Large-scale conversion of lignin to liquid through formic acid assisted solvolysis in aqueous and ethanolic reaction media: comparison of yields and product compositions

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Thesis for the degree of Philosophiae Doctor (PhD)
University of Bergen, Norway
2020

UNIVERSITY OF BERGEN

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Date of defense: 17.01.2020

Year: 2020

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Name: Solmaz Ghoreishi

Print: Skipnes Kommunikasjon / University of Bergen

Scientific environment

This thesis, submitted for the degree of Philosophiae Doctor at the University of Bergen, consists of two parts. The first part includes an introduction, an experimental section, a combined summary and discussion of the main results of the research papers presented in the second part, and ends with overall conclusions and suggestions for future work. The second part consists of four research papers and manuscripts.

The main part of the work has been performed at the Department of Chemistry, University of Bergen in the period September 2013–September 2019. Part of the work has been carried out in collaboration with the Chemical Engineering Department (ENTEG) at the University of Groningen and the Department of Chemical Engineering at the University of the Basque Country (UPV/EHU).

This project was partially funded by the Norwegian Research Council (grant no. 190965/S60) and Ltl NOR AS (grant no. 203527/E20). The main feedstock used during this project was provided by SEKAB.

The aim of the work conducted was to investigate the formic acid assisted conversion of lignin to liquid in an aqueous and ethanolic media at 5 L scale. In this context, several reaction conditions, including catalytic LtL-solvolysis, were investigated to identify the critical parameters affecting the large-scale conversion of lignin with respect to product yield and product quality. This approach provided good perspectives for further development of LtL-solvolysis conditions, e.g. investigation of several catalytic formulations. In addition, the large product volume made the investigation and development of various separation, fractionation and upgrading processes possible.

Acknowledgments

First and foremost I would like to thank my supervisor Tanja Barth for her excellent supervision as well as for giving me the opportunity to carry out this PhD. She has always been helpful and has provided invaluable personal and professional support during all my time at the University of Bergen. I would also like to thank my dear colleagues Stian H. Hegdahl, Hilde V. Halleraker and Camilla Løhre and the master students who helped me with the laboratory work, Hailegebrel Derribsa and Dag H. Hermundsgård. A special thanks goes to my dear colleague Andrea E. Carpinteyro Diaz for proofreading this work.

I would further like to thank the staff at the Department of Chemistry, and specially Steinar Vatne for his technical assistance and creative solutions emerging from his workshop, Inger Johanne Fjellanger for her assistance with the elemental analysis, and Terje Lygre and Bjarte Holmelid for the valuable assistance and scientific support with the gas chromatography analysis.

My sincerest gratitude goes to Idoia Hita at the University of Groningen for her productive and interesting collaboration. Working with her has been a real pleasure.

I would also thank my dear friends Mona Riyahi, Lena Kokab and Maziar Poursina for their valuable support and encouragement through this long journey.

Most of all I thank my beloved mom and sister and my dearest Feri. You all have stood by my side through my tedious time at the University of Bergen, beared me with your compassion through all my ups and downs, trusted on me and believed my abilities. I doubt I would have been able to finish this strenuous journey without your love and support.

Abstract

Biomass has recently received much attention as an attractive renewable energy resource and a promising alternative to fossil carbon resources for production of renewable biofuels and other value-added chemicals due to being the only viable feedstock for carbon based fuels and chemicals. Within the biorefinery concept, sustainable use of biomass involves optimal exploitation of all fractions of the raw material to make products with high value. Production of 2nd generation bioethanol from the carbohydrate fraction of non-edible lignocellulosic biomass is already established and the technical feasibility of this process is well demonstrated. However, this process leaves significant amounts of lignin, a cross-linked amorphous copolymer of phenylpropane units with unique properties as by-product.

Lignin is the third most abundant biopolymer as well as the most important source of bio-based aromatics in nature, which accounts for 10–30 wt. % of the feedstock. Thus, the viability of lignocellulosic biorefinery is highly dependent on the development of efficient lignin valorisation routes. Production of value-added chemicals from lignin requires the simultaneous depolymerization of the lignin structures with subsequent hydrodeoxygenation of the lignin monomers and alkylation of aromatic rings to prevent repolymerization and char production. Thermochemical conversion of lignin through Lignin-to-Liquid (LtL) process is an innovative conversion method, which can be considered as a solvolytic process in a liquid or near-critical reaction medium at high temperature and high pressure, using an *in situ* hydrogen donor solvent instead of molecular hydrogen.

The Lignin-to-Liquid process and the chemical composition and bulk properties of LtL-oils produced in small laboratory scale is well developed and there is ongoing research on this approach. However, in case of development towards industrial scale production, the effect of increasing the scale must be investigated and the conversion must be optimized at larger scale. Optimizing process conditions yielding high amount of the desired products is challenging and time-consuming, especially due to the interactions between different experimental conditions. Thus, some important reaction

parameters such as shorter reaction time, lower reaction temperature, and reduction of low-value side stream products, i.e. gas and solid residues, need to be improved in order to make LtL-oils competitive with petroleum-based fuels and chemicals.

The main focus in this thesis was therefore to evaluate the impact of upscaling on LtL-process efficiency in terms of bio-oil yield and bio-oil composition. Lignin conversion conducted at small laboratory scale (0.025 L) was scaled up by a factor of 200 and re-performed using a 5 L stirred reactor to explore the effect of increased volume and stirred reaction on the product yield and product quality. Various reaction parameters were investigated and the relationship between the product yields and reaction conditions were systematically evaluated using principal component analysis (PCA). Additionally, the catalytic conversion of lignin through LtL-solvolysis was explored using two different types of catalysts, an alumina supported noble metal catalyst and an iron-based mineral catalyst.

The overall results showed similar trends relative to reaction parameters at both reaction scales, but oil yields in some cases tended to decrease from small laboratory scale to 5 L scale when using water as reaction medium. The purest lignin feedstocks resulted in highest oil yields at both scales. Comparison of the investigated solvent systems (water vs. ethanol system) showed that the highest oil yields from eucalyptus lignin-rich residue were achieved from the ethanol system at reaction temperatures below 350 °C, indicating a higher tendency for repolymerzation of lignin components to give char formation at elevated temperatures. In addition, a major increase in oil yield and a significantly decrease in char yield was observed as a function of increased stirring rate and increased level of loading in the reactor. Goethite as catalyst did not shown good conversion efficiency, while Ru/Al_2O_3 was found to be very efficient with oil yields above 69 wt. % on lignin intake. Overall, the highest bio-oil yield and a significant low char yield was obtained from experiment Ru/Al_2O_3.S1000.Max.305, indicating that combination of high stirring rate with maximum loading in the reactor in the presence of Ru/Al_2O_3 as catalyst at low temperature is the most optimal condition investigated in this thesis.

The bio-oil comprises a complex mixture of monomeric phenols, aromatics and more hydrogenated products, with a high H/C and a low O/C ratio. However, bio-oils from the ethanol system had higher H/C values due to the incorporation of the ethyl groups, which increased the number of alkyl units in the product. Based on results from GC-MS analysis, there was no clear differences in the composition of LtL-oils from the same solvent system, while ethanol-based experiments generated bio-oils with a more complicated pattern of substitution than water-based experiments. However, concentration of the most abundant compounds identified in each solvent system showed to be mainly dependent on reaction temperature.

Furthermore, the large product volume made it possible to test fractionation ability of the produced bio-oils by means of solid phase extraction (SPE) where 65–92 wt. % of the bio-oils were separated and recovered as polarity-based fractions. The most volatile fractions were then identified using GC-MS analysis, which showed good perspectives for further development.

Moreover, the lignin-enriched eucalyptus residue was investigated as feedstock in a comparative study between a direct one-step hydrodeoxygenation (HDO) and a 2-step hydrothermal liquefaction-hydrodeoxygenation (HTL-HDO) approach using Ru/C and Pd/C as catalysts in terms of product yields, quality and composition of the produced bio-oils. A general observation was that bio-oil yields decreased as a function of increased temperature, while the volatility of the bio-oils as well as total monomer yields increased with temperature. 2-step HTL-HDO significantly improved the total monomer yields while preventing char formation.

The identified compounds comprising the lignin-oils were classified as alkylphenolics, aromatics, naphthalenes, linear and cyclic alkanes, guaiacols, catechols and ketones. Alkylphenolics and aromatics were the main chemical groups identified. However, a significant increase in alkane formation was observed with increased temperature, which can be due to enhanced depolymerization and hydrogenation at more severe temperature conditions. In terms of interesting monomers, the preferred pathways were

the 2-step HTL-HDO of LES using Ru/C at 410 °C, and the direct HDO of LES using Pd/C at 450 °C.

Overall, the results obtained in this project showed that increase in reaction volume was a promising option in terms of product yields and product composition, giving oil yields up to 79 wt. % on lignin intake. However, further studies to map out the optimal experimental conditions towards desired bio-oil yield and bio-oil quality as well as the development of appropriate fractionation methods to separate bio-oil components into fractions with similar chemical properties are the next steps needed to strength the bio-oil potential as a source for platform chemicals.

List of Publications

Paper I. Ghoreishi S., Barth T., Derribsa H. Formic acid assisted liquefaction of lignin in water and ethanol, investigated for a 0.025 and a 5 L batch reactor: Comparison of yields and compositions of the products. *Biomass and Bioenergy* **2019**, 124, 1–12.[I]

Paper II. Ghoreishi S., Barth T., Derribsa H. Stirred and non-stirred lignin solvolysis with formic acid in aqueous and ethanolic solvent systems at different levels of loading in a 5-L reactor. *Biofuel Research Journal* **2019**, 21, 937-946.[II]

Paper III. Ghoreishi S., Barth T., Hermundsgård D.H. Effect of reaction conditions on catalytic and non-catalytic lignin solvolysis in water media investigated for a 5 L reactor. *ACS Omega* **2019**. (Revised version submitted)

Paper IV. Hita I., Ghoreishi S., Barth T., Heeres H.J. A lignin-enriched stillage (LES) as a source for platform chemicals through a liquefaction-hydrodeoxygenation approach. (Manuscript)

Research not within the scope of this thesis:

Halleraker H.V, Ghoreishi S., Barth T. Formic acid's role in Lignin to Liquid solvolysis. (Manuscript ready for submission)

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Abbreviations

BSTFA	Bis(trimethylsilyl)triflouriacetamide
CI	Chemical ionization
CP/MAS	Cross Polarization Magic Angle Spinning
DCM	Dichloromethane
EA	Elemental analysis
EI	Electron ionization
ESI	Electron spray ionization
EtAc	Ethylacetate
FA	Formic acid
FAME	Fatty acid methyl ester
FID	Flame ionization detector
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography mass spectrometry
GPC	Gel permeation chromatography
H/C	Hydrogen to carbon ratio
HDO	Hydrodeoxygenation
HTL	Hydrothermal liquefaction
LtL	Lignin-to-Liquid
MeOH	Methanol
MSD	Mass spectrometry detector
NMR	Nuclear magnetic resonance
O/C	Oxygen to carbon ratio
OVAT	One-factor-at-a-time
PCA	Principal component analysis
PLSR	Partial least square regression
SPE	Solid phase extraction
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TOFMS	Time-of-flight mass spectrometer

Contents

Part I

Chapter 1. Introduction

1.1 Background: from current fossil carbon based energy system to future biomass based energy system

The increasing industrialization and motorization of the world has led to a steep rise in the demand for fossil fuels. Sources of these fossil fuels are becoming exhausted and excessive consumption of fossil fuels to fulfill the energy demand will contribute to greenhouse gas (GHG) emissions and global warming leading to many negative effects including climate change, shrinkage of glaciers, rise in ocean level, loss of biodiversity, etc. [1].

Fossil fuels accounts for more than 80 % of the global energy consumption. However, according to the latest report published by the International Energy Agency (IEA), energy demand worldwide grew by 2.3 % last year, which was the fastest pace this decade. Together, China, the United States and India accounted for nearly 70 % of the increase in energy demand around the world. The United States had the largest increase in oil (1.3 %) and gas (4.6 %) demand worldwide. Global coal consumption rose 0.7 % for a second year in 2018 led by some countries in Asia, such as China, India and a few countries in South and Southeast Asia, due to increased demand for power generation in these countries. Thus, the global coal demand has exceeded 10 Gt, accounting for one third of total CO_2 emissions last year. As a result, global energy-related CO_2 emissions increased by 1.7 % to 33 Gigatonnes (Gt) in 2018, with China, India, and the US accounting for 85 % of the net increase in emissions [2].

Furthermore, our environment and quality of life are affected by the devastating consequences of global population growth. The current world population of 7.6 billion is expected to reach 8.6 billion in 2030, 9.8 billion in 2050 and 11.2 billion in 2100, according to a report launched by United Nations in 2017. It will be increasingly difficult to provide food and energy for such a dense population [3, 4]. Population growth and recent economic developments in many countries all around the world have heightened the need for alternative energy resources, based mainly on renewable,

sustainable, and economically viable energy sources due to environmental concerns, declining availability of fossil fuels as well as increased crude oil prices [5–7].

Sustainable energy means continuous supply of energy for today's needs without compromising the ability of future generations to meet their needs. Sustainable bioenergy production requires comprehensive knowledge and skills for the analysis and design of sustainable biomass production, bioenergy processing, and biorefinery systems [8]. Bioenergy is renewable energy derived from biomass. Utilization of biomass as a renewable and sustainable feedstock has recently received great attention as a promising alternative to fossil resources for production of renewable biofuels and other value-added chemicals [9–11].

The amount of biomass that is technically available for production of bioenergy in the future depends on the evaluation of a variety of social, political and economic factors, e.g. land tenure and regulation, diets, trade and technology. Most of the research projects indicate that from 10 to 245 EJ yr^{-1} bioenergy can be supplied to global primary energy supply by 2050 [9]. Competition between biomass feedstocks as well as their applications is intensified because of increased demand for biomass. Thus, to ensure sustainable use of biomass, we need to know which routes are the most promising for producing heat, power, fuels and materials in terms of their technological, economic and environmental performance [12].

1.2 The ‘‘biorefinery’’ concept

The concept of a “biorefinery” describes all the processes and technologies that are involved in optimal and profitable use of the renewable biological resources, where the incoming raw material is completely transformed into a number of different products [10, 13]. As depicted in figure 1.1, the feasible utilization of biomass in a biorefinery involves taking advantages of all fractions of the biomass to make products with high value to ensure economic sustainability [10, 14]. Products from bioenergy systems, biofuels, can be deployed as solid, liquid and gaseous fuels in a wide range of applications, including transport, heating, electricity production, and cooking [9].

Biofuels have become one of the most strategically important sustainable fuel sources and are considered as an alternative to fossil fuels and future leading supplier of energy sources. Biofuels have the ability to increase the security of supply, reduce the vehicle emissions and provide a steady income for farmers [1].

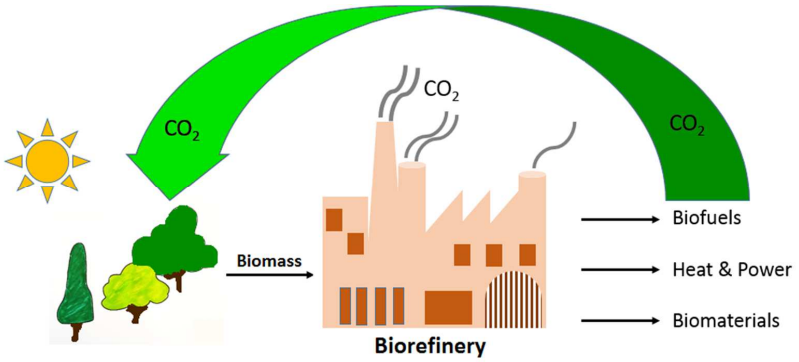


Figure 1.1. Graphical illustration of an integrated biomass-biofuel-biopower-biomaterial cycle.

The greatest challenge in biofuel area is to produce renewable liquid fuels that are suitable for use in motor vehicles. Produced fuels from renewable sources should preferably be compatible with the existing motor technology and infrastructure. This means direct substitution and mixing of conventional and renewable fuel types would be possible [10]. Bioethanol, biodiesel (FAMEs), and biogas are well-known examples of renewable and petroleum compatible first-generation biofuels. Crops such as sugar cane (in Brazil), wheat (in Europe) and corn (in USA) are used as feedstocks in production of first-generation bioethanol. However, there is tow major challenges within the large-scale production of first-generation bioethanol; (1) it is a huge challenge to achieve the economically equivalence between the cost of bioethanol production and the cost of oil-refining and petrochemical processing, and (2) use of edible crops for the production of bioethanol leads to competition between food industry and bioethanol production. The latter point can be assumed as the greatest disadvantage of first-generation biofuels since the competition between food industry and bioenergy production can lead to increased energy crops, fuel and food prices [15].

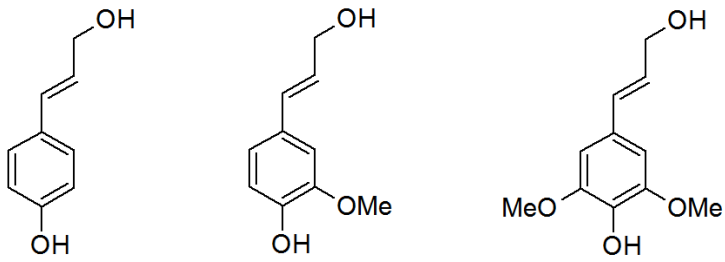
Thus, due to the limitations with first-generation biofuels, many efforts have been carried out to develop new processes for the production of second-generation biofuels

from a variety of non-edible biomass. The production and storage of biofuels and bulk chemicals from the lignocellulosic biomass which is abundant, sustainable and renewable has been considered to be an outstanding option as a biorefinery feedstock due to low cost and carbon neutrality [16–19]. Lignocellulosic biomass, found in forest and agriculture residues, has shown to be a beneficial platform for the production of second-generation biofuels and bio-based chemicals [9]. Lignocellulosic biomass is a heterogeneous feedstock composed of three basic polymeric components: cellulose (40–50 wt. %), hemicellulose (15–25 wt. %) and lignin (15–35 wt. %) [17, 20]. In many biorefinery concepts, the carbohydrate fraction of biomass (cellulose and hemicellulose) is converted to bioethanol trough the well-established lignocellulosic-to-ethanol process, leaving behind lignin as waste [17, 21, 22]. Since the high cost of cellulosic ethanol has limited its market, it would be essential for the overall process economy to develop an efficient and appropriate thermochemical method/catalytic technology for conversion of waste lignin streams into fuels and specialty chemicals, such as aromatics, phenols, aromatic ethers, vanillin, etc. However, the conversion technology of lignin is still lagging behind [17–19].

Another aspect to be considered is that increased demand for bio-based products and biopower can lead to changes in land-use and may put pressure on biodiversity. Changes in land-use may occur for direct and indirect reasons. Direct land-use change occurs when bioenergy crops replace other crops or forests. Indirect land-use change occurs when the implementation of bioenergy causes the expansion of green areas [9]. The negative impacts of bioenergy implementation on land-use changes can be mitigated by reducing land demand for food, fiber and bioenergy production, and creating synergies between different land-use systems using adapted feedstocks, e.g. cultivating of hardy plants on degraded lands that are not suitable for conventional food crops [9].

1.3 Lignin

The third major constituent comprising lignocellulosic biomass, i.e. lignin, is a cross-linked amorphous copolymer consisting of three main aromatic units; *p*-coumaryl alcohol (H-lignin), coniferyl alcohol (G-lignin) and sinapyl alcohol (S-lignin) units (figure 1.2), which are bonded together through different C-O-C and C-C linkages depending on the biomass source and processing conditions. The most frequent coupling linkage in lignin structure is the β-O-4-aryl ether bond accounting for 46 % of the bonds existing in softwood and 60 % of the bonds found in hardwood [4, 22, 23].



(a) (b) (c)

Figure 1.2. The three monolignols comprising lignin: (a) p-coumaryl (H-lignin), (b) coniferyl (G-lignin) and (c) sinapyl (S-lignin) alcohols.

Lignin is the most abundant renewable source composed of aromatic units in nature, which accounts for 23–33 % of the mass of softwoods, 16–25 % of the mass of hardwoods and 15–25 % of the mass of grasses and carries the highest specific energy content compared to cellulose and hemicellulose. Furthermore, composition of lignin varies from species to species, tree to tree, and even in woods from different parts of the same tree. For instance, hardwood lignin contains a mixture of guaiacyl and syringyl units, softwood lignin contains more guaiacyl units, while grass lignin is a mixture of all three aromatic units. The role of lignin in all higher vascular plants is to provide the plant rigidity and water-impermeability and protects hemicellulose and cellulose against chemical and microbial decay to a large extent [4, 21–24].

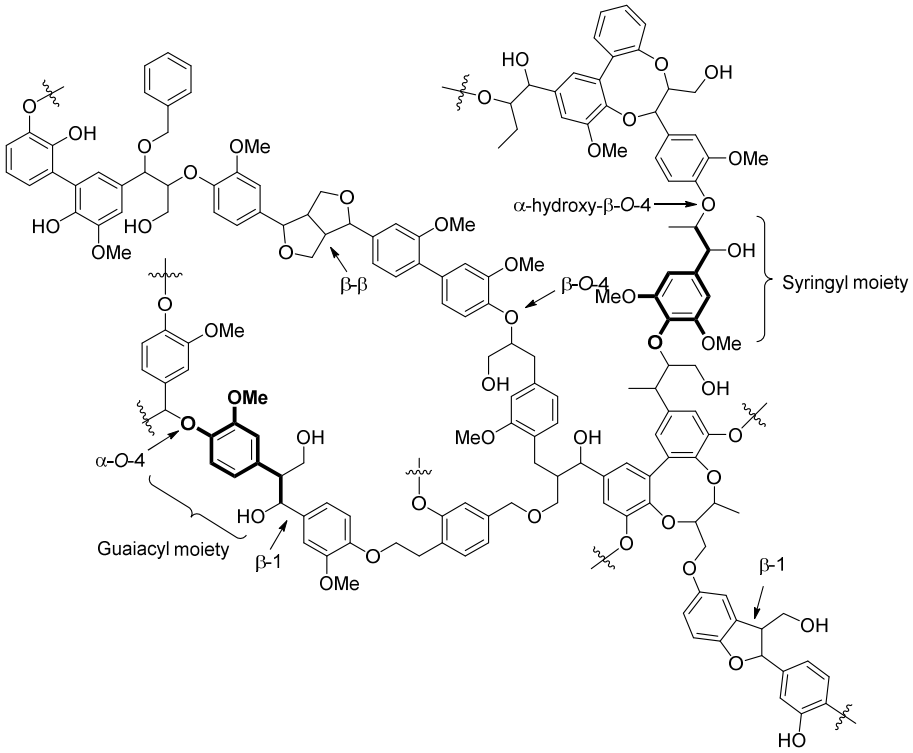


Figure 1.3. Schematic representation of a typical softwood lignin macro structure. Figure is reprinted from "Reactivity and reaction pathways in thermochemical treatment of selected lignin-like model compounds under hydrogen rich conditions" by Holmelid et al., 2012, Journal of Analytical and Applied Pyrolysis, 98, 37–44 [25]. Lisence by © 2012 Elsevier B.V.

Lignin is a low-cost, wide- spread renewable by-product from pulp- and paper and bioethanol production. At present, it is mostly burned as low value fuel for process energy purposes and only approximately 2 % is used commercially [26].

1.4 Isolation methods and lignin types

The nature and structure of lignin is determined by the pretreatment method used for isolation of lignin. Various technologies involving physical, chemical, physiochemical and biological processes have been used for pretreatment of lignocellulosic biomass. Physical pretreatment involves mechanical processes such as milling and grinding to reduce particle size and increase surface area as well as methods such as high energy

radiation to enhance the digestibility and solubility of lignocellulosic biomass. Chemical pretreatment involves acid and alkaline hydrolysis processes, in addition to methods such as solvent fractionation (organosolv) and oxidative delignification. Physiochemical pretreatment methods involve processes such as steam explosion, ammonia fibre explosion, torrefaction and CO_2 explosion. Biological pretreatment includes degradation of biomass employing microorganism, e.g. fungi, through processes such as enzymatic hydrolysis based on their enzymatic system [27, 28].

This section gives a detailed overview of the most common processes used for isolation of lignin, in which the methods employed for the extraction of the lignins used in this dissertation were of more interest. Biomass pretreatment methods that were of less interest such as mechanical methods, oxidative delignification, ammonia fibre explosion, torrefaction, CO_2 explosion and biological methods are not considered.

The most common pretreatment processes can be broadly divided into two major groups. The first group includes methods such as acid and enzymatic hydrolysis and steam explosion, in which cellulose and hemicelluloses are dissolved and removed, leaving lignin as insoluble residue. The second group includes processes such as alkaline hydrolysis and solvent fractionation (organosolv), in which lignin is dissolved and removed, retaining cellulose and a portion of hemicelluloses in solid fraction. Lignin available as by-product from lignocellulosic bioethanol production belongs to the first category, while lignin from the pulp and paper industries, commonly known as kraft lignin, sometimes also called alkali lignin belongs to the second category [22].

1.4.1 Enzymatic hydrolysis

Enzymatic hydrolysis of biomass is typically performed after a first dilute acid hydrolysis or steam explosion step. Cellulolytic enzymes, known as cellulases, are used to convert the insoluble cellulose to soluble sugars through hydrolysis of the β-1,4 glucosidic linkages in cellulose. This process occurs at mild conditions (pH 4.8 and temperature 45–50 °C) and includes three steps: (1) adsorption of cellulase enzymes onto the surface of the cellulose, (2) the biodegradation of cellulose to fermentable

sugars, and (3) desorption of cellulose [27, 29]. However, the enzymatic digestibility for hydrolysis and fermentation of native biomass are influenced by the feedstock composition and structure. The crystalline structure of cellulose, which is protected and sheathed by lignin and hemicellulose, along with its accessible surface area and the heterogeneity of biomass particles all contribute to the recalcitrance of lignocellulosic biomass to hydrolysis [30].

1.4.2 Acid hydrolysis

The acid fractionation method is divided into dilute and concentrated acid hydrolysis depending on the concentration of the acid used in the process. Pretreatment of lignocellulosic biomass using dilute and concentrated acid is among the most effective fractionation methods. Different types of inorganic and organic acids have been used in this process, but sulphuric acid and hydrochloric acid are the most common acids used. During the acid hydrolysis, hemicelluloses are the first constituents of lignocellulosic biomass that are broken down to their monomers, xylose and other 5-carbon and 6-carbon sugars, followed by break down of xylose to furfural [27].

Concentrated acid hydrolysis is normally conducted using concentrated inorganic acids, e.g. H_2SO_4, H_3PO_4 and HCl, at temperatures below 160 °C. Concentrated acids are powerful agents for cellulose hydrolysis, and therefore no enzymes are needed after the acid hydrolysis. However, concentrated acids are toxic, corrosive, hazardous, and thus require recators that are resistant to corrosion. Since this process requires large amounts of acids, the concentrated acid must be recycled to make the process economically viable [27, 29].

A well-established concentrated acid hydrolysis, which has been tested in our research group, is the so-called Weyland acid hydrolysis. In this method, the feedstock is mixed with an acid solution consisting of 46.67 wt. % H_2SO_4, 23.33 wt. % H_3PO_4 and 30 wt. % H_2O, and then the mixture is stirred for 1 hour at 40 °C. After 1 hour with stirring, the mixture is diluted with cold water to adjust the acid content to 3 wt. % sulfuric acid and is stirred for further 10 minutes. Then, the mixture is filtered, and the filter cake is

again mixed with water to adjust the sulphuric acid content to 3 wt. %. The solution is then transferred to an autoclave and is heated for 2 hours at 120 °C. After heating, the lignin is filtered and washed with water to remove sugar residues. The resulting filter cake consists of lignin, some unhydrolyzed cellulose and extractives [31].

Dilute acid hydrolysis has been considered to be among the most effective and most promising pretreatment technologies that can enhance biomass sugar release performance [32]. This process uses less severe conditions and achieves high xylan to xylose conversion yields [29]. During the dilute acid hydrolysis, only hemicelluloses are completely converted to their monomers and organic compound (e.g. furfural and HMF), while cellulose and lignin remain unaffected. There are two types of dilute acid pretreatment processes that are generally carried out using low acid concentration (< 4 wt. %): (1) a high temperature (T > 160°C), continuous-flow process for low solids loading (5–10 wt. % substrate concentration), and (2) a low temperature (T < 160°C), batch process for high solids loading (10–40 wt. % substrate concentration) [27, 32, 33].

1.4.3 Steam explosion

Steam explosion refers to a physiochemical pretreatment technique, where breakdown of lignocellulosic biomass structure is carried out using high-pressure saturated steam. This process is composed of two main stages. In the first stage, the biomass is treated with steam at high temperatures (between 160 °C and 260 °C) and pressures (10–48 bar) for several seconds to a few minutes. The biomass/steam mixture is held for a period of time to promote hemicellulose hydrolysis. Then, in the second stage, the pressure is reduced rapidly and the process is terminated by an explosive decompression. Combined effects of both stages include modification of the physical properties of the material, hydrolysis of hemicellulose and modification of the lignin structure. Furthermore, the sudden pressure drop defibrillates the cellulose bundles that increases the potential of subsequent hydrolysis of cellulose into fermentable sugars. Lignin is removed only to a limited extent during the pretreatment but is redistributed

on the fiber surfaces as a result of melting, and thus can be later recovered as the solid residue from the combination of the steam explosion and hydrolysis process [27, 33].

1.4.4 Alkaline hydrolysis

Alkaline treatment of woody biomass also known as kraft pulping is the most common chemical process used for the fractionation of lignocellulosic biomass. The general principle behind this process is the removal of lignin remaining cellulose and a portion of hemicelluloses in the solid fraction [27]. Some bases can be used for pretreatment of lignocellulosic materials and the effect of alkaline pretreatment depends on the lignin content of the materials. Alkali pretreatment processes utilize lower temperatures and pressures than other pretreatment technologies [29, 33]. In this process, wood is heated in the presence of sodium hydroxide or sodium sulphide at temperatures above 150 °C for several hours [27]. Kraft treatment cleaves the α-ether linkages between lignin and hemicelluloses and the ester bonds between lignin and/or hemicelluloses [34]. Traditionally, the lignin is precipitated from black liquor by neutralization using CO_2 gas. The precipitated lignin is then dissolved in acidified water (using sulphuric acid) to remove the remaining sodium from the lignin [27]. Kraft lignin is hydrophobic, has a lower molecular weight compared to the original lignin and has low sulphur content [21].

1.4.5 Solvent fractionation/organosolv

In the organosolv process, the biomass is treated with an organic solvent or a mixture of an organic solvent and water to remove lignin before enzymatic hydrolysis of the cellulosic fraction. A variety of organic solvents including methanol, ethanol, acetone, ethylene glycol, triethylene glycol and tetrahydrofurfuryl alcohol have been used in this process. Organic acids such as oxalic, acetylsalicylic, and salicylic acids can also be used as catalysts [27, 29, 33]. This process is conducted at high temperatures (up to 200 °C). Organosolv fractionation typically results in more than 50 % lignin removal through hydrolysis of interunit ether linkages in lignin (β-O-4) and lignin-carbohydrate bonds and subsequent solubilization in the organic solvent. Lignin obtained from

organosolv fractionation has a less modified structure than Kraft lignin and is sulphur-free with low molecular weight and of high purity. After pretreatment, lignin is isolated and recovered by acid precipitation. However, only Alcell® and Organocell lignins are commercially available [24, 35, 36].

1.5 Thermochemical conversion of lignin

Thermochemical conversion of lignin or lignin-rich residues to produce value-added functional materials has recently attracted increasing attention [37]. Various thermochemical processes [38] such as pyrolysis or catalytic pyrolysis [39], liquefaction [40], gasification [41], solvolysis [6, 13, 42] and hydrogenolysis [43] are among the most interesting concepts investigated in this respect.

1.5.1 Pyrolysis

Pyrolysis is the thermal decomposition of biomass in the absence of oxygen, where the potentially volatile components of biomass or lignin are converted into gaseous (mainly consisting of CO, CO_2, H_2, CH_4, C_2H_6 and C_2H_4), liquid (pyrolysis oil) and solid (char) products. An increase in the severity of the treatment will increase the efficiency of biomass degradation to low-molecular weight components. However, pyrolysis of lignin is a complex process and is affected by several factors, such as the feedstock type, heating rate, reaction temperature, additives, etc. [22, 23]. Thus, depending on the reaction temperature and heating rate, pyrolysis can be divided into three different processes: slow pyrolysis, fast pyrolysis and flash pyrolysis. Slow pyrolysis of biomass, also defined as conventional pyrolysis of biomass, occurs under slow heating rate and is associated with production of charcoal. While, fast pyrolysis is associated with production of 60–75 wt. % of liquid bio-oil, 15–25 wt. % of solid char, and 10–20 wt. % of non-condensable gases, depending on the feedstock used. However, the conversion of biomass to bio-oil through flash pyrolysis has shown to have an efficiency of up to 70 wt. %, depending on the biomass and operating conditions used [23, 44, 45]. The pyrolysis oil from fast and flash pyrolysis of biomass has a high content of oxygen, including water and water-soluble components, and is not miscible

with petroleum-based liquids. In addition, the oil is very acidic and corrosive and chemically unstable over time and has a very high viscosity and a low pH [10]. However, use of proper catalyst and conditions during biomass pyrolysis have shown to improve the quality of bio-oil, making this bio-oil more stable than bio-oil from fast pyrolysis [46].

