Research paper

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

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A B S T R A C T

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

## 1. Introduction

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

The concept of a "biorefinery" describes all the processes and

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

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

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

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

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

Furthermore, Huang et al. (2014) reported that hydrogenolysis of lignin using formic acid as an *in situ* hydrogen donor in the presence of a water-ethanol solvent mixture has contributed to more than 90 wt% depolymerized lignin yield from Kraft lignin even without any catalysts [26]. In a study by Kloekhorst et al. (2015), the catalytic solvolysis of Alcell® lignin using formic acid as hydrogen donor and Ru/C as the catalyst in an alcoholic reaction solvent has been shown to enhance the hydrodeoxygenation and thus reduce the oxygen content of the bio-oil

significantly. The best result reported in this study was conversion of approx. 71 wt% of lignin input to bio-oil with low O/C ratio (0.09). High yields of valuable chemical compounds such as alkylphenolics and aromatics were determined using GCxGC-FID [27]. Hita et al. (2018) recently reported that 16–29 wt% of lignin can be converted directly into valuable platform chemicals through solvent-free hydrotreatment using a Fe-based limonite catalyst at 450 °C for 4 h 67–81% of the lignin oil components were detectable by 2D GCxGC-FID confirming that the majority of the lignin oil is composed by volatile components with low molecular weight [28].

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

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

## 2. Materials and methods

### 2.1. Chemicals

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

### 2.2. Type of lignins

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

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

### 2.3. Experimental conditions

#### 2.3.1. Experimental set-up

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

**Table 1**
Lignin feedstock types and characteristics.

| Feedstock | Botanical species and isolation method | Lignin content (mass %) | Ash content[a] (mass %) | H/C ratio | O/C ratio |
|---|---|---|---|---|---|
| Eucalyptus | Origin: Thailand, produced at the Biorefinery Demo Plant (BDP) in Örnsköldsvik, Sweden, using weak acid and enzymatic hydrolysis | ~50 | ~4.4 | 1.41 | 0.586 |
| Stat417 | Norway Spruce-30% cellulose, produced at SEKAB from weak acid hydrolysis, SO$_2$-treated in bioethanol production process | ~70 | ~1.0 | 1.37 | 0.559 |
| BL | Norway Spruce, produced at Processum (Sweden) by acid precipitation from Kraft pulp mill black liquor | NA[b] | ~4.9 | 1.30 | 0.442 |
| Stat416 | Norway Spruce-30% cellulose, Produced at SEKAB from enzymatic hydrolysis in bioethanol production process | ~70 | NA | 1.20 | 0.451 |
| AL | Alkali lignin purchased from Sigma Aldrich | ~98 | NA | 1.25 | 0.730 |

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

**Table 2**
Extended overview of experimental conditions.

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

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

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

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

#### 2.3.2. Sample work-up

*5 L scale*; After the completed reaction time, the reactor heater was turned off and the reactor was cooled to ambient temperature by flowing cold water through the reactor's cooling coil. The final products after the LtL-process included a gas phase, a liquid phase and a solid phase, which contains both unreacted starting material and char produced during the conversion. A small amount of the produced gases was collected in a gas bag and analysed by gas phase GC before venting the rest. After opening the reaction container, the liquid phase was separated from the solid phase by opening the valve on the container bottom. Then a mixture of ethyl acetate:tetrahydrofuran (90:10 V:V) was added to the reactor container to extract the organic phase from the solid phase (unreacted lignin and char). The organic phase was dried over Na$_2$SO$_4$, and solvents and unreacted ethanol were removed from the LtL-oil on a rotary evaporator at reduced pressure (25–17.5 kPa) at 40 °C to yield a dark brown liquid. The oil yield was determined by mass. The char yield was determined by mass after drying. The oil fraction was characterized by gas chromatography mass spectroscopy (GC-MS) and elemental analysis. Some of the selected gas phases were characterized by gas chromatography.

