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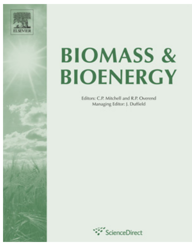

Research paper

Catalytic hydrodeoxygenation and hydrocracking of Alcell® lignin in alcohol/formic acid mixtures using a Ru/C catalyst

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ABSTRACT

The catalytic conversion of Alcell® lignin in iso-propanol/formic acid mixtures (1:1 mass ratio) was explored in a batch set-up using Ru/C as the catalyst (673 K, 4 h, 28% mass lignin intake on solvent). Lignin oils were obtained in good yields (71% mass yields on lignin input) and shown to consist of a mixture of mainly aromatics (10.5% mass yields on lignin input), alkylphenolics (6% mass yields on lignin input), catechols (8.7% mass yields on lignin input), guaiacols (1.3% mass yields on lignin input), and alkanes (5.2% mass yields on lignin input), the remainder being soluble higher molecular weight compounds (GCxGC-FID and GPC). The results for the catalytic experiments using formic acid were compared with those of a non-catalysed experiment and a catalytic hydrotreatment with molecular hydrogen and Ru/C in the absence of a solvent. Distinct differences in product yields and compositions were observed, and highest lignin oil yields were obtained by catalytic solvolysis (71% mass yields on lignin input) versus 18% mass yields on lignin input for non-catalytic solvolysis and 63% mass yields on lignin input for catalytic hydrotreatment. The effect of reaction time on oil yields and product composition was established and a reaction network involving depolymerisation, and hydro(-deoxy)genation pathways is proposed to explain the product yields and composition. Besides iso-isopropanol, the use of ethanol and methanol in combination with formic acid was also explored for catalytic solvolysis. Best results were obtained in methanol (4 h, 673 K) leading to a lignin oil (68% mass yields on lignin input) containing 11% mass yields on lignin input of alkylphenolics and 19% mass yields on lignin input of aromatics.

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1. Introduction

Due to declining fossil resources and associated negative environmental impact, the search for renewable resources for energy, transportation fuels and chemicals is high on the research agenda. Biomass is a promising alternative for carbon based transportation fuels (ethanol, biodiesel) and biobased chemicals [1–4]. Major breakthroughs have been made in the field of cellulose and hemi-cellulose conversions. However, valorisation of lignin, the third major biopolymer in lignocellulosic biomass, is still at a state of infancy. Nowadays, lignin is primarily used as a source for energy generation, a well-known example being the paper and pulp industry where 50 million Mg of lignin was produced as a by-product in 2004 [5]. The chemical composition of lignin makes it an excellent feedstock for the production of biobased chemicals, like aromatics (benzene, toluene, xylene) and alkylphenolics, and this has attracted considerable interest by academia and industry [6,7]. A number of conversion technologies are already actively explored, aiming to depolymerise lignin and subsequent (*in-situ*) conversion to higher value aromatics and alkylphenolics. An example is the base catalysed depolymerisation of lignin. Thring obtained 30% Alcell® lignin conversion, among others low molecular weight phenolics (3% mass yields on lignin input), by a treatment with NaOH (4% mass on lignin input) in a water–ethanol mixture [8]. More severe reaction conditions (613 K and 90 min reaction time) led to the formation of large amounts of coke. More recently, Roberts et al. succeeded in converting 52% mass yields on lignin input of organosolv lignin with the use of boric acid in combination with NaOH and water as solvent (543–633 K, 20–60 min reaction time), however with the formation of a large amount of char [9]. The main monomeric compounds present in the product oil were syringol, guaiacol, syringylaldehyde, and 3,5-dimethoxy-4-hydroxyacetophenone.

Another example of a lignin depolymerisation/upgrading technology involves thermal or catalytic cracking, the latter commonly performed with common petrochemical cracking catalysts (e.g. zeolites like H-ZSM-5). Thring et al. showed a 40% liquid yield which contained up to 90% mass yields of aromatics for the catalytic pyrolysis of Alcell® lignin (773–923 K) dissolved in acetone (1:2 mass ratio) using H-ZSM-5 in a packed bed reactor [10].

Catalytic hydrotreatment of lignin has also been explored extensively and involves the conversion of lignin in the presence of a (heterogeneous) catalyst with molecular hydrogen at elevated temperatures [7]. An early catalytic hydrotreatment example is from Pepper et al. who performed hydrogenation experiments with Raney nickel on extracted Maple wood lignin in a dioxane–water mixture (1:1) at 446 K and 20.7 MPa initial hydrogen pressure, for 6 h [11]. The main compounds found were syringols and guaiacols. Later research by Pepper et al. was more focused on noble metal catalyst, like Rh/C, Rh/Al_2O_3, Pd/C, Ru/C, and Ru/Al_2O_3, for the catalytic hydrotreatment of spruce lignin in dioxane–water mixtures, at 468 K, for 5 h, and 3.5 MPa [12,13]. Also this time the compounds were mainly syringols and guaiacols, however lignin conversion was much higher with noble metal catalyst then for Raney nickel. Oasmaa et al. performed catalytic hydrotreatment reactions using sulphided NiMo/Al_2O_3 and Cr_2O_3/Al_2O_3 for various types of lignin in the absence of an external solvent (668 K for 30 min with 10 MPa of hydrogen) and a maximum of 10.5% mass on lignin intake of aromatics and 9.3% mass of lignin intake of phenolics was obtained [14].

A well-known industrial example of the catalytic hydrotreatment of lignin is the Lignol process which was patented in 1983 by Huibers et al. [15,16]. In this process, (Co or Ni-promoted) iron or molybdenum oxides on alumina are used and a yield of 37% mass on lignin intake of phenolics is claimed (713 K and 7 MPa of hydrogen).

A promising, relatively new, lignin conversion methodology involves the use of a hydrogen donor instead of molecular hydrogen. A well known hydrogen donor is formic acid (FA), which is *in-situ*, either thermally or catalytically, converted to hydrogen and CO/CO_2. Commonly used solvents are alcohols (ethanol, methanol, isopropanol (IPA)), and water, see Table 1 for an overview.

Temperatures between 573 and 653 K have been explored, with reaction times ranging from 2 to 17 h. Kleinert et al. were able to convert alkaline extracted lignin from spruce, pine, birch, and aspen wood to a liquid products in 93% mass on lignin intake yield at 653 K with a reaction times of 17 h using FA in isopropanol [17,18]. The molar H/C ratio of the product oil ranged between 1.3 and 1.8, and the O/C ratio between 0.05 and 0.1, indicative for a substantial reduction in the oxygen content. Recent research by Liguori et al. showed that the reaction times and temperature can be reduced dramatically when using a heterogeneous catalyst (Pd/C) in water (Table 1) [19]. Major products were guaiacols (4.6% mass on lignin intake) and catechols (4.7% mass on lignin intake). It was hypothesized that the heterogeneous catalyst leads to higher FA decomposition rates at lower temperature. As such, it has a positive effect on lignin depolymerisation rates [20] and enhances the rate of the subsequent deoxygenation of the lower molecular weight fragments. More recent work from Xu et al. shows the use of Pt/C with ethanol and formic acid for the conversion of switchgrass lignin. The elemental compositions of the product oils for different reaction times were determined, though the molecular structures of major components were not reported.

This paper describes the use of a Ru/C catalyst for the catalytic conversion of Alcell® lignin with FA as the hydrogen donor in an alcohol as the solvent. The objective is to maximize the amounts of low molecular weight products and particularly aromatics and phenolics as these have the highest economic potential (>1000 euro/Mg). Recent studies, also in our group, has shown that Ru/C is an promising catalyst for the catalytic hydrotreatment of pyrolysis and lignin oils to stabilised liquid products with a higher H/C ratio than the feed. These product oils could serve as a feed for transportation fuels and biobased chemicals [25–28]. Alcell® lignin, an organosolv lignin, was used because of its very low sulphur content, which is beneficial for catalyst performance when noble metal catalysts are used. In addition, the molecular weight of the lignin is relatively low (around 2000 g/mol) and as such is a good choice for the conversion to low molecular weight products [29]. The effect of process conditions (reaction time and type of solvent) on low molecular weight oil yield was studied and the resulting products oils were

Table 1 – Summary of research on lignin conversion using FA as a hydrogen donor.

Lignin source	Solvent	Catalyst	Temp., K	Reaction time, h	Oil yield,[a] % mass	Solids,[b] % mass	Composition	Ref.
Enzymatic/hydrolysis lignin	IPA, EtOH	–	643–663	2–16	93	16–30	Phenolics	[21]
Multiple lignins	IPA,EtOH, MeOH	–	653	8–54	82–130	n.d.	Phenolics (25–35%)[a] H/C 1.3–1.8 O/C 0.05–0.1	[17,18]
Enzymatic/weak acid hydrolysis lignin	IPA, EtOH	–	653	–	–	2–15	Aliphatic hydrocarbons/phenolics H/C 1.2–1.8 O/C 0.16–0.5	[22]
Protobind 1000 lignin	EtOH	–	633	0.25–20	n.d.	2–5	Phenolics	[23]
Desulfonated Kraft lignin	Water	Pd/C	573	2	–	10–20	Mixture of phenols	[19]
Switchgrass lignin	EtOH	Pt/C	623	1–20	n.d.	12.3–32.6	Phenolics, guaiacols H/C 1.3–1.2 O/C 0.33–0.15	[24]

[a] % Mass on lignin intake.
[b] % Mass on total amount.

analysed using various techniques (GC–MS-FID, GCxGC-FID, GPC) to gain insights in the molecular composition. Finally, a reaction network is proposed to explain the product yields and compositions.

