

Catalytic Hydrotreatment of Alcell Lignin Using Supported Ru, Pd, and Cu Catalysts

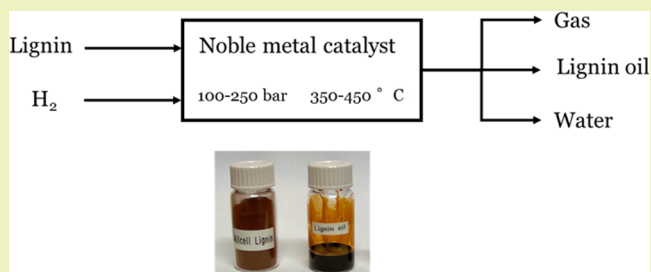
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Supporting Information

ABSTRACT: A catalyst screening study on the catalytic hydrotreatment of Alcell lignin in a batch setup was performed using supported Ru (C, Al₂O₃/TiO₂), Pd (C, Al₂O₃), and a Cu/ZrO₂ catalyst with the objective to determine the best catalyst for high yields of biobased aromatics and alkylphenolics. Experiments were performed at 400 °C, 4 h reaction time and an initial hydrogen pressure of 100 bar. Best results were obtained with Ru/TiO₂ and a lignin oil (78 wt % on lignin intake) with 9.1 wt % alkylphenolics, 2.5 wt % aromatics, and 3.5 wt % catechols on lignin intake were obtained. The reaction products were characterized using advanced GC×GC-FID and GC×GC-TOFMS techniques in combination with GPC, ¹³C NMR, and GC-MS-FID measurements. Systematic studies with the Ru/C catalysts using variable batch times (0–8 h, 400 °C, and an initial hydrogen pressure of 100 bar) gave insights in the reaction pathways occurring during the catalytic hydrotreatment and these include depolymerization, hydrogenation, hydrodeoxygenation, and dehydration reactions.

KEYWORDS: Lignin, Aromatics, Phenolics, Heterogeneous catalyst, Ruthenium, Palladium, Copper



INTRODUCTION

Lignocellulosic biomass is a promising alternative to replace fossil resources for carbon based transport fuels (e.g., bioethanol, biodiesel) and biobased chemicals.^{1–4} Major breakthroughs have been realized in the past decade for the conversion of carbohydrates from lignocellulosic biomass sources (cellulose and hemicellulose). Examples are the development of second generation biofuels (bioethanol from lignocellulosic biomass, (upgraded) pyrolysis oils) and biobased chemicals (lactic acid, succinic acid, levulinic acid, and derivatives). However, valorization of lignin, the third major biopolymer in lignocellulosic biomass, is still in a state of infancy, the major product outlet being the use as a fuel in, e.g., paper mills. Because of its aromatic nature (Figure S1, Supporting Information), lignin is expected to serve as an excellent starting material for the synthesis of aromatics and alkylphenolics, which are important chemical intermediates in the petrochemical industry with a value exceeding 800 euro/ton.^{5,6} Several methodologies have been developed to depolymerize lignin to more valuable monomeric compounds, examples are enzymatic conversions (lignin peroxidases),^{7,8} thermal depolymerization (pyrolysis),⁵ base assisted depolymerization,^{9,10} and oxidative depolymerization.^{11,12} An alternative upgrading technology for lignin involves catalytic hydrotreatment using molecular hydrogen in combination with a supported metal catalyst. An overview of studies on the catalytic hydrotreatment of lignin is given in Table 1. Typically, harsh conditions are employed, viz. temperatures between 170 and 450 °C and pressures between 34 and 360 bar. The product oil yield ranges from 10 to 100%, depending on

catalyst and reaction conditions. The exact chemical composition of the oil is often not given, and this hampers the identification of the best catalyst systems to obtain high aromatics and alkylphenolics yields.

The majority of the research has been performed in a solvent. In most cases, the solvent is not inert under the harsh reaction conditions giving rise to a more complex reaction mixture. In addition, the solvent may also react with lignin fragments or monomers (e.g., alkylation reactions) or serve as an additional hydrogen source (e.g., ethanol, tetralin, formic acid). This seriously complicates product analyses and mass balance closures. A limited number of solvent free approaches have been reported. In these cases, molten lignin acts as the initial solvent, later diluted with low molecular weight lignin products when the reactions are carried out in batch. For instance, Oasmaa et al. reported the use of (non-) sulfided NiMo catalysts on supports for the catalytic hydrotreatment of different lignin sources at elevated temperatures (395–430 °C) and pressures (90–101 bar H₂) in the absence of a solvent.²¹ The highest oil yield was obtained with an organosolv lignin at 400 °C for a reaction time of 30 min with sulfided NiMo on Cr₂O₃/Al₂O₃ (1:1) as the catalyst. Highest yields of aromatics and phenolics on lignin intake were 10.8 and 9.4 wt %, respectively. Meier et al. screened various catalysts (Pd/C, red mud, Raney Nickel, and NiMo on several supports) for the catalytic hydrotreatment of an organosolv lignin in the absence

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Table 1. Overview of Research on the Catalytic Hydrotreatment of Lignins