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

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

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

Product yield (wt.%) = (dry mass of oil or char (g)

/dry mass of input lignin (g))*100

### 2.3.3. Reproducibility

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

### 2.4. Characterisation of the products

#### 2.4.1. Elemental analysis

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

#### 2.4.2. Mass spectrometry

*5 L scale*; The LtL-oil (1.0 mg) was dissolved in 1 cm³ ethyl acetate:tetrahydrofuran (90:10 V:V) and the sample was analysed using GC–MS on a Trace Ultra GC coupled with a DSQ II quadrupole MS detector from Thermo scientific. The injection was run in splitless mode at 260 °C (injector temperature) on a 25 m Ultra 2 Silica capillary column ((5% phenyl)-methylpolysiloxane), 200 μm ID from Agilent Technologies. The following GC-MS instrumental conditions were applied:

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

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

*0.025 L scale*; The LtL-oil (1.0 mg) was dissolved in 1 cm³ ethyl acetate:tetrahydrofuran (90:10 V:V) and the sample was analysed using an Agilent Technologies 7890A GC-system with auto-sampler, coupled with an Agilent 5977A MSD. The injection was run in splitless mode at 280 °C (injector temperature) on a 30 m HP-5ms column with 250 μm ID and thickness of 0.25 μm from Agilent Technologies. The following GC-MS instrumental conditions were applied:

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

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

#### 2.4.3. Gas phase analysis

Gas phase GC analysis was performed on a GC-FID/TCD (HP 6890A)

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

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

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

and a 30 m Porapak Q Molsieve column equipped with a FID front detector and a TCD back detector, which was controlled by an HPChem laboratory data system. The following GC instrumental conditions were applied:

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

#### 2.4.4. Experimental design and multivariate data analysis

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

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

## 3. Results and discussion

### 3.1. Product yields

In the water-system, the liquid phase consisted of a single aqueous phase and the LtL-oil was not present as a separate phase, but was
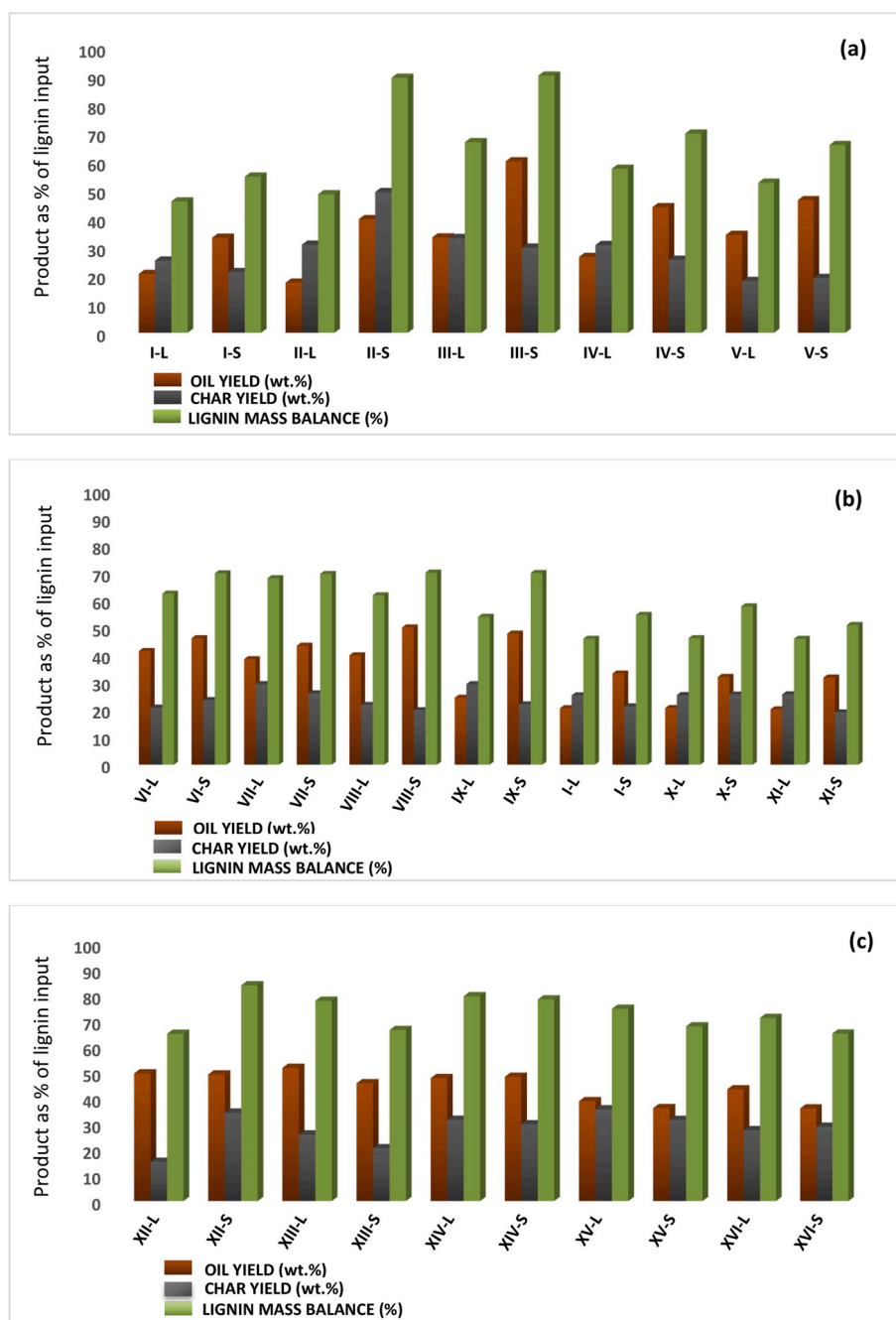
**Fig. 1.** Column diagrams showing product yields and lignin mass balances as mass fraction of lignin input at both scales as a function of different (a) lignin types in water system at 380 °C for 2 h (b) reaction temperatures from 320 to 380 °C (experiment VI to I) and reaction times from 0.75 to 3 h at 380 °C (experiment X, I and XI) in water system (c) reaction temperatures in ethanol system from 320 to 380 °C for 2 h. The lignins are identified in Table 1 and the temperature and duration of each experiment is given in Table 2.

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

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

Experiments I-V have been run at the same conditions, but with different feedstocks. The purity of the lignin input ranges from a very pure (98%) Alkali lignin (Exp. V) and a pure precipitated lignin from Black liquor with a comparable lignin content as Lignoboost lignin

(Exp. III) to a hydrolysis residue containing around 50% lignin (Exp. I), as specified in Table 1. All the experiments were run at 380 °C for 120 min. The mass yields of oil and char for both scales are given in Fig. 1a, together with the recovery of the input lignin mass in these fractions.

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

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

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