2. Material and methods

2.1. Chemicals

Ruthenium on carbon (5% mass of Ru on support, powder) was obtained from Sigma Aldrich and used as received. Hydrogen (>99.999%) and nitrogen gas (>99.8%) were obtained from Hoekloos. Alcell® lignin, produced by Repap, Canada from mixed hardwood, was kindly supplied by the Wageningen University and Research Center (WUR), The Netherlands. Analytical details are provided in Ref. [30]. Tetrahydrofuran (THF), methanol, ethanol, formic acid (FA), isopropyl alcohol, and di-n-butylether (DBE) were obtained from Sigma Aldrich (99.99%) and used as received.

2.2. Catalytic solvolysis experiments

Solvolytic hydrotreatment experiments were performed in a 100 cm^{-3} batch autoclave (Parr). The autoclave has a maximum operation temperature of 773 K and pressure of 35 MPa. The reactor was heated using an electric heater and the temperature was controlled using cooling water. The reactor content is stirred mechanically using a Rushton type turbine with a gas induced impeller. Temperature and pressure were monitored online and logged on a PC. Typically, the reactor is loaded with 25 g of reactants/solvents consisting of 71% mass of a mixture of alcohol and FA on total feed (1:1 mass ratio), 27.6% mass intake of lignin on total feed and 1.4% mass intake of Ru/C on total feed (5% mass on lignin feed). For the non-catalytic solvolysis experiments a glass insert was used to eliminate catalytic effect of the reactor wall.

The reactor was filled with lignin, the alcohol/FA mixture and catalyst, and subsequently flushed with hydrogen and pressurized to 10 MPa at room temperature for testing on leakage. Subsequently, the pressure was released to 0.1 MPa and stirring was started (20 Hz). The reactor was then heated to the intended reaction temperature with a rate of about 10 K min^{-1}. The reaction time is set at $t = 0$ when the pre-determined temperature is reached. The pressure is recorded during reaction. After the pre-determined reaction time, the reactor was cooled to room temperature with a rate of about 40 K min^{-1}. The pressure at room temperature was recorded for determination of the amount of gas phase components produced during reaction and the gas was collected in a 10 dm^3 tedlar gasbag for determination of the composition. The reactor was weighed after reaction to determine the total liquid and solid product weights. The liquid phase was removed using a syringe and filtered through a 4 μm PTFE filter. The solids in the PTFE filter were rinsed with acetone and dried before weighing. The remaining solids in the reactor were washed with acetone, filtered, dried, and weighed. The solids content is the sum of the weight of the solids in the filter and reactor. The total liquid weight is the difference between the known weight of the reactor contents after reactions minus the solids content. For some experiments, the amount of gas phase components produced during the reaction was determined by volumetric water displacement. For this purpose, the gas collected in the 10 dm^3 tedlar gasbag after reaction was submersed in a vessel filled with water. The amount of displaced water was determined and used to calculate the amount of gas phase components formed during reaction.

The liquid phase typically consists of two immiscible layers, a clear colourless aqueous phase on the bottom and a dark black oil phase on top. The liquid layers were separated using a syringe and the weights of both phases were determined. The water content of both phases was analysed using a Karl Fischer titration. Afterwards a sample of the oil phase was heated at 303 K under vacuum (1000 Pa) to remove the volatiles and the solvent. The amount of the volatile fraction or volatiles was determined gravimetrically. The remaining oil phase is designated as the lignin oil throughout this paper. The reported elemental compositions are for the lignin oils. For GCxGC-FID and GC–MS-FID analyse, the original oil phase from the reactor was used including volatiles. The product composition is compensated for the presence of the volatile fraction and reported on a volatile free basis.

2.3. *Liquid phase analyses*

Before GCxGC-FID and GC–MS-FID analyses, the organic samples were diluted with tetrahydrofuran (THF) and 1 mg g^{-1} di-n-butylether (DBE) was added as an internal standard.

GCxGC-FID analysis were performed on organic samples with a trace GCxGC from Interscience equipped with a cryogenic trap system and two columns: a 30 m × 0.25 mm i.d. and 0.25 μm film of RTX-1701 capillary column connected by a meltfit to a 120 cm × 0.15 mm i.d. and 0.15 ìm film Rxi-5Sil MS column. An FID detector was applied. A dual jet modulator was applied using carbon dioxide to trap the samples. Helium was used as the carrier gas (continues flow 0.8 cm^3 min^{-1}). The injector temperature and FID temperature were set at 553 K. The oven temperature was kept at 313 K for 5 min then heated up to 523 K at a rate of 3 K min^{-1}. The pressure was set at 70 kPa at 313 K. The modulation time was 6 s.

For product identification, GCxGC-TOFMS was performed on a standard lignin oil sample obtained by a hydrotreatment of Alcell® lignin with 5% mass of Ru/γ-Al_2O_3 on lignin intake, 4 h reaction time and 10 MPa initial H_2 pressure. The sample was analysed on a GCxGC-HRTOFMS from JEOL equipped with a cryogenic trap system and two columns: a 30 m × 0.25 mm i.d. and 0.25 μm film of RTX-1701 capillary column connected by a meltfit to a 200 cm × 0.15 mm i.d. and 0.15 μm film Rxi-5Sil MS column. A TOFMS JMS-T100GCV 4G detector was used with a scanning speed of 50Hz with a mass range of 35–600 *m*/z. Helium was used as the carrier gas (continues flow 0.8 cm^3 min^{-1}). The injector temperature and TOFMS temperature were set at 523 K. The oven temperature was kept at 313 K for 5 min then heated up to 523 K at a rate of 3 K min^{-1}. The pressure was set at 77.5 kPa at 313 K. The modulation time was 6 s. The MS-Spectra plot was analysed with GC Image® software and a homemade Matlab routine.

GC–MS-FID analyses were performed on organic product samples using a Hewlett Packard 5890 series II plus with a Quadrupole Hewlett Packard 5972 MSD and an FID. The GC was equipped with a 60 × 0.25 mm i.d. and 0.25 μm film Restek RTX-1701 capillary column which is split 1:1 to the MSD and FID. The injector temperature was set at 553 K. The oven temperature was kept at 313 K for 5 min then heated up to 523 K at a rate of 3 K min^{-1}.

GPC analyses were performed on organic samples with an HP1100 from Hewlett Packard equipped with three 300 × 7.5 mm PLgel 3 μm MIXED-E columns in series. Detection was made with a GBC LC 1240 RI detector. Calculations of the average molecular weight were made with the software PSS WinGPC Unity from Polymer Standards Service. The following operating conditions were maintained: THF as eluent (used as delivered), flow rate, 1 cm^3 min^{-1}; 14 MPa, column temperature of 315 K, 20 mm^{-3} injection volume, 10 mg cm^{-3} sample concentration. Toluene was used as a flow marker and polystyrene samples with different molecular weight were used as the calibration standard.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer differential scanning calorimeter Pyris 1 under a N_2 atmosphere. The sample was first heated from 298 K to 453 K and then cooled to 298 K. The heating and cooling rates were set at 10 K min^{-1} throughout the measurement. The first cycle was used for determination for glass point and melt point of the Alcell® lignin.

Elemental analysis (C, H and N) was performed on lignin oils using an Euro Vector 3400 CHN-S analyser. The oxygen content was determined by difference. All experiments were carried out in duplicate and the average value is taken.

The water content in the organic and water samples was determined by Karl Fischer titration using a Metrohm Titrino 758 titration device. A small amount of sample (ca. 0.03–0.05 g) was added into an isolated glass chamber containing Hydranal® (Karl Fischer Solvent, Riedel de Haen). The titrations were carried out using the Karl Fischer titrant Composit 5K (Riedel de Haen). All measurements were performed in duplicate and the average value is reported.

2.4. *Gas phase analysis*

The gas phases were collected after reaction and stored in a gasbag (SKC Tedlar 10 dm^3 sample bag) with a polypropylene septum fitting. GC-TCD analyses were performed on a Hewlett Packard 5890 Series II GC equipped with a Porablot Q Al_2O_3/Na_2SO_4 column and a molecular sieve (5 Å) column. The injector temperature was set at 423 K, the detector temperature at 363 K. The oven temperature was kept at 313 K for 2 min then heated up to 363 K at 20 K min^{-1} and kept at this temperature for 2 min. The columns were flushed for 30 s with the gas sample before starting the measurement.

A reference gas was used to quantify the results. The reference gas contains a known composition of gasses (55.19% H_2, 19.70% CH_4, 3.00% CO, 18.10% CO_2, 0.51% ethylene, 1.49% ethane, 0.51% propylene and 1.50% propane). The reference gas was used to identify the peaks by retention time and to quantify the amounts.

3. Results and discussion

3.1. *Screening experiments*

Initial screening experiments were performed using Alcell® lignin (27.6% mass intake on total feed) in a 71% mass of a mixture of IPA and FA (1:1% mass ratio) in presence or absence of Ru/C (1.4% mass on total feed). The reactions were carried out in a batch autoclave at 673 K for a reaction time of 4 h. During heating, the pressure in the reactor increased typically to 20 MPa when the temperature approached 673 K, likely due to the catalytic decomposition of formic acid to hydrogen and CO_x and the formation of other gas phase components (*vide infra*). After reaction, the liquid phase consisted of two immiscible layers, a dark brown organic phase on top and a clear aqueous phase at the bottom. In addition, solids were detected after reaction, the exact amounts depending on experimental conditions. The solvent in the organic phase was removed by evaporation (313 K, 1000 Pa), giving a dark brown oil, which will be designated as “lignin oil” throughout this paper.