1.5.2 Liquefaction

Liquefaction is also a thermochemical process to convert biomass to biofuel. Biomass is reacted in liquid water at a temperature of 300–400 °C and high pressure (120–200 bar). In the liquefaction process, macromolecule compounds in biomass depolymerize and decompose into fragments of low-molecular weight. These fragments are unstable and reactive, and repolymerize into oil products of different molecular mass distribution. Hydrothermal liquefaction produces bio-oils with low residual water content and high heating value. The major reactions involved during hydrothermal liquefaction are hydrolysis, pyrolysis, solvolysis, depolymerization, decarboxylation, hydrogenolysis and hydrogenation [12, 27, 47, 48].

1.5.3 Gasification

Thermal conversion of lignocellulosic biomass into gases through incomplete combustion at high temperature (800–900 °C) and limited access to oxygen is called gasification. The major products from lignin gasification include CO, CO_2, H_2 and CH_4. Some char and tars can also be formed. Biomass gasification is typically followed by a Fischer-Tropsch process, in which a mixture of hydrogen and CO (syngas) is converted into hydrocarbons and other various products, such as diesel and other chemicals via polymerization reactions [22, 27, 38].

1.5.4 Hydrodeoxygenation

As described in section 1.5.1, pyrolysis-oil has high oxygen content and is highly unsaturated, which makes the bio-oil thermal and chemical unstable. Hence, this bio-

oil must be upgraded to total or partial elimination of oxygenates and unsaturated degree, before it can be used as conventional liquid transportation fuel [46]. Hydrodeoxygenation is considered as a paramount process for upgrading of bio-oil, but is also utilized in the direct conversion of lignin. HDO involves removal of oxygen in form of water and/or carbon oxides under a high pressure of hydrogen resulting in an increase in H/C ratio and a decrease in O/C of the bio-oil [21, 49].

Since bio-oil from catalytic pyrolysis has lower oxygen content compared to bio-oil from fast pyrolysis, an advanced biofuel production process can be proposed, where biomass is first converted into stable bio-oil by catalytic pyrolysis and then this bio-oil is hydrodeoxygenated into hydrocarbon biofuel. However, it is not clear that if the hydrodeoxygenation of bio-oil derived from catalytic pyrolysis will be easier than bio-oil from fast pyrolysis [46].

In general, hydrodeoxygenation of lignin proceeds through two main pathways: hydrogenation−deoxygenation (through prehydrogenation of the aromatic ring leading to cycloalkenes and cycloalkanes) or direct deoxygenation (involving direct C–O bond cleavage yielding aromatic products) [49]. Recent studies have published results from a novel one-step lignin liquefaction process based on reductive depolymerization of lignin at temperatures above 300 °C with the participant of formic acid as an *in situ* hydrogen donor that facilitate the HDO of lignin into low-oxygen content fuel and monomeric phenols. This method has provided a liquid product, so-called bio-oil, with significant lower oxygen content and higher carbon yield compared to bio-oil from conventional pyrolysis [10, 13, 50–53].

1.5.5 Lignin-to-Liquid

In 2008, Kleinert and Barth reported an innovative conversion method for reductive conversion of lignin termed Lignin-to-Liquid (LtL). The LtL-process can be considered as a thermochemical solvolytic process that comprises simultaneous depolymerization of the lignin structures with subsequent hydrodeoxygenation of the lignin monomers in a polar solvent such as water and alcohols at high temperature and high pressure.

Lignin-to-Liquid conversion involves the use of a hydrogen donor solvent instead of molecular hydrogen.

A well-known hydrogen donor is formic acid. In the reductive conversion of lignin, formic acid has been proved to be more reactive than molecular hydrogen [54]. During the LtL-process, formic acid is converted *in situ* to molecular hydrogen and CO/CO_2 creating a reductive environment. However, the formic acid acts not only as an *in situ* hydrogen source, but also as assists in the depolymerization of the lignin molecule, and thus results in higher oil yields than comparable reactions with H_2 as reductant. Based on recent studies, the decomposition of formic acid and the chemical reaction between lignin and formic acid are competing reactions, thus a formylation–elimination–hydrogenolysis mechanism for the formic acid aided lignin conversion is proposed [10, 52, 53].

Various type of solvents, including water, methanol, ethanol and isopropanol, have been tested to create a more homogeneous reaction environment and enhance the mass and heat transfer. However, commonly used solvents are water and ethanol. Water has shown to be a promising reaction solvent due to low cost, green nature and its availability. However, water does not have the ability to solubilize most of the lignin types. Ethanol is also considered as one of the most promising reaction solvent alternatives due to its good solvent properties for biomass and low critical temperature.

As shown in figure 1.4, the product from solvolytic conversion of lignin consists mainly of a liquid, a gaseous and an organic solid phase. Depending on the reaction solvent used, the liquid fraction consist of (i) a well-separated mixture of a dark brown organic top layer and an aqueous bottom layer (for water system), or (ii) only a dark brown organic phase (for ethanol system). The liquid organic phase is a bio-oil with a high H/C and a low O/C ratio relative to the starting feedstock that comprise a complex mixture of monomeric phenols, e.g. phenol, cresol, guaiacol, catechol, etc., and more hydrogenated products, e.g. low molecular weight hydrocarbons, esters and ketones that are believed to be derived from the bridging units of the polymer along with the solvents.

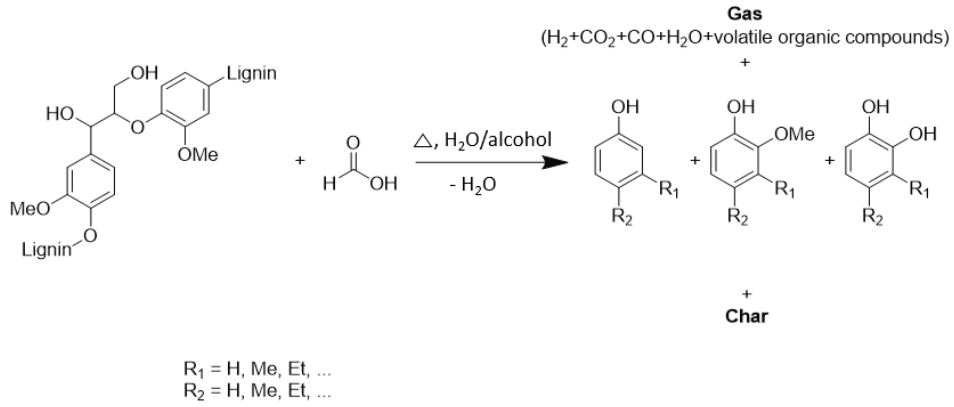


Figure 1.4. A simplified schematic overview of the Lignin-to-Liquid conversion route and its degradation products.

The properties of a good quality oil can be defined as high energy content, high stability, low viscosity, high H/C and low O/C ratio and low average molecular weight. The bio-oil produced in the LtL-process compared to pyrolysis-oil has a lower oxygen content, is much less polar and acts as a solvent that makes it miscible with petroleum-based fuels. The Van Krevelen diagram in figure 1.5 depicts the H/C and O/C ratios of different biomass and fossil materials. A high H/C and a low O/C value is ideal for the bio-oil. However, the higher quality of the LtL-oils over flash pyrolysis-oils is evident. In addition, the similarity between the LtL-oils and petroleum-based oil is also evident [10, 50].

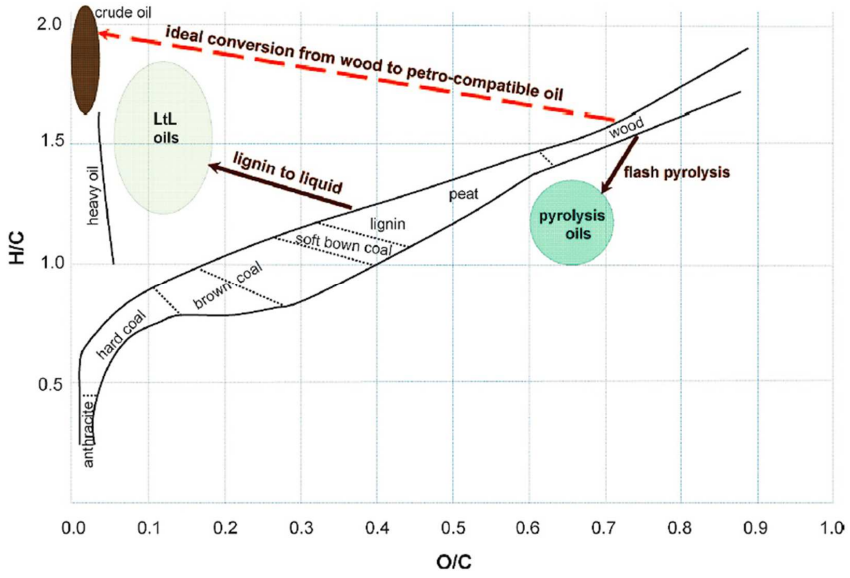


Figure 1.5. Van Krevelen diagram showing the H/C vs O/C ratios of different biomass and fossil materials. The arrows indicate conversion pathways for the flash pyrolysis and the Lignin-to-Liquid process as well as the "ideal" theoretical conversion from wood to crude petroleum (dashed arrow). Figure is reprinted from "Towards a Lignincellulosic Biorefinery: Direct One-Step Conversion of Lignin to Hydrogen-Enriched Biofuel" by Kleinert and Barth, 2008, Energy & Fuels, 22, 1371–1379 [10]. Lisence by © 2008 American Chemical Society.

Within a biorefinery, the integration of conversion optimization with the achievement of the desired product composition are key issues. The major challenge in developing an appropriate process for lignin conversion is to obtain high amounts of good quality oils while decreasing the reaction temperature, time and the amount of low-value side products, i.e. gas and solid residues. However, this kind of process optimization will be time-consuming due to the interactions between different experimental factors. Nevertheless, there is ongoing research on this approach, and a number of papers have been published addressing subjects such as reaction mechanisms [25, 52], kinetic modelling [55], and the effect of catalyst to increase energy efficiency [13, 56]. Most of the reported results have been obtained at small laboratory scale though. Thus, in the next step, upscaling towards industrial production scale is necessary. In addition, the effect of upscaling must be investigated, and the large scale conversion needs to be optimized.

1.6 Objectives of the thesis

The aim of this thesis is to systematically explore the role of upscaling on lignin conversion efficiency, to investigate the effect of different reaction parameters on lignin solvolysis and to evaluate product quality based on the product composition. A major objective of this thesis is to compare results obtained from laboratory scale (0.025 L) with results from 5 L pilot scale. In this context, all experiments done in laboratory scale (0.025 L) is multiplied by a factor of 200 and performed in a 5 L pilot scale to investigate whether the effect of the reaction variables are similar for the different reactors. Unlike the 0.025 L reactor, the 5 L reactor is equipped with a stirrer, which can improve the mass transfer in the system and give a faster reaction.

Another main focus in this thesis is to investigate the potential of a lignin-rich residue resulting from a mild acid pretreatment followed by an enzymatic hydrolysis of eucalyptus in the LtL-solvolysis at 5 L pilot scale. Then, the relationship between the yields and reaction conditions are systematically explored using principal component analysis (PCA). Another major objective is to explore the use of catalysts in the Lignin-to-Liquid conversion at 5 L scale.

Furthermore, a comparative study between a direct one-step hydrodeoxygenation (HDO) and a 2-step hydrothermal liquefaction-hydrodeoxygenation (HTL-HDO) approach (using Ru/C and Pd/C catalysts) has been assessed in terms of product yields, quality and composition of the produced bio-oils. This study is a collaborative work between the University of Bergen, the University of Groningen and the University of the Basque Country.

Basic studies on the fractionation of the bio-oils are also investigated (using solid phase extraction (SPE)) to separate and identify the volatile low molecular weight oil components from the heavier non-volatile fraction of the bio-oils.

Chapter 2. Experimental procedures & methods

This chapter introduces the general Lignin-to-Liquid experimental procedures and main analytical methods and tools used throughout this thesis. In the experimental section, the LtL-process and work-up procedure is described for both laboratory scale and 5 L scale. Additionally, a short description of the technique used for fractionation of the bio-oils, i.e. solid phase extraction (SPE) is also given. The main topics described in the method section includes techniques employed for chemical characterisation of the resulting products from the thermochemical conversion of lignin, including elemental analysis (EA) and gas chromatography provided with mass spectrometry detection (MSD) and flame ionization detector (FID) as well as tools employed for statistical evaluation of LtL-solvolysis results such as principal component analysis (PCA) and partial least square regression analysis (PLSR). Less central techniques and characterisation methods such as silylation, gas phase analysis, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), Fourier Transformed Infrared spectrometry (FT-IR) and solid-state ^{13}C Nuclear Magnetic Resonance spectrometry (CP/MAS ^{13}C NMR) are described in the individual papers in part II of this thesis.

2.1 Experimental procedures

In all cases, the Lignin-to-Liquid experiments were performed in a stirred 5.3 L high pressure autoclave reactor from ESTANIT GmbH (see figure 2.1A). In addition, half of the LtL-experiments presented in paper I were conducted in a non-stirred 0.025 L stainless steel high pressure Parr reactor from 4742-series (see figure 2.1B). Furthermore, the catalytic hydrotreatment experiments performed at the University of Groningen were carried out in a 0.1 L stainless steel high pressure Parr reactor, which has been equipped with a Rushton-type turbine. A detailed description of the applied reaction conditions and the amount of reactants are given in the *Experimental section* of each paper.

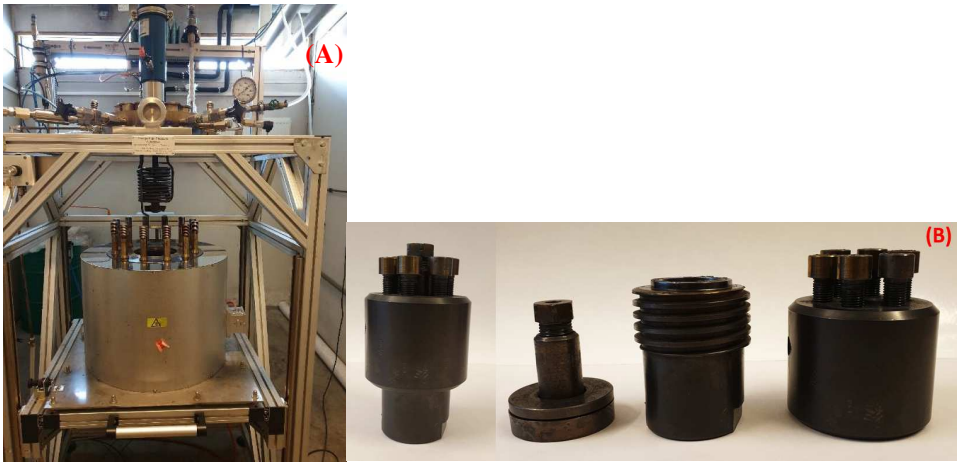


Figure 2.1. (A) High pressure 5 L pilot reactor, (B) High pressure 0.025 L Parr rector (assembled and disassembled).

2.1.1 Experimental set-up

- ***Experiments carried out at the University of Bergen***

5 L scale; Lignin, formic acid, the solvent (distilled water or ethanol) and in some cases catalyst (Ru/Al_2O_3 or goethite) were added into the reactor. The autoclave was then closed and heated to the desired temperature with an approximate heating rate of 5 °C min^{-1} under specific stirring condition. Reaction time was measured in addition to the heating period from room temperature to the desired temperature. The pressure and torque of the stirrer were continuously monitored during the experiment.

Laboratory scale (0.025 L); Briefly summarized, Lignin, formic acid and the solvent (water or ethanol) was added into the reactor. The Parr reactor was then closed directly and heated in a preheated Carbolite high temperature oven to the desired temperature with an approximate heating rate of 20 °C min^{-1}. The heating period was included in the reaction time.

- ***Experiments carried out at the University of Groningen***

In all the experiments, the reactor was loaded with either ball-milled lignin-rich eucalyptus residue (direct HDO) or LtL-solvolysis oil (HTL+HDO approach) and catalyst (Ru/C or Pd/C). After loading the reactor, it was flushed several times with H_2 to expel air, and then pressurized to 180 bar for a leak test at room temperature. Subsequently, the H_2 pressure was set at 100 bar and stirring was started at 1200 rotation per minute (rpm). After that, the reactor was heated up to the desired reaction temperature at an approximate rate of 10 °C min^{-1}, and reaction time was measured in addition to the heating period. During the experiment, the pressure and torque of the stirrer were continuously monitored online.

2.1.2 Sample work-up

- ***Experiments conducted at the University of Bergen***

5 L scale; After the completed reaction time, the reactor heater was turned off and the reactor was cooled to ambient temperature by flowing cold water through the reactor's cooling coil. The final products after the LtL-process included a gas phase, a liquid phase and a solid phase. A small amount of the produced gases was collected in a gas bag and analysed by gas phase GC before venting the rest. After opening the reaction container, the liquid phase was separated from the solid phase by opening the valve on the container bottom. Then a mixture of EtAc:THF (90:10 v:v) was added to the reactor container to extract the organic phase from the solid phase (unreacted lignin and reaction products (and catalyst if used)).

In the ethanol system, the liquid phase consisted of two immiscible layers; a dark brown LtL-oil phase and a small clear ethanol/water phase. The two layers were separated using the same work-up procedure as in the water system to ensure compatibility and reproducible results.

The organic phase was dried over Na_2SO_4, and solvents and unreacted ethanol were removed from the LtL-oil on a rotary evaporator at reduced pressure (175 mbar was

set as standard pressure to avoid any inconsistencies about the work-up procedure between the solvent-systems) at 40 °C to yield a dark brown liquid. The yields were determined by mass and the bio-oil fraction and char was characterized by several analytical techniques as described in section 2.2.

Laboratory scale (0.025 L); After the completed reaction time, the reactor was taken out of the oven and cooled in an air stream to ambient temperature. Just like at 5 L scale, the final products after the LtL-process included a gas phase, a liquid phase and a solid phase. The amount of produced gas phase was determined by weighting the reactor before and after venting the gas phase. After opening the reaction container, the liquid reaction mixture was extracted with a mixture of EtAc:THF (90:10 v:v) and the solid phase (unreacted lignin and organic solid products) was filtered. Two well-separated liquid phases were obtained (an organic phase on the top and an aqueous phase on the bottom). They were separated by decanting, and the organic phase was dried over Na_2SO_4 and concentrated using the same procedure as in 5 L scale. The yields were determined by mass, and the same analysis were done for the oil fraction and char in laboratory scale as in 5 L scale. A simplified flow chart of LtL-solvolysis sample work-up procedure is displayed in figure 2.2.

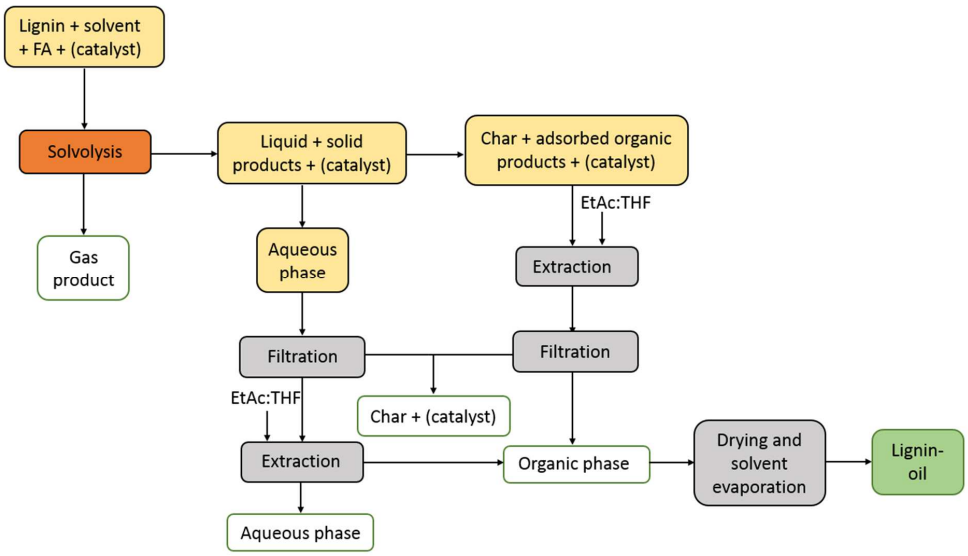


Figure 2.2. A simplified flow chart for the LtL-solvolysis sample work-up procedure.

➢ ***Experiments conducted at the University of Groningen***

Upon the completion of the determined reaction time, the reactor was turned off and the reactor was cooled down to room temperature and the pressure at room temperature was recorded allowing determination of the total amount of H_2 consumed during the reaction. Gas products were collected in a 3 L Tedlar gas bag to determine its composition. After reaction, an aqueous phase and an organic phase (bio-oil) were obtained. The bio-oil and aqueous phase were easily separated from the rest of the products by decantation. After that, a solvent wash was used to recover the remaining organic products absorbed on the solid phase. The procedure involved treatment of the solid phase with dichloromethane (DCM) and acetone, from where organic DCM and acetone soluble phases were obtained, respectively. The remaining solid fraction (consisting of char formed during the reaction and catalyst) was dried and the yields (bio-oil and char) were determined by weight. Then, for the identification of individual components in the lignin oil, gas chromatography analyses were performed. Figure 2.3 depicts a simplified schematic overview of the lignin hydrotreatment work-up procedure.

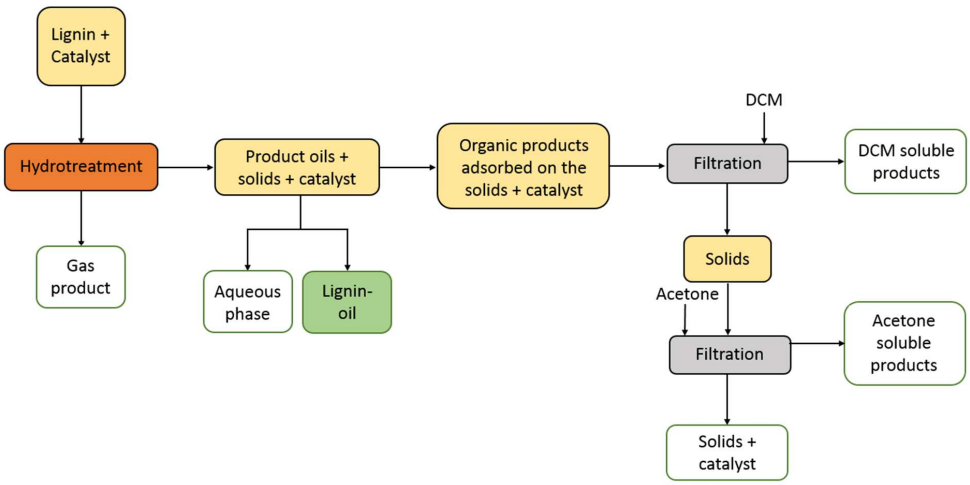


Figure 2.3. A simplified flow chart for the lignin hydrotreatment work-up procedure.

2.1.3 Solid phase extraction

In paper III of this thesis, normal phase chromatography separation has been applied using a column material consisting of silica modified with cyanopropyl groups, which is more suitable than silica and C18 columns for separation of lignin-derived compounds due to its intermediate polarity.

A very small amount of the LtL-oil was dissolved in DCM: MeOH (93:7 v:v). The SPE column was wetted with the first eluent before the dissolved oil sample was gently applied to the top of the column material. Then, the column was placed on top of the SPE vacuum manifold by Supelco Visiprep^{TM}, the extraction vacuum was kept on 20 mHg and the flow rate through the column was adjusted to 0.3 cm^3 per minute (see figure 2.4). Three different eluents were used in increasing polarity order. The different fractions were collected in sample vials, concentrated and then weighted. Furthermore, fraction 2 and 3 were prepared for GC-MS analysis. A more detailed description about the eluents used and sample preparation for GC-MS analysis (silylation) is given in paper III.

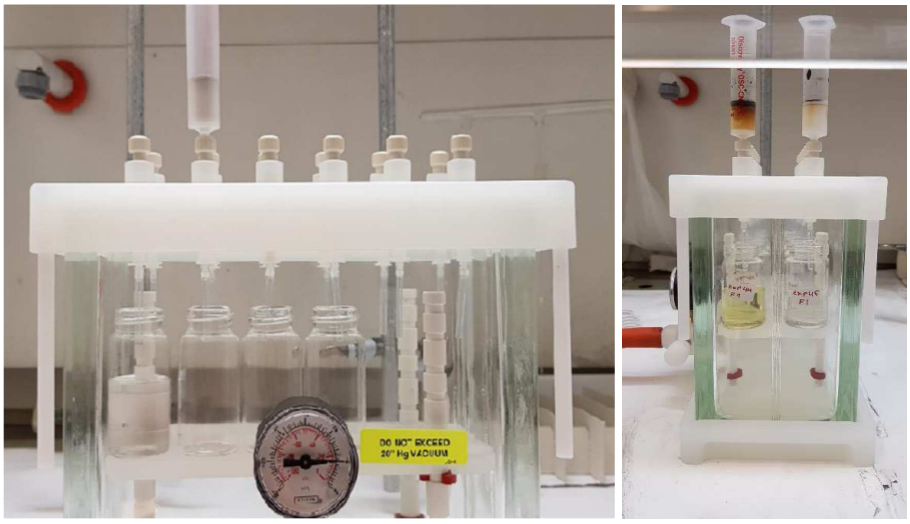


Figure 2.4. Supelco Visiprep^{TM} apparatus together with the CN column used for Solid phase extraction of bio-oil samples.

2.2 Product characterisation

In this section, the major characterisation techniques used in this study are described. Identification studies are performed both qualitatively and quantitatively on products from LtL-solvolysis.

2.2.1 Elemental analysis

This technique was employed to determine the elemental composition of feedstocks, bio-oils and solid products by measuring mass contribution of elements such as C, H, N, and O (by difference). The S content was not considered in this thesis. The samples were placed in an oven and combusted in the presence of oxygen excess at temperatures above 1000 °C. During the combustion, C, H, N and (S) elements were converted to their oxidized form, mainly CO_2, H_2O, O_2, NO_x and SO_x gases in addition to molecular nitrogen, N_2. Helium worked as the carrier gas and tungsten trioxide inside the combustion unit worked as a catalyst in order to bind alkaline or earth alkaline elements and to avoid non-volatile sulfates. Later, NO_x and SO_x gases were reduced into N_2 and SO_2, respectively. Thus, the remaining gas stream consisted of CO_2, H_2O, SO_2 and N_2, which were separated in specific adsorption columns and analysed by a thermal conductivity detector (TCD) [57].

This method can confirm the substantial reduction in oxygen content from lignin to bio-oil caused by hydrodeoxygenation of lignin during the LtL-solvolysis. A reduction in the oxygen content from lignin to bio-oil is necessary to increase the heat value of lignin-oil if the main application for this bio-oil is to be utilized as transportation fuel. In addition, the elemental composition of solid products has also been characterized to evaluate the efficiency of the LtL-conversion process by measuring the oxygen and carbon content of the solid residues to indicate if the solid phase products consisted mainly of unreacted lignin or char. Furthermore, mass balance calculations were done based on elemental composition data from bio-oils and solid residues (paper II and III).

2.2.2 Gas chromatography

One of the main objectives of this PhD thesis was to obtain a more detailed characterisation/identification of bio-oil components using gas chromatography. Gas chromatography involves separation of the individual components in the sample based on their volatility, their affinity to a stationary and mobile phase, which is an inert gas, and their stability within the operating temperature range. The currently accepted status is that GC can be used up to 350 °C, which corresponds to an upper molecular weight limit of 600 Da [58]. The column containing the stationary phase (a non-volatile or bound liquid) is placed inside a heating chamber and is connected on the one side to an injector and on the other side to a detector. Briefly summarized, the separation itself is done by elution, where the analyte is injected through an injector and vaporized rapidly. Then, an inert carrier gas transports the gaseous analyte through a heated column and the components of the analyte elute the GC-column at a rate depending on their affinity to the stationary phase [58–60]. There are many different types of detectors used in gas chromatography, but in this thesis, gas chromatography provided with mass spectrometry detector (MSD) and flame ionization detector (FID) was used for the identification and quantification of bio-oils.

The lignin-derived oil comprises a complex mixture of phenolic compounds of varying volatility. The more volatile compounds can be identified using GC-MS analysis, while the majority of the LtL-oil consists of high molecular weight components with poor GC-properties (high polarity and low volatility), which will be retained by the column, and thus can not be identified.

In paper III, sample components in fraction 3 form solid phase extraction have been silylated to facilitate the analysis. Silylation is a derivatisation technique, in which a specific functional group within the sample molecule (herein the hydroxyl substituents of the lignin monomers) is introduced a silyl group substituent (R_3Si). Silylation of the polar compounds of the bio-oil fraction gives derivatives with enhanced volatility and reduced polarity, which improves the separation and detection of components and makes them more suitable for GC-analysis.

2.2.3 2D gas chromatography (GCxGC)

In the last decade, 2D gas chromatography has been introduced for many applications. For complex samples such as fragrances, petrochemical products and bio-oils, two-dimensional chromatography is a good alternative to increase chromatographic resolution, in which improved chromatographic resolution enhances product identification [61]. GC×GC is a versatile technique that can be applied to essentially all GC-amenable, complex samples and analyte classes and has high separation capacity, improved analyte detectability and generation of structured chromatograms [62].

Briefly, sample separation is conducted in two different columns, typically of different lengths and different affinities (for example, a 20–30 m non-polar first column that retains non-polar compound and a short 0.5–1 m polar that retains polar compounds). A modulator, often referred to as the "heart" of the system, is connected to the two columns that collects the separated compounds from the first column, usually refocus it into a narrow band, and then periodically re-injects the focused fraction into the second column [62, 63].

However, the orthogonality of the tow separation dimensions (independent separation mechanisms) enables different separation mechanisms accessible for separation of different chemical compounds or classes in a sample, which is very helpful for identification purposes. Structured retention is one the most important property of GCxGC that relates the positions of peaks in the two-dimensional separation space to the trends in chemical properties of the sample set. This means that members of the same chemical class, e.g. those containing the same functional group, exhibit a related second-dimension retention time and show up as bands or clusters, which can easily be interpreted and recognised in the 2D GC×GC space, as illustrated in figure 2.5 [62, 64, 65].

Several detectors have been combined with GCxGC, including flame ionization detector (FID), time-of-flight mass spectrometer (TOFMS) and quadruple mass spectrometry (MS). In this thesis, two-dimensional gas chromatography coupled with

flame ionization detector was employed for characterisation of the organic liquid product samples.

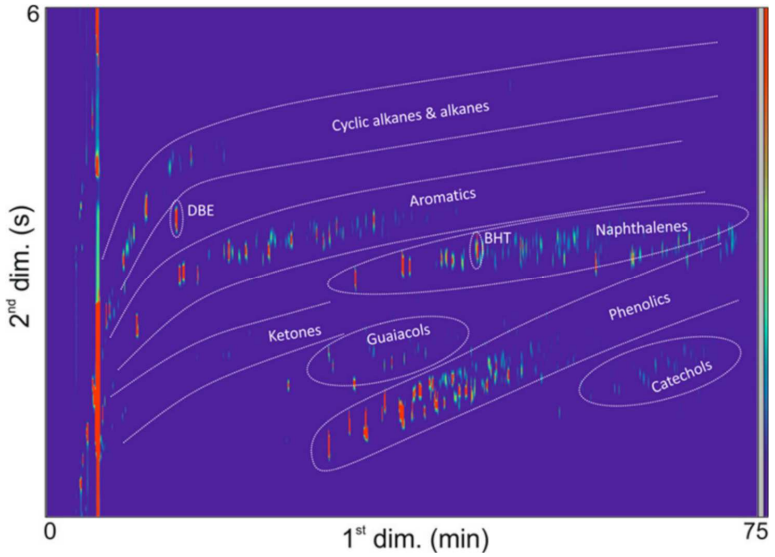


Figure 2.5. GC×GC-FID chromatogram for the lignin oil. Figure is reprinted from "Experimental Studies on the Hydrotreatment of Kraft Lignin to Aromatics and Alkylphenolics Using Economically Viable Fe Based Catalysts" by Agarwal et al., 2017, ACS Sustainable Chemistry & Engineering, 5, 2668−2678 [65]. License by © 2017 American Chemical Society.

