 1-propanol and 1-butanol respectively. Dimethyl ether is most likely also formed but lost due to evaporation during filtration.

Esters of varying sizes are formed in all experiments; however, the alkyl parts are mainly of similar length to the alcohol solvent used. For solvolysis both with and without the addition of lignin at 400°C the esters ethyl acetate, propyl propanoate and butyl butanoate are found when using the solvent ethanol, 1-propanol and 1-butanol respectively. This corresponds well with a Cannizzaro/Tishchenko type reaction.[204,205] Many of the esters where the acid part is either propanoic acid or acetic acid are identified only in the reaction products of lignin solvolysis and not in solvent blanks. This indicates that these acid functionalities are breakdown products of the lignin rich biomass. In particular acetic acid esters may come from transesterification reactions from the natively acetylated biomass to acetylated solvent.

5.1.2.3 Solvent to Gas Reactions

Figure 5.7 shows gaseous decomposition products of solvolysis in methanol, ethanol, 1-propanol and 1-butanol at 400 °C both with and without the addition of lignin. Absalam-Gadzhievich and Ramazanovich[201] equally reported non-catalytic gaseous decomposition of these alcohols at temperatures below 300 °C. In the solvent blanks the combined amount of CO and H_2 comprise more than 50 mole% of the total amount of identified gaseous species. It was previously observed for solvolysis in ethanol at varying degrees of lignin loading that CO is solely a product of solvent decomposition and CO_2 was mainly formed as a product of lignin decomposition (see section 4.1.1.3). Barnard and Hughes[198] equally demonstrated that thermal decomposition of ethanol facilitates cleavage between C1 and C2 yielding CH_4, CO and H_2. Solvent decomposition through decarbonylation was equally observed for all primary alcohols as hydrocarbons of a chain length one shorter than the starting alcohol was observed in the solvent blanks in Figure 5.7(b) (e.g. 1-butanol forms mainly CO, H_2 and propane). Solvent decarbonylation is the main path for reaction (b) in Figure 5.3.

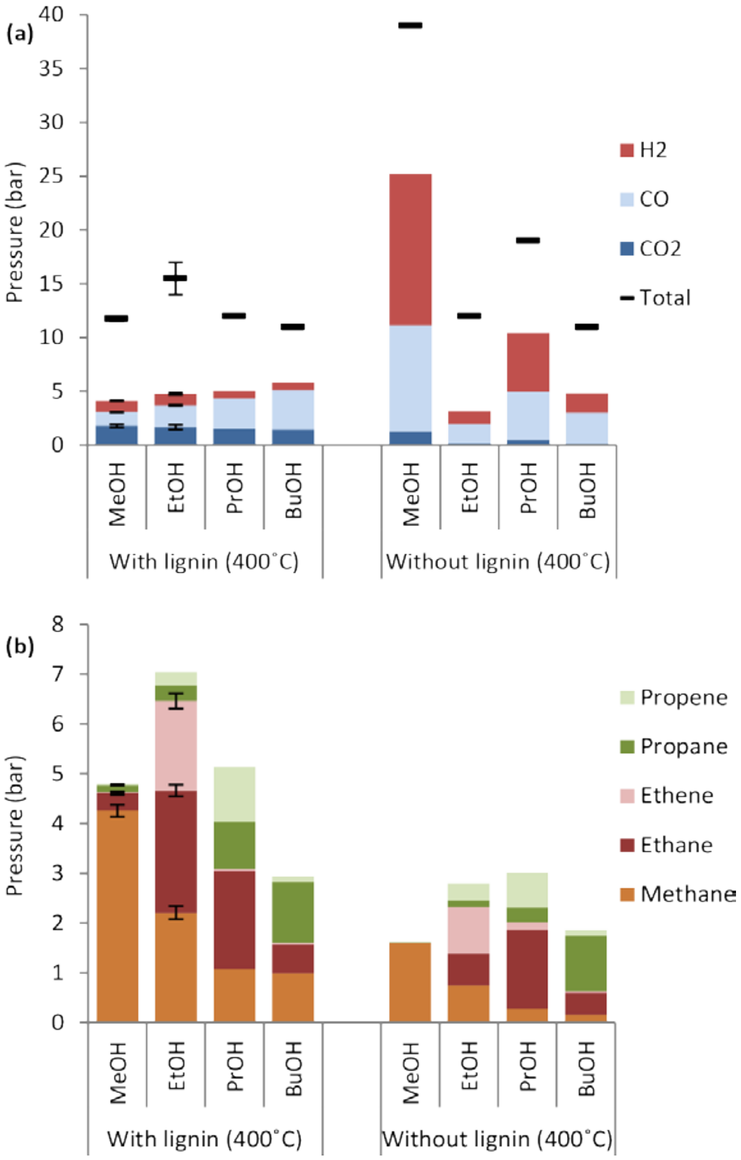


Figure 5.7 Gas species produced after 4 h reaction at 400 °C in 100 ml alcohol solvent both with addition of 10 g lignin and without. For ease of comparison the top chart (a) shows yield of H_2, CO and CO_2 and total gas yield and bottom chart (b) shows yield of gaseous hydrocarbons. Error bars represent standard error of the mean.

Lignin decarboxylation is unaffected by the type of primary alcohol used as the CO_2 yield is nearly unchanged. Interestingly the CO formation increases from 1.3 to 3.7 bar as the alcohol chain length increases from C1 to C4 in the lignin solvolysis experiments.

The chain length of hydrocarbon species found in highest amounts in the gas phase after lignin solvolysis corresponds to the chain length of the alcohol used. In particular lignin solvolysis in methanol yields the highest methane yield, lignin solvolysis in ethanol yields the highest combined ethane/ethane yield and lignin solvolysis in 1-propanol yields the highest combined propane/propene yield. C4-hydrocarbons and longer may have been present but limitations due to the GC-TCD gas analysis conducted did not allow for its detection. This shows that the majority of hydrocarbons found in the gas phase comes from solvent to gas reactions. Strikingly there is a higher degree of up to two or three times more gaseous hydrocarbons formed when lignin is added compared to the solvent blank experiments. These gaseous species may in fact be reaction products of a reaction between solvent and lignin. Such a reaction could be an initial incorporation of the solvent alcohol in the depolymerized lignin products and subsequent bond cleavage causing the gaseous hydrocarbon of chain length equal to the solvent to be released. Such reactions will be responsible for reaction (e) in Figure 5.3.

5.1.2.4 Solvent to Bio-Oil Reactions

Incorporation of the solvent alcohol into the depolymerized lignin polymer through reaction (c) in Figure 5.3 or higher alcohol synthesis through reaction (d) in Figure 5.3 will increase bio-oil yield. A direct transformation of alcohol solvent to heavy bio-oil is not necessarily undesirable depending on the price of alcohol relative to the price of the final oil product.

Figure 5.8 shows the molar H/C in the oils obtained from the solvolysis in different alcohols at temperatures 300 °C to 400 °C. When the chain length of the alcohol is increased the molar H/C equally increases with the highest value of ~1.65 obtained using 1-butanol. An increased molar H/C ratio corresponds to an increase in saturated carbon. The molecular size distribution is equally shifted towards larger species in the oil product obtained as the chain length of the solvent alcohol is increased (see Figure 5.9). This effect is more pronounced at lower temperatures and at 300 °C in particular where the shoulders in the SEC curves represent monomer and dimer species there is a clear shift towards more dimers relative to monomers as the chain length of the alcohol solvent is increased. The SEC uses a UV-detector at 280 nm and hence only detects aromatic compounds. The increased molecular weight of the bio-oil combined with increased aliphatic content therefore indicates that the alcohol solvent is incorporated into the bio-oil through covalent bonding to aromatic species.

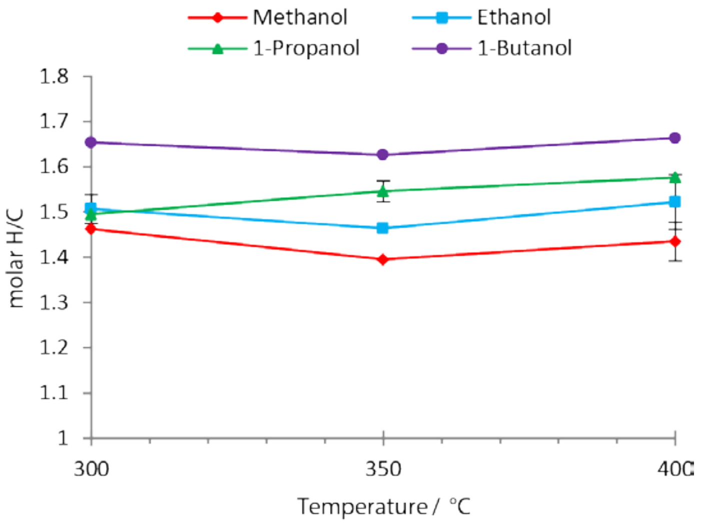


Figure 5.8 Molar H/C of the oil product resulting from treatment of 10 g lignin in 100 ml alcohol solvent at different reaction temperatures for 4 h. The lignin feedstock has a molar H/C of 1.3. Error bars represent standard error of the mean.

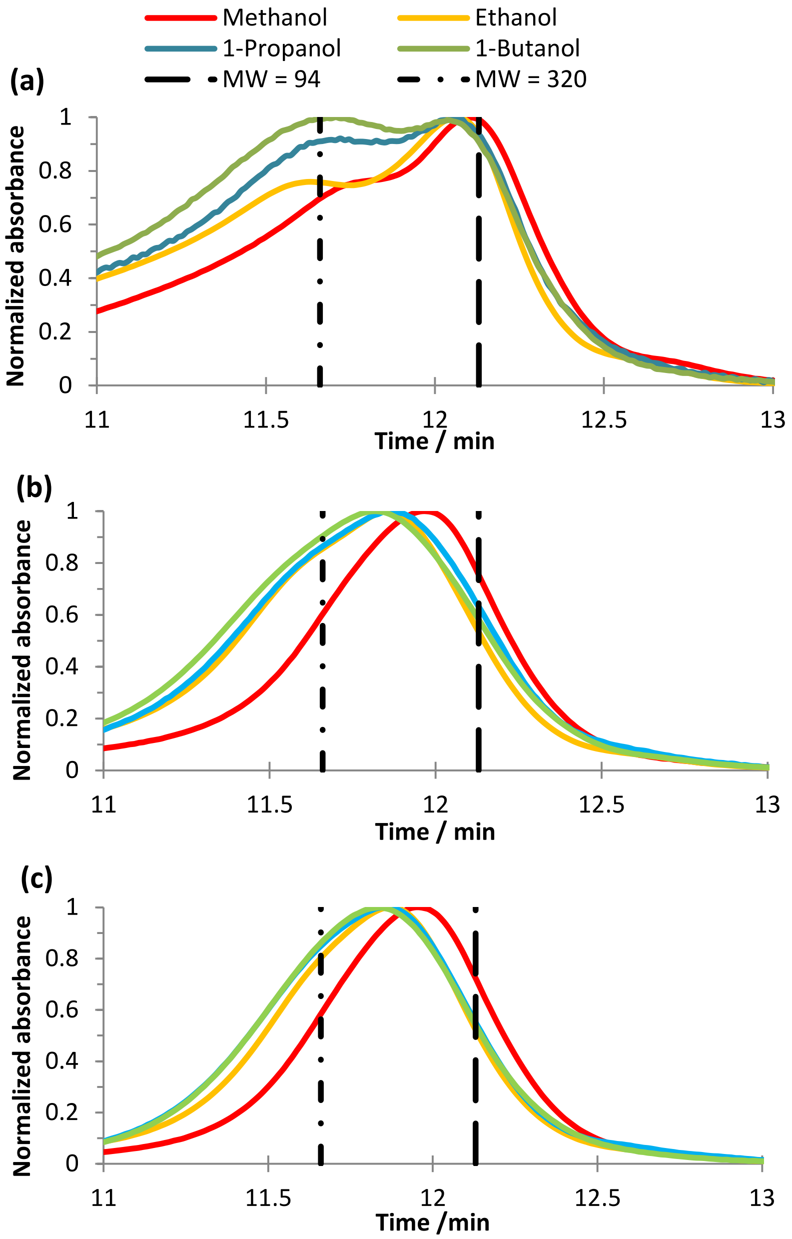


Figure 5.9 Molecular size distribution of oil product obtained from solvolysis in the different alcohols at similar reaction conditions. 10 g lignin was treated for 4 h in 100 ml of alcohol solvent at different reaction temperatures: (a) 300 °C; (b) 350 °C; (c) 400 °C.

^{1}H-TOCSY NMR spectra shown in Figure 5.10 allow for identification of solvent incorporation in the oil as cross peaks corresponding to the alcohol solvent chain length are observed. At least two different ways in which the solvent is incorporated are found at 4 ppm and 3.5 ppm. At 2.5 ppm bond identification was not possible; however, as the signal is at lower ppm it is suspected that the solvent is reduced and incorporated through a C-C bond. This is explained by the mechanism by Zhao *et al.*[75] where lignin depolymerization by ether bond cleavage is facilitated by an OH-radical and solvent alkyl radical ultimately leading to incorporation of the alkyl chain through C-C bonding. The ^{1}H peak found at 4 ppm in the ^{1}H-TOCSY spectra corresponds to incorporation of the solvent as an ester, as a correlation peak is found at 170 ppm in the ^{13}C-HMBC spectra. The ^{1}H peak at 3.5 ppm has no correlation peak >100 ppm in the ^{13}C-HMBC spectrum, showing that the alcohol is incorporated as an ether (^{13}C-HMBC spectra are supplied in Appendix B). The oils obtained from solvolysis in the different alcohols have seemingly similar ^{13}C-HSQC spectra; however, there are less methoxy groups in the bio-oils produced in ethanol, 1-propanol and 1-butanol compared to the bio-oil produced in methanol (HSQC spectra are supplied in Appendix B). This indicates alcohol incorporation through transetherification.

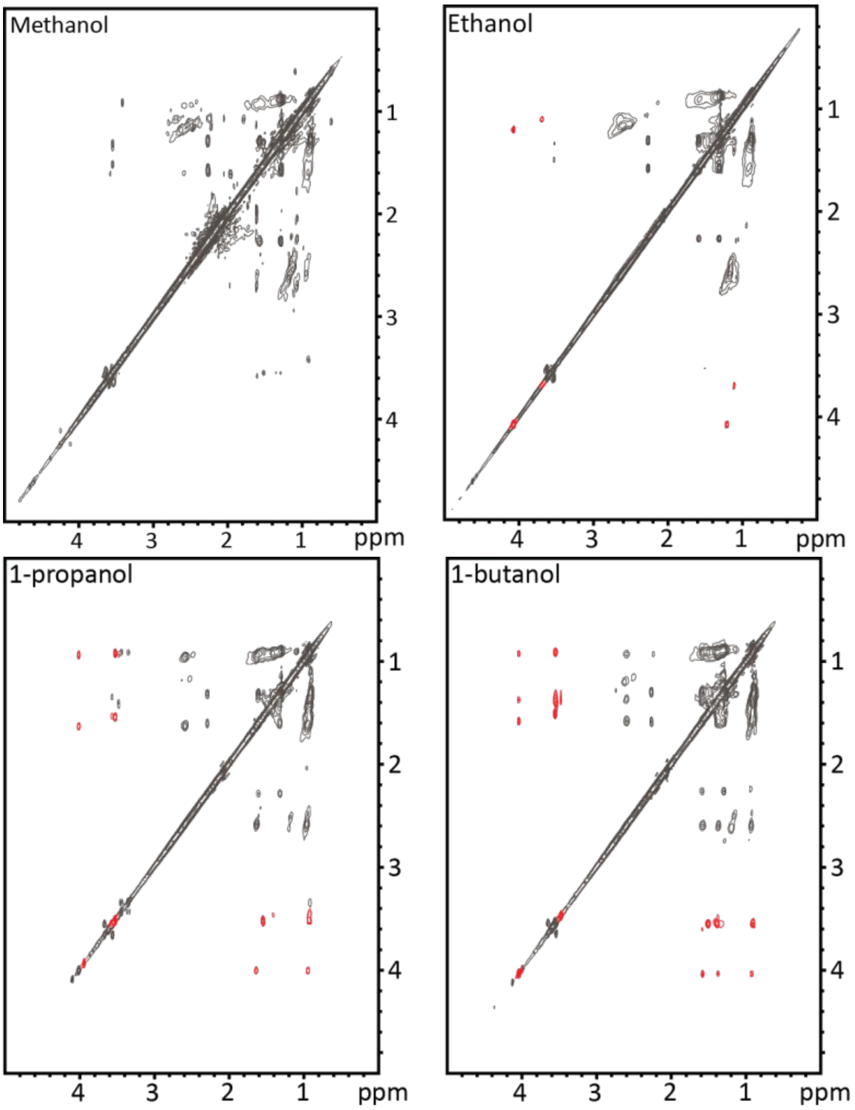


Figure 5.10 ^{1}H-TOCSY NMR spectra on oils obtained from solvolysis of 10 g lignin in 100 ml alcohol for 4 h. Correlated protons of alkyl groups with chain length identical to the chain length of the solvent used are shown in red.

5.2 Conclusions

The irreversible reaction of solvent with depolymerized lignin species is beneficial as a means of inhibiting repolymerisation and effectively lowering the oxygen content of the bio-oil. However, loss of solvent by reaction to gas and higher alcohols is undesired as the loss of solvent challenges a commercial process as the solvent cannot be recovered after reaction.

All of the primary alcohol solvents methanol, ethanol, 1-propanol and 1-butanol performed similar with respect to oil product composition. Methanol was an outlier with respect to bio-oil yield (~0.2 g/g lignin) which was only half the value of 0.4 g/g lignin obtained when conducting the lignin solvolysis in the three other solvents at 400 °C.

By comparing the products of lignin solvolysis in the four different alcohols a mechanism for solvent consumption was highlighted by identifying reaction products directly stemming from the alcohols. Solvent consumption mainly takes place through three different reactions: Direct decomposition to gas through decarbonylation, formation of light condensation products and incorporation of the alcohol into the bio-oil through covalent bonding.

CHAPTER 6

Economic Assessment of the LDO Process

In this chapter a simple economic assessment is made on the lignin-diesel oil (LDO) process as described in the parameter study in Chapter 4. Profitability is evaluated as output value minus input value and an example is given on large scale annual production of LDO where the energy balance is equally discussed.

The market for low sulfur marine fuels is increasing as emission control areas (ECA) in coastal areas are expanding now requiring less than 0.1 % S in the fuel (see Figure 6.1). In year 2020 the maximum sulfur content in fuels globally outside ECAs is lowered from 3.5 % to 0.5 % (MARPOL Annex VI).[209] This clearly shows the great market potential for a low sulfur LDO that readily blends with existing fossil diesels.

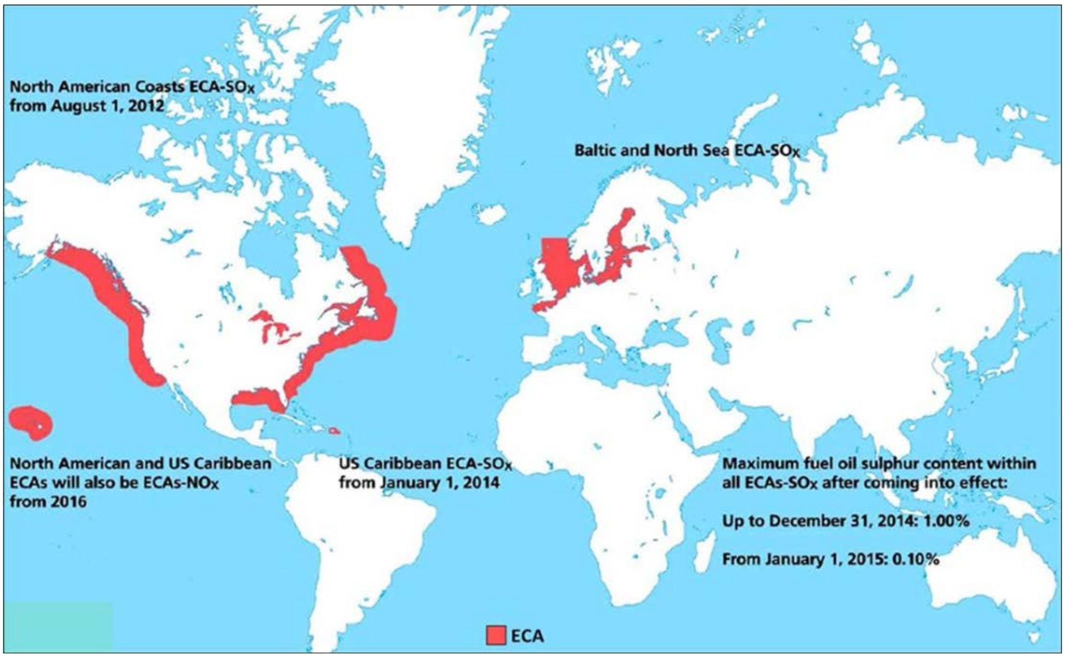


Figure 6.1 Map showing existing emission control areas where large ships are required to use low sulfur fuels.[209]

The availability of lignin from 2nd generation biorefineries may become a limiting factor as the vast majority of lignin produced worldwide comes from the pulp and paper industry which yields undesired sulfur rich lignin.[10–12] The calculations herein are therefore based on using a lignin rich feedstock in quantities that are actually obtainable from a large scale production of 2nd generation bioethanol. One such large scale bioethanol production may be the Maabjerg Energy Center (MEC) which is a consortium owned by DONG Energy, Novozymes, Vestforsyning and Struer Forsyning[210] using the same biorefinery technology as Inbicon, DONG Energy, thereby providing a feedstock similar to the hydrothermally pretreated enzymatic hydrolysis lignin used in this study. MEC is currently a work in progress as a final 2nd generation bioethanol production facility will only be constructed if a Danish fuel blend requirement (2.5 % 2nd generation bioethanol in gasoline) among other requirements are satisfied in order to provide a business case.[211] MEC will annually process 300,000 ton of biomass (straw) for the production of 2nd generation bioethanol. This will yield 60,000 ton lignin rich solid residual p.a. which forms the basis for this economic assessment of the LDO process.

