

The effect of input material pretreatment on product yield and composition of bio-oils from LtL-solvolytic

A continuous process for organosolv fractionation of lignocellulosic biomass and solvolytic conversion of lignin

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I think like a proton and stay positive

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PREFACE

This thesis, submitted for the degree of Philosophiae Doctor at the University of Bergen, has been structured in two parts. The first part includes an introduction, thesis scope, methods conducted throughout, a summary of the work and main results in the research papers included in the second part, and ends with overall conclusions and suggestions for future outlook and approaches. The second part contains four research papers and manuscripts. The papers are based on experimental work carried out at the Department of Chemistry at the University of Bergen in the period August 2012 – October 2016.

The aim of the work conducted was to investigate input material pretreatment on product yield and composition of bio-oils from thermochemical conversion of lignin by LtL-solvolytic. This approach led to the development of a continuous process for organosolv fractionation of lignocellulosic biomass and solvolytic conversion of lignin.

ABSTRACT

As the world's population and subsequent energy demand increases, there is a need to supplement existing energy technology with new and alternative approaches. Lignocellulosic biomass represents the vast bulk of terrestrial plant material and possesses both an enormous store of energy and a great potential as a source for biomass derived products. Production of bioethanol from the carbohydrate components of this biomass type is already established, while the remaining 10-25 % of the biomass, comprised by an amorphous phenylpropane copolymer called lignin, also holds unique characteristics. Lignin is the most important source of bio-based aromatics in nature, and lignin derived fuels or platform chemicals are approachable by lignin depolymerisation.

Thermochemical conversion of lignin by Lignin-to-Liquid solvolysis depolymerises the lignin copolymer through hydrodeoxygenation and yields an energy rich bio-oil high in alkylphenols. In Lignin-to-Liquid solvolysis, formic acid and a co-solvent (ethanol or water) are added to the lignin, and the reaction mixture is exposed to a high temperature and high pressure as a closed system. A major focus within this thesis was to investigate the impact of initial feedstock species and feedstock fractionation and/or pretreatment method on yields of LtL-oil and LtL-oil composition.

All feedstock species and pretreatment methods applied generated lignin rich fractions suitable for LtL-solvolytic. Multiple feedstocks were screened through systematic LtL-experiments with ethanol or water as co-solvent and early results lead to water being chosen as preferred solvent in consecutive experiments due to low cost, availability and its benign nature. Optimal substitution order of the generated phenols within the bio-oils depends on desired utilisation area, and ethanol-system experiments generated phenols with a more complex substitution order than water-system experiments.

The produced bio-oils were high in aromatic content and water-system experiments produced phenolic components with similar substitution patterns regardless of feedstock preprocessing. The initial oxygen content of the feedstock used in LtL-solvolytic, e.g. due to carbohydrate residues from biomass fractionation, determined the bio-oil yield due to substantial depletion of oxygen through hydrodeoxygenation. This observation shifted the choice of feedstock towards lignin extracted by organosolv fractionation. Organosolv fractionation treats biomass with an organic solvent or mixtures of organic solvents and water to remove lignin. The lignin obtained is of low molecular weight and of high purity. Lignin extracted by organosolv fractionation provided high yields of bio-oil after LtL-solvolytic, and the yields also showed a positive correlation with the amount of formic acid in the reaction process. The O/C ratio of the phenolic monomers comprising the bio-oils displayed a reduction with increasing reaction temperature.

As organosolv extracted lignin thus proved to be highly suitable for LtL-solvolytic, a process for *continuous* organosolv fractionation of lignocellulosic biomass and solvolytic conversion of lignin was proposed. A semi-continuous flow-through setup for organosolv fractionation was designed and optimal fractionation conditions were determined for a softwood mixture predominantly containing Norway spruce (and ~ 10 % pine). The extracted and isolated lignin

was of high purity, in high yields and proved to be very well suited for LtL-solvolyis in subsequent LtL-experiments.

LtL-solvolyis of lignin extracted by semi-continuously fractionated lignocellulose displayed high conversion ratios and yields of bio-oil. The bio-oils' structural composition were investigated and quantified to examine the impact of experimental parameters and the bio-oils potential industrial employment. Alkylated phenols are presently being used as fuel additives, while phenols rich in oxygenated substituents are valuable for the chemical and pharmaceutical industry. Solvolyis experiments showed reproducible results with high mass recovery and gave a similar response to the reaction conditions as previously observed, confirming that an increased addition of formic acid input increased the bio-oil yield, and an increased reaction temperature reduced the O/C ratio (oxygen content) within the bio-oils. Quantification of the ten most abundant components identified in the oils showed their concentration to be mainly temperature dependent. Hence, tuning experimental conditions towards desirable bio-oil composition, and the development of methods to separate the bio-oils into series of homologs or similar compounds are both necessary and will strengthen the LtL-oils potential as a future platform chemical.

LIST OF PUBLICATIONS

Paper I Løhre, C.; Barth, T.; Kleinert, M., The effect of solvent and input material pretreatment on product yield and composition of bio-oils from lignin solvolysis. *Journal of Analytical and Applied Pyrolysis* **2016**, 119, 208-216.

Paper II Løhre, C.; Aakre Laugerud, G. A.; Huijgen, J. J. W.; Barth, T., Lignin-to-liquid-solvolysis (LtL) of organosolv extracted lignin. *Journal of Analytical and Applied Pyrolysis* **2016** (Submitted)

Paper III Løhre, C.; Kleinert, M.; Barth, T., Organosolv extraction of softwood combined with lignin-to-liquid-solvolysis as a semi-continuous system. *Biomass & Bioenergy* **2016**, (Final revisions submitted)

Paper IV Løhre, C.; Halleraker, V. H.; Barth, T., Composition of Lignin-to-Liquid solvolysis oils from lignin extracted in a semi-continuous organosolv process (Manuscript)

ABBREVIATIONS

BSTFA	Bis(trimethylsilyl)trifluoroacetamide
DCM	Dichloromethane
EA	Elemental analysis
EtAc	Ethylacetate
EtOH	Ethanol
FA	Formic acid
GC-MS	Gas chromatography mass spectrometry
LCBM	Lignocellulosic biomass
LtL	Lignin-to-Liquid
NMR	Nuclear magnetic resonance
PCA	Principal Component analysis
PLS	Partial least square
THF	Tetrahydrofuran

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Part I

1.

INTRODUCTION

1.1 Current and future energy situation

The UN's 17 suggested sustainability goals from 2016 direct a substantial focus on target changes in global and environmental energy challenges within the year 2030. Goal 7 aims to "Ensure access to affordable, reliable, sustainable and modern energy for all", goal 12 aims to "Ensure sustainable consumption and production patterns" and goal 13 aims to "Take urgent action to combat climate change and its impacts" (1).

If the sustainability goals are to be met, a growing human population, a consequently enhanced energy demand and increased *per capita* consumption are current and future challenges that need to be dealt with in a sustainable manner. According to the Brundtland Report, sustainable development is

“development that meets the needs of the present without compromising the ability of future generations to meet their own needs” (2).

As the current main energy resources still comprise fossil fuels and crude oil it is self-explanatory that a growth in the use of resources and consumption on a finite providing planet is not sustainable indefinitely. Fossil fuels accounts for more than 80 % of the world’s global energy consumption, and predicted shortages in petroleum resources, a rapid population growth and an increasing energy demand, makes it necessary to supplement existing energy technology with new and alternative approaches (3, 4).

Fossil fuels and resources do not only provide energy for electricity and liquid fuels for the transportation sector, but are also manufactured into building blocks and final products for use and consumption in both the general industry and in every home. Renewable energy such as wind-power, solar-power, hydro-power, geothermal power etc. can contribute when aiming at replacing fossil resources for the sake of pure energy and power, but they cannot replace frequently used fossil based products and building blocks such as e.g. plastics, dyes, resins and/or key components in the pharmaceutical and chemical industry.

1.2 Biomass

Renewable resources are now seen an important factor in meeting the increasing global energy demands. Moreover, shifting the energy-dependence from fossil resources towards renewable biomass resources is now generally viewed as an important contributor to the development of a sustainable industrial society and effective management of potential environmental consequences from the use of fossil fuels, such as greenhouse gas emissions (5). The earth's biomass represents an enormous store of energy. It has been estimated that about one eighth of the global total of renewable biomass produced annually would theoretically cover all of humanity's current demand for energy (6). The vast bulk of terrestrial plant material is called *lignocellulosic* biomass (LCBM). LCBM refers to all inedible plant materials made up of primarily (on dry weight basis) cellulose (40-60 %) hemicelluloses (20-40 %) and lignin (10-25 %) such as: forestry materials, agricultural materials and residues, and fractions of municipal and industrial waste (6).

According to Ragauskas et al. (2006) "the integration of agroenergy crops and biorefinery manufacturing technologies offers the potential for the development of sustainable biopower and biomaterials that will lead to a new manufacturing paradigm" (5). And the International Energy Agency's Task 42 defines a concept termed "biorefining" as sustainable processing of biomass into a spectrum of biobased products (chemicals, materials, human food and animal feed) and bioenergy (fuels, power and/or heat) (7).

Feasible and profitable utilization of LCBM in a biorefinery involves taking advantage of all its constituents and building blocks, as seen in Figure 1.1, depicting a biorefinery-concept including a complete biomaterial-biopower cycle.

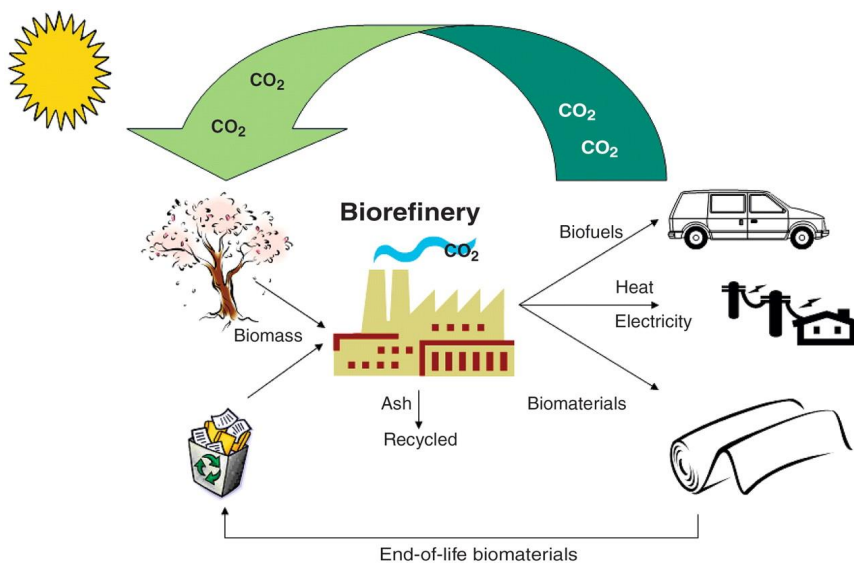


Figure 1.1 – The fully integrated agro-biofuel-biomaterial-biower cycle for sustainable technologies (5).

For biopower and biofuels to be viable substitutes for fossil fuels, the alternative fuel should not only have superior environmental benefits over the fossil fuel it displaces, it should also be economically competitive with it, be producible in sufficient quantities to make a meaningful impact on energy demands and it should also provide a net energy gain over the energy sources used to produce it (8).

1.2.1 Feedstock resources

International focus on sustainable forestry management has revealed losses of e.g. tropical forests due to deforestation. However, Europe has seen a forest expansion of 33 % over the last 25 years (215 million HA total), and Norwegian forests are also expanding, much due to an increase in temperatures and increased atmospheric CO_2 levels and nitrogen-rich rainfall (9-12).

The shift from paper based to digital platforms for news media and entertainment has resulted in a massive global over-capacity in the pulp and paper industry. This, in turn, creates great potential for the very same paper mills to continue operation by producing bioenergy and other biomaterials from the feedstock previously used for pulp and paper production (13, 14).

A sustainable biorefinery should avoid using food crops for the production of fuels and biobased products. Therefore, modifying existing production sites and utilising residue materials, such as forestry- and agricultural waste, is crucial to minimise the need for resources to meet necessary energy and consumption levels.

1.2.2 Land use change

Current development towards biopower and biobased production has led to farmland being utilised with the aim of producing fuel, such as rapeseed and soybean for the production of bio-diesel (fatty acid methyl esters, FAMES), so that the worldwide increasing energy demand can be met. As farmland is a limited resource, a discussion on how to best utilize this resource is vital when addressing the UN's goals for sustainable development. The needs of the present might be covered by this development in fuel production, but predictions regarding whereas future generations could experience food shortage and malnutrition due to the chosen utilisation of land are less promising (15-17). Hunger and malnutrition are already global issues, and devoting agricultural land that could be used for food production to produce fuel crops will prevent helping future generations meet their needs. Our population is increasing rapidly, and producing enough food to help cover the increasing demand is crucial. As the geographical distribution of fossil resources is

unbalanced, using LCBM grown land and land that is not farmland or suitable for food production is thus a unique possibility and an essential global resource for the future growth of fuel crops.

1.3 Lignin

One of the three main constituents comprising lignocellulosic biomass is lignin, a cross-linked amorphous copolymer synthesized from random polymerisation of three phenylpropane monomers; *para*-coumaryl alcohol (H-lignin), coniferyl alcohol (G-lignin) and sinapyl alcohol (S-lignin), bonded through different C-O-C and C-C interunit linkages (see Figure 1.2) (18).

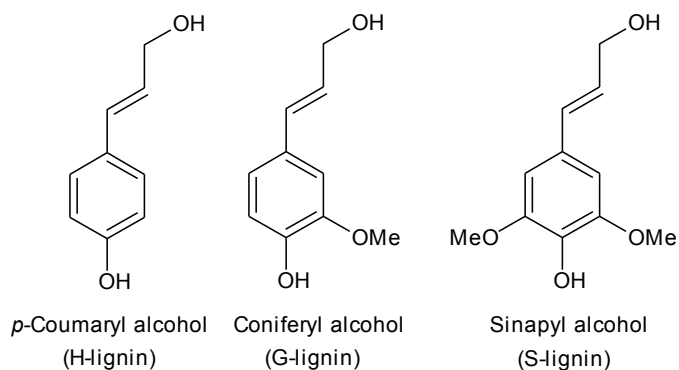


Figure 1.2 – The three phenylpropane monolignols comprising lignin.

Lignin provides all vascular plants, such as woody plants and trees, their rigidity and water-impermeability and protects them against microbial and fungal destruction of cellulosic fibres (19). Being an amorphous aromatic copolymer, lignin is the most important source of bio-based aromatics in nature (see Figure 1.3 for a typical lignin structure).

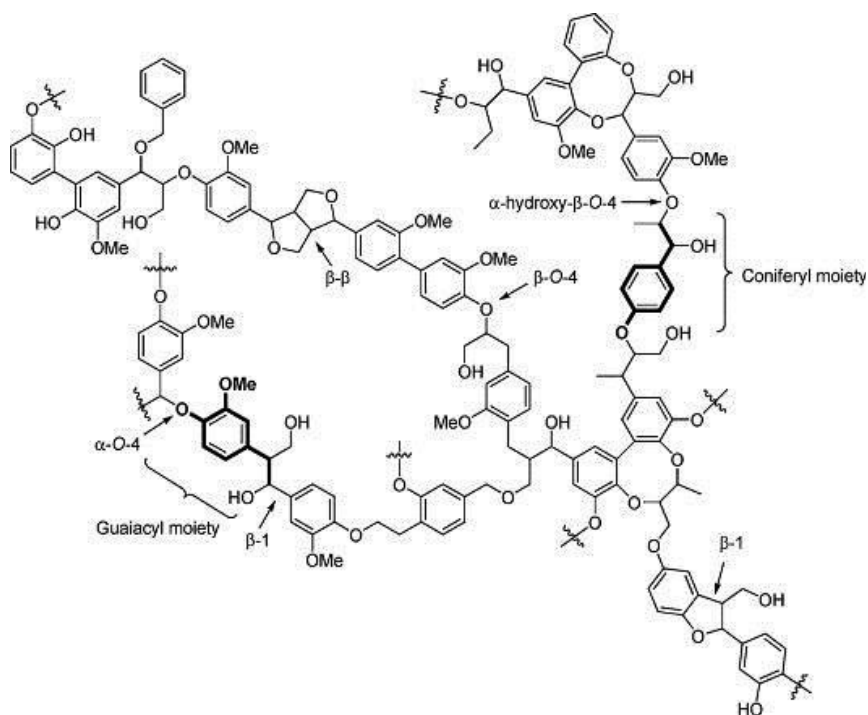


Figure 1.3 – Schematic representation of a typical softwood lignin macro structure (20).

Traditionally, lignin has been a by-product from the pulp and paper industry after delignification of cellulose in Kraft or sulphite pulping. The Kraft process produces the largest amounts of pulp to be used for paper production, and the Kraft lignin can be recovered in reasonably high yields. However, very few Kraft mills process lignin for sale, while the bulk of the non-recovered spent liquor lignin is processed to recover pulping chemicals or burned for the production of energy (21). The development of biorefining operations to convert lignocellulosic biomass into ethanol or other liquid fuels has also led to the generation of large fractions of residual lignin. Lignin's unique aromatic characteristics provides this highly abundant material with great potential as feedstock in the industry, and researchers are exploring extensively how to transform the lignin into more diverse and valuable products (22).