Mass spectrometry detector (MSD)

Most of the GC-analysis carried out in this thesis were coupled to a mass spectrometry detector (MSD). The combination of gas chromatography and mass spectrometry is called GC-MS. Mass spectrometry detector consists of an ionization source, a mass separator and a mass analyser. The separated molecules from GC need to be ionised in order to be analysed by mass spectrometry. There are several sources of ionization, e.g. chemical ionization (CI), electron spray ionization (ESI) and electron ionization (EI). The most common ionization source is electron ionization where a beam of high-energy electrons strike the analyte molecule causing the loss of an electron from the analyte molecule and converting the molecule to a cation ($M^{+\bullet}$). Since the molecular cation ($M^{+\bullet}$) contains so much energy, the ionization is followed by fragmentation of the cation. After ionization, the beam of ions is accelerated by an electric field and

passes into a mass analyser. In the mass analyser, in this case a quadrupole mass analyser, the formed ions are separated according to their mass-to-charge ratio, m/z. The quadrupole mass analyser consists of four cylindrical rods placed parallel to the direction of the ion beam from the ionization source. A direct-current (DC) voltage and a radiofrequency (RF) is applied to the rods to ensure that ions with the desired m/z value pass through the quadrupole analyser without hitting the rods and reach the identifying detector [66, 67]. Each compound has a unique or almost unique fragmentation pattern that can be compared with parent molecules in a library base so that structural identification can take place.

Flame ionization detector (FID)

Quantification studies in paper IV included the use of flame ionization detector (FID). Flame ionization detector (FID) is based on that the electrical conductivity of a gas is proportional with the concentration of charged particles in the gas. The gaseous sample from GC separation is introduced into a FID through column input and burned in a hydrogen–air flame, producing ions in the process. In order to detect these ions, two electrodes are used to measure the current from the ions. This current is directly proportional with the amount of substance burned. The flame ionization detector (FID) is one of the most efficient detectors for organic compounds as it detects the amount of carbon in a sample [58, 68].

2.3 Solid phase extraction

Solid phase extraction (SPE) is a rapid and inexpensive chromatographic technique, which is reproducible and requires low sample and solvent amounts. The versatility of SPE allows use of this technique for many purposes, such as purification, trace enrichment, desalting, derivatisation and class fractionation. Solid phase extraction is achieved through the interaction of three components: the sorbent, the analyte and the solvent, where the analytes have stronger affinity for, and adsorb to, the sorbent rather than the sample matrix [69].

SPE is a separation technique based on partition principles that involves passing the sample matrix through a column containing an adsorbent that retains the analytes. After adsorption, retained analytes can be removed from the sorbent material and subsequently recovered using eluents with appropriate polarity [70, 71].

In this method, a small amount of a sample (herein bio-oil sample) is dissolved in a small amount of a solvent and then transferred to the stationary phase of a certain polarity. The column is usually composed of an inert substance such as silica, which is covered with the stationary phase. Compounds in the sample will have varying affinity for the stationary phase depending on the interactions between the sorbent and analyte of interest. Additionally, the solvent, an eluent, must be of known polarity and should not react with either the sample or the stationary phase.

Based on the polarities of the solvent and the stationary phase, SPE can be divided into two types: normal and reverse phase SPE.

- Normal phase involves a polar analyte, a mid- to nonpolar matrix (for instance acetone, chlorinated solvents and hexane) and a polar stationary phase. Retention of an analyte under normal phase conditions is primarily due to interactions between polar functional groups of the analyte and polar groups on the sorbent surface. These include hydrogen bonding, л- л interactions, dipole-dipole interactions, and dipole-induced dipole interactions, among others. A compound adsorbed by these mechanisms is eluted by passing a solvent that disrupts the binding mechanism, usually a solvent that is more polar than the sample's matrix. In normal phase SPE, the least polar analyte elutes first.
- Reverse phase involves a polar or moderately polar sample matrix (mobile phase) and a nonpolar stationary phase. The analyte of interest is typically mid- to nonpolar. Several SPE materials, such as the alkyl or aryl-bonded silicas (e.g. C8, C18) are in the reverse phase category. Retention of organic analytes from polar solutions (for instance water) onto these SPE materials is due primarily to the non-polar–nonpolar attractive forces (van der Waals forces or dispersion forces) between the carbon-hydrogen bonds in the analyte and the functional

groups on the sorbent surface. To elute an adsorbed compound from a reversed phase SPE tube or disk, a nonpolar solvent, which can disrupt the forces between the sorbent and compound, is used. In reverse phase SPE, the most polar analyte elutes first [69, 71].

An SPE method always consists of three to four successive steps, as illustrated in figure 2.6. In the first step, the solid sorbent should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step enables the wetting of the packing material and the solvation of the functional groups, thus is crucial. The second step is the percolation of the sample through the solid sorbent. The sample flow-rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration. During this step, the analytes are concentrated on the sorbent. In addition, some of matrix components may also be retained by the solid sorbent enabling some purification of the sample. The third step is optional. In this step, the solid sorbent may be washed with an appropriate solvent, having a low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes. The final step involves elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The flow-rate and solvent volume should be correctly adjusted to ensure efficient elution and quantitative recovery of the analytes [70].

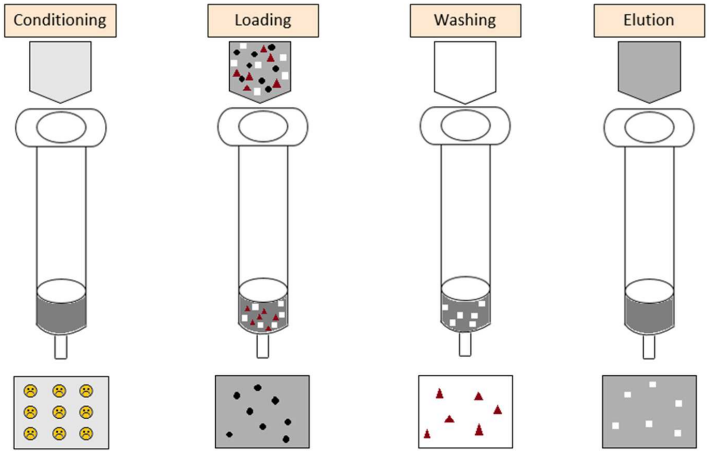


Figure 2.6. Solid Phase Extraction operation steps.

2.4 Experimental design

“One-factor-at-a-time” (OVAT) approaches have commonly been used in the explanation and optimization of reaction systems, where reaction parameters are singularly altered from selected starting point. The approach requires that the chosen parameters have a defined single effect and are independent of each other, which can lead to a false maximum due to a reduced potential range for response. Additionally, this method does not consider that the combination of several parameters, and thus the interaction between the parameters, may have multiple effect in the experimental plane. In most cases, parameters in an experimental set are dependent of each other, i.e. although they can be adjusted individually, but can still affect each other in the system [72, 73]. However, results obtained from experiments that are performed randomly will also be random. Therefore, in complex reaction systems, such as LtL-solvolysis experiments that involve a multitude of various reaction parameters, it is of a major importance to design the experiments in such a way that the interesting information will be obtained [74]. For best performance, statistical tools such as experimental design, which reveal the statistical value of parameters or combination of parameters, can simplify the processing of the collected laboratory data [75].

For this purpose, a variety of experimental designs has been developed. However, the selection of an appropriate design is highly dependent on the reaction system. A full factorial design includes all minimum and maximum level combinations of the individual factors in an experimental set. In a full factorial design, the number of experiments will increase dramatically if the number of factors is increased. In such a situation, a fractional factorial design would be useful. Fractional factorial designs have been developed to effectively reduce the number of experiments, including both single factors and combination of factors. In this thesis, fractional factorial designs were applied in paper I and II, which included a balanced half of all possible combinations of the factors to reduce the number of experiments performed [72].

2.4.1 Principal component analysis

Principal component analysis (PCA) is a multivariate technique used to interpret large amounts of data by analysing a data table representing observations described by several inter-correlated dependent variables. This technique aims to reduce the dimensionality of the data while retaining most of the variation in the data set. This is done by extracting the important information from the data table and presenting it as a new set of latent variables called "principal components" [76–78]. The first principal component, PC1, is a linear combination of the original data that explains most of the variance in the data set. The second principal component, PC2, which is extracted by removing PC1, explains the maximum of the variance that cannot be explained by PC1. PC3 is the component explaining the residual variance that is not described by PC1 and PC2 and so forth [76]. PC1 and PC2 are orthogonal (figure 2.7), while PC3 is orthogonal to PC1 and PC2.

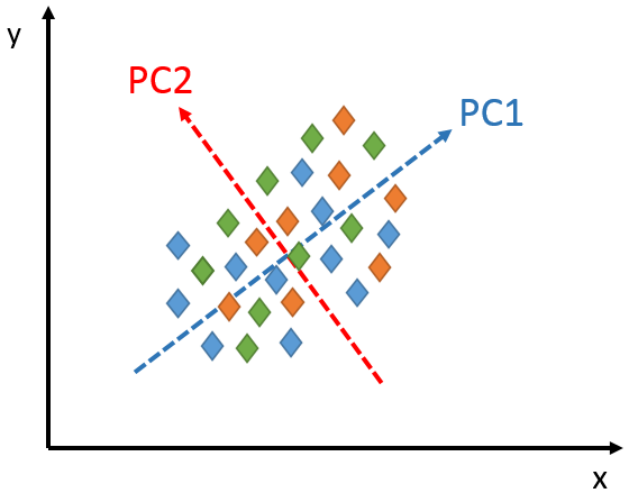


Figure 2.7. Graphical presentation of principal component 1 and 2.

2.4.2 Partial least square regression analysis (PLSR)

In many cases, principal components are not the ideal latent variables. Partial least square regression (PLSR) has proven to be a very versatile method for multivariate data analysis and is the simplest and most used form of PLS approach in chemistry and

technology. It is a supervised method established to address the problem of making good predictions in multivariate problems. PLSR is used to establish quantitative relations between two blocks of data, e.g. a block consisting of descriptor data for a series of reaction systems (X-block) and a block consisting of response data measured on these systems (Y-block). By using the quantitative relationship between these blocks, it is possible to predict expected responses for a new system [75, 79]. It can thus be said that in PLSR one can extract as much information as possible from X that correspond to the information in Y, which improves the results in comparison with traditionally multiple regression approaches [76, 80]. In this thesis, PLS regression analysis was employed in paper I and II and the results from PLSR were described by several regression equations for the most interesting dependent variable “y”.

Chapter 3. Main results & discussion

This chapter summarizes the main results achieved within this PhD project. The conducted laboratory- and analytical work is attached as four individual papers in Part II of this thesis. The order of the presented papers from I–IV depends on results obtained in each paper with respect to the work objectives in its following paper. Each paper in this chapter gives a summarized description of the main focus and the main findings.

3.1 Paper I. Formic acid assisted liquefaction of lignin in water and ethanol, investigated for a 0.025 and a 5 L batch reactor: Comparison of yields and compositions of the products

One of the primary objectives of this PhD project was to investigate the influence of reaction scale on LtL-solvolysis product yields and composition. This paper addresses depolymerization of lignin at small and large laboratory scales and includes characterisation of the products. Lignin conversion was performed using a 5 L stirred reactor and a 0.025 L unstirred reactor to evaluate the effect of increased volume and stirring on the oil yield and oil quality. In this context, the amount of yields was investigated for different types of lignin/lignin-rich residues, reaction temperatures, reaction times and reaction solvents.

Table 3.1 shows the different types of lignins used in this paper, selected based on availability, to represent both purified lignins and lignin-rich residues from bio-ethanol production. The feedstocks used in this work were not directly soluble in the reaction media at low temperatures, and thus the initial state of the reaction system was a suspension of lignin particles in the liquid reaction medium. Further heating melted the lignin and increased the solubility. The physical state of the reaction system at the selected temperatures was not explicitly known, but torque readings during the heating period indicated that lignin melted into a viscous liquid, which dissolved at higher temperatures.

In most cases, experiments performed at small laboratory scale gave higher oil yields than large laboratory scale experiments. Oil yields measured on lignin intake ranged from 33 to 60 wt. % for experiments conducted at 0.025 L scale and were in a range of 17 to 52 wt. % for experiments performed at 5 L scale. The amount of the original lignin mass recovered as oil and char was calculated as lignin mass balance. As expected, both the oil yields and the lignin mass balances varied between the lignin types, and lignins with high purity, i.e. BL- and AL-lignins, provided the quantitatively highest oil yields at both scales. However, the lignin-rich residues, i.e. Eucalyptus, Stat 417 and Stat416 lignins, resulted in the lowest amounts of lignin-derived oils at both

scales. These feedstocks contained significant amounts of residual carbohydrate that contributed substantial amounts of oxygen, confirming that feedstock composition along with pretreatment method influenced the O/C ratio of the feedstock and then conversion yields. Hence, much of the mass loss can be associated with the loss of oxygen since the oxygen content was reduced from 39.1–46.7 wt. % in the lignins to a range of 10.5–25.3 wt. % in the bio-oils.

Table 3.1. Lignin feedstock types and characteristics used in paper I [81].

Feedstock	Botanical species and isolation method	Lignin content (mass %)	Ash content** (mass %)	H/C ratio	O/C ratio
Eucalyptus	Origin: Thailand, produced at the Biorefinery Demo Plant (BDP) in Örnsköldsvik, Sweden, using weak acid and enzymatic hydrolysis	~50	~4.4	1.41	0.586
Stat417	Norway Spruce-30% cellulose, produced at SEKAB from weak acid hydrolysis, SO_2-treated in bioethanol production process	~70	~1.0	1.37	0.559
BL	Norway Spruce, produced at Processum (Sweden) by acid precipitation from Kraft pulp mill black liquor	NA*	~4.9	1.30	0.442
Stat416	Norway Spruce-30% cellulose, Produced at SEKAB from enzymatic hydrolysis in bioethanol production process	~70	NA	1.20	0.451
AL	Alkali lignin purchased from Sigma Aldrich	~98	NA	1.25	0.730

*: Comparable lignin content as Lignoboost lignin (95–98 %).

**: Ash content was measured by combustion at 575 °C according to protocol NREL/TP-510-42622 [82].

Nevertheless, the lignin-rich eucalyptus residue was selected to be used in subsequent experiments due to its availability. For experiments conducted at different reaction temperatures, results showed a trend of decreasing for oil yields with temperature, which was more marked at 5 L scale. Product yields from the two scales were quite similar at lower and intermediate temperature range, e.g. 320–350 °C, and then they diverged at the highest temperatures, e.g. at 365–380 °C. At large scale the oil yield dropped more rapidly with temperature, indicating that secondary lignin oil cracking was more efficient at 5 L scale than 0.025 L scale. The duration of the experiments at the investigated temperature (380 °C) did not significantly influence the yields at either

scale, indicating a moderate effect of the reaction duration at each scale. Comparison of yields obtained from parallel experiments using water and ethanol as solvent showed that the ethanol-based experiments gave higher oil yields than the water-based experiments and were to some extent equivalent at both scales. The addition of ethyl groups to the aromatic ring structures gave a net mass contribution and enhanced the oil yields relative to lignin intake. The bio-oil yields from ethanol-based experiments also tended to decrease at higher temperatures just as in water-based experiments.

Results obtained from elemental analysis showed a substantial removal of oxygen from the lignin structure through LtL-solvolysis. Deoxygenation of feedstock was considerably higher for eucalyptus lignin than AL- and BL-lignins, while bulk hydrogenation did not seem to have occurred since the H/C ratios of the bio-oils were also reduced slightly relative to the starting feedstocks (see figure 3.1a). The lower H/C ratios of the bio-oils compared to starting feedstocks can be explained by the elimination of hydrogen-rich molecules such as methanol from the lignin structure as aqueous products. As depicted in figure 3.1b, a trend of reduction was observed for both H/C and O/C ratio of the oils with increased operating temperature at both large and small scale. The ethanol-based conversion systems gave higher H/C ratios (see figure 3.1c), supporting previous observation that ethanol as reaction solvent together with formic acid works as an alkylation agent [25]. The incorporation of the ethyl groups increases the number of alkyl units in the product, and thus increases the H/C ratio. Nevertheless, an H/C value in the range of 1–1.2 suggested that aromatic rings were predominant.

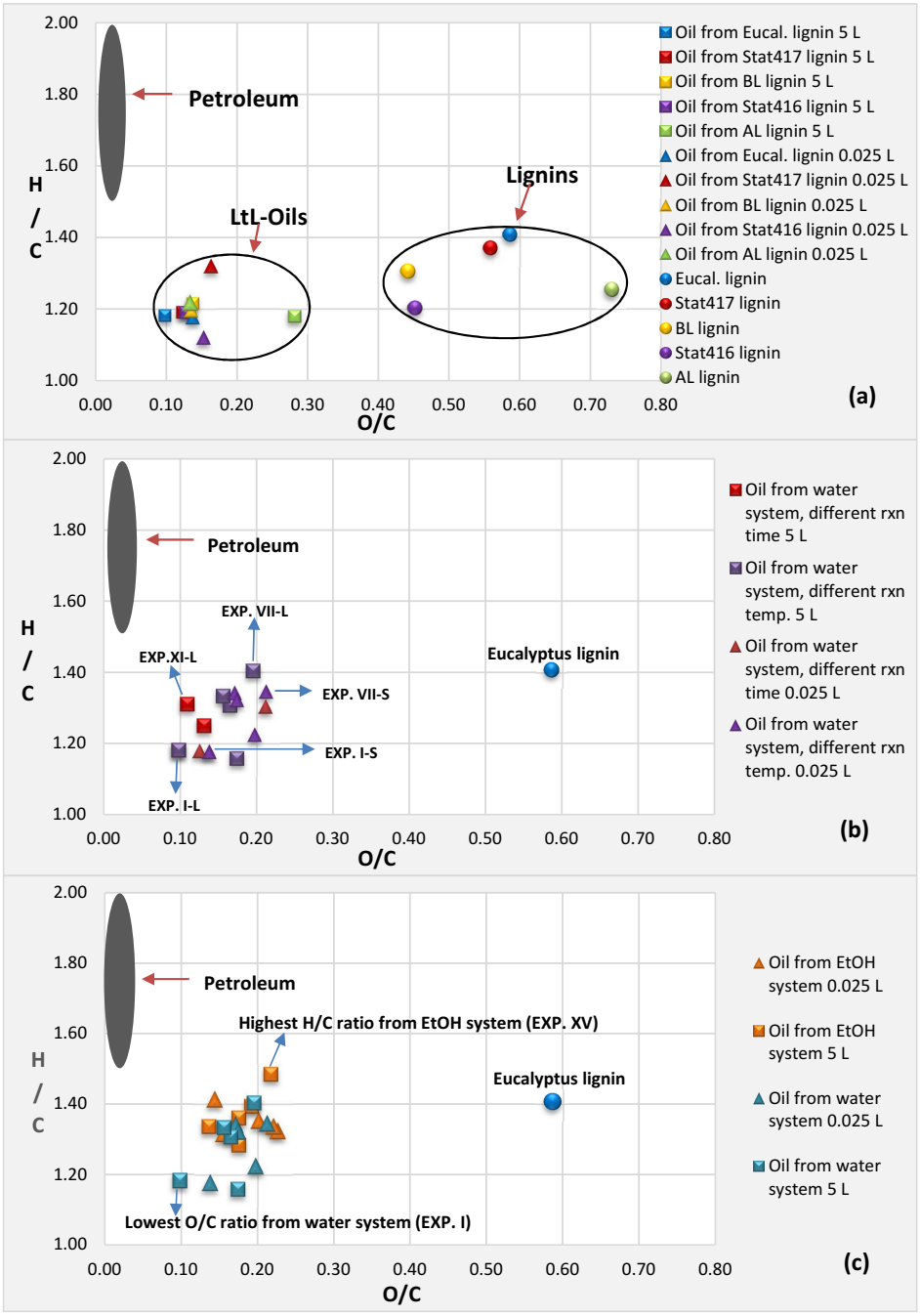


Figure 3.1. Van Krevelen diagrams showing H/C and O/C ratios of all feedstocks and bio-oils in paper I. For experimental coding, see Table A in the Appendix. Figure is adapted from Ghoreishi et al., 2019 [81].

In addition to recovery by mass, yields on carbon basis were also measured using the elemental composition data. Carbon recovery was calculated based on the net recovery of the target compounds, and thus was very dependent on the oil recovery by mass. A major source of uncertainty was the lack of data for aqueous and gas phase products, thus the carbon balance data were most useful for comparative use.

However, in a study reported by Løhre et al. (2017), high levels of dissolved organic carbons were detected in the aqueous phase using ^{1}H-NMR analysis. The results from ^{1}H-NMR showed a presence of methanol, ethanol and considerable amounts of aromatics and carboxylic acids in addition to the extraction solvents, ethyl acetate and tetrahydrofuran [83]. Hydrogenation of a methoxy substituent in a methoxyphenol will lead to the formation of phenol and methanol [25]. The methanol formed will be found in the aqueous phase and will be removed during work-up procedure. However, the other components such as aromatics and carboxylic acids are believed to originate from lignin and formic acid, respectively. Carbon recovery was highest in bio-oils produced in experiment XIII (at 5 L scale) and experiment III (at 0.025 L scale) and reached approx. 75 and 80 wt. % of initial carbon content of the feedstock, respectively.

For water-based experiments, the composition of the GC-MS detectable part of the oils was quite similar for experiments at large and small scale when keeping other variables constant. However, the variations in proportion of the compounds between the oils from different scales were most likely due to the lack of stirring at small scale. As shown in figure 3.2, phenol (#1), methylphenol (#3&4), 2-methoxyphenol (#5), ethylphenol (#6) and 2,3-dihydro-1H-inden-5-ol (#9) were the most abundant components in bio-oils from water-based experiments.

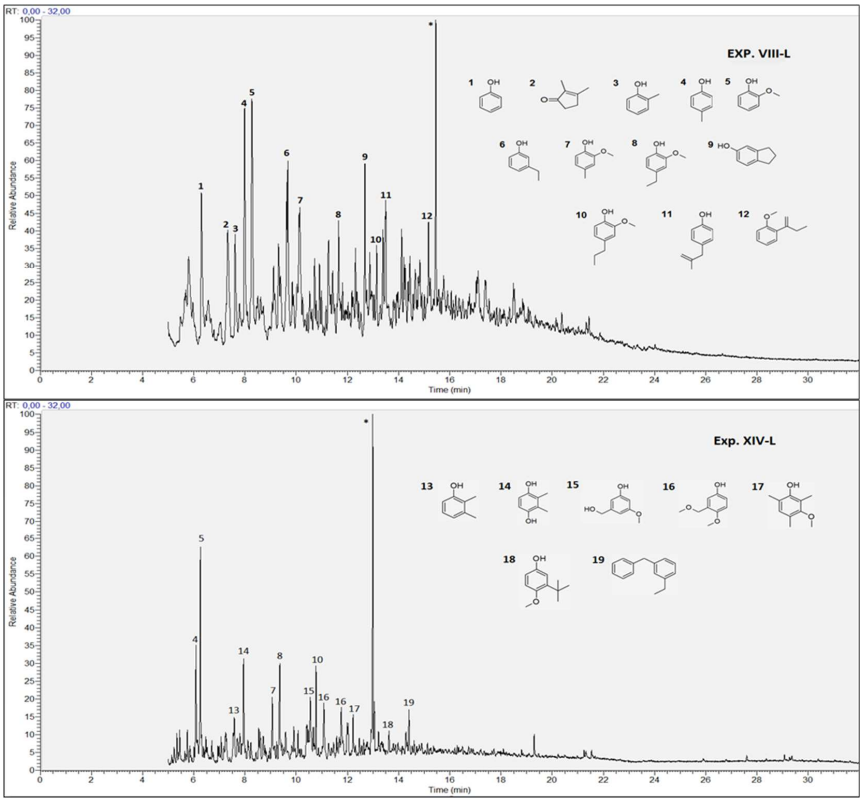


Figure 3.2. GC-MS chromatogram from LtL-oils produced using eucalyptus lignin as feedstock and water (on top) and ethanol (at bottom) as reaction solvent at 5 L scale. Compound (*) is an inhibitor (Butylated hydroxytoluene) in the solvent (THF) used. A more detailed comparison of composition of the LtL-oils performed at different scales is given in paper I.

A comparable chromatogram from an ethanol-based experiment is also presented in figure 3.2. A general observation was that the bio-oil composition was significantly influenced by ethanol as solvent, whereas 2-methoxyphenol (guaiacol) was still the most abundant compound. In addition, a significant increase in number of components that included an alkyl substituent was observed, leading to a higher H/C ratio of the LtL-oils from the ethanol-based experiments. Furthermore, the increase in phenol-/methoxy-/ethoxy-substituted compounds resulted in significantly higher O/C ratio and higher molecular weight in the bio-oils obtained from ethanol system. Bio-oils performed at 5 L scale using ethanol as solvent gave a different range of highly

substituted phenols compared to bio-oils from small scale experiments, but the reason for these differences is not well understood at present.

Results obtained from principal component analysis confirmed all observations described above. As shown in figure 3.3, oil yield was strongly positively correlated with carbon recovery, oxygen recovery and O/C ratio of the oils, which indicated that high oil yield recovered a high amount of carbon and retained a high amount of oxygen, while the latter was not optimal in terms of the oil quality. In addition, the negative correlation between the oil yields and reaction temperature indicated that high reaction temperature reduced the oxygen content of the oil. This design confirmed also that the ethanol-based experiments gave higher oil yields than the water-based experiments. In addition, char yield was found to be independent of the oil yield and carbon recovery. Since there was a positive correlation between the char yield, the reaction temperature and the H/C ratio of the oil, a disproportionation of the oil components producing carbon-rich char and hydrogen-enriched liquid product was suggested at higher temperatures. Overall, the influence of the variables on the yields were similar for the two scales.

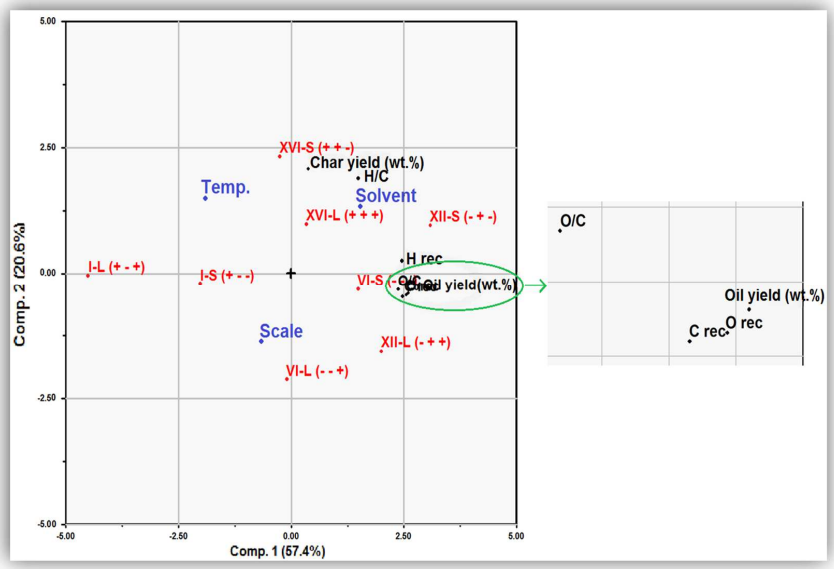


Figure 3.3. Biplot of objects and variables from fractional factorial design presented in Table 3 in paper I. Figure is adapted from Ghoreishi et al., 2019 [81].

3.2 Paper II. Stirred and non-stirred lignin solvolysis with formic acid in aqueous and ethanolic solvent systems at different levels of loading in a 5-L reactor

The conversion of eucalyptus lignin to bio-oil as well as the bio-oil quality have shown to be influenced by reaction parameters such as reaction temperature, reaction solvent type and stirring condition in paper I. Thus, the main focus in paper II was to evaluate the product yield and product composition of bio-oils derived from eucalyptus lignin through LtL-solvolysis at 5 L scale as a function of the reaction parameters solvent type, level of loading in the reactor, and reaction temperature under stirred and non-stirred conditions.

The lignin conversion was investigated at two different temperatures (320 and 350 °C) using two different reaction solvents (water and ethanol) by changing the stirring rate from 0 to 400 rpm at different levels of loading in the reactor. For detailed experimental conditions and coding, see Table A in the Appendix.

The quantitative results from all the LtL-solvolysis experiments are presented in figure 3.4. For the water-based experiments, it was not possible to use the maximum level of loading due to pressure limitations, and thus the results from water-based experiments with high loading level would not be completely comparable with the results of the ethanol-based experiments with maximum loading level.

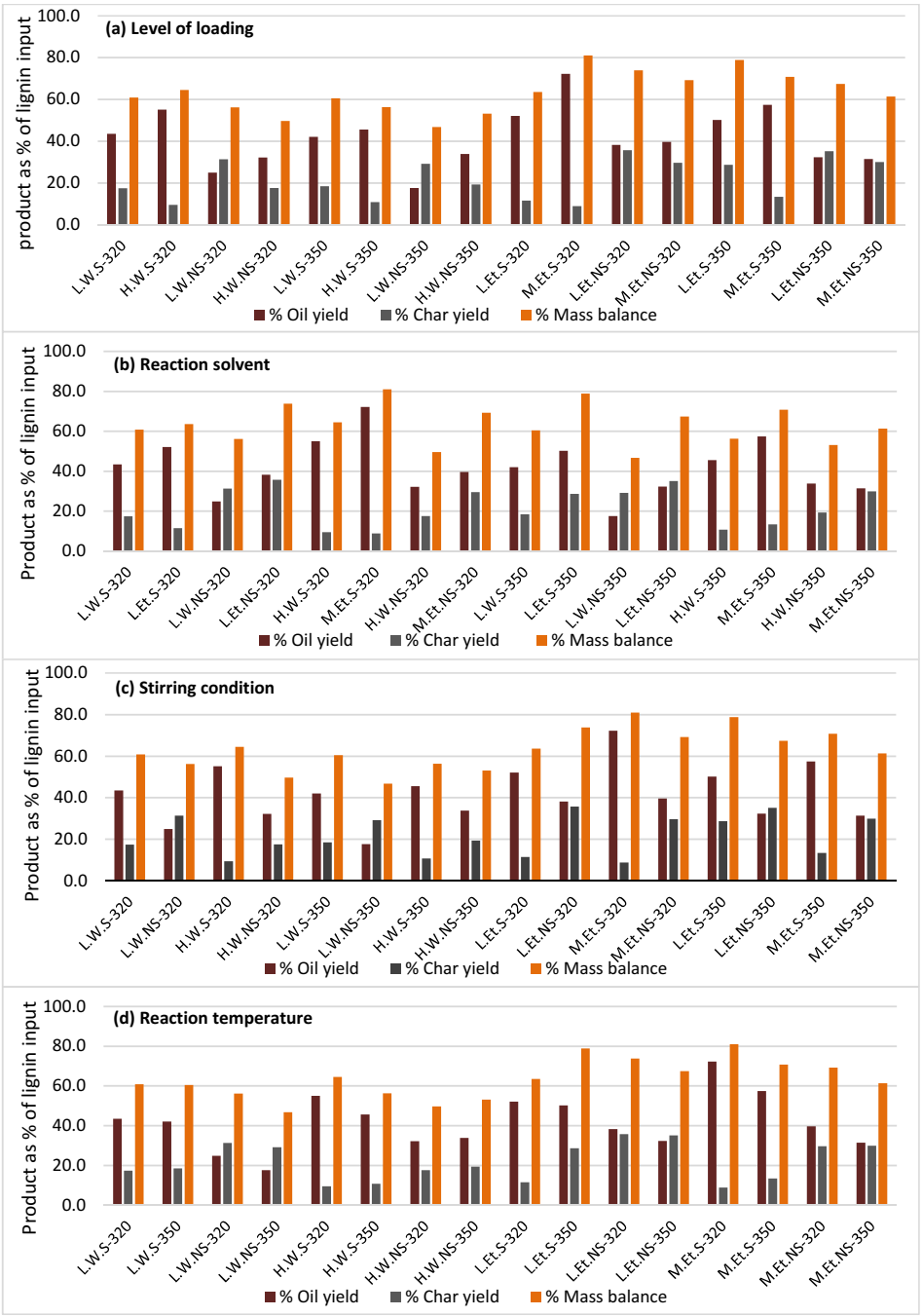


Figure 3.4. Product yields and lignin mass balance given as mass fraction on lignin intake plotted according to the different reaction conditions investigated. Figure is adapted from Ghoreishi et al., 2019 [84].

Figure 3.4a displays distinct variations in the product yields on lignin basis (wt. %) as a function of different levels of loading in the reactor when keeping all the other conditions constant. The bio-oil and char yields ranged, respectively, from 18 to 72 wt. % and from 9 to 36 wt. % of the lignin input. The amount of the original lignin mass recovered was in the range of 47–81 wt. % on lignin intake. The results showed that increased loading in the reactor from a low to a high/maximum level led to an increase in bio-oil yield. The increased bio-oil yield when reactor was loaded to a high level can be associated with a higher overall conversion due to more efficient stirring and higher operating pressure. The 5 L reactor was equipped with two stirrers above each other on the stirring rod, in which the contact of both stirrers with the reaction medium when a high level of the reactor was loaded resulted in a more efficient mixing and consequently better lignin depolymerization. In addition, the pressure in the reactor showed to be proportional with the level of loading in the reactor, especially with the liquid level (formic acid and reaction solvent), which means that increased amount of reaction medium elevated the pressure during the reaction, which also increased the efficiency of the conversion. For the char yields, a decreasing trend was observed as a function of increased level of loading. The reaction was optimal when a high amount of oil and a low amount of char was produced, so high loading levels were preferable.