The method for assessing the profitability of the LDO process and definitions and prices of inputs and outputs are given in section 6.1. The results of the economic assessment using data from the parameter study in Chapter 4 are discussed in section 6.2. In section 6.3 an example on a full scale LDO process is given and the energy balance is briefly discussed. Supplementary information is supplied in Appendix C.

6.1 Method

The simple economic assessment of the LDO process entails assessing the value gain from the main experimental series conducted in the parameter study in Chapter 4. The value gain is defined in the following as the difference between value of output products and input feedstock/reactants for the one step processing of lignin in ethanol. Utility costs and other operating as well as fixed costs are not considered. The cost of further downstream processing and waste handling is equally not considered. For ease of comparison between the results of the parameter study conducted the value gain is defined on a per lignin added basis:

$$\text{Value gain} = \frac{(\textit{value of outputs - value of inputs})}{\textit{mass of lignin}} \quad (\$/\text{kg}) \tag{6.1}$$

The currency used for all calculations is USD ($). The value gain as defined in equation (6.1) is equally used to calculate the total annual profit for the processing of the annual lignin yield of 60,000 ton from MEC. The inputs and outputs of the process are defined in the following as:

Inputs

Lignin (feedstock): Dried lignin as used in the parameter study (see section 3.1.2). In the parameter study 2–40 g lignin was added to the reaction. A wet filter cake comprising the lignin rich solid residual with more than 50 wt% water is typically the form in which the lignin is obtained. Drying is thus required and using wet lignin may instead ultimately be preferred. The HHV of the lignin is 18 MJ/kg.

Ethanol (solvent): 96 vol% is used as higher purity ethanol is significantly more costly to obtain (additional requirements for removal of water-ethanol azeotrope). Depending on the reaction parameters an increased concentration of water negatively impacts oil yield and quality, but the 4 vol% water present in the solvent is assumed to have a negligible influence. The effect on oil yield and oil quality by adding water to the solvent mixture was highlighted in the patent application[8] and is shown in Appendix C. In the parameter study 79 g ethanol (100 ml) was added to the reaction.

Outputs

Gas: Gas is formed during the reaction. This gas can be separated and used for heating the process. For experiments with high lignin loading the gas consisted of around 50 % noncombustible gasses (CO_2) (see section 4.1.1). An energy content equal to half the value of natural gas is therefore assumed. Due to limited gas data the gas composition is assumed constant with a mass directly proportional to the final gas pressure of the reaction vessel after cooling. This corresponds to a gas yield of 0.4 ($\pm 8\cdot10^{-2}$) g/bar.

Solids: Unconverted solid lignin and/or char comprise the solid fraction. The ash content of the lignin feedstock is preserved and also found in the solid fraction. The mass of solids was determined as the weight of the dried filter cake after reaction. Due to limited elemental compositional data on solids obtained the composition of the solid fraction is assumed constant. The composition is assumed identical to solids obtained from a reaction in which 10 g lignin was treated in 100 ml ethanol for 4 h at 400 °C. The composition with respect to C, H, O and ash is 59.6 wt%, 3.6 wt%, 8.5 wt% and 28.2 wt%.

Oil: The oil fraction is fully dissolved in the liquid fraction, and is easily isolated by evaporating the light fraction and water yielding the heavy oil fraction which was weighed. The oil is ash and sulfur free and the elemental composition was determined for all experiments conducted.

Water and other light reaction products: Hold little to no value. The water and other organic light products can be removed from the liquid fraction by distillation and thus ethanol can be recycled for the LDO process. It is unknown how organic solvent-solvent reaction products impact the process but water needs to be removed in order to avoid accumulation and negatively impact oil yield and quality.[8]

Ethanol: The solvent is isolated by evaporation from the oil. Some of the ethanol is lost due to reaction or handling. Solvent consumption was determined as described in section 3.1.4 as the best case scenario assuming mass balance closure when remaining mass is comprised of light products (unreacted ethanol, other light organics and water).

The value (price) of ethanol is easily obtained from market data, but for the remaining inputs and outputs market data is not readily obtainable. The solid lignin as well as the solid output (char) of the LDO process is priced according to the price per energy for thermal coal. Since the oil product substitutes a low sulfur diesel this product is priced according to the price per energy for an Ultra Low Sulfur Diesel (ULSD). The gas product is priced according to the price per energy for natural gas. Calorimetric measurements were not carried out but elemental compositional data on oil and solid products allow for the calculation of the higher heating value (HHV) as shown in equation (3.4) in section 3.2.2.

All products of reaction vary as a function of reaction parameters. Only compositional data for the oil fraction exists for all of the experiments conducted in the parameter study. The price of gas and solid product are therefore assumed constant as a function of reaction parameters and the respective values depend only on the yields. The price of oil changes as a function of reaction parameters and the value therefore depends on both yield and HHV.

Table 6.1 shows the value of all inputs and outputs of the process. It is seen that the oil product (HHV of 43 MJ/kg) has a price comparable to that of the solvent ethanol. Incentives to use biomass derived fuels may however further positively increase the oil value. It is equally seen that liquefaction can increases the value of the lignin by up to a factor ten and none of the other products of the solvolysis provide a significant value increase relative to the lignin feed.

Table 6.1 Price and higher heating value (HHV) of inputs and outputs of the LDO process. HHV is fixed for all inputs/outputs except for the oil product. All prices are also fixed except for the oil price which scales with the HHV of the oil obtained at specific reaction conditions. [a]HHV of typical low sulfur diesel (ULSD). [b]Price of Australian thermal coal scaled with respect to HHV of lignin relative to typical HHV for thermal coal (28 MJ/kg) (January 2015)[212]. [c]Bulk price of 96 % ethanol (February 2015)[213]. [d]Price of natural gas scaled with respect to HHV of gas product relative to typical HHV for natural gas (46 MJ/kg) (February 2015)[212]. [e]Price of ULSD (February 2015)[212]. [f]Price of Australian thermal coal scaled with respect to HHV of solid product relative to typical HHV for thermal coal (28 MJ/kg) (January 2015)[212].

Input/output	HHV (MJ/kg)	Price ($/t)
Lignin	18	43.7[b]
Ethanol	-	483[c]
Gas	23	71.1[d]
Oil	43[a]	508[e]
Solids (char)	24	57.4[f]

6.2 Results and Discussion

Figure 6.2 shows the value gain per lignin and the total annual value gain on a lignin processing scale equivalent to 60,000 ton from MEC as a function of different process parameters used in the parameter study. The parameters changed are reaction temperature, reaction time and amount of lignin added shown in Figure 6.2a, Figure 6.2b and Figure 6.2c respectively. Figure 6.2d shows the value gain from the experimental series in which the reaction temperature was kept at 350 °C with high lignin loading of 1:2 (w:w) lignin to ethanol ratio and reaction times of 0 to 2 h. These reaction conditions are more favorable as was highlighted in Chapter 4 where a reduced reaction time, increased lignin loading and 350 °C relative to 400 °C provided the best tradeoff with respect to obtaining high oil yield and quality and at the same time limiting solvent consumption/loss. Price data was acquired early 2015 and changes in commodity prices and in particular the oil price may change the overall profitability but the trends observed will remain.

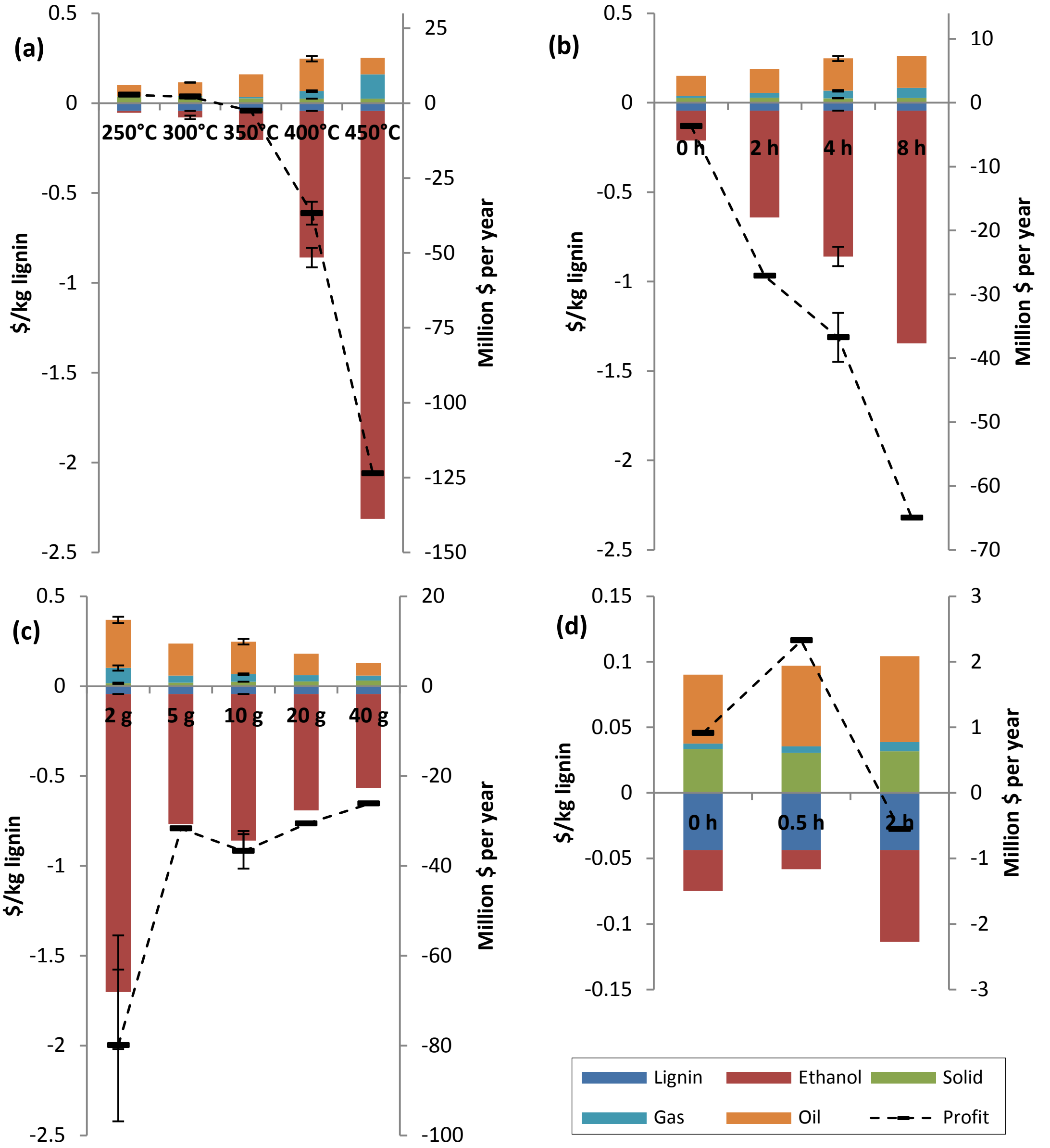


Figure 6.2 Value gain from inputs and outputs and total annual profit for processing of 60,000 ton lignin are shown for the LDO process conducted at different operating conditions as a function of reaction temperature (a), reaction time (b) and lignin loading (c). Data from reaction conditions more favorable with respect to the oil yield and solvent consumption tradeoff is shown as a function of reaction time in (d). Reaction conditions: (a) 10 g lignin treated in 100 ml ethanol for 4 h at different reaction temperatures; (b) 10 g lignin treated in 100 ml at 400 °C for different reaction times; (c) different amounts of lignin added to 100 ml ethanol treated for 4 h at 400 °C; (d) 40 g lignin treated in 100 ml ethanol at 350 °C for different reaction times. Error bars represent standard error of the mean.

The biggest cost driver is ethanol consumption for all experiments conducted and for experiments at 400 °C and lower the biggest revenue driver is the oil yield. For all experiments the value of the solid fraction per lignin added is comparable to the value of the lignin feed. As the reaction temperature is increased up to 400 °C in Figure 6.2a the added loss from ethanol consumption increases more significantly than the added value increase arising from an increased and more deoxygenated oil yield. At 450 °C the value gained from the gas produced exceeds the value of the oil yield, but this gas is in fact mainly the result of solvent to gas reactions as described in Chapter 4 making it highly disadvantageous. The annual profit from processing lignin equivalent to the MEC scale shows a small profit of 2.7 million $ p.a. at 250 °C but a rapidly declining profit as the reaction temperature is increased. A reaction temperature of 250 °C does however not indicate an optimum for operation as the oil is less depolymerized (see section 4.1.2) and has a substantially higher viscosity making the product less oil like which the calculations herein do not take into account.

The profitability decreases as the reaction time increases for a fixed reaction temperature of 400 °C (see Figure 6.2b). This corresponds to the 0^{th} order solvent consumption reaction that exceeds the rate at which oil yield increases while deoxygenation is unchanged as a function of reaction time (see section 4.1.1.2). These results again emphasize that a reaction time as short as possible is necessary to increase profitability and provide commercial viability.

In Figure 6.2c where the value gain is represented as a function of lignin loading for a fixed reaction temperature of 400°C it is clear that the economics improve on a per lignin basis as lignin loading is increased. The value gain from the oil product per lignin added decreases as the lignin loading is increased showing that the increased value of the oil from increased degree of deoxygenation is not enough to offset the reduced oil yield equally arising. Figure 6.3 shows the oil yield per solvent consumption as a function of lignin loading. When the amount of lignin added is increased from 5 to 40 g the amount of oil produced per solvent consumed drops from 0.26 to 0.15 showing no advantage of increasing lignin loading in order to directly lower solvent consumption. Therefore the overall improvement of profitability is mainly due to a reduced solvent loss per lignin added as less solvent is required overall.

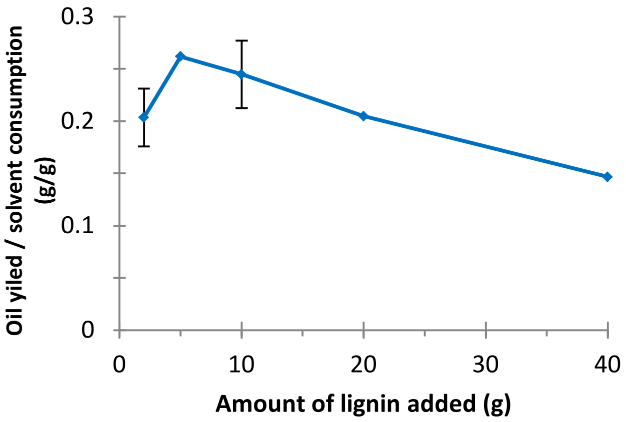


Figure 6.3 Oil yield per solvent consumption (g/g) shown as a function of lignin loading for experiments with lignin in 100 ml ethanol treated for 4 h at 400°C. Error bars represent standard error of the mean.

In the case where the reaction temperature is 350 °C and lignin loading is high (see Figure 6.2d) the profitability improves substantially over the other scenarios represented. An annual profit of 2.3 million $ is obtained for a reaction time of 30 min for lignin processing on MEC scale. The value of the gas phase is insignificant and due to the reduced oil yield per lignin added the value of the solid product contributes relatively more to the increased profit. Equally the lignin feed contributes relatively more to decreased profitability. Increased uncertainties are however attributed to the solid and oil yields at these conditions of high lignin to solvent ratio as an increased amount of char fraction was difficult to isolate from the reaction vessel after experiments (see Chapter 4). The solvent consumption as defined herein represents a best case scenario where mass balance closure is assumed but a mass balance closure better than 90 % was not possible in any of the experiments conducted (see section 3.1.4). None of the experiments conducted show a profit if the actual solvent consumption as defined for Chapter 4 and 5 is used for the calculation of the profitability. This further adds to the uncertainty of the profitability. It is however clear that short reaction times and in particular a reaction time of 30 minutes at 350 °C and high lignin to solvent ratio of 1:2 (w:w) substantially improves the profitability of the LDO process and may on a large scale be profitable.

Different processing parameters may impose different advantages and disadvantages on the process economy of a production facility on an industrial scale that equally need to be taken into account. Reaction temperature and reaction time serve as indicators of the severity of the process. Higher process severity implies higher equipment costs as the autogenous pressure increases with higher temperature. Also, both higher temperature and longer reaction time impose higher energy demands. The reaction time and relative amount of lignin to solvent ratio are equally important measures in order to assess the viability of lignin direct liquefaction on an industrial scale. Long reaction times and low ratio of lignin to solvent impose increased processing cost as a larger facility is required to ensure a production of oil on a large scale. However, if the reaction time becomes too short in the order of only a few minutes it may be more difficult to ensure proper heat recovery in heat exchangers. A high lignin to solvent ratio may be advantageous from a processing point of view; however, it may also be disadvantageous if a stable lignin-solvent slurry cannot be formed hence imposing difficulties in processing the lignin-solvent slurry continuously due to pumping difficulties which are effects that cannot be highlighted from a study in batch autoclaves only. An exact measure for profitability of lignin solvolysis in ethanol is therefore impossible based on the data obtained in this study alone. In the following an example is provided with realistic estimates for inputs and outputs for a large scale annual production of bio-oil from lignin. This example and the assumptions made are similar to data that was given to Maersk Maritime Technology for further economic evaluation of the LDO process and the data was equally supplied as justification for filing of an additional patent[9] covering continuous processing of the LDO process.

6.3 Example on Large Scale LDO Production

In this example the annual profit is calculated disregarding any cost other than material costs. The example is based on processing of 60,000 ton lignin p.a. (lignin rich solid residual) equivalent to 100 % utilization of the annual yield of solid waste from

MEC's 2nd generation bioethanol production. Material prices given in Table 6.1 and real input-output data was scaled up from an experiment in lab scale in which 40 g lignin was treated for 30 min in 100 ml of ethanol at 350 °C (see Figure 6.2d) which provided one of the best tradeoffs between oil yield, degree of deoxygenation and solvent consumption. The degree of solvent consumption and yield of oil are the biggest cost and revenue driver respectively hence these values are of great significance and special assumptions regarding these have been made in order to assess the potential for a large scale production of lignin oil.

Ethanol consumption:

The ethanol consumption is assumed to achieve a theoretical value that is lower than the values obtained in lab scale experiments. By assuming that solvent loss through solvent to gas and solvent-solvent reactions can be eliminated completely some degree of incorporation into the oil product or loss of solvent due to reactions facilitating lignin depolymerization/inhibition of repolymerization is still expected. One molecule of ethanol is assumed to be consumed by reaction with one molecule of lignin monomer unit. This corresponds to roughly a ratio of 1:5 (w:w) ethanol to lignin monomer. The ethanol is assumed to be incorporated into the depolymerized lignin oil product. The resulting ratio between ethanol consumption and oil becomes 1:6 (w:w) which forms the basis for a theoretical solvent consumption in this example.

Oil yield:

A theoretical oil yield of 40 $\text{wt\%}_{\text{d.a.f.}}$ is assumed for this example. In the lab scale experiment with similar operating conditions to the ones in this example only 18 $\text{wt\%}_{\text{d.a.f.}}$ oil yield was obtained. Larger amounts of char and possibly oil product were difficult to completely remove and isolate from the reaction vessel after reaction meaning the actual yield was most likely higher. Furthermore a continuous industrial scale processing may allow for faster heat up in particular and significantly different conditions of the lignin ethanol slurry that could potentially enhance oil yield. Different liquefaction techniques described in the literature including both direct liquefaction[4] and pyrolysis/gasification techniques[79,214] have demonstrated that 40 wt% liquid organic yields are feasible justifying the assumptions herein.

