PAPER

Liquid-phase reforming and hydrodeoxygenation as a two-step route to aromatics from lignin

Anna L. Jongerius, Pieter C. A. Bruijnincx and Bert M. Weckhuysen*

A two-step approach to the conversion of organosolv, kraft and sugarcane bagasse lignin to monoaromatic compounds of low oxygen content is presented. The first step consists of lignin depolymerization in a liquid phase reforming (LPR) reaction over a 1 wt% Pt/γ-Al$_2$O$_3$ catalyst at 225 °C in alkaline ethanol–water. The first LPR step resulted in a decrease in lignin molecular weight of 32%, 57% and 27% for organosolv, kraft and bagasse lignin, respectively. GC analysis of the depolymerized lignin reaction mixture furthermore showed the formation of alkylated phenol, guaiacol and syringol-type products in 11%, 9% and 5% yields from organosolv, kraft and bagasse lignin, respectively. The lignin-oil that was isolated by extraction of the ethanol–water solution was subjected to a subsequent hydrodeoxygenation (HDO) reaction in the second conversion step. HDO of the lignin-oil was performed in dodecane at 300 °C under 50 bar hydrogen pressure over CoMo/Al$_2$O$_3$ and Mo$_2$C/CNF catalysts. GC analysis of the product mixture obtained after the two-step LPR–HDO process revealed the formation of, amongst others, benzene, toluene, xylenes and ethylmethylbenzenes. Of the total observed monomeric products (9%), 25% consisted of these oxygen-free products. Notably, such products cannot be obtained by direct HDO of lignin. HDO of the lignin-oil at 350 °C resulted in the conversion of all tris-oxygenated products, with 57% of the observed monomeric products now identified as mono-oxygenated phenolics.

1. Introduction

The valorization of the lignin component of lignocellulosic biomass would greatly aid the development of economically viable biorefinery processes.[1] Lignin is highly aromatic and can thus be regarded as a major source of aromatics in a bio-based economy; however, selective conversion of this relatively recalcitrant resource has proven to be difficult and requires the development of new technologies. Many of the recent efforts in this direction have focused on single-step routes for the conversion of lignin into monomeric aromatic compounds. Oxygen-rich fine chemicals such as vanillin and benzoquinones are, for instance, readily obtained *via* oxidative routes as was shown by Werhan *et al.* and Stärk *et al.*[2,3] and by the commercial production of vanillin from lignosulfonate lignin through the Borregaard biorefining processes.[4] Reductive one-step conversion routes, on the other hand, typically lead to the formation of mixtures of (alkylated) guaiacol and syringol-type molecules. Recently, yields of up to 50% of propyl-substituted guaiacol and syringol have been reported *via* a nickel-catalyzed fragmentation–hydrolysis[5] or the nickel/tungsten carbide-

catalyzed hydrocracking of birch wood.[6] Other reported reductive processes generally resulted in lower yields and more complex product mixtures consisting of multiple aromatic products,[7,8] or even ring-hydrogenated monomeric products.[9] Such one-step, reductive processes generally lead to the formation of bis- or tris-oxygenated mono-aromatic molecules, however. No one-step lignin conversion processes have been reported to date for the production of oxygen-free or low-oxygen content monomeric aromatics.

Rather than performing the conversion of lignin in a single step, a two-step conversion strategy allows a general depolymerization step to be followed by a subsequent, independently chosen second conversion step to further upgrade the product mixture of the depolymerization process. In the first step of such a process, a (catalytic) depolymerization reaction is applied to yield lignin monomers, dimers and small oligomers. The reaction product of this first step can both be a solution of depolymerized lignin fragments or a lignin-oil. Such oils, for instance those obtained from lignin pyrolysis reactions, commonly consist of a complex mixture of phenolic molecules including (substituted) guaiacols, catechols and syringols.[10–12] Other (thermochemical) processes are also available for the production of lignin-oils, with a base-catalyzed hydrogenolysis reaction being most commonly studied.[13–15] As the second conversion step can be independently chosen, there are many possibilities such as oxidation, hydrogenation,

Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands. E-mail: B.M.Weckhuysen@uu.nl
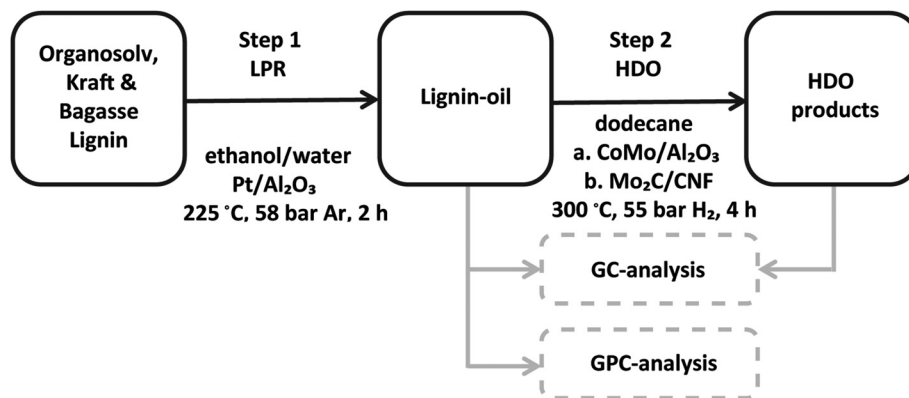
Fig. 1 Two-step approach to valorization of various lignins. After a liquid-phase reforming (LPR) reaction, the extracted lignin-oil is subjected to a second hydro-deoxygenation (HDO) step.

or hydrodeoxygenation (HDO), with especially the latter two being often explored. Indeed, the choice of catalyst and the type of conversion in the second step can be based on the targeted end products. Here, we focus on the use of an HDO step for the upgrading of the depolymerized lignin streams. The combination of lignin depolymerization with a separate HDO step allows one to obtain products with a lower oxygen content than is customarily obtained with one-step processes.

HDO studies aimed at the deoxygenation of lignin-oils mostly make use of industrial CoMo and NiMo catalysts or noble metal Ru, Pt and Pd-based catalysts. However, it must be noted that most of the catalytic studies that are concerned with HDO of lignin-related compounds are actually performed with model compounds. The use of either a single molecule or a library of compounds, rather than real lignin-derived feeds, greatly simplifies product analysis and kinetic studies.[1,16] Performing HDO reactions on real depolymerized lignin feeds poses considerable challenges that are not encountered when model compounds are used, primarily because lignin-derived bio-oils consist of a complex mixture of oxygen-rich aromatic molecules, a mixture that in addition to monomeric compounds will also contain dimers and oligomers. These higher molecular weight components are prone to repolymerization and coke formation at the relatively high temperatures (>300 °C) generally needed for HDO. Of the relatively few reports that have appeared on the HDO of real lignin depolymerization products, Shabtai *et al.* were one of the first to report a combination of a lignin depolymerization step with a second HDO step.[17] The process consisted of a sequential base-catalyzed depolymerization and a CoMo/Al$_2$O$_3$-catalyzed HDO and hydrocracking step to ultimately produce hydrocarbon gasoline. More recently, several studies on the HDO of (lignin) pyrolysis oils[18,19] showed that higher degrees of deoxygenation could be obtained with noble metal catalysts than with the traditional CoMo and NiMo catalysts.[18] Noble metal catalysts, however, also showed a high ring-hydrogenation activity leading to the formation of cycloalkanes rather than aromatic products.[20]

Here, we report the integration of a lignin depolymerization step, *i.e.* a liquid phase reforming (LPR) reaction, with a second HDO step over CoMo/Al$_2$O$_3$ or Mo$_2$C/CNF catalysts with the aim of obtaining aromatics of low oxygen content (Fig. 1). We present a rare example of actual BTX (Benzene, Toluene, Xylenes) formation from real lignin sources. The LPR reaction of organosolv, kraft and bagasse lignin is performed in ethanol–water over a Pt/Al$_2$O$_3$ catalyst at 225 °C as reported by Zakzeski *et al.*[21] The LPR product mixture containing the depolymerized lignin is extracted and a lignin-oil is obtained after evaporation of the solvent. The lignin-oil is then used as the feed for HDO reactions performed in dodecane at 300 °C under 50 bar hydrogen atmosphere over CoMo/Al$_2$O$_3$ or Mo$_2$C/CNF. These catalysts were tested previously under similar conditions but in the HDO of (a library of) lignin model compounds.[22,23]