The ethanol-based experiments resulted in significantly higher bio-oil yields compared to the water-based experiments (see figure 3.4b). The bio-oil yields were in a range of 18–55 wt. % and 31–72 wt. % for water- and ethanol-based experiments, respectively. The char formation also showed an increase in the ethanol-based experiments, and thus a better mass balance was achieved for all the ethanol-based experiments, due to the lack of data on aqueous products when using water as solvent.

Furthermore, significantly higher bio-oil yields were achieved in the stirred experiments compared to the non-stirred experiments. Char formation was considerably decreased as a result of stirring. The results revealed that under stirred conditions, over 40 wt. % of the lignin was converted to bio-oil regardless of the solvent type and the degree of filling in the reactor. Overall, the highest bio-oil yield was

achieved from ethanol-based experiment with a high level of loading in the reactor under stirred conditions.

In addition, variations in yields were observed as a function of reaction temperature. A trend of slight reduction was observed for oil yields with increased reaction temperature. The decreasing trend was more marked in the experiments performed under stirred conditions with a high filling in the reactor. However, char yields were not significantly affected by the reaction temperature, showing a minor increase by elevating the temperature from 320 °C to 350 °C. Nevertheless, in experiments conducted at 320 °C with high/maximum level of loading in the reactor under stirred condition over 55 wt. % of the lignin was converted to bio-oil regardless of the solvent type.

Results obtained from elemental analysis indicated a substantial reduction of oxygen content in the bio-oils relative to the starting feedstock through LtL-process. However, in bulk, hydrogenation did not seem to have occurred since the H/C ratio of the bio-oils was also reduced relative to the starting material, just as described in paper I. In the LtL-process, hydrogen can be removed as aqueous products when hydroxyl groups are cleaved from lignin structure. Since the carbon content of the bio-oils produced in this work was increased relative to the carbon content of the starting lignin, see table 3.2, it is unlikely that hydrogen which was bound to carbon was removed as alcohol and/or aldehyde during the LtL-solvolysis [10, 25]. Deoxygenation of lignin was considerably higher in water-based experiments, while bio-oils from the ethanol-based experiments showed a higher degree of hydrogenation. This means that replacing water with ethanol as reaction solvent while keeping the other reaction parameters constant, led to a clear increase in both H/C and O/C ratios of the bio-oils. For water-based experiments, high reaction temperature together with stirring contributed to a more efficient hydrogenation of lignin constituents, while for the ethanol-based experiments, it was not possible to have a specific conclusion since neither the H/C nor the O/C ratios of the bio-oils followed a clear trend.

Calculations showed a carbon recovery between 68–92 wt. % and 89–115 wt. % for water- and ethanol-based experiments, respectively. It became clear that the incorporation of ethyl groups from ethanol has contributed significantly to the high carbon recovery in the products from ethanol-based experiments. Furthermore, a lower amount of carbon was recovered in the non-stirred experiments, which can most likely be due to increased gasification under non-stirred conditions. However, carbon recovery did not appear to be influenced by variations in either level of loading in the reactor or reaction temperature.

Table 3.2. Total carbon recovered in oil and char in LtL-process experiments performed in paper II [84].

Experiment	**L.W.S-320**	**L.W.NS-320**	**H.W.S-320**	**H.W.NS-320**	**L.W.S-350**	**L.W.NS-350**	**H.W.S-350**	**H.W.NS-350**
Carbon added as lignin (g)	95.84	95.84	143.76	143.76	95.84	95.84	143.76	143.76
Carbon recovered in oil (%)	64.42	39.04	82.87	50.18	62.59	27.56	67.51	52.87
Carbon recovered in char (%)	20.02	41.36	9.29	22.71	24.63	39.96	11.10	24.33
Total carbon recovered (%)	84.44	80.40	92.16	72.89	87.22	67.52	78.61	77.20
Experiment	**L.Et.S-320**	**L.Et.NS-320**	**H.Et.S-320**	**H.Et.NS-320**	**L.Et.S-350**	**L.Et.NS-350**	**H.Et.S-350**	**H.Et.NS-350**
Carbon added as lignin (g)	95.84	95.84	167.72	167.72	95.84	95.84	167.72	167.72
Carbon recovered in oil (%)	76.51	54.49	102.68	54.33	73.83	46.81	85.79	45.47
Carbon recovered in char (%)	13.95	51.99	8.78	43.03	41.11	52.37	16.10	43.55
Total carbon recovered (%)	90.46	106.48	111.46	97.36	114.94	99.18	101.89	89.02

Results from GC-MS analysis showed that the identified compounds comprising the bio-oils from the same solvent system were quite similar, with only minor variations in the abundance of each compound peak caused by reaction conditions. However, the

compositional differences were more significant when comparing oils from water and ethanol systems, as shown in figure 3.5.

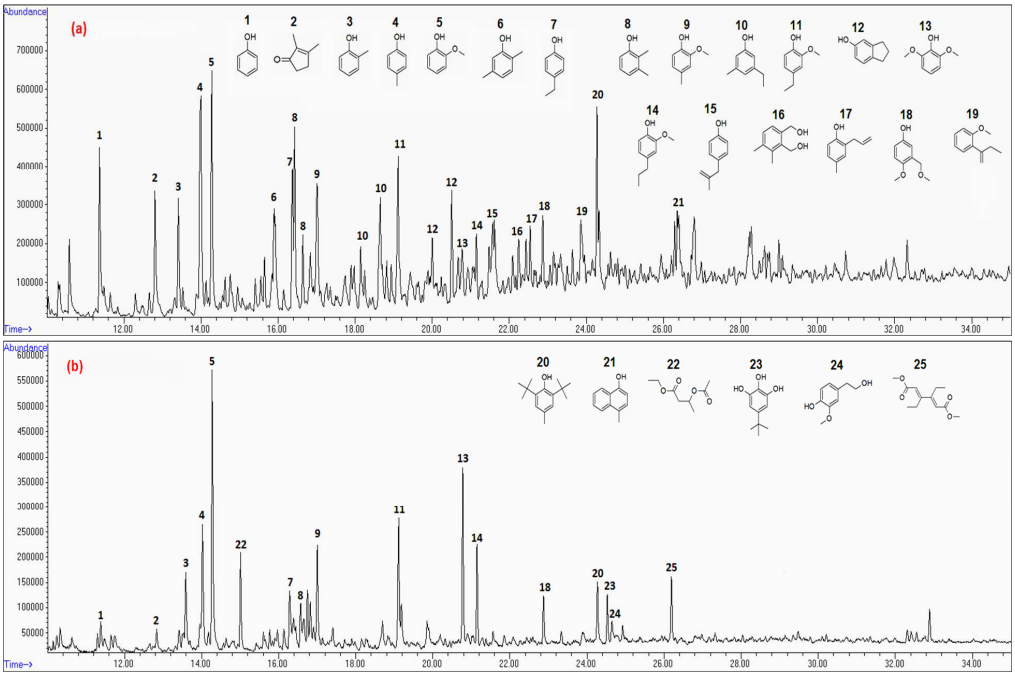


Figure 3.5. GC-MS chromatogram from experiments (a) L.W.NS-320 and (b) L.Et.S-320. Butylated hydroxytoluene (#20) is an inhibitor in the solvent (THF) used.

A general observation was that guaiacol (#5) was the most abundant compound in almost all the LtL-oils produced in this study. In addition, phenol (#1), 2,3-dimethyl-2-cyclopenten-1-one (#2), alkylated phenols (#3,4,6,7,8&10), alkylated methoxyphenols (#9&11), and 2,3-dihydro-1H-inden-5-ol (#12) were the dominating compounds in bio-oils produced in the water-based experiments. Moreover, identification of the most abundant peaks in the chromatograms related to the ethanol-based experiments showed a higher amount of methoxy-substituted phenols such as 2,6-dimethoxyphenol (#13), 2-methoxy-4-propylphenol (#14), and 4-methoxy-3-methoxymethylphenol (#18), indicating a significantly higher O/C ratio and a higher average molecular weight in the oils obtained from this solvent system.

The lower content of oxygen-containing compounds in bio-oils from water-based experiments corroborated the results obtained from elemental analysis, i.e. lower O/C

ratio of the bio-oils from water system. While the higher degree of alkyl-substitution in bio-oils from water system have not resulted in higher H/C ratio compared to bio-oils from ethanol system. Therefore, it was not possible to have a specific understanding relative to H/C ratio since only the volatile fraction of the bio-oils was analysed by GC-MS, and the composition of the heavier portion of the oils was unknown.

The quantitative experimentally data obtained from LtL-solvolysis experiments in this study were subjected to principal component analysis and partial least square regression analysis. Results obtained from the experimental design confirmed all the observations discussed above. Oil yield was negatively correlated with reaction temperature, and positively correlated with stirrer rate, level of loading in the reactor and solvent type. These observations were also confirmed by the fitted equation obtained from the PLSR analysis, which indicated that the highest bio-oil yield was obtained in the experiment performed in the ethanol system combined with high level of loading in reactor under stirred conditions at lower reaction temperatures. Results from PCA and PLSR analysis showed that the char yield was negatively correlated with filling degree in the reactor and stirrer rate, while positively correlated with solvent type and reaction temperature. Thus, the highest char formation was attributed to the experiment performed in ethanol system combined with low level of loading in the reactor under non-stirred conditions at higher reaction temperatures. The carbon balance was found to be positively correlated with stirrer rate and solvent type, confirming the results presented in table 3.2. Furthermore, the positive correlation between the carbon balance with oil and char yield indicated that the highest yield overall recovered highest amount of carbon with the lowest loss of lignin-derived carbon to aqueous and gas-phase products.

The H/C ratio of the bio-oils was well modelled and well predicted when only experiments performed at 320 °C were considered, and was positively correlated with solvent type and loading level in the reactor. Hence, the highest H/C ratio was achieved for bio-oil produced in ethanol-based experiment using high level of loading in the reactor regardless of stirring conditions. Moreover, the O/C ratio of the bio-oils

performed under non-stirred conditions was found to be negatively correlated with reaction temperature and positively correlated with solvent type and reactor filling, indicating that bio-oil from water-based experiment performed using low level of loading in the reactor at higher reaction temperature had the lowest O/C ratio.

3.3 **Paper III.** Effect of reaction conditions on catalytic and non-catalytic lignin solvolysis in water media investigated for a 5 L reactor

From the results obtained in paper II, it was concluded that product yields have been mainly influenced by two reaction factors, namely level of loading in the reactor and stirrer rate. In addition, water as reaction solvent has been shown to lead into lower oxygen content of the bio-oils. Thus, in this study, the efficiency of lignin conversion to bio-oil through LtL-solvolysis in water media was investigated as a function of increased stirrer rate from zero to 1000 rpm at 305 °C as well as increased level of loading from a minimum to a maximum level at 350 °C. Furthermore, two parallel experiments performed at different reaction temperatures were re-performed to explore the influence of feedstock storage on bio-oil yield.

As an additional option for improving oil yields, catalysts were used. Based on published studies, supported noble metal catalysts and the economically viable iron-based catalysts have shown to significantly improve the bio-oil yields on a lignin basis, with yields up to approximately 92 wt. % of the input lignin [13, 65]. In this paper, the catalytic LtL-solvolysis was investigated using a supported noble metal catalyst and an iron-based catalyst, namely Ru/Al_2O_3 and goethite. Finally, the non-catalysed experiment conditions giving the highest bio-oil yields were combined and re-performed using the most efficient catalyst of the two catalysts.

The quantitative results from all LtL-solvolysis experiments are presented in figure 3.6. For experimental coding, see Table A in the Appendix. Experiments shown in figure 3.6a were performed at the same reaction conditions (305 °C and 2 hours), while the stirring rate was changed stepwise from zero to 1000 rpm. The oil and char yields ranged, respectively, from 44 to 67 wt. % and from 12 to 24 wt. % on lignin basis. The total organic mass recovered as oil and char was in the range 65–78 wt. %. Overall, the oil yield along with the organic mass balance was increased as a function of increased stirrer rate and was consistently higher for experiments with stirring rates above 400 rpm. Furthermore, char formation was significantly reduced with increased stirring rate. As mentioned previously, the observed trends for the product yields can be

understood as a better mass transfer due to more efficient stirring, and thus high stirring rates are preferred.

The only difference between experiments shown in figure 3.6b is the degree of filling in the reactor while all the other conditions were kept constant (350 °C with a stirring rate of 400 rpm and 2 hours). Oil yield increased from 28 wt. % to 62 wt. % and char yield decreased form 31 wt. % to 11 wt. % on lignin basis as a function of increased loading in the reactor. In addition, over 70 wt. % of the original lignin mass was directly recovered as oil and char in the maximum level loaded experiment. The impressive increase in bio-oil yield when the reactor was loaded at the maximum level can be due to the higher operating pressure as well as a more efficient blending of lignin with the reaction medium, which improved the reaction efficiency and led to better lignin depolymerization.

The quantitative results shown in figure 3.6c indicated some variations between the duplicate experiments. The difference in organic mass balance between experiments performed at 305 °C was approx. 13 wt. % on lignin basis, indicating that the composition of the raw material was changed during storage. Previous studies conducted at 0.025 L scale has reported less than 5 % variation between duplicates [53] and 2–6 % standard deviation for three replicates [13] for product yields (oil and char), supporting the reproducibility of the reactions and the work-up procedures at small laboratory scale. However, since variations in product yields from conversion tests over time were higher than expected, the results from duplicate experiments performed in this work cannot be assumed to be reproducible, and thus comparisons should be done with considerable caution.

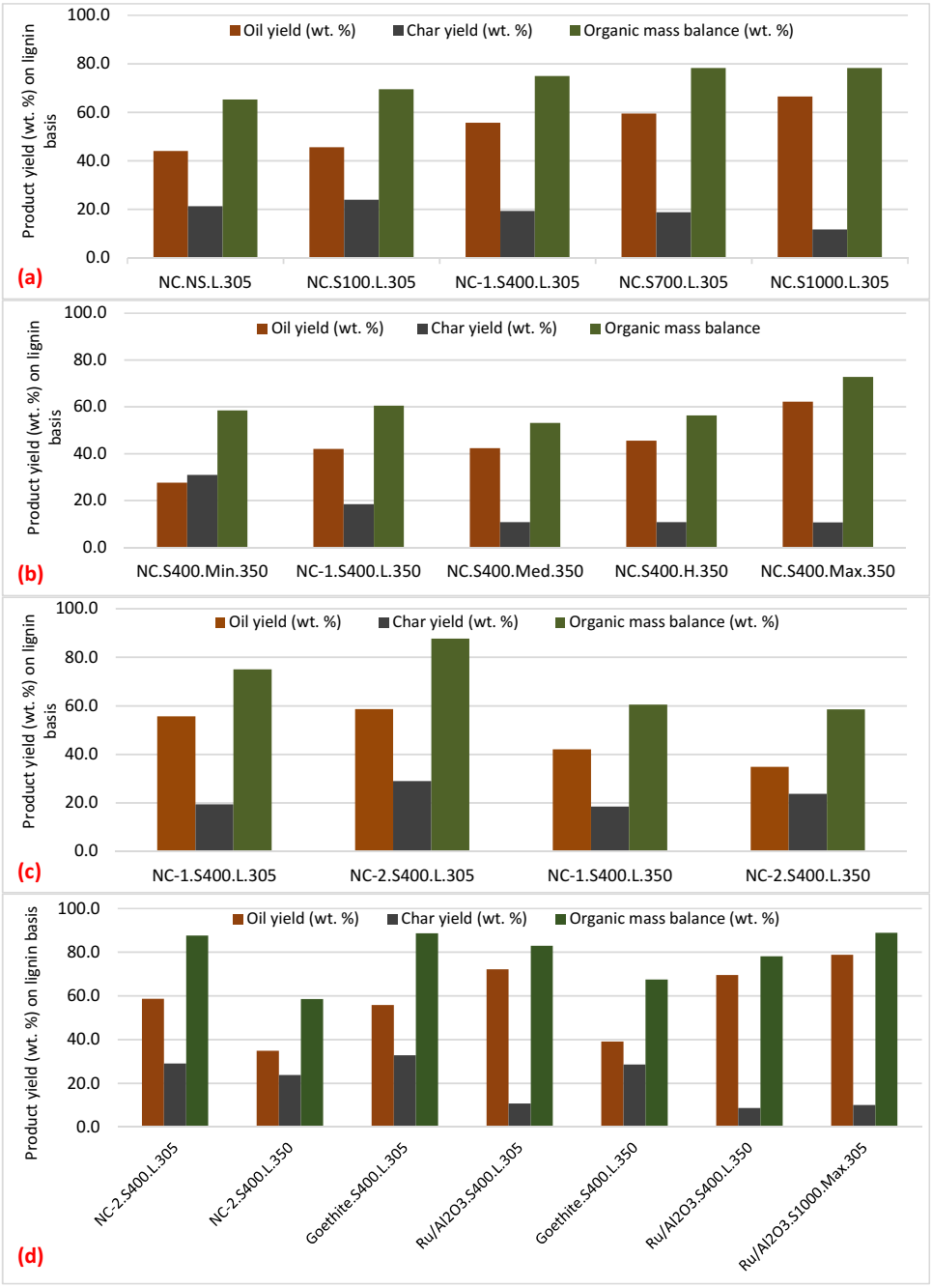


Figure 3.6. Column diagrams showing product yields and lignin mass balances as mass fraction of lignin input as a function of (a) different stirrer rate at 305 °C (b) different levels of loading in the reactor at 350 °C (c) long-term storage of the feedstock at both 305 and 350 °C, and (d) catalyst use at both 305 and 350 °C. Figure is adapted from paper III.

Comparison of results obtained from the non-catalysed and catalysed experiments at 305 °C showed small reduction in oil yield when using goethite as reaction catalyst (approx. 3 wt. %), and a significant increase in oil yield when using Ru/Al_2O_3 as catalyst (ca. 13 wt. %). In case of experiments performed at 350 °C, oil yields increased as a function of catalyst use, to a small extent when using goethite (approx. 4 wt. %), and considerably when using Ru/Al_2O_3 (approx. 35 wt. %). However, char yields increased, between 3–5 wt. % on lignin intake, when using goethite, and decreased significantly, between 13–15 wt. % on lignin basis, when using Ru/Al_2O_3 depending on reaction temperatures. The positive effect of Ru/Al_2O_3 as catalyst can be explained by reaction pathways and kinetics of the lignin decomposition being controlled by the catalyst [13]. The first step in lignin solvolysis is a fast depolymerization of the lignin structure, which is followed by competing reactions giving hydrodeoxygenation or repolymerization of the depolymerized monomers. Use of catalyst in the LtL-process probably reduced the activation energy of hydrodeoxygenation process, and thus the likelihood of repolymerization of depolymerized lignin monomers was also reduced [54]. Thus, at the selected reaction conditions, Ru/Al_2O_3 showed to be a more suitable catalyst than goethite for lignin solvolysis.

Furthermore, as shown in figure 3.6d, experiment Ru/Al_2O_3.S1000.Max.305 that combined the best reaction conditions, resulted in the highest bio-oil yield and consequently the highest organic mass balance of 79 and 89 wt. % on lignin basis, respectively. However, char yield was not affected to the same extent as the bio-oil yield under this reaction condition.

The Van Krevelen diagram depicted in figure 3.7 shows a prominent difference in hydrogen and oxygen content between the fresh and stored feedstocks. The higher content of hydrogen and oxygen in the fresh lignin was attributed to the high content of carbohydrates in this feedstock. Thus, the significantly reduction in the hydrogen content and the moderate depletion of oxygen content of the biomass during the storage might be due to microbial/bacterial degradation of the carbohydrate residues.

The distinct reduction of oxygen content in the bio-oils relative to the starting feedstocks confirmed the occurrence of deoxygenation during the LtL-process. The lower H/C ratio of the bio-oils compared to the fresh lignin can be caused by the elimination of hydrogen as aqueous products, i.e., water, methanol, ethanol, short chain organic acids and furfural from the degraded carbohydrate residues, while the increase in H/C ratio of the bio-oils produced from stored lignin can be due to bulk hydrogenation of the starting feedstock.

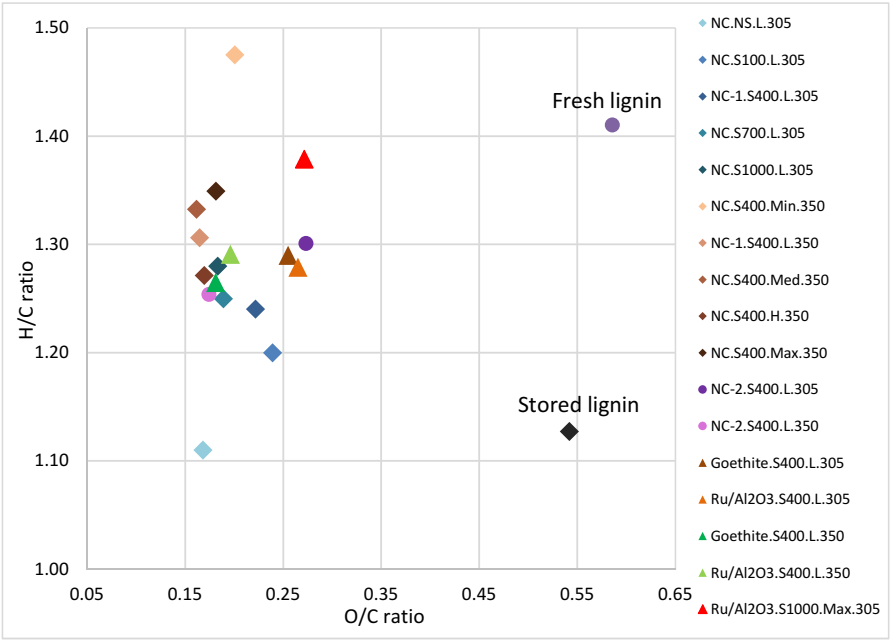


Figure 3.7. Van Krevelen diagram showing H/C and O/C ratio of the feedstocks and all LtL-oils in paper III. Figure is adapted from paper III.

The O/C values of the oils did not seem to be influenced by the variations in level of loading in the reactor, while the H/C values appeared to be more affected, but variations in H/C ratios do not follow a specific trend. In case of experiments performed under different stirring conditions, the H/C ratio of the oils showed an increasing trend as a function of increased stirring rate, while the O/C values did not follow a specific trend.

Moreover, for bio-oils produced from fresh lignin, a trend of reduction in O/C ratio was observed in addition to a trend of increase in H/C ratio as a function of increased

reaction temperature, indicating more efficient hydrodeoxygenation at higher reaction temperatures. However, the same trend was not common for bio-oils performed from stored lignin and both H/C and O/C ratios were decreased as a function of increased reaction temperature.

In addition, the H/C and O/C ratios of the bio-oils were not significantly affected by catalyst use (catalysed vs. non-catalysed) and catalyst type (Goethite vs. Ruthenium on Alumina), confirming that the distribution of the elemental composition was primarily based on the temperature of the conversion process. However, among all bio-oils produced from stored lignin, the highest H/C ratio belongs to experiment Ru/Al_2O_3.S1000.Max.305, indicating that a combination of maximum stirring rate and maximum level of loading in the reactor is preferred for a better hydrogenation of the lignin-derived oils.

In addition, carbon balance calculations displayed carbon recovery in the range of 75–108 wt. %. Carbon balances over 100 wt. % can be associated with a potential carbon contribution from formic acid to the bio-oil. The carbon balance increased significantly as a function of increased stirring rate (from 89 to 108 wt. %), which can indicate a better incorporation of carbon from formic acid to the lignin structure at elevated stirring conditions, while variations in the reactor filling did not influenced the carbon recovery, except the maximum loading in experiment NC.S400.Max.350, which gave a carbon balance of approx. 101 wt. %. The carbon balance was not particularly affected by catalyst use at lower temperature, while showed an increase of approx. 10.3 and 24.7 wt. % when using goethite and Ru/Al_2O_3 at 350 °C.

Results obtained from GC-MS analysis indicated that the reaction temperature influenced the composition of the GC-MS detectable part of the bio-oils, while the abundance of peaks depended on the other reaction conditions used, i.e. stirring rate, level of loading in the reactor and catalyst use. A general observation was that 2-methoxyphenol (guaiacol) was the most abundant compound in almost all cases. However, catechol was one of the major components in bio-oils produced using goethite. Bio-oils produced at 305 °C consisted mainly of methoxy-substituted phenols

in high concentration, confirming results obtained from elemental analysis that indicated higher content of oxygen, and thus a higher O/C value in bio-oils produced at 305 °C. Identification of the most abundant peaks in the bio-oils produced at 350 °C showed a higher amount of alkylated phenols. The higher content of hydrogen in bio-oils produced at 350 °C resulted in significantly higher H/C ratio of the oils, again confirming the results obtained from the elemental analysis.

Results from solid phase extraction (SPE) showed that more than 65 wt. % of the input bio-oil can be fractionated using the eluents given in Table 3 in paper III. A general observation was that bio-oils from non-catalysed experiments showed a better recovery from fractionation compared to bio-oils from catalysed experiments performed at the same reaction temperature. Bio-oils produced at 350 °C contained a larger proportion of non-polar or less-polar components compared to bio-oils produced at 305 °C, which can be due to an increase in hydrocarbon content of the oils, caused by more effective lignin depolymerization and hydrodeoxygenation at higher reaction temperature. In addition, considerably amounts of long-chained fatty acids and alcohols were identified in the non-polar/less-polar fraction of the bio-oils produced at 305 °C (see figure 6 in paper III).

The amount of the collected fractions as well as the retained portion in the SPE column confirmed that approx. 80 wt. % of the bio-oils consisted of polar phenolic compounds. Most of the polar phenolic compounds in the bio-oils were hard to quantify using gas chromatography due to poor GC-properties. Therefore, silylation was used to enhance the elution properties of the polar compounds and to improve the quantification of the different phenolic compounds. Results from GC-MS analysis of the silylated bio-oil fractions (fraction #3) showed that the most abundant components identified were quite similar and independent of the reaction temperature and catalyst use. Furthermore, the polarity of the compounds identified in fraction #3 were increased compared to the polarity of compounds identified in fraction #2, which was as expected. The major components identified in fraction #3 were catechol, 3,5-dihydroxytoluene, 2-(2-hydroxyethyl)phenol, and 2-hydroxymandelic acid ethyl ester.

3.4 **Paper IV.** A lignin-enriched stillage (LES) from bioethanol production as a source for platform chemicals through a liquefaction-hydrodeoxygenation approach

In this study, a lignin-enriched residue (LES), also termed as eucalyptus lignin in the previous papers, was investigated as a source of sustainable platform chemicals. The paper was intended to provide a comparative study between a direct one-pot hydrodeoxygenation (HDO) and a 2-step hydrothermal liquefaction-hydrodeoxygenation (HTL-HDO) approach using Ru/C and Pd/C catalysts, in terms of product yields and the composition of the produced bio-oils at different operating temperatures.

The feedstock (LES) was characterised using several analytical techniques to gain a better understanding of its reactivity and structural features. Results from elemental analysis of the LES showed a hydrogen content of 5 wt. % and a nitrogen content of <1 wt. %, which were similar to those of commercial lignins, while the carbon (48 wt. %) and oxygen (46 wt. %) contents differed notably to those typically measured for commercial lignins. The high oxygen content in LES is related to the significant amount of residual sugar/carbohydrates present in this feedstock, which significantly affects the product yields. Discrepancies between the elemental data presented above and the elemental data presented in previous papers (I–III) can be attributed to changes in the raw material composition over time since the elemental analyzes were performed at different times.

TGA analysis showed that a residue of 16 wt. % was left by the LES, which evidenced a lower polymerization degree in comparison with technical lignins. Results obtained showed that the lignin was decomposed mainly in the range of 200–500 °C due to the degradation of oligomeric components in the lignin structure through breakage of C–O and C–C bonds. At temperatures above 500 °C, the aromatic components were repolymerized, leading to the formation of considerably amounts of char.

For further insights into structural features of the LES, FTIR analysis was applied. Table 3.3 gives an overview of the most representative bands for the LES. The intense

bands in the 1029–1100 cm^{-1} range were attributed to the residual carbohydrate structures.

Table 3.3. Overview of the most representative bands in the lignin-enriched stillage structure.

Wavelength (cm^{-1})	Band type
3334	O–H stretch in aromatic and aliphatic structures
2926	C–H stretch in CH_2 and CH_3 groups
1710	C=O bonds in carboxylic acids
1591, 1507 and 1422	Aromatic ring stretch
1268	C–O bond characteristic for guaiacyl unit
913	C–O bond characteristic for syringyl unit
1163	Antisymmetric C–O stretching of ester groups

Moreover, results obtained from solid-state CP/MAS ^{13}C NMR showed intense peaks at 64 ppm (C5), 75 ppm (C2–C4) and 102 ppm (C1) positions, which again confirmed the presence of residual sugars in this feedstock (LES). Figure 3.8 depicts the lignin-characteristic bands that were observed. Peak at 56 ppm indicated the presence of methoxy functionalities. Peaks in the 110–160 ppm and 165–180 ppm ranges were attributed to olefins/aromatics and C=O bonds in lignin, respectively. The methoxy content in the LES was estimated to be 5.2 %, which seemed to be about half the amount of methoxy groups present in commercial lignins [85], indicating the low purity of LES, mainly due to the high content of residual sugars.

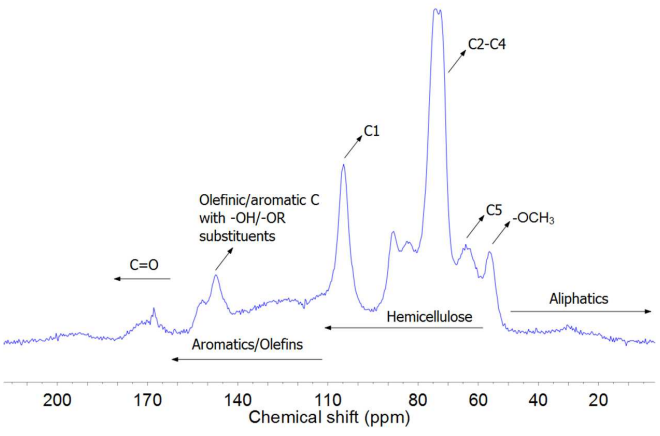


Figure 3.8. Solid-state CP/MAS ^{13}C NMR spectra of the LES (figure is adapted from paper IV).

The hydrothermal liquefaction (HTL) experiments were carried out at the University of Bergen under two different experimental conditions, while the catalytic hydrotreatment of the LES (direct HDO) and HTL-oils (HTL-HDO approach) were conducted at the University of Groningen using different experimental conditions. The experimental conditions of all the experiments investigated in this paper are shown in figure 3.9.

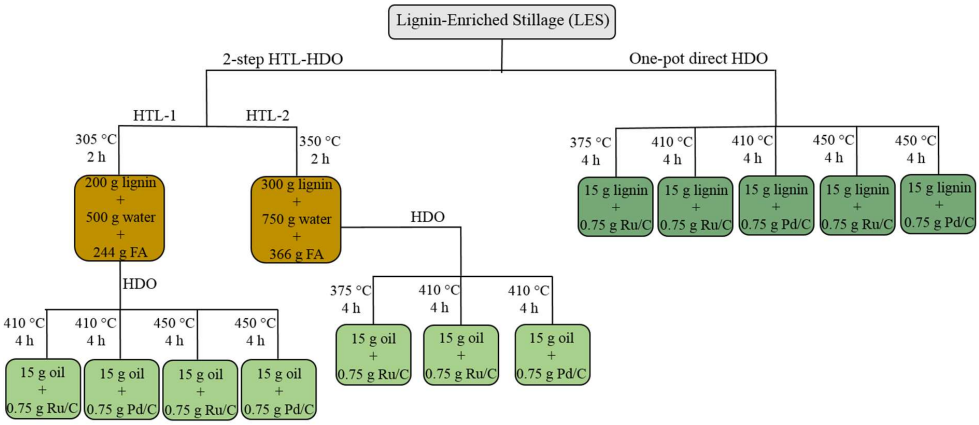


Figure 3.9. Extended overview of experimental conditions investigated in paper IV.

Results from direct hydrodeoxygenation (HDO) showed that organic products (comprising lignin-oil together with DCM and acetone soluble fractions) were the main product fraction in all cases with yields ranging from 28.0 to 39.2 wt. % on lignin intake. However, gas products, aqueous phase and char yields accounted for 20.8–23.8 wt. %, 15.1–20.3 wt. % and 13.5–17.6 wt. % on lignin basis, respectively. In addition, mass balances over 84 wt. % were achieved in all cases. Higher organic product yields as well as more accurate mass balances at lower hydrotreatment temperatures indicated limited gasification at these temperature conditions.