Table 6.2 Inputs, outputs and respective value gains as well as total profit for annual processing of 60 kt lignin rich solid residual based on an example with operating conditions similar to previously conducted experiment on lab scale: reaction temperature of 350 °C and 30 min reaction time. The 7,300 ton required on the output side to close the mass balance consists of water and other light organic liquid reaction products. [a]Based on prices given in Table 6.1 and the HHV scaled price for oil. [b]Value gain is the price of the material multiplied with the difference between output and input. [c]The lignin feed contains 13 wt% ash and 2 wt% water and thus the dry ash free (d.a.f.) fraction is 85 wt% of the lignin input. [d]Ethanol input is based on 1:2 (w:w) lignin to solvent ratio and output is based on a 1:6 (w:w) solvent to oil ratio. [e]Actual gas yield obtained in lab experiments at the reaction conditions and the HHV is assumed half the value of natural gas as given in Table 6.1. [f]Assuming 40 wt%$_{\text{d.a.f.}}$ oil yield and the HHV is the actual calculated value based on elemental composition of oil obtained in lab scale experiments at similar reaction conditions. [g]Actual solid yield obtained in lab experiments at the reaction conditions and HHV and price is given in Table 6.1. Ash from the lignin feedstock is fully retained in the solid fraction.

Material	Input (t)	Output (t)	HHV (MJ/kg)	Price ($/t)[a]	Value gain p.a. ($)[b]
Lignin[c]	60,000	-	18	43.7	-2,622,000
Ethanol[d]	120,000	116,600	-	483	-1,642,200
Gas[e]	-	4,200	23	71.1	298,620
Oil[f]	-	20,400	34	402	8,200,800
Solids (char)[g]	-	31,500	24	57.4	1,808,100
TOTAL					6,043,320

Table 6.2 shows the value of inputs and outputs for annual processing of 60,000 ton lignin. The table shows that 120,000 ton ethanol is required; however, the actual requirement for ethanol to be on site is much lower as ethanol is recycled. The annual value gain as defined herein equals 6 million $. The value of the oil product is the greatest contributor to revenue and with the assumptions used in this example the value of the lignin feed becomes the biggest cost driver. The total annual profit is more than double the initial value of the feedstock lignin. The transformation from lignin to oil corresponds to a value increase by three times showing that even with 40 wt% oil yield the process may be profitable.

In Figure 6.4 energy inputs and outputs of the process example are shown based on 1 ton of dry lignin rich solid waste. The energy requirements for heating the process and the solvent loss/consumption are not shown due to difficulties in estimating these values.

The transformation from a solid fuel (lignin feedstock) to a liquid fuel provides a value increase of around five times going from 2.4 $/GJ to 12 $/GJ. The biomass provides a gross energy of combustion of 18 GJ if used as a low value solid fuel. It is seen that the total gross energy of combustion for the gas, solid and oil phase combined exceed the energy of combustion of the feedstock by 8.6 GJ. This is most likely due to the high estimate of 40 wt%$_{\text{d.a.f.}}$ oil yield as the actual oil yield obtained experimentally at similar reaction conditions (see Figure 6.2d) was only 18 wt%$_{\text{d.a.f.}}$. This lower yield results in a reduction from 12 GJ to 5.2 GJ for the gross energy of oil product combustion. At these conditions 29 % of the energy content of the lignin feedstock is retained in the oil product. The gas phase contributes only to very little energy and the solid product of the reaction may therefore be a preferred candidate for providing energy for the process in terms of combustion; however, the energy requirement for bringing 2 ton of ethanol to the operating temperature of 350 °C requires only 1.7 GJ (calculated using standard enthalpy of evaporation and assuming constant average heat capacity of supercritical ethanol)[215]. Assuming an energy recovery from heat exchangers of at least 50 % and a relative negligible contribution to heating requirements from the reaction and heating of the biomass the gas produced may be sufficient for heating of the process.

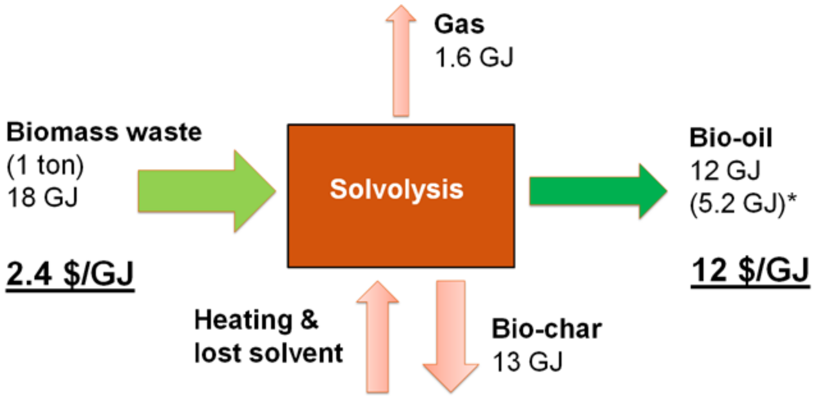


Figure 6.4 Gross energy inputs and outputs of the LDO process as given in the example for processing of lignin in 1:2 (w:w) ratio of lignin to ethanol (96 vol%) at 350 °C for 30 min. Price per energy for feedstock and oil product is based on early 2015 economic data as given in Table 6.1. *Gross energy of combustion for the oil product where the actual oil yield was 18 wt%$_{\text{d.a.f.}}$ as obtained in lab scale experiments.

6.4 Summary of Economic Assessment

The results of the parameter study as given in Chapter 4 were evaluated economically as a value gain obtained as the difference between outputs and inputs disregarding other production costs and fixed costs. The total annual profit using this method was calculated based on processing 60,000 ton lignin rich solid residual which is equivalent to the annual yield of solid waste from Maabjerg Energy Center (MEC) which is a 2$^{\text{nd}}$ generation bioethanol plant that might be built in the near future.

The biggest cost driver of the LDO process is by far the ethanol consumption and the biggest revenue driver is the oil product for experiments conducted at 400 °C and lower. As low operating temperature as possible is preferred due to the increased rate at which solvent is lost/consumed as the temperature is increased. It is equally preferred to keep the reaction time as short as possible as the rate of solvent consumption exceeds the rate of oil formation and a short reaction time is also more favorable from a cost of processing perspective. Increased lignin loading results in increased profitability mainly due to a reduced requirement for ethanol solvent on a per lignin added basis. Lab scale experiments yielded an optimum tradeoff between oil yield, quality and solvent consumption when using a high lignin loading at 350 °C for short reaction times. At these conditions the profitability was substantially improved yielding an annual profit of up to 2.3 million $. Increased uncertainties are however attributed to the solid and oil yields at these reaction conditions and the solvent consumption is determined based on an assumption of mass balance closure.

An example based on large scale processing of 60,000 ton lignin p.a. with assumptions regarding improved oil yield and lowered solvent consumption showed that a net annual profit of around 6 million $ may be possible. This corresponds to a value increase of three times from the original lignin feedstock. The solvent consumption was assumed substantially reduced in relation to what was achieved in lab scale experiments.

An energy balance on the process showed that the heat of combustion for the gas products may be sufficient for heating of the LDO process and at least 29 % of the gross energy content of the lignin feedstock is retained in the oil product after reaction.

The results of this simple economic study indicates that going from batch mode operation as conducted in the parameter study to scalable continuous processing may yield a process that is profitable if solvent consumption is reduced.

CHAPTER 7

Conclusions and Outlook

Direct liquefaction of lignin in alcohols is a promising technology as alcohols are efficient solvents/reactants as they both facilitate aryl ether cleavage but also stabilize depolymerized radical species. The process of direct liquefaction is thermally more efficient than indirect liquefaction such as pyrolysis and can provide improved oil yield and quality. The heterogeneous structure of lignin is advantageously utilized to target production of a liquid fuel rather than fine chemical production and a simple process is therefore needed.

A process in which lignin-diesel oil (LDO) is obtained by solvolysis in ethanol was designed. The LDO process is easily integrated with existing 2nd generation biorefineries as both lignin and ethanol are product streams. The lignin rich solid residual is obtained as a waste product from biorefineries and may advantageously be sulfur free.

Experiments conducted in a batch autoclave have demonstrated that supercritical ethanol solvolysis of a biorefinery lignin can yield a substantially diesel soluble and sulfur free bio-oil without the need for exhaustive deoxygenation. The LDO process does not require addition of a catalyst or reducing agent such as hydrogen. The oil product is shelf stable and acid free with no detectable carbonyl functionalities which makes it superior to conventional pyrolysis oil.

A parameter study in which lignin was liquefied in 100 ml ethanol revealed the effects of different reaction temperatures, reaction times and degree of lignin loading. The highest oil yield of 50 $\text{wt\%}_{\text{d.a.f.}}$ was obtained for solvolysis of 10 g lignin for 8 h at 400 °C but 47 wt% of the solvent was also disadvantageously consumed. A lower reaction temperature and short reaction time (<1 h) yielded an improved tradeoff between oil yield and solvent consumption.

In this study the lignin to solvent ratios tested were higher than previously reported values. Increased lignin loading showed substantial improvement of oil quality. In an experiment with 2:1 (w:w) ethanol to lignin ratio the resulting oil product had a very low molar O/C ratio of 0.09 and an increasingly narrowed molecular size distribution dominated by species <300 g/mol (lignin monomers and dimers). Decarboxylation is the main contributor to the lignin deoxygenation as the majority of CO_2 formed comes from the lignin whereas CO is mainly the result of alcohol solvent decomposition.

A study was conducted on the effects of using different primary alcohols for the LDO. The study revealed that methanol, ethanol, 1-propanol and 1-butanol performed similar with respect to oil product composition; however, methanol was an outlier with respect to bio-oil yield (~0.2 g/g lignin) which was only half the value of 0.4 g/g lignin obtained when conducting the lignin solvolysis in the three other solvents at 400 °C. A comparison of the products of the reaction in the four different alcohols allowed for identification of reaction products directly stemming from the alcohols. Three main routes in which solvent consumption occurs were identified: Direct decomposition to gas through decarbonylation, formation of light condensation products and incorporation of the alcohol into the bio-oil through covalent bonding. The latter was in the form of ethers and esters and possibly also C-C bonding.

It is inherently difficult to propose a reaction mechanism for depolymerization when using a real lignin feedstock. A question that arises is whether lignin bonds are first thermally broken and then reacts with ethanol or whether the alcohol is directly facilitating cleavage. Both reaction mechanisms have been proposed in the literature and most likely a combination occurs (see section 2.3.3.1). Many model compound studies exist on lignin depolymerization and catalytic hydrodeoxygenation; however, neither of these studies has demonstrated commercial viability. The study herein provides a simplified approach which highlights that the key challenges of lignin solvolysis are lignin liquefaction yield versus solvent consumption and the more traditional approach involving maximization of depolymerization while minimizing repolymerization is less important. This means that a future commercially relevant process for producing an LDO must utilize the more readily convertible part of the lignin feedstock as extensive processing requirements may result in disadvantageous added costs. This implies that there is a low hanging fruit of the lignin suitable for solvolysis by ethanol and the remainder is not suited for liquefaction in solvents such as alcohols as solvent consumption/loss is not a tolerable tradeoff.

The LDO process was economically assessed by evaluating the value gain obtained as the difference between outputs and inputs for the full parametric study. The biggest cost driver of the LDO process is by far the ethanol consumption and the biggest revenue driver is the oil product for experiments conducted at 400 °C and lower. Optimum profitability was observed with high lignin loading, short reaction time and lower reaction temperature such as 350 °C instead of 400 °C. Increased uncertainties are however attributed to the solid and oil yields at these reaction conditions and the solvent consumption is determined based on an assumption of mass balance closure. An example was designed in which the total annual profit was calculated based on processing 60,000 ton lignin rich solid residual from a real 2nd generation biorefinery. The example showed that a net annual profit of around 6 million $ may be possible which corresponds to a value increase of three times from the original lignin feedstock.

An energy balance on the process showed that the heat of combustion for the gas products may be sufficient for heating of the LDO process and at least 29 % of the gross energy content of the lignin feedstock is retained in the oil product after reaction. The solid product of the LDO process has reduced oxygen content relative to the lignin feed making it a candidate for use as a biochar.

7.1 Future Work

The results of this study showed some limitations of the experimental setup. The heat-up was slow (5-10 °C/min) resulting in unnecessarily extended reaction time, the mass balance closure was less than 90 % which makes accurate determination of solvent consumption impossible and relatively small amounts of oil (<10 g) were produced which makes further product oil valorization or actual engine performance tests difficult. A higher oxygen content of a diesel fuel may typically increase NO_x emissions but also lower particle emissions.[216] The LDO may benefit combustion as the soot-NO_x tradeoff has been reported to be improved in the presence of aromatic and cyclic oxygenates in diesel fuel.[217–221] This highlights an implementation in which the LDO may also benefit as a diesel additive.

The batch autoclave used does not represent a scalable setup and in fact a continuous experimental setup is preferable for that reason. Testing of continuous mode operation for the LDO process can be conducted in a continuously stirred tank reactor (CSTR) using a design as shown in section 2.2.1 for a hydrothermal liquefaction (HTL) process where rapid heat up is achieved with a large recycled solvent stream. The issue of excessive solvent consumption may however still be present if an alcohol stream is recycled. For that reason a flow reactor designed to adequately allow for pumping of a lignin-ethanol slurry without settling of solids is a preferred option.

The design of flow reactor experiments for the LDO process will overcome the challenges of the current batch reactor setup. A faster heat-up and shorter reaction times directly dependent on the flow rate can be achieved and mass balance closure will be improved if the amount of solvent volume processed greatly exceeds the total flow reactor volume. Experiments designed for a continuous flow reactor also allow for investigation of pressure changes by using a backpressure regulator.

A scalable operation of the LDO process by continuous processing will allow for greater quantities of oil to be isolated and thus further routes for valorization of the oil product can be explored. The LDO is superior to pyrolysis oils due to particularly shelf stability and lack of aldehydes and carboxylic acid functionalities. This may allow for upgrading over a catalyst for hydrodeoxygenation (HDO) without extensive charring that deactivates the catalyst compared to upgrading of pyrolysis oils.

The use of alternative feedstocks for the LDO process should also be explored. Other lignin types than enzymatic hydrolysis lignin and low sulfur feedstocks, in particular whole nonedible biomass such as woods and grasses, are relevant in this context.

An alternative strategy for the future of biorefineries involves a lignin first concept where lignin is isolated under less severe conditions (e.g. organosolv extraction) prior to valorization of cellulose and hemicellulose. Such approach may allow for a higher quality lignin feedstock better suited for chemical valorization than a typical hydrolysis lignin obtained as a solid residual waste product after several processing steps.

The future of lignin valorization requires establishing a commercially viable and scalable process which satisfies a substantial market size. Such valorization is advantageously very simple such as the LDO process and future valorization of product streams or alternative valorization strategies may then yield improved profit streams. This is similar to fossil crude oil valorization which has grown over decades from targeting bulk fuel markets to generate increased profit from higher value fossil-derived chemicals. Biorefineries can achieve profitability through subsidization and increased taxation of fossil resources but if a process independently on this can demonstrate profitability in a market competing against fossil resources (bio-crude versus fossil crude) the end of fossil-based fuels may be near. A small step in this direction might be lignin valorization by the LDO process.

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Appendices

Supplementary information for the different chapters is supplied in appendices in the following.

Appendix A - Supplementary information for Chapter 4

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Appendix A - Supplementary Information for Chapter 4

Additional Product Yield Data

Additional experimental series where lignin was solvolytically treated in ethanol at varying temperatures, residence times and with different degrees of lignin loading were carried out using the methods described in the main text. Fig. A. 1 shows oil yield, solid yield, gas yield and solvent consumption which were quantified using the methods described in the main text. Fig. A. 2 shows linear fits to oil yield and solvent consumption as a function of reaction time for an experiment in which 40 g lignin was treated in ethanol at 350 °C. Fig. A. 3 shows the gas yields from treating 40 g lignin in ethanol at 350 °C at different reaction times using methods described in the main text.

The gas yield increases proportionally as a function of reaction time at 350 °C and high lignin loading (40 g) which was equally observed for the experiments described as a function of reaction time in the main text (400 °C reaction temperature and 10 g lignin loading). The yield of oil plus char as a function of reaction time remained constant at 350 °C and high lignin loading whereas it increased for the experiments described in the main text; however, additional gas formed over time must still be the result of solvent decomposition which was highlighted in the main text. Solvent consumption at 350 °C and high lignin loading equally increases linearly as a function of reaction time as described in the main text at 400 °C and lower lignin loading.

For a reaction temperature of 350 °C and high lignin loading the relative increase in ethane and methane yield over time is larger than the formation of CO and CO_2 as was also highlighted in the main text for a reaction temperature of 400 °C and lower lignin loading.

For solvolysis at reaction temperatures between 250 °C and 450 °C with only 2 g lignin loading the oil yields are substantially higher and solid char and gas yields lower compared to a higher lignin loading of 10 g as described in the main text.

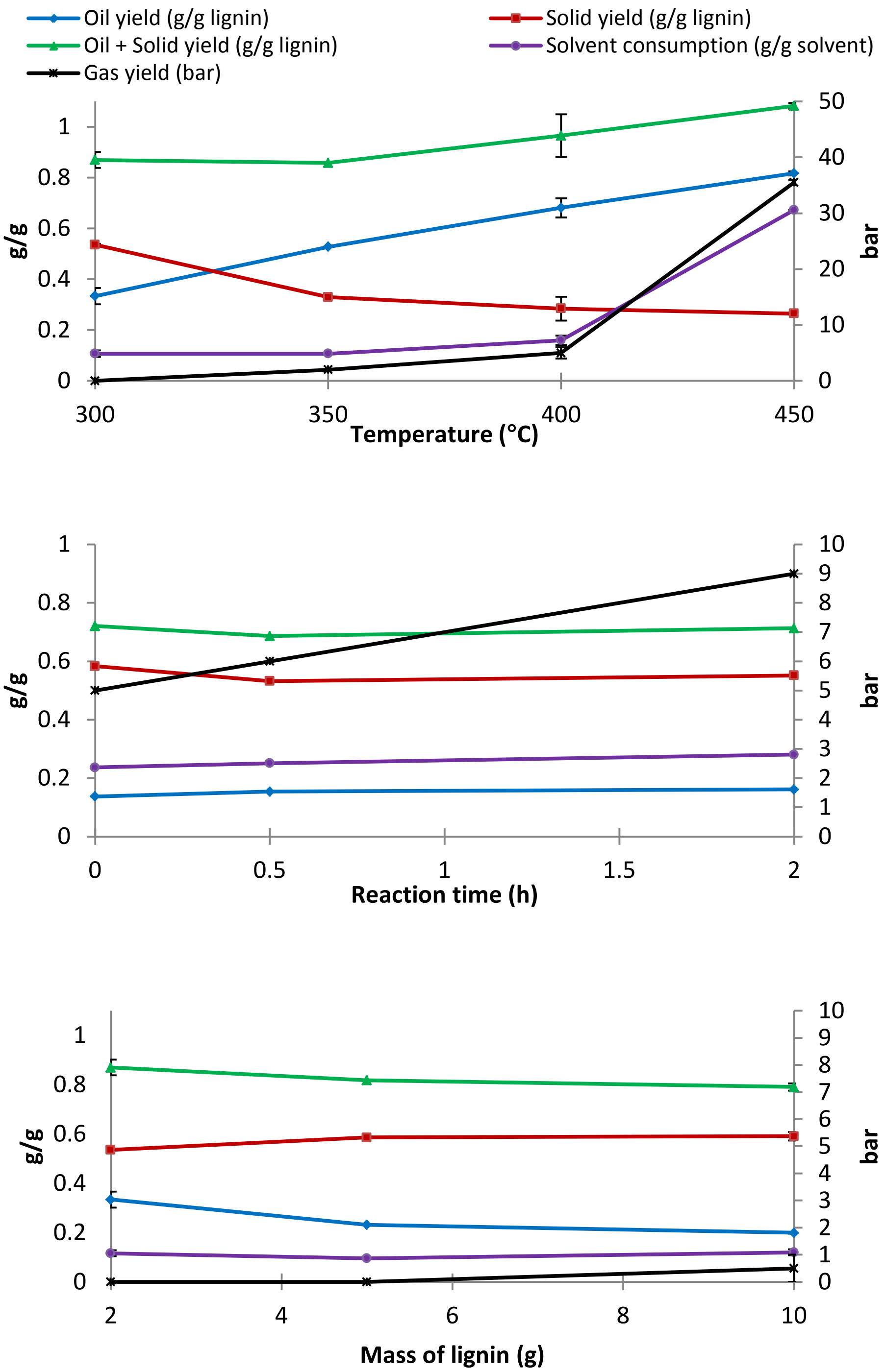


Fig. A. 1 The oil yield, residual solid char yield and sum of oil and residual char yield are represented together with gas yield and amount of solvent consumed/lost as a function of reaction temperature (top), reaction time (middle) and amount of lignin added (bottom). Oil yield, residual solid yield and sum of oil and residual solid yield are represented per lignin added (w:w) and amount of solvent consumption/loss is represented per solvent initially added (w:w). Conditions: 2 g lignin and 4 h reaction time (top); 40 g lignin and 350 °C reaction temperature (middle); 4 h reaction time and 300 °C reaction temperature (bottom). Error bars represent standard error of the mean.