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

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

### 3.1.3. Variations in yields with ethanol as solvent

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

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

### 3.1.4. Comparison with published values

In our systems, the oil yields lie in the range of 17–60 wt% of lignin input, reflecting that the yields are strongly dependent on the reaction conditions. When comparing with recent studies, it must be noted that they mostly have taken advantage of the benefits of using catalysts. As mentioned in the introduction section, Kloekhorst et al. explored that the catalytic solvolysis of Alcell® lignin in the presence of formic acid as hydrogen donor and Ru/C as the catalyst in an alcoholic reaction media has given over 70 wt% bio-oil with very low oxygen content [27]. In a recent study from 2017, Kristianto et al. reported that over 66 wt% of CAHL-lignin (Concentrated Acid Hydrolysis Lignin) can be converted to bio-oil using the same reaction medium and catalyst as Kloekhorst' research group [32]. In that study, Kristianto et al. have shown that an increase in formic acid amount and prolonged reaction time in the presence of Ru/C increases oil yield, as well as reduces the oxygen

content of the bio-oil substantially. These studies are based on pure lignin as input, and thus are comparable with our yields from the purest lignins (47–67 wt%). The results reported in both mentioned studies above are quite comparable with results obtained by Oregui-Bengoechea et al. (2015) from the catalytic hydrodeoxygenation of acid hydrolysis lignin in water/formic acid reaction medium using $Ru/Al_2O_3$ as catalyst, which lies in the range of 86–98 wt% of lignin input [21].