The total monomer yields obtained from the lignin-oils were in a range of 10.8–25.2 wt. % on LES intake. As expected, the volatility of the products were higher at elevated temperatures, resulting in total monomer yields of 21.6–25.2 wt. % at 450 °C, decreasing to 11.5–10.8 wt. % yields at 375–410 °C. Bio-oils produced at 375 and 410 °C were more viscous, and the recovery of these oils were carried out by solvent

extraction (mainly DCM), while bio-oil produced at 450 °C was directly retrieved from the reactor. Gas products consisted mainly of significant amounts of CO_2 and CH_4, also with considerably amounts of unreacted excess hydrogen.

The chemical composition of the organic product fraction was identified using GCxGC-FID analysis and classified as alkylphenolics, aromatics, naphthalenes, linear and cyclic alkanes, guaiacols, catechols and ketones (as shown in figure 3.10a). Overall, alkylphenolics were the main chemical group identified, followed by significant amounts of aromatic compounds, alkanes and oxygenates, respectively. The amount of linear and cyclic alkanes was significantly increased with temperature increase from 375–410 °C to 450 °C, which can be explained by the enhancement of both cracking and hydrogenation reactions at more severe temperature conditions. The total monomer yields from LES were comparable with commercial lignins, but provided lower amount of alkylphenolics due to low content of lignin (50 wt. %) in this feedstock.

In addition, results obtained from GPC analysis also confirmed this fact that the volatility of the bio-oils was affected by the reaction temperature, where the average molecular weight of the bio-oils was reduced with increased temperature. Moreover, a substantial removal of oxygen was indicated by elemental analysis since the oxygen content in the LES was reduced from 46.3 wt. % to values of 3.9–6.3 wt. % in the organic product fractions.

Hydrothermal liquefaction of LES provided an oil yield of 53.2 wt. % on lignin intake in experiment HTL1 with a char formation of 22.9 wt. %, while elevated temperature condition in experiment HTL2 provided an oil yield of 43.5 wt. % with a partially reduced char formation of 14.7 wt. % on lignin basis. Moreover, the total organic mass balance was decreased from 76.1 wt. % at 305 °C to 58.2 wt. % at 350 °C due to increased gasification at 350 °C.

Results obtained from GCxGC-FID analysis revealed that the bulk of the volatile fraction of the HTL-oils consisted of catechols, guaiacols, alkylphenolics, ketones and volatile fatty acids (see table 2 in paper IV). As expected, the volatility of the HTL-oils

increased with reaction temperature from 10.0 % in HTL1-oil to 26.6 % in HTL2-oil due to a significant increase in the content of hydrocarbons, caused by more effective hydrogenation at harsher conditions. The elemental composition data of the HTL-oils showed a significant depletion of oxygen through HTL-process. Oxygen content was reduced to 22.9 wt. % and 15.8 wt. % in the HTL1- and HTL2-oils, respectively, implying better deoxygenation at higher reaction temperature.

Since the identification provided by GC analysis was limited due to poor GC-properties of the HTL-oils, ^{13}C NMR analysis was applied for further characterisation of these oils as a whole. The quantification results (given in table 3 in paper IV) showed that aromatic compounds were predominant (49–60 %) in both HTL-oils, while side chain aliphatics accounted for about 38 % in both cases.

Despite the significant removal of oxygen through HTL-process, the HTL-oils still had a high oxygen content, and thus low volatility. Therefore, further hydrodeoxygenation of the HTL-oils was investigated in the next step.

Results from 2-step HTL-HDO approach showed that char formation was avoided at all temperature conditions regardless of the catalyst type. Oil yields were in the range of 50.7–64.1 wt. % and 76.4–85.7 wt. % for HTL1 and HTL2, respectively. Just as direct HDO of LES, a better mass balance was achieved at lower temperatures. 2-step HTL-HDO significantly improved the total monomer yields (higher than 30 wt. %) in all cases compared to direct HDO, where only the most severe conditions (450 °C) led to yields higher than 20 wt. %. In addition, the higher amount of CO in the gas phase products from 2-step HTL-HDO approach indicated that in addition to decarboxylation, decarbonylation was also relevant in the 2-step HTL-HDO-process.

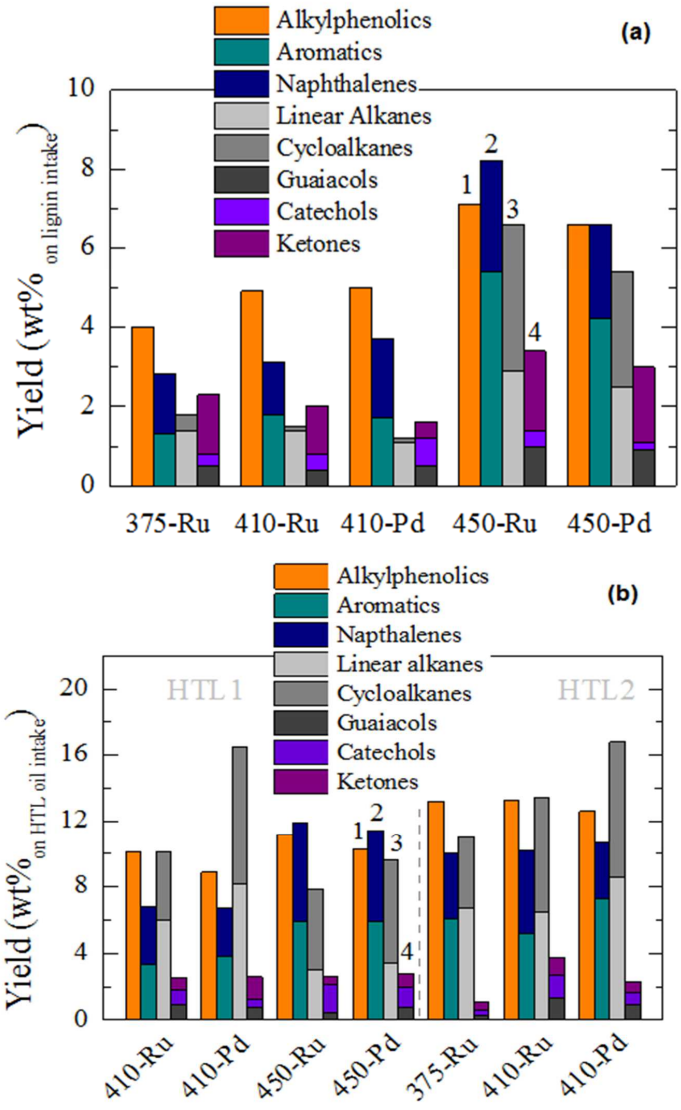


Figure 3.10. A schematic overview of organic product composition obtained from the one-pot direct HDO (a) and the 2-step HTL-HDO (b) of LES using the Ru/C and Pd/C catalysts classified as alkylphenolics (1), aromatics (2), alkanes (3) and other oxygenates (4). Figure is adapted from paper IV.

Identification of the molecular composition of the upgraded bio-oils indicated that alkylphenolic and aromatic monomers were predominant (see figure 3.10b). In addition, a significant increase in alkane formation was also observed, most probably due to the conversion of organic acids in the HTL-oils. Alkane formation was more

evident in experiments using Pd/C catalyst, mainly caused by a higher hydrogenation capacity of the Pd/C catalyst [86]. Since Ru/C catalyst showed lower selectivity towards alkane formation, this catalysis is found to be preferable for 2-step HTL-HDO approach.

In terms of total oxygen removal from the feedstock, there was no significant effect of including a first HTL-step since the oxygen content of all the hydrotreated oils was quite similar. Whereas, bio-oils derived from the direct HDO to some extent had lower H/C ratio compared to oils from the 2-step HTL-HDO caused by higher alkane concentrations in the oils from 2-step HTL-HDO.

Figure 3.11 depicts distinct variations in total monomer, alkylphenolic and aromatic yields between HDO and HTL-HDO processes. For experiments conducted at 410 °C, an improvement in the total monomer yields of 4–7 wt. % was observed when 2-step HTL-HDO route was selected, while the same trend of increase was not observed in case of alkylphenolics and aromatic yields. Monomer yields were slightly higher when treating the HTL2-oil, referring to the more depolymerized and volatile nature of the HTL2-oil. Additionally, the simultaneous depolymerization of LES with subsequent hydrodeoxygenation of the lignin monomers, has limited the yields of phenolic and aromatic monomers in favor of alkane formation when processing HTL-oils.

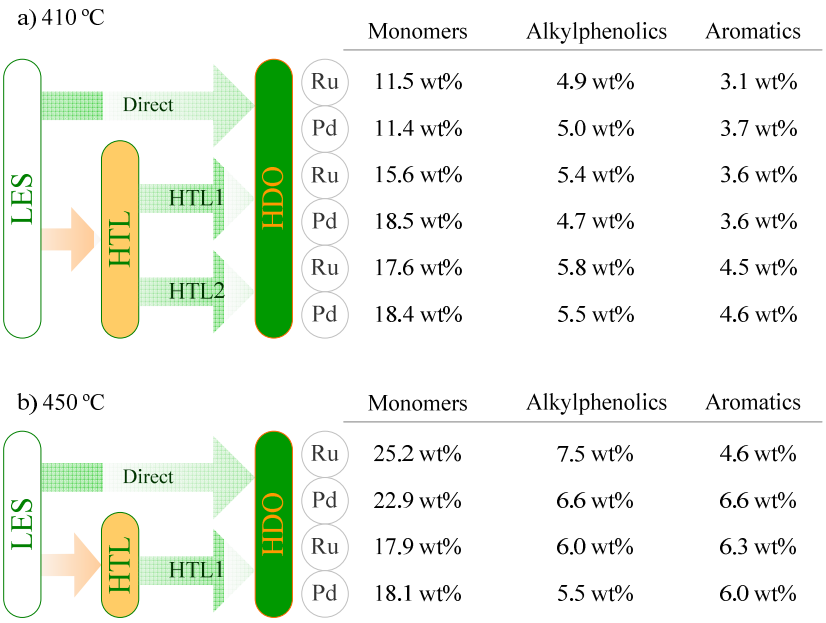


Figure 3.11. Overview of total monomer, alkylphenolic and aromatic yields obtained from the hydrotreated oils on a starting LES feed intake basis for the direct HDO and 2-step HTL-HDO approach at a) 410 °C and b) 450 °C using the Ru/C and Pd/C catalysts. Figure is adapted from paper IV.

An opposite trend in terms of total monomer yields was observed at 450 °C. Thus, at 450 °C, direct HDO of LES was preferred in terms of interesting monomers, despite the limited volatility of the HDO-oils compared to oils from HTL-HDO approach. However, in case of alkylphenolics and aromatics yields, minor variations were observed in between direct HDO and 2-step HTL-HDO at this temperature.

Overall, the results indicated that high operating temperature (450 °C) is preferred for direct conversion of LES through HDO, while processing the HTL2-oil at 410 °C provided highest total monomer yields as well as alkylphenolics and aromatics.

Chapter 4. Conclusions & future work

4.1 Summary and main conclusions

To integrate the LtL-solvolysis technique into a biorefinery concept, the formic acid assisted conversion of lignin was performed at two different scales. On this basic, conclusions regarding the differences in amount of oil yields and the quality of the produced oils in between the two scales were drawn in paper I. Overall, similar trends were observed with respect to reaction parameters at both reaction scales, yet oil yields decreased from small laboratory scale to 5 L scale with water as reaction medium. Since it takes longer time to reach the target temperature in 5 L scale compared to laboratory scale, lignin-oil components can undergo secondary lignin oil cracking, which will significantly influence relative amounts of oil and char at this scale. This can be confirmed by the increase in char formation in 5 L scale experiments compared to 0.025 L scale experiments, most likely caused by repolymerization of lignin components.

All feedstocks investigated in paper I had lignin contents above 50 wt. %, providing lignin-oils with high aromatic content. Feedstocks with low purity and/or high content of residual carbohydrates contained significant amounts of oxygen, which contributed to lower bio-oil yields. Much of the mass loss can be due to loss of oxygen due to substantial removal of oxygen through LtL-process. Bio-oils from ethanol-based experiments had to some extent higher H/C and O/C values compared to bio-oils from water-based experiments due to a higher fraction of alkylated phenols with a more complicated substitution pattern.

As results from paper I showed good perspectives for further investigation at 5 L scale, conversion of eucalyptus lignin in aqueous and ethanolic reaction media was given main focus in paper II. One of the main observations was that ethanol as reaction solvent resulted in higher bio-oil yields as well as higher H/C and O/C ratios compared to bio-oils derived from water-based experiments. Moreover, the incorporation of ethyl groups from ethanol contributed to a higher carbon recovery in the products. Stirred

reaction condition led to higher oil yield, lower char yield and higher carbon recovery due to increased reaction rate, improved mass transfer and limited gasification. Increased level of loading in the reactor also gave an increase in bio-oil yield and a decrease in char yield due to enhanced reaction efficiency at higher operating pressure. Oil yields tended to be somewhat reduced at higher temperatures. Bio-oils consisted mainly of aromatic components with guaiacol (2-methoxyphenol) as the major component in almost all cases. Overall, the highest bio-oil yields were achieved under stirred condition combined with high filling in the reactor at lower reaction temperature.

Since results from paper I and II provided a detailed insight into the effect of different reaction conditions on LtL-solvolysis performed at 5 L scale, the previously tested reaction conditions were further-developed and re-investigated with new parameters in paper III. Results obtained in paper III showed a major increase in oil yield and a significant decrease in char yield as a function of gradual increase in stirring rate as well as level of loading in the reactor. The use of goethite as reaction catalyst did not shown good conversion efficiency at either reaction temperatures, while Ru/Al_2O_3 as reaction catalyst contributed to significantly higher oil yields and lower char yields. Overall, the highest oil yield was obtained from experiment conducted under maximum stirring rate combined with maximum level of loading in the reactor when using Ru/Al_2O_3 as catalyst at lower reaction temperature.

The significant reduction in the H/C ratio of the raw material from storage over time did not affect the H/C ratio of the bio-oils, and the H/C values appeared to be quite similar between oils derived from the two raw materials at the same reaction conditions. In addition to guaiacol, alkyl-substituted methoxyphenols and alkylated phenols were the most abundant compounds identified in bio-oils produced at 305 and 350 °C, respectively, confirming more efficient hydrodeoxygenation at elevated temperatures. In addition, catechol was one of the major components in bio-oils when using goethite as catalyst. Results from SPE showed that more than 65 wt. % of the bio-oils can be recovered as polarity-based fractions, giving good perspectives for further development.

Detailed characterization of the lignin-enriched stillage (eucalyptus lignin) in paper IV confirmed the low purity of the LES feedstock compared to commercial lignins due to a notably amount of residual sugars/carbohydrates present in the LES, and consequently high oxygen content.

The organic products, comprising lignin-oil together with DCM and acetone soluble fractions, were the main product fraction from both processes with yields ranging from 28.0 to 39.2 wt. % on LES intake in direct HDO, and ranging from 50.7 to 85.7 wt. % on HTL-oil intake in 2-step HTL-HDO. However, char formation was avoided in 2-step HTL-HDO approach. Overall, higher organic product yields as well as better mass balances were achieved at lower temperatures. In terms of direct HDO of the LES, harsher conditions (450 °C) was required in order to produce lignin-oils with high volatility and improved monomer yields, while a significant increase in total monomer yields was observed when processing HTL-oils at 410 ℃.

The chemical composition of the organic product fraction was classified as alkylphenolics, aromatics, naphthalenes, linear and cyclic alkanes, guaiacols, catechols and ketones. In both conversion processes, alkylphenolics and aromatic compounds were the main chemical groups identified, followed by significant amounts of alkanes and oxygenates, respectively. Alkane formation was more evident in 2-step HTL-HDO approach compared to direct HDO and was significantly higher in experiments using Pd/C catalyst at 410 °C. Moreover, in terms of the interesting target monomers, Pd/C and Ru/C were the most preferred catalysts for direct HDO and 2-step HTL-HDO, respectively.

The oxygen content of the lignin-oils obtained from both hydrotreatment methods, i.e. direct HDO and 2-step HTL-HDO was quite similar. Hence, involving a first step hydrothermal liquefaction is not relevant in terms of oxygen depletion from the LES. All in all, the highest total monomer yields, including alkylphenolics and aromatics were obtained when treating the HTL2-oil at 410 °C and converting LES through direct HDO at 450 °C.

According to the results obtained in this thesis, increased LtL-process volume/scale from a small laboratory scale to a large pilot scale proved to be a successful process, yielding bio-oils consisting of phenolic components with high H/C and low O/C values. The phenolic components of the LtL-oils have high complexity and are still rich in oxygen, which make the LtL-oils of greater interest as a source of chemical building blocks than as a fuel.

4.2 Future work

The lignin-rich eucalyptus residue used in this project had a lignin content of approx. 50 wt. %, which was significantly low compared to commercial lignins. Therefore, further fractionation, e.g. organosolv fractionation, of this raw material prior to the LtL-process would enhance the lignin purity and improve the product yields. The structure and properties of lignin is highly dependent on the lignin origin as well as isolation methods used. Thus, a better characterization of the feedstock will lead to better understanding of the depolymerization behavior of the feedstock. However, exploitation of other types of lignins also is highly recommended. Additionally, utilization and screening of different types of catalysts, including homogenous and heterogeneous catalysts, is an essential option to overcome some of the major challenges associated with the catalytic LtL-process.

Moreover, the exploitation of the gas, aqueous and solid products from the LtL-process can also be beneficial. The gas phase products mainly consist of decomposition products of formic acid, i.e. CO, CO_2 and H_2, which can be converted to short-chain hydrocarbons such as methane, ethane and propane via Fisher-tropsch process. The aqueous phase contains residual solvents, methanol, ethanol, short chain organic acids and aromatics, which can be recovered by extraction. Utilization of the low-value char streams in the production of activated carbons, which can be used as catalyst supports can also be a promising option.

Results from Paper III showed carbon balances over 100 %, which suggests that exploration of the formic acid role in the LtL-solvolysis reaction mechanisms is

required. As mentioned earlier, there is ongoing research in this field and the results indicate that yet more detailed information on this is needed in the aim of further development and integration of the LtL-process into a biorefinery concept.

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Appendix

Table A. *Extended overview of experimental conditions investigated in the LtL-experiments.*

Experiment	Feedstock type	Feedstock (g)	Water (g)	Ethanol (g)	FA (g)	Catalyst (g)	Temp. (°C)	Time (h)	Stirrer rate (rpm)
Paper I									
I	Eucalyptus	200	500		244		380	2	400
II	Stat 417	200	500		244		380	2	400
III	BL	200	500		244		380	2	400
IV	Stat 416	200	500		244		380	2	400
V	AL	200	500		244		380	2	400
VI	Eucalyptus	200	500		244		320	2	400
VII	Eucalyptus	200	500		244		335	2	400
VIII	Eucalyptus	200	500		244		350	2	400
IX	Eucalyptus	200	500		244		365	2	400
X	Eucalyptus	200	500		244		380	0.75	400
XI	Eucalyptus	200	500		244		380	3	400
XII	Eucalyptus	200		394.5	244		320	2	400
XIII	Eucalyptus	200		394.5	244		335	2	400
XIV	Eucalyptus	200		394.5	244		350	2	400
XV	Eucalyptus	200		394.5	244		365	2	400
XVI	Eucalyptus	200		394.5	244		380	2	400
Paper II									
L.W.S-320	Eucalyptus	200	500		244		320	2	400
L.W.NS-320	Eucalyptus	200	500		244		320	2	0
H.W.S-320	Eucalyptus	300	750		366		320	2	400
H.W.NS-320	Eucalyptus	300	750		366		320	2	0
L.W.S-350	Eucalyptus	200	500		244		350	2	400
L.W.NS-350	Eucalyptus	200	500		244		350	2	0
H.W.S-350	Eucalyptus	300	750		366		350	2	400
H.W.NS-350	Eucalyptus	300	750		366		350	2	0
L.Et.S-320	Eucalyptus	200		394.5	244		320	2	400
L.Et.NS-320	Eucalyptus	200		394.5	244		320	2	0
M.Et.S-320	Eucalyptus	350		690.4	427		320	2	400
M.Et.NS-320	Eucalyptus	350		690.4	427		320	2	0
L.Et.S-350	Eucalyptus	200		394.5	244		350	2	400
L.Et.NS-350	Eucalyptus	200		394.5	244		350	2	0
M.Et.S-350	Eucalyptus	350		690.4	427		350	2	400
M.Et.NS-350	Eucalyptus	350		690.4	427		350	2	0

Paper III									
NC.NS.L.305	Eucalyptus	200	500		244		305	2	0
NC.S100.L.305	Eucalyptus	200	500		244		305	2	100
NC-1.S400.L.305	Eucalyptus	200	500		244		305	2	400
NC.S700.L.305	Eucalyptus	200	500		244		305	2	700
NC.S1000.L.305	Eucalyptus	200	500		244		305	2	1000
NC.S400.Min.350	Eucalyptus	150	375		183		350	2	400
NC-1.S400.L.350	Eucalyptus	200	500		244		350	2	400
NC.S400.Med.350	Eucalyptus	250	625		305		350	2	400
NC.S400.H.350	Eucalyptus	300	750		366		350	2	400
NC.S400.Max.350	Eucalyptus	350	875		427		350	2	400
NC-2.S400.L.305	Eucalyptus	200	500		244		305	2	400
NC-2.S400.L.350	Eucalyptus	200	500		244		350	2	400
Goethite.S400.L.305	Eucalyptus	200	500		244	5.25	305	2	400
Ru/Al_2O_3.S400.L.305	Eucalyptus	200	500		244	5.07	305	2	400
Goethite.S400.L.350	Eucalyptus	200	500		244	5.36	350	2	400
Ru/Al_2O_3.S400.L.350	Eucalyptus	200	500		244	5.01	350	2	400
Ru/Al_2O_3.S1000.Max.305	Eucalyptus	1000	875		427	5.16	305	2	1000

Part II

Paper I

Formic acid assisted liquefaction of lignin in water and ethanol, investigated for a 0.025 and a 5 L batch reactor: Comparison of yields and compositions of the products

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Ghoreishi S., Barth T., Derribsa H.

Published on:
Biomass & Bioenergy **2019,** 124, 1–12.

Biomass and Bioenergy 124 (2019) 1–12

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

Research paper

Formic acid assisted liquefaction of lignin in water and ethanol, investigated for a 0.025 and a 5 L batch reactor: Comparison of yields and compositions of the products

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ARTICLE INFO

Keywords:
Lignin
Formic acid assisted
Lignin-to-Liquid
Hydrodeoxygenated
Reactor volume
Phenols

ABSTRACT

Formic acid assisted conversion of lignin to liquids (LtL-process), where lignin is hydrodeoxygenated in a one-step conversion, produces bio-oils with a molecular weight range of 300–600 Da that comprise a complex mixture of monomeric phenols, e.g., phenol, cresol, guaiacol, catechol, etc., and more hydrogenated products. This paper addresses depolymerisation of lignin at small and large lab scales and includes characterisation of the products. Lignin conversion is performed using a 5 L stirred reactor and a 0.025 L unstirred reactor to evaluate the effect of increased volume and stirring on the oil yield and oil quality. The amount of oil yields is investigated for different types of lignin/lignin-rich residues, reaction temperatures (320–380 °C), reaction times (0.75–3 h) and reaction solvents (aqueous or ethanolic), and have been shown to be highest for the 0.025 L reactor. Furthermore, the relationship between the yields and reaction conditions are systematically explored using principal component analysis (PCA). For the Eucalyptus lignin-rich residue, ethanol tends to give higher oil yields (36–52 wt%) at most of the operating temperatures compared to water as reaction solvent (20–50 wt%). At both reaction scales and both solvent-systems, oil yields tends to decrease at reaction temperatures above 350 °C due to increased char formation. Reaction time does not seem to have any significant effect on oil yield at either scale. More than 40 wt% of the input lignin can be recovered as oil at 320 °C at both scales and solvent systems.

1. Introduction

Our environment and quality of life are affected by the devastating consequences of global population growth. It will be increasingly difficult to provide food and energy for such a dense population [1]. Recent economic developments in many countries all around the world have heightened the need for alternative energy resources, based mainly on renewable sources due to the depletion of fossil fuel, increasing energy demand, greenhouse gasses emission and global warming. All the mentioned perspectives have strengthened the interest in alternatives that are renewable, sustainable, and economically viable [2,3]. Biomass has recently received increasing attention as an attractive energy resource for the production of renewable biofuels and other value-added chemicals due to being a significant renewable resource and the only viable feedstock for carbon based fuels and chemicals [3–5].

The concept of a “biorefinery” describes all the processes and technologies that are involved in optimal use of biomass resources. The incoming raw material is completely converted to a range of products such as fuels and value-added chemicals [6–8]. In this context, research on second-generation biofuel is focused on the more abundant and often relatively cheap plant-derived lignocellulosic biomass. The bulk of the lignocellulosic biomass consists of three basic polymeric components: cellulose, hemicellulose and lignin. Cellulose and hemicellulose are complex polysaccharides [9]. Lignin is an amorphous, highly branched phenolic polymer and the third most abundant biopolymer in nature, which accounts for 10–30 wt% of the feedstock and carries the highest specific energy content of all the three fractions. Lignin can be obtained as a cheap byproduct either from the pulp and paper industry or from bio-ethanol production. At present, it is mostly burned as low value fuel for process energy purposes and only approximately 2% is used commercially [1,5,9–12].

Sustainable use of biomass must include using all fractions of the raw material to make products with high value [8,13]. Various types of

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https://doi.org/10.1016/j.biombioe.2019.03.004
Received 29 June 2018; Received in revised form 11 March 2019; Accepted 14 March 2019

biofuels and value-added chemicals have been produced from cellulose and the technical feasibility of this process has been well demonstrated [14]. However, major challenges must be addressed to develop the valorization of lignin to provide chemicals and fuels [11,15]. Lignin as a feedstock has significant potential for sustainable production of fuels and bulk chemicals and is regarded as the major aromatic resource of the bio-based economy [7,16]. However, the amount of lignin and the structural and monomeric composition of lignin within the lignocellulosic biomass varies from tree to tree, species to species, and even in samples from different parts of the same tree [1,9,12].

Different pathways have been explored for the conversion of lignin and lignin-rich residues to fuels and bulk chemicals. Thermochemical processes such as pyrolysis or catalytic pyrolysis, liquefaction, gasification, solvolysis and hydrogenolysis are among the most interesting concepts investigated in this respect [3,5,17–21]. In a review by Mohan et al. (2006), products from fast pyrolysis of biomass in the absence of oxygen were shown to be potentially useful both as an energy source and a feedstock for chemical production [22]. Yan et al. (2008) explored cleavage of ether bonds present in the lignin structure during reductive depolymerisation of lignin with hydrogen [23]. In this study, birch wood sawdust was converted to four main monomers, namely guaiacylpropane, syringylpropane, guaiacylpropanol, and syringylpropanol using an organic solvent and a series of active carbon supported catalysts, such as Ru/C, Pd/C, Rh/C, and Pt/C, at 523 K and 4 MPa H_2 pressure for 0.5–2 h. The maximum monomer yields were 46% relative to the initial lignin mass for Pt/C catalyzed conversion in dioxane.

Production of value-added chemicals from lignin requires the simultaneous depolymerisation of the lignin structures with subsequent hydro-deoxygenation of the lignin monomers and alkylation of aromatic rings, and is thus very complex [11,15,24]. Several studies have shown that the use of formic acid as a hydrogen donor enhances the depolymerisation of lignin. In 2008, Kleinert and Barth reported an innovative conversion method for valorization of lignin termed lignin to liquid (LtL). The LtL-process can be considered as a thermochemical solvolysis process in a liquid or near-critical reaction medium at high temperature and high pressure. Lignin to liquid conversion involves the use of a hydrogen donor solvent instead of molecular hydrogen. A well-known hydrogen donor is formic acid. At the given conditions, the formic acid acts not only as an *in situ* hydrogen source, but also as assists in the depolymerisation of the lignin molecule, and thus results in higher oil yields than comparable reactions with H_2 as reductant. A recent study reported by Oregui-Bengoechea et al. (2017) has revealed that the decomposition of formic acid and the chemical reaction between lignin and formic acid are competing reactions, and based on this study, a formylation–elimination–hydrogenolysis mechanism for the formic acid aided lignin conversion has been proposed. Commonly used solvents are water and ethanol [8,11,26]. The reaction product consists of a well-separated mixture of an organic top layer and an aqueous bottom layer with a total liquid yield of up to 90 wt%. The liquid organic phase is an oil with a high H/C and a low O/C ratio relative to the lignin input. GC-MS analysis show that the liquid organic fraction mainly consists of phenols and aromatic compounds, and this makes it a potential source of components for blending in motor fuels, or for utilization in fine chemical production. The isolated phenolic fractions were reported to be within 25–35 wt% of the lignin input and are quite high compared to the reported values from pyrolysis of similar feedstocks at the same reaction severities [8,9,12,13,24,25].

Furthermore, Huang et al. (2014) reported that hydrogenolysis of lignin using formic acid as an *in situ* hydrogen donor in the presence of a water-ethanol solvent mixture has contributed to more than 90 wt% depolymerized lignin yield from Kraft lignin even without any catalysts [26]. In a study by Kloekhorst et al. (2015), the catalytic solvolysis of Alcell® lignin using formic acid as hydrogen donor and Ru/C as the catalyst in an alcoholic reaction solvent has been shown to enhance the hydrodeoxygenation and thus reduce the oxygen content of the bio-oil significantly. The best result reported in this study was conversion of approx. 71 wt% of lignin input to bio-oil with low O/C ratio (0.09). High yields of valuable chemical compounds such as alkylphenolics and aromatics were determined using GCxGC-FID [27]. Hita et al. (2018) recently reported that 16–29 wt% of lignin can be converted directly into valuable platform chemicals through solvent-free hydrotreatment using a Fe-based limonite catalyst at 450 °C for 4 h 67–81% of the lignin oil components were detectable by 2D GCxGC-FID confirming that the majority of the lignin oil is composed by volatile components with low molecular weight [28].

However, optimizing process conditions yielding high amount of the desired products is challenging and time-consuming, especially since it is probable that there are interactions between different experimental factors. In a study reported by Kleinert et al. (2009), optimizing experiments have shown that high-pressure conditions give high product yield [24]. However, some important reaction parameters such as (i) shorter reaction time, (ii) lower reaction temperature and (iii) reduction of low-value side products, i.e., gas and solid residues need to be improved to make LtL-oils competitive with fuels and chemicals obtained from petroleum [21].

The development of the LtL-process and the chemical composition and bulk properties of LtL-oils produced in small laboratory scale have been described in previous papers [8,11,12,21,24,25]. In the next step of development towards industrial scale production, the effect of increasing the scale must be investigated, and the conversion needs to be optimized at larger scale. The larger product volumes also makes testing of separation and upgrading processes, e.g., distillation, possible. In this work, all experiments done in laboratory scale have been multiplied by a factor of 200 and performed in a 5 L reactor where pressure readings and stirrer torque were continuously recorded and controlled, to investigate whether the effect of the reaction variables are similar for the different reactors. In addition, the 5 L reactor is equipped with a stirrer, which could improve the mass transfer in the system and give a faster reaction. The main purpose of the work reported here is: (i) to compare amount of oil and char produced in stirred 5 L scale with 0.025 L laboratory scale, (ii) to find reaction conditions that give high oil yields of good quality in large scale, (iii) to provide an evaluation of product distribution and product composition in terms of reaction scale and various reaction parameters, such as lignin type, reaction temperature, reaction time and reaction solvent.

2. Materials and methods

2.1. Chemicals

Tetrahydrofuran (˃99.9%), ethyl acetate (˃99.8%) and formic acid (˃98%) were purchased from Sigma Aldrich and used without further purification. Ethanol, absolute prima, was purchased from Kemetyl Norway AS.

2.2. Type of lignins

The different types of lignins used in this work are given in Table 1.

All lignin types used in this work (except AL), were ground and sieved to a dry powder of < 500 μm particle size. Eucalyptus lignin was received as wet sample and was dried in an oven at 60 °C until constant mass before further preparation. Raw materials used in this work are chosen to represent both purified lignins and lignin-rich residues from ethanol production, and have been selected on the basis of availability.

2.3. Experimental conditions

2.3.1. Experimental set-up

5-L scale: Lignin (200 g), formic acid (244 g) and the solvent (500 g of water or 394.5 g of ethanol) were added to a stirred 5.3 L high pressure autoclave reactor from ESTANIT GmbH. Then the autoclave

Table 1
Lignin feedstock types and characteristics.