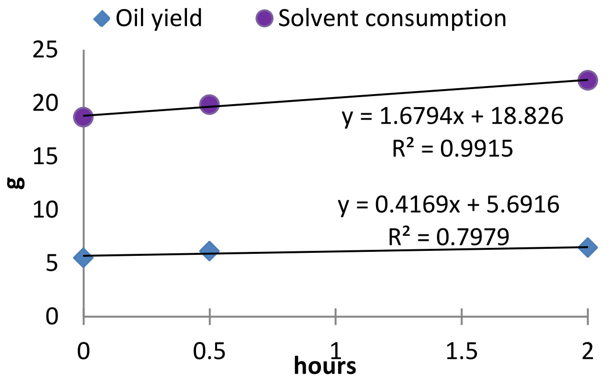


Fig. A. 2 Linear fit to oil yield and solvent consumption as a function of time obtained for solvolysis of 40 g lignin in 100 ml ethanol at 350 °C.

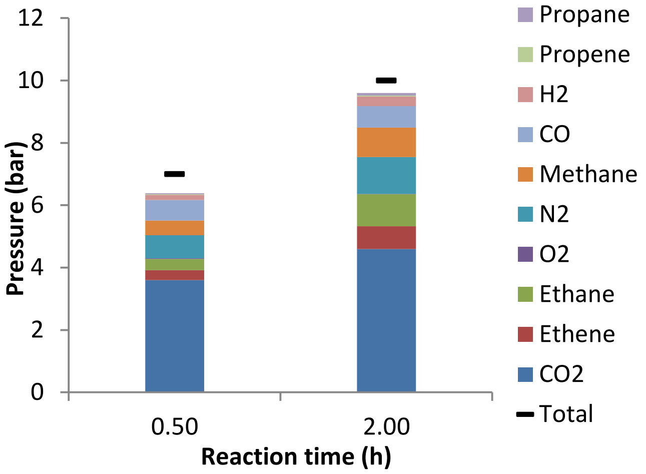


Fig. A. 3 Final pressure at room temperature of different gasses formed as a function of reaction time for the solvolysis of 40 g lignin in 100 ml ethanol at 350 °C.

Water Gas Shift Reaction

At the reaction conditions herein with long residence time of 4 h and a reaction temperature of 400 °C the water-gas shift reaction could have an influence on the CO_2 yield as high amounts of water is present in the reaction vessel (reactants and products of the water-gas shift reaction are shown in Fig. A. 4). The equilibrium constant for the water gas shift reaction (shown in the equation below) is calculated for the given reaction conditions and Gibbs' free energy of formation for the reactants and products.[215]

(A.1) $H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad K_{eq}(T = 400°C) = 12.0$

The experimental equilibrium ratio at reaction conditions are shown in Table A. 1. Partial pressures of CO_2, H_2 and H_2O are obtained from quantified masses and real isothermal properties at 400 °C retrieved from NIST. Ideal gas behavior is assumed for CO.

The experimental equilibrium ratio in this study yields values that are too small by a factor of $\sim 10^2$ indicating that the water-gas shift reaction is far from being at equilibrium and therefore it has a negligible influence on the high CO_2 yield.

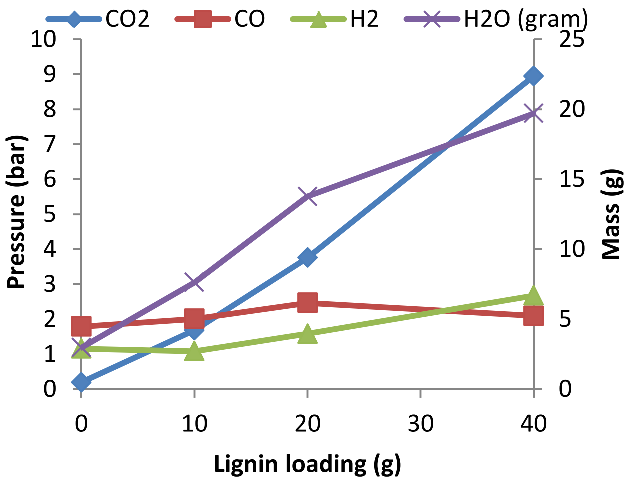


Fig. A. 4 Final amount of water and pressure at room temperature of different gasses formed as a function of degree of lignin loading for the lignin solvolysis in 100 ml ethanol at 400 °C for 4 h.

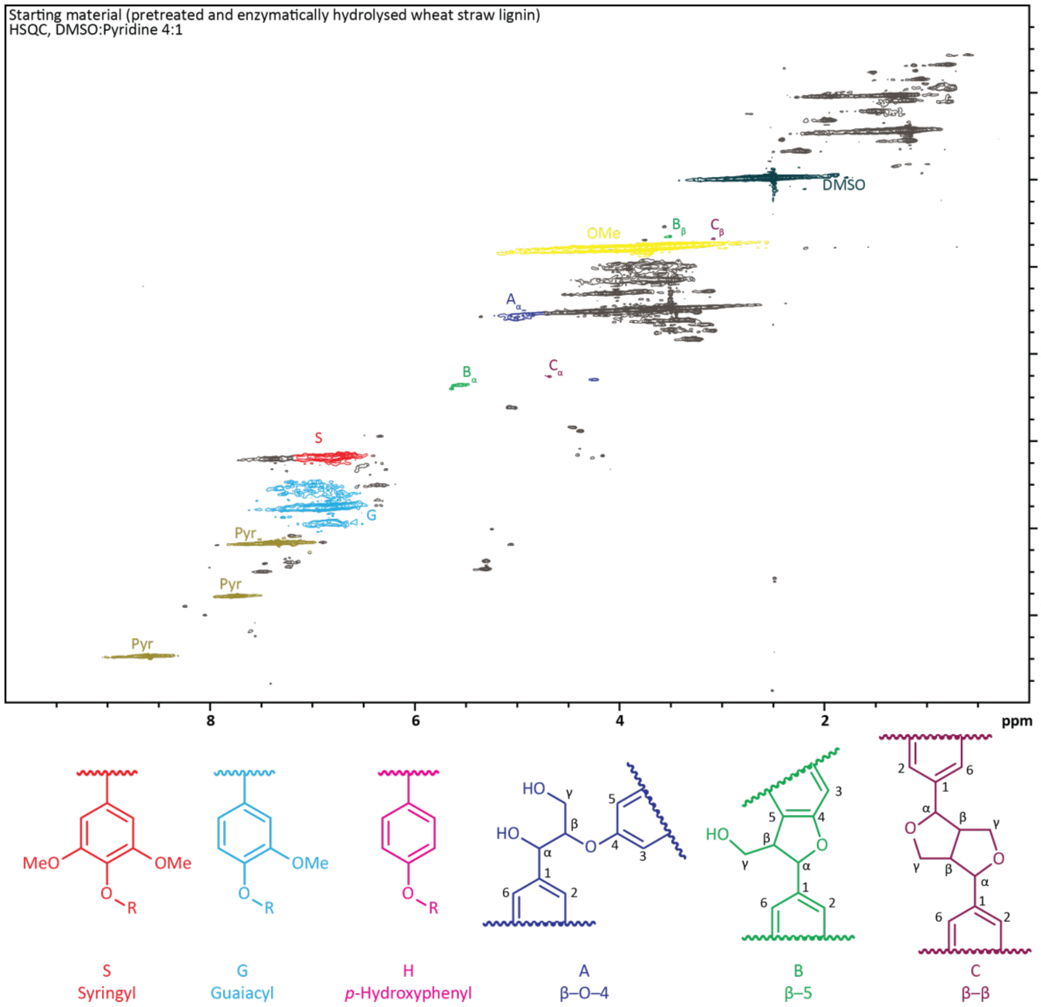
Table A. 1 Experimental equilibrium ratios for the water-gas shift reaction at 400 °C. The theoretical equilibrium constant has a value of 12.0[215]

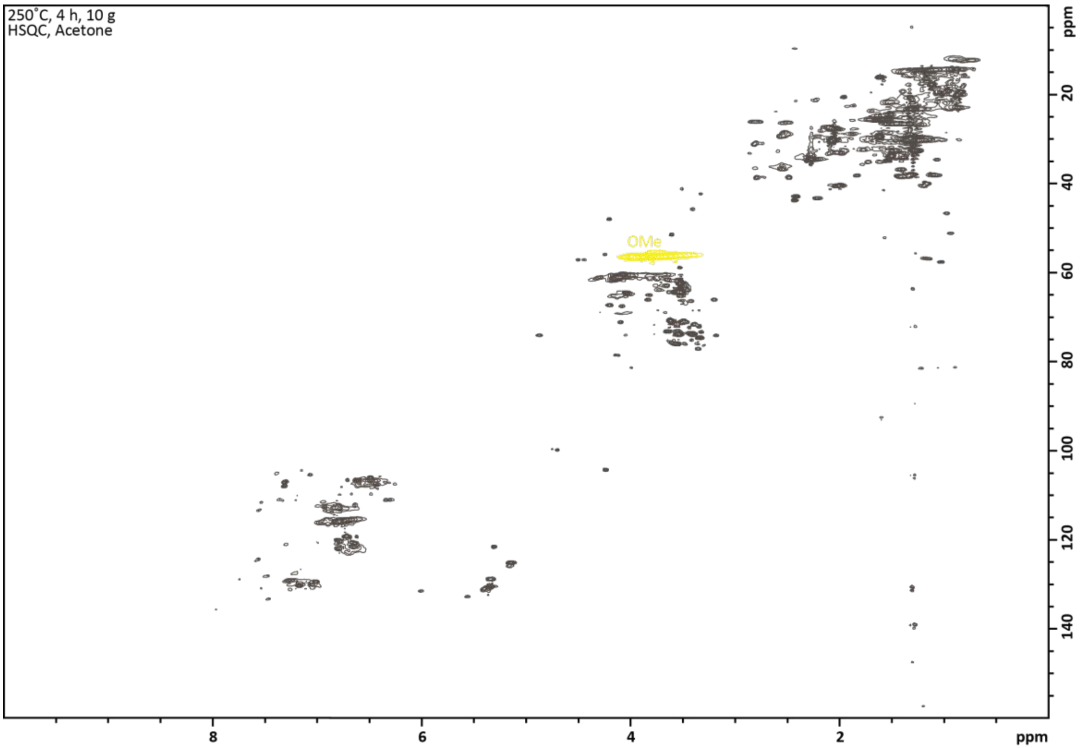
Lignin loading (g)	$K_{experimental} = (P_{CO2}P_{H2})/(P_{CO}P_{H2O})$
0	0.015
10	0.038
20	0.056
40	0.19

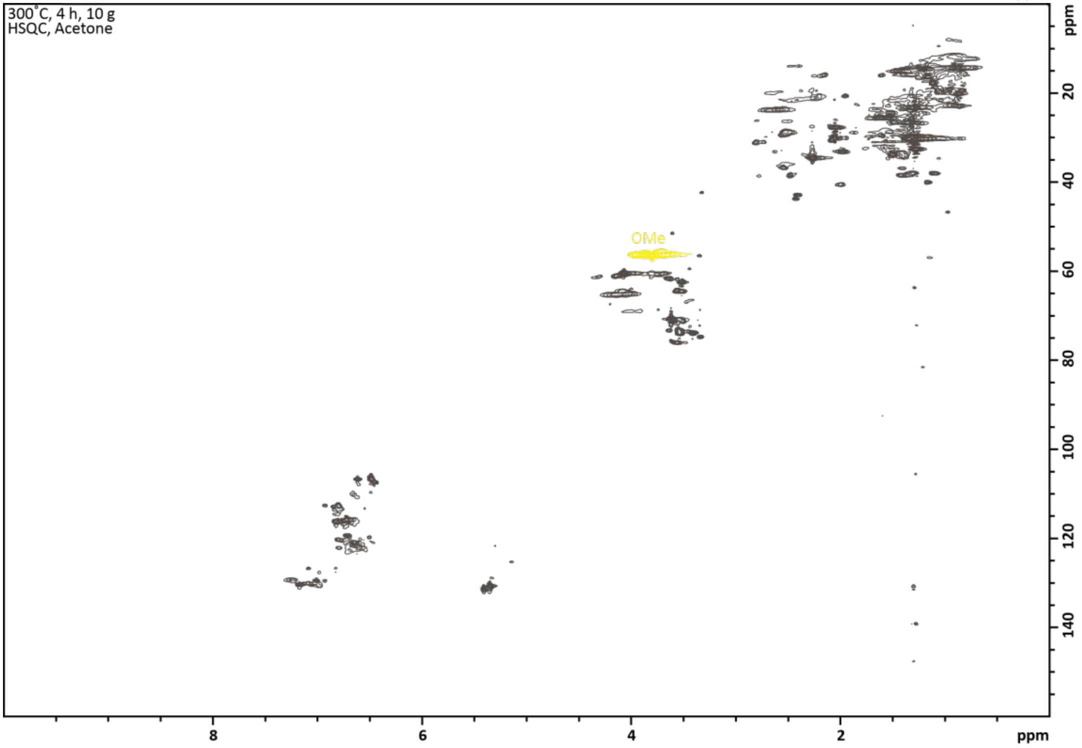
^{1}H-^{13}C-HSQC NMR Data

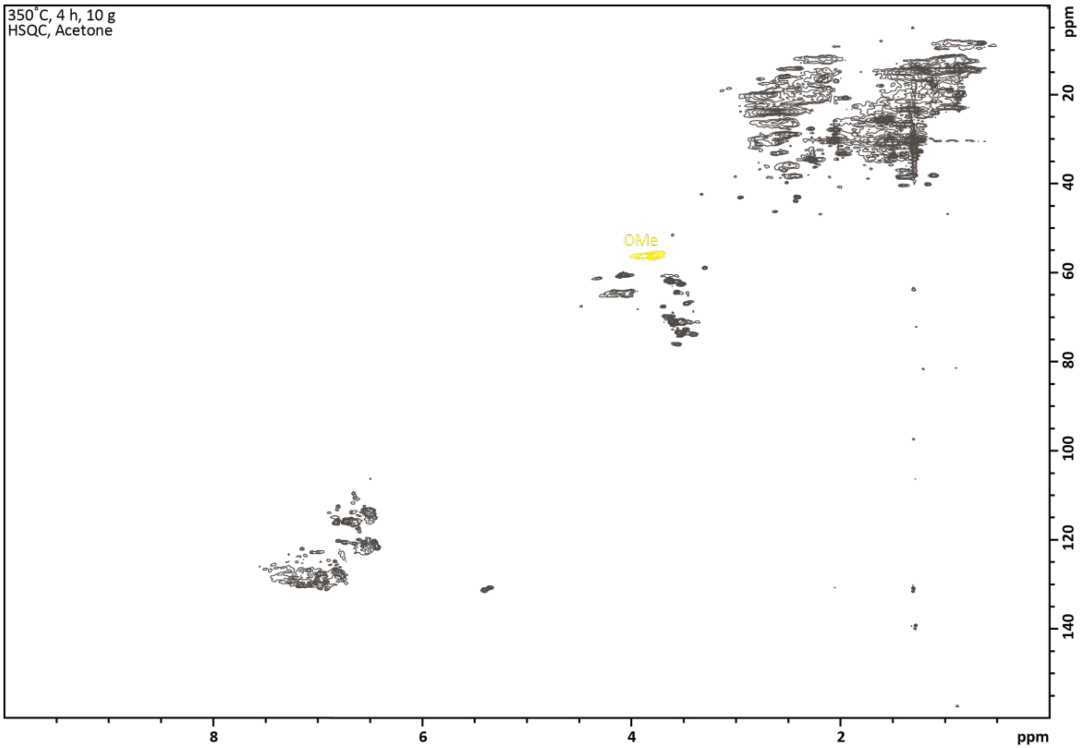
^{1}H-^{13}C-HSQC NMR was conducted as described in the main text. Fig. A. 5 shows the spectra for the oils obtained by treating 10 g lignin in 100 ml ethanol at different reaction temperatures and an additional spectrum shows the unreacted lignin rich feedstock. As can be seen, the NMR spectra of the starting material are typical for enzymatically hydrolysed wheat straw lignin rich residue.[29,31] Original lignin unit linkages are broken after solvolysis at all temperatures.

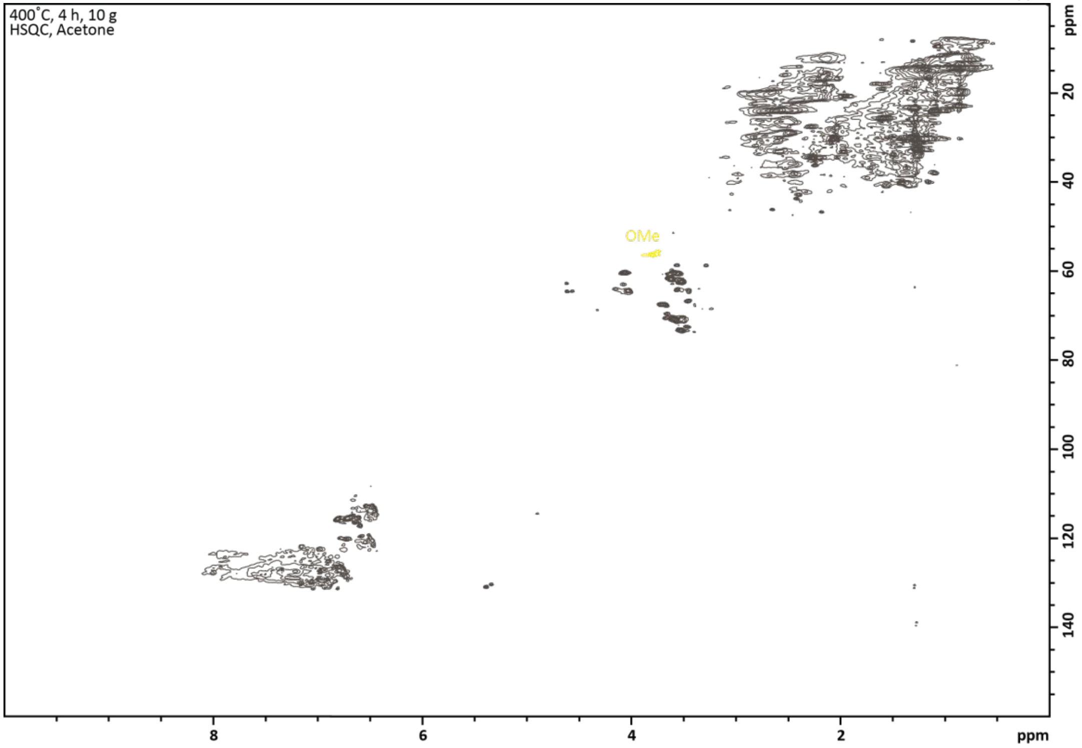
Fig. A. 5 ^{13}C-HSQC spectra of the lignin and oil product obtained at different reaction temperatures using 10 g lignin, 100 ml ethanol and a reaction time of 4 h. The first spectrum shows the lignin rich feedstock. The spectra cover multiple pages.

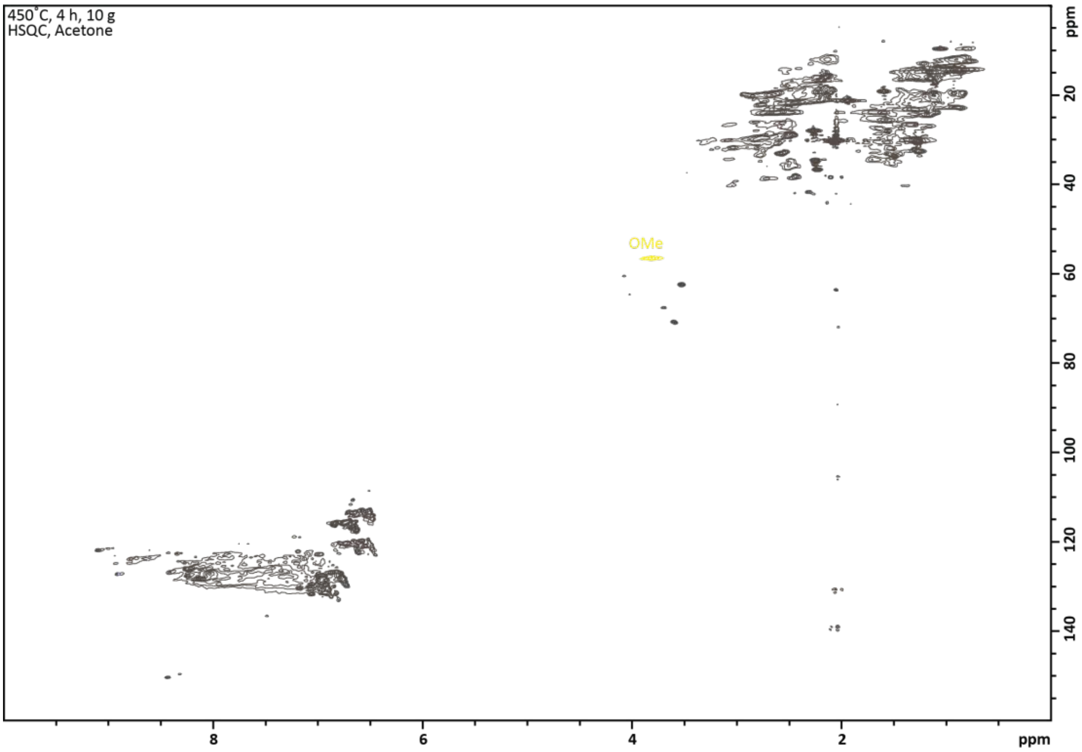



250˚C, 4 h, 10 g
HSQC, Acetone
OMe
ppm
20
40
60
80
100
120
140
8
6
4
2
ppm


300˚C, 4 h, 10 g
HSQC, Acetone
OMe
ppm
20
40
60
80
100
120
140
8
6
4
2
ppm


350˚C, 4 h, 10 g
HSQC, Acetone
OMe
8
6
4
2
ppm
20
40
60
80
100
120
140
ppm


400˚C, 4 h, 10 g
HSQC, Acetone
OMe
8
6
4
2
ppm
20
40
60
80
100
120
140
ppm


450°C, 4 h, 10 g
HSQC, Acetone
OMe
ppm
20
40
60
80
100
120
140
8
6
4
2
ppm

Additional Elemental Analysis Data

Elemental analysis was conducted as described in the main text on three additional experimental series where also reaction temperature, reaction time and lignin loading were varied. The results are shown in Fig. A. 6.