feed	solvent	catalyst	T (°C)	t (min)	P (bar)	major products	yield ^a (wt % on lignin intake)			ref
							oil	Ph.	Ar.	
ethanol extracted aspen lignin	dioxane	Cu–CrO	250–260	1080	200–350	cyclohexanols	70	NR	NR	13
maple/spruce wood lignin	dioxane:water 1:1 NaOH (3%)	Cu–CrO, Raney Ni, Pd/C, Rh/C, Ru/C, Ru/Al ₂ O ₃	170–250	300–360	34–200	lignin monomers	13–27	NR	NR	14–16
indulin AT lignin	phenolics tetralin, cat. cracker bottom	Ni–W/SiO ₂ –Al ₂ O ₃ (PO ₄)	300–450	30–60	35–240	cresols, xylenols	77–100	1–5	NR	17
organosolv lignin	1-methyl-naphthalene	Ni/Mo, Co/Mo/Al ₂ O ₃ (S)	404–428	60	70	phenol (~30%), cresols (~40%)	51–90	2–10	NR	18
rye straw lignin	tetralin	red mud (S), CoMo γ -Al ₂ O ₃	400	240	150	NR	75–78	18–21	NR	19
multiple lignin sources		Fe ₂ O ₃ , Raney Ni, Pd/C, NiMo on various supports	350–450	0–120	30–120	phenolics	15–81	6–16	NR	20
multiple lignin sources		Ni/Mo on Cr ₂ O ₃ and alumina	395–430	20–60	90–100	aromatics, phenolics	50–65	4.7–9.4	5.6–10.8	21
BCD lignin	alcohol water mixture	CoMo/Al ₂ O ₃ , NiMo, NiW (S)	350–385		100–150	alkylphenolics/aromatics	≈70	NR	>30	22, 23
white birch lignin	water, dioxane	H ₃ PO ₄ , Ru/C, Pd/C, Rh/C, Pt/C	200	240	40	synglypropanolguaiacylpropanol	NR	NR	5–46	24
pyrolytic alcell lignin oil	dodecane	Ru/C	350	120	100	cyclic alkanes, alkylated cyclohexanols, linear/branched alkanes	NR	NR	NR	25
organosolv cornstalk lignin	65% vol ethanol–water	Ru/C, Pt/C, Pd/C	225–300	30–180	20	alkylated phenolics, guaiacols, syringols	NR	NR	NR	26, 27
alkali lignin	1:1 ethanol–water	Ru/Al ₂ O ₃ , Pt/C, Ru/C, Ni/Al ₂ O ₃ , Ni/C	200–325	15–360	50	alkylphenolics	NR	NR	NR	28
olive tree organosolv lignin frac.	formic acid	10% Ni, AISBA15	200	30		syngaldehyde, desaspidinol	10–35	NR	NR	29
organosolv lignin	ethanol	Ru/Al ₂ O ₃ , Ni/C	300–350	120	50		33–95	NR	NR	30

^aPh., phenolics; Ar., aromatics; NR, not reported.

of a solvent.²⁰ The highest oil yield (80.6%) was obtained for Pd/C (380 °C, 100 bar initial H₂ pressure, 15 min reaction time). The main compounds in the lignin oil from Pd/C were methyl-, ethyl-, and propylcyclohexanones and minor amounts of phenols, guaiacols, and catechols (2.4 and 5.8 wt % on lignin intake, respectively).

In this study, we report a systematic catalyst screening study in a batch reactor setup for the catalytic hydrotreatment of a typical organosolv lignin (Alcell) in the absence of a solvent with the objective to obtain high yields of monomeric alkylphenolics and aromatics. All catalytic reactions were carried out under similar conditions, allowing a proper comparison between the catalysts. Several commercially available supported noble metal catalysts (Ru and Pd) and a Cu on zirconia catalyst, prepared in our laboratory, were screened. The resulting product oils were characterized using various analytical techniques (GC×GC-FID, GC×GC-TOFMS, GPC, and GC-MS-FID) to determine the chemical composition of the lignin oils. Finally, for a selected catalyst (Ru/C), the effect of reaction time on product composition was established to (i) determine the optimum reaction time to obtain high yields of aromatics/alkylphenolics and (ii) to gain insights in reaction pathways during the catalytic hydrotreatment of lignins.

■ EXPERIMENTAL SECTION

Chemicals. The catalysts Ru/C, Ru/Al₂O₃, Pd/Al₂O₃, and Pd/C (all 5 wt % metal loading, powder) were obtained from Sigma-Aldrich. Ru/TiO₂ (5 wt % metal loading, powder) was obtained from Degussa. Cu/ZrO₂ (32 wt % metal loading) was prepared by an incipient wetness impregnation using powdered zirconia and Cu(NO₃)₂ in water. The catalyst was subsequently calcined for 5 h at 500 °C. Cu(NO₃)₂ was obtained from Sigma-Aldrich; zirconia pellets were supplied by BASF and crushed and sieved before use. Hydrogen and nitrogen gases were obtained from Hoekloos and were both of analytical grade (>99.9999%). Alcell lignin was supplied by the Wageningen University and Research Center, relevant properties are given in Table S1 (Supporting Information).

Catalytic Hydrotreatment Experiments. The catalytic hydrotreatment reactions were performed in a stainless steel (14S71) batch autoclave (Buchi, 100 mL). The autoclave has a maximum operation temperature of 400 °C and a pressure of 350 bar. The reactor is surrounded by a metal block containing electrical heating elements and channels allowing the flow of cooling water. The reactor content was stirred mechanically using a Rushton type turbine with a gas induced impeller. Temperature and pressure were monitored online and logged on a PC.

The reactor was filled with lignin (15 g) and catalyst (0.75 g catalyst, 5 wt % on lignin intake) and subsequently flushed with hydrogen and pressurized to 120 bar at room temperature for leak testing. After the leak test, the pressure was reduced to the required initial hydrogen pressure (100–125 bar). Stirring was started (1200 rpm) and the reactor content was heated to 400 °C with a rate of about 8 °C min⁻¹. The reaction time was set at zero when the reaction temperature (400 °C) was reached. The reactions were performed in a batch mode without hydrogen supply during an experiment. The pressure and temperature profile were recorded during the reactions. After the predetermined reaction time, the reactor was cooled to room temperature with a rate of about 10 °C min⁻¹. The pressure at room temperature was recorded to determine the amount of gas phase components produced during reaction. Subsequently, the pressure was released to atmospheric pressure and the gas phase was collected in a 3 L Tedlar gasbag to determine the composition. The liquid product was collected and weighed. In most cases, the liquid phase consisted of an organic layer and an aqueous layer which were separated by decanting. The water content in each phase was determined using a Karl Fischer titration. The reactor was rinsed several times with acetone and the

combined acetone fractions were filtered and collected. After evaporation of the acetone overnight at room temperature, the weight of the remaining liquid was measured and added to the organic product phase.

Liquid Phase Analyses. Details regarding the liquid phase analyses by GC-MS-FID, GC×GC-FID, elemental analyses, TOC, and water determinations are given in ref 34.