Feedstock	Botanical species and isolation method	Lignin content (mass %)	Ash content[a] (mass %)	H/C ratio	O/C ratio
Eucalyptus	Origin: Thailand, produced at the Biorefinery Demo Plant (BDP) in Örnsköldsvik, Sweden, using weak acid and enzymatic hydrolysis	~50	~4.4	1.41	0.586
Stat417	Norway Spruce-30% cellulose, produced at SEKAB from weak acid hydrolysis, SO_2-treated in bioethanol production process	~70	~1.0	1.37	0.559
BL	Norway Spruce, produced at Processum (Sweden) by acid precipitation from Kraft pulp mill black liquor	NA[b]	~4.9	1.30	0.442
Stat416	Norway Spruce-30% cellulose, Produced at SEKAB from enzymatic hydrolysis in bioethanol production process	~70	NA	1.20	0.451
AL	Alkali lignin purchased from Sigma Aldrich	~98	NA	1.25	0.730

[a] Ash content was measured by combustion at 575 °C according to protocol NREL/TP-510-42622 [29].
[b] Comparable lignin content as Lignoboost lignin (95–98%).

Table 2
Extended overview of experimental conditions.

Experiment	Lignin type	Time (min)	Temperature (°C)	Solvent
Test of lignin quality				
I	Eucalyptus	120	380	Water
II	Statoil 417	120	380	Water
III	Black liquor	120	380	Water
IV	Statoil 416	120	380	Water
V	Alkali	120	380	Water
Test of temperature and time				
VI	Eucalyptus	120	320	Water
VII	Eucalyptus	120	335	Water
VIII	Eucalyptus	120	350	Water
IX	Eucalyptus	120	365	Water
X	Eucalyptus	45	380	Water
XI	Eucalyptus	180	380	Water
Test of solvent type				
XII	Eucalyptus	120	320	Ethanol
XIII	Eucalyptus	120	335	Ethanol
XIV	Eucalyptus	120	350	Ethanol
XV	Eucalyptus	120	365	Ethanol
XVI	Eucalyptus	120	380	Ethanol

was closed and heated to the desired temperatures (320–380 °C) with a stirring rate of 400 rotations per minute (rpm) for a given reaction time of 0.75–3 h. The heating time from room temperature to the desired temperature (320–380 °C) was tested to be in a range of 60–75 min, giving an approximate heating rate of 5 °C min^{-1}. Reaction time (0.75–3 h) was measured in addition to the heating period. The pressure and torque of the stirrer were continuously monitored.

Laboratory scale: A detailed description is given elsewhere by Kleinert and Barth [8]. Briefly summarized, Lignin (1.0 g), formic acid (1.22 g) and the solvent (2.5 g of water or 1.97 g of ethanol) was added to a 0.025 L stainless steel high pressure Parr reactor from 4742-series without stirring, closed directly and heated in a preheated Carbolite high temperature oven to the desired conditions. The heating time from room temperature to the desired temperature (320–380 °C) was tested to be in a range of 16–19 min, giving an approximate heating rate of 20 °C min^{-1} [8]. The heating period was included in the reaction time (0.75–3 h).

The experimental conditions of all the experiments are given in Table 2.

2.3.2. Sample work-up

5 L scale; After the completed reaction time, the reactor heater was turned off and the reactor was cooled to ambient temperature by flowing cold water through the reactor's cooling coil. The final products after the LtL-process included a gas phase, a liquid phase and a solid phase, which contains both unreacted starting material and char produced during the conversion. A small amount of the produced gases was collected in a gas bag and analysed by gas phase GC before venting the rest. After opening the reaction container, the liquid phase was separated from the solid phase by opening the valve on the container bottom. Then a mixture of ethyl acetate:tetrahydrofuran (90:10 V:V) was added to the reactor container to extract the organic phase from the solid phase (unreacted lignin and char). The organic phase was dried over Na_2SO_4, and solvents and unreacted ethanol were removed from the LtL-oil on a rotary evaporator at reduced pressure (25–17.5 kPa) at 40 °C to yield a dark brown liquid. The oil yield was determined by mass. The char yield was determined by mass after drying. The oil fraction was characterized by gas chromatography mass spectroscopy (GC-MS) and elemental analysis. Some of the selected gas phases were characterized by gas chromatography.

Laboratory scale; After the completed reaction time, the reactor was taken out of the oven and cooled in an air stream to ambient temperature. Just like at 5 L scale, the final products after the LtL-process included a gas phase, a liquid phase and a solid phase. The

amount of produced gas phase was determined by weighting the reactor before and after ventilating the gas phase. After opening the reaction container, the liquid reaction mixture was extracted with a solution of ethyl acetate:tetrahydrofuran (90:10 V:V) and the solid phase (unreacted lignin and reaction products) was filtered. Two well-separated liquid phases were obtained (an organic phase on the top and an aqueous phase on the bottom). They were separated by decanting, and the organic phase was dried over Na_2SO_4 and concentrated using the same procedure as in 5 L scale. The yields were determined by mass, and the same analysis were done for the oil fractions in laboratory scale as in 5 L scale.

The mass percentage of oil and char yields is calculated using the formula shown below.

$$\text{Product yield (wt.\%)} = (\text{dry mass of oil or char (g)} / \text{dry mass of input lignin (g)}) * 100$$

2.3.3. Reproducibility

Replicate experiments for accuracy measurements have been omitted in this study due to the extensive sample work-up procedure in 5 L scale. However, previous studies using the same equipment at 0.025 L scale has reported less than 5% variation between duplicates [12] and 2–6% standard deviation for three replicates [21] for product yields (oil and char) supporting the reproducibility of the reactions and the work-up procedures.

2.4. Characterisation of the products

2.4.1. Elemental analysis

All samples were analysed for their elemental composition in the CHNS mode with a Vario EL III instrument using helium as carrier gas. The amount of oxygen was calculated by difference.

2.4.2. Mass spectrometry

5 L scale; The LtL-oil (1.0 mg) was dissolved in 1 cm^3 ethyl acetate:tetrahydrofuran (90:10 V:V) and the sample was analysed using GC–MS on a Trace Ultra GC coupled with a DSQ II quadrupole MS detector from Thermo scientific. The injection was run in splitless mode at 260 °C (injector temperature) on a 25 m Ultra 2 Silica capillary column ((5% phenyl)-methylpolysiloxane), 200 μm ID from Agilent Technologies. The following GC-MS instrumental conditions were applied:

Start temperature: 40 °C; Heating rate 1: 8 °C min^{-1}; Final temperature 1: 220 °C; Heating rate 2: 10 °C min^{-1}; Final temperature 2: 300 °C; Ion-source temperature for MS: 220 °C; Mass range: 50–400 Da.

The GC–MS inter phase valve delay was set to 5 min and the MS detector operated in positive mode at 70 eV. Compounds were identified using Xcalibur software and the NIST 2.0 library.

0.025 L scale; The LtL-oil (1.0 mg) was dissolved in 1 cm^3 ethyl acetate:tetrahydrofuran (90:10 V:V) and the sample was analysed using an Agilent Technologies 7890A GC-system with auto-sampler, coupled with an Agilent 5977A MSD. The injection was run in splitless mode at 280 °C (injector temperature) on a 30 m HP-5ms column with 250 μm ID and thickness of 0.25 μm from Agilent Technologies. The following GC-MS instrumental conditions were applied:

Start temperature: 50 °C; Heating rate 1: 8 °C min^{-1}; Final temperature 1: 220 °C; Heating rate 2: 10 °C min^{-1}; Final temperature 2: 300 °C; Ion-source temperature for MS: 230 °C; Mass range: 50–400 Da.

The GC–MS inter phase valve delay was set to 5 min and the MS detector operated in positive mode at 70 eV. Compounds were identified using Enhanced MSD Chemstation software F.01.00.1903 and the NIST 2.0 library.

2.4.3. Gas phase analysis

Gas phase GC analysis was performed on a GC-FID/TCD (HP 6890A) and a 30 m Porapak Q Molsieve column equipped with a FID front detector and a TCD back detector, which was controlled by an HPChem laboratory data system. The following GC instrumental conditions were applied:

Initial temperature: 50 °C; Heating rate 1: 5 °C min^{-1}; Final temperature 1: 85 °C; Heating rate 2: 20 °C min^{-1}; Final temperature 2: 180 °C; Injection temperature: 200 °C; FID detector temperature: 300 °C; TCD detector temperature: 200 °C; The pressure was kept constant at 255 kPa.

Table 3
Experimental details for experiments comprising the experimental design: Variable 1 (−) = 320 °C, Variable 1 (+) = 380 °C, Variable 2 (−) = water, Variable 2 (+) = ethanol, Variable 3 (−) = 0.025 L, Variable 3 (+) = 5 L.

Experiment[a]	Temperature (°C)	Solvent type	Scale (L)
VI-S (—)	320	Water	0.025
VI-L (−+)	320	Water	5
XII-S (- + -)	320	Ethanol	0.025
XII-L (-++)	320	Ethanol	5
I-S (+−)	380	Water	0.025
I-L (+-+)	380	Water	5
XVI-S (++-)	380	Ethanol	0.025
XVI-L (+++)	380	Ethanol	5

[a] The letters S and L, written by the experiment names, explain Small and Large scale.

2.4.4. Experimental design and multivariate data analysis

A fractional factorial design was used to explore the effect of the processing conditions on the amount and composition of the products. A high (+) and low (−) value for each of the three selected experimental variables; reaction temperature (V1), type of reaction solvent (V2) and reactor scale (V3), was used in the design. A fractional factorial design (2^{3-1}) which includes a balanced half of all possible combinations of the variables was used to reduce the number of experiments required. The duration of the experiments were kept constant (2 h). Table 3 Gives an overview of the experimental parameters.

All the response factors, quantitative yields (oil and char yields as wt.% relative to the dry lignin input), H/C and O/C ratios, and H, C and O recoveries from the design were interpreted using principal component analysis (PCA) and Sirius 10.0 software. PCA is a commonly used technique in statistics for simplifying the data by reducing multivariable to a two-dimensional plot in order to analyse the results. Multivariate methods such as PCA are necessary to detect hidden correlations between reaction parameters and product properties [17,30]. In order to interpret the data set in PCA, biplots are used. A biplot in PCA shows the relationship between objects, between variables, and between objects and variables. This means that a biplot shows correlations between loadings and their potential association with the properties of an object. Loadings that are projected close to each other with respect to the origin are positively correlated, and loadings that are projected oppositely to each other are negatively correlated. If the loadings have strong influence on the model they will be projected far from the origin, and loadings that appear close to the origin have negligible or minor influence on the model. PLS (Partial least squares) regression was used to establish quantitative equations for the individual response factors. The use of multivariate analysis in interpretation of experimental data is covered in depth in by Carlson and Carlson (2005) [31].

3. Results and discussion

3.1. Product yields

In the water-system, the liquid phase consisted of a single aqueous phase and the LtL-oil was not present as a separate phase, but was

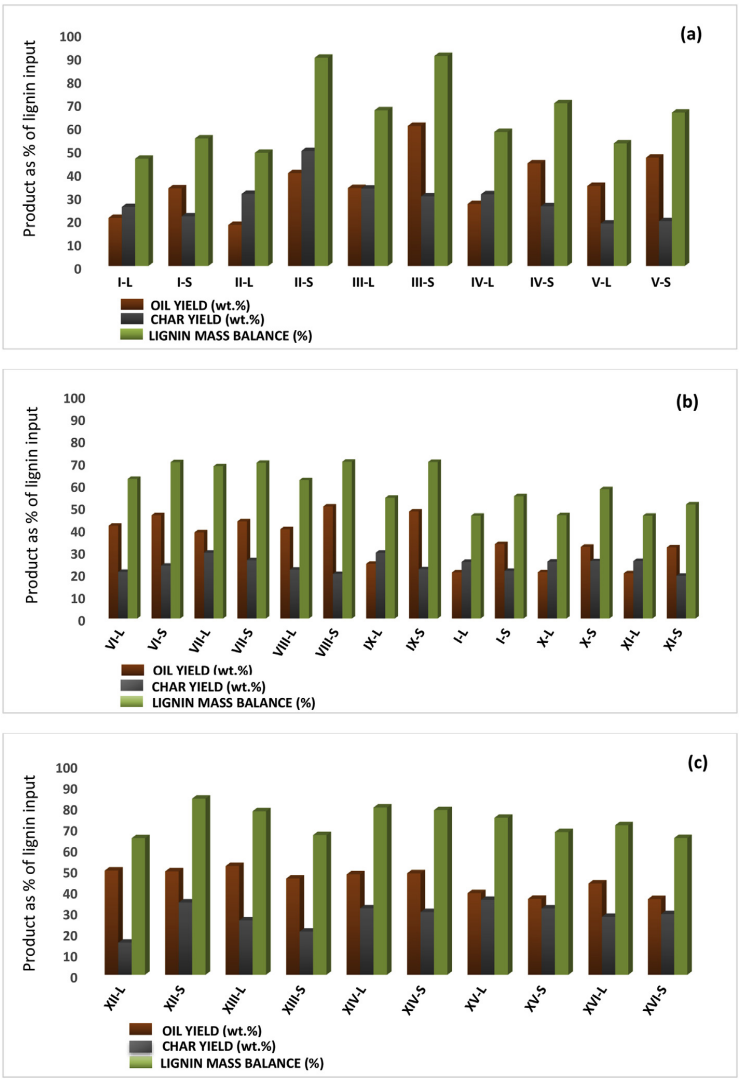

Fig. 1. Column diagrams showing product yields and lignin mass balances as mass fraction of lignin input at both scales as a function of different (a) lignin types in water system at 380 °C for 2 h (b) reaction temperatures from 320 to 380 °C (experiment VI to I) and reaction times from 0.75 to 3 h at 380 °C (experiment X, I and XI) in water system (c) reaction temperatures in ethanol system from 320 to 380 °C for 2 h. The lignins are identified in Table 1 and the temperature and duration of each experiment is given in Table 2.

adsorbed onto the solid phase. In the ethanol-system, the liquid phase consisted of two immiscible layers: a dark brown LtL-oil phase and a small clear ethanol/water phase. The two layers were separated using the same work-up procedure as in the water-system, and can thus be compared. The quantitative results from lignin degradation from all the experiments are shown in the supplementary material (Table S1).

3.1.1. *Variations in yields for lignins from different feedstocks*

Experiments I-V have been run at the same conditions, but with different feedstocks. The purity of the lignin input ranges from a very pure (98%) Alkali lignin (Exp. V) and a pure precipitated lignin from Black liquor with a comparable lignin content as Lignoboost lignin (Exp. III) to a hydrolysis residue containing around 50% lignin (Exp. I), as specified in Table 1. All the experiments were run at 380 °C for 120 min. The mass yields of oil and char for both scales are given in Fig. 1a, together with the recovery of the input lignin mass in these fractions.

The yields of liquid ranges from 17 to 52 wt% on lignin basis at 5 L scale, and from 33 to 60 wt% at 0.025 L scale. The char yields are in the ranges 15–36 wt% and 19–50 wt%, respectively. The amount of the original lignin mass recovered as oil and char as calculated in the lignin mass balance lies in the range 46–80 wt% in the 5 L reactor, and 51–90 wt% in the 0.025 L scale. The difference in the mass balance will comprise gas phase and aqueous products, including water produced in

the thermal decomposition reactions. A precise mass balance of all products is thus difficult to obtain; and the carbon recovery data presented below are more pertinent for an overall evaluation of yields. However, the general observation is that the oil yields are consistently higher at 0.025 L scale at this level of conversion. As expected, both the oil yields and the total recovery vary between the lignin types [12], where the most pure lignins, AL lignin (Exp. V), and BL lignin (Exp. III) produce the highest oil yield at both scales. This confirms that the purity of the raw material is an important factor, and should be optimized using pretreatment techniques prior to the LtL-process.

3.1.2. Variation in yields as a function of temperature and time

These experiments were run using the lignin-rich Eucalyptus residues as feedstock. The temperature range was 320–380 °C, and the holding time at the target temperature was between 45 and 180 min for experiments performed at 380 °C, and 120 min for the experiments performed at lower temperatures. The solvent used in this section was water. The mass yields from both scales are shown in Fig. 1b.

The results show a trend of decreasing oil yields with temperature, which is more marked at 5 L scale. The char yields increase somewhat with temperature. The results for the two scales are quite similar in the lower and intermediate temperature range (320–350 °C, Exp. VI–VIII), and then they diverge at the highest temperatures, e.g., at 365 °C (Exp. IX). Here, 0.025 L scale experiment gives nearly 50 wt% oil, while the 5 L scale experiment gives only 25 wt% oil yield. Thus, at large scale the oil yield decreases more rapidly with temperature. As mentioned in section 2.3.1, it takes longer time to reach the target temperature in 5 L scale experiments compared to laboratory scale. This can be interpreted as that secondary lignin oil cracking is more efficient at 5 L scale than 0.025 L scale, which will significantly influence relative amounts of oil and char at the two scales. This is supported by the general observation that the amount of char increases at higher reaction temperatures, which can be caused by the repolymerisation of lignin components. The duration of the experiment at 380 °C (45–180 min, Exp. X, I and XI) does not significantly influence the yields at either scale, confirming previous results showing only a moderate effect of the duration and supporting the premise that the differences in heating rate will not strongly influence the yields from Eucalyptus lignin at the two reactor scales.

3.1.3. Variations in yields with ethanol as solvent

In this series of experiments, ethanol was used as the reaction medium, with Eucalyptus as the feedstock. The temperature was varied between 320 and 380 °C for 120 min (Exp. XII–XVI). The mass yields from both scales are given in Fig. 1c.

For the ethanol experiments, the oil yields were higher than for the water based experiments shown in Fig. 1b and more or less equivalent at both scales. The yields are similar at around 50 wt% in the 320–350 °C temperature range (Exp. XII–XIV), and then tend to decrease at higher temperatures.

3.1.4. Comparison with published values

In our systems, the oil yields lie in the range of 17–60 wt% of lignin input, reflecting that the yields are strongly dependent on the reaction conditions. When comparing with recent studies, it must be noted that they mostly have taken advantage of the benefits of using catalysts. As mentioned in the introduction section, Kloekhorst et al. explored that the catalytic solvolysis of Alcell® lignin in the presence of formic acid as hydrogen donor and Ru/C as the catalyst in an alcoholic reaction media has given over 70 wt% bio-oil with very low oxygen content [27]. In a recent study from 2017, Kristianto et al. reported that over 66 wt% of CAHL-lignin (Concentrated Acid Hydrolysis Lignin) can be converted to bio-oil using the same reaction medium and catalyst as Kloekhorst' research group [32]. In that study, Kristianto et al. have shown that an increase in formic acid amount and prolonged reaction time in the presence of Ru/C increases oil yield, as well as reduces the oxygen content of the bio-oil substantially. These studies are based on pure lignin as input, and thus are comparable with our yields from the purest lignins (47–67 wt%). The results reported in both mentioned studies above are quite comparable with results obtained by Oregui-Bengoechea et al. (2015) from the catalytic hydrodeoxygenation of acid hydrolysis lignin in water/formic acid reaction medium using Ru/Al_2O_3 as catalyst, which lies in the range of 86–98 wt% of lignin input [21].

The main purpose of our study is to find reaction conditions that are favorable at both scales without the use of catalysts. The results obtained in this study are comparable with results obtained from similar conversion processes reported by other research groups. For instance, Huang et al. (2014) has reported that over 90 wt% of Kraft lignin can be depolymerized using an *in situ* hydrogen donor in a water/ethanol (1:1 V:V) reaction solvent mixture at 300 °C without any catalysts [26]. Among the different lignin types and reaction conditions we have tested in this study, BL-lignin, a Kraft lignin, has yielded the highest oil yield (approx. 60 wt%) using water as reaction media at 380 °C in small scale, and Eucalyptus lignin has yielded the highest oil yield (approx. 52 wt%) in ethanol based experiment performed in large scale at 335 °C. The differences between the results presented in this paper and results reported by Huang et al. [26] are most likely due to the variation in the procedure and reaction parameters used in these two studies. The use of acetone as extracting solvent by Huang et al. [26] rather than the less polar ethyl acetate/THF mixture used in this work may have a major influence on the recovery values, as this would incorporate a wider range of oligomeric lignin degradation products in the depolymerized lignin fraction. Using different lignin feedstocks also makes the quantitative comparison difficult, as well as the different reaction temperature ranges (320–380 °C vs. 200–330 °C), reaction solvents (water or ethanol vs. 50:50 V:V water:ethanol mixture), formic acid-to-lignin mass ratio (1.22 vs. 0.7), stirrer speed (400 vs. 200 rotations per minute), and reactor size (0.025 and/or 5 L vs. 0.01 L).

3.2. Elemental composition and carbon recovery

The elemental composition of all oil samples are presented in Table 4., and compared with the composition of the original lignins in

Table 4
Elemental composition of all LtL-oils and feedstocks.

Experiments	5 L scale Mass %				0.025 L scale Mass %			
	C	H	N	O	C	H	N	O
I	80.6	7.99	0.89	10.5	77.2	7.63	1.02	14.1
II	78.4	7.83	0.92	12.9	74.6	8.27	0.88	16.2
III	77.5	7.91	0.43	14.2	77.6	7.80	0.60	14.0
IV	78.1	7.80	0.82	13.3	77.0	7.24	0.16	15.6
V	67.7	6.68	0.37	25.3	77.8	7.95	0.50	13.8
VI	74.4	7.23	1.18	17.2	73.9	8.32	1.04	16.8
VII	72.1	8.49	0.63	18.8	71.2	8.04	0.70	20.1
VIII	74.7	8.19	0.79	16.4	72.1	7.41	1.50	19.0
IX	74.9	8.39	1.07	15.6	73.8	8.19	0.89	17.1
X	77.4	8.12	1.00	13.5	71.3	7.81	0.79	20.1
XI	79.0	8.70	0.80	11.5	78.5	7.77	0.67	13.1
XII	73.7	7.93	1.16	17.2	70.2	7.80	0.92	21.1
XIII	72.0	8.42	1.19	18.4	71.7	8.14	0.97	19.2
XIV	73.8	8.43	0.50	17.3	70.1	7.87	1.38	20.6
XV	69.9	8.71	1.15	20.3	75.2	8.31	0.99	15.5
XVI	76.4	8.56	1.21	13.9	75.3	8.93	1.38	14.4

Lignins Mass %				
	C	H	N	O
Eucalyptus	50.1	5.92	0.44	39.1
Stat417	53.2	6.12	0.07	39.6
BL	55.9	6.12	0.17	32.9
Stat416	58.3	5.89	0.73	35.1
AL	48.1	5.07	0.10	46.7

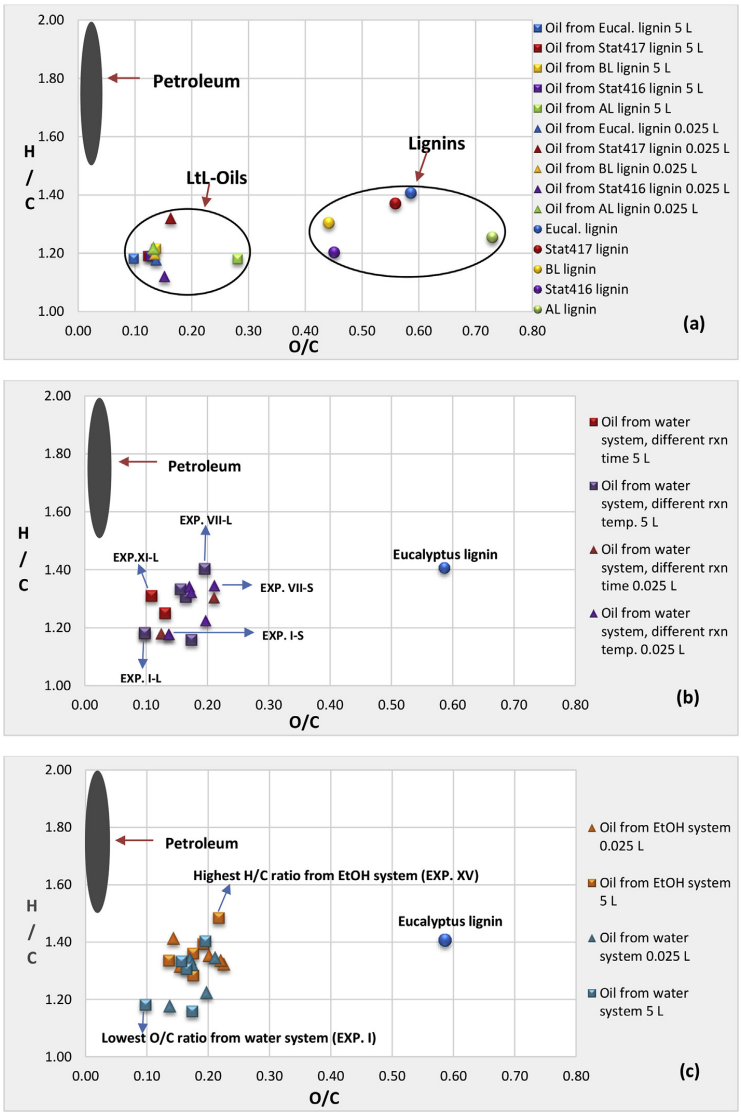

Fig. 2. Van Krevelen diagram (a) shows H/C ratio and O/C ratio of all lignin types and LtL-oils produced from different lignin types in large and small scale. Van Krevelen diagram (b) shows H/C ratio and O/C ratio of Eucalyptus lignin and LtL-oils produced at different reaction times and reaction temperatures using aqueous solvent in large and small scale, and (c) shows H/C ratio and O/C ratio of Eucalyptus lignin and LtL-oils produced using ethanolic or aqueous solvents in large and small scale.

Fig. 2. Fig. 2a shows a clear deoxygenation for all bio-oils since the O/C ratios of the LtL-oils are significantly reduced relative to the starting biomasses. However, bulk hydrogenation does not seem to have occurred since the H/C ratios of the bio-oils seem also to be reduced slightly relative to the starting materials. The H/C value is in the range 1–1.2, suggesting that aromatic rings can be predominant. The lower H/C ratios of the oils compared to starting feedstocks can be caused by the elimination of hydrogen from the lignin structure as aqueous products, i.e., water and methanol.

Fig. 2b shows a trend of reduction in both H/C and O/C ratio for the oils with increasing temperature of conversion at both large and small scale. The H/C and O/C ratio of all oils are presented in the supplementary material, Table S2. The ethanol based conversion systems give higher H/C ratios (Fig. 2c) supporting the previous observation of addition of ethyl groups to the aromatic ring structures [25]. The incorporation of the ethyl groups will increase the number of alkyl units in the product and thus increase the H/C ratio.

The elemental compositional data also makes it possible to calculate the yields on a carbon basis in addition to recovery by mass. Since the oxygen content of the oil is reduced from, e.g., 39.1 wt% in the Eucalyptus lignin to a range of 10.5–25.3 wt% in the lignin derived oils, much of the mass loss will be due to loss of oxygen. Hydrogen can both

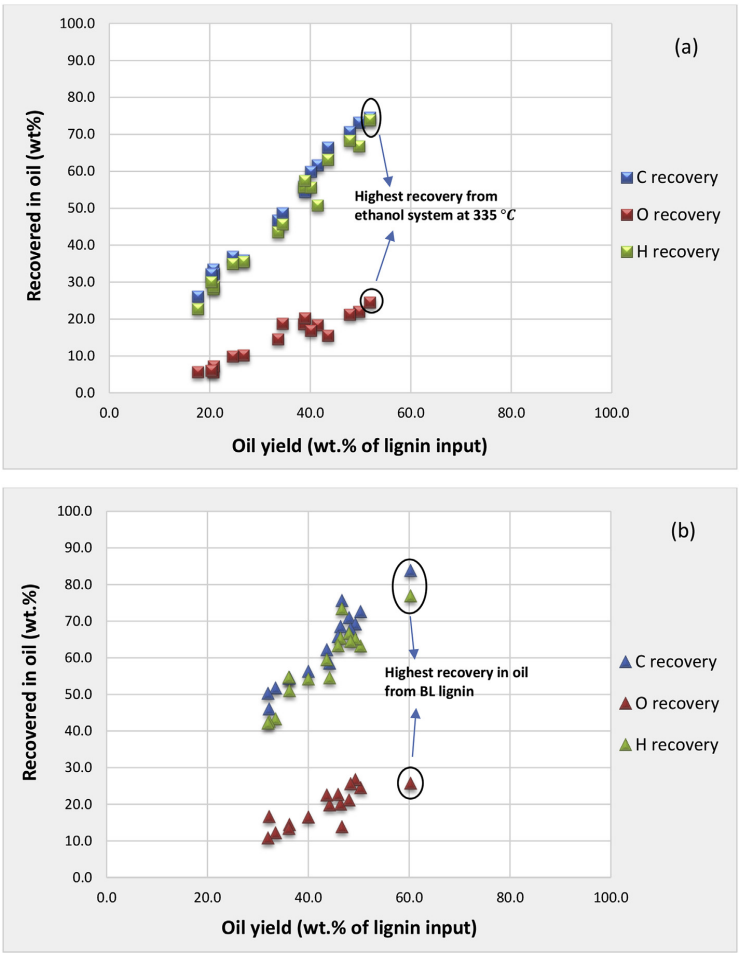

Fig. 3. (a) Percentage of C, O and H recovered in % LtL-oils produced in large scale and (b) Percentage of C, O and H recovered in % LtL-oils produced in small scale.

be lost and added in the conversion process. Calculating the recovery of oil from lignin on a carbon basis will focus on the net recovery of the target compounds, with no distraction from the loss of oxygen which is not wanted in the products.

Fig. 3 gives an overview of the carbon recovery in oil from all experiments. The carbon recovery is very dependent on the oil recovery by mass, and reaches approx. 75 wt% of initial carbon content of the feedstock in experiment XIII (Eucalyptus residue, ethanolic reaction medium, 335 °C for 120 min). The incorporation of ethyl groups from the solvent will contribute to the calculated carbon recovery. At lab scale, the highest value for carbon recovery is more than 80 wt% in oil from the Black liquor lignin in experiment III (water as reaction medium, 380 °C for 120 min). At both these conditions, nearly 80 wt% of the oxygen has been removed from the liquid products compared to the initial feedstock.

3.3. Molecular composition of LtL-oils

The liquid phase product comprises a complex mixture of phenolic compounds. The more volatile compounds can be identified using GC-MS analysis. Examples of major components are given in Table S3. In the supplementary material, and their relative amounts are shown in Fig. 4. Examples of GC-MS chromatograms containing representative compound distributions are given in the supplementary material (Fig. S1 and Fig. S2).

The composition of the GC-MS detectable part of the oils is quite similar for experiments at large and small scale when other variables are kept constant. Fig. 4a and 4b illustrate this, showing that the most abundant compounds are the same at large and small scale for experiments VIII-L and VIII-S (Eucalyptus lignin, 350 °C, 120 min, water as solvent). However, the proportion of the compounds relative to 2-methoxyphenol (guaiacol) varies between the oils from the large and small reactor. This can tentatively be caused by the lack of stirring at small scale, which seems to influence the degree of conversion somewhat, as also seen on the total yield (see section 3.1.2).

In Fig. 4c and 4d, the comparable experiments with ethanol as solvent are presented. Although 2-methoxyphenol still is the highest peak, the ethanol solvent influences the oil composition to a significant degree. The number of components that include an ethyl substituent has increased significantly, including (19) 1-ethyl-3-phenylmethylbenzene, (20) 2-ethoxyphenol and (21) 2,5-diethylphenol, and other substituted compounds like (15) vanillyl alcohol are also

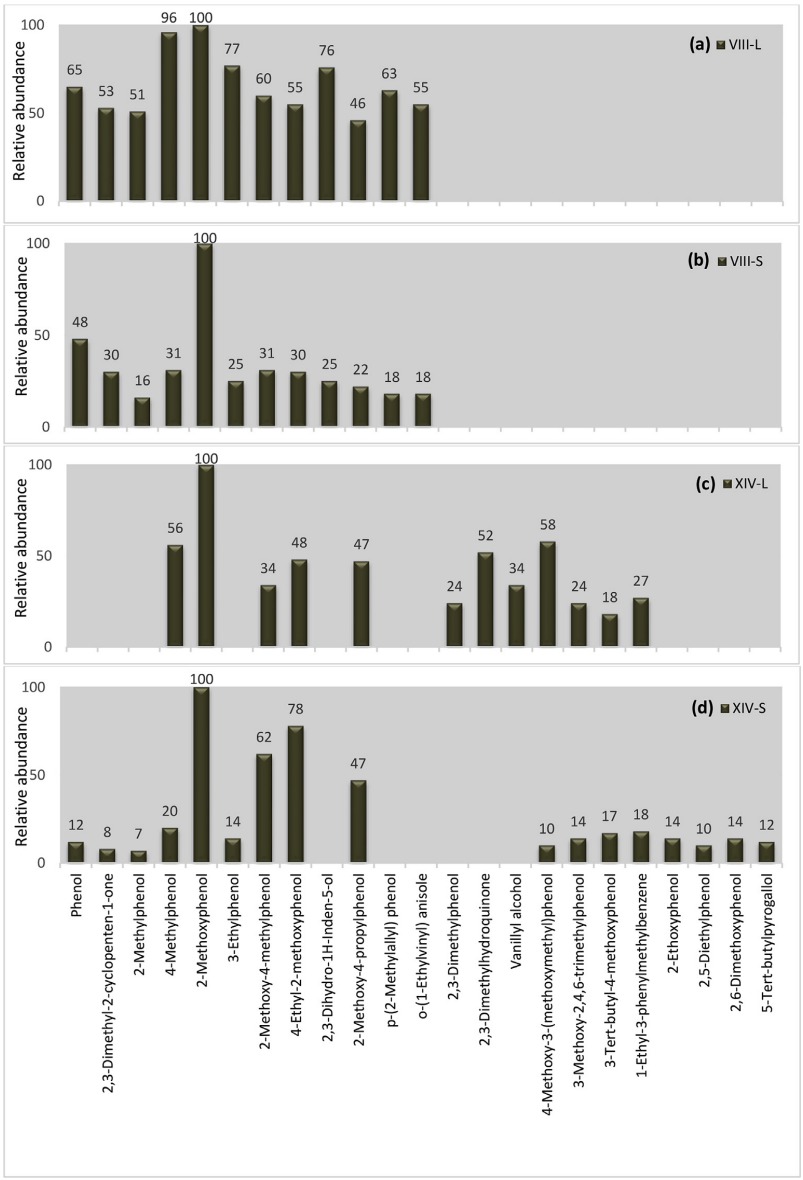

Fig. 4. GC-MS data from experiments VIII-L, VIII-S (Eucalyptus, 350 °C, 120 min, water as solvent) and XIV-L and XIV-S (Eucalyptus, 350 °C, 120 min, ethanol as solvent) showing the relative peak height of the most abundant compounds present in the bio-oils. The sequence of identified compounds on x-axis refers to the same structure numeration shown in Fig. S1 and Fig. S2 in the supplementary material. 2-methoxyphenol represents peak height of 100% due to highest relative abundance, and peak heights are measured relative to this peak.

more abundant. This indicates that ethanol has a double effect as both reaction solvent and as an alkylation agent. The increase in alkyl-substituted compounds mirrors the tendency to a higher H/C ratio in the oils from the ethanol based system. Furthermore, the increase in phenol-/methoxy-/ethoxy-substituted compounds results in significantly higher O/C ratio and higher molecular weight in the oils obtained from ethanol-system.