2. Experimental

2.1 Chemicals and lignins

The INDULIN AT kraft lignin (63.25% C, 6.05% H, 0.94% N, 1.64% S, 28.12% O by difference), ash content 1.2%, provided by ECN was obtained from pine and is free of all hemi-cellulosic materials. The Alcell organosolv lignin (66.47% C, 5.96% H, 0.15% N, 27.43% O by difference), ash content 0.1%, provided by Wageningen University was obtained from hardwoods and isolated by the organosolv extraction method. The lignin from sugarcane bagasse (58.90% C, 4.90% H, 0.14% N, 1.53% S, 34.53% O by difference), estimated ash content 2.4%,[24] provided by Dow Chemical was derived from Brazilian sugarcane. Demineralized water was purified using a MilliQ system. Reagents, catalysts, solvents and gasses were purchased commercially: NaOH (Merck), HCl (Merck, 37%), ethanol (Scharlau, HPLC grade), dichloromethane (Biosolve), ethyl acetate (Biosolve), dodecane (Acros, 99%), diethylether (Biosolve), hexadecane (Sigma, 99%), anisole (Acros, 99%), Pt/Al$_2$O$_3$ (1 wt% Pt, Aldrich), argon and hydrogen (Linde, 5.0).

2.2 Catalytic reactions

The LPR reactions were conducted in a 100 mL stainless steel high-pressure Parr batch autoclave reactor equipped with a thermocouple, a pressure transducer and gauge and a magnetic driver (750 rpm). During a typical LPR reaction, 1 g of lignin was added to the autoclave along with 0.5 g Pt/Al$_2$O$_3$, 25 mL 1 M NaOH in water and 25 mL ethanol. The reactor was purged three times with argon and pressurized with argon to 58 bar. The reaction mixture was heated to 225 °C and depressurized regularly to maintain a pressure of around 58 bar. The reaction was stopped after 2 h by cooling rapidly to room temperature. The reaction mixture was filtered to remove all solids and subsequently acidified with HCl to pH 1. After a second filtration under reduced pressure to remove any precipitated lignin, the liquid phase was extracted with dichloromethane. After evaporation of the dichloromethane and ethanol a lignin-oil was obtained.

The HDO reactions were performed in a 25 mL stainless steel high-pressure Parr batch autoclave reactor. The temperature was monitored using a thermocouple, and stirring was performed using a magnetic driver equipped with an impellor at 750 rpm. In a typical reaction, the autoclave was loaded with 500–800 mg of the lignin-oil, 50 mg of the catalyst material, 0.35 g of hexadecane as an internal standard, and 7.5 g of the solvent dodecane. A fresh batch of catalyst was used in every run. The reactor was purged three times with argon, and the reaction mixture was heated to 300 °C and then pressurized with H$_2$ to 50 bar, and the catalytic reaction was carried out for 4 h. The reaction was stopped by cooling and release of pressure, after which the reaction mixture was diluted with an equal volume of diethyl ether in order to dissolve all of the products; condensed lignin solids and the solid catalyst were removed by filtration and washed with diethyl ether.

2.3 Analysis

The chemical composition of the isolated product mixtures was determined by a Varian GC equipped with a VF-5 ms capillary column and an FID detector. Anisole was used as an internal standard for the LPR reactions. The products were quantified using response factors determined for phenol, guaiacol and syringol. Product identification was conducted using a Shimadzu GCMS-QP2010 equipped with a VF-5 ms capillary column and by comparison with pure compounds when available.

The M_w of depolymerized lignin was analyzed by GPC performed on an alkaline SEC using a Waters Alliance system equipped with a manually packed column (4.6 mm × 30 cm) with the ethylene glycolmethacrylate copolymer TSK gel Toyopearl HW-55F, according to the work of Gosselink et al.[25] Sodium polystyrene sulfonates (M_w range 891–976 000 Da) were used for the calibration of the molar mass distribution. The LPR lignin solutions were diluted to a concentration of 1 mg mL^{-1} lignin in 0.5 M NaOH. GPC runs were performed at 40 °C with 0.5 M NaOH eluent at a flow rate of 1 mL min^{-1} and UV detection at 280 nm.

X-ray powder diffraction (XRD) patterns were obtained on a Bruker-AXS D2 Phaser powder X-ray diffractometer using Co K$_{\alpha 1,2}$ with λ = 1.79026 Å. Measurements were carried out between 10 and 100° 2θ using a step size of 0.09° 2θ and a scan speed of 1 s.