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

### 3.2. Elemental composition and carbon recovery

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

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

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

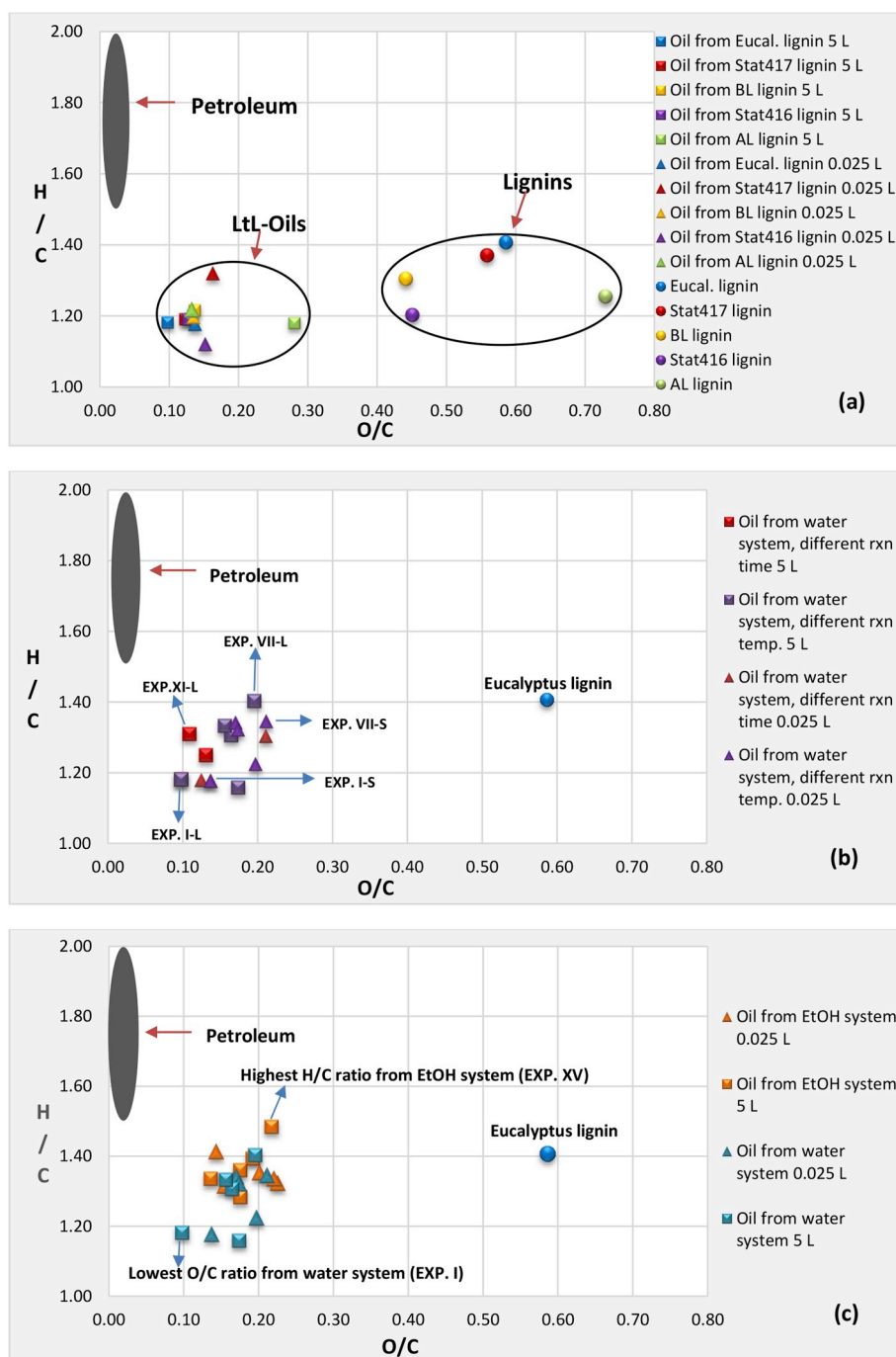| Lignins Mass % | | | | |
|---|---|---|---|---|
| | C | H | N | O |
| Eucalyptus | 50.1 | 5.92 | 0.44 | 39.1 |
| Stat417 | 53.2 | 6.12 | 0.07 | 39.6 |
| BL | 55.9 | 6.12 | 0.17 | 32.9 |
| Stat416 | 58.3 | 5.89 | 0.73 | 35.1 |
| AL | 48.1 | 5.07 | 0.10 | 46.7 |