For experiments conducted with 2 g lignin at different temperatures relative to use of 10 g lignin (as shown in the main text) the latter case yielded a lower molar O/C for the oil obtained at all temperatures; however, the oil yield was equally reduced. Increased deoxygenation is further demonstrated at 300 °C where the molar O/C in the oil is plotted as a function of lignin loading which corresponds to the observation in the main text where the molar O/C drops as a function of lignin loading at 400 °C.

For a reaction temperature of 350 °C and a high lignin loading (40 g) the molar O/C decreases from 0.21 after 0 h to 0.16 after only 2 h. This is different from that described in the main text for a reaction temperature of 400 °C, 10 g lignin loading and a reaction time up to 8 h where no clear change in O/C was observed. The molar H/C in the oil increases slightly as a function of reaction time at 350 °C and 40 g lignin loading equally to what is described in the main text at 400 °C and 10 g lignin loading.

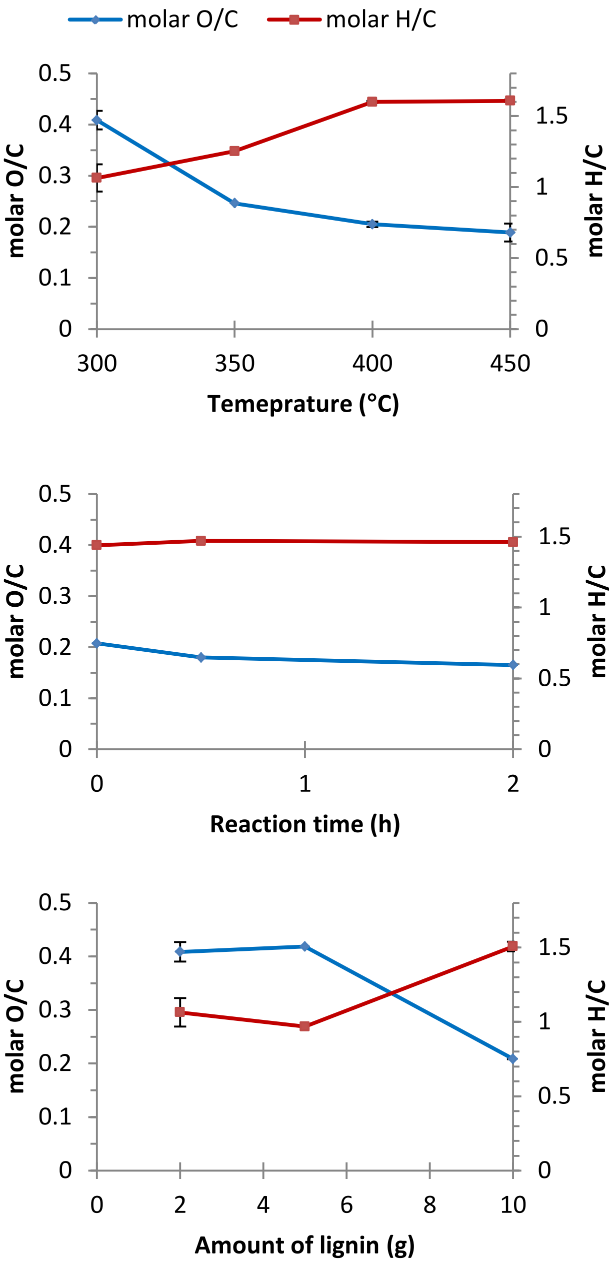


Fig. A. 6 Molar O/C and H/C ratio in the oil product plotted as a function of reaction temperature (top), reaction time (middle) and degree of lignin loading (bottom) for different reaction conditions. Reaction conditions: 2 g lignin and 4 h reaction time (top); 40 g lignin and 350 °C reaction temperature (middle); 4 h reaction time and 300 °C reaction temperature (bottom). Error bars represent standard error of the mean.

Additional Size Exclusion Chromatography Data

Size exclusion chromatography was conducted as described in the main text on oils obtained after solvolysis in 100 ml ethanol for 4 h at different lignin loadings. This is shown in Fig. A. 7.

When the lignin loading is increased going from 2 g to 5 g and to 10 g at 300 °C a shift towards lower molecular mass species is observed where two distinct size fractions possibly represent a monomeric and dimeric fraction. Increased lignin loading at 400 °C as described in the main text equally showed a decrease in molecular size distribution.

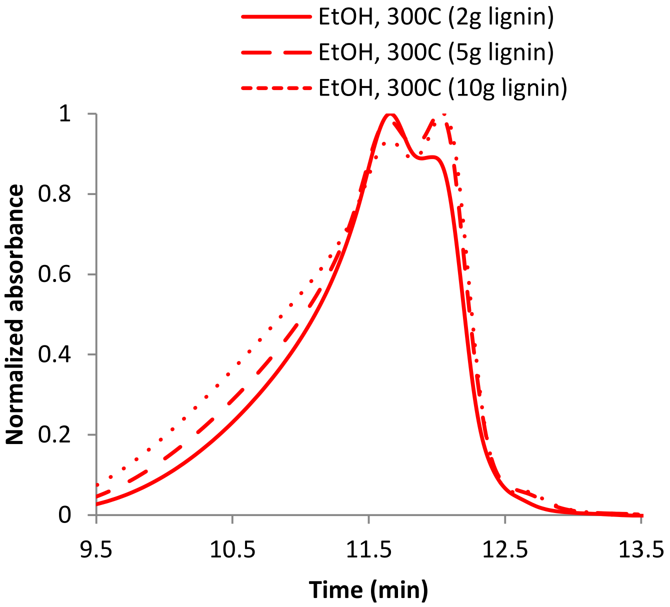


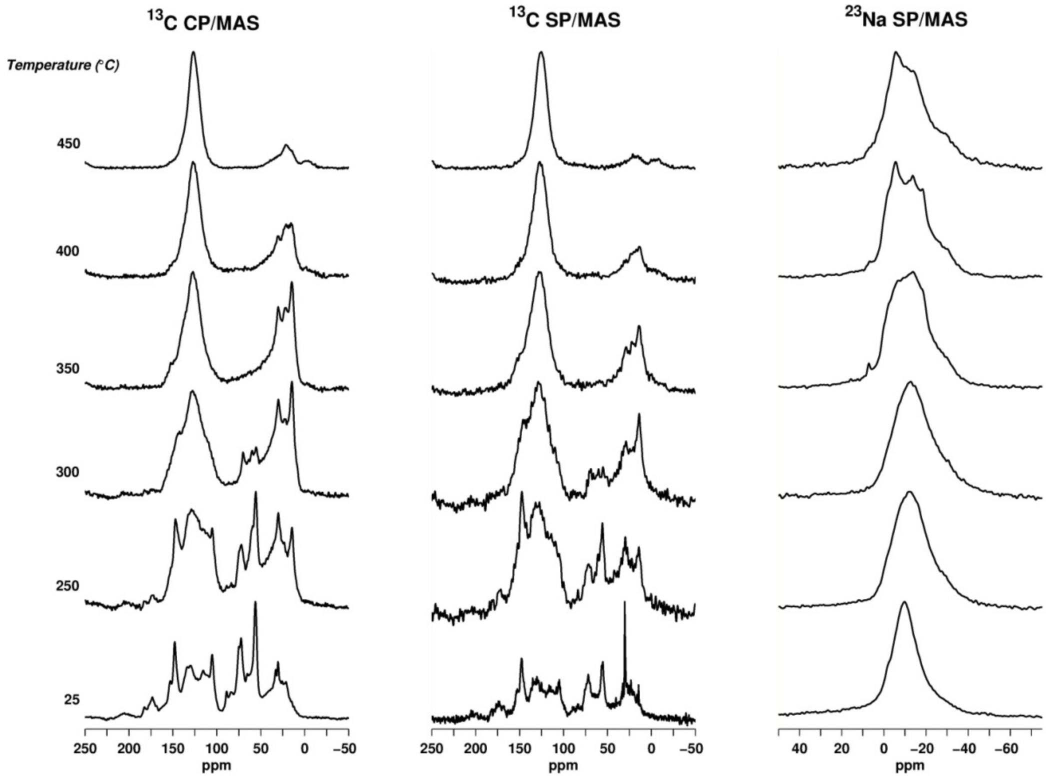
Fig. A. 7 Molecular size distribution for the solvolysis of 2 g, 5 g and 10 g lignin in 100 ml ethanol at 300 °C for 4 h.

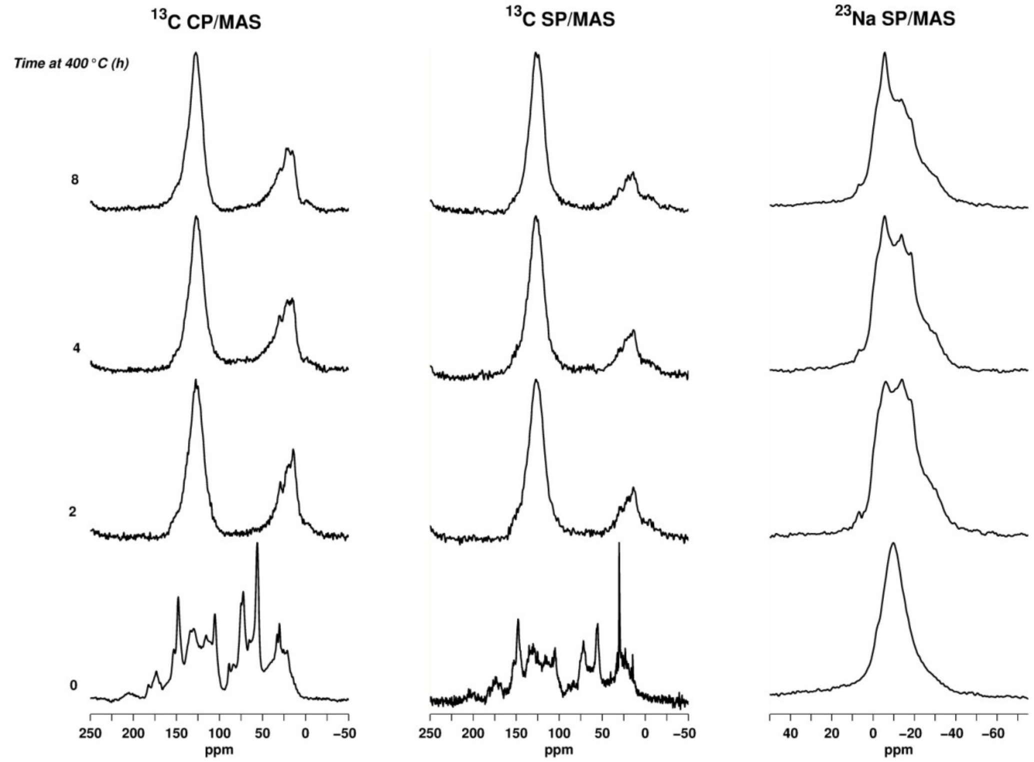
Full Solid State NMR Data

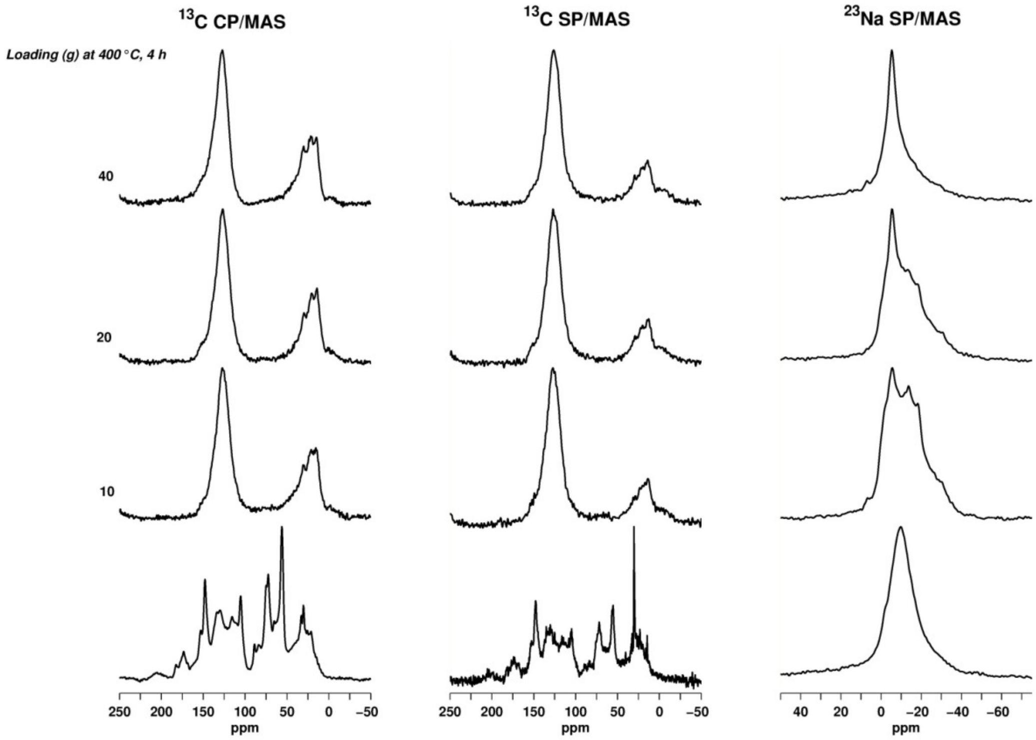
Solid state data was obtained using the methods described in them main text. Fig. A. 8 shows the ^{13}C and ^{23}Na solid-state MAS NMR spectra for residual chars obtained as a function of varying reaction temperature (also shown in the main text), reaction time and lignin loading.

In the lower rows the spectra of the lignin feedstock are presented. The ^{13}C CP/MAS spectrum contains resonances from lignin at 56 ppm from the methoxy groups, at 147 ppm from C1 and C4 in G units (guaiacyl) as well as the non-etherified C3 and C5 in H units (*p*-hydroxyphenyl), whereas the etherified C3 and C5 in S units (syringyl) are observed at 153 ppm. Moreover a broad resonance ~175 ppm originates from the carbonyl in esters and carboxylic acids. In the spectral region 60-107 ppm specific resonances from cellulose are observed at 60, 72-75, 84-90 and 105 ppm. Below 50 ppm resonances from aliphatic residues in the lignin are observed. Additional narrow resonances in the spectral region 10-40 ppm originating from fatty acids were observed in the ^{13}C SP/MAS spectrum.

Fig. A. 8 ^{13}C and ^{23}Na solid state MAS NMR of the residual solids at varying reaction conditions: 10 g lignin, 100 ml ethanol, 4 h (top); 10 g lignin, 100 ml ethanol, 400 °C (middle); 100 ml ethanol, 400 °C, 4 h (bottom). The figure spans multiple pages.




^{13}C CP/MAS
^{13}C SP/MAS
^{23}Na SP/MAS
Time at 400 °C (h)
8
4
2
0
250 200 150 100 50 0 −50
ppm
250 200 150 100 50 0 −50
ppm
40 20 0 −20 −40 −60
ppm


^{13}C CP/MAS
^{13}C SP/MAS
^{23}Na SP/MAS
Loading (g) at 400 °C, 4 h
40
20
10
250 200 150 100 50 0 −50
ppm
250 200 150 100 50 0 −50
ppm
40 20 0 −20 −40 −60
ppm

Elemental Analysis Data (O/C and H/C)

Elemental analysis of the oil and residual solid fraction was conducted as described in the main text. Full elemental analysis data represented as the molar O/C and H/C for oils and solids as a function of reaction temperature is shown in Fig. B. 1.

A comparison between the effects of the different alcohols solvents shows that the obtained oil product and residual solids have similar molar O/C. This highlights similar effects of the solvent on the lignin depolymerization. The molar O/C of the oil is reduced to a minimum of around 0.15 to 0.20 at 350˚C to 400˚C. The molar O/C of the residual solid fraction drops almost linearly as a function of reaction temperature with similar values as the oil product at 300˚C and 350˚C but at 400˚C the O/C achieves values of 0.1 or lower which is lower than for the oil product.

Despite similarities in molar O/C for oils and solids the molar H/C of the solids is much lower for all temperatures with a value of less than 1.0. The molar H/C for the solids drops as the reaction temperature is increased which shows increased aromaticity and possibly due to presence of poly aromatic hydrocarbons (PAH). The molar H/C of the oils is nearly unchanged as a function of reaction temperature with values between 1.4 and 1.7. It is clearly seen that the molar H/C of the oil product at all reaction temperatures is increased as the chain length of the alcohol solvent used is increased. This may be due to the alcohol solvent alkylating the depolymerised lignin as described in the main text.

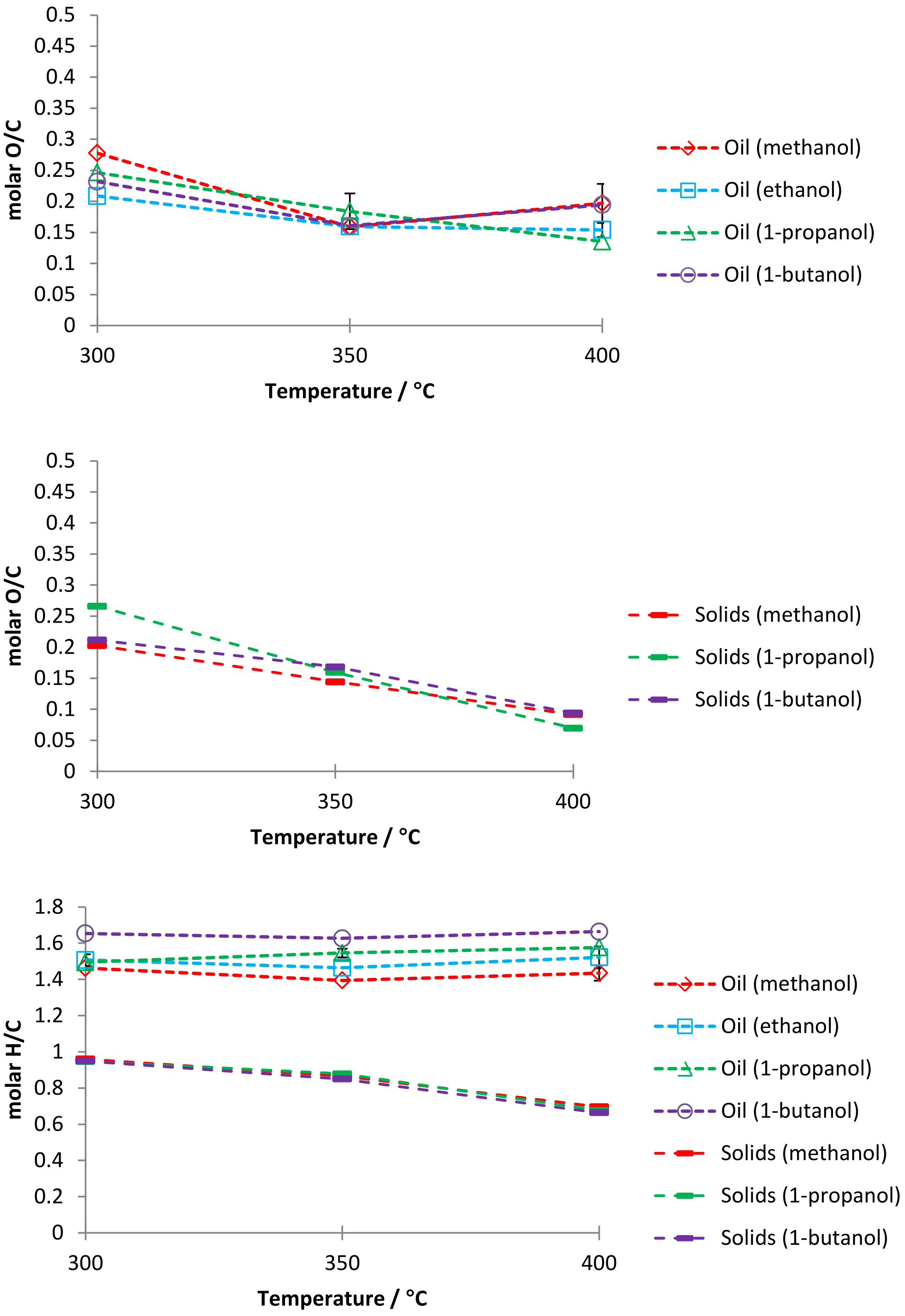


Fig. B. 1 molar O/C and H/C of isolated oil and dried solids shown as a function of reaction temperature and different alcohol solvent. The lignin feedstock has a molar H/C of 1.3 and molar O/C of 0.4. Top: molar O/C of oils; middle: molar O/C of solids; bottom: molar H/C of oils and solids. Reaction conditions: 10 g lignin in 100 ml alcohol was treated for 4 h.