The identification of main GC×GC component groups (e.g., alkanes, aromatics, alkylphenolics) in the lignin oils was done by spiking with representative model compounds for the component groups, GC-MS-FID analysis, and GC×GC-TOFMS analysis for a representative sample (see the Supporting Information). Quantification was performed by using an average relative response factor (RRF) per component group with di-*n*-butyl ether (DBE) as the internal standard. For instance, for the alkylphenolics group the average RRF was determined by determination of the RRF values for 5 representative model components (phenol, 4-ethylphenol, 4-methylphenol, 4-propylphenol, and 2,3 dimethylphenol). This procedure was followed for each component group and a minimum of 3 model components were used to determine the average RRF. More information about the calibration of the GC×GC-FID spectra is provided in the Supporting Information.

For enhanced product identification, GC×GC-TOFMS was performed on the lignin oil sample obtained from the hydrotreatment of Alcell lignin at 400 °C with Ru/TiO₂ (5 wt % on lignin intake), 4 h reaction time and 100 bar initial H₂ pressure. The sample was analyzed on a GC×GC-HR TOFMS from JEOL equipped with a cryogenic trap system and two columns: a RTX-1701 capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness) connected by a Meltfit to a Rxi-5Sil MS column (120 cm × 0.15 mm i.d. and 0.15 μm film thickness). A TOFMS JMS-T100GCV 4G detector was used with a scanning speed of 50 Hz with a mass range of 35–600 *m/z*. Helium was used as the carrier gas (0.8 mL min⁻¹). The injector temperature and TOFMS temperature were set at 250 °C. The oven temperature was kept at 40 °C for 5 min then heated up to 250 °C at a rate of 3 °C min⁻¹. The pressure was set at 77.5 kPa at 40 °C. The modulation time was 6 s. The MS-spectra plot was analyzed with GC Image software and a homemade Matlab routine. Detailed grouping and examples found through MS identification (>90% hit) for the lignin oil sample is shown in the Supporting Information separated in nonoxygen and oxygen containing groups.

GPC analyses of the lignin oils and the feed were performed on a HP1100 from Hewlett-Packard equipped with three MIXED-E columns (300 × 7.5 mm, PLgel 3 μm) in series and a GBC LC 1240 RI detector. The average molecular weights were determined using the PSS WinGPC Unity software from Polymer Standards Service. The following operating conditions were used: THF as eluent at a flow rate of 1 mL min⁻¹; a pressure of 140 bar, column temperature of 42 °C, an injection volume of 20 μL with sample concentrations of 10 mg mL⁻¹. Toluene was used as a flow marker and polystyrene samples with different molecular weights were used as the calibration standards.

Thermogravimetric analysis (TGA) were determined using a TGA 7 from PerkinElmer. The samples were heated under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹ from 20 °C until 900 °C.

Gas Phase Analysis. The gas phases were collected after reaction and stored in a gasbag (SKC Tedlar 3 L sample bag) with a polypropylene septum fitting. GC-TCD analyses were performed as provided in ref 34.

■ RESULTS AND DISCUSSION

Catalyst Selection. Five noble metal catalysts (Ru/C, Ru/TiO₂, Ru/Al₂O₃, Pd/C, and Pd/Al₂O₃ with 5 wt % metal loading) were tested together with a Cu/ZrO₂ catalyst (32 wt % Cu). Ru and Pd were selected as the metal of choice as both have shown good performance for the catalytic hydrotreatment of lignin model components and pyrolytic lignin.^{15,16,20,25,27,28,31–34} A Cu catalyst was also selected because

Table 2. Overview of Experiments for the Catalytic Hydrotreatment of Alcell Lignin^a

catalyst	Ru/C ^b	Ru/Al ₂ O ₃	Ru/TiO ₂	Pd/C	Pd/Al ₂ O ₃	Cu/ZrO ₂ ^c
organic phase (wt % on lignin intake)	63.9	75.3	78.3	67.5	75.1	71.8
aqueous phase (wt % on lignin intake)	11.4	6.6	— ^d	11.5	— ^d	11.2
gas phase (wt % on lignin intake)	9.2	8.9	10.2	9.3	11	8.8
carbon dioxide (mol %)	14.5	8.7	10.1	13.6	12.4	6.3
carbon monoxide (mol %)	2.2	2.1	2.0	1.6	4.0	2.0
ethylene (mol %)	0.0	0.0	0.0	0.0	0.0	0.0
ethane (mol %)	2.1	2.7	3.7	2.8	4.0	2.1
propylene (mol %)	0.0	0.0	0.0	0.0	0.0	0.0
propane (mol %)	0.9	1.0	1.7	0.8	1.4	0.9
methane (mol %)	23.1	19.2	37.0	23.3	28.2	14.1
hydrogen (mol %)	57.2	66.3	47.6	57.9	49.9	74.6
total mass balance (wt % on lignin intake)	85	91	88	88	86	92
total carbon balance (%)	90	104	106	94	101	98
hydrogen uptake NI/kg lignin	340	290	360	330	340	320
water content organic phase (wt %)	3.6	5.8	7.2	4.8	8.3	3.6
carbon content aqueous phase (wt %)	1.5	2.7	— ^c	3.2	— ^c	2.6
elemental composition organic phase (wt %, dry basis)						
carbon	83.2	88.3	87.3	86.5	87.1	84.6
hydrogen	9.6	8.2	8.6	9.65	8.7	8.2
oxygen	7.2	3.5	3.9	3.65	3.9	7.0

^a400 °C, 4 h, 100 bar H₂ initial pressure, 5 wt % catalyst. ^baverage data for two experiments (see Table S2, Supporting Information for additional data). ^c400 °C, 4 h, 125 bar H₂ initial pressure, 5 wt % catalyst. ^dNo phase separation observed after reaction.

Cu catalysts are known to exhibit unique selectivity for the hydrodeoxygenation of aromatic hydroxyl- and methoxy groups when compared to conventional sulfided Ni, Co, and Mo catalysts and supported noble metal catalysts.³⁵ In addition, Cu on alumina is known to be an active catalyst for the selective depolymerization of lignin dimers. Over hydrogenation of aromatic rings to saturated hydrocarbons is known to be reduced when using certain Cu catalysts.³⁶ Furthermore, the use of relatively cheap Cu catalysts is economically more attractive than the use of noble metal catalysts.