For solvolysis in the presence of Ru/C (experiment 1, Table 2) the resulting lignin oil yield was about 70% mass on lignin feed and negligible solids formation was observed (<0.3% mass on lignin). A significant amount of water was produced

Table 2 – Product yields and composition for lignin solvolysis using Ru/C.

Experiment	1[a]	2[a]	3[b]	4[c]
Lignin	Alcell	Alcell	Alcell	–
Solvent	IPA/FA	IPA/FA	None	IPA/FA
Catalyst	Ru/C	None	Ru/C	Ru/C
Initial hydrogen pressure (MPa)	–	–	10	–
Top organic phase, % mass on total feed	38.2	25.0	–	–
Bottom aqueous phase, % mass on total feed	11.9	25.0	–	–
Solids (acetone insoluble), % mass on total feed	0.3	12.2	<0.1	–
Water formation, % mass on total feed[e]	9.6	13.1	13.3	–
Gas phase, % mass on total feed	n.d.	n.d.	n.d.	n.d.
Gas phase, mol fractions (dry basis) %				
Carbon dioxide	54.1	50.4	15.5	48.9
Carbon monoxide	4.8	8.2	2.9	1.9
Ethane	1.0	2.0	2.8	3.0
Propylene	1.0	1.9	0.0	0.1
Propane	11.1	11.8	0.9	6.2
Methane	6.5	8.5	25.6	32.0
Hydrogen	21.4	17.3	52.2	7.8
Lignin oil, % mass on lignin intake[d]	71.2	18.2	63.1	–
Elemental composition lignin oil (% mass, dry basis)				
Carbon	80.76	79.88	82.5	–
Hydrogen	10.16	8.90	9.6	–
Oxygen	8.94	11.16	7.72	–

[a] Reaction with Alcell® lignin 27.6% mass intake in a mixture of 71% mass of IPA and FA (1:1 mass ratio) with Ru/C (1.4% mass on total feed at 673 K for 4 h.

[b] Solvent free reaction with Alcell lignin with 5% mass of Ru/C on lignin intake at 673 K for 4 h.

[c] Reaction with an 18 g mixture of IPA and FA in a 1:1 mass ratio with 0.75 g Ru/C at 673 K for 4 h.

[d] In case of IPA/FA, it is the oil yield after removal of the solvent from the top organic phase by evaporation.

[e] Total amount of water formed during reaction.

(9.6% mass on lignin intake), likely due to FA decomposition as well as the catalytic hydro-deoxygenation of depolymerised lignin (fragments).

In the absence of the catalyst (experiment 2, Table 2), only 18% mass of lignin oil on lignin feed was obtained (compared to 70% mass of lignin on lignin feed for the reaction in presence of Ru/C) and a large amount of solids (12.2% mass on total feed, corresponding to 46% mass on lignin intake) was present after reaction. These solids may either consist of unconverted lignin or product from the repolymerisation of reactive low molecular weight lignin fragments. Thus, either lignin depolymerisation rates or the rate of repolymerisation or a combination of the two are affected by the presence of Ru/C. Clearly, the catalyst has a positive effect on the oil yield.

In this respect, it is of interest to make a comparison between the catalytic solvolysis of lignin with Ru/C and pyrolysis oil upgrading by a catalytic hydrotreatment reaction using Ru/C. Pyrolysis oils also contains a significant lignin fraction (up to 30%% mass), consisting of lower molecular weight lignin fragments. The catalytic hydrotreatment reaction aims to improve the product properties of fast pyrolysis oil by hydro(-deoxy)genation, ultimately leading to hydrocarbons. In this case, thermal repolymerisation is also a serious issue, leading to excessive solids formations [25,31,32]. The most effective way to reduce solids formation is to increase the rate of hydro(-deoxy)genation reactions, i.e. by using very active catalysts in combination with a high hydrogen pressure. These observations may also be valid to explain the reduction in solids yields for catalytic solvolysis compared to the non-catalytic version. Likely, in the presence of a catalyst, the hydro(-deoxy)genation reactions are accelerated leading to less repolymerisation (solids). In this respect, the catalyst has two functions, i) create an on average higher hydrogen pressure during the reaction due to rapid catalytic decomposition of FA [20,33] and ii) rapid catalytic hydrogenation of reactive fragments prone to polymerization to less reactive products.

Further proof that Ru/C is indeed an active hydrotreatment catalyst for Alcell® lignin was obtained by performing an experiment in the absence of an external solvent using molecular hydrogen (10 MPa initial pressure at room temperature, 16–18 MPa at reaction conditions, Ru/C, (5% mass on lignin intake), 673 K, 4 h). At these conditions, Alcell® lignin is expected to be present in the liquid state and acts as both as solvent and reactant. This was confirmed by DSC measurements, clearly showing endothermic peaks between 423 and 448 K, which are associated with the melting of lignin (Fig. 1) [34].

Like with the solvolysis experiments, two liquid phases were observed after reaction. The lignin oil yield was 63.1% mass on lignin intake (Table 2, experiment 3), which is similar to the catalytic solvolysis experiments. Thus, when considering lignin oils yields, catalytic solvolysis using formic acid as the hydrogen donor can be an attractive alternative for the use of molecular hydrogen. However, the product composition for both methodologies differs considerably (*vide infra*).

3.2. *Reproducibility experiments*

The catalytic solvolysis reaction with Ru/C in IPA/FA (experiment 1, Table 2) was performed in triplicate to gain insights in the reproducibility of the reaction. In addition, these experiments were designed in such a way that the amount of gas phase components formed during reaction could be

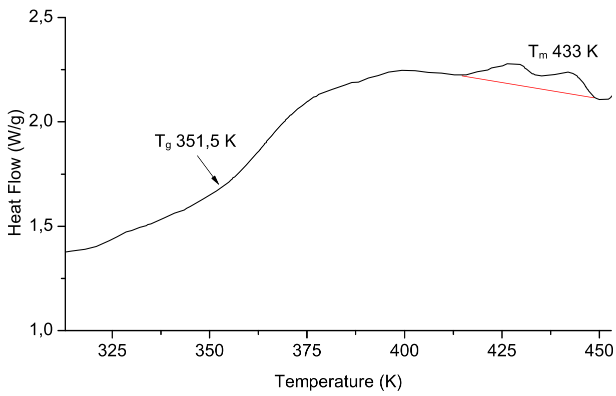


Fig. 1 – DSC curve of Alcell® lignin.

determined accurately, allowing assessment of the complete mass balance for the reaction. Good mass balance closures were obtained (>95% mass on total feed) and the results were found to be reproducible (Table 3). Remarkably, the amount of gas phase components after reaction turned out to be high (about 43% mass on the total feed (lignin, FA/IPA), indicative for the occurrence of gas forming reactions to a considerable extent. Gas phase composition and formation pathways will be discussed in upcoming paragraphs.

4. Composition of the gas and liquid phase

4.1. Gas phase composition

By far the most abundant gas phase component after a typical solvolysis reaction with Ru/C in FA/isopropanol is CO_2 (>50 mol%), followed by hydrogen (20 mol%), propane (10 mol %), and methane (7 mol%, Tables 2 and 3). Part of these gas phase components is likely formed by reactions of the solvents, partly by depolymerisation/deoxygenation reactions of lignin. To study the relative importance of both pathways, a catalytic solvolysis experiment with FA/IPA in the absence of lignin was performed (experiment 4, Table 2). The major gas phase component was CO_2, like with experiments in the presence of lignin. However, the amounts of hydrocarbons (methane, ethane, propane) for a reaction in the absence of lignin are significantly higher (41 mol%) than for the experiments with lignin (18 mol%), whereas the amount of hydrogen is much lower. These experiments suggest that i) the solvents (IPA/FA) are the major source for the gas phase components and ii) that gas phase hydrogenation reactions, e.g. CO/CO hydrogenation to hydrocarbons, which are known to be catalysed by Ru on supports [35], occur to a significant extent.

Table 3 – Reproducibility data for catalytic solvolysis experiments in IPA/FA using Ru/C.

Experiment	5	6	7
Solvent	IPA/FA	IPA/FA	IPA/FA
Catalyst	Ru/C	Ru/C	Ru/C
Top organic phase, % mass on total feed	36.4	35.8	37.9
Bottom aqueous phase, % mass on total feed	13.7	12.7	14.5
Solids (acetone insoluble), % mass on total feed	2.7	2.5	2.7
Gas phase, % mass on total feed	43.3	43.6	40.1
Gas phase, mol fractions (dry basis) %			
Carbon dioxide	52.7	53.4	57.9
Carbon monoxide	6.0	5.9	4.8
Ethane	5.4	2.6	1.9
Propylene	0.7	0.9	0.7
Propane	10.3	10.9	10.4
Hydrogen	18.2	20.0	17.0
Methane	6.6	6.3	7.3
Water formation, % mass on total feed	5.7	5.5	5.7
Mass balance closure, % mass on total feed	96.1	94.6	95.2

Reactions performed with 27.6% mass of Alcell® lignin on solvent, 1.4% mass of Ru/C on total feed, in a mixture of FA and IPA (71% mass, 1:1 mass ratio) at 673 K for 4 h.

4.2. Composition of the organic phase and lignin oil

The elemental composition of the lignin oils from the (catalytic) solvolysis experiments and the catalytic hydrotreatment experiment in the absence of solvents were determined and the results are given in Table 2. The oxygen content (7.7–11.2% mass) of all lignin oils is considerably lower than the original Alcell® lignin (C, 65.2% mass, H, 5.8% mass, O, 29.0% mass), a clear indication for the occurrence of deoxygenation reactions and formation of compounds with a lower oxygen content. The lignin oil obtained after catalytic solvolysis has a lower O content (8.9% mass) than the oil from a non-catalytic experiment (11.2% mass). Apparently, during the catalytic solvolysis, the formation of components with on average lower oxygen content occurs to a larger extent. This is in line with the molecular composition of the lignin oil, which is richer in hydrocarbons for the catalytic solvolysis product (*vide infra*). The largest reduction in oxygen content was observed for the catalytic hydrotreatment reaction (7.7% mass), though levels were close to those of the (catalytic)-solvolysis experiments (8.8–9% mass).