Full GC-MS Data

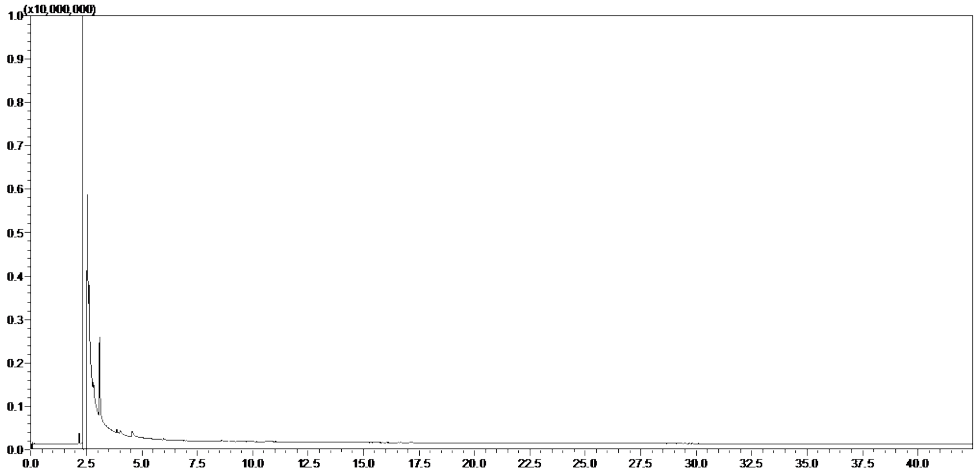
GC-MS was conducted on the light solvent fractions after reaction as described in the main text. GC-MS chromatograms obtained from all reaction temperatures using the four different solvents are shown in Fig. B. 2 (methanol), Fig. B. 3 (ethanol), Fig. B. 4 (1-propanol) and Fig. B. 5 (1-butanol) and identified species are listed in Table B. 1 (methanol), Table B. 2 (ethanol), Table B. 3 (1-propanol) and Table B. 4 (1-butanol).

The GC-MS chromatograms for solvent phase products using the four different alcohols show that species formed at 300 °C are equally formed at higher temperatures but as the temperature was increased more species are seen. The species formed in the solvent blanks resemble the ones formed with lignin present during solvolysis.

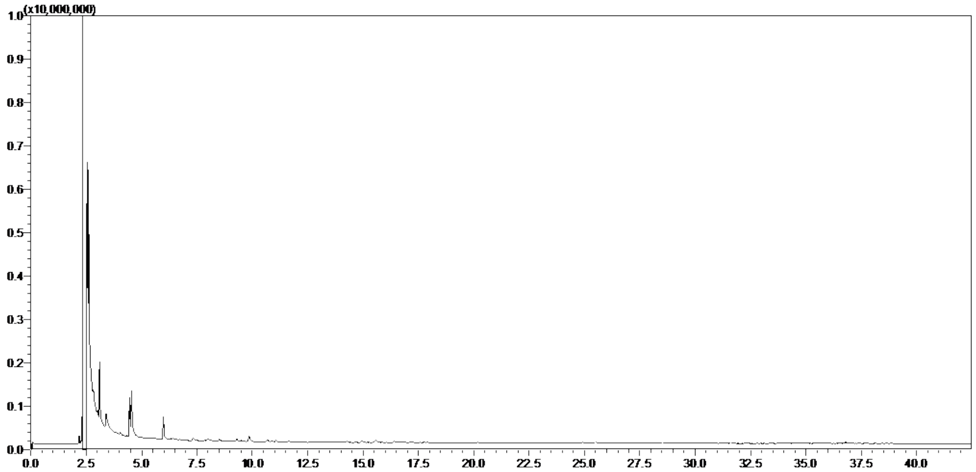
Methanol:

Fig. B. 2 GC-MS chromatograms of the light solvent fraction (solvent: methanol) after reaction. When experimental replicates exist multiple chromatograms are shown. Reaction conditions: 10 g lignin, 100 ml methanol and 4 h reaction at different reaction temperatures. The figure spans multiple pages

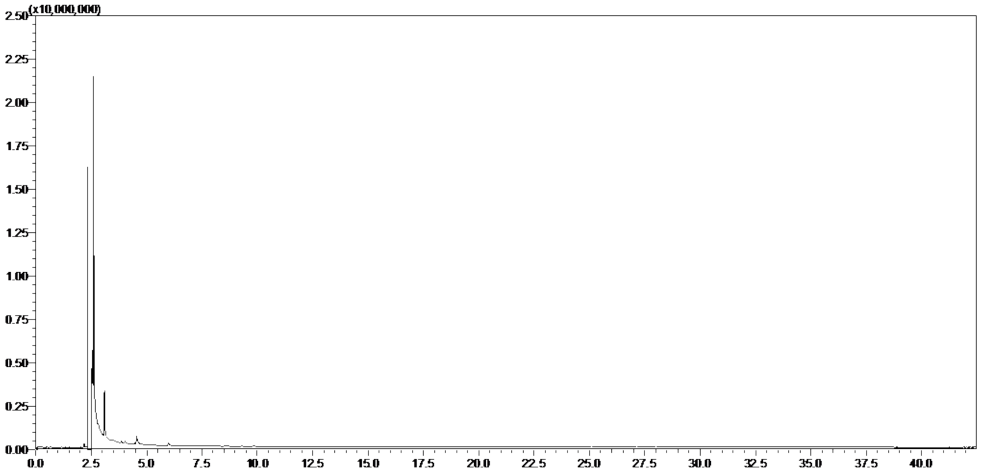
300˚C:

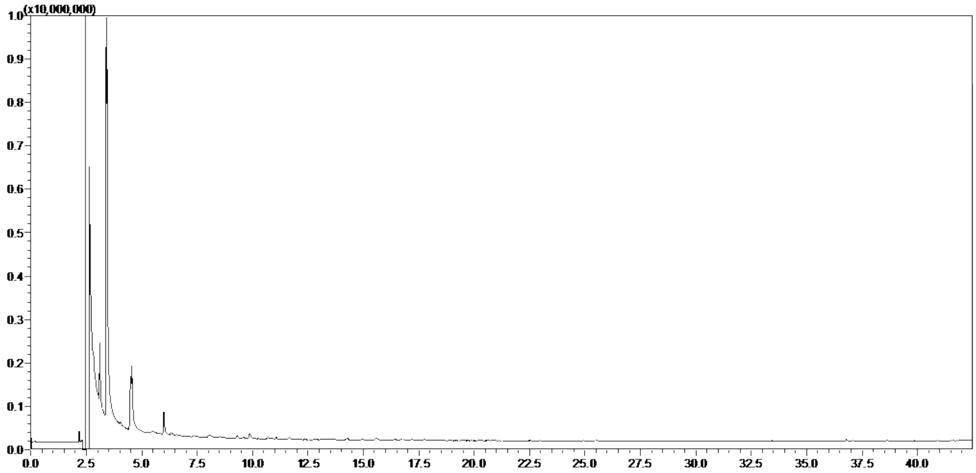


350°C:


(x10,000,000)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0

400°C:


(x10,000,000)
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0


(x10,000,000)
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0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
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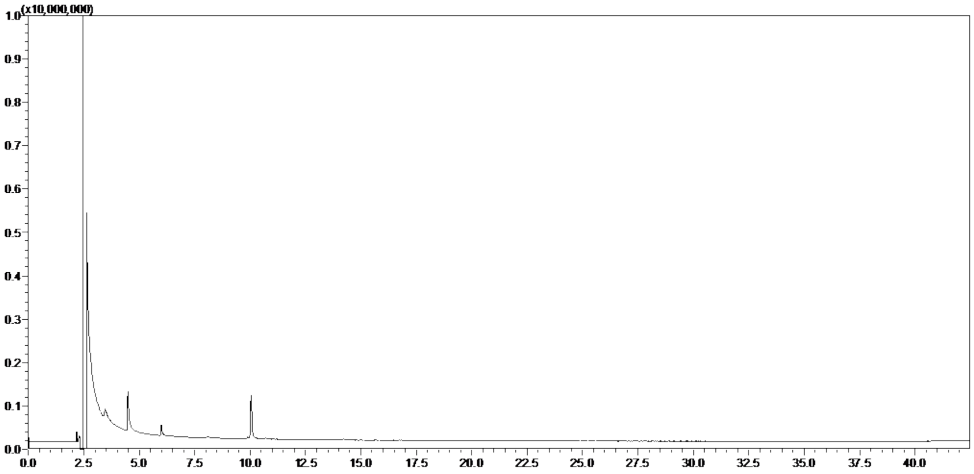
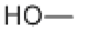
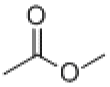
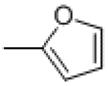
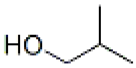
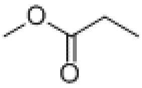
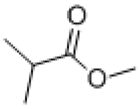
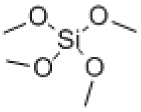
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0



400˚C (solvent blank):

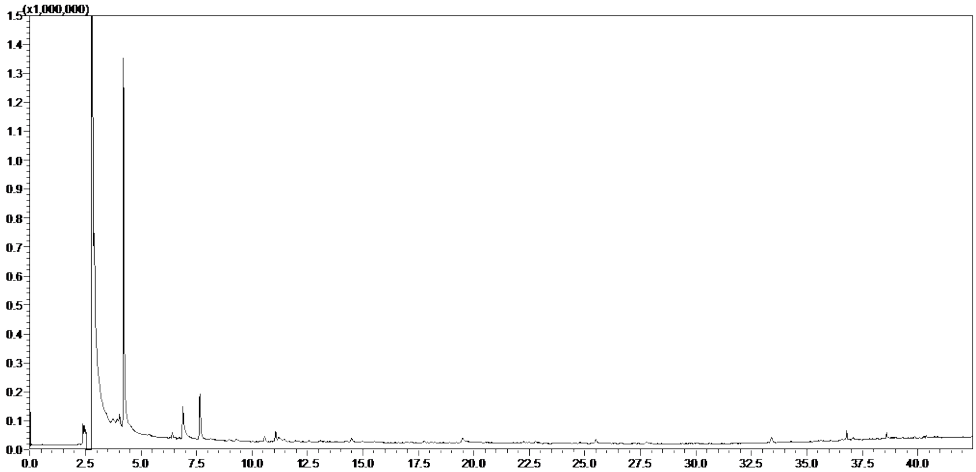
Table B. 1 Identified peaks from the GC-MS chromatograms (solvent: methanol). Species were identified automatically using the software GCMSsolution Version 2.70 software and NIST library search. Identified species are marked with an x at the given reaction temperature. Reactions conditions: 10 g lignin treated for 4 h in 100 ml methanol.

Time [min]	**Similarity index**	**Name**	**Drawing**	**Temperature**			
				300°C	**350°C**	**400°C**	**400°C (blind)**
2.393	96	methanol		x	x	x	x
2.607	92	ethanol		x	x	x	x
2.813	96	acetone		x	x	x	x
3.093	95	methyl acetate		x	x	x	x
3.400	96	1-propanol			x	x	x
3.863	92	1,1-dimethoxyethane		x	x	x	
4.027	94	2-methylfurane		x	x	x	
4.450	94	2-methylpropan-1-ol			x	x	
4.570	95	methyl propanoate		x	x	x	x
5.900	97	methyl-2-methyl propanate			x	x	x
10.043	95	tetramethyl orthosilicate					x

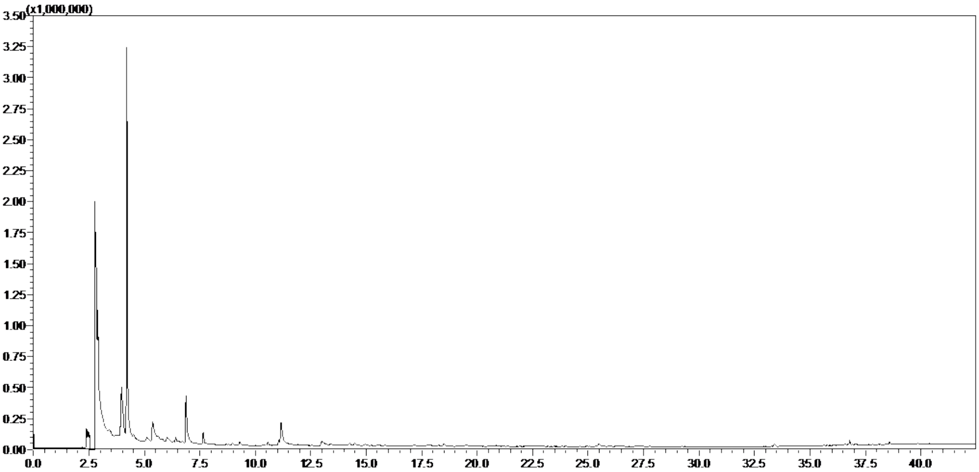
Ethanol:

Fig. B. 3 GC-MS chromatograms of the light solvent fraction (solvent: ethanol) after reaction. When experimental replicates exist multiple chromatograms are shown. Reaction conditions: 10 g lignin, 100 ml ethanol and 4 h reaction at different reaction temperatures. The figure spans multiple pages.

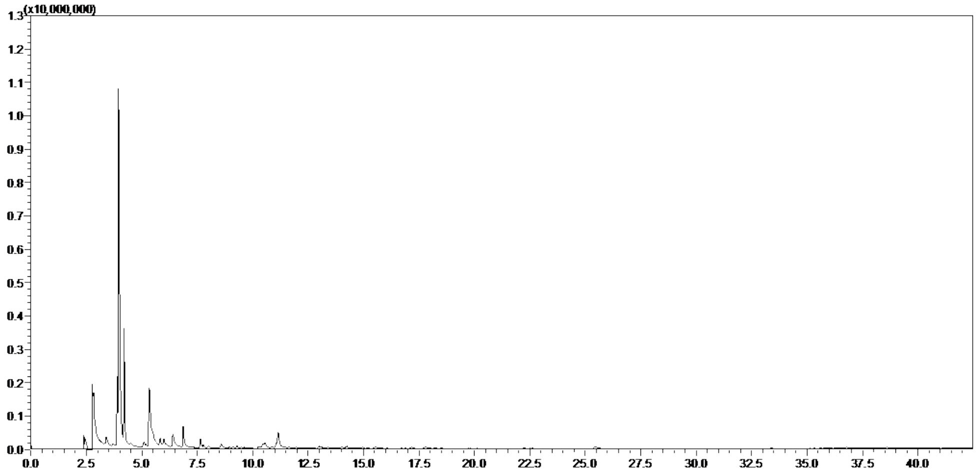
300˚C:

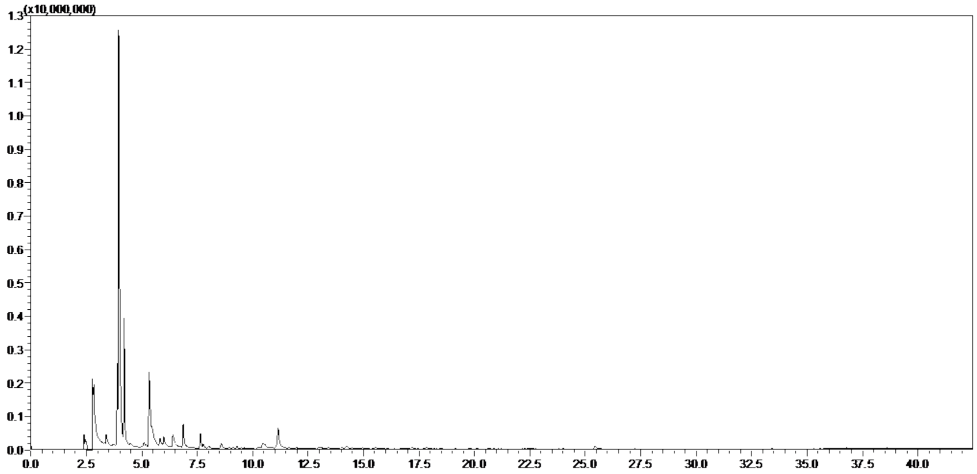


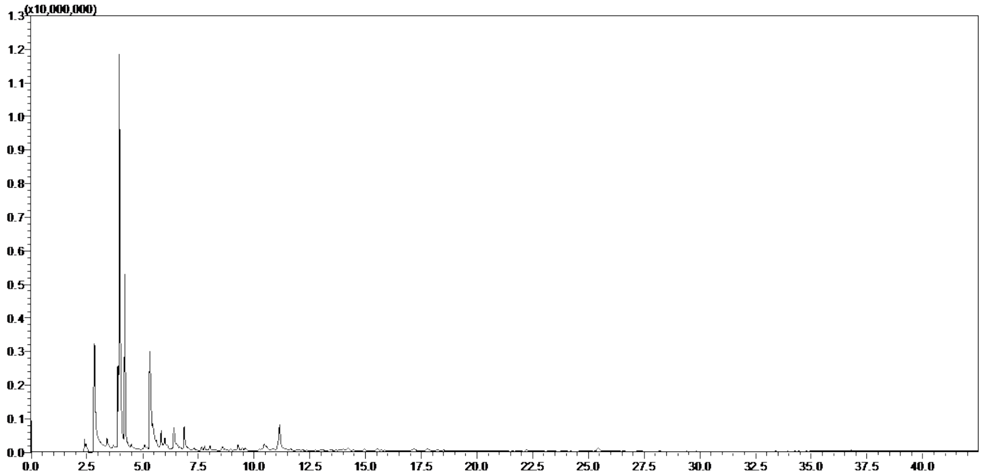
350˚C:



400˚C:


(x10,000,000)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0


(x10,000,000)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0


(x10,000,000)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
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32.5
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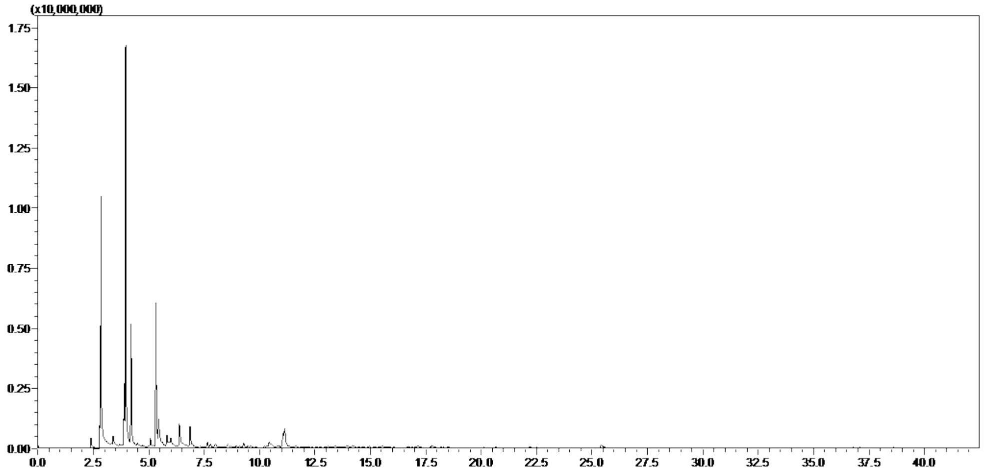
37.5
40.0



400˚C (solvent blank):

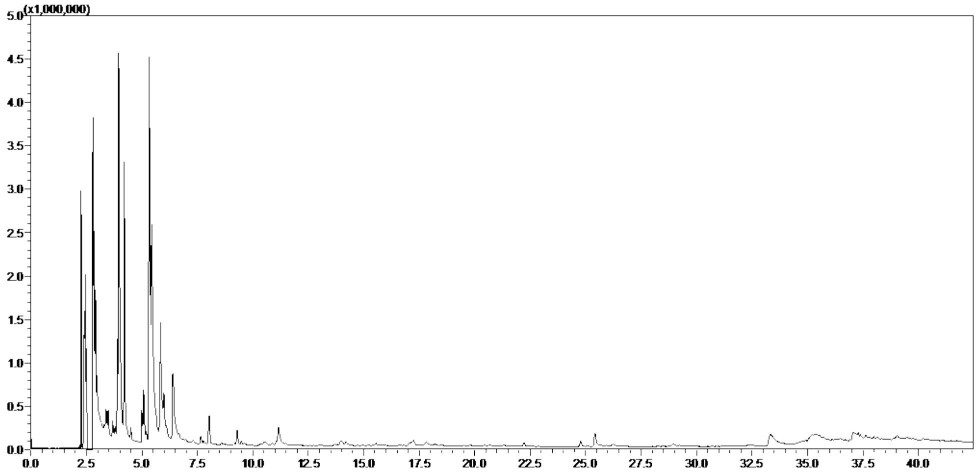
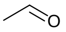
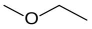
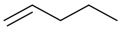
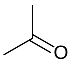
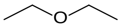
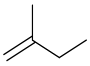
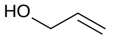
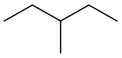
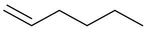
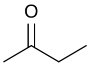
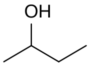
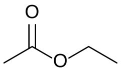
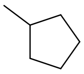
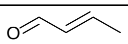
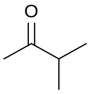
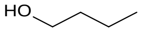
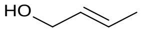
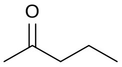
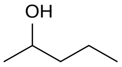
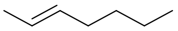
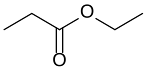
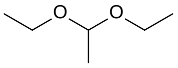
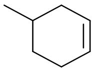
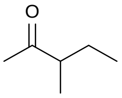
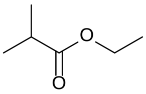
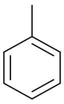
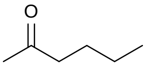
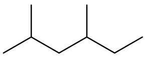
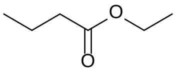
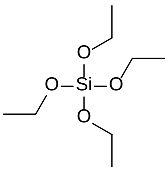
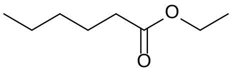
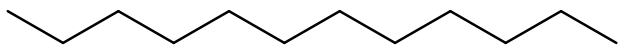