1.4 Biomass fractionation

Complete exploitation of lignocellulosic biomass in a biorefinery involves the pretreatment and/or fractionation of feedstock into its major or singular constituents.

LCBM can be pretreated physically, chemically, physicochemically or biologically. *Physical treatment* involves e.g. mechanical processes such as grinding, to reduce particle size and increase surface area, but also techniques such as high energy radiation to increase solubility or to ensure sterilisation. *Chemical treatment* involves hydrolysis processes, such as acid- and alkaline hydrolysis (e.g. pulping), in addition to methods such as organosolv extraction and oxidative delignification. *Physicochemical treatment* includes processes like steam explosion, torrefaction and hydrothermal carbonisation, while *biological treatment* involves degradation of the biomass by fungi or enzymes, as in enzymatic hydrolysis (6, 21, 23, 24).

The choice of method for pretreatment and fractionation depends on the desired form and quality for further processing of the biomass fractions. LCBM's three major intermingled constituents, being cellulose, hemicelluloses and lignin, provide rigidity and recalcitrance to a plant against exterior attack. Cellulose is a crystalline and water insoluble linear polymer of D-anhydroglucopyranose (glucose) units linked together by β -1,4-glucosidic bonds. Hemicellulose functions as an interphase between cellulose and lignin in the cell wall to form the matrix in which the cellulose fibrils are embedded, and is comprised by a variety of 5-carbon- and 6-carbon sugars. Lignin binds to cellulose and hemicellulose and are therefore highly resistant to hydrolysis because of extensive cross linking within the copolymer (6). Many fractionation processes target the cellulose fraction quality to efficiently produce large quantities of cellulose conversion products, as in bioethanol production and paper pulping.

Biomass hydrolysis in bioethanol production targets the carbohydrate fraction and leaves the lignin fraction in a mixture containing residual carbohydrates and inorganic extractives (25). Enzymatic digestibility for hydrolysis and/or fermentation of native biomass is low due to the feedstocks compositional characteristics. Cellulose's accessible surface area, its heterogeneity, its crystalline structure, it being protected by lignin and sheathed by hemicellulose makes it resilient to hydrolysis into fermentable sugars (26). From Kraft and sulphite processes, the lignin fraction also often remains structurally altered and/or partly condensed within a residual mixture with other components such as sulphur containing residues from the pulping process, hemicelluloses, ash and inorganic extractives also present within LCBM. The pulping industry also has serious shortcomings, such as air and water pollution (27, 28).

Purity and quality of biomass fractions are important characteristics if they are to be effectively utilised and converted into valuable products, and *organosolv fractionation* is, unlike hydrolysis and pulping, an effective separation method which can provide both carbohydrate fractions and a lignin fraction of high purity.

1.4.1 Organosolv fractionation

Organosolv approaches treat biomass with an organic solvent or mixtures of organic solvents and water, with or without the use of a catalyst, to remove lignin. A great variety of solvents can be used, such as methanol, ethanol, acetone and ethylene glycol (27, 29).

Organosolv treatment typically results in more than 50 % lignin removal from biomass through cleavage of lignin-carbohydrate bonds and β -O-4 interunit linkages (see Figure 1.3) and subsequent lignin solubilisation in the organic

solvent (22). Lignin obtained from organosolv fractionation is sulphur free, with low molecular weight and of high purity. Characteristics such as these are beneficial in the processing of lignin towards desirable end products, and for some downstream processes even essential.

Organosolv fractionation can be used as a pre-processing step before hydrolysis of the LCBMs' cellulose fraction in bioethanol production, and reports of high saccharification yields from enzymatic hydrolysis of organosolv pretreated biomass frequently emerge (30-33).

1.5 Thermochemical conversion of lignin

Converting lignin or lignin-rich residues into advantageous end products entails a great variety of techniques and methods. The lignin copolymer's aromaticity provides its beneficial characteristic and thus pyrolysis, gasification, chemical oxidation, hydro-cracking, and hydrolysis under supercritical conditions are some of the major methods developed aiming at lignin depolymerisation (34). *Pyrolysis* is essentially the thermal decomposition of biomass or lignin into gaseous, liquid and solid products in the absence of oxygen or steam (35). *Gasification* converts lignin (or biomass) into gases, and the main lignin gasification products include H₂, CO, CO₂ and CH₄ (36). *Chemical oxidation* involves thermal treatment (high temperature/high pressure) of lignin in the presence of oxygen for the production of chemicals such as vanillin and/or aldehydes (37, 38). *Hydro-cracking/hydrogenolysis* means thermal treatment in the presence of hydrogen, so that the cleavage of bonds is assisted by the addition of hydrogen, generating a liquid comprised by monomeric phenols (39). *Hydrolysis* utilises water to break down the polymer (40).

1.6 Lignin-to-Liquid

The first papers on thermochemical conversion of lignin to an alkylphenol- and aliphatic containing bio-oil using the *Lignin-to-Liquid (LtL)* technique were published by Kleinert and Barth in 2008, entitled “Towards a Lignin-cellulosic Biorefinery: Direct One-Step Conversion of Lignin to Hydrogen-Enriched Biofuel” and “Phenols from lignin” (41, 42). The topic on utilisation and valorisation of lignin has been the basis for major research on multiple arenas the recent years, and the LtL-technique has accordingly developed substantially since its appearance.

The thermochemical conversion method itself is termed Lignin-to-Liquid-solvolyis. The experimental procedure includes addition of lignin, a hydrogen donor (formic acid) and a solvent into a high pressure/high temperature reactor and heating the reaction mixture, as a closed system, to a desired reaction temperature (see Chapter 3.2 for detailed work-up procedure). Various solvent systems, including pure solutions and various mixtures, using methanol, ethanol, isopropanol and/or dimethyl carbonate have been thoroughly tested through the LtL-methods developing process. Due to availability, low cost, its benign nature and partly due to results obtained in paper I in part II of this thesis, the recently determined choice on solvent system is formic acid in water (43).

Formic acid (FA) acts, together with a co-solvent, as an *in situ* hydrogen donor in the liquid reaction medium during LtL-solvolyis, providing depolymerisation and hydrodeoxygenation of the lignin copolymer. Thermal degradation products of FA provide CO and H₂O or CO₂ and H₂ with the latter as the preferred decomposition pathway (44). FA has shown to deliver reactive hydrogen upon degradation during LtL-solvolyis, together with CO₂, in a more reactive way than for H₂ gas (45). Figure 1.4 depicts the main conversion route during LtL-

solvolysis, excluding aliphatic reaction products from the equation, as the most recent publications report aromatics to be the dominating product structures.

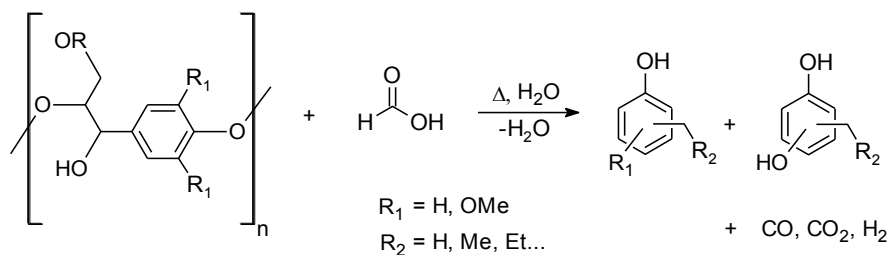


Figure 1.4 – Overview of the main conversion route; Lignin is a methoxylated, phenolic polymer which in course of the solvolytic reaction is degraded to phenol monomers with different substitution patterns and aliphatic compounds. Simultaneously a hydrodeoxygenation occurs in which formic acid (FA) serves as the hydrogen donor. Water is generated during the reaction (43).

The thermochemical conversion method is a solvolysis reaction producing a low viscous bio-oil with high H/C ratios and low O/C ratios, an aqueous product fraction, a gas fraction and a small fraction of solid residue. The choice of utilisation area for the aromatic LtL-oil as a fuel or as a basis for building blocks in the chemical industry provides different criteria for physical and structural properties. The oxygenated functional groups and phenolic character of the aromatic monomers comprising the LtL-oils can be beneficial in the chemical industry by e.g. transforming them to high-performance plastics and/or a variety of fine chemicals (22). High conversion-level LtL-oils have solvent properties similar to petroleum products, which makes them fully miscible with petroleum-based fuels. The van Krevelen diagram in Figure 1.5 illustrates this by showing the H/C and O/C ratios in different biomass and fossil materials (41). Comparing LtL-oils to fossil fuel (HHV = 42-45 MJ/kg) shows an estimated higher heating value for LtL-oil (HHV = 35.6-44 MJ/kg) compared to e.g. flash pyrolysis bio-oil (HHV = 21-25 MJ/kg), and efficiently enables the LtL-oil to be utilised as a fuel or as a fuel additive (41).

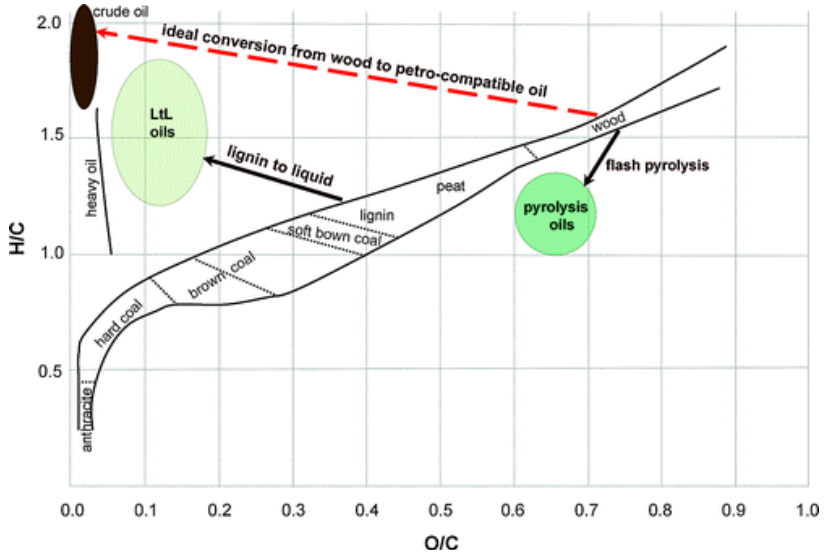


Figure 1.5 - Van Krevelen diagram showing the H/C vs O/C ratios of different biomass and fossil materials. The arrows indicate conversion pathways for flash pyrolysis and the lignin to liquid process as well as the "ideal" theoretical conversion from wood to crude petroleum (dashed arrow) (41).

2.

SCOPE

Following the first publications on the L_tL-solvolytic process in 2008, studies on optimisation and kinetics have been published by Kleinert et al. (2009 & 2011) and Gasson et al. (2012). Among other, mechanistic and structural studies were published by Holmelid et al. (2012) and Gellerstedt et al. (2008), studies aiming at the use of catalyst in L_tL-solvolytic process have been published by Liguori and Barth (2011) and Oregui Bengoechea et al. (2015). Optimisation of the L_tL-technique has been, and still is, necessary as a step for proceeding closer to the commercialisation of the technology, including detailed investigation of various effects based on the role of lignin feedstock origin, feasibility of integrating the process in a biorefinery-concept, product composition and applicability as well as upscaling and catalytic adjustments.

The main focus in this thesis is the role of the lignin feedstock origin, the biorefinery integration potential and an evaluation of product applicability based on the product composition. To investigate LtL conversion's application potential within a biorefinery it is necessary to examine the role of biomass feedstock origin and/or pretreatment on quantitative product yields. Based on biorefinery integration potential it is of essence to achieve high conversion yields from lignin to LtL-oil, and in a biorefinery scenario the preparation and conversion parameters are optimised. With the aim of finding a suitable feedstock species and pretreatment method to generate lignin for LtL-solvolyis, thus providing high oil yields, multiple feedstocks are screened through systematic LtL-experiments.

Conversion optimisation, together with targeting the desired product composition, are key issues for integration within a biorefinery. Organosolv extraction causes delignification of the biomass through intramolecular ether linkage cleavage and provides high yield biomass fractions of high purity (52). A focus in this thesis therefore directed towards the impact of this conceptual feedstock pretreatment on LtL-solvolyis results. The final objective is to develop a *continuous process*, in which fractionation of lignocellulosic biomass and thermochemical conversion of its lignin fraction using LtL-solvolyis are combined (see Figure 2.1 for a conceptual sketch). Combining fractionation and thermochemical conversion of lignocellulosic biomass will increase the application potential for the LtL-solvolyis technology as a complementary industrial approach.

The combination of organosolv fractionation and LtL-solvolyis is designed as a continuous flow-through system for separation with following LtL-solvolyis experiments on the separated lignin fraction. Delignification by organosolv fractionation and LtL-solvolyis as a continuous process enables the dissolved

hemicelluloses, lignin and extractives to be moved downstream from the cellulose fraction in order for the separated fractions to be further processed.

Extraction efficiency, LtL conversion ratio and quantitative bio-oil composition are examined to evaluate the application potential for the concept and the final bio-oil products.

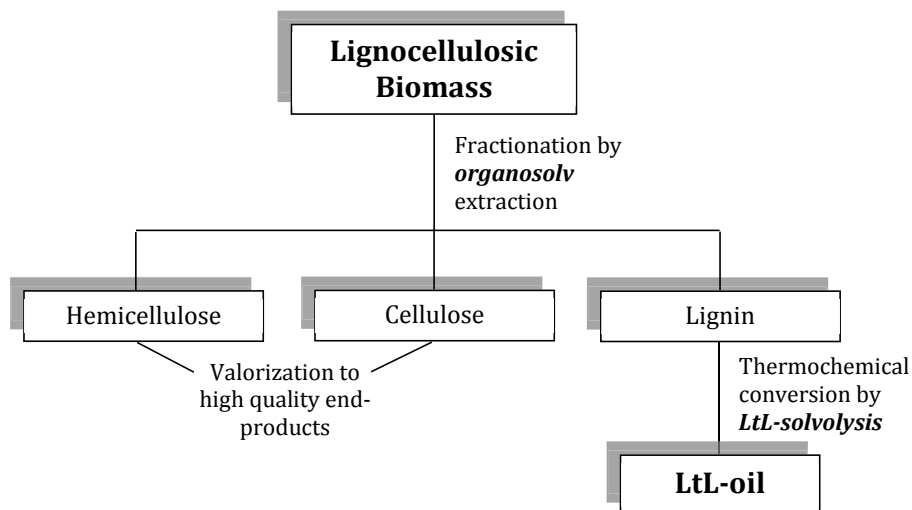


Figure 2.1 – Conceptual sketch including fractionation of LCBM and thermochemical conversion of lignin by LtL-solvolyis.

3.

METHODS AND EXPERIMENTAL PROCEDURES

This chapter describes the most frequently used experimental procedures and analytical methods used throughout this PhD project. Techniques outside the following descriptions are given in the individual papers in Part II of this thesis. The main topics chosen to be described are: semi-continuous organosolv fractionation of biomass, LtL solvolysis, tools used for statistical evaluation of product outputs such as principal component analysis (PCA) and partial least square (PLS) regression analysis. Additionally, techniques used for chemical characterisation of the resulting products from biomass fractionation and thermochemical conversion of lignin are also described herein, including a brief conceptual description of Fourier transform infrared spectroscopy (FT-IR) and elemental analysis (EA) and a more detailed description of gas chromatography coupled with mass spectrometry (GC-MS).

3.1 Semi-continuous organosolv fractionation

About

As part of investigating the biorefinery integration potential for LtL-solvolyis, a setup for semi-continuous fractionation of LCBM was developed. By this method, lignin was dissolved in an in-line separation process, the lignin containing organosolv liquor was collected and finally lignin was isolated from the liquor by precipitation before thermochemical conversion using LtL-solvolyis.

Experimental

In each fractionation experiment a solvent, containing an acid catalyst, was pumped by a Gilson 307 piston pump through coiled tubing heated by a heating cord (type HTC452002, Brisk Heat, USA) and controlled by a benchtop thermocouple controller (type SDC240JC-A, Brisk Heat, USA) to the desired temperature. Heated solvent then reached a high pressure column packed with biomass for the extraction to take place. The column was provided with end-filters of 104 μm (S4020-5EA, Sigma Aldrich, USA). After filling the entire system with solvent, the column was heated to the desired reaction temperature by a Samox heavy insulated heating tape (type BWH102060L, Brisk Heat, USA) which was also controlled by a benchtop thermocouple controller (type SDC240JC-A, Brisk Heat, USA). The lignin is then solubilised within the high pressure column. The dissolved lignin was pumped out of the column in a continuous stream by the supplying Gilson 307 piston pump, through an in-line particulate filter (SS-2F-60, 60 μm , Swagelok Company, USA) to filter off potential particles, into heat exchanging coiled tubing for condensation, through a back-pressure regulating valve (SS-4R3A, Swagelok Company, USA) and subsequently collected in a beaker. All coiled tubing was made from Cajon Special stainless steel seamless tubing (SS-T2-S-035-6ME, Swagelok Company, USA). The system temperature was continuously monitored in three positions

by mineral insulated metal sheathed thermocouples (type K, length 300 mm, TC Direct, UK) connected to a Digi-Sense 4-input data logging T/C thermometer (type K/J, Davis Instruments, USA). The solvent flow was kept constant at 1.500 mL/min throughout every experiment and the pressure in the system was held at 2.0 MPa to ensure the solvents being kept in liquid state during extraction. This was controlled and monitored via the piston pump. Extraction time was kept at 10 hours in all experiments. Figure 3.1 and Figure 3.2 display the laboratory setup.