The organic phase of the catalytic and non-catalytic solvolysis experiments as well as the lignin oil from the catalytic hydrotreatment experiment was analysed using GCxGC-FID and GC–MS-FID to determine the product composition. A representative example of a GC–MS-FID is given in Fig. 2.

Clearly, a large number of components are present, belonging to various compound classes (aromatics, ketones, and phenolics). More detailed information on molecular composition was obtained by GCxGC-FID chromatography (Fig. 3). This technique is very informative and allows rapid assessment of major organic compound classes present within a liquefied biomass sample [36,37]. Typically up to three hundred components are visible in the organic phase and, for clarity, these were divided into a number of organic product classes. The classification and main components within each class are given in Table 4. The component groups are well separated in the GCxGC-FID spectra and visible as discrete regions.

A typical organic phase was also measured by GCxGC-TOFMS for enhanced identification of the organic compounds and to improve the classification system.

The main GC detectable product classes for the catalytic solvolysis experiments with Ru/C are ketones, followed by aromatics, catechols and alkylphenolics (Fig. 4).

Typical contents for the desired alkylphenolics and aromatics are 6 and 10% mass on lignin intake. Major ketones are methyl isobutylketone (MIBK) and mesityloxide (MO), typically in a 3–4 to 1 ratio. These compounds are not formed by lignin depolymerisation/hydro(-deoxy)genation reactions but are likely reaction products from acetone dimerisation through an aldol condensation reaction (Scheme 1) [38].

Here, the required acetone may be formed by dehydrogenation of IPA. Thus, the solvent IPA is not inert under these conditions and prone to reaction. Similar reactivity of IPA has also been observed by Kleinert et al. for the non-catalytic solvolysis of lignin in IPA/FA mixtures [17].

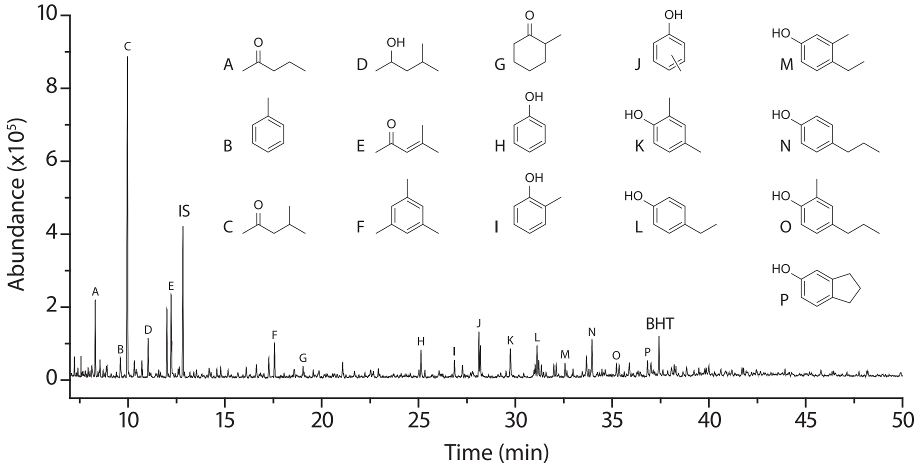


Fig. 2 – Part of a representative GC–MS-FID chromatogram for the organic phase of a catalytic solvolysis experiment.

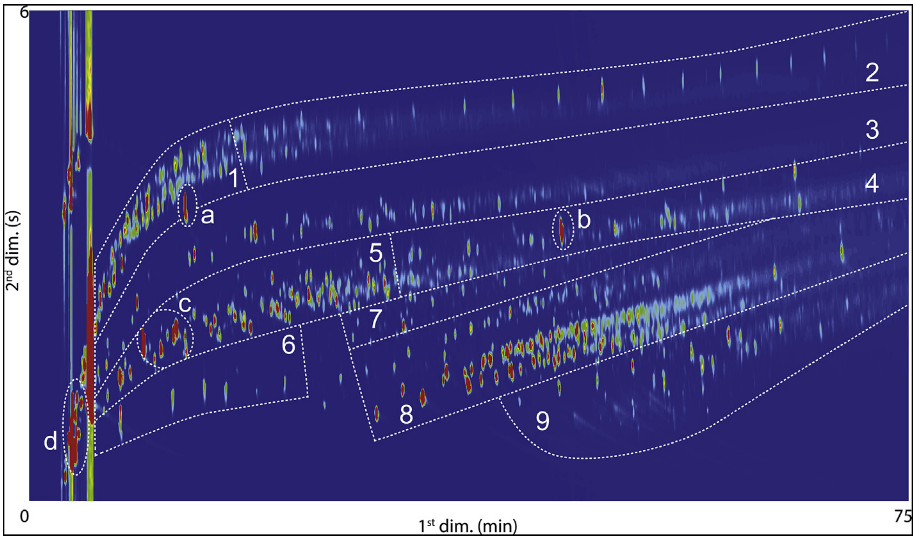


Fig. 3 – GCxGC-FID measurement of an organic phase from a typical catalytic solvolysis experiment. (exp 1, Table 2). 1 = cyclic alkanes, 2 = linear alkanes, 3 + 4 = aromatics, 5 = ketones/alcohols, 6 = acids, 7 = guaiacols 8 = alkylphenolics, 9 = catechols. Also a = IS, b = BHT (stabilizer in THF solvent), c = aldol condensation products (MIBK, mesityl oxide), d = IPA and acetone.

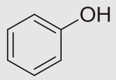
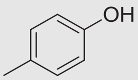
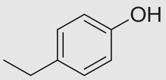
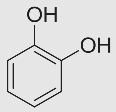
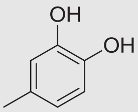
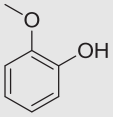
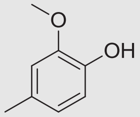
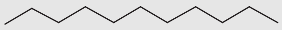
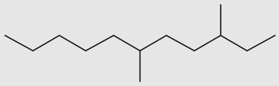
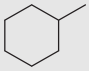
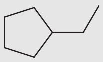
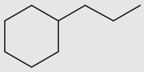
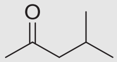
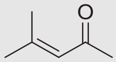
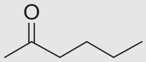
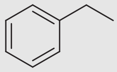
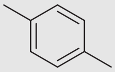
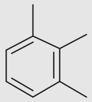
The catechols, guaiacols and alkylphenolics likely arise from lignin depolymerisation followed by catalytic hydro(deoxy)genation reactions (Scheme 2). The presence of significant amounts of aromatics and aliphatic hydrocarbons indicates that the catechols, guaiacols and alkylphenolics are not inert under reaction conditions and subsequently hydro(deoxy)genation with molecular hydrogen (*vide infra*). The oxygenated aromatics likely react in two parallel pathways to alkanes, viz. i) hydrogenation of the aromatic C–C double bonds to form saturated cyclic ketones and alcohols followed by subsequent hydrogenation reactions [39] and ii) the hydrodeoxygenation of the oxygenated aromatics to aromatics, followed by over hydrogenation to alkanes.

The product composition of the organic phase from a non-catalytic solvolysis experiment differs significantly from that of a catalytic solvolysis experiment with Ru/C. Ketones like MIBK and MO are present, though in much lower amounts and, like with catalytic solvolysis, originate mainly from IPA.

The total amounts of aromatics, alkanes and alkylphenolics (21.6% mass on lignin intake) are much higher than for the catalytic solvolysis (14.8% mass on lignin intake). However when alkylphenolics are the desired products, non-catalytic solvolysis seems the method of choice (8% versus 6% mass on lignin intake). This is evident from the work of Kleinert et al. on non-catalytic solvolysis, who claimed a highest phenolic yield of 25–35% mass on lignin intake [17,18,21,22].

The amount of hydrocarbons in lignin oil from non-catalytic solvolysis is much lower than for the catalytic version. The presence of the latter indicates that hydro(deoxy)genation also occurs to some extent in the non-catalytic reaction. The most likely explanation is catalysis by metal reactor parts. The non-catalytic solvolysis experiments

Table 4 – Major compounds classes in organic product oils as determined by GCxGC-FID, GCxGC-TOFMS, and GC–MS-FID.

Alkylphenolics	 phenol  4-methylphenol  4-ethylphenol
Catechols	 pyrocatechol  4-methylbenzene-1,2-diol
Guaiacols	 2-methoxyphenol  2-methoxy-4-methylphenol
Alkanes	 undecane  3,6-dimethylundecane
Cyclic alkanes	 methylcyclohexane  ethylcyclopentane  propylcyclohexane
Ketones	 methyl isobutyl ketone  mesityl oxide  hexan-2-one
Aromatics	 ethylbenzene  *p*-xylene  1,2,3-trimethylbenzene

were carried out with a glass insert to minimize contact of the reactor content with the walls. However, a steel stirrer is applied which is in contact with the solution and likely catalytically active. This explanation was supported by performing an experiment without the glass insert, leading to higher yields of low molecular weight deoxygenated compounds.