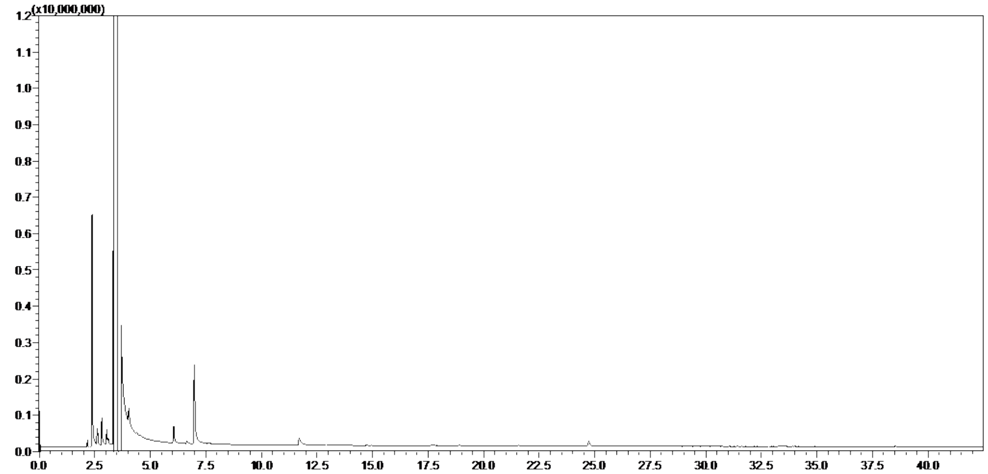
Table B. 2 Identified peaks from the GC-MS chromatograms (solvent: ethanol). Species were identified automatically using the software GCMSsolution Version 2.70 and NIST library search. Identified species are marked with an x at the given reaction temperature. Reactions conditions: 10 g lignin treated for 4 h in 100 ml ethanol. The table spans multiple pages.

Time [min]	**Similarity index**	**Name**	**Drawing**	**Temperature**			
				300°C	**350°C**	**400°C**	**400°C (blind)**
2.45	98	acetaldehyde		x	x	x	x
2.51	94	ethyl methyl ether			x		
2.79	96	1-pentene					x
2.81	94	acetone			x		
2.90	96	diethyl ether		x	x		
2.98	98	2-methyl-1-butene					x
3.30	92	2-propen-1-ol					x
3.68	93	3-methyl-pentane					x
3.79	92	1-hexene					x
3.89	97	2-butanone			x	x	x
3.96	97	2-butanol			x	x	x
4.20	98	ethyl acetate		x	x	x	x
4.50	96	methyl-cyclopentane					x
4.99	95	2-butenal					x
5.20	96	3-methyl-2-butanone				x	x
5.34	91	1-butanol			x	x	x
5.44	94	2-buten-1-ol					x
5.99	96	2-pentanone				x	x
6.39	96	2-pentanol					x
6.68	93	2-heptene					x
6.87	96	ethyl propanoate		x	x	x	
7.65	96	1,1-diethoxy-ethane		x	x	x	x
8.03	97	4-methyl-cyclohexene					x
8.58	90	3-methyl-2-pentanone				x	

8.95	92	ethyl 2-methylpropanoate				x	
9.29	95	toluene				x	x
10.46	93	2-hexanone				x	
11.05	92	2,4-dimethyl-hexane			x		
11.15	94	ethyl butanoate			x	x	x
24.77	92	tetraethyl silicate					x
25.42	93	ethyl hexanoate					x
36.79	95	*n*-dodecane			x	x	

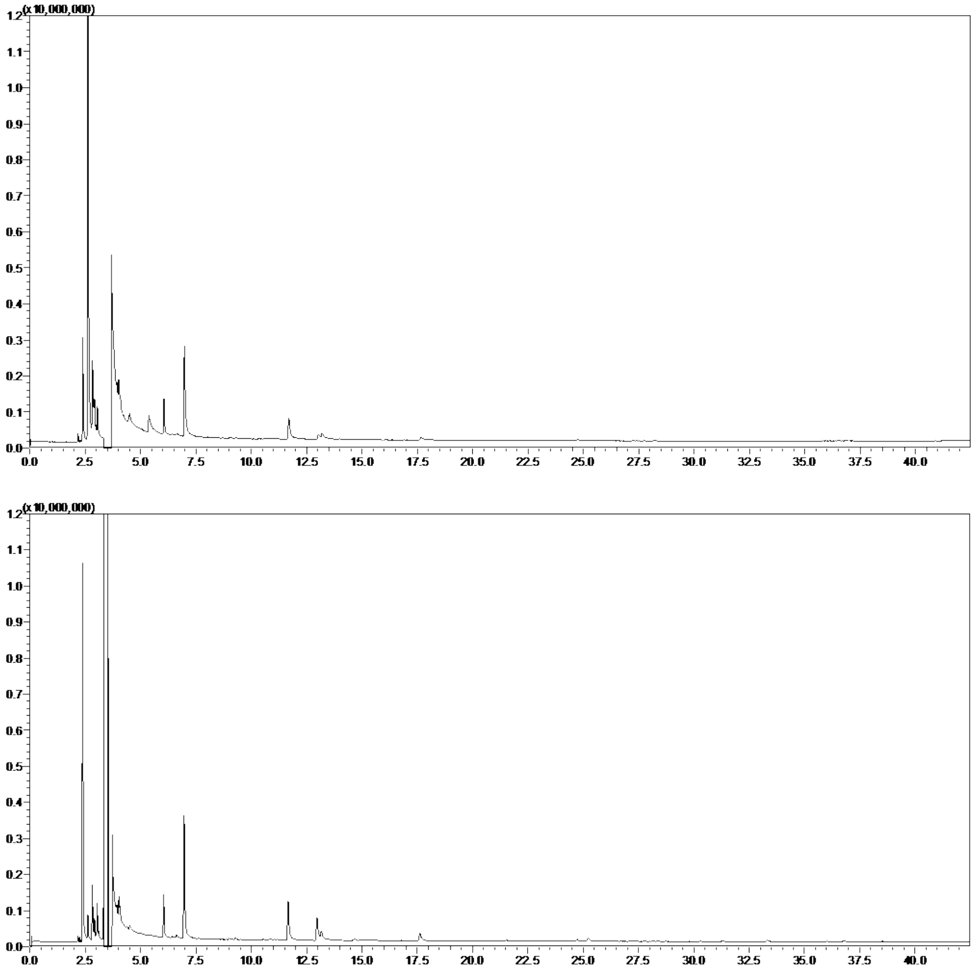
1-Propanol:

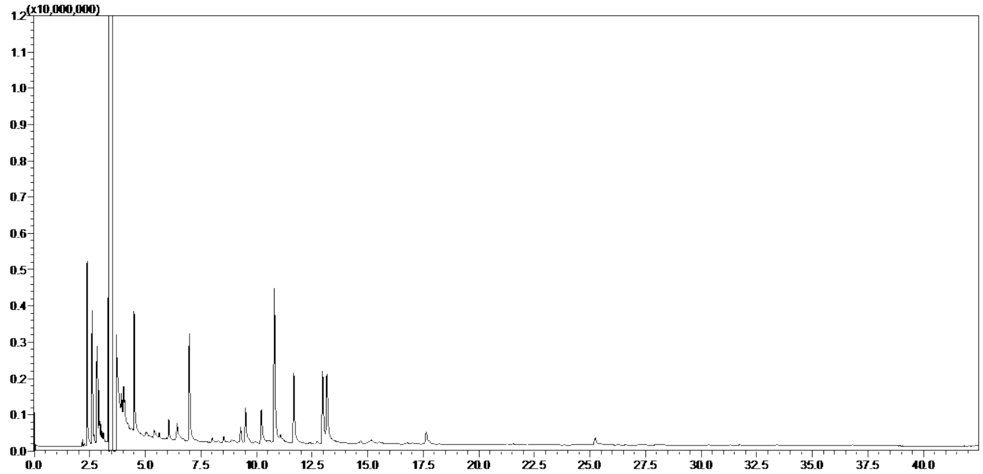
Fig. B. 4 GC-MS chromatograms of the light solvent fraction (solvent: 1-propanol) after reaction. When experimental replicates exist multiple chromatograms are shown. Reaction conditions: 10 g lignin, 100 ml 1-propanol and 4 h reaction at different reaction temperatures. The figure spans multiple pages.



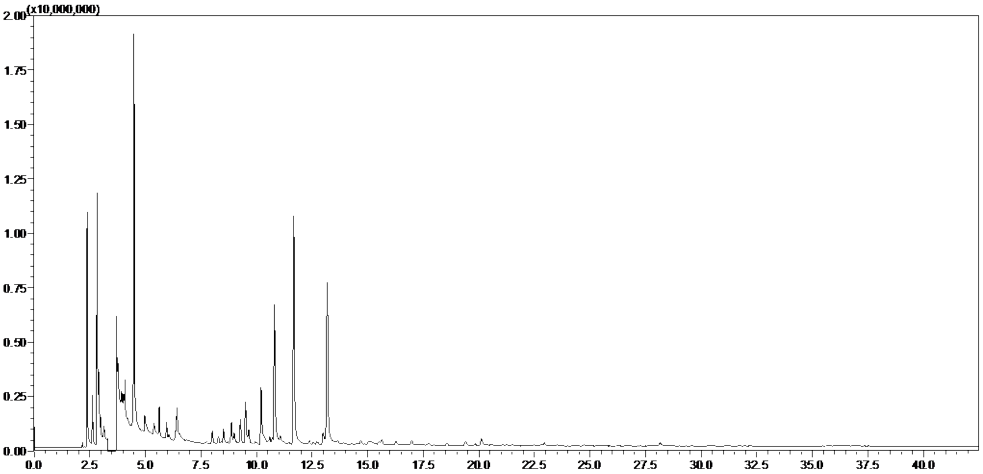
300˚C:

350˚C:


(x10,000,000)
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0
(x10,000,000)
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0

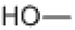
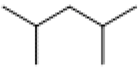
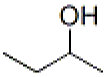
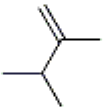
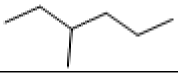
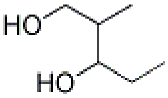
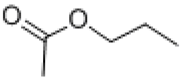
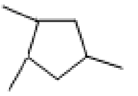


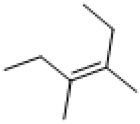
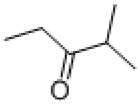
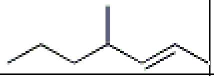
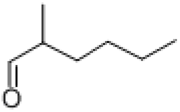
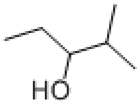
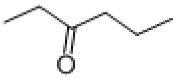
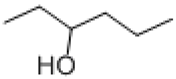
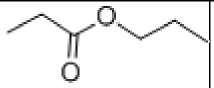
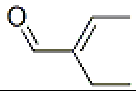
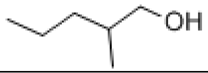
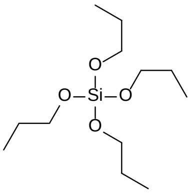
400˚C:



400˚C (solvent blank):

Table B. 3 Identified peaks from the GC-MS chromatograms (solvent: 1-propanol). Species were identified automatically using the software GCMSsolution Version 2.70 and NIST library search. Identified species are marked with an x at the given reaction temperature. Reactions conditions: 10 g lignin treated for 4 h in 100 ml 1-propanol. The table spans multiple pages.

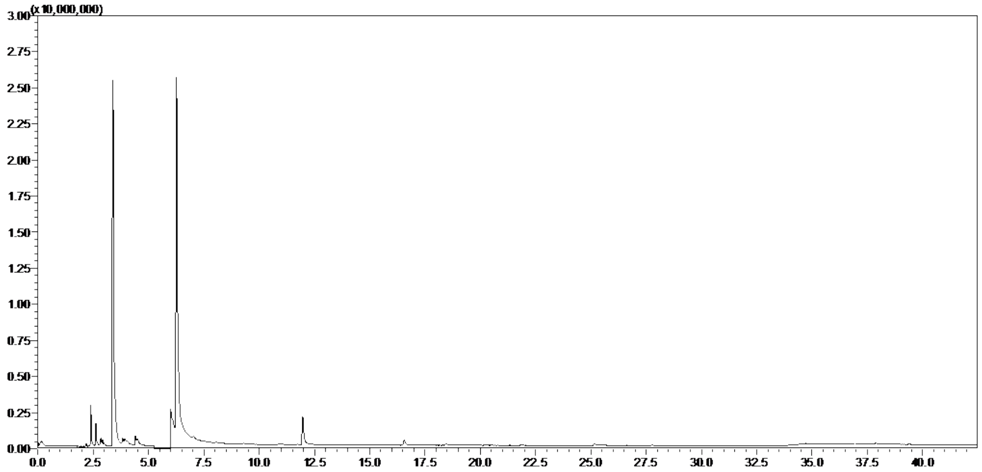
Time [min]	**Similarity index**	**Name**	**Drawing**	**Temperature**			
				300°C	**350°C**	**400°C**	**400°C (blind)**
2.393	96	methanol		x	x	x	x
2.607	92	ethanol		x	x	x	x
2.980	96	2-pentene			x	x	x
3.043	97	methyl propyl ether		x	x	x	
3.117	90	propanal				x	x
3.400	96	1-propanol		x	x	x	x
3.920	93	2,4-dimethylpentane			x	x	x
4.023	93	1-methylpropan-1-ol		x	x	x	
4.080	91	2,3-dimethylbut-1-ene			x	x	x
4.450	94	2-methylpropan-1-ol		x	x	x	x
4.963	94	2-methylprop-2-en-1-ol					x
5.373	93	1-butanol			x	x	x
5.630	96	3-methylhexane				x	x
5.957	97	3-ethylpentane				x	x
6.053	91	dipropyl ether		x	x	x	x
6.430	91	2-methyl-1,3-pentandiol				x	x
6.90	97	propyl acetate		x	x	x	
8.017	95	1,2,4-trimethylcyclopentane					x

8.283	93	2,3-dimethylhex-3-ene					x
8.520	94	2-methylpentan-3-one				x	x
8.867	95	4-methylhept-2-ene					x
8.983	92	2-methylhexanal					x
9.507	96	2-methyl-pentan-3-ol				x	x
10.223	98	hexan-3-one				x	x
10.807	94	hexan-3-ol				x	x
11.707	96	propyl propanoate		x	x	x	x
12.967	95	2-ethyl-but-2-enal			x	x	x
13.167	94	2-methyl-1-pentanol			x	x	x
38.360	86	tetrapropyl orthosilicate					x

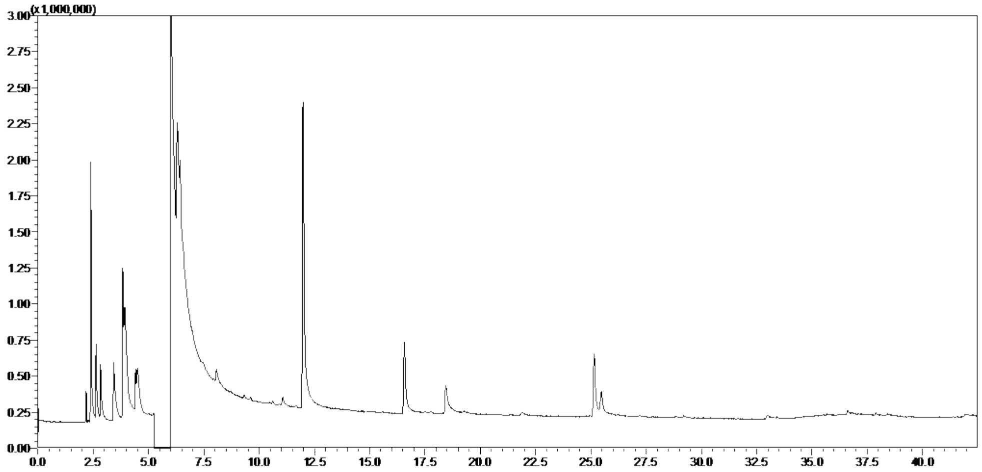
1-Butanol:

Fig. B. 5 GC-MS chromatograms of the light solvent fraction (solvent: 1-butanol) after reaction. When experimental replicates exist multiple chromatograms are shown. Reaction conditions: 10 g lignin, 100 ml 1-butanol and 4 h reaction at different reaction temperatures. The figure spans multiple pages.

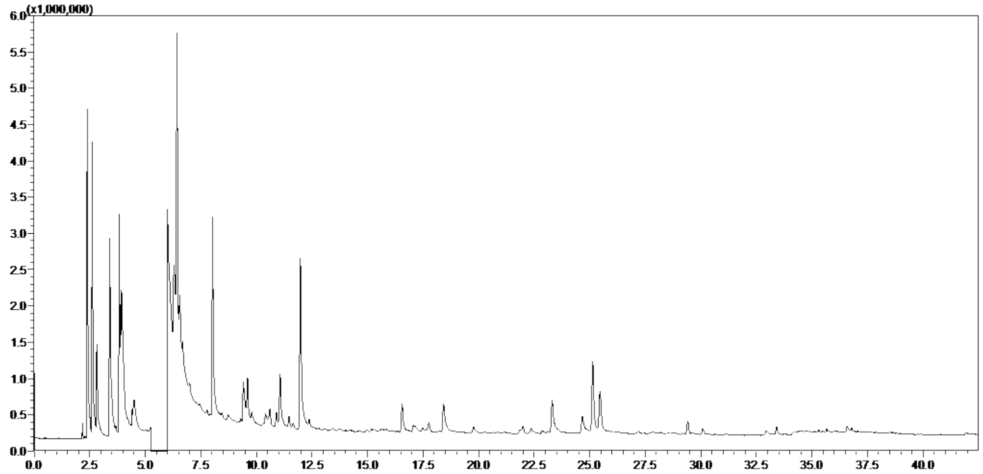
300˚C:



350˚C:



400˚C:



400˚C (solvent blank):

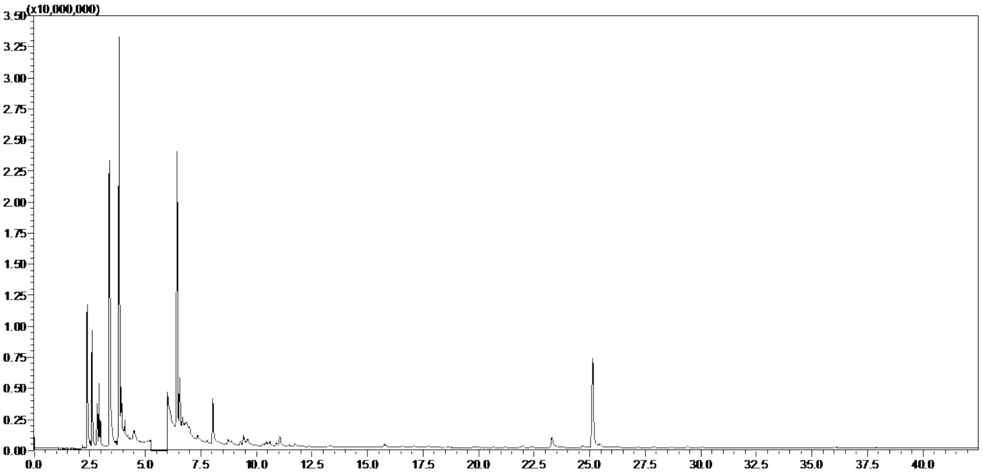
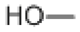
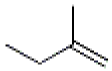
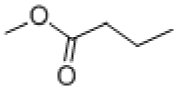
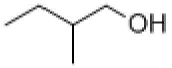
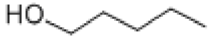
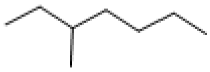
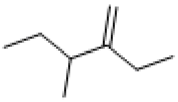
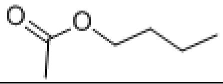
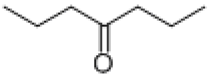
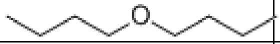
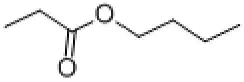
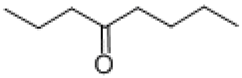
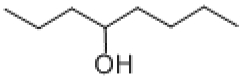
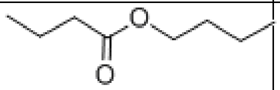
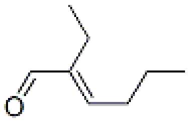


Table B. 4 Identified peaks from the GC-MS chromatograms (solvent: 1-butanol). Species were identified automatically using the software GCMSsolution Version 2.70 and NIST library search. Identified species are marked with an x at the given reaction temperature. Reactions conditions: 10 g lignin treated for 4 h in 100 ml 1-butanol. The table spans multiple pages.