With the total volume of the system being 255 mL, an equivalent amount of solvent was pumped through to collect residual extract and to wash the solid residue when the system reached ambient temperature after completed extraction. The washing solution was combined with the organosolv liquor. After washing, the solid residue was removed from the column and dried at ambient temperature to constant mass. The organosolv liquor was diluted with distilled water in a ratio of 1:3 v/v (organosolv liquor : H₂O), cooled to 4 °C and left for precipitation. The precipitated lignin was filtered off over a Whatman 1 filter and dried at ambient temperature to constant mass.

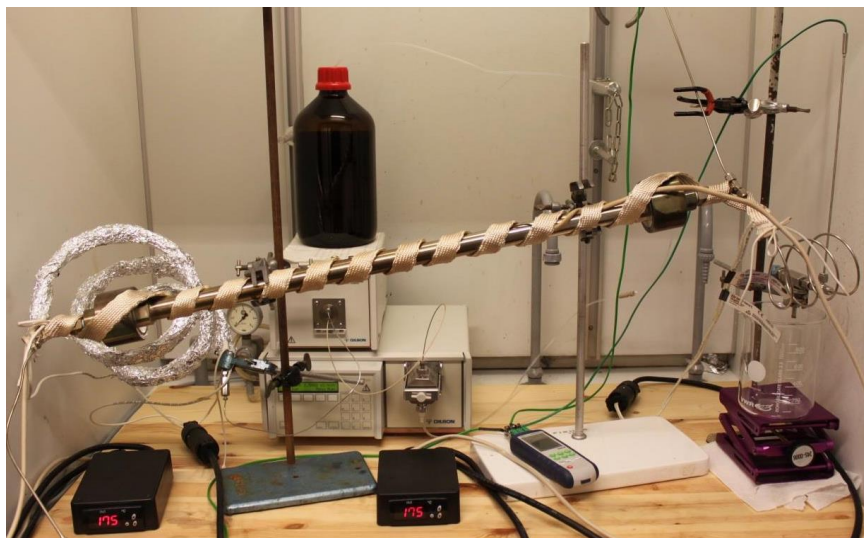


Figure 3.1 – System for continuous organosolv fractionation of lignocellulosic biomass. The separation column is here wrapped with Samox heavy insulated heating tape.

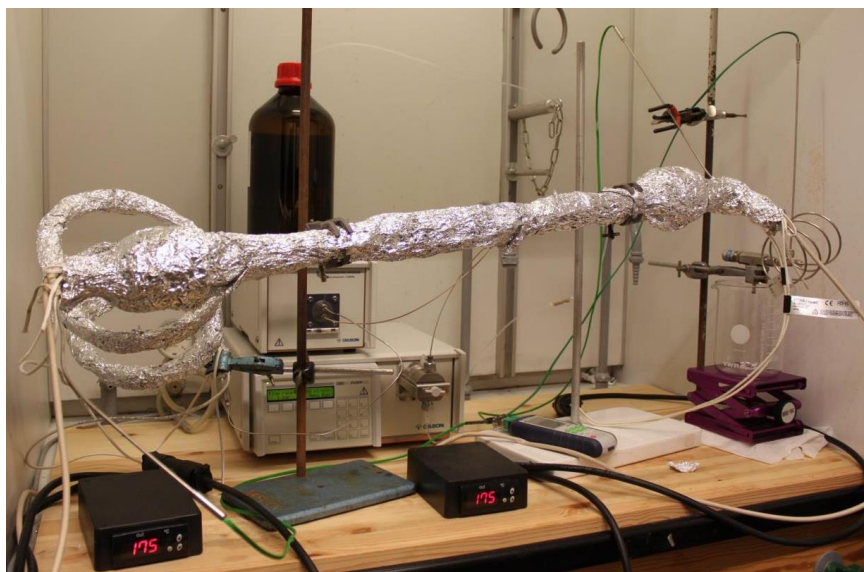


Figure 3.2 – System for continuous organosolv fractionation of lignocellulosic biomass. The separation column is wrapped with Samox heavy insulated heating tape and isolated with glass fibre paper and aluminium foil to minimize the heat loss during the extraction process.

3.2 LtL-solvolysis

About

LtL-solvolysis experiments conducted with water or ethanol (EtOH) as co-solvent have the same workup-protocol regardless of solvent system. This is to ensure comparability and reproducible results.

Detailed up-to-date laboratory workup protocol for LtL-solvolysis

Lignin, distilled water and formic acid were added to a non-stirred 25 mL high pressure Parr reactor from the 4740-series (see Figure 3.3) and placed in a preheated Carbolite Laboratory High Temperature oven. After completed reaction time, the reactor was removed from the oven and cooled to ambient temperature. The resulting products after solvolysis include a gas phase, a liquid phase and a small amount of solid phase. The amount of gaseous product was determined by weighing the reactor before and after venting the gases.

The liquid product consisted of a single aqueous phase. Dark brown LtL-oil was not present as a separate phase, but adsorbed onto the solid residue due to its hydrophobic character. The LtL-oil is miscible in an ethyl acetate (EtAc) and tetrahydrofuran (THF) mixture and the liquids were therefore separated from the solid phase using EtAc:THF (9:1 v/v) and filtered through a 0.45 μm Puradisc™ 25 NYL filter. The aqueous phase and organic phase were separated using a separatory funnel, and the remaining aqueous phase was extracted with EtAc:THF (9:1 v/v) three times before combining the organic phases and drying it over Na_2SO_4 (s). The aqueous phase in ethanol-system experiments was of significantly smaller volume and was hence diluted by a known quantity of distilled water before separation from the organic phase in a separatory funnel.

The solvent was removed from the LtL-oil on a rotary evaporator at a temperature of 40 °C and a pressure of 175 mbar until stable mass. This

pressure was set as standard conditions for all LtL-oils to ensure the same workup-protocol for all LtL-experiments regardless of solvent system. A simplified flow sheet for LtL-solvolysis laboratory workup is displayed in Figure 3.4.

Gas composition analysis was not performed as part of this project, but relevant data for gas composition is published showing that the main components of the gas phase are the decomposition products of formic acid (51).

Paper I in this thesis describes an experimental protocol using dichloromethane (DCM) as solvent during workup, and the aqueous phase to be extracted with DCM three times, followed by EtAc:THF (9:1 v/v) three times. For safety-, simplicity- and practical reasons the workup solvent was altered to EtAc:THF (9:1 v/v) as single workup solvent in consecutive LtL-experiments, displaying equally good properties for extraction as DCM (53-55).



Figure 3.3 – A: Disassembled 25 mL Parr reactor. B: Assembled 25 mL Parr reactor.

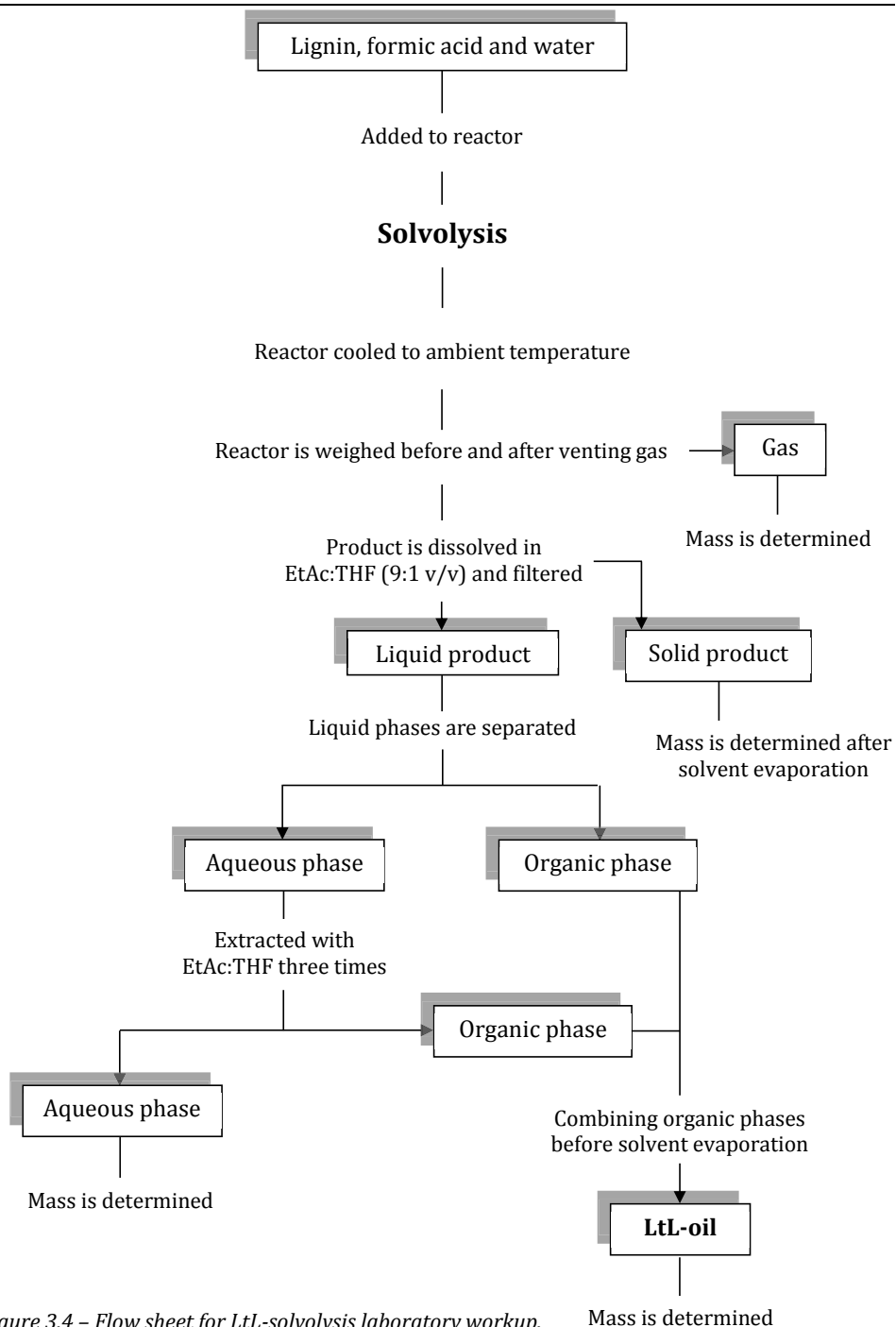


Figure 3.4 – Flow sheet for LtL-solvolyis laboratory workup.

3.3 Experimental designs and optimisation

Multiple LtL-solvolysis experiments require the use of analytical tools in order to process the yielded sets of complex data. If experiments are performed randomly, the results obtained will also be random. Therefore, it is necessary to plan the experiments in such a way that the interesting information will be obtained (56). Statistical methods, such as the use of experimental design, can simplify the processing of laboratory results in a way that reveal which factors, or combination of factors, that are necessary to control to achieve acceptable results (yields, side product production, shortening of reaction time etc.) (57). The classical approach whereby an experimental response is investigated, is each experimental factor or variable in turn, while all the other factors are held at a constant level. One of the main reasons for preferring an experimental design to a classical design is that a design can detect and estimate interactions between factors/variables which classic designs cannot (58). By varying only “one-variable-at-a-time” (OVAT) and keeping all but one variable fixed, a false maximum can be found due to a reduced potential range for response. In most cases, variables in an experimental setup are dependent of each other. They are only independent in such a way that they can be adjusted independently. When a variable exerts its influence on a chemical system, the level of one variable may well modify the influence of other variables. This can lead to both compensating and amplifying effects (57).

A complete factorial design includes all factors and all combinations of factor levels in an experimental setup. To effectively reduce the number of experiments, including both single variables and combinations of variables, *fractional* factorial designs have been developed (59). Fractional factorial designs are also key solutions when time and resources are limited. Within this thesis full factorial designs were applied in paper II and IV. A fractional factorial

design was applied in paper III, reducing the number of experiments to a balanced half fraction of semi-continuous organosolv extractions.

3.3.1 Principal component analysis

Principal component analysis (PCA) is a multivariate technique that analyses a data table representing observations described by several dependent variables which are, in general, inter-correlated (60). PCA is most easily described geometrically by extracting latent variables called “principal components”. Extracting the first principal component (PC1) is done by finding the linear combination of the original data which explains the maximum of its variance. PC2 is extracted by removing PC1, and PC2 describes the maximum of the variance which cannot be described by PC1 (PC1 and PC2 are orthogonal), see Figure 3.5. PC3 will then be the component explaining the variance not described by PC1 and PC2 and so forth (PC3 is orthogonal to PC1 and PC2). The target of PCA is variable reduction, and the number of extracted components equals the number necessary to explain all the information in the dataset (61).

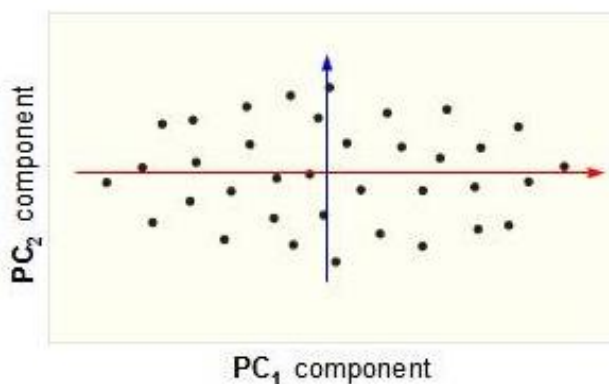


Figure 3.5 – Projection of a dataset into two PCs describing maximum variance (62).

3.3.2 Partial least square regression analysis

In a partial least square (PLS) regression analysis, quantitative relations can be established between blocks of variables, e.g. a block of descriptor data for a series of reaction systems (X-block) and a block of response data measured on these systems (Y-block). By the quantitative relation between the blocks, it is possible to enter data for a new system to the X block and make predictions of the expected responses (57). Meaning, rather than letting latent variables (such as PCs) explain the variance of X, one can extract as much information as possible from X that correspond to the information in Y (61). In this thesis PLS regression analysis was employed in paper II, where feedstock for LtL-solvolyis was divided into blocks before PCA so that maximum variance within each feedstock could be described independently.

3.4 Product characterisation

Identification studies were performed both qualitatively and quantitatively on bio-oils from LtL-solvolyis. The bio-oils are complex mixtures containing a wide range of compound classes and multiple functional groups.

Selected bio-oils were tested by Fourier transform infrared spectroscopy (FT-IR) to examine potential change in functional groups present in the oils by comparing them to their feedstock and product differences based on solvent system (paper I). This technique is a mere qualitative way of investigating structural change from sample to product, but it does not provide detailed information towards compound identity.

Elemental composition of feedstocks, bio-oils and solid residues/char by measuring mass contribution of elements such as nitrogen, hydrogen, carbon and oxygen (by difference) was also investigated. This was done to verify hydrodeoxygenation of lignin during the LtL reaction process with a special focus on O/C ratio to confirm substantial reduction in oxygen content from feedstock to bio-oil. A reduction in oxygen content from feedstock to bio-oil is desirable if the main application for the oil-product is to be utilised as fuel components with high heating values (41). Elemental composition of solid residue/char was performed as a standard procedure to monitor thermochemical conversion efficiency by indicating whether the residue had levels of oxygen suggesting unreacted lignin, or was high in carbon, suggesting a char fraction as a result of efficient lignin-to-liquid conversion. Elemental composition of bio-oils and solid residues was also used for mass balance calculations (paper IV).

3.4.1 Gas chromatography

To obtain a more detailed identification of bio-oil constituents, the main focus in this PhD project was gas chromatography coupled with mass spectrometry. Gas chromatography (GC) focuses on separating components in a sample based on volatility and thermal stability within the applicable temperature range. Standard GC can be used up to 350 °C, corresponding to an upper molecular weight limit of 600 Da (63). Published data on gel permeation chromatography-size exclusion chromatography (GPC-SEC) of LtL-oils show molecular weight distributions <500 Da, which verify GC as an analysis technique covering the relevant structural range (51). Simplified, the separation itself is done by elution, where the sample is injected and quickly vaporised, an inert carrier gas transports the sample through a heated GC-column and the components in the sample elutes at a rate determined by their retention onto the solid packing within the GC-column. If the differences in sorption are sufficient or the column is long enough, a complete separation is possible (64). When investigating complex samples, compounds with similar boiling point may elute simultaneously, giving a chromatographic peak overlap signal in the chromatographic detector. This possibility demonstrates a weakness within the separation method, and may exclude compounds from detection and identification. By “spiking” a sample with a component standard (adding a known quantity of the specific compound to the investigated sample) one can positively identify the retention time of the interesting compound by simply comparing chromatograms, and peak area in the chromatograms, from pure and “spiked” samples. Peak overlap may still occur, but as in this case, by the use of a detector such as a mass spectrometer, one can identify a compound based on its fragmentation pattern as described below.