Catalyst Screening Experiments. The catalyst screening experiments were performed in batch using Alcell lignin as the feed in the absence of a solvent. Typically, 5 wt % of the catalyst on lignin intake was used and the reactions were carried out at 400 °C for 4 h with an initial pressure of 100 bar of hydrogen (125 bar for the Cu catalyst). For Cu, a higher pressure was used as an initial experiment at 100 bar lead to substantial amounts of char, resulting in a paste like product after reaction which was impossible to handle and characterize. No external solvents were used and as such the molten lignin acts both as a reactant and solvent. The absence of a solvent is positive regarding product analyses as solvents are often not inert under the harsh reaction conditions and lead to additional products that interfere with the lignin product analyses. After reaction, typically two liquid phases were obtained, an organic dark/brown phase and a transparent yellowish aqueous phase. The only exceptions were experiments with Ru/TiO₂ and Pd/Al₂O₃, where only a single liquid phase was obtained. The gas, organic, and water phase were determined gravimetrically to obtain overall mass balances (Table 2). Only minor amounts of solid residues were observed after reaction. These amounts were too low to allow for proper quantification. Besides one or two liquid phases, also about 10 wt % of gas phase components are formed (*vide infra*).

For comparison, also a blank experiment was performed in the absence of a metal containing catalyst but in the presence of a support (carbon) at standard conditions (400 °C, 4 h, 100 bar

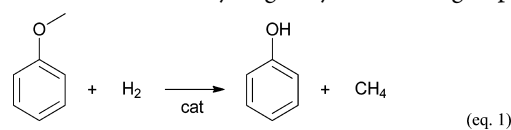
initial H₂ pressure). The main products after reaction were only char (Figure S2, Supporting Information) and gas phase products, which clearly indicates that an active metal is required to obtain a lignin oil.

Mass balance (>85 wt %) and overall carbon balance closures (>90%) were satisfactory. Mass balance closures are not quantitative due to workup losses after reaction. The organic product (lignin oil) yields are between 64 and 78 wt % on lignin intake. The lignin oils still contain significant amounts of water, the exact amount depending whether a single or two liquid phases are formed after reaction. For two phase systems, the water content varies between 3.6–6%, compared to 7–8.5 wt % for the single phase products. Water is typically formed in catalytic hydrotreatment processes of oxygen rich biofeeds by hydrodeoxygenation reactions.³⁷ The aqueous phases also contain limited amounts of carbon (<3.2 wt %), indicative for the presence of some polar organic molecules in the water phase.

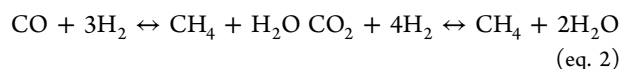
With the C-balances available, the amount of carbon from the feed ending up in the lignin oil can be estimated and are found to be more than 80% in all cases (Figure S3, Supporting Information). Thus, losses of carbon to the water phase and gas phase are limited, and as such, the catalytic hydrotreatment of Alcell lignin has a good carbon efficiency.

COMPOSITION OF THE GAS- AND LIQUID PHASE

Gas Phase Composition. Quantification of the gas phase after reaction shows that considerable amounts (about 10 wt % on lignin intake) of noncondensable gases are formed during the reaction (Table 2). The main components are CH₄ (14–37 mol %), and CO₂ (6–15 mol %). A possible pathway for methane formation is the hydrogenolysis of OMe groups eq. 1.



Another pathway for methane formation involves gas phase reactions of CO/CO₂ with H₂ eq. 2, which are known to be catalyzed by supported Ru catalysts.^{32,37,38}



The CO₂ and CO are likely formed by gasification reactions of various reactive lignin fragments. For instance, it is well-known that Ru catalysts are active for the gasification of Alcell lignin in supercritical water at 400 °C (3.3 wt % Alcell in water).³⁹ Though in our case the water content is much lower, such gasification reactions may also occur to a significant extent. Methane formation is not desired as it both consumes expensive hydrogen gas and reduces the carbon yields and as such should be avoided.

Composition of the Lignin Oils. The elemental compositions of the lignin oils from the catalyst screening study were determined and the results are given in Table 2. A graphical representation is given in a van Krevelen plot in Figure 1. The oxygen content of the lignin oils after catalytic

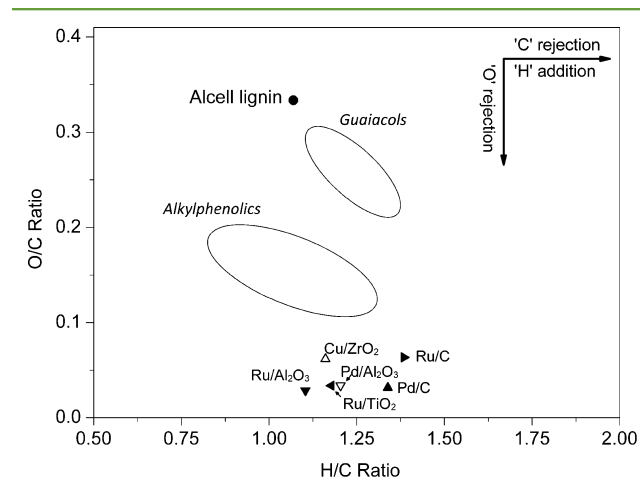


Figure 1. Van Krevelen plot for the catalytic hydrotreatment of Alcell lignin with various catalysts (400 °C, 4 h). Circles represent typical component classes, e.g., alkylphenolics (phenol, methylphenol, ethylphenol) and guaiacols (guaiacol, methylguaiacol, ethylguaiacol).

hydrotreatment on a dry bases is below 7 wt %, which is considerably lower than for the Alcell lignin feed (28.9 wt %). This is a clear indication for the occurrence of hydro(-deoxy)genation reactions and the formation of compounds with an on average lower oxygen content than the feed.

The product oils from the carbon supported Pd and Ru catalysts have a much higher H/C ratio than for the other supports. This suggests an on average higher hydrogenation activity for the carbon supported catalysts during the batch runs. However, sound conclusions cannot be drawn from the batch experiments as the deactivation rates during the 4 h batch time for each catalyst may be different. Detailed studies in continuous set ups will be required to assess catalyst stability.