For the catalytic hydrotreatment experiments in the absence of IPA/FA but using molecular hydrogen, the amount of alkylphenolics and alkanes (15.9% mass on lignin intake) is higher than for the catalytic solvolysis experiments (11.5% mass on lignin intake), indicating higher hydro(-deoxy)genation activity during the catalytic hydrotreatment reaction. This is probably due to an on average higher hydrogen partial pressure during the catalytic hydrotreatment experiments in comparison with the catalytic solvolysis experiments, where FA has to decompose at elevated temperatures

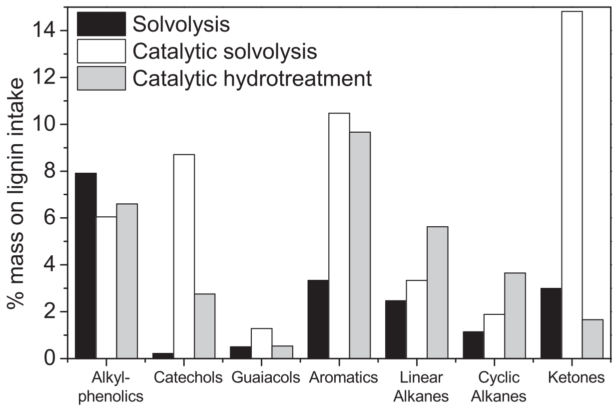
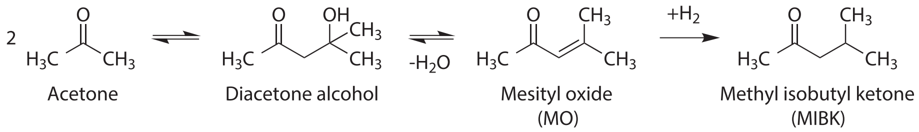
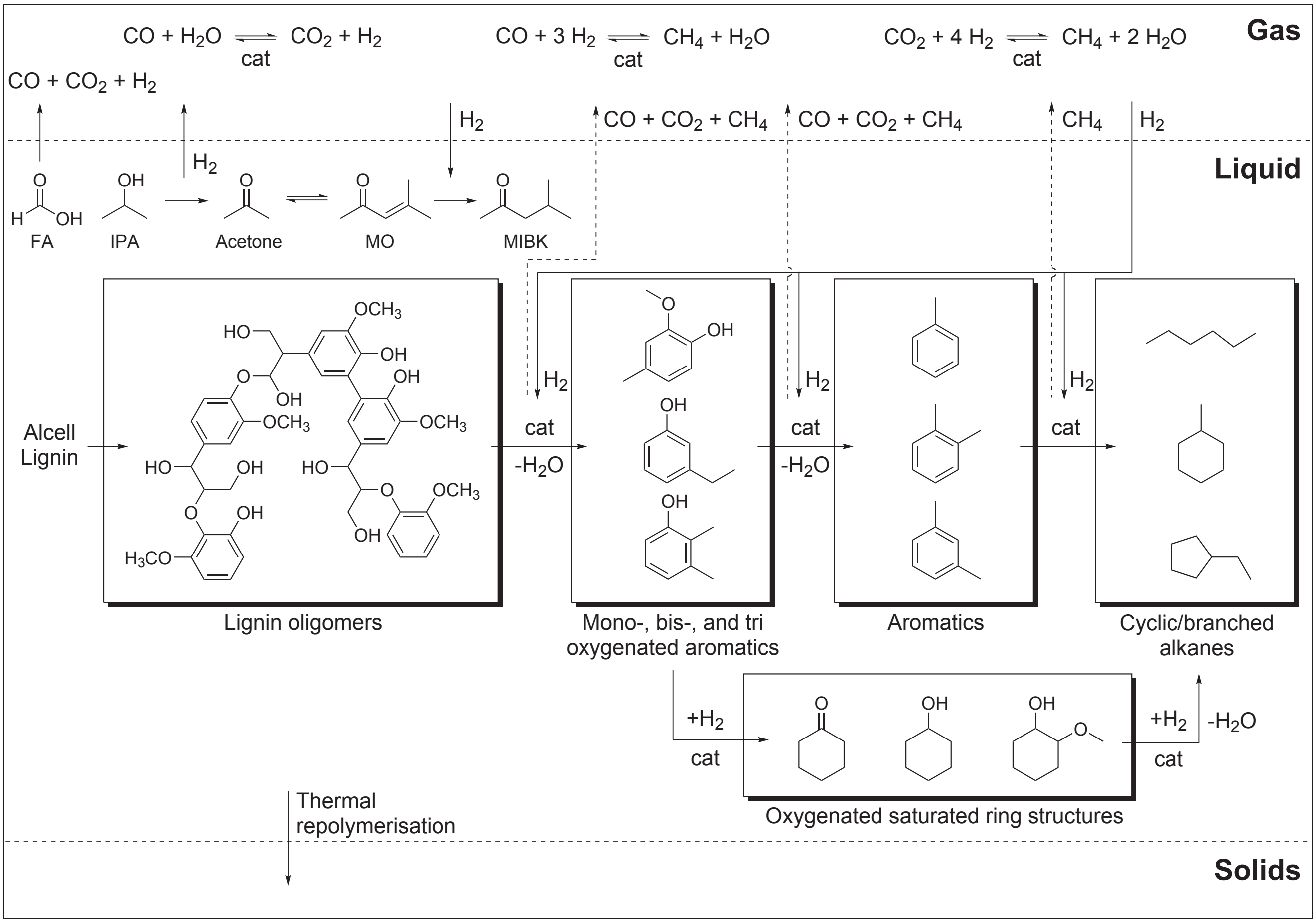


Fig. 4 – Product distribution for the three types of lignin liquefaction experiments (673 K and 4 h).



Scheme 1 – Reaction scheme for acetone conversion to mesityloxide and methyl isobutyl ketone.



Scheme 2 – Proposed reaction pathways for the catalytic solvolysis of lignin.

to form hydrogen and CO$_x$. Furthermore, a much lower amount of ketones is present in the organic phase. The ketone fraction now consists mainly of 3-pentanone and 2-hexanone and, as expected, IPA derived compounds like MIBK and MO are absent. This observation confirms that the MIBK and MO in the catalytic solvolysis experiments are formed by reactions of the solvent.

The total amount of detectable species using GC techniques is less than the total amount of organic product oils present after reaction. This is due to the presence of a higher molecular weight, non-volatile fraction in the oils (typically >250 Da) that are not detectable by GC techniques. To gain insights in the amounts of higher molecular weight products, the organic product phases were subjected to GPC analyses and the results are shown in Fig. 5.

In Fig. 5, the molecular weight distribution of the Alcell® lignin feed is also provided. Clearly, the molecular weight of

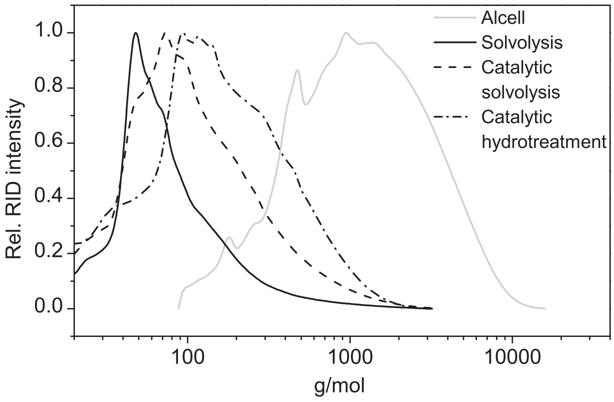


Fig. 5 – Molecular weight distribution of the organic product phases for the three liginin upgrading methodologies.

the organic phases of the catalytic/non-catalytic and the catalytic hydrotreatment experiment are much lower than for the Alcell® lignin feed, indicating that all three methodologies lead to molecular weight breakdown. The molecular weight of the product oil from a non-catalytic solvolysis experiment is remarkably low and actually lower than for the oils from both catalytic methods. A possible explanation is a higher rate of repolymerisation of reactive lignin fragments in case catalysts are absent, as the rate of hydrogenation of these reactive fragments is limited or even negligible in the absence of a catalyst. This is also supported by the observation that considerable amounts of char are formed for non-catalytic experiments. As such, only the thermally very stable monomers/oligomers that are not prone to repolymerisation are present in the product oil for non-catalytic reactions. In the case of the catalytic experiments, reactive fragments are hydrogenated and not repolymerised (limited/negligible amounts of char), leading to an on average higher molecular weight of the product oils.

4.3. *Effect of reaction time and solvent on liquid yields and product composition for the catalytic solvolysis of lignin using Ru/C*

The effects of reaction time and type of alcohol on the liquid product yield and molecular composition were assessed for the catalytic solvolysis of Alcell® lignin in isopropanol/FA mixtures using Ru/C, with the main objective to optimize the amounts of valuable low molecular weight product classes (alkylphenolics and aromatics).

4.3.1. *Effects of batch time*

The effect of batch time was explored by performing reactions at 0, 1, 4, and 6 h (673 K, 27.6% mass of Alcell® lignin on solvent, 1.4% mass of Ru/C on total feed, 71% masss of FA and IPA in a 1:1 mass ratio). Initial pressure at reaction temperature was around 20 MPa for all experiments. The heating time for each experiment was 45 min and the reaction time was set at zero when the temperature reached 673 K. Phase separation for the liquid phase was not observed for the only heating up (0 h) and 1 h experiments, whereas the experiments at prolonged reaction times resulted in the formation of two liquid phases after reaction, a clear water phase and a dark-brown oil phase. An additional experiment was performed at 1.5 h, and here a biphasic system was also obtained, indicating that phase separation occurs for products made between 1 and 1.5 h reaction time. Apparently, after this batch time, sufficient soluble apolar molecular weight components are formed that lead to the formation of a separate apolar organic phase.

The mass balances for each reaction are given in Fig. 6a. The lignin oil yield is highest after heating up the reactor to reaction temperature (92% mass on lignin intake), and steadily reduces to 70% mass on lignin intake after 6 h, see Fig. 6b.