Derivatisation is also a useful method to ensure GC suitability for a sample. Non-volatile samples can be derivatised, thus forming volatile samples. In the same

way, highly volatile samples can be derivatised to ensure sufficient separation and detection of components. Derivatisation is done with the purpose of improving detectability and/or selectivity, often by sample substitution reactions prior to injection (63, 65).

Mass Spectrometry Detector (MSD)

As gas chromatography only separates the sample components, using a mass spectrometry detector can aid in identifying the components. The combination of gas chromatography and mass spectrometry is designated GC-MS. In order for the separated molecules from GC to be analysed by mass spectrometry, they need to be ionised. Ionisation can be done by e.g. chemical ionisation (CI), electron spray ionisation (ESI) or desorption ionisation (DI). Ionisation is in this case done by a beam of high-energy electrons (ion source), to provoke the loss of an electron and converting the molecules to molecular ions ($M^{+\bullet}$), a process called electron impact ionisation mass spectrometry (EIMS). Ionisation is followed by fragmentation of the $M^{+\bullet}$ in ways characteristic for the structure of the fragmenting ion. Further fragmentation occur before the ions leave the ion source and high vacuum ensures that, once the ions formed in the ion source begin to move toward the detector, they will not collide with other molecules to prevent further fragmentation or divert them from reaching the analyser (66, 67). In the analyser, in this case a heated gold quadrupole, the formed ions are separated according to their mass to charge ratio (m/z), and an adjusting voltage and radiofrequency applied to the rods in the quadrupole ensure that ions with the correct m/z ratio travel down the rods and into the identifying detector (67). The identifying detector ensures that the compound unique fragmentation patterns are conveyed so that structural identification can take place.

Flame ionisation detector

Quantification studies in paper IV included the use of a flame ionisation detector (FID). A FID is a small oxygen-hydrogen flame in which the sample fractions from GC separation are burned, producing ions in the process. The ions are collected, form a small current, amplified and sent to a data system. Ionisation efficiency in flame ionisation is high and sufficient to give good sensitivity, and an FID detects all organic compounds (63).

4.

MAIN RESULTS

This chapter focuses on main results achieved within this PhD project. The performed laboratory- and analytical work is presented as four individual papers in part II of this thesis. The order of the papers from I-IV is a consequence derived from results obtained in one paper influencing the work objective in its following paper. Each paper is in this chapter presented with a condensed summary describing the main focus and the main findings.

4.1 **Paper I** – The effect of solvent and input material pretreatment on product yield and composition of bio-oils from lignin-solvolyis

As one of the primary focuses of this PhD project was to investigate the influence of feedstock pretreatment on LtL-solvolyis product yields and bio-oil composition, this was also the primary focus of paper I. A second topic in this study was to compare two different solvent systems, water and ethanol, and their impact on product yield and product composition.

Table 4.1 displays the different lignin types used in this study. From multiple LtL-solvolyis screening experiments of the chosen lignin types it was clear that SKL lignin provided the quantitatively largest conversion of lignin to LtL-oil based on lignin input mass (75 wt. %). SKL lignin was subjected to re-dispersion and thorough cleaning in a Kraft pulping process and has thus high purity. SSEH lignin resulted in the lowest conversion of lignin to LtL-oil (50 wt. %), and originated from steam exploded Norway spruce, followed by enzymatic hydrolysis. This material also contained substantial amounts of carbohydrates.

Table 4.1 – Lignin feedstock types and characteristics (paper I).

Feed-stock	Characteristics	Ratio		Lignin Content (%)	Ash Content (%)
		H/C	O/C		
SEH	Norway Spruce (<i>picea abies</i>) – 30 % cellulose, Enzymatic Hydrolysis – bioethanol production process	1.20	0.45	~ 70 %	NA
SAH	Norway Spruce – 30 % cellulose, weak Acid Hydrolysis, SO ₂ - treated – bioethanol production process	1.37	0.57	~ 70 %	< 1.0
SKL	Norway Spruce – cleaned lignin from paper production – lignin from Kraft pulp mill black Liquor (Lignoboost)	1.10	0.36	95-98 % (68)	< 1.5
SSEH	Norway Spruce – Steam exploded, Enzymatic Hydrolysis – bioethanol production process	1.40	0.70	~ 60 %*	1.16
BEH	Birch (<i>betula pubescens</i>) – Enzymatic Hydrolysis, tempered at 210 °C for 10 min – bioethanol production process	1.31	0.51	~ 70 %*	1.25

* Estimated from the elemental composition

In this study it became clear that feedstock purity was influencing conversion yields. High fractions of residual carbohydrates in the feedstock provide a significant contribution of oxygen, and results from EA displayed a substantial depletion of oxygen through LtL-solvolyis. Deoxygenation of feedstock was considerably higher for SSEH than SKL as seen in Figure 4.1. Conversion yields from feedstock to LtL-oil were evidently proven to increase with decreasing oxygen content in feedstock, and the feedstocks' conversion ratios at optimal conditions were distributed in the following descending order: SKL > SEH > BEH > SAH > SSEH. Oil yields were thus showed to depend to some degree on biomass origin, but more strongly on pretreatment method, which influences the O/C ratio of the feedstock utilised for LtL-solvolyis.

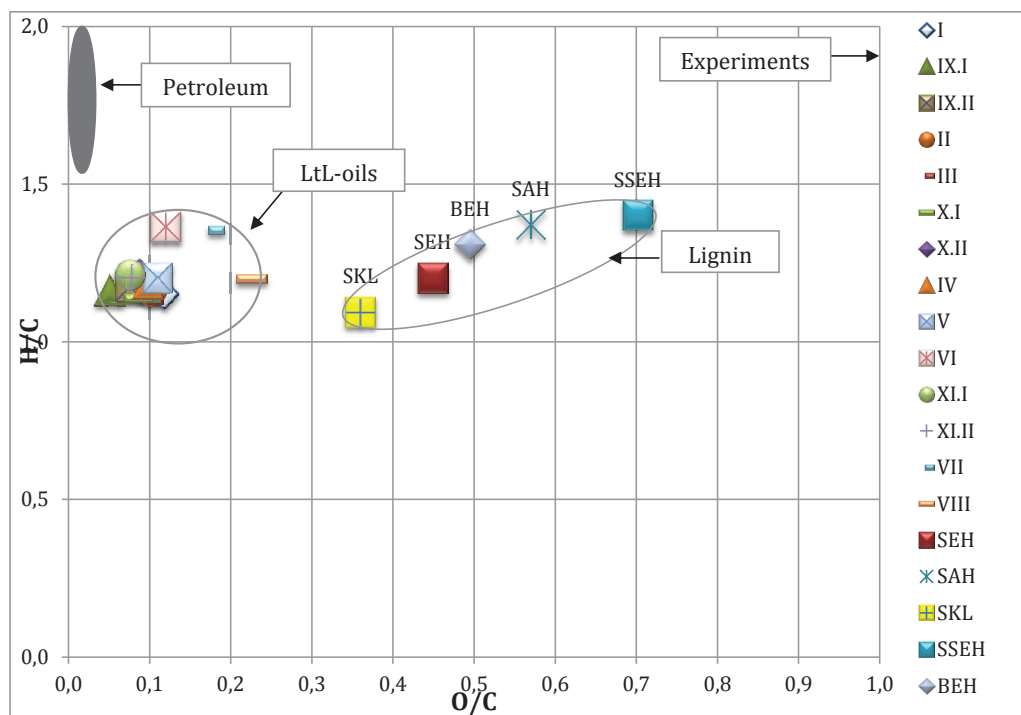


Figure 4.1 – Van Krevelen plot showing H/C ratio and O/C ratio of all feedstocks and LtL-oils in paper I. Experimental coding refers to LtL experiments in Løhre et al. (2016).

When comparing parallel experiments using water or ethanol as solvent, it was clear that the ethanol system gave higher oil yields than the water system. The alcohol used as co-solvent together with formic acid, also functions as an alkylation agent in the LtL system, which has previously been published by Holmelid et al. (2012) using ^{13}C -labeled methanol. The alkylation gives a net mass contribution to the lignin monomers, and therefore enhances the oil yield relative to lignin input. The alkylation property was in addition evident when examining GC-MS spectra from the parallel experiments. Compositional differences showed that the bulk of the dominating compounds comprising bio-oil from ethanol solvent systems were of a more complex substitution order, as a result of alkylation from ethanol, in addition to the phenolic substituents originating from the depolymerisation, as shown in Figure 4.2 (20, 43). The

difference in substitution order can be beneficial depending on utilisation area for the specific compounds.

GC-MS analysis showed that the compound identity comprising the bio-oils from water system reactions were similar regardless of which wood species the lignin stemmed from. The dominating peaks were primarily represented by the same compound peaks, with minor variations in abundance caused by reaction conditions.

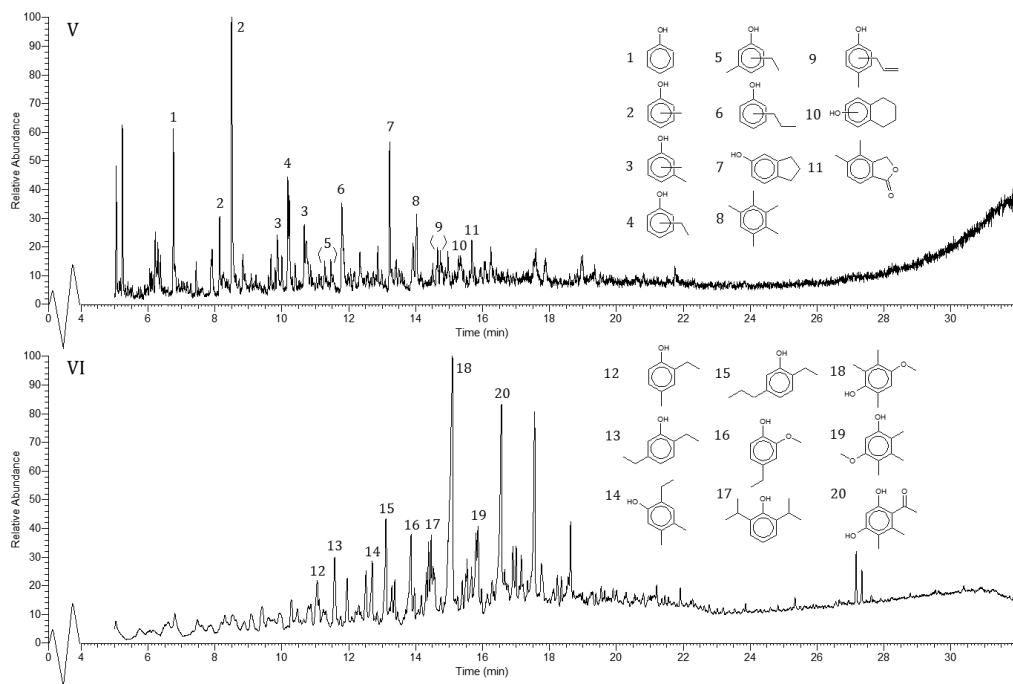


Figure 4.2 – GC-MS chromatogram of experiments using Norway spruce pre-treated with steam explosion and enzymatic hydrolysis (SSEH). Experiment V is a water-system reaction, while VI is an ethanol system reaction (figure adapted from Løhre et al. (2016)).

The alkylation effect of ethanol on the oil yield was considered not to be substantial (5-10 %), and water was nonetheless evaluated as a more environmentally friendly solvent system largely due to low cost, high availability and its benign nature.

4.2 Paper II – Lignin-to-Liquid solvolysis (LtL) of organosolv extracted lignin

As feedstock purity was found to influence the conversion yield from lignin to LtL-oil in paper I, organosolv extracted lignin was chosen as main focus for feedstock in paper II. Organosolv extracted lignin is known to be of high purity, sulphur free and to have low molecular weight (27). ^{31}P -NMR was used to investigate the type of hydroxyl groups (-OH) present in the LtL-oils, and ^{31}P -NMR results, combined with results from GC-MS and EA, were used to evaluate the distribution of phenolic monomers present in the bio-oils according to experimental conditions.

Table 4.2 displays the different lignin types used in this study. Two of the organosolv extracted lignins (BO and WSO) were supplied from the Energy Research Centre of the Netherlands (ECN), while the third organosolv extracted lignin (EEHO) was extracted as part of the experimental procedures.

All four feedstocks described in Table 4.2 were subjected to an identical series of experimental conditions. Organosolv extraction of feedstock EEH, to give feedstock EEHO, close to doubled the bio-oil yield after LtL-solvolysis. Average oil yields, in descending order based on feedstock input mass, were: BO (64 wt. %) > WSO (61 wt. %) > EEHO (57 wt. %) > EEH (32 wt. %).

Table 4.2 – Lignin feedstock types and characteristics (paper II).

Feed-stock	Characteristics	Ratio		Lignin Content (%)	Ash Content* (%)
		H/C	O/C		
EEH	Eucalyptus – Origin: Thailand, produced at Biorefinery Demo Plant (BDP) in Örnsköldsvik, Sweden Lignin rich residue from weak acid- and Enzymatic Hydrolysis	1.53	0.74	~50**	~ 4
EEHO	Eucalyptus – Origin: Thailand, produced at University of Bergen (UoB), Norway Lignin rich residue after Enzymatic Hydrolysis processed with Organosolv conditions: 178°C, EtOH-H ₂ O 63% w/w, without acid, 3 h 20 min (69)	1.12	0.34	ND	< 0.6
BO	Birch – Origin: Finland, produced at Energy research Centre of the Netherlands (ECN), The Netherlands Organosolv conditions: 200°C, EtOH-H ₂ O 50% w/w, 5 mM H ₂ SO ₄ , 30 min carbohydrates <<1% w/w	1.16	0.32	96.4***	< 0.9
WSO	Wheat Straw – Origin: Champagne-Ardennes region, France, produced at Energy research Centre of the Netherlands (ECN), The Netherlands Organosolv conditions: 210°C, EtOH-H ₂ O 50% w/w, without acid, 90 min carbohydrates <<1% w/w	1.14	0.27	ND	< 0.9

* Ash content was measured by combustion at 575 °C according to protocol NREL/TP-510-42622 (70).

** Estimated from elemental composition.

*** Sum of AIL (acid insoluble) and ASL (acid soluble) lignin was determined using analytical procedures described in Wildschut et al. (2013) (71).

The experimentally obtained data in this study was subjected to principal component analysis and partial least square regression analysis. PCA showed a negative correlation between reaction temperature and O/C ratio in the LtL-oils, meaning higher temperatures provide lower O/C ratios (effective deoxygenation at high temperatures). This was also verified with ³¹P-NMR and GC-MS, by a decrease in phenols with one and two methoxy groups and an increase in phenols with no methoxy substituents caused by increased reaction

temperature. The results from ^{31}P -NMR of all LtL-oils are displayed in Figure 4.3.

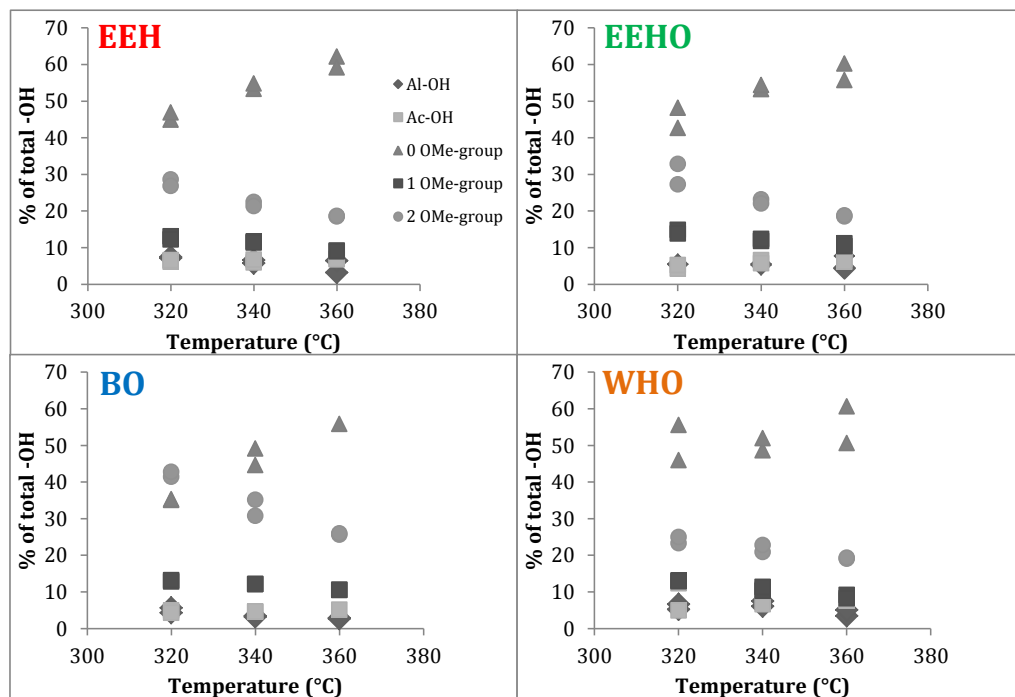


Figure 4.3 – Relative amounts of hydroxyl groups in each lignin type relative to conversion temperature.