The lignin oil samples were analyzed by GC×GC-FID to determine the various product classes present in the oil. This technique allows rapid assessment of major organic compound classes (e.g., aromatics, alkylphenolics, aliphatic hydrocarbons,) in an organic biomass derived liquid.^{40,41} A representative chromatogram of a product oil is given in Figure 2, including the major organic compound classes. Clearly, good separation between the various organic compound classes is possible and

discrete regions are visible. The lignin oil obtained using Ru/TiO₂ was also measured using GC×GC-TOFMS for enhanced identification of the organic compounds and to improve the classification system.

Quantification of the various product classes was performed with an internal standard and the use of an average response factor per product class. The results are given in Table 3. The main GC detectable product classes in the lignin oils are aromatics (1.3–4.3 wt %), alkylphenolics (4.7–9.1 wt %), and cyclic/linear/branched alkanes (2.5–6.9 wt %). Considerable differences in oil composition were observed for the various catalysts. The highest combined amounts of alkylphenolics and aromatics, the target component classes in this study, were obtained using Pd/C (12.4 wt %), Ru/C (12.2 wt %), and Ru/TiO₂ (11.6 wt %) whereas Cu/ZrO₂ showed the lowest value (6.0 wt %). It is difficult to compare these values with the available literature data given in Table 1 due to large differences in reaction conditions (batch or residence time, hydrogen pressure, catalyst intake) and the presence of solvents. The lignin oils obtained by Meier et al. using Pd/C (organocell lignin, solvent free, 400 °C, 180 bar, 15 min) were shown to consist of substituted cyclohexanones (2.5 wt % on lignin intake) and quantities of alkylphenolics of about 2 wt % on lignin intake.²⁰ The larger amount of alkylphenolics found in our study is likely related to the longer reaction time (4 h versus 15 min).

The main individual components in the various product classes are given in Table S4 (Supporting Information).

The molecular composition of the starting feed Alcell lignin and the product oil after catalytic hydrotreatment with Ru/C was also determined by ¹³C NMR. Quantification was performed by dividing the ¹³C NMR spectra in characteristic regions based on the occurrence of representative carbon atoms.³⁴ The normalized integration results for the starting feed and the hydrotreated oil (Ru/C) are given in Table 4 and the spectra are shown in Figure 3.

The ¹³C NMR spectra indicate an almost complete removal of the methoxy groups (δ 52–58 ppm), which is in line with the limited amount of methoxylated phenolic components found by GC×GC analysis. Furthermore, the strong increase in the amount of carbons in the aliphatic region indicate the formation of significant amounts of linear/branched/cyclic alkanes, which is also supported by the GC×GC measurements and elemental analysis.

Pd/C gave a lignin oil with the largest amount of GC detectable components (22.8 wt %). This indicates that the lignin oils also contain large amounts of non-GC detectable, thus nonvolatile, larger oligmeric fragments. The presence of such higher molecular weight low volatile compounds is also supported by TGA measurements (see Supporting Information, Figure S4). The product oils were analyzed using GPC to gain insights in the molecular weight distribution and the results (including the Alcell feed) are provided in Figure S5 (Supporting Information). The molecular weights of the product oils are considerably lower than the original lignin feed, indicative for substantial depolymerization during the catalytic hydrotreatment process. Distinct differences between the product oils for the various catalysts are observed and, when considering the molecular weight tail, the degree of depolymerization is Ru/C > Pd/Al₂O₃ > Ru/TiO₂ > Pd/C > Cu/ZrO₂ > Ru/Al₂O₃.

These findings suggest that the noble metal catalysts outperform the Cu catalyst when considering the degree of

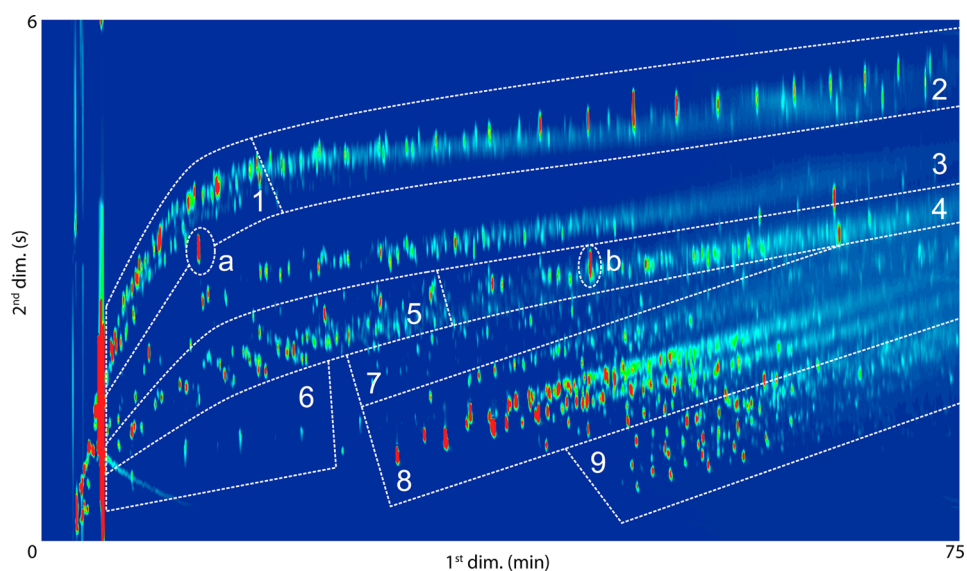


Figure 2. GC×GC-FID chromatogram of the organic phase using Ru/TiO₂ as the catalyst. (1) Cyclic alkanes, (2) linear/branched alkanes, (3 + 4) aromatics, (5) ketones/alcohols, (6) organic acids, (7) guaiacols (8) alkylphenolics, (9) catechols, (a) internal standard, and (b) BHT (stabilizer in THF).