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

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

Fig. 2b shows a trend of reduction in both H/C and O/C ratio for the oils with increasing temperature of conversion at both large and small

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

The elemental compositional data also makes it possible to calculate the yields on a carbon basis in addition to recovery by mass. Since the oxygen content of the oil is reduced from, e.g., 39.1 wt% in the Eucalyptus lignin to a range of 10.5–25.3 wt% in the lignin derived oils, much of the mass loss will be due to loss of oxygen. Hydrogen can both
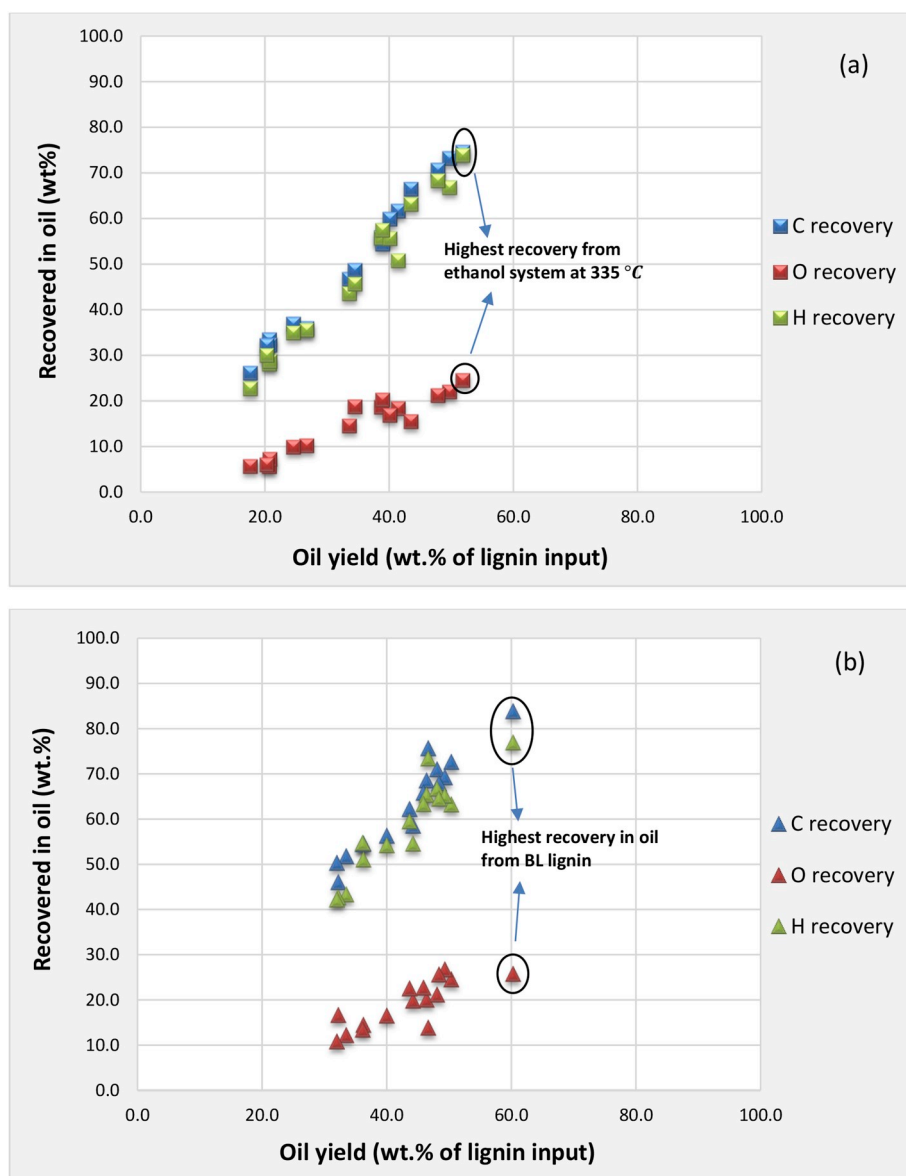
**Fig. 3.** (a) Percentage of C, O and H recovered in % LtL-oils produced in large scale and (b) Percentage of C, O and H recovered in % LtL-oils produced in small scale.