The oil yield proved to be positively correlated with the initial volume of formic acid in the reactor, yet uncorrelated with reaction temperature. However, the H/C ratio showed a minor negative correlation to temperature, and a positive correlation to oil yield. This, supported by results from PLS regression analysis (by dividing responses into blocks of feedstock), suggested that high temperatures might inhibit hydrogenation of the feedstock or, most probably, promotes condensation reactions that reduce the hydrogen content of the products.

Both impure lignin, such as feedstock EEH, and pure lignin, such as organosolv extracted BO, proved to be suitable for LtL-solvolytic. In line with the findings detailed in paper I, the bio-oil yield depends on the purity of the lignin, and organosolv extracted lignin yielded high conversion of lignin to bio-oil compared to (the carbohydrate rich) EEH feedstock. Formic acid was suggested to have only a limited impact on the structural composition of LtL-oils, yet solvolysis reactions need sufficient amounts (excess) of FA to yield successful experiments with high oil yields. The oxygen content of the resulting bio-oils also depends on sufficiently high reaction temperature for effective depolymerisation and hydrogenation.

4.3 Paper III – Organosolv extraction of softwood combined with lignin-to-liquid-solvolyis as a semi-continuous system

From the study conducted in paper II it was concluded that organosolv extracted lignin was suitable for LtL-solvolyis providing considerable bio-oil yields. In order to approach commercialisation of the technology it is desirable to implement LtL-solvolyis into the concept of a biorefinery as described in Chapter 2. In this context the idea of biomass extraction, by organosolv fractionation, combined with LtL-solvolyis as a continuous process arose.

Organosolv fractionation of biomass as a continuous flow-through system was the first focus towards a complete continuous setup with lignocellulosic biomass as feedstock and LtL-oil as final product. Figure 4.4 displays a process flow diagram setup designed for flow-through organosolv extraction of wood shavings.

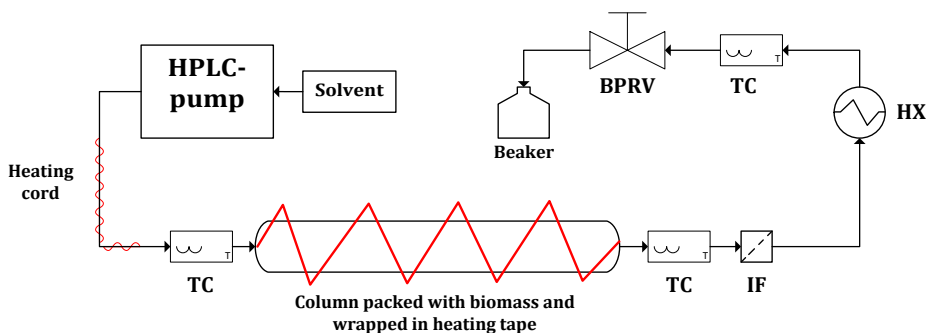


Figure 4.4 – Process flow diagram (PFD) of semi-continuous organosolv extraction. TC = Thermocouple; IF = In-line Filter; HX = Heat Exchanger; BPRV = Back Pressure Regulating Valve.

The experimental description of flow-through organosolv processing of Norway spruce (~90 %) and pine (~10 %) using the setup depicted in Figure 4.4 is described in detail in Chapter 3.1.

Data obtained from this study was subjected to PCA to investigate optimal conditions for organosolv fractionation. Within the variable range it was found that fractionation depended on the presence of a catalyst for optimal extraction yields, with sulfuric acid (H_2SO_4) improving lignin yields compared to formic acid (HCOOH). A solvent ratio of 63:37 EtOH:H₂O (by mass), a temperature of 175 °C and $[\text{H}_2\text{SO}_4] = 6.00 \text{ mM}$ yielded optimal lignin recovery of up to 86 % of the initially determined lignin mass content in the biomass feedstock. The solubilized and subsequently precipitated lignin had a purity of ~95 % and the fractionation experiments were found to be reproducible. This, together with initial LtL testing of the flow-through organosolv extracted lignin, giving LtL-solvolytic conversion results of 90 % based on lignin mass input, showed that the continuous flow fractionation of lignocellulosic biomass is a promising route for biorefinery processing.

Descriptions of further technology development for the concept to be included in a biorefinery are suggested in Chapter 5.2.1.

4.4 **Paper IV** – Composition of Lignin-to-Liquid solvolysis oils from lignin extracted in a semi-continuous organosolv process

Utilisation of lignin as feedstock for production of renewable and sustainable aromatics is expanding and shows great potential. The successful flow-through organosolv fractionation in paper III gave rise to a systematic set of LtL-solvolysis screening experiments on the relevant lignin feedstock produced and subsequent quantification studies. Identifying bio-oil components will help map out the product commercialisation potential in the case of LtL-solvolysis being implemented in a biorefinery.

LtL-solvolysis experiments were part of an experimental design in which both the effects of reaction conditions on quantitative product yields and the quantitative bio-oil compositions were subjected to PCA.

To study the bio-oil composition, the LtL-oils were derivatised by silylation to ensure complete gas chromatography compatibility and quantification properties, and subsequently quantified by an FID (see Chapter 3.4.1). Silylation with, in this case, bis(trimethylsilyl)trifluoroacetamide (BSTFA) is an addition reaction in which the hydroxyl protons on phenolic compounds are replaced with a trimethylsilyl derivative yielding trimethylsilyl derivatives of the aromatics.



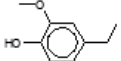
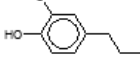



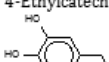

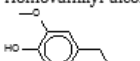
Similar to the findings detailed in paper II, the bio-oil yields were positively correlated with the initial volume of formic acid in the reactor. O/C ratio was negatively correlated with reaction temperature, thus decreasing the oxygen content of the bio-oils with increasing temperature within the variable range.

Bio-oil yields from this specific lignin feedstock reached as high as 94 % based on lignin mass input. Compositional quantification of their ten major compounds yielded ≤ 9.5 % identification of total composition, where reaction temperature was the dominating parameter on structure formation, and the effect of FA was limited. The temperature dependency of the identified compounds was evident when examining the compositional results displayed in Table 4.3. Guaiacol, 2-naphtol, catechol and catechol derivatives were clearly positively correlated to temperature, illustrated by higher abundance at the upper temperature setting (360 °C). Guaiacol derivatives were (limitedly) negatively correlated to initial input of formic acid in the reactor, or not correlated to neither variable.

Quantification results from this study indicated the possibility of tuning experimental LtL-solvolytic conditions towards preferable product composition for utilisation in the chemical industry. The components that were quantified showed structural similarities, including similar substitution patterns and functional groups, between the phenolic monomers. Quantification studies were suggested to be rather aimed at series of homologs or otherwise similar compounds, as suggested by Carlson et al. (2012). Separation of LtL-oil into desired homological series, followed by further separation and/or quantification, would increase the LtL-application potential even further.

The flow-through fractionation of lignocellulosic biomass provided high purity lignin well suited for LtL-solvolytic. Mass balance calculations on LtL-solvolytic experiments were performed as part of this study. Carbon count from lignin to LtL-oil and solid residue exceeded 100 % and the results suggested contributions from formic acid beyond hydrogenation in the reaction mechanism. ^{13}C -labeled formic acid was suggested to be used to clarify whether FA is incorporated in the products in future experimental proceedings.

Table 4.3 – Mass percentages from quantification studies of selected compounds in LtL-oils. Experimental coding refers to LtL experiments in paper IV in part II of this thesis.

Compound	O/C	320 °C				340 °C				360 °C			
		1.1a	1.1b	1.2a	1.2b	2.1a	2.1b	2.2a	2.2b	3.1a	3.1b	3.2a	3.2b
Guaiacol 	0.29	1.95	1.84	1.64	1.60	2.00	2.08	1.71	1.63	2.89	3.00	2.46	2.57
4-Methylguaiacol 	0.25	0.89	0.90	0.74	0.73	1.02	1.02	1.01	0.90	0.41	0.40	0.23	0.28
4-Ethylguaiacol 	0.22	0.61	0.61	0.46	0.48	0.70	0.73	0.65	0.62	0.58	0.65	0.10	0.09
4-Propylguaiacol 	0.20	0.40	0.37	0.40	0.40	0.46	0.48	0.43	0.42	0.42	0.44	0.40	0.43
Catechol 	0.33	0.44	0.46	0.52	0.49	0.44	0.37	0.51	0.39	2.54	2.66	2.48	2.49
3-Methylcatechol 	0.29	No trace								0.24	0.26	0.18	0.20
4-Methylcatechol 	0.29	Trace amounts								1.06	1.08	1.14	1.22
4-Ethylcatechol 	0.25	0.08	0.08	0.09	0.07	0.10	0.10	0.08	0.11	0.52	0.55	0.49	0.52
2-Naphthol 	0.10	No trace				0.02	0.03	0.02	0.02	0.11	0.12	0.10	0.09
Homovanillyl alcohol 	0.33	0.37	0.34	0.40	0.38	0.24	0.24	0.25	0.38	0.30	0.31	0.27	0.31
Total identified (wt. %)		4.74	4.60	4.25	4.14	4.99	5.05	4.66	4.47	9.08	9.47	7.88	8.20

5.

CONCLUSIONS AND OUTLOOK

5.1 Condensed summary and main conclusions

For the purpose of integrating the LtL-solvolytic technique in a biorefinery concept, conclusions regarding feedstock quality and solvent system for LtL-solvolytic were drawn in paper I. High fractions of residual carbohydrates give a significant contribution of oxygen to the feedstock. All feedstocks and pretreatment methods tested in paper I provided lignin rich fractions suitable for LtL-solvolytic, resulting in the desired bio-oils with high aromatic content. Yet, the oxygen content of the feedstock determined the bio-oil yield due to substantial depletion of oxygen through hydrodeoxygenation.

Water as solvent was selected for the thermochemical conversion reactions in subsequent studies on LtL-solvolysis, over ethanol, due to low cost and availability. Bio-oils from the ethanol solvent-system comprise alkylated phenols of a more complex substitution order compared to water solvent-system experiments. The importance of substitutional differences depends on desired utilisation area for the specific compounds.

As lignin originating from organosolv fractionation generates a high purity lignin fraction, this feedstock was given main focus for LtL-solvolysis in paper II. Organosolv extracted lignin proved to generate good bio-oil yields, with birch wood providing the highest conversion ratio among the tested lignins. A screening of reaction conditions showed, inter alia, a positive correlation between oil yields and formic acid input and a reduction in the oxygen content of the LtL-oils with increasing reaction temperature, thus displaying effective hydrodeoxygenation.

As organosolv extracted lignin proved to be well suited for LtL-solvolysis, the next target was to combine organosolv fractionation and LtL-solvolysis as a continuous flow. A continuous-flow organosolv extraction system was designed and constructed in paper III, and optimal extraction conditions were determined for a softwood mixture predominantly containing Norway spruce (and ~ 10 % pine). Lignin was isolated by precipitation, to determine extraction efficiency by terms of yield per fraction, before batch LtL-solvolysis. The extracted and precipitated lignin from flow-through organosolv extraction in paper III was of high purity, in high yields and showed promising results in preliminary LtL-solvolysis testing experiments.

In paper IV the lignin from flow-through organosolv fractionation was used in an experimental setup producing LtL-oils with subsequent quantification of the bio-oil products. The lignin proved to be very suitable for LtL-solvolytic, with high conversion yields to bio-oil ($\leq 94\%$) and possessing compositional similarities, both structural and regarding H/C and O/C ratios, as the LtL-oils produced in paper I and II. Screening of reaction conditions showed, as in paper II, a positive correlation between oil yields and formic acid input and a reduction in the oxygen content of the LtL-oils with increasing reaction temperature, thus displaying effective hydrodeoxygenation. Quantification studies of selected components showed structure concentration to be mainly temperature dependent. Mass balance calculations were performed and showed carbon balances exceeding 100 % on average based on lignin input and LtL-oil plus solid residue output. Experiments using ^{13}C -labeled formic acid were suggested to determine whether FA is incorporated in the aromatic products in future experimental proceedings to further clarify reaction mechanisms.

5.2 Outlook

According to the results obtained in paper I-IV, the LtL reaction mechanisms do need further studies to map out the possibility of tuning experimental conditions towards desired product composition. Phenolic compounds rich in oxygenated substituents are of great value to the chemical industry, while low oxygen content is desirable, to increase HHV and achieve a net energy gain, if the LtL-oil is to be used as a fuel for energy (see Figure 5.1). Based on the oil-components' aromaticity and complexity the LtL-oils will yield greater value if used as a source of building blocks rather than as a fuel.

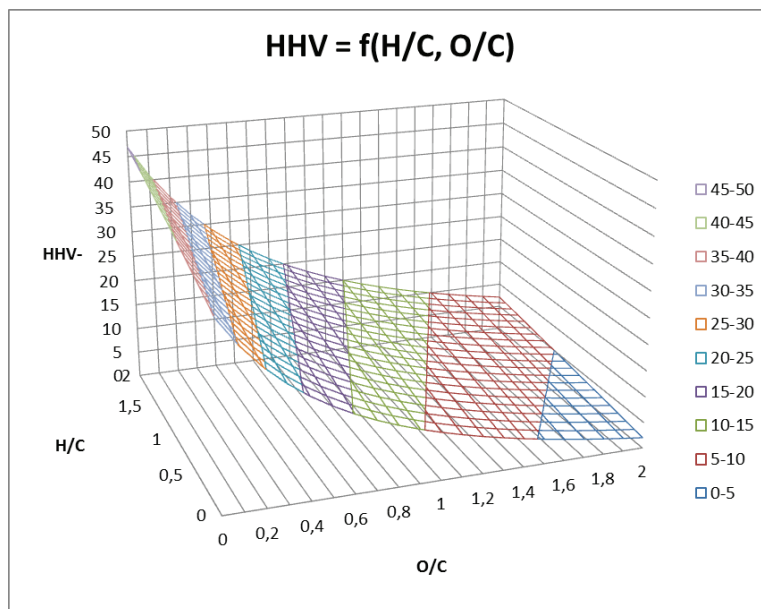


Figure 5.1 – Higher heating value as a function of H/C and O/C ratio. HHV was calculated according to Channiwala and Parikh (2002) (74).

Manufacturing of bioethanol from the carbohydrate fractions in lignocellulosic biomass is already commercially available. Furthermore, cellulosic fibres are being converted into viscose fibres, and hemicelluloses are also being used to generate platform chemicals and/or additives used in e.g. food and feed products to adjust properties such as texture, binding ability and stability (6). Hence, combining fractionation of LCBM with LtL-solvolyis is a unique opportunity when it comes to applicability of the LtL-technique and the product value in a biorefinery. According to the observations and conclusions in this project, the most successful fractionation method of LCBM providing lignin for LtL-solvolyis is organosolv extraction. The fractions are of high purity and in high yields and can hence easily be processed further towards desirable end products. Developing the continuous flow fractionation setup from paper III

into a continuous flow fractionation and thermochemical conversion setup is thus necessary and would yield greater continuity to the concept.

5.2.1 Combined organosolv fractionation and LtL-solvolyis

As adjustments for the flow-through setup described in Chapter 3.1 to function as a continuous process, a carousel-like attachment is a relevant approach for the biomass-containing columns. Mounting an attachment of biomass containing columns on a heat resistant carousel would yield continuity by switching/rotating the carousel towards a new column after completed extraction. While the next fractionation is starting up, the used column can simply be detached, emptied, refilled and reattached for a new run.

To increase efficiency, the heating source should be changed from insulated heating tape and into a larger scale oven. A feasible solution is to attach the active column on to its position in the processing line for solvents to be pumped through, sliding it into the oven, and exposing it to the targeted temperature when it has been filled with solvent. After completed extraction it can easily be slid back onto the carousel for refilling and a new column takes its place in the processing line and moves into the oven.

Heating and cooling of the oven can be time consuming and is not energy efficient, so a station-like solution for the oven to be at a constant temperature level is preferable, thus; the carousel generates a column, the column is connected to the solvent supplying line, the column is filled with solvent before being moved inside the oven (to not burn off the biomass inside the column prior to extraction), the column is withdrawn from the oven after completed extraction, and subsequently replaced with a new one. Residual fractionation solvent in the column can easily be rinsed off the cellulose fraction as solvent

residues inhibits the growth of organisms during e.g. enzymatic hydrolysis (27). The column needs to be cooled and depressurised before being disconnected from the processing line and emptied.