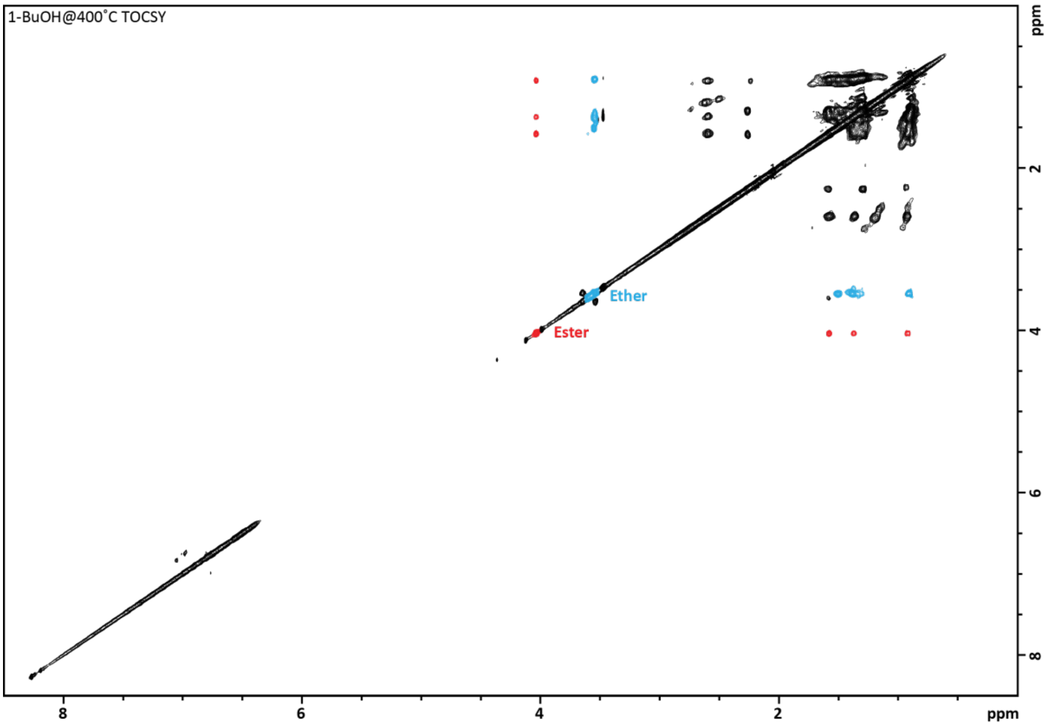
Time [min]	**Similarity index**	**Name**	**Drawing**	**Temperature**			
				300°C	**350°C**	**400°C**	**400°C (blind)**
2.393	97	methanol		x	x	x	x
2.620	95	ethanol		x	x	x	x
2.823	90	acetone		x	x	x	x
2.927	97	2-methylbut-1-ene		x	x	x	x
3.433	96	1-propanol		x	x	x	x
3.830	94	butanal		x	x	x	x
3.933	92	hexane		x	x	x	x
4.407	96	methyl butyl ether		x	x	x	x
4.450	90	2-methylpropan-1-ol		x	x	x	x
5.373	93	1-butanol		x	x	x	x
6.293	91	*n*-butyl formate		x	x	x	
6.423	90	*n*-heptane				x	x
6.557	96	hept-3-ene					x
7.030	96	propyl acetate		X	x	x	
7.363	94	methyl butanoate					x
8.067	98	2-methylbutan-1-ol			x	x	x
9.407	94	1-pentanol				x	x
9.603	93	3-methylheptane				x	x

10.613	94	3-methyl-4-methylenehexane				x	x
11.070	91	2,4-dimethylhexane				x	x
11.463	96	2-octene				x	x
11.977	97	butyl acetate		x	x	x	
15.767	96	4-heptanone					x
16.567	96	*n*-butyl ether		x	x	x	x
17.763	93	*n*-nonane				x	
18.447	98	butyl propanoate			x	x	
23.310	94	4-octanone				x	x
24.657	95	4-octanol				x	x
25.160	94	butyl butanoate		x	x	x	x
25.473	95	2-ethylhex-2-enal			x	x	x

NMR Data

^{1}H-TOCSY NMR, ^{13}C-HMBC NMR and ^{13}C-HSQC NMR was conducted on isolated oil products as described in the main text. Spectral data from ^{1}H-TOCSY NMR and ^{13}C-HMBC NMR on isolated oil from treatment of 10 g lignin at 400°C in 1-butanol is shown in Fig. B. 6 and alkylation is identified as both butyl ether and ester. Fig. B. 7 shows ^{13}C-HSQC NMR data on oil isolated after treatment of 10 g lignin at 400 °C in the four different alcohols. The spectral data shows very similar oil composition independent on alcohol chain length; however, methoxy groups are presented in a noticeably higher amount in the oil produced in methanol solvent. This shows that a transetherification takes place.

Fig. B. 6 ^{1}H-TOCSY and ^{13}C-HMBC spectra of oils produced at 400 °C for 4 h in 100 ml 1-butanol. Butyl ester and butyl ether is highlighted in the figure.



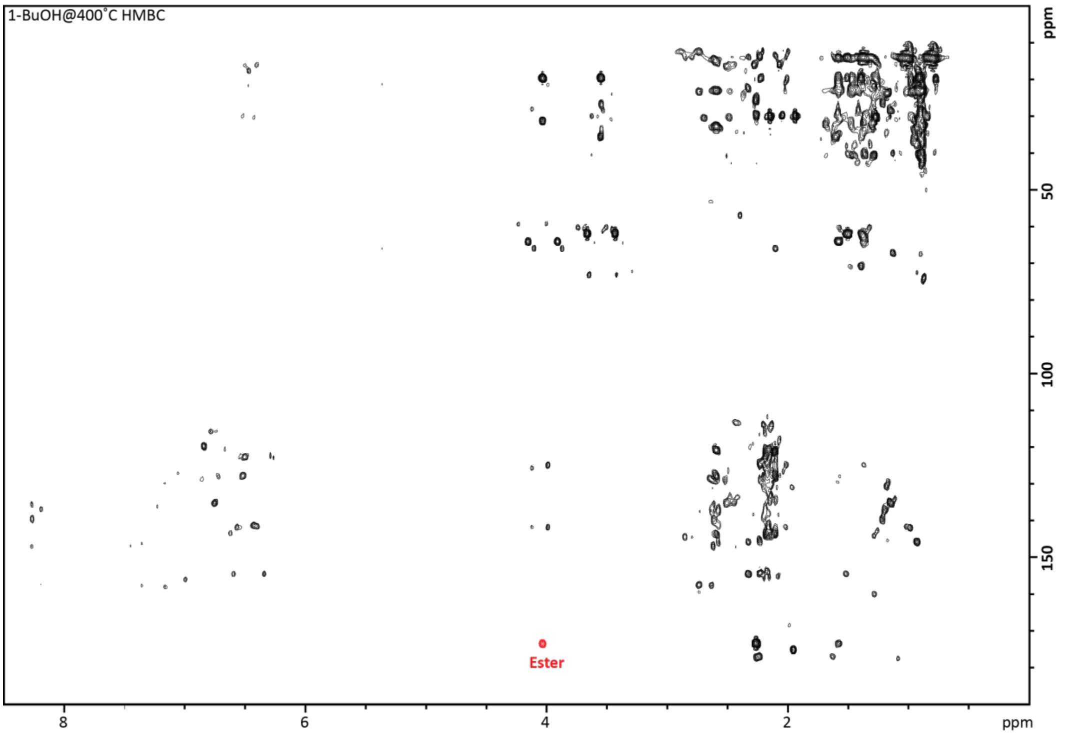
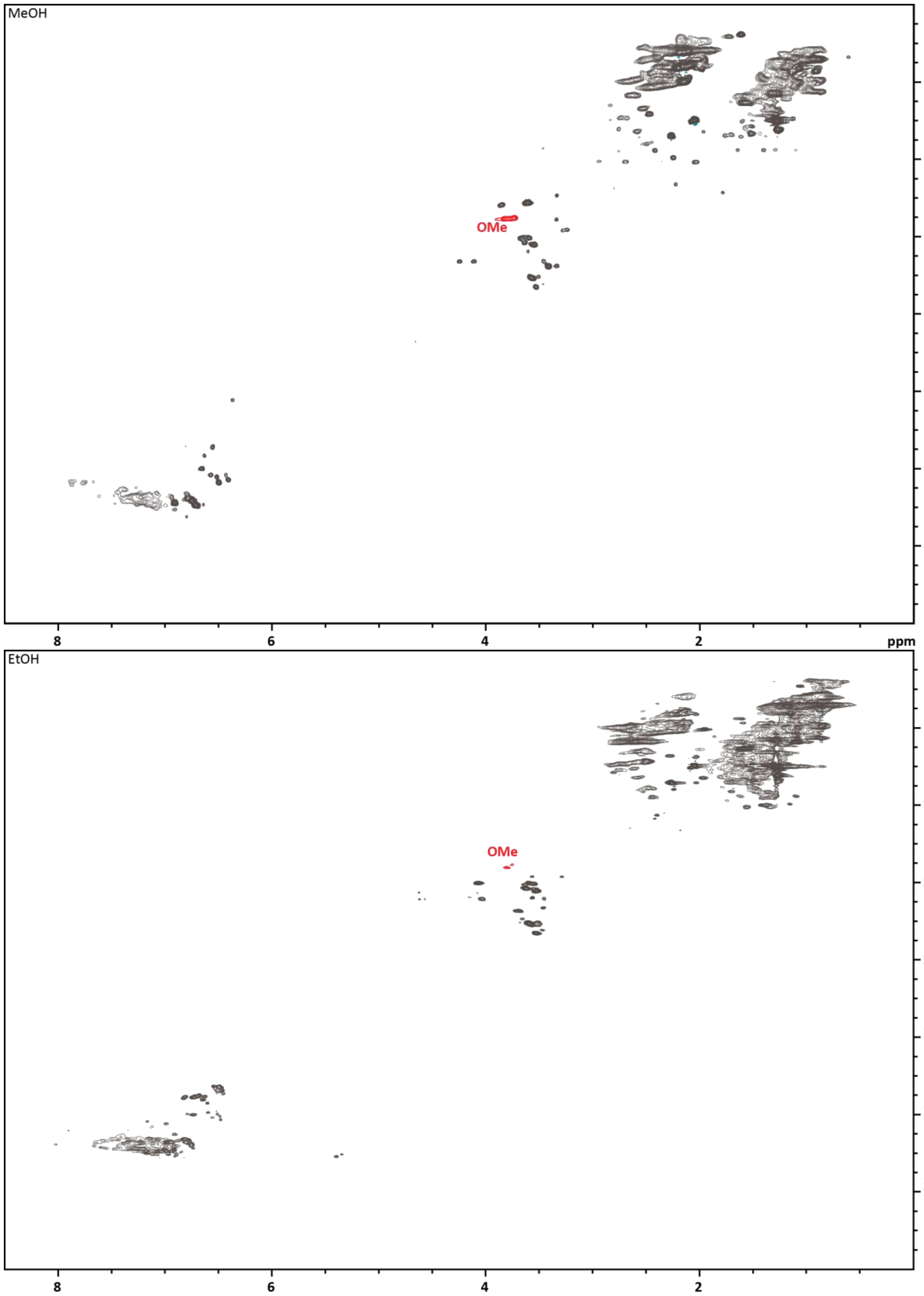
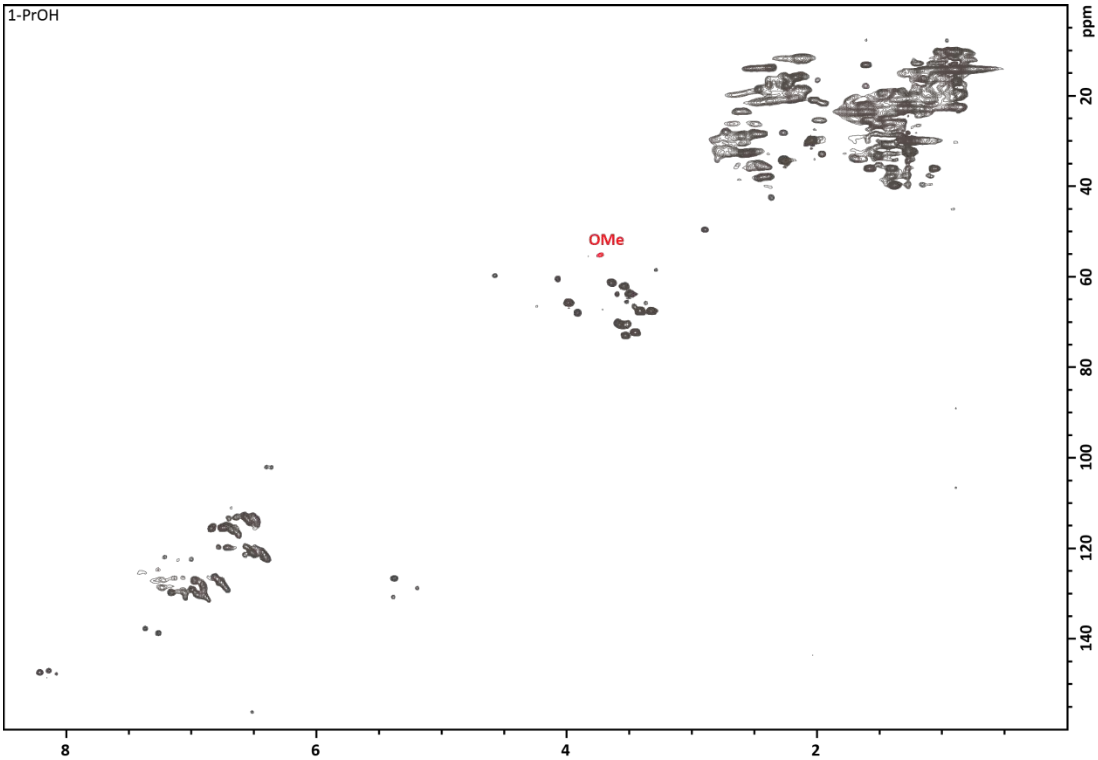


Fig. B. 7 ^{13}C-HSQC NMR of oils produced from 10 g lignin reacted for 4 h at 400 °C in 100 ml alcohol. The methoxy groups are highlighted. The figure spans multiple pages.

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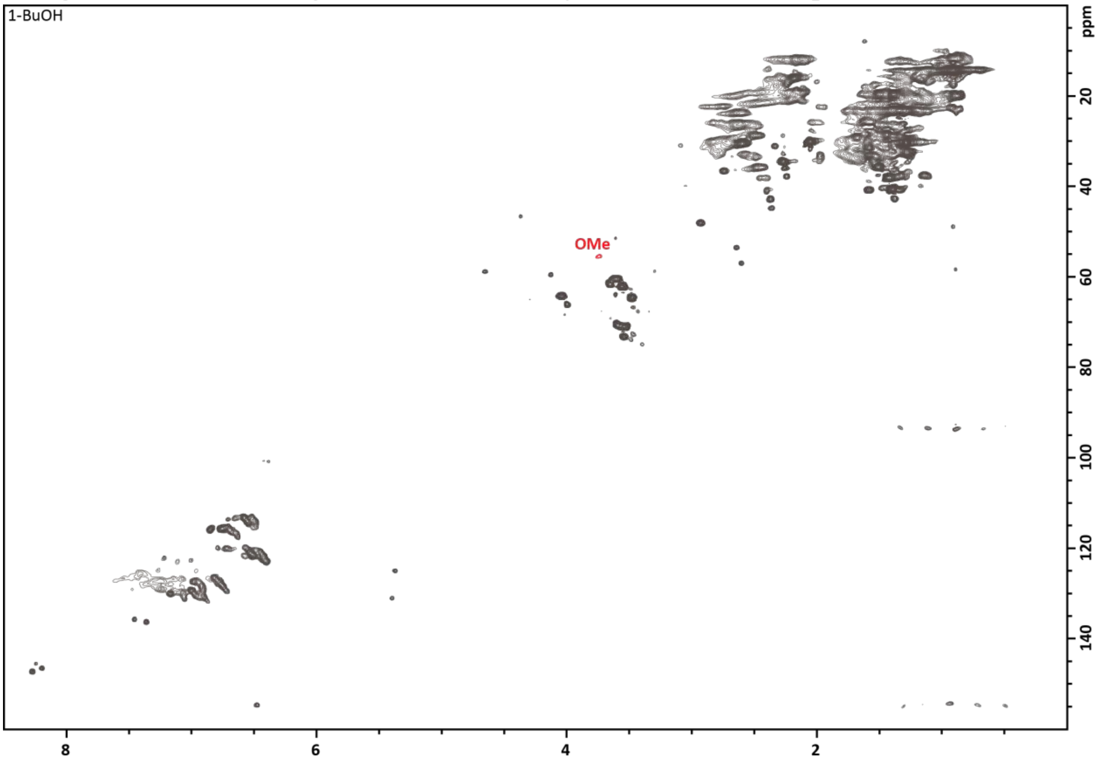
OMe
ppm
20
40
60
80
100
120
140
8
6
4
2


1-BuOH
OMe
ppm
20
40
60
80
100
120
140
8
6
4
2

Effects of Water Content with Various Process Parameters

A series of experiments at various reaction conditions were designed similar to those described in Chapter 4 where different amounts of water was added to high purity ethanol (99.9 %) maintaining a solvent volume of 100 ml. Fig. C. 1 shows the result of these experiments represented as the effect of water content in the solvent ethanol on oil yield and molar O/C of the oil product. The specific water content of the solvent was calculated by including the water content of the lignin feedstock (2 wt%). A decrease in oil yield is seen for a reaction temperature of 400 °C when the water concentration increases and no clear effect on oil yield is seen with the other reaction parameters tested. The oil quality is however clearly reduced (molar O/C increases) for all of the reaction conditions tested as the water content of the solvent is increased. A small amount of water in the ethanol solvent such as in the case of using 96 vol% rather than high purity (99.9%) ethanol only has a small negative impact on oil yield and quality in particular for lower reaction temperatures (<400 °C).

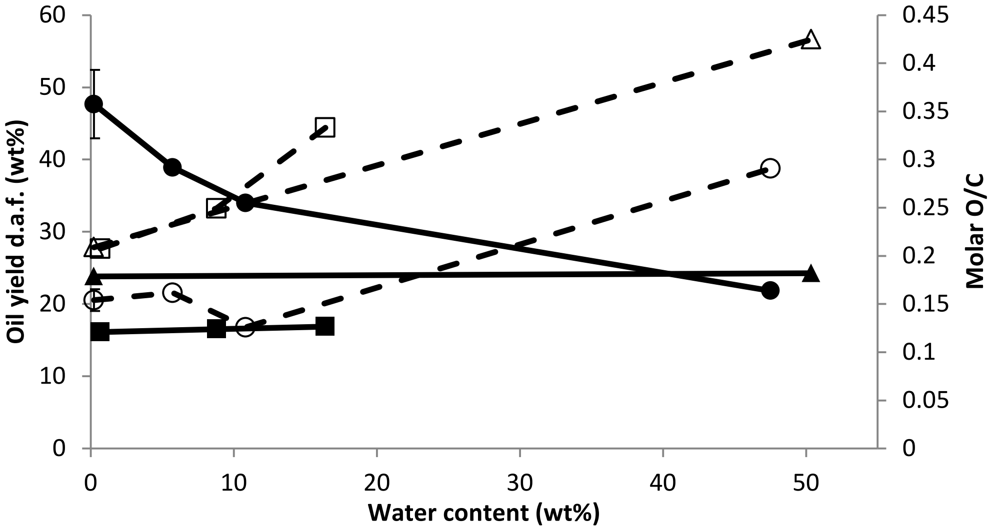


Fig. C. 1 The oil yield (solid lines) and molar O/C (dashed lines) of the oil product represented as a function of water content in 100 ml ethanol-water solvent mixture at different reaction conditions. The water content of the lignin added (2 wt%) is included. Reaction conditions: (circles) 10 g lignin treated at 400 °C for 4 h; (squares) 40 g lignin treated at 350 °C for 0 h [only heating up and cooling down]; (triangles) 10 g lignin treated at 300 °C for 4 h. Error bars represent standard error of the mean.