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

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

### 3.3. Molecular composition of LtL-oils

The liquid phase product comprises a complex mixture of phenolic compounds. The more volatile compounds can be identified using GC-MS analysis. Examples of major components are given in Table S3. In

the supplementary material, and their relative amounts are shown in Fig. 4. Examples of GC-MS chromatograms containing representative compound distributions are given in the supplementary material (Fig. S1 and Fig. S2).

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

In Fig. 4c and 4d, the comparable experiments with ethanol as solvent are presented. Although 2-methoxyphenol still is the highest peak, the ethanol solvent influences the oil composition to a significant degree. The number of components that include an ethyl substituent has increased significantly, including (19) 1-ethyl-3-phenylmethylbenzene, (20) 2-ethoxyphenol and (21) 2,5-diethylphenol, and other substituted compounds like (15) vanillyl alcohol are also
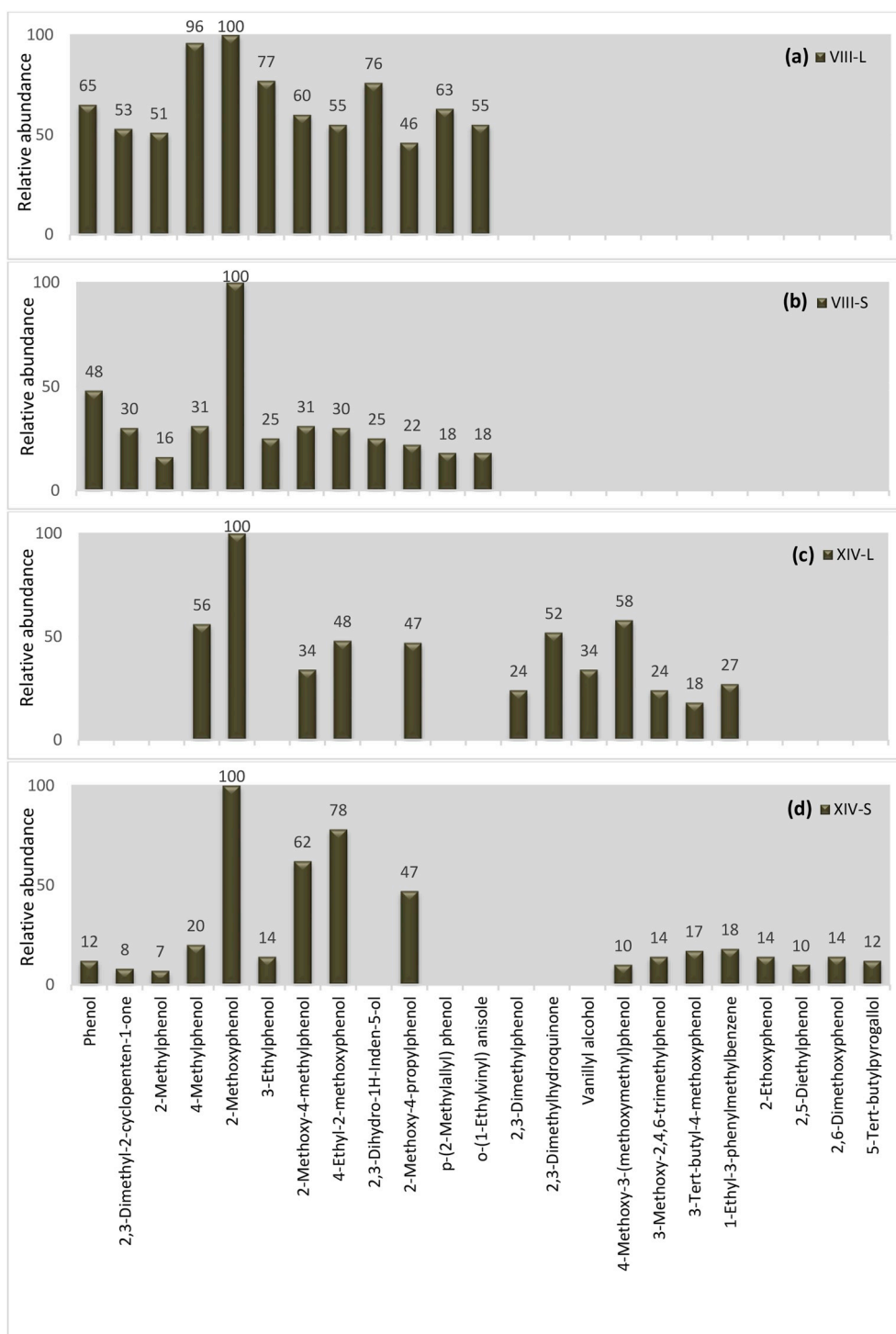
**Fig. 4.** GC-MS data from experiments VIII-L, VIII-S (Eucalyptus, 350 °C, 120 min, water as solvent) and XIV-L and XIV-S (Eucalyptus, 350 °C, 120 min, ethanol as solvent) showing the relative peak height of the most abundant compounds present in the bio-oils. The sequence of identified compounds on x-axis refers to the same structure numeration shown in Fig. S1 and Fig. S2 in the supplementary material. 2-methoxyphenol represents peak height of 100% due to highest relative abundance, and peak heights are measured relative to this peak.