Table 3. GC×GC-FID Results (wt % on Lignin Intake) for the Hydrotreated Alcell Lignin with Different Catalysts^a

catalyst	Ru/C ^b	Ru/TiO ₂	Pd/C	Pd/Al ₂ O ₃	Cu/ZrO ₂ ^c
alkylphenolics	9.0	9.1	8.1	7.3	4.7
guaiacols	0.5	0.1	0.2	0.2	0.2
catechols	1.1	3.5	0.5	1.1	0.8
aromatics	3.2	2.5	4.3	2.0	1.3
linear/branched alkanes	3.2	2.2	3.8	2.3	0.9
cyclic alkanes	3.7	2.1	3.2	2.7	1.6
ketones/alcohols	1.4	2.6	2.7	3.5	2.5
total GC×GC	22.1	22.1	22.8	19.1	11.8

^a400 °C, 100 bar H₂, 4 h, 5 wt % catalyst, ^baverage of two experiments (see Table S3 in the Supporting Information) ^c125 bar H₂ initial pressure.

Table 4. ¹³C NMR Integration Data for Alcel Lignin and a Hydrotreated Oil (Ru/C)

chemical shift region (ppm)	type of carbon	carbon content (% of total carbon)	
		Alcell lignin	Ru/C
0–36	aliphatic chains	17.1	47.0
52–58	methoxy groups	16.6	0.7
58–100	ether bonds (α , β , and γ)	6.3	0.0
100–160	total aromatics	59.5	51.9
100–123	nonbranched aromatics	25.1	17.9
123–160	branched aromatics	34.4	34.0
160–195	carbonyl structures	0.5	0.3
	aliphatic/aromatic ratio ^a	0.29	0.91

^aratio of the area of aliphatic carbons (δ 36–0 ppm) and aromatic carbons (δ 160–100 ppm).

depolymerization and the amount of valuable monomeric alkylphenolics and aromatics in the product oils. However, further detailed catalyst characterization studies (e.g., active site determinations by chemisorption experiments) will be required to support this statement. The highest amounts of valuable components is obtained with the Ru/TiO₂ catalyst (9.1 wt % alkylphenolics, 3.5 wt % catechols, and 2.5 wt % aromatics), though these values are close to those found for Ru/C.

However, for commercial applications, the use of the titania support is favored as regeneration of the catalyst (e.g., by mild oxidation at elevated temperatures) is feasible, in contrast to carbon based catalysts.

Effect of Reaction Time on Lignin Oil Yield and Product Composition for the Catalytic Hydrotreatment of Lignin Using Ru/C. The effect of reaction time on the lignin oil yield and elemental and molecular composition was assessed for the catalytic hydrotreatment of Alcell lignin with Ru/C with the objective to determine the optimum reaction times for high yields of aromatics/alkylphenolics. Reaction times were in the range 0–8 h with increments of 2 h (400 °C, 100 bar initial H₂, and 5 wt % Ru/C on lignin intake). The reaction time was set at zero when the temperature in the reactor reached 400 °C. For all the reactions, two liquid phases were observed, a clear aqueous phase and a dark brown/black organic phase. An overview of the time experiments are given in Table 5. Mass balance closures were satisfactory (>85 wt %). The oil lignin oils yields are between 64.7 and 73.3 wt % on lignin intake and a clear trend between the lignin oil yield and reaction time is absent. The water content of the organic phase is reduced in time (from 4.2 to 1.3 wt %), indicating that apolar compounds are formed in the course of the reaction that reduce the polarity of the lignin oil phase (*vide infra*).

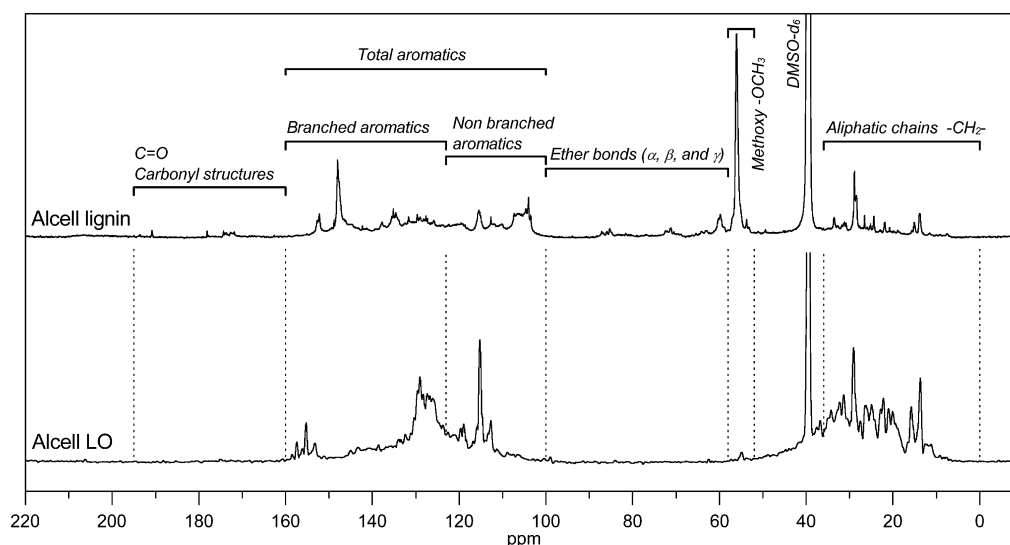


Figure 3. ^{13}C NMR spectra of Alcell lignin and a product oil (Alcell LO) after a catalytic hydrotreatment experiment with Ru/C at 400 °C, 4 h, 100 bar H_2 initial pressure, 5 wt % Ru/C on lignin intake.

Table 5. Overview of Catalytic Hydrotreatment Experiments of Alcell Lignin Using Ru/C at Different Batch Times^a

time (h)	0	2	4	8
organic phase (wt % on intake)	73.3	70.3	63.9	72.8
aqueous phase (wt % on intake)	14.2	3.1	11.4	10.1
gas phase (wt % on intake)	9.6	12.5	9.2	9.9
carbon dioxide (mol %)	7.8	16.7	14.5	13.3
carbon monoxide (mol %)	0.5	0.85	2.2	1.9
ethylene (mol %)	0.0	0.0	0.0	0.0
ethane (mol %)	0.8	2.0	2.1	2.3
propylene (mol %)	0.0	0.0	0.0	0.0
propane (mol %)	0.4	0.8	0.9	1.5
methane (mol %)	31.4	27.1	23.1	21.5
hydrogen (mol %)	59.0	52.5	57.2	59.6
total mass balance (wt % on intake)	97	87	85	93
total carbon balance (%)	90	91	90	100
water content organic phase (wt %)	4.2	3.0	3.6	1.3
carbon content aqueous phase (wt %)	1.9	2.3	1.5	1.4
elemental composition organic phase (wt %, dry basis)				
carbon	76.9	80.4	83.2	84.9
hydrogen	8.1	9.2	9.6	9.6
oxygen	14.9	10.3	7.0	5.3

^a400 °C, 100 bar initial H_2 , 5 wt % Ru/C on lignin intake

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 (Figure 4).