3. Results and discussion

3.1 Step 1: liquid-phase reforming

Organosolv lignin, kraft lignin and sugarcane bagasse were first depolymerized through the LPR process.[21]

In a typical reaction, 1 g of dried lignin was dispersed in 50 mL ethanol–water (1/1 v/v) with 0.5 g of a commercial 1 wt% Pt/γ-Al$_2$O$_3$ catalyst and 1 g of NaOH as a co-catalyst. The reaction was performed for 2 h under 58 bar Ar at 225 °C. As previously reported, the solvent combination ethanol–water is used in the LPR process to aid lignin solubilization and to prevent (re)condensation.[21] An acid or base is used as a co-catalyst to increase monomer yields. Although sulfuric acid was previously shown to be somewhat more effective as a co-catalyst,[21] here we chose to perform our reactions with NaOH instead. The general solubility of lignin in basic solutions prevents coke formation at higher lignin concentrations and the use of NaOH simplifies the isolation of lignin after reaction. Compared to the previously reported typical LPR conditions, the reaction was scaled up and lignin concentration, as well as the lignin to catalyst ratio, was doubled to allow a sufficient amount of lignin-oil to be isolated for the second HDO step. After the reaction, any solids formed were removed by filtration and a lignin-oil was obtained by extraction of the acidified product mixture with dichloromethane followed by solvent evaporation. Reactions performed on sugarcane bagasse contained larger amounts of insoluble matter (0.2 g) than the reactions performed with organosolv and kraft lignin (less than 0.02 g). Complete evaporation of carried over ethanol proved to be difficult and small quantities were present in the lignin-oil that was used for the second step. Almost no lignin-derived solids were obtained after the LPR reaction because of the excellent solubility of lignin in alkaline solutions; in addition, the lignin-derived LPR products were found to be almost completely soluble in ethanol–water even after acidification to pH 1. Lignin-oil yields were generally around 0.8 g for organosolv and kraft lignin; bagasse yielded less oil (around 0.65 g), because of the relatively large amount of insoluble ash that the bagasse sample contained.

GPC analysis of the crude reaction mixture after simple dilution of the LPR reaction mixture with alkaline H$_2$O reveals a decrease in molecular weight for all three types of lignin. The chromatograms depicted in Fig. 2 show the formation of a shoulder at longer retention times, indicating the formation of lower molecular weight components. Only for the kraft lignin a shift of the peak maximum towards longer retention times was observed, which indicates that all polymer chains, including the larger ones, were shortened. Our previous results also showed LPR of kraft lignin to be most effective.[21] Calculated

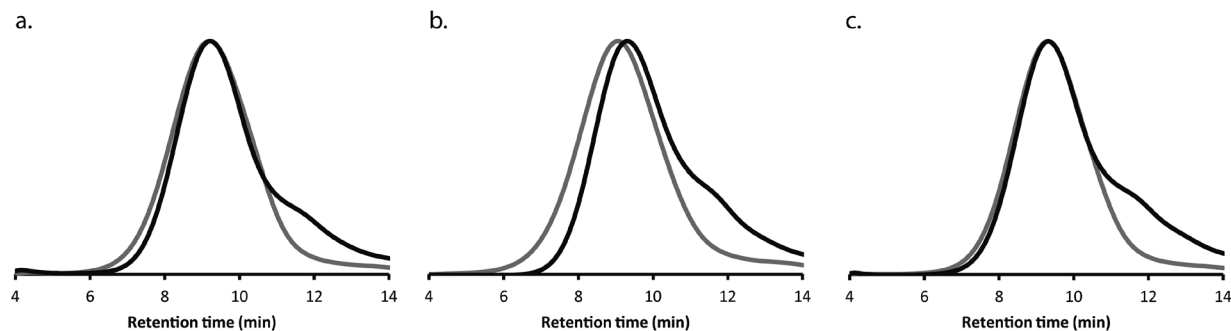a.   b.   c.

Fig. 2 GPC chromatograms of (a) organosolv, (b) kraft and (c) bagasse before (grey) and after (black) LPR. The peak maxima were normalized to the same value.

Table 1 M_w and PDI decrease for organosolv, kraft and bagasse lignin after LPR with NaOH as a co-catalyst

	M_w before (Da)	M_w after (Da)	Decrease (%)	PDI before	PDI after	Decrease (%)
Organosolv	3900	2700	32	4.8	5.6	−17
Kraft	5000	2200	57	5.9	5.5	7
Bagasse	3000	2200	27	4.3	5.8	−35

average molecular weights (M_w) and polydispersity indices (PDI) of the lignins and depolymerized lignins are shown in Table 1. Despite the 30–50% decrease in average molecular weight that was observed after the LPR reaction, the M_w of 2200–3000 Da of the depolymerized lignins after reaction indicates that a large fraction of the product mixture still consists of larger lignin molecules. The increase in signal intensity at the longest retention times, *i.e.* around 12 min, nonetheless revealed that low molecular weight monomers and dimers are formed as well. The retention time of phenol under these conditions is 12.2 min and any molecules eluting at around 12 min are most likely monomers.