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

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

### 3.4. The composition of the gas phase

A considerable amount of gas is produced during the reaction. Decomposition of formic acid is the source of the major part of the gas in the form of $CO_2$ and $H_2$ from the direct decomposition and CO from
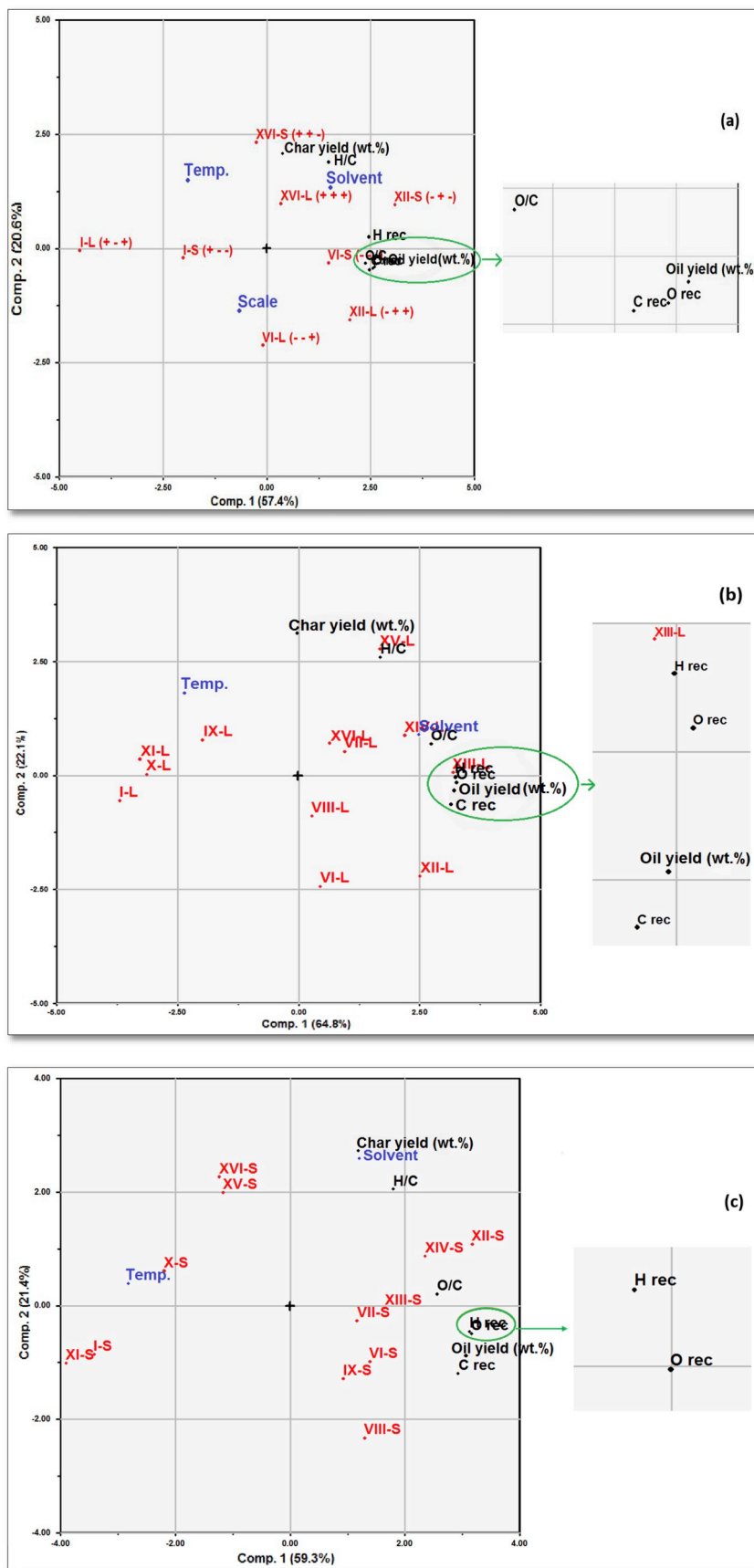
**Fig. 5.** (a) Biplot of objects and variables from fractional factorial design shown in Table 3. (b) biplot of objects and variables from all experiments done with Eucalyptus lignin in large scale and (c) biplot of objects and variables from all experiments done with Eucalyptus lignin in small scale.

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

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

*3.5. Principal component analysis*

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

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

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

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

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

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

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

The factorial design also makes it possible to compare the large and small scale experiments on a systematic basis. Separate PCA models based on all experiments are given in Fig. 5b (large scale) and Fig. 5c (small scale). Even though the models are not statistically balanced, they provide a good basis for comparing the systems. Overall, the influence of the variables on the yields are similar. The main difference is in the effect of the solvent, which is strongly positively correlated with the char yield at small scale. This observation can be explained by lack of stirring in the small reactors, as the stirring will distribute the lignin better in the reaction medium and thus reduce the tendency towards recondensation reactions. The overall slightly lower oil yields at 380 °C seen in Fig. 1b and 1c can also be an effect of improved mass transport

at stirred conditions, giving a higher degree of conversion in the stirred systems. Since the lignin is not directly soluble in the reaction media at low temperatures, the initial state of the reaction system will be a suspension of lignin particles in the liquid reaction media. Further heating melts the lignin and increases the solubility. The physical state of the reaction system at the selected temperatures is not explicitly known, but torque readings during the heating period at large scale indicate that lignin melts to a viscous liquid which dissolves at higher temperatures.

## 4. Conclusion

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

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

## Appendix A. Supplementary data

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

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