A clear trend is visible for the elemental composition of the lignin oils versus the batch time. The O/C ratio decreases whereas the H/C ratio increases over time. Remarkable is the large difference between the composition of the Alcell feed and the lignin oil after heating up to reaction temperature (0 h). Apparently, hydrodeoxygenation reactions already occur to a significant extent in the heating up phase. In addition, it appears that reactivity is limited between 4 and 8 h as the elemental composition remains about constant.

The molecular weight distribution of the product oils versus time is given in Figure S6 (Supporting Information). Clearly, the molecular weight is reduced in time and lowest values are found after 8 h reaction time. Apparently, depolymerization is a

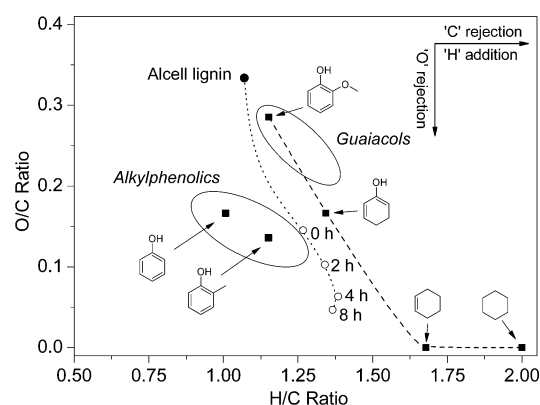


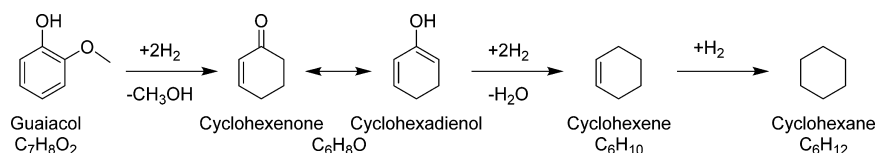
Figure 4. Van Krevelen plot for the catalytic hydrotreatment of Alcell lignin at different batch time (400 °C, 100 bar initial H_2 , 5 wt % of Ru/C on initial lignin intake). Included are the theoretical line for the conversion of guaiacol to cyclohexane and areas representing alkylphenolics (phenol, methylphenol, ethylphenol) and guaiacols (guaiacol, methylguaiacol, ethylguaiacol).

relatively slow process and occurs in parallel with the deoxygenation reactions. Again, the trend also reveals that depolymerization already occurs to a significant extent during the heating up phase. It is well established from model studies that the various linkages in the lignin ($\text{S}-\text{S}$, $\beta-1$, $\beta-5$, $\alpha-\text{O}-4$, and $\beta-\text{O}-4$) show different reactivity.^{42,43} It is likely that the $\beta-\text{O}-4$ linkages, which are known to be very reactive, are cleaved in the heating up phase, whereas the more persistent linkages, like the $\text{S}-\text{S}$ and $\beta-1$, are cleaved at prolonged reaction times.

The observed experimental trend for the elemental composition versus time is indicative for the occurrence of a combination of hydrogenation (higher H/C ratios) and dehydration reactions (lower O/C and H/C ratios). This is supported by the trend calculated for the theoretical reaction of guaiacol to cyclohexane with cyclohexadienol (or its tautomer cyclohexenone) and cyclohexene as the intermediate (Scheme 1).

Clearly, the slope of the experimental and theoretical lines are rather similar (Figure 4), indicating that the model reactions given in Scheme 1 occur to a significant extent.

Scheme 1. Reaction Pathway for the Conversion of Guaiacol to Cyclohexane



The product composition of the organic phase after the reaction was determined with GC×GC-FID and GC–MS-FID and the results are given in Table 6. The GC detectables after

Table 6. GC×GC-FID Results (wt % on Lignin Intake) for the Hydrotreated Alcell Lignin at Different Times with Ru/C^a

time (h)	0	2	4 ^b	8
alkylphenolics	5.6	10.3	9.0	12.2
guaiacols	1.1	0.1	0.5	0.1
catechols	2.1	0.7	1.1	0.8
aromatics	1.3	3.6	3.2	5.2
linear/branched alkanes	0.6	3.7	3.2	5.7
cyclic alkanes	0.3	0.3	3.7	4.4
ketones/alcohols	1.9	1.8	1.4	1.3
total GC×GC	12.9	20.5	22.1	29.7

^a400 °C, 100 bar H₂, 0–8 h, 5 wt % catalyst. ^bAverage of two experiments.

heating up (0 h) mainly consists of aromatics, catechols and ketones/alcohols. These findings are in line with the elemental composition and GPC data and indicate that depolymerization and hydro-deoxygenation reactions already occur to a significant extent in the heating up phase. At prolonged reaction times, the total GC detectables increases from 12.9 (0