The large-scale experiments with ethanol as solvent give a different range of highly substituted phenols than the small-scale experiments. The reason for these differences is not well understood at present.

3.4. The composition of the gas phase

A considerable amount of gas is produced during the reaction. Decomposition of formic acid is the source of the major part of the gas in the form of CO_2 and H_2 from the direct decomposition and CO from

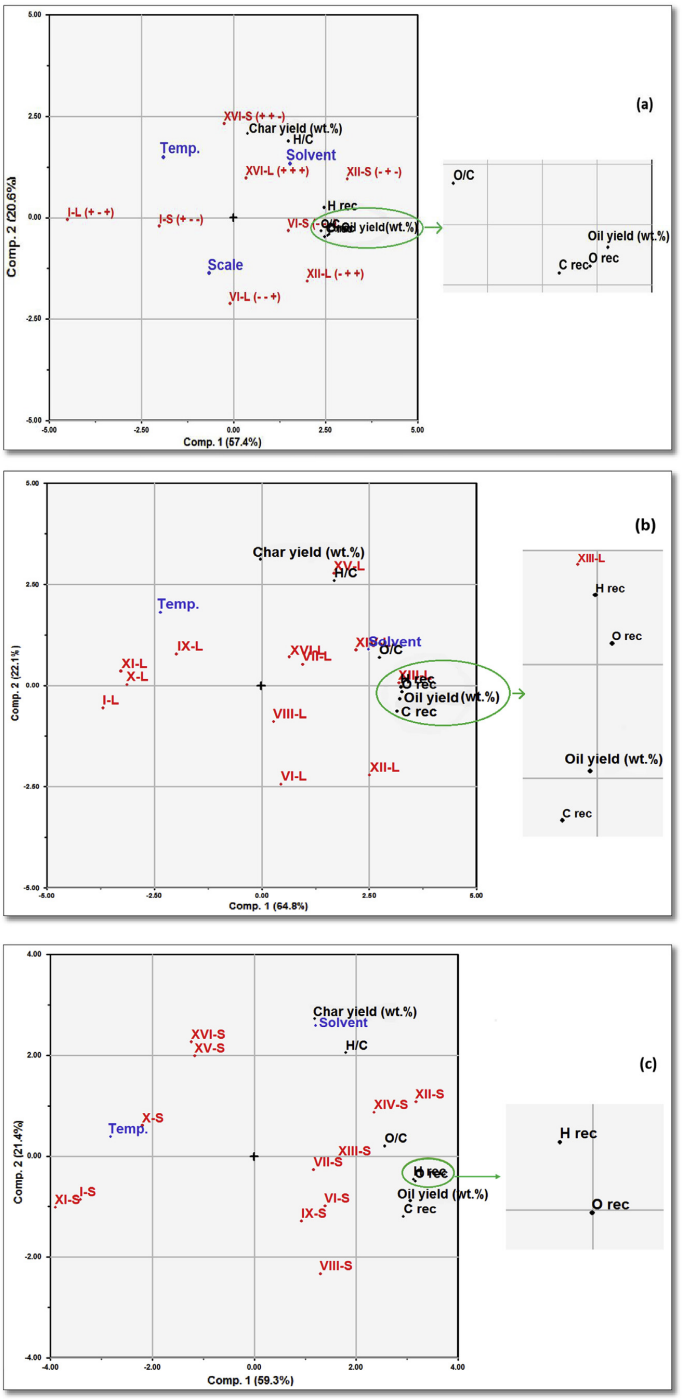

Fig. 5. (a) Biplot of objects and variables from fractional factorial design shown in Table 3. (b) biplot of objects and variables from all experiments done with Eucalyptus lignin in large scale and (c) biplot of objects and variables from all experiments done with Eucalyptus lignin in small scale.

the water–gas shift reaction [1,24]. In the water-system, these are the major gas components, with traces of CH_4 also present. In the ethanol-system, a homologous series of hydrocarbon gases are also present, reflecting dehydration reactions of ethanol. Examples of chromatograms of gas phase samples are given in the supplementary material, Fig. S3.

The gas phase yields are monitored as the overpressure after cooling in the 5 L reactor and in the small scale reactions as the difference in mass of the reactor before and after venting the overpressure gas. At present, no reliable method for converting these data to precise yields have been established, so the gas yields are not discussed in detail. However, the compositional data will be useful in evaluation of the overall process.

3.5. Principal component analysis

In the defined experimental setup from Table 3 The following parameters were studied: oil yield (wt.%), char yield (wt.%), H/C ratio of the bio-oils, O/C ratio of the bio-oils, carbon recovery, hydrogen recovery and oxygen recovery.

A biplot of the experimental design using the design variables and all the experimental responses is given in Fig. 5a. The design confirms that a high carbon recovery is associated with a high oil yield, and also places the oxygen recovery and O/C ratio as highly correlated with the oil yield on PC1. This implies that the highest oil yields overall retain oxygen, and thus may not be optimal in terms of the oil quality. These yields are negatively correlated with the reaction temperature, so a higher temperature gives a lower mass yield but also reduces the oxygen content of the oil. The yields are positively correlated with the solvent variable, again confirming the observation that the ethanol based experiments produce higher yields than the water based experiments. The char yield is described on PC2, and thus independent of the oil yield and carbon recovery. It is positively correlated with the temperature and H/C ratio of the oil, suggesting a disproportionation of the oil components producing carbon-rich char and hydrogen-enriched liquid product at higher temperatures.

Using the design variables to calculate multivariate regression equations for the yields mostly produce models with a significant uncertainty and a considerable degree of scatter when the additional experiments on the Eucalyptus feedstock are predicted in the models. This implies that a larger design would be needed for reliable yield predictions, since only linear relationships will be well described in the screening model based on the factorial design. The exception is the oxygen recovery and O/C ratio, which are well modelled and well predicted using the following regression equations (based on standardized experimental variables):

$$O/C = 13.4 - 0.82*Temp. + 0.36*Solvent - 0.33*Scale$$

(Predictions: 90.5% of variance explained, R = 0.95 in the design, 0.71 with all samples included)

$$O\ recovered = 11.8 - 0.83*Temp. + 0.44*Solvent - 0.22*Scale$$

(Predictions: 92.7% of variance explained, R = 0.96 in the design, 0.84 with all samples included).

The factorial design also makes it possible to compare the large and small scale experiments on a systematic basis. Separate PCA models based on all experiments are given in Fig. 5b (large scale) and Fig. 5c (small scale). Even though the models are not statistically balanced, they provide a good basis for comparing the systems. Overall, the influence of the variables on the yields are similar. The main difference is in the effect of the solvent, which is strongly positively correlated with the char yield at small scale. This observation can be explained by lack of stirring in the small reactors, as the stirring will distribute the lignin better in the reaction medium and thus reduce the tendency towards recondensation reactions. The overall slightly lower oil yields at 380 °C seen in Fig. 1b and 1c can also be an effect of improved mass transport at stirred conditions, giving a higher degree of conversion in the stirred systems. Since the lignin is not directly soluble in the reaction media at low temperatures, the initial state of the reaction system will be a suspension of lignin particles in the liquid reaction media. Further heating melts the lignin and increases the solubility. The physical state of the reaction system at the selected temperatures is not explicitly known, but torque readings during the heating period at large scale indicate that lignin melts to a viscous liquid which dissolves at higher temperatures.

4. Conclusion

The overall result shows similar trends relative to reaction parameters at both reaction scales, but that the oil yields in some cases decrease from small laboratory scale to 5 L scale with water as reaction medium. The maximum difference in the oil yield produced at the two scales is approx. 32 wt% on lignin basis (EXP. II). AL lignin, which is the most pure lignin feedstock, has given the highest oil yields at both scales. In both solvent systems, the highest oil yields from Eucalyptus lignin-rich residue are achieved at reaction temperatures up to 350 °C, indicating that repolymersation of lignin components to give char formation becomes significant at higher reaction temperatures. The oil yields remain constant at 380 °C when the reaction times were increased from 0.75 to 3 h, and was highest in the small scale experiments.

Furthermore, results from elemental analysis shows no obvious differences in the H/C ratios of the oils as a function of reactor scale. However, bio-oils produced at large scale, regardless of solvent type, seem to have lower O/C ratios, which confirms increased deoxygenation at large scale experiments and thus better oil quality. The stirring equipment used in the 5 L reactor will give improved mass transfer and enhance the reaction rates. Bio-oils from ethanol-system have higher H/C values compared to bio-oils from water-system due to the increase in alkyl-substituted compounds. Results from GC-MS analysis shows no clear differences in the composition of LtL-oils based on the reaction scale. However, comparison of the composition of LtL-oils produced in water-system vs. Ethanol-system shows clear variations due to a more complicated pattern of substitution in the bio-oil components from ethanol-system. Guaiacol is the major component in most of the LtL-oils produced in both solvent-systems and scales. In this study, the highest oil yields were obtained using ethanol at reaction temperatures below 350 °C at 5 L scale. In addition, one of the main benefits of bio-oil production at 5 L scale is the large product volume, which makes testing of different separation, fractionation and upgrading processes, e.g., distillation, solid phase extraction, possible. Overall, the results show good perspectives for further experiments on 5 L scale, but indicate that the optimal conditions must be established for the specific reactor setup to be used.

Acknowledgements

We gratefully acknowledge Ltl NOR AS, Norway (grant no. 203527/E20) and the Norwegian Research Council, Norway (grant no. 190965/S60) for financial support and use of the 5 L reactor. The authors would also like to thank I. J. Fjellanger for assisting with elemental analysis and Sekab for providing lignin.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2019.03.004.

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Paper II

Stirred and non-stirred lignin solvolysis with formic acid in aqueous and ethanolic solvent systems at different levels of loading in a 5-L reactor

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Ghoreishi S., Barth T., Derribsa H.

Published on:
Biofuel research journal **2019,** 21, 937–946.

Biofuel Research Journal 21 (2019) 937-946

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Original Research Paper

Stirred and non-stirred lignin solvolysis with formic acid in aqueous and ethanolic solvent systems at different levels of loading in a 5-L reactor

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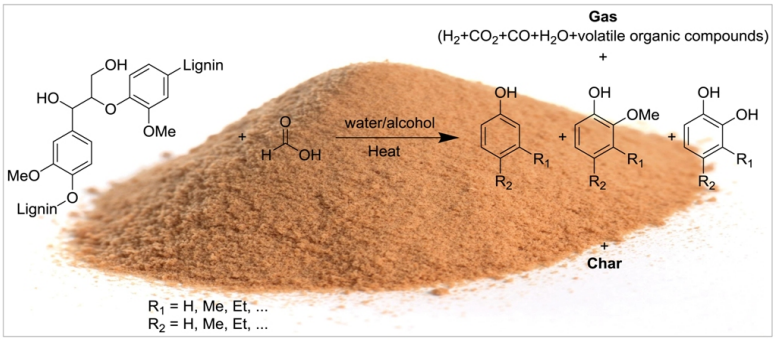
HIGHLIGHTS

- Oil yields increased and char yields decreased with a high loading in the reactor at stirred condition.
- In comparison with water-based system, ethanol-based system tended to give higher oil yields.
- Oil yields decreased, more or less, with increasing reaction temperature regardless of solvent type.
- The bio-oils from ethanol-based experiments had the highest H/C and O/C ratios.
- The bio-oil composition produced in each solvent system was quite stable and independent of other reaction conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 November 2018
Received in revised form 23 January 2019
Accepted 17 February 2019
Available online 1 March 2019

Keywords:
Lignin de-polymerization
Stabilization
Lignin-to-Liquid
5-L Scale
Stirring

ABSTRACT

Lignin polymer is biologically and chemically stable and requires highly vigorous conditions for de-polymerization, and subsequent stabilization of the monomeric conversion products to prevent re-polymerization and char production. The Lignin-to-Liquid (LtL) process is a solvolytic conversion of lignin with formic acid. Formic acid has been shown to both catalyze the de-polymerization and supply hydrogen that stabilizes the de-polymerization products. In this paper, lignin from Eucalyptus wood was used as the feedstock, and the LtL-process was performed in both aqueous and ethanolic solvent systems. The experimental variables were different levels of loading in the reactor, stirred and non-stirred conditions, and different reaction temperatures. The bio-oil consisted mostly of phenolic compounds, and the bio-oil yields differed with type of the solvent used, level of loading in the reactor, stirring condition, and operating temperature. More than 55 wt.% of the lignin was recovered as bio-oil at 320 °C at stirred conditions when the reactor was loaded at high level. Overall, the ethanolic solvent together with maximum level of loading in the reactor under stirred condition resulted in the highest bio-oil yield. Elemental balance data for bio-oil and char yields and the molecular composition of the bio-oils were also investigated using, respectively, elemental analysis and GC-MS. Finally, principal component analysis was used as well to systematically explore the relationship between the bio-oil and char yields and the reaction conditions.

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Please cite this article as: Ghoreishi S., Barth T., Derribsa H. Stirred and non-stirred lignin solvolysis with formic acid in aqueous and ethanolic solvent systems at different levels of loading in a 5-L reactor. Biofuel Research Journal 21 (2019) 937-946. DOI: 10.18331/BRJ2019.6.1.5

1. Introduction

Environmental preservation is one of the major concerns in the 21st century. Population growth, increasing living standards, increasing industrialization, and the motorization of the world have led to a steep rise in energy and fossil fuel consumption. Excessive consumption of fossil fuels to fulfill the energy demands has not only resulted in the depletion of the resources but also has largely contributed to greenhouse gas (GHG) emissions and global warming (Nigam and Singh, 2011; Tanaka et al., 2012). Thus, it is necessary to develop a bio-based economy, mainly based on renewable, sustainable, and economically viable energy sources. Since there is no single solution to the challenges faced, there will be a need for combined actions, including changes in behavior, changes in vehicle technology, expansion of public transport, and introduction of innovative fuels and technologies (Cherubini, 2010; Singh et al., 2010; Haghighi Mood et al., 2013; Kim et al., 2013). Utilization of biomass as a renewable and sustainable raw material for production of biofuels and other value-added chemicals through a biorefinery approach has recently received a great deal of attention as a promising alternative to fossil resources (Cherubini and Jungmeier, 2010; Bu et al., 2012; Kim et al., 2013). A biorefinery system comprises optimal and sustainable use of the renewable resources where the incoming raw material is completely converted into a range of products with high values (Kleinert and Barth, 2008; Gasson et al., 2010; Oregui-Bengoechea et al., 2015).

Emerging technologies for production of fuels from biomass have become an important subject because of their potential environmental impacts. Competition over biomass feedstocks as well as their different applications has been intensified because of increasing demands for biomass. Thus, to ensure sustainable use of biomass, one needs to identify the most promising routes for producing heat, power, fuels, and materials in terms of their technological, economic, and environmental performance (Gerber et al., 2011; Gerssen-Gondelach et al., 2014). Biofuels, as an alternative to fossil fuels and a future leading supply of energy, are believed to increase supply security, reduce vehicle emissions, and provide farmers with a steady income (Nigam and Singh, 2011; Creutzig et al., 2015).

The greatest challenge faced in the biofuel arena is to produce renewable liquid fuels, which are suitable for use in motor vehicles. New fuels generated from renewable sources should preferably be compatible with the existing motor technology and infrastructure. This in fact facilitates direct substitution and mixing of conventional and renewable fuel types. Bioethanol produced from edible sources of carbohydrates and biodiesel produced from edible vegetable oils, are well-known examples of renewable and petroleum compatible first-generation biofuels. However, there are major challenges associated with large-scale production of these first-generation biofuels such as food *vs.* fuel conflicts, etc. Thus, much effort has been put into developing new processes for the production of second-generation biofuels from a variety of non-edible resources such as lignocellulosic biomass (Kleinert and Barth, 2008).

Lignocellulosic biomass is in fact considered as a suitable carbon raw material for the synthesis of functional carbon materials. It is cheap, abundant and does not negatively affect the human food supply chain (Zhang et al., 2011; Liu et al., 2015). Lignocellulosic biomass is a heterogeneous feedstock composed of three principal components of different nature: cellulose, hemicelluloses, and lignin. Various types of biofuels and value-added chemicals have been already produced from cellulose and hemicellulose, and the technical feasibility of the processes involved have been well demonstrated. The third major consistent, i.e., lignin, is a cross-linked amorphous copolymer, defined as a complex polyphenolic network of three basic phenylpropane monomers (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol). Lignin as a feedstock has a significant potential for the production of bio-based aromatic fuels and chemicals (Azadi et al., 2013; Løhre et al., 2016). Since, the high cost of cellulosic ethanol has limited its market, it will be essential to develop an efficient and appropriate thermochemical method for conversion of waste lignin streams into fuels and valuable bulk and specialty chemicals like aromatics, phenols, aromatic ethers, vanillin, etc. However, there are still major challenges faced for the valorization of lignin to these valuable commodities (Singh et al., 2014; Kristianto et al., 2017; Oregui-Bengoechea et al., 2017).

Various methods have been, and are being, explored to develop high-yield processes for the conversion of lignin-rich residual materials to fuels and bulk chemicals. One of such processes aimed at lignin valorization was reported by Kleinert and Barth (2008), comprising simultaneous de-polymerization of the lignin structures with subsequent hydro-deoxygenation of the lignin monomers in a solvent with an *in-situ* hydrogen donor. This approach has been termed as the Lignin-to-Liquid (LtL) process. It is in fact a thermochemical solvolytic process performed in polar solvents such as water and alcohols at high temperatures and high pressures. In the LtL process, formic acid is used as hydrogen donor, which is converted *in situ* to molecular hydrogen and CO/CO_2. The reaction product is a mixture of monomeric alkylated phenols and aliphatic hydrocarbons, with a high H/C and a low O/C ratio. As shown by previous studies, the decomposition of formic acid and the chemical reaction between lignin and formic acid are competing reactions, and therefore, a formylation–elimination–hydrogenolysis mechanism for the formic acid aided lignin conversion has been proposed (Kleinert et al., 2009; Oregui-Bengoechea et al., 2015; Løhre et al., 2017; Oregui-Bengoechea et al., 2017). However, as highlighted in these works, optimization of such a process would be challenging and time-consuming due to the interactions between different experimental conditions. Nevertheless, there is ongoing research on this approach, and a number of papers have been published addressing subjects such as reaction mechanisms (Holmelid et al., 2012; Oregui-Bengoechea et al., 2017), kinetic modelling (Gasson et al., 2012), and the effect of catalyst to increase energy efficiency (Liguori and Barth, 2011; Oregui-Bengoechea et al., 2015). Most of the reported results have been obtained at small laboratory scale though. In addition, upscaling is necessary to develop the process to industrial level and for the conversion needs to be optimized at larger scales.

Therefore, the aim of this study is to evaluate the product yields and product composition of bio-oils through thermochemical conversion of lignin at a 5-L pilot scale as a function of reaction parameters such as solvent type, level of loading in the reactor, and reaction temperature under stirred and non-stirred conditions. In this study, lignin conversion was investigated at two different temperatures (320 and 350 °C) using two different reaction solvents (water and ethanol) by changing the stirring rate from 0 rpm to 400 rpm at different levels of loading in the reactor. For the LtL-experiments carried out in this work, a fractional factorial design was set up to determine the impacts of the experimental parameters on yields and product composition as well as to find the conditions leading to highest oil yields and quality.

2. Materials and Methods

2.1. Chemicals

All reagents and solvents used in this experimental work were purchased from Sigma Aldrich and were used without any further purification (≥98%). Ethanol, absolute prima, was purchased from Kemetyl Norway AS.

2.2. Feedstock characterization

The feedstock used in this work, herein termed as Eucalyptus lignin, was a lignin rich residue isolated through the application of weak acid and enzymatic hydrolysis of Eucalyptus, at the Biorefinery Demo Plant (BDP) located in Örnsköldsvik, Sweden. The lignin content of the feedstock estimated from its elemental composition, was ~ 50.1%. The ash content of the feedstock was determined to be approximately 4.4% according to protocol NREL/TP-510-42622 (Sluiter et al., 2008). The H/C and O/C ratios of the feedstock also estimated through elemental analysis, were 1.41 and 0.59, respectively. The feedstock contained traces of cellulose and hemicellulose, which could explain the high value of the O/C ratio compared to that of pure lignin.

Eucalyptus lignin was received as wet sample and was dried in an oven at 60 °C until constant weight before further grinding and sieving to a dry powder of <500 µm particle size. The dried lignin powder was used as it was without further purification.

2.3. Lignin to Liquid (LtL) experiments

2.3.1. Experimental set-up

Lignin (200 – 350 g), formic acid (244 – 427 g), and the solvent (500 – 750 g of water or 394.5 – 690.4 g of ethanol) were added to a stirred 5.3 L

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high-pressure autoclave reactor (ESTANIT GmbH). The autoclave was then closed and heated to the desired temperatures (320 – 350 °C) with a stirring rate of 0 – 400 rpm for a reaction time of 2 h. The heating time from room temperature to the desired temperature (320 – 350 °C) ranged from 60 to 70 min, giving an approximate heating rate of 5 °C/min. Reaction time (2 h) was measured in addition to the heating period. The pressure and torque of the stirrer were continuously monitored during the experiments.

The experimental conditions investigated are given in Table 1. The experiments are coded as shown below:

X.Y.Z-T
X: Loading in the reactor; Y: Reaction solvent; Z: Stirring condition; T: Reaction temperature

For instance;
L.W.S-320 indicating: Low level of loading Water as reaction solvent. Stirred reaction at 320 °C.

Table 1.
Experimental conditions investigated in the LtL-process experiments.

Experiment*	Lignin** (g)	Formic acid (g)	Water (g)	EtOH (g)	Stirrer speed (rpm)	Temperature (°C)
L.W.S-320	191	244	500	—	400	320
L.W.NS-320	191	244	500	—	0	320
H.W.S-320	287	366	750	—	400	320
H.W.NS-320	287	366	750	—	0	320
L.W.S-350	191	244	500	—	400	350
L.W.NS-350	191	244	500	—	0	350
H.W.S-350	287	366	750	—	400	350
H.W.NS-350	287	366	750	—	0	350
L.Et.S-320	191	244	—	394.5	400	320
L.Et.NS-320	191	244	—	394.5	0	320
M.Et.S-320	335	427	—	690.4	400	320
M.Et.NS-320	335	427	—	690.4	0	320
L.Et.S-350	191	244	—	394.5	400	350
L.Et.NS-350	191	244	—	394.5	0	350
M.Et.S-350	335	427	—	690.4	400	350
M.Et.NS-350	335	427	—	690.4	0	350

* L: Low loading; H: High loading; M: Maximum loading; W: Water; Et: Ethanol; S: stirred; NS: Non-stirred.
**: Lignin-enriched eucalyptus residue, measured on ash-free basis.

2.3.2. Work-up procedure

Upon the completion of the determined reaction time, the reactor heater was turned off and the reactor was cooled to the ambient temperature by flowing cold water through the reactor's cooling coil. The final products of the LtL-process included a gas phase, a liquid phase, and a solid phase, containing both unreacted starting materials and the char produced during the conversion. Nevertheless, based on the published literature, the bulk of the solid phase produced under the given reaction conditions would be expected to be mainly in the form of char (Gasson et al., 2012). The produced gas was vented by opening the gas-valve. Analysis of the gas composition was not performed as a part of this study, but relevant data for the gas composition can be found in a previous work performed by our group (Oregui-Bengoechea et al., 2015), showing that the decomposition of formic acid was the source of the major part of the gas produced.

After the gas phase was vented, the reactor was opened and the liquid phase was separated from the solid phase. In the water system, the liquid phase consisted of a single aqueous phase while the LtL-oil was adsorbed to the solid phase. The liquid phase was separated from the solid phase by opening the valve on the container bottom. Then, the organic phase was extracted by adding a solution of EtAc:THF (90:10) and subsequently, the solid phase was filtered off.

In the ethanol system, the liquid phase consisted of two immiscible layers; a dark brown LtL-oil phase and a small clear ethanol/water phase. The two layers were separated using the same work-up procedure as in the water system.

The extracted organic phase was dried over Na_2SO_4, while the solvent and unreacted ethanol was removed from the LtL-oil using a rotary evaporator at 40 °C and 250 mbar (in the water system) and 175 mbar (in the ethanol system) to yield a dark brown liquid. The final oil and solid yields were determined by weight after solvent evaporation and drying, respectively. The mass balance was calculated as the sum of % oil and char yield. The oil fraction was characterized by gas chromatography-mass spectroscopy (GC-MS) and elemental analysis. The chars were characterized by elemental analysis.

2.4. Elemental analysis

All samples were analyzed for their elemental composition in the CHNS mode with a Vario EL III instrument using helium as carrier gas. The amount of oxygen was calculated by difference.

2.5. GC–MS

The LtL-oil (1.0 mg) was dissolved in 1 mL ethyl acetate:tetrahydrofuran (90:10) and the sample was analyzed using an Agilent Technologies 7890A GC-system with auto-sampler, coupled with an Agilent 5977A MSD. The injection was run in splitless mode at 280 °C (injector temperature) on a 30 m HP-5ms column with 250 µm ID and thickness of 0.25 µm from Agilent Technologies. The following GC-MS instrumental conditions were applied:

Start temperature: 40 °C; Heating rate 1: 6 °C/min; Final temperature 1: 280 °C; Heating rate 2: 40 °C/min; Final temperature 2: 300 °C; Ion-source temperature for MS: 250 °C; and Mass range: 50 – 400 u.

The GC–MS inter phase valve delay was set to 5 min and the MS detector was operated in positive mode at 70 eV. Compounds were identified using the Enhanced MSD Chemstation software F.01.00.1903 and the NIST 2.0 library.

2.6. Experimental design

As mentioned earlier, for the LtL-experiments carried out in this work, a fractional factorial design was set up. Experimental variables, which were studied, were (1) level of loading in the reactor (the sum of input amounts of the reactants), (2) reaction solvent, (3) stirring condition, and (4) reaction temperature. A high (+) and low (–) value for the experimental variables was selected for use in the design. The duration of the experiments was kept constant (2 h) in both reaction systems. A fractional factorial design (2^{4-1}) which included a balanced half of all possible combinations of the variables was used to reduce the number of experiments required in each reaction system. An overview of the experimental parameters is tabulated in Table 2.

All the response factors, quantitative yields (% oil and % char), H/C and O/C ratios, C recovery, H recovery, and O recovery from the design were interpreted using principal component analysis (PCA) and Sirius 10.0 software. A biplot of a PCA reveals correlations between loadings/descriptors and their potential association with the same properties of an object. Loadings, which are projected close to each other with respect to the origin, are positively correlated, while loadings, which are projected oppositely to each other, are negatively correlated. Loadings that have a strong influence on the model will be projected far from the origin, and loadings with negligible or minor influence on the model will appear close to the origin in the biplot (Carlson and Carlson, 2005).

In many cases, principal components are not the ideal latent variables. Partial Least Squares (PLS) regression analysis is a method that can establish quantitative relations between two blocks of data, e.g., a block consisting of descriptor data for a series of reaction systems and a block

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consisting of response data measured on these systems (Carlson and Carlson, 2005). In line with that, such regression analysis was applied to each yield variable in the data set.

Table 2.
Experimental details of the LtL-process experiments: Variable 1 (–) = low loading (g), Variable 1 (+) = high or maximum loading, Variable 2 (-) = water, Variable 2 (+) = ethanol Variable 3 (–) = 0 rpm, Variable 3 (+) = 400 rpm, Variable 4 (–) = 320 °C, Variable 4 (+) = 350 °C.

Experiment	Loading water-/ethanol-system (Lignin + solvent + FA (g))	Solvent type	Speed of stirrer (rpm)	Temperature (°C)
L.W.S-320 (- - + -)	935	Water	400	320
L.W.NS-320 (- - - -)	935	Water	0	320
H.W.S-320 (+ - + -)	1403	Water	400	320
H.W.NS-320 (+ - - -)	1403	Water	0	320
L.W.S-350 (- - + +)	935	Water	400	350
L.W.NS-350 (- - - +)	935	Water	0	350
H.W.S-350 (+ - + +)	1403	Water	400	350
H.W.NS-350 (+ - - +)	1403	Water	0	350
L.Et.S-320 (- + + -)	830	Ethanol	400	320
L.Et.NS-320 (- + - -)	830	Ethanol	0	320
M.Et.S-320 (+ + + -)	1452	Ethanol	400	320
M.Et.NS-320 (+ + - -)	1452	Ethanol	0	320
L.Et.S-350 (- + + +)	830	Ethanol	400	350
L.Et.NS-350 (- + - +)	830	Ethanol	0	350
M.Et.S-350 (+ + + +)	1452	Ethanol	400	350
M.Et.NS-350 (+ + - +)	1452	Ethanol	0	350

3. Results and Discussion

3.1. Product yields

The quantitative results of all the LtL-process experiments are presented in Figure 1 and TableS1 in the supplementary material.

For the water-based experiments, it was not possible to use the maximum level of loading due to pressure limitations, and thus, the results from water-based experiments with high loading level would not be completely comparable with the results of the ethanol-based experiments with maximum loading level.

The feedstock used in this work was not directly soluble in the reaction media at low temperatures, and thus, the initial state of the reaction system was a suspension of lignin particles in the liquid reaction medium. Further heating melted the lignin and increased the solubility. The physical state of the reaction system at the selected temperatures was not explicitly known, but torque readings during the heating period indicated that lignin melted into a viscous liquid, which dissolved at higher temperatures.

3.1.1. Variation in yields as a function of different loadings in the reactor

In the first part of this work, the effect of two different levels of loading on product yield was considered. The yields of oil (wt.%) and char wt.%), together with the lignin mass balance (%), for all the experiments are shown in Figure 1a. The difference between two consecutive experiments, presented in Figure 1a, was the degree of filling in the reactor while all the other conditions were kept constant.

The yields of oil and char ranges, respectively, from 18 to 72% and from 9 to 36% by weight of the lignin input. The amount of the original lignin mass recovered as oil and char was calculated as lignin mass balance and was in the range 47 – 81% relative to lignin input weight. The difference between the input and the measured mass balance would comprise gas phase and aqueous products, which were produced in the thermal decomposition reactions. Since a precise mass balance of all products was difficult to obtain, the carbon recovery data presented in *Section 3.2* could be more pertinent for an overall evaluation of yields.

The results showed that increasing the loading in the reactor from a low to a high/maximum level, when all other reaction conditions were kept constant, led to an increase in bio-oil yield percentage. The increased oil yield could be associated with a higher overall conversion due to more efficient stirring and higher operating pressure when the reactor was loaded to a high level (see Table S1). The reactor was equipped with two stirrers above each other on the stirring rod, and thus, the different filling levels in the reactor were one of the main factors for investigating changes in product yields as a function of two simultaneously rotating stirrers. The results also showed that when the maximum level of the reactor was loaded, rotation of both stirrers would result in a more efficient mixing of lignin with the reaction medium and consequently, better lignin de-polymerization. As mentioned above, the pressure in the reactor was proportional with the level of loading, and in particular with liquid level (formic acid and reaction solvent), in the reactor. That means that increasing the amount of reaction media would increase the pressure during the reaction, which might also increase the reaction efficiency. A maximum difference of 20% in oil yield was observed as a function of the reactor filling, while the char yields tended to decrease when increasing the level of loading. The reaction was optimal when a high amount of oil and a low amount of char was produced, so high loading levels were found preferable.