In an ideal scenario, the lignin-containing organosolv liquor would be transferred to the last position in the continuous stream where LtL-solvolyis takes place. Additional organosolv liquor components, such as dissolved hemicelluloses and extractives, can accompany lignin in LtL conversion, as seen from the results in paper I, yet serve a greater value if they are extracted before LtL-solvolyis and utilised. LtL-solvolyis can be performed in batch after reactor filling, one or multiple reactors, followed by cooling and final work up. The workup step needs an addition of solvent for the solids to be filtered off, liquid-liquid extraction, drying of the organic phase to remove water residuals and solvent removal. The aqueous phase should be processed to extract desirable compounds (such as methanol, ethanol, aromatics etc., see paper IV) before efficient waste water treatment for regeneration. Solvents in the organic phase can easily be recovered by evaporation.

So far, the organosolv liquor has a too large volume and it needs to be reduced before further processing in LtL-solvolyis. Effective lignin precipitation is achieved when the liquor is diluted with a ratio of 1:3 v v⁻¹ (organosolv liquor : H₂O), which increases the volume even further (if precipitation is desirable). This step needs adjustment for the process to be suitable for combined fractionation and thermochemical conversion. According to the results in paper III, sulphuric acid proved to yield greater degree of lignin extraction than formic acid. In the concept for this to be a continuous process, formic acid would be preferred as acid catalyst in the fractionation step so that the organosolv liquor needs no more than volume reduction, and additional formic acid addition, before direct use in LtL-solvolyis. Figure 5.2 shows a conceptual sketch

demonstrating organosolv fractionation and LtL-solvolyis as a continuous system.

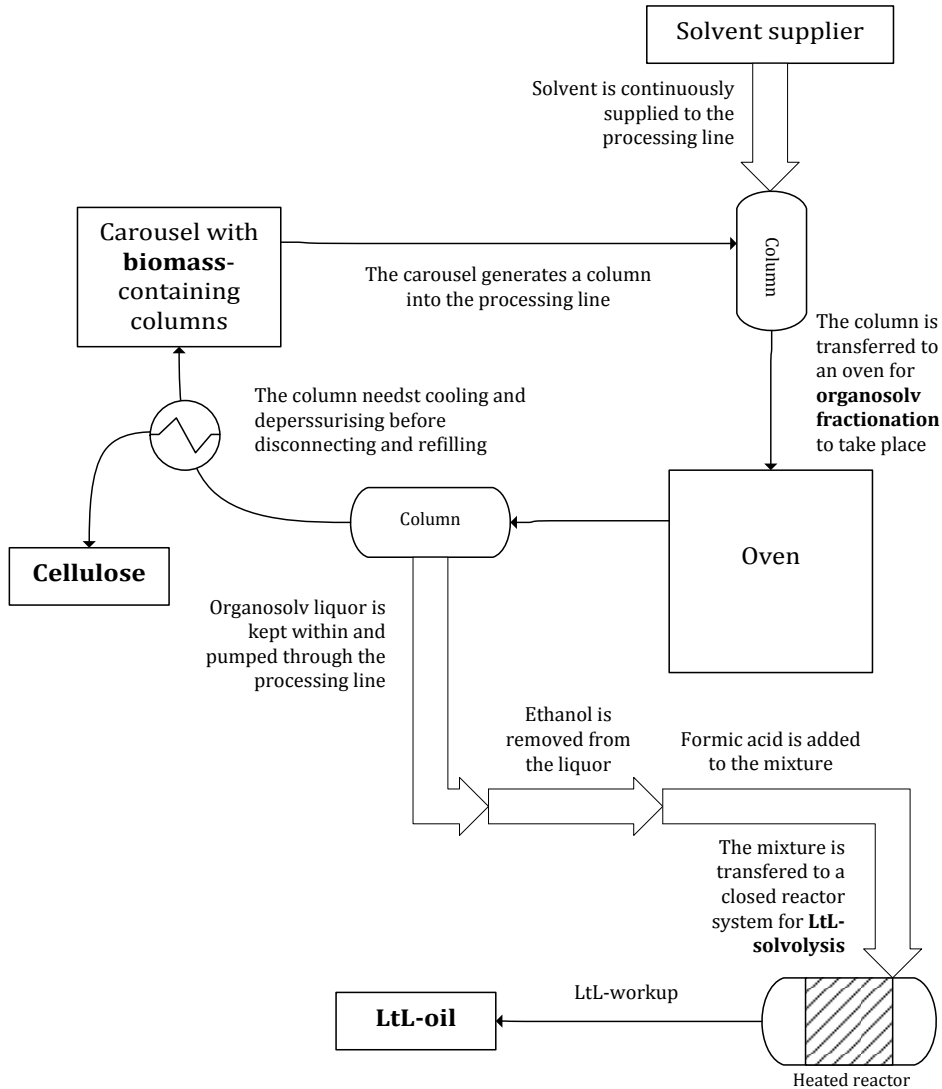


Figure 5.2 – Conceptual sketch displaying organosolv fractionation of lignocellulosic biomass and LtL-solvolyis as a continuous system.

5.2.2 LtL-solvolyis optimisation

For the LtL-oil to function as a resource for energy it is important that it provides a net energy gain over the energy sources used to produce it. Catalytic investigations are ongoing and aiming at increasing the energy efficiency of the conversion process by decreasing the activation energy, hence, decreasing the energy consumption. Tests on up-scaling the process are also progressing, including experiments with continuous stirring inside the reactor during the thermochemical conversion, and where the physical conditions during the reaction are monitored.

The gas-, solid- and aqueous fraction also possess advantages that can be exploited. The gas phase comprises mainly decomposition products of formic acid (CO_2 , CO and H_2), readily convertible through e.g. Fischer-Tropsch synthesis, but also limited fractions of short chained alkanes such as methane, ethane, propane and butane (51). The solid phase has high carbon content (see paper IV), and work on using it as carbon support for catalysts in LtL-solvolyis is advancing. The aqueous phase still contains valuable compounds such as residual solvent, methanol, ethanol and various aromatics, and should be processed and extracted for recovery.

5.2.3 Product applicability

Further quantification and structural identification studies are vital to adjust conversion conditions towards preferable product composition, so that valuable compounds can be separated and sold in the case of LtL-oil being used for building blocks and not fuel. Accordingly, upscaling and the development of applicable bio-oil fractionation methods are necessary in future work on identification and quantification. As lignin is the most abundant source of renewable phenolic groups, lignin has been seen as a potential replacement of phenol in different types of dispersing agents or thermoset resins, such as phenol-formaldehyde (PF) resins. Lignin is seen to be used in low-cost carbon fibres, converted into engineered plastics and thermoplastic elastomers, polymeric foams, fungible fuels and commodity chemicals (e.g. vanillin). Lignin, in its pure form, presents a good capacity to adsorb heavy metals ions and has thus been studied as a potential low cost adsorbent for wastewater purification (22, 75-77).

Quantification results from paper IV indicate the possibility of tuning experimental LtL-solvolytic conditions towards preferred product compositions for utilisation in the chemical industry. Guaiacol, which is found in large quantities in all of the analysed LtL-oils, is an agent thought to have disinfectant properties and is used as an expectorant in the pharmaceutical industry. Guaiacol can be found as a flavour in foods as roasted coffee and also contributes to the taste of smoked meat (78, 79). 4-Methylguaiacol, 4-ethylguaiacol and 4-propylguaiacol are all phenol derivatives that can be used as flavouring agents (80). Catechol is commonly used as a photographic developer, as an intermediate for antioxidants in rubber and lubricating oils, in polymerisation inhibitors, in fur dyes and leather tanning, as well as in pharmaceuticals (81, 82). 2-Naphthol is a widely used intermediate for the production of dyes (83).

Interestingly, homovanillyl alcohol (HVA) is found as a key component of Queen mandibular pheromone (QMP), produced by honey bee queens, and used to regulate the behaviour and physiology of their nest mates. QMP has shown to block aversive learning in young worker bees, an effect that can be mimicked by treating bees with HVA (84). This supports the search for other bio-active compounds in the LtL-oils.

Results from paper IV based on carbon balances exceeding 100 % display the need to investigate the role of formic acid in the reaction mechanism during LtL-solvolysis. Studies performed by Holmelid et al. (2012) approaches LtL-solvolysis reaction mechanisms, yet more detailed information on this is needed in the aim of designing desired product compositions.

Detailed separation of the LtL-oil into series of homologs or similar components demands development of extensive separation methods. Structural results from paper I-IV and quantitative results from paper IV suggest that the LtL-oil holds high value, and strengthens its potential as building blocks for the chemical and pharmaceutical industry in the future.

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Part II

Paper I

The effect of solvent and input material pretreatment on product yield and composition of bio-oils from lignin solvolysis

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The effect of solvent and input material pretreatment on product yield and composition of bio-oils from lignin solvolysis

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ABSTRACT

Solvolytic conversion of lignin from wood with formic acid as a hydrogen donor can provide a renewable source of aromatic compounds, especially phenols. In this paper, lignin or lignin-enriched fractions from Norway spruce and white birch are compared with regard to yields of bio-oil in solvolytic conversion. Water as a green solvent is also compared to ethanol as the reaction medium, and the yields and composition of the produced oils are presented. Maximum yields by weight are inversely connected to the oxygen content of the feedstock, showing that pure lignins give the highest yields while carbohydrate-containing feedstocks undergo more deoxygenation and thus give lower yields. The overall composition of the bio-oils produced is quite stable and independent of the feedstock type and pretreatment, though some difference in the quantitative distribution of the individual components is observed. The use of water or ethanol as reaction media has a significant impact on the bio-oil yields and composition due to the alkylation of the aromatic rings by the ethyl group from the solvent.

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1. Introduction—purpose of the work

Lignin is the third most abundant biopolymer in nature, and a promising feedstock for production of aromatic fuels and chemicals. Solvolysis with formic acid is an innovative conversion method for producing aromatic compounds from the lignin. A considerable amount of work has been completed to establish this conversion pathway [1–5]. However, lignins from different plants have differences in their structural and monomeric composition. The lignin concentration within lignocellulosic biomass varies from species to species and even in samples from different parts of the same tree [6,7]. Guaiacyl lignin is dominated by coniferyl monomeric units and found predominantly in softwoods, while guaiacyl-syringyl lignin is typically found in many hardwoods. The copolymer consists of both the coniferyl and sinapyl phenylpropane units, and the fraction of sinapyl units is therefore higher in hardwood lignin than in softwood lignin [8]. The structural abundance of each monomeric unit in the raw material could thus have a strong influence on the aromatic compounds being produced during lignin solvolysis.

Previous literature on lignin liquefaction with formic acid focused on the utilization of ethanolic solvent systems. In order to investigate the use of a more readily available solvent, with the aim

of incorporation of the technique in a biorefinery concept, water was selected as an alternative to ethanol in the majority of the following investigation of lignin conversion to bio-oils. The overall reaction system for thermochemical conversion of solid lignin in a solvent system of formic acid (FA) as hydrogen donor in ethanol is shown in Fig. 1 [1].

FA delivers reactive hydrogen upon degradation, together with CO₂, in a more reactive form than for H₂ gas [9]. This hydrogen combines with oxygen stemming from methoxy groups from the lignin to form water, resulting in a reduced oxygen content of the phenolic fraction of the complex product mixture [2]. The degradation of FA to carbon dioxide and hydrogen ensures that there is no acid remaining to lower the pH of the formed product mixture [10]. Formic acid in itself can be produced by thermal treatment of biomass, which gives perspectives for a biorefinery approach with production of all of the ingredients in an integrated biorefinery concept [11].

The quantitative results from experiments using the Lignin-to-liquid-technique (LTl), with formic acid as hydrogen donor, depend largely on the reaction conditions [5]. The known variations in structural composition and monomeric distribution affects depolymerisation rates and conversion rates, and experience with the LTl-system, indicates that each new lignin quality needs to be screened through systematic experimental designs to obtain the maximum conversion conditions and ratios [1]. In our experiences, to treat all lignins only at one set of conditions and ratios does not

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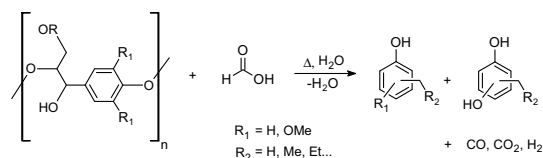


Fig. 1. Overview of the main conversion route; lignin is a methoxylated, phenolic polymer which in course of the solvolytic reaction is degraded to phenol monomers with different substitution patterns and aliphatic compounds. Simultaneously a hydrodeoxygenation occurs in which formic acid (FA) serves as the hydrogen donor. Water is generated during the reaction [1].

necessarily result in a correct or justified determination of optimal oil yields.

In this work we compare bio-oils, from different lignins stemming from various pretreatment techniques and wood species. Most of the oils are produced in a water-based LtL-solvent system, but some ethanol-based experiments are included for comparison. The results provide a basis for evaluation of variation due to feedstock relative to product distribution and product composition. Selected experiments have been duplicated to screen the reproducibility of the conversion method.

2. Experimental

2.1. Lignin starting materials and chemicals

The different lignin types used in this work are given in Table 1. SEH and SAH lignins were produced at SEKAB for Statoil ASA. The carbohydrate content was determined by supplier. SKL lignin was kindly supplied by Innventia Sweden and SSEH and BEH were received from the Norwegian University of Life Sciences in the context of the LignoRef research project. The raw materials are of different degrees of purity and some of them have carbohydrate residues depending on the pretreatment applied.

Samples of SEH, SAH and SKL were not sieved or exposed to any other preparation steps after they were received as dry powder of <500 μm particle size. SSEH and BEH were received as wet samples and were dried at ambient temperature until constant weight before use.

All other reagents and solvents were purchased from Sigma-Aldrich and used without further purification ($\geq 99.5\%$).

Table 1
Lignin feedstock types and characteristics.

Feed-stock	Characteristics	Ratio		Lignin Content (%)	Ash Content (%)
		H/C	O/C		
SEH	Norway Spruce (<i>Picea abies</i>)— 30% cellulose, Enzymatic Hydrolysis —bioethanol production process	1.20	0.45	~70%	NA
SAH	Norway Spruce— 30% cellulose, weak Acid Hydrolysis, SO_2 -treated —bioethanol production process	1.37	0.57	~70%	<1.0
SKL	Norway Spruce— cleaned lignin from paper production —lignin from Kraft pulp mill black Liquor (Lignoboost)	1.10	0.36	95–98% [12]	<1.5
SSEH	Norway Spruce— Steam exploded, Enzymatic Hydrolysis —bioethanol production process	1.40	0.70	~60% ^a	1.16
BEH	Birch (<i>Betula pubescens</i>)— Enzymatic Hydrolysis, tempered at 210 °C for 10 min —bioethanol production process	1.31	0.51	~70% ^a	1.25

^a Estimated from the elemental composition.

2.2. Solvolysis system and conditions

Biomass and solvent was added to a 25 mL high pressure Parr reactor from the 4740-series without stirring, closed directly and placed in a preheated Carbolite Laboratory High Temperature oven. After the completed reaction time, the reactor was taken out of the oven and cooled by an air stream to ambient temperature. The resulting products after solvolysis included a gas phase, a liquid phase and a small solid phase. The amount of gaseous product was determined by weighing the reactor before and after venting the gas.

In the water system the liquid phase consisted of a single aqueous phase. The dark brown LtL-oil was not present as a separate phase, but adsorbed to the solid residue due to its hydrophobic character. The LtL-oil was miscible in dichloromethane (DCM) and therefore separated from the solid phase using DCM and filtered through a 0.45 μm Puradisc™ 25 NYL filter. The entire liquid phase was then extracted with DCM three times and the organic phases were combined and dried over Na_2SO_4 . The aqueous phase was in addition extracted with a mixture of ethyl acetate (EtAc) and tetrahydrofuran (THF) in 90:10 v/v ratios respectively to increase the recovery of the most polar compounds. The organic phases were combined and dried over Na_2SO_4 .

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

DCM in the first extraction step was removed from the LtL-oil on a rotary evaporator at a temperature of 40 °C and a pressure of 175 mbar for removal of ethanol. These conditions were replicated for all LtL-oils to ensure the same work-up protocol. EtAc:THF in the second extraction step was left for evaporation under atmospheric conditions. The two organic phases adds up to the total oil yield. The oil yields were determined by weight after solvent evaporation. The char yield was determined by weight after drying.

2.3. Mass spectrometry

The LtL-oil was analysed shortly after workup using GC-MS on a Trace Ultra GC coupled with a DSQ II quadrupole MS detector from Thermo Scientific. DCM and EtAc:THF were used as solvents for the respective product fractions and the samples were analysed using splitless injection at 260 °C (injector temperature) on a 25 m Ultra 2 Silica capillary column ((5% phenyl)-methylpolysiloxane),

Table 2
Quantitative results.