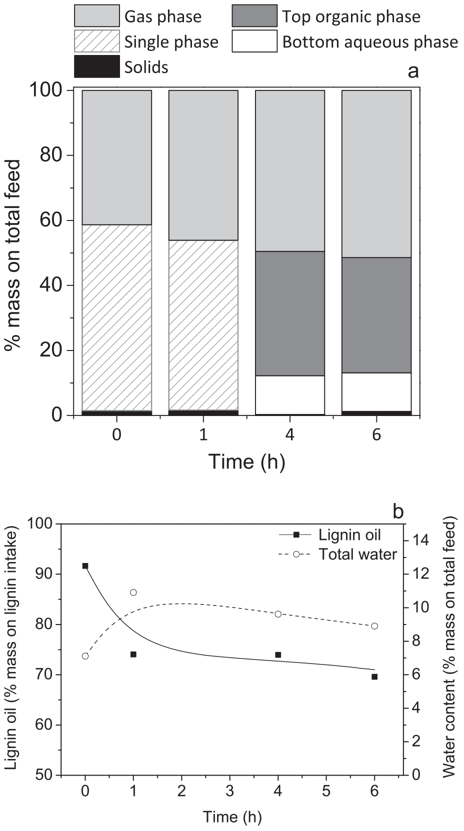


Fig. 6 – a) Mass balance results for catalytic solvolysis experiments at different batch time (27.6% mass of Alcell® lignin, 1.4% mass of Ru/C on total feed, 71% mass FA and IPA in a 1:1 mass ratio, 673 K, gas formation was not measured and is taken as the difference), b) lignin oil and total water on lignin intake.

A significant amount of water is formed, particularly during the first hour of reaction (Fig. 6b), likely by hydro(-deoxy) genation reactions of various oxygenated molecules in the reaction mixture. The amount of solids present after reaction is low (<6% mass on lignin intake) and remains about constant, an indication that repolymerisation does not occur to a significant extent, even at prolonged reaction times. These findings indicate that lignin depolymerisation and other main reaction pathways (e.g. hydrodeoxygenation) occur in the initial stage of the reaction. In line with these findings is the

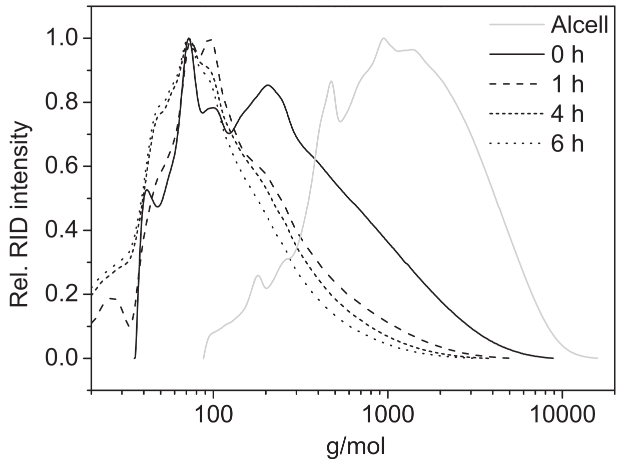


Fig. 7 – Molecular weight distribution of the organic products from catalytic solvolysis at different reaction times (1:1 mass ratio FA and IPA, 1.4% mass Ru/C on total feed, 673 K, 20 MPa pressure at reaction temperature).

Table 5 – Gas composition of the catalytic solvolysis at different batch times.

Reaction time (h)	0	1	4	6
Gas phase, mol fractions (dry basis)%				
Carbon dioxide	54.6	53.6	54.1	54.0
Carbon monoxide	8.3	7.6	4.8	4.8
Ethane	0.5	0.8	1.0	1.3
Propylene	0.5	3.7	1.0	0.8
Propane	4.3	7.5	11.1	12.1
Hydrogen	28.7	21.7	21.4	19.7
Methane	3.2	5.0	6.5	7.0

Reaction performed with 27.6% mass of Alcell® lignin, 1.4% mass of Ru/C on total feed, in a 71% mass mixture of FA and IPA (1:1 mass ratio) at 673 K.

molecular weight development as a function of the batch time (Fig. 7). Clearly, molecular weight breakdown also takes place mainly in the initial stage of the reaction.

The amount of gas phase components slightly increases in time (Fig. 6). This is likely due to catalytic reactions involving the solvent/hydrogen donor FA and IPA (Scheme 2). In addition, the gas phase composition is also changing in time (Table 5), and the amount of methane and particularly propane increases over time. Methane formation may be related to both lignin reactivity (e.g. hydrogenolysis of OMe groups) as well as by various gas phase hydrogenation reactions (Scheme 2). Propane formation may be due to IPA dehydration to propene and subsequent hydrogenation of propene to propane.

The product composition of the organic phase after reaction was determined using GCxGC-FID and the results are given in Fig. 8. It clearly shows an optimum for guaiacols and catechols and an increase in aromatics and alkanes in time. This is in line with the anticipated deoxygenation pathways as given in the reaction network in Scheme 2.

The elemental composition of the lignin oils obtained at various batch times was determined and a graphical representation is given in a van Krevelen plot (Fig. 9a).

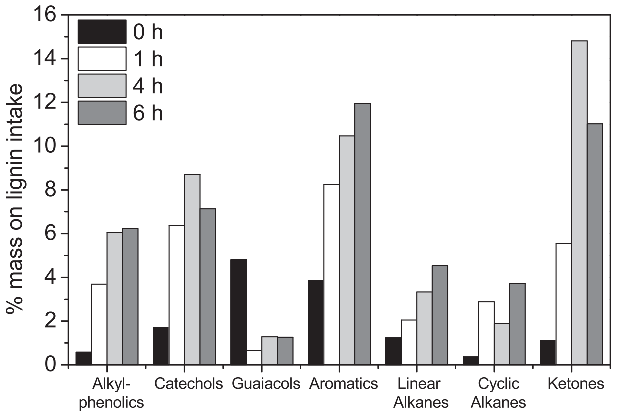


Fig. 8 – Product distribution of catalytic solvolysis at different batch times by GCxGC (27.6% mass of Alcell® lignin, 1.4% mass of Ru/C on total feed, 71% mass of FA and IPA in a 1:1 mass ratio, 673 K).

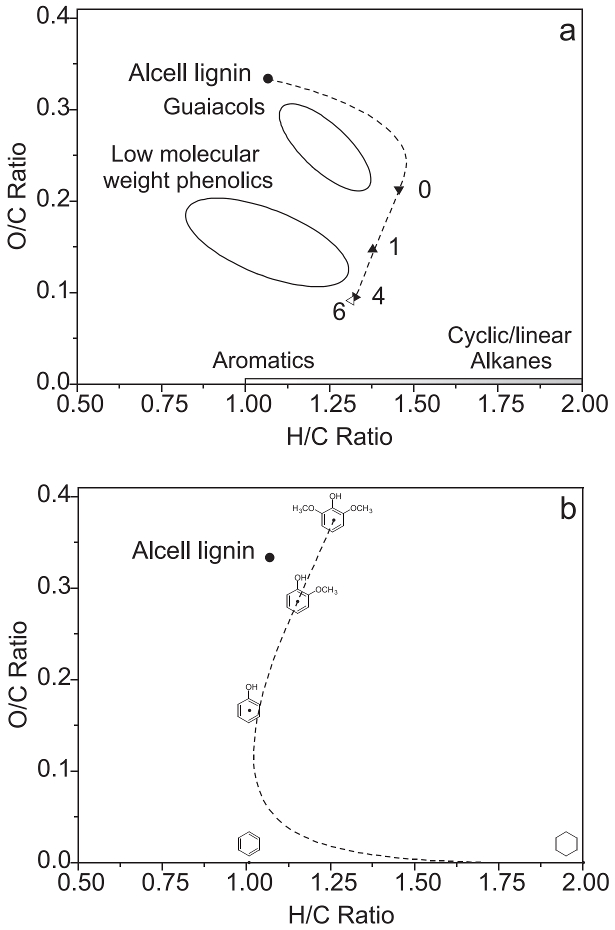
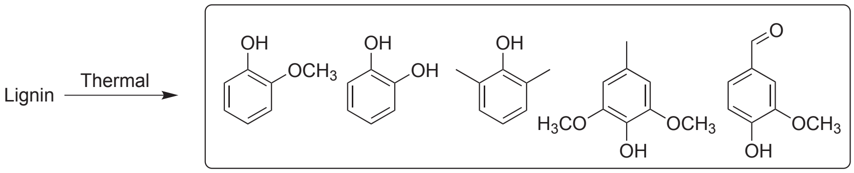


Fig. 9 – a) van Krevelen plot for the catalytic solvolysis at different batch times (71% mass 1:1 mass ratio of FA and IPA, 1.4% mass Ru/C on total feed and 673 K, b) theoretical hydrotreatment line of syringol towards phenolics, aromatics, and cyclic alkanes.