3.1.2. Variation in yields as a function of solvent type

The effect of reaction solvent on product yields was considered by replacing water with ethanol as reaction solvent. The two successive experiments differed from each other in terms of the type of reaction solvent while all the other reaction parameters were kept constant.

For the ethanol experiments, as shown in Figure 1b, the oil yields were significantly higher than for the water-based experiments, except for the maximum loaded, non-stirred experiment at 350 °C. The yields were in a range of 18 – 55% and 31 – 72% for water- and ethanol-based experiments, respectively. In terms of the char yield, it can be observed that the ethanol-based experiments yielded higher amounts of char than the water-based experiments, except in low loaded, stirred experiment at 320 °C. Moreover, a better mass balance was achieved for all the ethanol-based experiments. As mentioned above, the main reason for this might be the lack of data on aqueous products when using water as solvent.

3.1.3. Variation in yields as a function of stirring condition

Figure 1c presents a comparison of mass yields (%) among all the experiments based on their differences in stirring condition. The two consecutive experiments presented in Figure 1c were performed at the same reaction conditions, while the rate of stirring was changed from 400 rpm to the non-stirred condition (0 rpm).

The general observation was that the oil yields, which were obtained at the stirred conditions, were consistently much higher than those recorded at the non-stirred conditions. The results showed that the difference in oil yields ranged from 12 to 33 wt.% of the lignin input between the stirred and non-stirred experiments. Furthermore, the char formation was shown to be significantly decreased by stirring when all the other reaction parameters were kept constant. The overall result revealed that at the stirred conditions, both water and ethanol-based experiments yielded over 40 wt.% oil, regardless of the level loaded in the reactor. However, ethanol-based experiments with a high level of loading in the reactor at the stirred conditions led to the highest bio-oil yields.

3.1.4. Variation in yields as a function of reaction temperature

The purpose of this part of the work was to compare the product yields recorded for the experiments performed at different reaction temperatures. Figure 1d shows an overview of the mass yield (%) for all the experiments in which the only difference between the two successive experiments was the operating temperature. Experiments were run using two different

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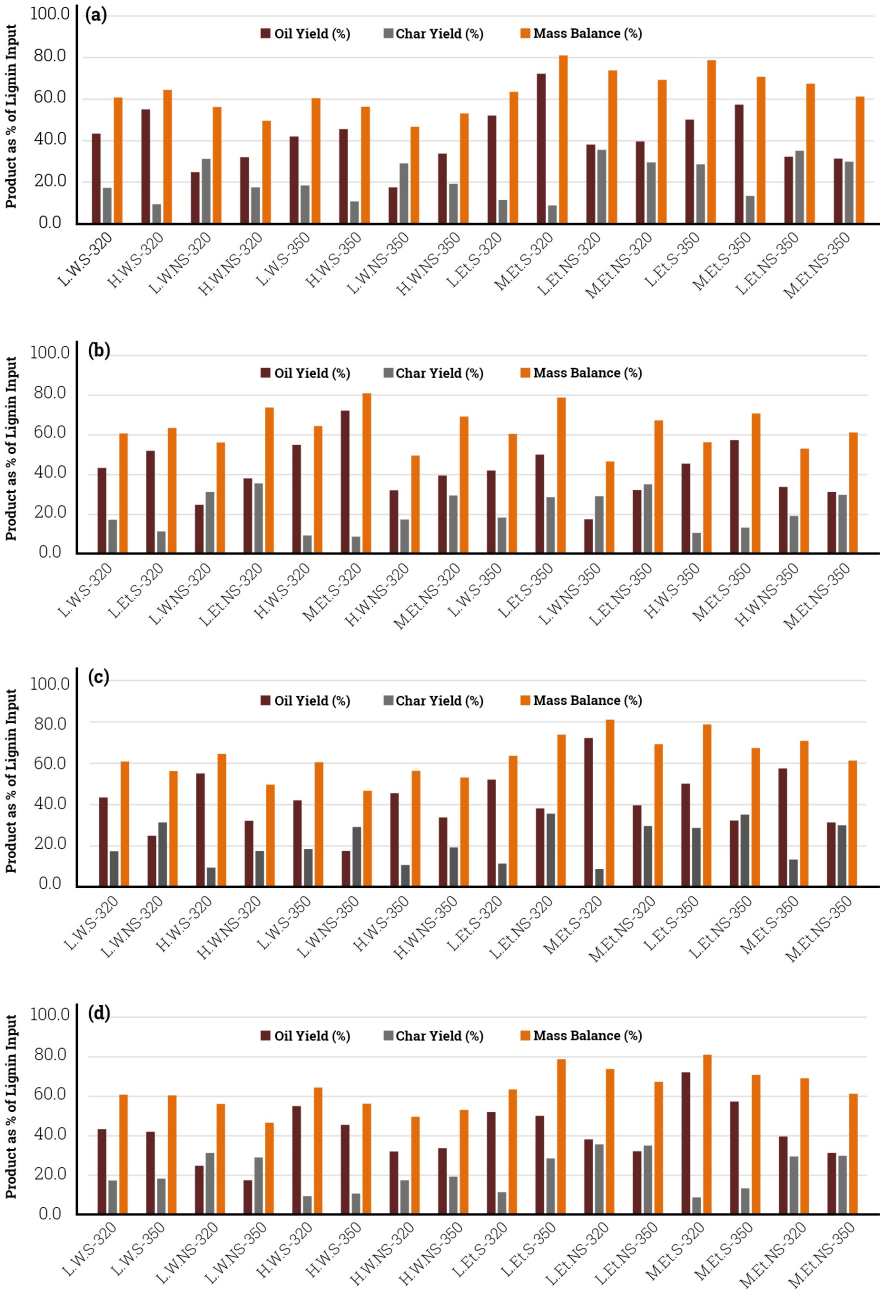

Fig. 1. Oil yield (wt.%), char yield (wt.%), and lignin mass balance (%) given as percentages of lignin input plotted according to different (a) levels of loading in the reactor (b) solvent types (c) stirring conditions, and (d) reaction temperatures (For coding; see Table 1).

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temperatures (320 and 350 °C), while all the other reaction parameters were kept constant.

The results showed a trend of slightly decreasing oil yields with temperature. The decreasing trend was more marked in the experiments performed at the stirred conditions with a high level of loading in the reactor. The char yields were not significantly influenced by the reaction temperature, showing a slight increase by elevating the temperature from 320 °C to 350 °C. The trends of the results obtained for the two solvent systems were quite similar at both temperatures. The experiments performed at 320 °C with high level of filling in the reactor under the stirred conditions led to over 55 wt.% oil regardless of the solvent type.

3.2. Elemental analysis and carbon balance

Figure 2 displays a Van Krevelen plot of H/C and O/C ratios for all the LtL-oils and the lignin feedstock. Deoxygenation was clear for all the 16 bio-oils since the O/C ratio of the LtL-oils was significantly reduced relative to the starting biomass (Eucalyptus lignin). However, in bulk, hydrogenation did not seem to have occurred since the H/C ratio of the bio-oils was also reduced relative to the starting material. This could in part be explained by the conversion of the carbohydrate residues to aqueous products. For lignin, in the LtL-process, hydrogen can both be added and lost. The highly reactive *in situ* formed hydrogen from the thermal decomposition of formic acid is responsible for converting the lignin constituents into hydrogen-rich, oxygen-depleted products. However, hydrogen can also be removed as aqueous products when hydroxyl groups are cleaved from lignin structure. Since the carbon content (%) of the bio-oils produced in this work increased relative to the carbon content (%) of the starting raw material (Eucalyptus lignin), it is unlikely that hydrogen which is bound to carbon, was removed as alcohol and/or aldehyde during the LtL-process (Kleinert and Barth, 2008; Holmelid et al., 2012). The H/C value was in the range of 1.15 – 1.44, suggesting that aromatic rings could be predominant. The general observation was that bio-oils from the water-based experiments had the lowest O/C indicating a higher degree of deoxygenation. However, bio-oils from the ethanol-based experiments were shown to have the highest H/C ratios indicating a higher degree of hydrogenation.

Figure 2 shows that for the water-based experiments, the highest H/C values were obtained in the stirred experiments performed at 350 °C regardless of the level of loading (Exp. L.W.S-350 and H.W.S-350), thus indicating that higher reaction temperature together with stirring contributed to a more efficient hydrogenation of lignin constituents. All the bio-oils produced at the non-stirred conditions showed a slight decrease in both H/C and O/C values compared to the bio-oils produced at the stirred conditions at the same temperature and level of loading. This indicated a higher degree of dehydrogenation and deoxygenation in the non-stirred experiments.

In addition, Figure 2 depicts that replacing water with ethanol as reaction solvent while keeping the other reaction parameters constant, led to a clear

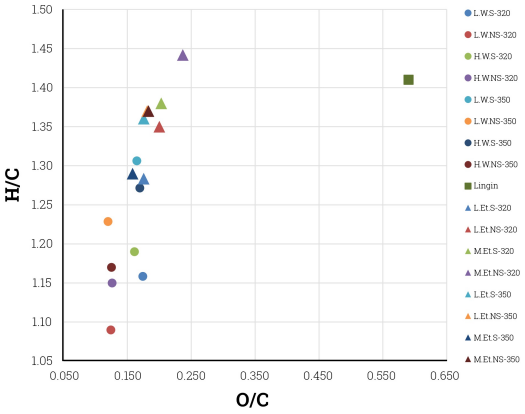

Fig. 2. Van Krevelen plot showing H/C ratio and O/C ratio of the LtL-oils and lignin.

increase in both H/C and O/C ratios for the bio-oils. Previous investigations revealed that the higher degree of hydrogenation in ethanol-systems was due to the substitution of ethyl groups on the aromatic ring structures, which would increase the number of alkyl units in the product and thus, increase the H/C ratio (Holmelid et al., 2012). However, among the bio-oils produced in the ethanol-based system, the bio-oil associated with the experiment M.Et.NS-320 had the highest H/C and O/C values. Since neither the H/C nor the O/C ratios of the bio-oils of the ethanol-based experiments followed a clear trend, it was not possible to draw a specific conclusion. Furthermore, Figure 2 reveals that the H/C and O/C values of the bio-oils produced in the experiments H.W.S-350 and M.Et.S-350 were quite similar even though they were produced in two different reaction systems.

The elemental compositional data also made it possible to calculate the yields on a carbon basis in addition to the recovery by weight. Table 3 tabulates the carbon recovery data from all the LtL-process experiments carried out in this work. The carbon recovery data were calculated using input of carbon in the form of lignin and output of carbon in the form of organic products (bio-oils and chars). Therefore, the recovery of carbon in the products would be dependent on the product recovery by weight. A

Table 3.
Carbon recovered in bio-oil and char of the LtL-process experiments.

Experiment	**L.W.S-320**	**L.W.NS-320**	**H.W.S-320**	**H.W.NS-320**	**L.W.S-350**	**L.W.NS-350**	**H.W.S-350**	**H.W.NS-350**
Carbon added as lignin (g)	**95.84**	**95.84**	**143.76**	**143.76**	**95.84**	**95.84**	**143.76**	**143.76**
Carbon recovered in oil (%)	64.42	39.04	82.87	50.18	62.59	27.56	67.51	52.87
Carbon recovered in char (%)	20.02	41.36	9.29	22.71	24.63	39.96	11.10	24.33
Total carbon recovered (%)	**84.44**	**80.40**	**92.16**	**72.89**	**87.22**	**67.52**	**78.61**	**77.20**
Experiment	**L.Et.S-320**	**L.Et.NS-320**	**H.Et.S-320**	**H.Et.NS-320**	**L.Et.S-350**	**L.Et.NS-350**	**H.Et.S-350**	**H.Et.NS-350**
Carbon added as lignin (g)	**95.84**	**95.84**	**167.72**	**167.72**	**95.84**	**95.84**	**167.72**	**167.72**
Carbon recovered in oil (%)	76.51	54.49	102.68	54.33	73.83	46.81	85.79	45.47
Carbon recovered in char (%)	13.95	51.99	8.78	43.03	41.11	52.37	16.10	43.55
Total carbon recovered (%)	**90.46**	**106.48**	**111.46**	**97.36**	**114.94**	**99.18**	**101.89**	**89.02**

* All calculations are carried out on ash free basis

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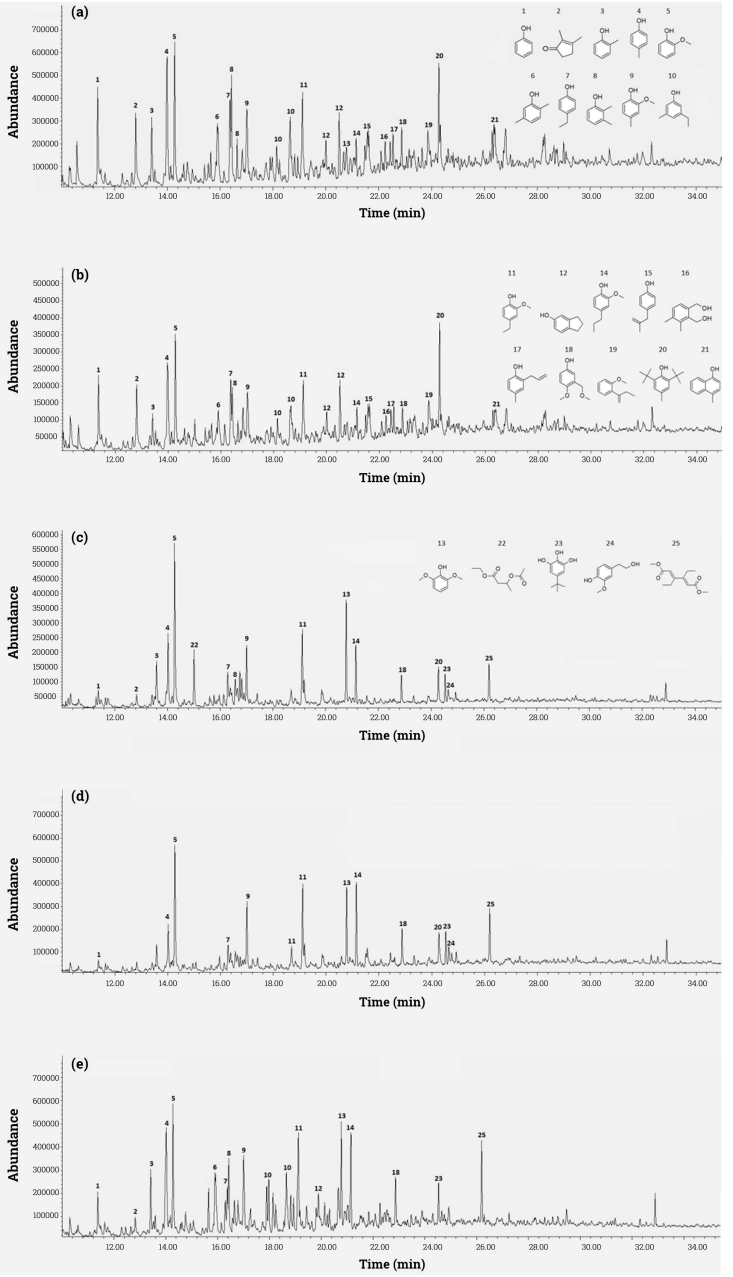

Fig. 3. GC-MS chromatograms of five selected experiments (a) L.W.NS-320 , (b) L.W.S-350, (c) L.Et.S-320, (d) M.Et.S-320, and (e) M.Et.NS-350, showing the relative peak height of the most abundant compounds present: (1) Phenol, (2) 2,3-Dimethyl-2-cyclopenten-1-one, (3) 2-Methylphenol, (4) 4-Methylphenol, (5) 2-Methoxyphenol, (6) 2,5-Dimethylphenol, (7) 4-Ethylphenol, (8) 2,3-Dimethylphenol, (9) 2-Methoxy-4-methylphenol, (10) 3-Ethyl-5-methylphenol, (11) 4-Ethyl-2-methoxyphenol, (12) 2,3-Dihydro-1H-inden-5-ol, (13) 2,6-Dimethoxyphenol, (14) 2-Methoxy-4-propylphenol, (15) p-(2-Methylallyl) phenol, (16) 6-Hydroxymethyl-2,3-dimethylphenyl methanol, (17) 2-Allyl-4-methylphenol, (18) 4-Methoxy-3-methoxymethylphenol, (19) o-(1-Ethylvinyl) anisole, (20) Butylated hydroxytoluene, (21) 4-Methyl-1-naphthalenol, (22) Ethyl-3-acetoxybutyrate, (23) 5-Tert-butylpyrogallol, (24) Homovanillyl alcohol, and (25) 3,4-Diethyl-2,4-hexadienedioic acid dimethyl ester.

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major source of uncertainty was the lack of data for aqueous products and gases produced from the lignin. However, unpublished results suggested that the aqueous products were methanol, short chain organic acids, furfural from carbohydrate residues, etc. The recovery figures were thus most useful for comparative use. Calculations showed a carbon recovery ranging from 68 to 92% for the water-based experiments, and a carbon recovery ranging from 89 to 115% for the ethanol based experiments. The incorporation of ethyl groups from ethanol contributed to the high carbon recovery compared to the lignin carbon input in the products of the ethanol-based experiments. Furthermore, a higher amount of carbon was recovered in the stirred experiments compared to the non-stirred ones (except Exp. L.Et.S-320) which may be explained by increased gasification at non-stirred conditions due to high temperature at the reactor walls above the solvent level. There was no clear trend showing reduction or increase in carbon recovery, neither with the level of loading in the reactor nor when the reaction temperature was changed. The elemental composition of all the bio-oil and char samples, including H/C and O/C ratios, are presented in **Table S2**.

3.3. Molecular composition of bio-oils identified with GC–MS

The LtL-oils comprised a complex mixture of phenolic compounds. **Figure 3** shows the chromatograms of five selected bio-oils. The volatile monomeric phenols were identified using GC-MS library search. The chromatograms presented in **Figure 3** show that the composition of the bio-oils were quite similar in different oil samples from the same solvent system, while the abundance of each component varied when the other reaction conditions were changed. However, the compositional differences were more significant when comparing oils from the water- and ethanol-based systems (**Figs. 3a** and **b** *vs.* **Figs. 3c**, **d** , and **e**).

A general observation was that 2-Methoxyphenol (Guaiacol) was the most abundant compound in almost all of the chromatograms depicted in **Figure 3**, while the proportion of the other compounds varied relative to this compound in the bio-oils produced at different reaction conditions. The GC-MS chromatograms depicted in **Figure 3a** and **b** indicate that the bio-oils produced in the water-based system, consisted mainly of alkylated phenols in high concentrations. More specifically, phenol, 2,3-dimethyl-2-cyclopenten-1-one, methyl- and ethylphenol, guaiacol, allylphenol, and butylated hydroxytoluene were the most abundant compounds identified. Identification of the most abundant peaks in the chromatograms related to the ethanol-based experiments showed a higher amount of methoxy-substituted phenols such as 2,6-dimethoxyphenol, 2-methoxy-4-propylphenol, 4-methoxy-3-methoxymethylphenol, and 5-tert-butylpyrogallol, corresponding to a significantly higher O/C ratio (**Figure 2**) and a higher average molecular weight in the oils obtained from this solvent system compared to the bio-oils associated with the water-based system. 3,4-diethyl-2,4-hexadienedioic acid dimethyl ester was also one of the most abundant compounds in bio-oils generated in the ethanol-based system which was possibly a condensations product of the ethanol in the reaction solvent.

The lower content of oxygen in the bio-oils of the water-based system resulted in lower O/C ratios of the oils, corroborating the results of the elemental analysis (**Figure 2**), while the higher degree of alkyl-substitution in the oils generated in the water-based system did not result in higher H/C ratios compared to the bio-oils of the ethanol-based system. This could be explained by the fact that only the volatile fraction of the bio-oils could be analyzed by GC-MS, and since the composition of the heavier portion of the oils was unknown, it was not possible to have a specific conclusion when it came to H/C ratio.

Water as a solvent is undoubtedly cheaper and more readily available relative to ethanol. However, in the LtL-process, ethanol has been found to be better suited as reaction solvent since it could act both as a solvent and as a reactant (Holmelid et al., 2012). Products produced in ethanol-based experiments were considered to be more useful in large-scale production of bio-oils and/or chemicals. Therefore, ethanol appeared to be more economically viable in terms of industrial investment in product quality and application. One may also propose isopropanol as solvent. However, since isopropanol is even more expensive than ethanol, it does not seem to be economically beneficial.

3.4. Principal component analysis (PCA)

In the defined experimental setup presented in **Table 2**, the following parameters were studied: oil yield (%), char yield (%), H/C ratio and O/C ratio of the bio-oils, and carbon recovery (%).

Figure 4 depicts a biplot of the experimental design using the design variables and all the experimental responses. All data were standardized, meaning that all values for each variable were weighted by division with the standard deviation. Standardization led to an equal variance from -1 to +1 for each variable.

The PCA confirmed that the oil yield (%) was highly correlated with the speed of stirring and a high level of loading in the reactor. Furthermore, there was a positive correlation between carbon balance (%) with oil (%) and char (%) yields, respectively, on PC1 and PC2. This implied that the highest carbon recovery with the lowest loss of lignin-derived carbon into aqueous and gas-phase products, was achieved in the experiments with the highest product yields (oil and char yields). The design also confirmed that both oil (%) and char (%) yields were positively correlated with the solvent type, again confirming the observation that the ethanol-based reactions led to higher oil and char yields, and thus, higher carbon recovery compared to the water-based reactions. In addition, a positive correlation between the solvent type and H/C and O/C ratios was also observed on PC1, which again confirmed the results obtained in the elemental analysis (i.e., the bio-oils of the ethanol-based experiments had higher H/C and O/C ratios compared to the bio-oils of the water-based experiments). A strong positive correlation between the experiment M.Et.NS-320 and H/C and O/C ratios was also shown, corresponding to the max H/C and O/C ratios shown in **Figure 2**.

Furthermore, the oil yield (%) and carbon balance (%) were negatively correlated with the reaction temperature and positively correlated with the stirring and level of loading, matching the results obtained in *Sections 3.1.1–3.1.4* (i.e., the stirred reaction performed at 320 °C with high level of loading in the reactor led to high oil yields, and thus, high carbon recovery). However, the char yield (%), which is described on PC2, was positively correlated with the reaction temperature and H/C ratio. This could be caused by a disproportionation of oil components to carbon-rich char and hydrogen-enriched liquid product at higher temperatures. The negative correlation between the char yield (%) and the level of loading in the reactor and stirring condition confirmed the observations of the positive effects of high reactor loading presented and discussed in *Sections 3.1.1* and *3.1.3*.

From the PLS analysis and the respective regression coefficients, it could be seen that the design variables were used to calculate multivariate regression models for the yields. The regression equations for the oil and char yields, H/C and O/C ratios, and carbon balance (%), which were well modelled and well predicted, are given in **Table 4**. For the other variables, models with a significant uncertainty and a considerable degree of scatter were produced. This implied that a larger design would be needed for reliable yield predictions, since only linear relationships could be well described in the screening model based on the factorial design.

Both oil and char yields were well explained by the model when all four variables were taken into account. According to the fitted equations, high level of loading and high speed of stirrer increased the oil yield and decreased the char yield, while high reaction temperature decreased the oil yield and increased the char yield. Ethanol as reaction solvent led to an increase in both oil and char yields. Moreover, the model provided a reasonable explanation for carbon recovery (%) using all the relevant variables. The regression equations in **Table 4** show that there was a significant positive correlation between the carbon recovery (%) with stirring of the reaction and usage of ethanol as reaction solvent. The H/C ratio of the bio-oils was well modelled and well predicted when the experiments were categorized based on the reaction temperature. According to the regression equations shown, the H/C ratio of the oils (based on the experiments performed at 320 °C) was increased when the reactor was loaded at the high level and ethanol was used as reaction solvent, while it was not influenced by the stirring condition in particular. The model best explained the O/C ratio of the oils when only the non-stirred experiments were taken into account. The fitted equations in **Table 4** also show that the O/C ratio of the bio-oils had a strong positive correlation with

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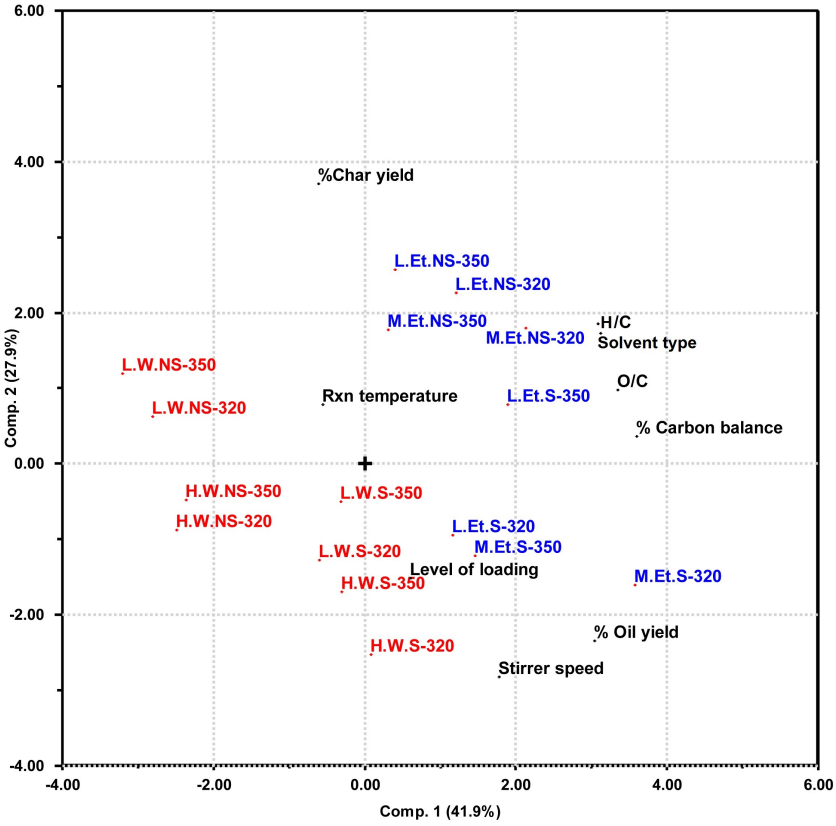

Fig. 4. Biplot for Principal Component Analysis (PCA) of the data set consisting of experimental variables and response factors.

Table 4.
Fitted regression equations for the oil and char yields (%), H/C and O/C ratios, and carbon recovery (%) using standardized design variable values.

Equation for	k	Loading	Stirrer speed	Experiental temperature	Solvent	Prediction*	Correlation (R)
% Oil yield	3.06	0.32	0.80	- 0.22	0.37	92.4 %	0.96
% Char yield	2.27	- 0.46	- 0.74	0.16	0.27	85.8 %	0.93
% Carbon recovery	6.42	- 0.01	0.39	- 0.16	0.77	77.2 %	0.88
H/C ratio	10.4	0.28	- 0.06	—	0.92	92.5 %	0.96
O/C ratio	3.66	0.14	—	- 0.24	0.92	96.1 %	0.96

* Indicates variance (%) which is explained by the model.

solvent type, a weak positive correlation with level of loading, and a negative correlation with reaction temperature. This confirms the systematic effect of the variables and the fact that the bio-oil produced in the ethanol-based experiment under non-stirred condition at 320 °C with high level of loading in the reactor had the highest O/C values.

4. Conclusions

This study was aimed at providing an insight into the yield and composition of the products generated through an LtL-process using a 5-L pilot scale at different reaction conditions. The maximum difference in bio-oil yields of the experiments performed in this work was above 50%.

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The main conclusions drawn include:

- Ethanol-based experiments yielded the highest amounts of bio-oil with the highest H/C and O/C ratios;
- Stirred reactions led to higher bio-oil yields, lower char yields, and higher carbon recovery compared to non-stirred reactions;
- Increased level of loading in the reactor led to an increase in bio-oil yield and a decrease in char yield.
- Guaiacol (2-Methoxyphenol) was the major component in most of the LtL oils produced in both solvent systems regardless of the other reaction conditions.
- The highest bio-oil yield and lowest char yield were obtained through the ethanol-based experiment performed under stirring at 320 °C with high level of loading in the reactor (i.e., Exp. M.Et.S-320).

Overall, the use of the 5-L pilot scale reactor was found very promising, as the highest yields of bio-oil were obtained at stirred, high loading conditions. It should be emphasized that such conditions could not be tested at small laboratory scale experiments.

Acknowledgements

We gratefully acknowledge LtLNOR, The Norwegian Research Council (grant no. 190965/S60) and Statoil As for financial support and the use of the 5-L reactor. The authors would also like to thank I. J. Fjellanger for assisting with elemental analysis and Sekab for providing lignin.

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Supplementary Material

Table S1.
Extended overview of the product output of the LtL-process experiments together with pressure and torque at the end of each experiment (for experimental conditions, see **Table 1**).

Experiment	Pressure (bar)	Torque (Nm)	Oil yield (%)*	Char yield (%)*	Lignin mass balance (%)*
L.W.S-320	195	0.534	43.43	17.36	60.78
L.W.NS-320	215	0	24.85	31.30	56.15
H.W.S-320	265	0.514	55.03	9.43	64.46
H.W.NS-320	292	0	32.11	17.50	49.61
L.W.S-350	251	0.509	42.02	18.42	60.44
L.W.NS-350	237	0	17.56	29.11	46.67
H.W.S-350	336	0.510	45.53	10.74	56.27
H.W.NS-350	323	0	33.80	19.27	53.07
L.Et.S-320	165	0.514	52.06	11.46	63.52
L.Et.NS-320	169	0	38.17	35.64	73.81
M.Et.S-320	269	0.519	72.17	8.81	80.98
M.Et.NS-320	279	0	39.61	29.56	69.18
L.Et.S-350	139	0.514	50.13	28.64	78.77
L.Et.NS-350	190	0	32.25	35.11	67.36
M.Et.S-350	310	0.552	57.38	13.37	70.75
M.Et.NS-350	341	0	31.34	29.92	61.26

* All yields are calculated on ash-free basis.

Table S2.
Elemental composition as well as the H/C and O/C ratios of all the LtL-oils and chars.

Experiment	Oil						Char					
	C	H	N	O	H/C	O/C	C	H	N	O	H/C	O/C
	Moles (%)						Moles (%)					
L.W.S-320	6.19	7.17	0.084	1.08	1.16	0.174	4.81	4.77	0.049	0.99	0.99	0.205
L.W.NS-320	6.56	7.14	0.076	0.81	1.09	0.124	5.51	4.20	0.051	1.00	0.76	0.182
H.W.S-320	6.28	7.50	0.057	1.01	1.19	0.161	4.11	3.75	0.047	0.84	0.91	0.204
H.W.NS-320	6.52	7.53	0.065	0.82	1.15	0.126	5.42	3.91	0.046	0.60	0.72	0.111
L.W.S-350	6.22	8.12	0.056	1.02	1.31	0.165	5.58	4.73	0.045	0.48	0.85	0.085
L.W.NS-350	6.55	8.05	0.049	0.78	1.23	0.120	5.73	4.45	0.047	0.78	0.78	0.136
H.W.S-350	6.19	7.87	0.071	1.05	1.27	0.169	4.31	3.87	0.042	0.86	0.90	0.200
H.W.NS-350	6.53	7.64	0.064	0.81	1.17	0.125	5.27	3.85	0.045	0.81	0.73	0.154
L.Et.S-320	6.13	7.87	0.083	1.08	1.28	0.176	5.08	4.69	0.046	0.32	0.92	0.062
L.Et.NS-320	5.96	8.02	0.092	1.19	1.35	0.200	6.09	4.34	0.054	0.65	0.71	0.106
M.Et.S-320	5.94	8.20	0.080	1.21	1.38	0.203	4.16	3.76	0.035	0.72	0.90	0.173
M.Et.NS-320	5.72	8.25	0.091	1.35	1.44	0.237	6.07	4.91	0.052	0.50	0.81	0.082
L.Et.S-350	6.15	8.36	0.036	1.08	1.36	0.176	5.99	4.70	0.050	0.55	0.78	0.092
L.Et.NS-350	6.06	8.30	0.097	1.09	1.37	0.181	6.23	4.01	0.054	0.56	0.64	0.089
M.Et.S-350	6.24	8.07	0.080	0.99	1.29	0.158	5.027	3.890	0.041	0.60	0.77	0.119
M.Et.NS-350	6.05	8.26	0.090	1.11	1.37	0.183	6.075	4.112	0.050	0.56	0.68	0.091

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Graphic design: Communication Division, UiB / Print: Skipnes Kommunikasjon AS

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ISBN: 9788230840269 (print)
9788230845059 (PDF)