Experiment	I	II	III	IV	V	VI	VII	VIII
Raw Material	SEH	SAH	SKL	SSEH	SSEH	SSEH	BEH	BEH
Solvent	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	EtOH	H ₂ O	EtOH
Time (h)	16	16	4	16	4	4	4	4
Temperature (°C)	380	380	390	360	380	380	360	360
Lignin (g)	1.00	1.01	1.01	2.00	2.01	2.01	2.00	2.01
Formic Acid (g)	3.10	3.14	3.08	3.10	3.05	3.09	3.10	3.16
Solvent (g)	5.10	5.14	4.15	5.06	5.09	4.10	5.00	4.03
Lignin input percentage (%)	10.9	10.8	12.3	19.7	19.8	21.9	19.8	21.8
Total mass input (g)	9.20	9.29	8.24	10.16	10.15	9.20	10.11	9.19
Total mass output (g)	8.98	8.10	7.90	9.59	9.24	5.26	8.32	5.03
Ltl-oil (g)	0.71	0.55	0.76	1.01	0.96	1.03	1.22	1.39
Solids (g)	0.03	0.03	0.04	0.17	0.16	0.18	0.17	0.04
Water-phase (g)	5.23	4.52	4.10	5.31	5.11	0.64	3.84	0.40
Gas (g)	3.0	3.0	3.0	3.1	3.0	3.4	3.1	3.2
Gas (% of FA input)	96.8	95.4	97.5	100.0	98.2	110.0	99.9	101.4
Water-phase (% of solvent input) ^a	102.6	87.9	98.7	105.0	100.4	15.7	76.7	9.9
Solids (% of lignin input)	3.39	3.06	4.29	8.30	8.15	9.11	8.27	2.08
Ltl-oil yield (% of lignin input)	71.0	54.4	75.5	50.5	47.9	51.1	60.9	69.3
Mass recovery (%) ^a	97.6	87.1	95.9	94.4	91.0	–	82.3	–

^a Solvent fractions from the process of evaporating extraction solvent have not been weighted or accounted for, and complete mass calculations are therefore NA for ethanol-system experiments.

0.200 mm ID, thickness 0.11 μm from Agilent Technologies. A constant gas flow rate of 1 mL/min and the following GC oven temperature program were applied:

Start temperature: 50 °C (1 min)

Heating rate 1: 8 °C/min (1 min) Final temperature: 220 °C

Heating rate 2: 10 °C/min (1 min) Final temperature: 300 °C

The GC–MS inter phase valve delay was set to 5 min and the MS detector operated in positive mode at 70 eV with an ion-source temperature of 220 °C. Compounds were identified using Xcalibur software and the NIST 2.0 library.

2.4. FT-IR

The FT-IR spectra were recorded by applying the sample to an attenuated total reflectance (ATR) crystal. The main measurement features were a spectral range from 4000 to 400 cm^{-1} , 16 scans, and a resolution of 4 cm^{-1} . The peaks were assigned based on correlation charts from Pavia et al. (2009) [13].

2.5. Elemental analysis

Selected Ltl-oils were analysed by elemental analysis in CHNS mode with a VarioEL III from Elementar. The amount of oxygen was calculated by difference.

3. Results and discussion

3.1. Product yields

A selection of the most relevant data is shown in Table 2. The reaction conditions and ratios represent *optimal conversion conditions* which were obtained in extensive previous screening experiments (data not shown).

During the Ltl-conversion process, the lignin undergoes hydrodeoxygenation, which means simultaneous removal of oxygen and addition of hydrogen to form water as by-product [1]. The total mass of oil product can therefore not add up to Ltl-product yield of 100% based on the mass of lignin input, because of the substantial mass of oxygen that is being removed from the raw material. Elemental composition analysis, shown in Section 3.6, proves the substantial depletion of oxygen. The amount of solvent in the reactor is always in excess of the amount of gas phase

required for hydrodeoxygenation. The pressure in the reactor is the gas-liquid equilibrium pressure at the given temperature. The air present in the reactor upon closing is hence negligible due to the amount of potentially reactive oxygen being insignificant compared to the vaporised formic acid during the reaction. The overall mass recovery, which includes both generated water and gases, confirms tight reactors and a plausible work-up protocol. The completeness of the lignin conversion reaction can be estimated by the comparison of the elemental composition of lignin SM, the Ltl-oil and the solid by-product, but this will be reported in a separate publication on different focus in due course. Compositional analysis of the gases and dissolved aqueous fractions were not performed since the objective is to maximise and compare oil yields. Relevant data for gas composition can be found in Oregui et al. (2015) [14].

The workup process includes a removal of the extraction solvent under reduced pressure. This will result in some loss of volatile, predominantly hydrocarbon, products during evaporation [1]. However, this shortcoming was estimated by checking the recovery of one of the key components previously proven to be present in the bio-oils from Ltl-conversion [5,15]. Guaiacol was subjected to rotary evaporation at a temperature of 40 °C and a pressure of 175 mbar for one hour and the loss was negligible.

The tabulated results show a considerable variation in maximum oil yield. The quantitatively largest conversion of lignin to Ltl-oil is according to Table 2 achieved when using SKL lignin. SKL lignin is subjected to re-dispersion and thorough cleaning in the Kraft pulping process [12], and thus has a high purity. SSEH results in the lowest conversion of lignin to Ltl-oil. SSEH is a lignin originating from steam exploded Norway spruce, followed by enzymatic hydrolysis, and the material also contains carbohydrate residues (see Table 1). The differing degrees of purity in terms of lignin content will play a role for the produced amount of monophenolic units, which are identified to be the most abundant class of oil constituents. A high content of carbohydrate residues increase the oxygen content of the solid starting material due to the higher O/C ratio values in carbohydrates compared to lignin. The conversion to monomeric phenols depends on a high fraction of lignin rather than carbohydrates; hence the yield is evidently dependent on the purity of the raw material. The effect of oxygen content has been further investigated and commented in Section 3.6 using elemental analysis.

Table 3
Reproducibility.

Experiment	IX.I	IX.II	X.I	X.II	XI.I	XI.II
Raw Material	SEH	SEH	SKL	SKL	SSEH	SSEH
Solvent	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O
Time (h)	16	16	20	20	10	10
Temperature (°C)	380	380	380	380	380	380
Lignin (g)	2.52	2.50	1.00	1.01	2.01	2.01
Formic Acid (g)	3.07	3.21	3.22	3.14	3.22	3.18
Solvent (g)	5.18	5.23	4.20	4.11	5.13	5.08
Lignin input percentage (%)	23.4	22.9	11.9	12.2	19.4	19.5
Total mass input (g)	10.77	10.95	8.42	8.26	10.36	10.27
Total mass output (g)	9.72	9.53	8.00	7.00	9.25	9.20
LtL-oil (g)	1.27	1.25	0.67	0.58	0.94	0.88
Solids (g)	0.47	0.22	0.01	0.17	0.05	0.05
Water-phase (g)	4.77	4.76	4.12	ND	5.05	4.98
Gas (g)	3.2	3.3	3.2	3.3	3.2	3.3
Gas (% of FA input)	104.2	102.8	99.4	105.1	99.4	103.8
Water-phase (% of solvent input)	92.2	91.0	98.2	71.6	98.5	98.0
Solids (% of lignin input)	18.8	9.0	1.3	17.4	2.7	2.3
LtL-oil yield (% of lignin input)	50.4	49.9	66.9	57.7	46.7	43.8
Mass recovery (%)	90.2	87.1	95.1	84.7	89.2	89.6

SEH and SAH both originate from Norway spruce, but have undergone different hydrolysis techniques during pretreatment. Previously mentioned parallel reaction series from preliminary screening experiments (not shown) indicates a slightly higher LtL-oil yield resulting from the enzymatically hydrolysed lignin compared to the weak acid hydrolysed lignin (SAH < SEH).

SEH and SSEH both originate from enzymatic hydrolysis of Norway spruce, and SSEH has also been exposed to steam explosion. SEH shows a generally higher conversion of lignin to oil than the steam exploded lignin SSEH. BEH is a lignin derived from birch and has also undergone enzymatic hydrolysis during pretreatment. Values from Table 2 indi-

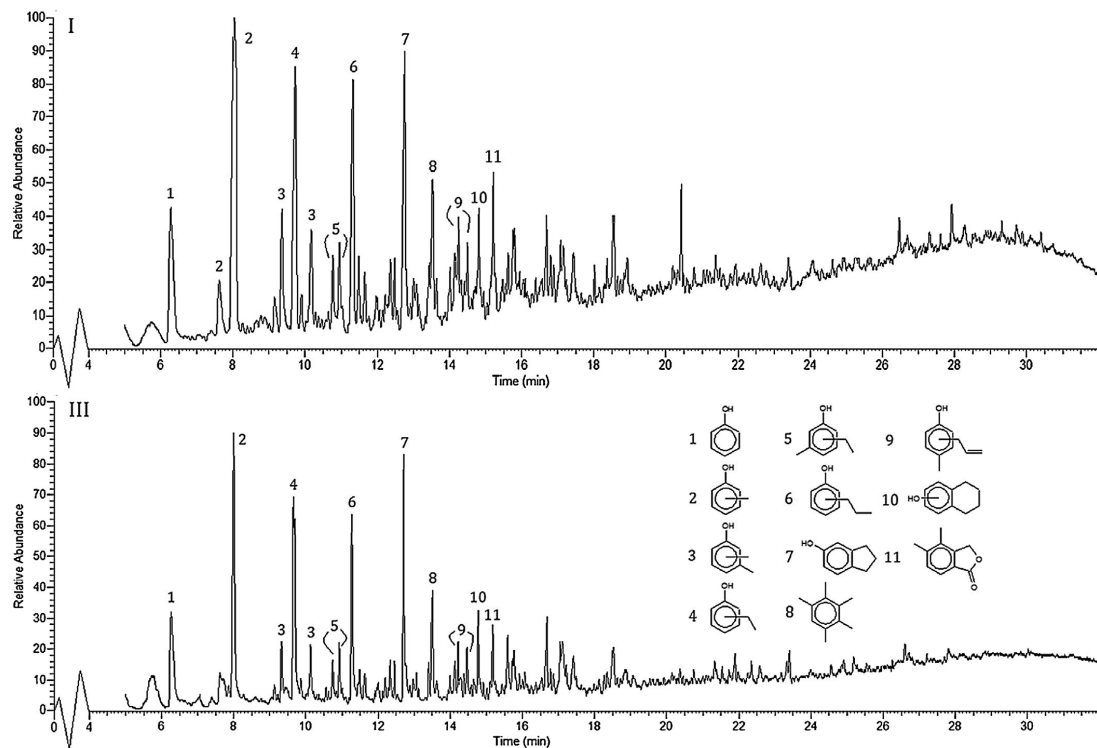


Fig. 2. GC-MS chromatogram of experiment I on top using Norway spruce, containing 30% cellulose and pre-treated with enzymatic hydrolysis (SEH). The bottom GC-MS chromatogram shows experiment III using lignin from the Lignoboost process as raw material (SKL). Both experiments were performed with water as solvent.

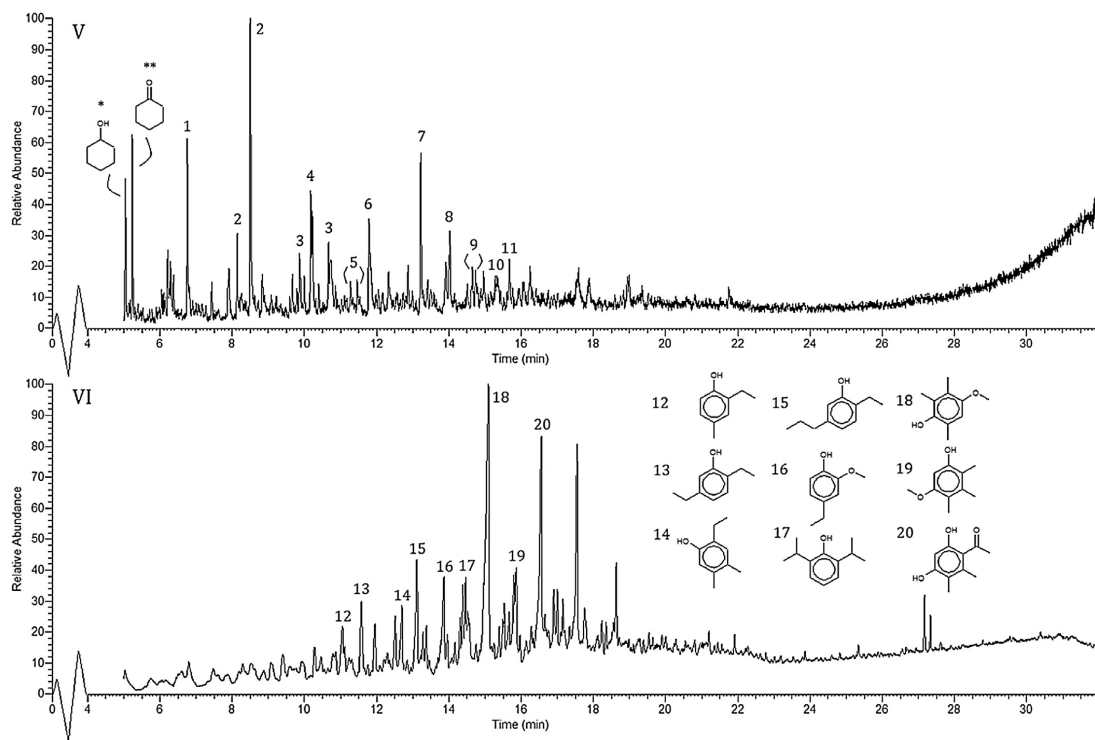


Fig. 3. GC-MS chromatogram of experiments using Norway spruce pre-treated with steam explosion and enzymatic hydrolysis (SSEH). Experiment V is a water-system reaction, while experiment VI is an ethanol-system reaction.

cate a slightly higher yield from LtL-conversion for BEH than for SSEH, but less efficient conversion for BEH than for SEH (SSEH < BEH < SEH).

The overall conversion efficiency of lignin to LtL-oil varies from 51.0–75.5% (24.5%) by weight for the compared lignins (see Table 2).

The amounts of solids produced are minimal, as given in Table 2 ($\leq 2.0\%$ of total product). This indicates a good conversion ratio of lignin to oil. Though the initial screening of raw material with different reaction conditions and ratios were aimed to maximize the oil yield and minimize the solid residue, the potential for further optimisation to give no solid products at all is still present.

The product values for gas in Table 2 are largely a function of the input of formic acid, and the product values for water phase are largely represented by the input of water. The extraction process between the two different phases is performed with a focus on the organic phase. The water phase may therefore contain traces of solvent residues, and the recovery of more than the input water phase as reaction products must be interpreted with caution.

Experiments performed with ethanol as solvent results in a significantly lower recovery of the solvent phase than parallel experiments in water-based systems. This is obvious when examining the water-phase quantities in Table 2. This is caused by the loss of major amounts of ethanol which remain in the organic phase and subsequently is evaporated off during work-up, and thus not measured or accounted for. Small amounts of ethanol also remain within the LtL-oil as alkyl substituents.

3.2. Reproducibility

Three experiments were performed in duplicate to gain insight to the reproducibility of the reaction process and to assess mass recovery (see Table 3).

The results were found to be reproducible with a variation in oil yield within $\pm 5.0\%$ comparing the respective duplicate experiments. The solids give a larger variation, but compared to the relative input of lignin and solvents, the variation is still negligible.

The experiments are performed in batch at laboratory scale and thus result in an inevitable loss of product during work-up. With this in mind, the mass balances obtained are considered acceptable.

3.3. Solvent system

When using SSEH as raw material the reaction conditions for experiment IV (16 h, 360°C , see Table 2) resulted in the highest oil yield. However, after GC-MS analysis it was concluded that a reaction time of 4 h and a temperature of 380°C was sufficient for effective hydrodeoxygenation and conversion to phenolic monomers for this specific raw material. The conclusion was made based on a decrease in presence of methoxy substituents in the bio-oil. Parallel experiments using an ethanol-based solvent system was therefore performed with duration of 4 h at 380°C on both SSEH and BEH. In Table 2 a selection of two parallel reaction sets (four experiments) are shown, and the trend of increased oil yields in ethanol-based systems is clear when examining these results.

In the previous optimisation, experiments performed with ethanol as solvent systematically give a higher oil yield than water-based systems. This is known to be largely due to the solvent system's alkylation properties. Previous work performed by Holmelid et al. using ^{13}C -labeled methylphenol has shown the double effect of alcohol as both co-solvent together with formic acid, and also as a reactant in the reaction system [4]. The alkylation gives a net mass contribution to the lignin-monomers, and therefore enhances the oil yield relative to lignin input. The effect on oil yield is not substantial (5–10%), and water might nonetheless be evaluated as a more environmentally friendly solvent system for LTL-conversion due to regeneration properties and availability.