Here, the atomic H/C ratio is plotted on the x-axis and the O/C ratio on the y-axis. In addition, typical ranges for product classes are given (Table 4). Clear trends are visible. In the heating phase, the H/C ratio increases from about 1 for Alcell® lignin to 1.5 for the lignin oil. A similar trend was observed by Xu et al. for switch grass lignin solvolysis in ethanol with Pt/C as the catalyst (see Table 1) [24]. In addition, the O/C ratio is lowered from 0.21 to 0.09. This trend is indicative for the occurrence hydrogenation reactions in combination with oxygen removal reactions, most associated with water and methanol formation. The initial phase of the reaction likely involves depolymerisation of lignin to low molecular weight fragments followed by subsequent conversions. This reaction may either by thermally or catalytically, in the latter case involving hydrogenolysis of ether bonds to monomers and lower molecular weight lignin fragments. Well known monomeric decomposition products of the thermal decomposition of lignin are catechols, phenolics, guaiacols, and syringols with various side chains [40]. For instance, de Wild et al. performed pyrolysis experiments (673 K) using Alcell® lignin and observed the formation of 13% mass on lignin intake of organic condensables with 2-methoxyphenol, 2,6-dimethylphenol, 4-methylsyringol, catechol, and vanillin as the main components (Scheme 3) [27]. The initial steps in the



Scheme 3 – Conversion of organosolv lignin by pyrolysis to pyrolytic lignin oil [27].

catalytic breakdown of lignin may, besides hydrogenolysis of lignin–ether bonds, also involve the hydrogenation of reactive aldehydes and ketone groups to alcohols, leading to products with a higher H/C ratio.

For longer batch times, both the H/C and the O/C ratio decrease considerably. It suggests the occurrence of mainly oxygen removal reactions. This is in line with the composition of the lignin phase versus batch time as found by GCxGC-FID analyses, implying the conversion of tri-oxygenated (syringols) and di-oxygenated catechols/guaiacols to mono-oxygenated alkylphenolics. For the latter, two pathways can be envisaged based on model component studies [7], i) demethoxylation to phenol, or ii) a two-step sequence consisting of demethylation to catechol and methane followed by hydrodeoxygenation to phenol and water (Scheme 4).

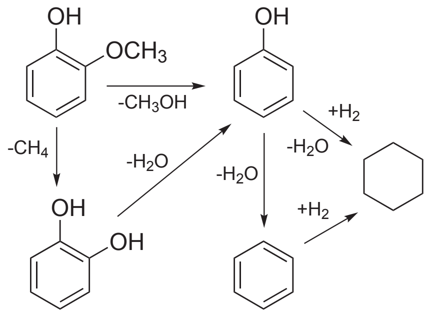
The presence of catechols in the reaction mixture (Fig. 8) suggests that the two step pathway occurs to a significant extent.

In Fig. 9b, the theoretical conversion line of syringol to cyclohexane via guaiacol, phenol, and benzene is provided in the form of a van Krevelen plot. The slope of the line is close to that observed experimentally, though shifted to lower H/C values. The latter is likely due to the presence of alkyl substitution of the aromatic rings (Table 4) in the lignin oil that will shift the curve to higher values. These strong similarities in slopes indicate that the chemistry occurring in the lignin oil is related to that for the model systems and involves i) methoxy removal from aromatic rings by either demethylation or demethoxylation and the formation of water, methanol, and methane and ii) aromatic OH removal by hydrodeoxygenation and the formation of water (Scheme 4).

4.3.2. *Solvent effects*

Previous research from Kleinert et al. showed that the solvent has a major influence on the product distribution in the organic product phase [17]. To probe solvent effects for catalytic solvolysis of Alcell® lignin with Ru/C, two other alcohols were tested in combination with FA and Ru/C, namely methanol, and ethanol. The experiments were performed with 27.6% mass of lignin intake on solvent and a 71% mas of 1:1 mass ratio of alcohol–FA (673 K, for 4 h, with 1.4% mass of Ru/C on total feed). After reactions, two liquid phases were observed for both alcohols, a dark brown organic phase on top of a clear water phase, similar as earlier observed for isopropanol. The product distributions for the three alcohols are provided in Table 6.

For methanol, the highest amount of lignin oil was obtained (68% mass, versus 63% mass yield on lignin intake for ethanol). Lower yields for ethanol are associated with a higher solids yield (5.2 versus 1.6% mass on total feed for methanol). Thus, from a yield perspective, methanol appears a better choice than ethanol. The yield data for methanol are close to those for isopropanol.



Scheme 4 – Conversion routes forguaiacols to phenol, benzene, and cyclohexane.

Table 6 – Product yields and mass balances for lignin solvolysis with different solvents.[a]

Experiment	1	S2	S3
Lignin	Alcell	Alcell	Alcell
Solvent	IPA/FA	Ethanol/FA	Methanol/FA
Catalyst	Ru/C	Ru/C	Ru/C
Top organic phase, % mass on total feed	38.2	35.8	29.6
Bottom aqueous phase, % mass on total feed	11.9	8.5	29.8
Solids (acetone insoluble), % mass on total feed	0.3	5.2	1.6
Water formation, % mass on total feed[b]	9.6	8.1	12.7
Gas phase, % mass on total feed	n.d.	n.d.	n.d.
Gas phase, mol fractions (dry basis) %			
Carbon dioxide	54.1	44	48.6
Carbon monoxide	4.8	13.8	10.9
Ethane	1.0	10.6	1.9
Propylene	1.0	0.1	1.2
Propane	11.1	1.3	7.9
Hydrogen	21.4	15.3	22.5
Methane	6.5	5.0	7.0
Lignin oil, % mass on lignin intake[c]	71.2	63.4	68.4
Elemental composition lignin oil (% mass, dry basis)			
Carbon	80.76	79.7	81.85
Hydrogen	10.16	8.98	8.72
Oxygen	8.94	11.2	9.33

[a] Reactions performed with 27.6% mass of Alcell® lignin intake, 1.4% mass of Ru/C on total feed, in a mixture of FA and solvent (1:1 mass ratio) at 673 K for 4 h.
[b] Total amount of water formed during reaction.
[c] Oil yield after removal of the solvent from the top organic phase by evaporation.

The gas composition after reaction is also remarkably different for the three alcohols. For ethanol, considerable higher amounts of ethane and lower amounts of hydrogen are present. This is indicative for dehydration to ethylene followed by hydrogenation to ethane. This reaction lowers the effective hydrogen concentration in the gas phase and will lead to lower hydro(-deoxy)genation rates. As such it may be the explanation for the higher amounts of solids present after reaction when using ethanol. Thus, in ethanol, the rate of hydro(-deoxy)genation reactions involving lignin is reduced and repolymerisation takes place to a larger extent ultimately leading to solids.

The molecular weight distribution of the organic phase after reaction for the different solvents is given in Fig. 10. For all solvents, a clear reduction in molecular weight is observed compared to the Alcell® lignin feed.

The elemental composition of the lignin oil for the three alcohols after reaction shows only minor differences. Of interest is the slightly higher oxygen content for ethanol, again indicating that the rate of hydro(-deoxy)genation reactions in ethanol is lightly lower than for the other alcohols, presumably due to an on average lower hydrogen partial pressure in the reactor due to hydrogen usage for the conversion of ethanol to ethane.

The product composition of the product oils for all alcohols is given in Fig. 11. Of particular interest is a higher aromatics (19% mass on lignin intake) and alkylphenolics yield (11% mass on lignin intake) for methanol, the most valuable and desired compounds. These values are considerably higher than for isopropanol and ethanol. So far, a sound explanation for the higher amounts of aromatics and alkylphenolics in methanol than in the other alcohols is lacking. A possibility is the formation of significant amounts of ring alkylated products, in this case with methyl substituents, which has been reported for catalytic solvolysis [41,42]. These ring alkylated products are expected to affect the rates of the various reaction pathways in Scheme 2, though it is not clear yet to which extent. Given the fact that methanol is also considerably cheaper than ethanol and isopropanol, this solvent appears to be the solvent of choice for the catalytic solvolysis of lignin.

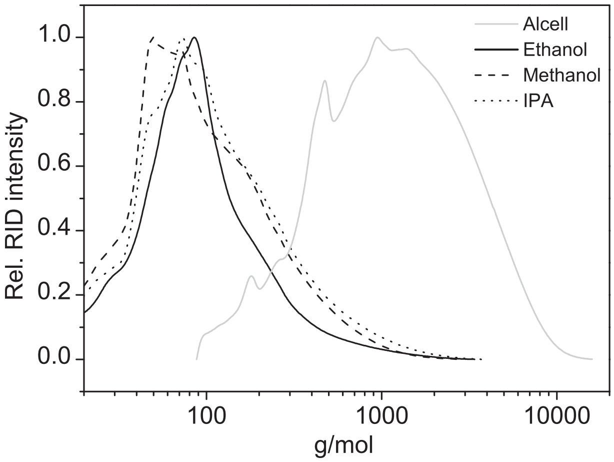


Fig. 10 – Molecular weight distribution of the catalytic solvolysis at different reaction temperatures with 27.6% mass of Alcell® lignin, 1.4% mass of Ru/C on total feed, in a 71% mass mixture of FA and alcohol in a 1:1 mass ratio for 4 h.

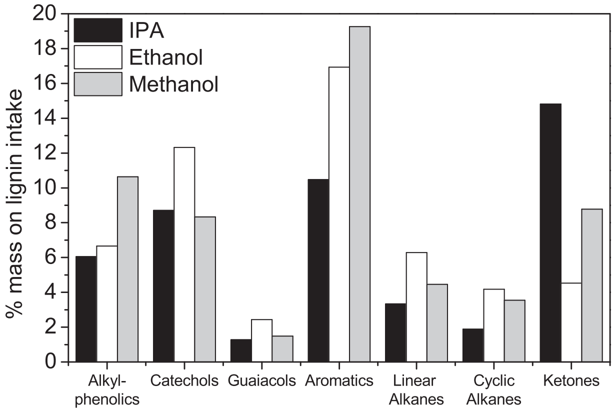


Fig. 11 – Product composition of the catalytic solvolysis at different reaction temperatures with 27.6% mass of Alcell® lignin, 1.4% mass of Ru/C on total feed, in a 71% mass mixture of FA and alcohol in a 1:1 mass ratio for 4 h.