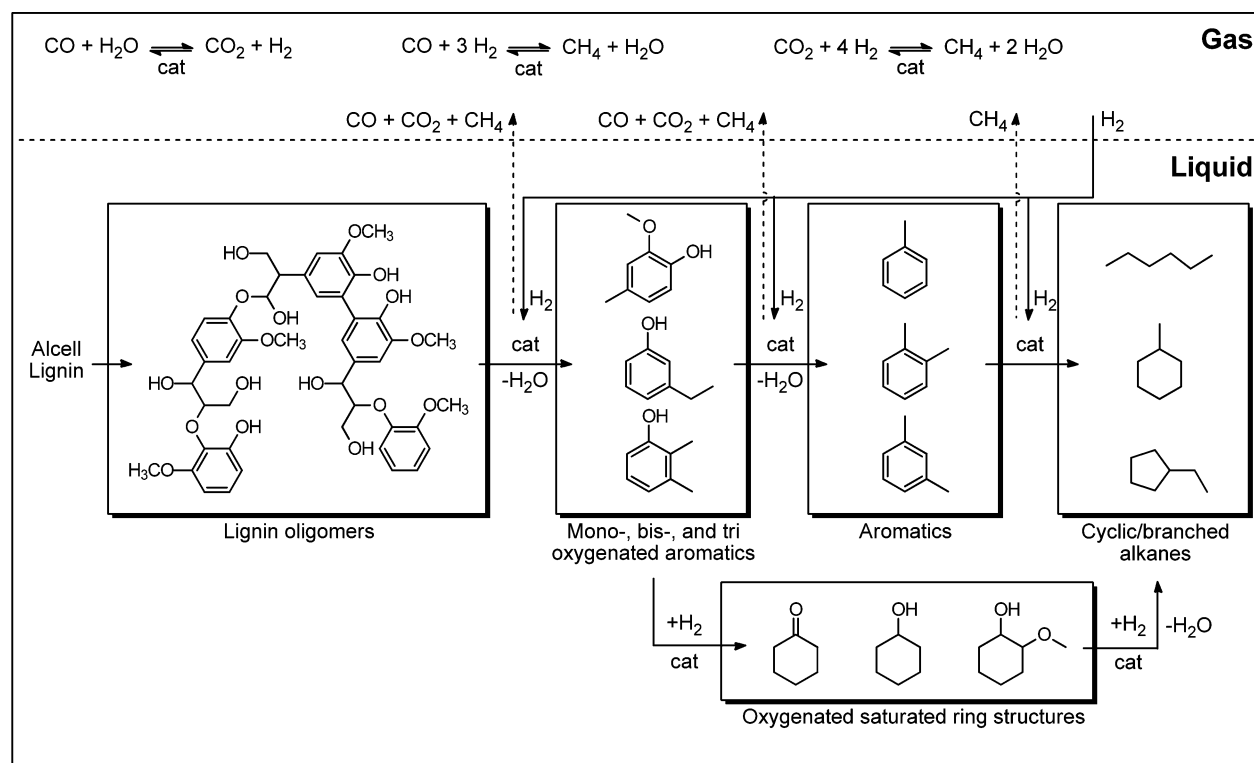
h) up to 29.7 wt % on lignin intake (8 h), which is in line with the molecular weight distributions versus batch time trends discussed earlier and indicate that molecular weight breakdown is a relatively slow process.

A decrease in the guaiacols, catechols, and ketones/alcohols content over time in combination with a concomitant increase in the amounts of cyclic ring alkanes, aromatics, alkylphenolics, and linear/branched alkanes is observed (Table 6).

On the basis of the current data set, it is not possible to determine the optimum reaction time for the highest aromatics and alkylphenolics yield. The data reveal that carbon–carbon double bond hydrogenation of aromatic rings is occurring to a significant extent at prolonged reaction times. This is an undesirable side reaction as it reduces the amounts of the desired alkylphenolics and aromatics to a significant extent. Thus, when aiming for high amounts of low molecular weight phenolics and aromatics, proper selection of batch times are of high importance to optimize the rate of depolymerization with that of undesired carbon–carbon double bond hydrogenation of aromatic rings.

Reaction Pathways. On the basis of the information provided in the previous sections and available literature data, a reaction network is proposed for the catalytic hydrotreatment of Alcell lignin with supported Ru and Pd catalysts (Scheme 2). Within the experimental window (high H₂ pressures, 400 °C, reaction times up to 8 h) lignin is converted by a number of

Scheme 2. Proposed Reaction Network for the Catalytic Hydrotreatment of Lignin with Ru/C



parallel and consecutive reaction pathways. In the initial stage of the reaction, the Alcell lignin melts around 170 °C and starts to depolymerize thermally to lower weight lignin oligomers at temperatures as low as 230–260 °C.⁴⁴

The presence of a catalyst may also have a positive effect on the depolymerization rates, e.g., by promoting splitting of ether and C–C linkages. Depolymerization is a relatively slow process and full conversion to monomeric compounds was not observed experimentally, not even after 8 h reaction time. Lignin contains a large number of different linkages between the aromatic nuclei and it is well possible that initially the more labile ether linkages are broken, whereas the C–C linkages are more difficult to open and require more harsh conditions. As such, depolymerization and subsequent reactions of the lower molecular weight fragments are parallel processes.

The lignin oligomers react further to lower molecular weight oxygenated aromatics with the concomitant formation of water and methane. 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 hydrogenations and (ii) the hydrodeoxygenation of the oxygenated aromatics to aromatics, followed by over hydrogenation to alkanes. For our target component classes (alkylphenolics and aromatics), hydrogenation of the aromatic rings should be avoided.

CONCLUSIONS

A catalyst screening study on the hydrotreatment of Alcell lignin was performed in a batch reactor using five noble metal catalysts (Ru/C, Ru/Al₂O₃, Ru/TiO₂, Pd/C, and Pd/Al₂O₃) and a Cu catalyst (Cu/ZrO₂ at relatively harsh conditions (400 °C with 100 bar initial H₂ pressure for 4 h). The main product was a lignin oil, which was obtained in yields up to 78 wt % on lignin intake whereas solids formation was negligible. The most promising catalyst was Ru/TiO₂ due to the formation of a high extent of monomeric aromatics and alkylphenolics in the product oil and a high degree of depolymerization. In addition, titania is known to be reactivated easily in air/steam to remove coke on the catalyst, possibly formed by repolymerization, which is an advantage for further scale up. More in-depth research on Ru/C with different batch time reactions (0–8 h) showed that a large amount of deoxygenation and depolymerization of the lignin structures takes already place during the heat-up time. Main reaction mechanisms during heat-up were found to be a parallel reaction of hydrogenation and hydrodeoxygenation. A reaction pathway for the depolymerization of lignin with Ru/C including a number of parallel and consecutive reactions is presented.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00041.

Structural model for lignin, relevant properties of the Alcell lignin source, picture of a char from an experiment in the absence of a catalyst, carbon- and mass balances for selected experiments, TGA profiles, molecular weight distributions, and GC×GC-FID and GC×GC TOFMS chromatograms of product oils, calibration procedure for GC×GC chromatograms (PDF)

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Notes

The authors declare no competing financial interest.

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