3.4. Compound identification with gas chromatography–mass spectrometry

GC–MS analysis shows that the types of compounds comprising the oil are similar in the different oil samples, while the abundance varies with the feedstock and reaction conditions. Fig. 2 shows chromatograms of two different LTL-oils and the monomeric alkyl phenols which are the most abundant compounds within the volatility range covered by the analysis.

The chromatograms in Fig. 2 show two experiments originating from different lignins, where the difference being the pretreatment technique. The chromatograms indicate that these different ways of pre-treating the same species of wood (the Lignoboost process and enzymatic hydrolysis) gives limited differences in product composition.

When comparing the chromatograms from different solvent-systems in Fig. 3, the compositional differences are more obvious. They are clearly a verification of the ethanol's double effect as both co-solvent and as an alkylation agent. The bulk of the dominating compounds comprising bio-oil from an ethanol solvent-system are of a more complex substitution order, and this is a result of alkylation from ethanol in addition to the phenolic substituents originating from the depolymerisation [4]. This difference in substitution order can be beneficial depending on utilisation area for the specific phenols. Alkylphenols are being used as antioxidants in diesel at present, and phenols are interesting as building blocks in both the pharmaceutical- and food industry. Propofol, identified as structure 17 in ethanol-system reaction VI as seen in Fig. 3, is commonly used as a general anaesthetic [16]. Cresol on the other hand, tentatively identified as structure 2 in water-system reactions I, III and V as seen in both Fig. 2 and Fig. 3, is an intermediate product in production of plastics, pharmaceuticals and pesticides.

The limited effect of difference in pretreatment technique of wood on product composition is again confirmed when comparing the chromatogram of experiment V with I and III. The same compound peaks dominate, while the relative abundance of each compound is the more selective characteristic.

Overall, when investigating chromatograms collected from LTL-oils stemming from Norway spruce (SEH, SAH, SKL and SSEH) in the water system and comparing them to chromatograms collected from LTL-oils from birch (BEH) in water system, the compounds do not differ significantly. The substitution patterns, e.g. the position of a single methyl group, are occasionally different, but the dominating peaks are primarily represented by the same compound groups regardless of which wood species the lignin stems from.

However, with guaiacyl lignin being the dominating monomer in softwoods [8], one would expect a more distinct presence of methyl phenol in oils from Norway spruce than from birch. Thus one would also expect a higher presence of dimethyl phenol in oils from birch than from Norway spruce. The reaction conditions that the lignin and the solvent system are exposed to are severe, which accelerates hydrodeoxygenation [17] and could thus make the substitution pattern thermodynamically controlled and independent

of the raw material used. Testing with milder conditions might give the possibility to tune the resulting abundance of each monomeric phenol being present. From Fig. 4 it is clear that methylphenol (2) is the dominating compound in oils from both spruce and birch, while 2,3-dihydro-1H-inden-5-ol (7), ethylphenol (4), propylphenol (6) and phenol (1) are also clearly represented in the LTL-oils from both wood species. Fig. 4 represents 11 of the most abundant structures observed.

When studying the chromatograms from the water systems in Fig. 2 and Fig. 3 (I, II and V), all retention times in chromatogram V are slightly longer than in I and III. During the experimental time passing, the column was renewed due to maintenance. Compounds * and ** indicated in V, which represent products with a high degree of hydrodeoxygenation, can therefore also be present in I and III, but have as a consequence eluted during the solvent delay and have therefore not been accounted for in Fig. 4.

Quantification of the observed constituents will be reported in a separate publication on different focus in due course.

3.5. FT-IR

The FT-IR spectra of the samples using the same lignin type with both solvent systems show that the solvent is the main factor that differentiates between the samples. Fig. 5 shows the spectra of one bio-oil from each solvent system. Both spectra are dominated by the same functional groups; hydrogen bonded –OH with a maximum absorbance around $3300\text{--}2400\text{ cm}^{-1}$, C–H stretch with a maxima from $2960\text{ to }2870\text{ cm}^{-1}$, carboxylic acid C=O at $1700\text{--}1707\text{ cm}^{-1}$, aromatic ring stretch at around $1600\text{ and }1450\text{ cm}^{-1}$ and C–O bonds at around 1200 cm^{-1} . The intensity of the absorption is higher for nearly all functional groups on the aromatic rings in the water system bio-oils, as also observed in the GC-chromatograms in Fig. 3. The carboxylic acid functional groups indicated in the IR-spectra are not found in the GC-chromatograms, probably because the carboxylic acids are too polar for direct analysis in such a non-polar GC-system.

3.6. Elemental analysis

The Van Krevelen plot in Fig. 6 displays a distinct reduction of oxygen content when comparing lignin starting material and resulting LTL-oil.

The difference in oxygen content among the raw materials is also prominent. SSEH contains the highest level of oxygen, thus providing the highest potential for deoxygenation among the five lignins. The high oxygen content can be an indication of a high fraction of carbohydrate residues, see Table 1. The significant loss of oxygen during hydrodeoxygenation can thus potentially result in a lower oil yield and correspondingly elevated water phase yield as shown in Fig. 1. Experiments using SSEH, which has the highest oxygen content, resulted in the lowest average oil yield among the experiments compared in this paper. The high purity of SKL provided by the Lignoboost process will by the same criterion provide high oil yields relative to lignin input in the LTL-conversion process, as also shown in Table 2. A reasonable interpretation is that a low O/C ratio corresponds to a more pure lignin, which will give higher oil yields since a lower amount of oxygen is left to remove, while the carbohydrate containing starting materials give deoxygenation of carbohydrates in addition to lignin and thus a lower oil yield by weight.

According to Table 2 the lignins, sorted by oil yield, give the following ascending order: SSEH < SAH < BEH < SEH < SKL. According to Fig. 6, the lignins, sorted by oxygen content, give the same ascending order. This indicates a clear reduction in oil yield with increasing oxygen content represented by high carbohydrate content.

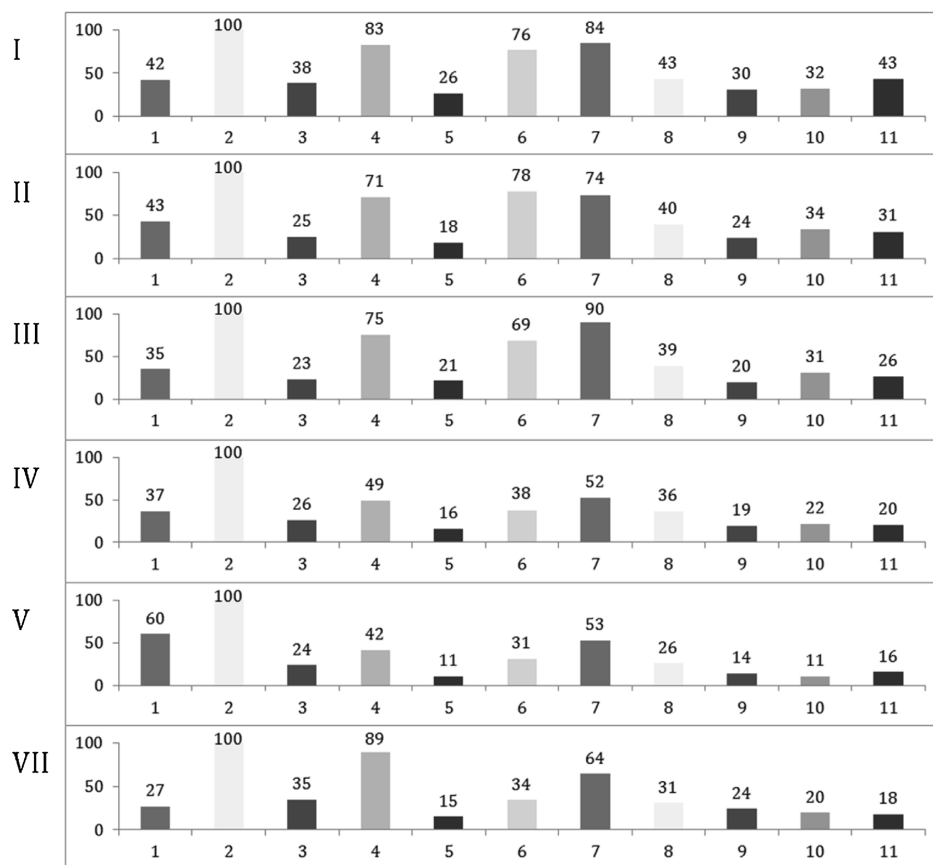


Fig. 4. Column diagrams of experiments I, II, III, IV, V and VII indicating relative peak height of the most abundant compounds present in Ltl-oils from water-system experiments in Table 2. Components presented include (1) phenol, (2) methylphenol, (3) 3,x-dimethylphenol, (4) ethylphenol, (5) x-ethyl-3-methylphenol, (6) propylphenol, (7) 2,3-dihydro-1H-inden-5-ol, (8) pentamethylbenzene, (9) x-allyl-4-methylphenol, (10) 5,6,7,8-tetrahydronaphthalenol and (11) 4,5-dimethyl-3H-isobenzofuran-1-one. Numeration on x-axis refers to the same structure numeration as in Fig. 2. Methylphenol (2) represents peak height of 100% due to highest relative abundance, and peak heights are measured relative to this peak. A high number indicates high abundance/peak height.

Experiment VI performed in ethanol-system show a higher O/C ratio than the parallel experiment V performed in water-system. This is a verification of the structural differences due to solvent-system, observed by GC–MS and discussed in Section 3.4. The same is the case for experiment VIII and VII where the ethanol-system gives the highest O/C ratio.

Alkylation takes place in the alcohol-based solvent-system which also increases the carbon content of the Ltl-oil constituents. The presence of highly oxygen-containing compounds are documented by GC–MS (see Fig. 3), but the change in O/C ratio between parallel experiments is not significant. The alkylation may thus be the preliminary explanation to this observation.

Experiment VII from birch shows the highest O/C ratio among Ltl-oils from water-system in the Van Krevelen plot. Birch lignin has a naturally higher content of oxygen than the lignins from spruce due to the guaiacyl-syringyl-copolymer that is typically found in many hardwoods [8]. The copolymer gives a higher fraction of the sinapyl phenylpropane unit and thus higher oxygen content in the birch-lignin than spruce-lignin. This can explain the value for oxygen content in oil VII and VIII. In Fig. 6 the deoxygenation from starting material SSEH to oils V and VI is the highest

according to the change in O/C ratio. Table 2 verifies this observation with the oil yields for SSEH being the lowest, indicating a greater loss of oxygen during the passing reaction time. SSEH most likely contains a high percentage of carbohydrate residues causing this major deoxygenation.

High oxygen content in the form of carbohydrate residues gives rise to initially elevated oxygen content in the raw material, followed by a significant deoxygenation of both lignin and carbohydrate fractions and thus a correspondingly low oil yield (by weight). This suggests that the purity of the lignin feedstock could be an important factor for evaluation of suitable pretreatment of the lignocellulosic feedstock.

It is clear that the steam exploded lignin, SSEH, and acid hydrolysed lignin, SAH, give the lowest oil yield due to the highest degree of deoxygenation. SEH and SAH contain the same amount of cellulose (30%), but no identifications of which phenyl propane units comprise the lignin SM have been performed. The impact and/or alteration of lignin structure in the raw material after steam explosion and acid- or enzymatic hydrolysis has not been characterized or investigated, but this could potentially influence the phenyl propane units incorporated in the raw materials [18–21].

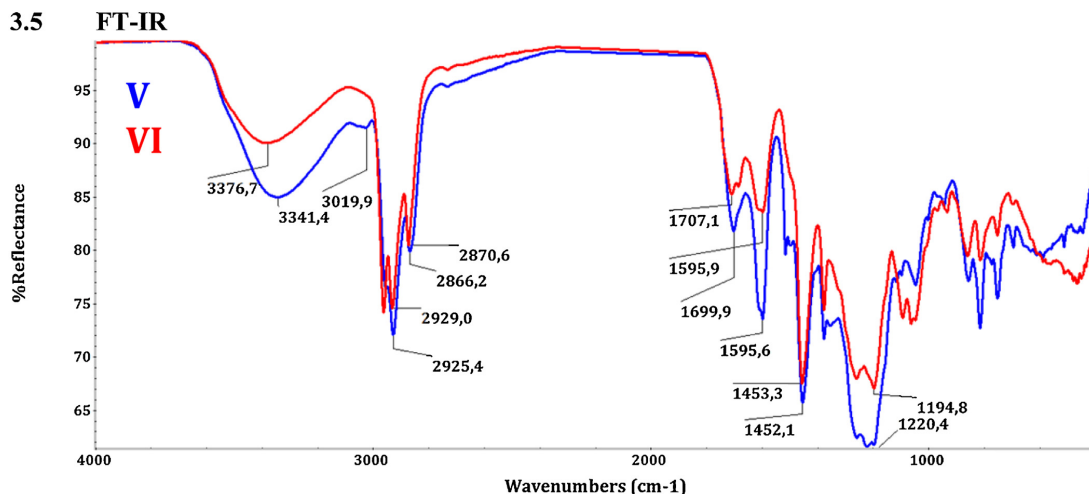


Fig. 5. FT-IR spectra of experiments using Norway spruce pre-treated with steam explosion and enzymatic hydrolysis (SSEH). Experiment V (blue) is a water-system reaction, while experiment VI (red) is an ethanol-system reaction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

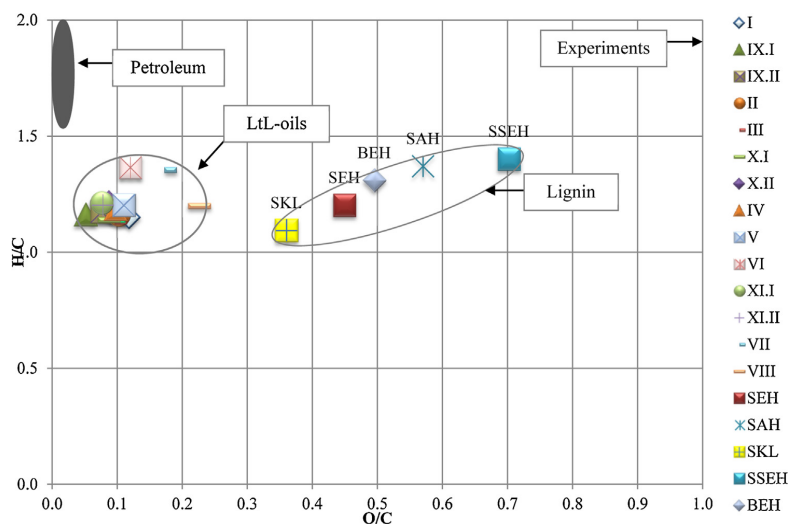


Fig. 6. Van Krevelen plot showing H/C ratio and O/C ratio of all LTL-oils.

4. Conclusions

This paper aimed to provide an insight into the variation in product distribution and product composition of bio-oils from different lignins stemming from various pretreatment techniques and wood species, mainly produced in a water-based LTL-solvent system. Selected experiments were duplicated to screen the reproducibility of the conversion method.

GC-MS analysis shows no obvious differences in the composition of LTL-oils from water-system experiments. Comparing chromatograms collected from LTL-oils stemming from Norway spruce (SEH, SAH, SKL and SSEH) in water-system with chromatograms collected from LTL-oils from birch (BEH) in water-system, the com-

pounds comprising the bio-oils do not differ significantly. The substitution patterns, e.g. the position of a single methyl group, are occasionally different, but the dominating peaks are represented by the same primary compound groups regardless of which wood species the lignin stems from. Small differences in the position of single methyl groups are to be expected due to the difference in monomers comprising the lignin.

Methylphenol (2) is the dominating compound in oils from both spruce and birch, while 2,3-dihydro-1H-inden-5-ol (7), ethylphenol (4), propylphenol (6) and phenol (1) are also present in high yields in the LTL-oils from both wood species.

Comparing the composition of LTL-oils stemming from water-systems vs. ethanol systems there are obvious variations. The

differences are a clear verification of the ethanol's double effect as both co-solvent and as an alkylation agent. The mass of the dominating compounds comprising bio-oil from an ethanol solvent-system are of a more complex substitution order, and this is a result of alkylation from ethanol in addition to the phenolic substituents originating from the depolymerisation [4].

The pretreatment techniques investigated did not show significant compositional differences among the LtL-oils, but rather a change in the oil yields relative to lignin input. However, elemental analysis clearly shows that the oil yields depend strongly on the oxygen content of the lignin feedstock. A high oxygen content, e.g. in the form of carbohydrate residues, gives rise to initially elevated oxygen content compared to pure lignin. Intensive deoxygenation during the reaction results in an oil yield lower than for raw material/lignin with an initially lower oxygen content. The purity of the raw material is a significant factor, and should be optimised during pretreatment of the lignocellulosic feedstock.

It is clear that the steam exploded lignin, SSEH, and acid hydrolysed lignin, SAH, give the lowest oil yield due to the highest degree of deoxygenation. SEH and SAH contain the same amount of cellulose (30%), but no identifications of which phenyl propane units comprise the lignin SM have been performed.

Acknowledgments

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