5. Conclusions

The catalytic solvolysis of Alcell® lignin in IPA using formic acid as the hydrogen donor and Ru/C as the catalyst was investigated and the results were compared with a non-catalytic solvolysis and a catalytic hydrotreatment with molecular hydrogen. Catalytic solvolysis resulted in the highest oil yield (71.2% mass yield on lignin intake), the lowest O/C ratio of the lignin oil (0.09), and highest yield in valuable chemical compounds (alkylphenolics (6% mass on lignin intake), and aromatics (10.5% mass on lignin intake)). The product compositions were determined using GCxGC-FID, a powerful technique for the analyses of complex organic matrices with hundreds of compounds belonging to various compound classes. Further improvements regarding the catalytic solvolysis methodology was obtained by using methanol as the solvent, which resulted in reduced O/C values (0.085), and a further increase in alkylphenolics (10.6% mass on lignin intake) and aromatics yield (19.2% mass on lignin intake) compared to isopropanol. Further techno-economic evaluation is required to determine the potential of catalytic solvolysis in methanol/FA mixtures compared to a catalytic hydrotreatment using molecular hydrogen.

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REFERENCES

[1] Balat M, Balat H, Oz C. Progress in bioethanol processing. Prog Energy Combust Sci 2008;34(5):551–73.

[2] Atabani AE, Silitonga AS, Badruddin IA, Mahlia TMI, Masjuki HH, Mekhilef S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. Renew Sust Energy Rev 2012;16(4):2070–93.

[3] Bozell JJ. Feedstocks for the future – biorefinery production of chemicals from renewable carbon. CLEAN-Soil Air Water 2008;36(8):641–7.

[4] Dickerson T, Soria J. Catalytic fast pyrolysis: a review. Energies 2013;6(1):514–38.

[5] Gosselink RJA, de Jong E, Guran B, Abacherli A. Co-ordination network for lignin - standardisation, production and applications adapted to market requirements (EUROLIGNIN). Ind Crops Prod 2004;20(2):121–9.

[6] Amen-Chen C, Pakdel H, Roy C. Production of monomeric phenols by thermochemical conversion of biomass: a review. Bioresour Technol 2001;79(3):277–99.

[7] Zakzeski J, Bruijnincx PCA, Jongerius AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. Chem Rev 2010;110(6):3552–99.

[8] Thring RW. Alkaline-degradation of Alcell® lignin. Biomass Bioenergy 1994;7(1–6):125–30.

[9] Roberts VM, Stein V, Reiner T, Lemonidou A, Li X, Lercher JA. Towards quantitative catalytic lignin depolymerization. Chem Eur J 2011;17(21):5939–48.

[10] Thring RW, Katikaneni SPR, Bakhshi NN. The production of gasoline range hydrocarbons from Alcell® lignin using HZSM-5 catalyst. Fuel Process Technol 2000;62(1):17–30.

[11] Pepper JM, Hibbert H. Studies on lignin and related compounds. LXXXVII. High pressure hydrogenation of maple wood. J Am Chem Soc 1948;70(1):67–71.

[12] Pepper JM, Lee YW. Lignin and related compounds. I. A comparative study of catalysts for lignin hydrogenolysis. Can J Chem 1969;47(5):723–7.

[13] Pepper JM, Lee YW. Lignin and related compounds. 2. Studies using ruthenium and Raney nickel as catalysts for lignin hydrogenolysis. Can J Chem 1970;48(3):477.

[14] Oasmaa A, Johansson A. Catalytic hydrotreating of lignin with water-soluble molybdenum catalyst. Energy Fuels 1993;7(3):426–9.

[15] Huibers DTA, Parkhurst HJ, inventors. Hydrocarbon research Inc., Assignee. Lignin Hydrocracking Process to Produce Phenol and Benzene; 1983. United States Patent US 4420644; 1983 Dec 13.

[16] Huibers DTA, Jones MW. Fuels and chemical feedstocks from lignocellulosic biomass. Can J Chem Eng 1980;58(6):718–22.

[17] Kleinert M, Barth T. Towards a lignincellulosic biorefinery: direct one-step conversion of lignin to hydrogen-enriched biofuel. Energy Fuels 2008;22(2):1371–9.

[18] Kleinert M, Barth T. Phenols from lignin. Chem Eng Technol 2008;31(5):736–45.

[19] Liguori L, Barth T. Palladium–Nafion SAC-13 catalysed depolymerisation of lignin to phenols in formic acid and water. J Anal Appl Pyrolysis 2011;92(2):477–84.

[20] Loges B, Boddien A, Gaertner F, Junge H, Beller M. Catalytic generation of hydrogen from formic acid and its derivatives: useful hydrogen storage materials. Top Catal 2010;53(13–14):902–14.

[21] Kleinert M, Gasson JR, Eide I, Hilmen A, Barth T. Developing solvolytic conversion of lignin-to-liquid (LtL) fuel components: optimization of quality and process factors. Cellul Chem Technol 2011;45(1–2):3–12.

[22] Kleinert M, Gasson JR, Barth T. Optimizing solvolysis conditions for integrated depolymerisation and hydrodeoxygenation of lignin to produce liquid biofuel. J Anal Appl Pyrolysis 2009;85(1–2):108–17.

[23] Gasson JR, Forchheim D, Sutter T, Hornung U, Kruse A, Barth T. Modeling the lignin degradation kinetics in an ethanol/formic acid solvolysis approach. Part 1. Kinetic model development. Ind Eng Chem Res 2012;51(32):10595–606.

[24] Xu W, Miller SJ, Agrawal PK, Jones CW. Depolymerization and hydrodeoxygenation of switchgrass lignin with formic acid. ChemSusChem 2012;5(4):667–75.

[25] Wildschut J, Iqbal M, Mahfud FH, Melian-Cabrera I, Venderbosch RH, Heeres HJ. Insights in the hydrotreatment of fast pyrolysis oil using a ruthenium on carbon catalyst. Energy Environ Sci 2010;3(7):962–70.

[26] Wildschut J, Melian-Cabrera I, Heeres HJ. Catalyst studies on the hydrotreatment of fast pyrolysis oil. Appl Catal B Environ 2010;99(1–2):298–306.

[27] de Wild P, Van der Laan R, Kloekhorst A, Heeres HJ. Lignin valorisation for chemicals and (transportation) fuels via (catalytic) pyrolysis and hydrodeoxygenation. Environ Prog Sustain Energy 2009;28(3):461–9.

[28] Burgess CE, Clifford DJ, Horvath JR. Catalytic effect of carbon-supported ruthenium on the depolymerization of hydrolytic lignin. Preprint Pap Am Chem Soc Div Fuel Chem 2002;47(1):376–9.

[29] Gosselink RJA, Abacherli A, Semke H, Malherbe R, Kauper P, Nadif A, et al. Analytical protocols for characterisation of sulphur-free lignin. Ind Crop Prod 2004;19(3):271–81.

[30] Baumberger S, Abaecherli A, Fasching M, Gellerstedt G, Gosselink R, Hortling B, et al. Molar mass determination of lignins by size-exclusion chromatography: towards standardisation of the method. Holzforschung 2007;61(4):459–68.

[31] Wildschut J, Mahfud FH, Venderbosch RH, Heeres HJ. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Ind Eng Chem Res 2009;48(23):10324–34.

[32] Venderbosch RH, Ardiyanti AR, Wildschut J, Oasmaa A, Heeres HJ. Stabilization of biomass-derived pyrolysis oils. J Chem Technol Biotechnol 2010;85(5):674–86.

[33] Columbia M, Thiel P. The interaction of formic-acid with transition-metal surfaces, studied in ultrahigh-vacuum. J Electroanal Chem 1994;369(1–2):1–14.

[34] Shukry N, Fadel SM, Agblevor FA, EI-Kalyoubi SF. Some physical properties of acetosolv lignins from bagasse. J Appl Polym Sci 2008;109(1):434–44.

[35] Jimenez V, Sanchez P, Panagiotopoulou P, Luis Valverde J, Romero A. Methanation of CO, CO_2 and selective methanation of CO, in mixtures of CO and CO_2, over ruthenium carbon nanofibers catalysts. Appl Catal Gen 2010;390(1–2):35–44.

[36] Marsman JH, Wildschut J, Mahfud F, Heeres HJ. Identification of components in fast pyrolysis oil and upgraded products by comprehensive two-dimensional gas chromatography and flame ionisation detection. J Chromatogr A 2007;1150(1–2):21–7.

[37] Marsman JH, Kloekhorst A, Rohrbach L, Heeres HJ. Product characterization of hydro-deoxygenated lignin (lignin oil) by comprehensive two-dimensional gas chromatography and evaluation of a simulation technique to construct

contourplots for apolar–polar and polar–apolar column sets, in preparation.

[38] Talwalkar S, Mahajani S. Synthesis of methyl isobutyl ketone from acetone over metal-doped ion exchange resin catalyst. Appl Catal Gen 2006;302(1):140–8.

[39] Zhao C, Kou Y, Lemonidou AA, Li X, Lercher JA. Hydrodeoxygenation of bio-derived phenols to hydrocarbons using RANEY® Ni and Nafion/SiO_2 catalysts. Chem Commun 2010;46(3):412–4.

[40] Brebu M, Vasile C. Thermal degradation of lignin – a review. Cellul Chem Technol 2010;44(9):353–63.

[41] Warner G, Hansen TS, Riisager A, Beach ES, Barta K, Anastas PT. Depolymerization of organosolv lignin using doped porous metal oxides in supercritical methanol. Bioresour Technol 2014;161(0):78–83.

[42] Huang X, Koranyi TI, Boot MD, Hensen EJM. Catalytic depolymerization of lignin in supercritical ethanol. ChemSusChem 2014;7(8):2276–88.