The monomer yields and composition of the product mixture after step 1 were determined by GC analysis of the lignin-oil. Typical monoaromatic product yields were 11%, 9% and 5% for organosolv, kraft and sugarcane bagasse lignin, respectively. These yields are comparable to the results reported before for the same lignin sources in the LPR reaction with NaOH as a co-catalyst.

A large number of different monoaromatics are obtained from the LPR reaction of organosolv and kraft lignin, including methyl-, ethyl-, propyl- and propanol-substituted guaiacol and syringol-type products as well as catechols, phenol and some aromatic products derived from reactions with the solvent. In contrast, the bagasse-derived product mixture contained only methyl- and ethyl-substituted guaiacol, phenol and syringol. The relatively simple product mixture formed after the LPR of sugarcane bagasse is most probably related to its relatively low natural abundance of syringyl units. Indeed, the product distribution and oxygen content of the observed monomers generally corresponded to the natural abundance of syringyl, guaiacyl and *p*-coumaryl units in the original lignin samples.[26,27] The monomeric products detected in the lignin-oil originating from the hardwood organosolv lignin
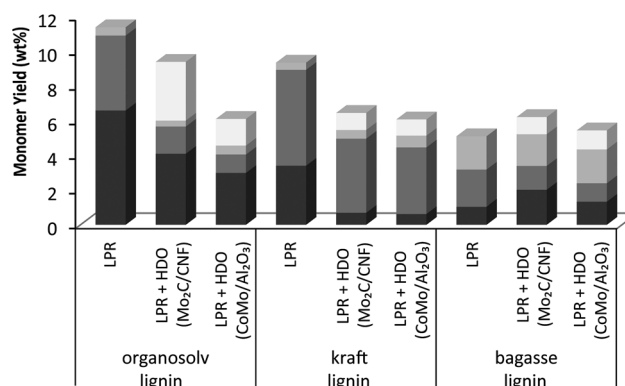

Fig. 3 Yield of monomeric aromatic products after LPR and LPR + HDO reactions of different lignins: ☐ oxygen-free products, ▨ mono-oxygenated products, ▨ products containing two oxygen functionalities, ■ products with three or more oxygen functionalities.

consisted of 58% of tris-oxygenated, syringol-like molecules. In the kraft lignin LPR product, 59% of the aromatics were bis-oxygenated as can be expected from a softwood lignin, while the grass-type bagasse yielded a mixture of 42% bis-oxygenated and 38% mono-oxygenated phenolics. Fig. 3 shows the monomer yields that were obtained during the first LPR step; products are grouped according to the number of oxygen atoms.

3.2   Step 2: hydrodeoxygenation

The lignin-oils obtained after LPR of organosolv, kraft and sugarcane bagasse lignin consisted of highly oxygenated oligo- and monoaromatic molecules. To lower the oxygen content of the lignin-derived products a subsequent HDO reaction was performed. Various types of catalysts have been previously reported for HDO of lignin model compounds, ranging from

alumina-supported CoMo and NiMo catalysts to supported noble metal catalysts.[16,22,28,29] Recently both bulk and supported tungsten and molybdenum carbide catalysts have been shown to be active in the HDO of fatty acids and other biomass-derived oxygenates.[30–32] Mo_2C on carbon nanofibers in particular showed a high activity and selectivity in the HDO of guaiacol.[23]

In our two-step approach, the lignin-oils were subjected to a HDO reaction over a $CoMo/Al_2O_3$ or Mo_2C/CNF catalyst at 300 °C in dodecane. Reactions were performed under 50 bar hydrogen atmosphere for 4 h; these conditions are comparable to those previously used for the HDO of lignin model compounds over $CoMo/Al_2O_3$.[22] The $CoMo/Al_2O_3$ catalyst was activated prior to use and the Mo_2C/CNF catalyst was freshly prepared; both catalysts were stored under an argon atmosphere to prevent deactivation over time. After the HDO reactions, the formation of solids was observed, probably caused by precipitation of the larger lignin molecules that were still present in the lignin-oil after the LPR reaction, components that are not soluble in dodecane. Individual catalyst particles could easily be distinguished from the formed insoluble organics.

Analysis of the liquid phase of the $CoMo/Al_2O_3$-catalyzed reactions showed the formation of (alkylated) syringol, guaiacol and phenol-type molecules. The composition of the product mixtures after the LPR and HDO step is depicted in Fig. 3 and 4. Total observed monomer yields were 6%, 6% and 5% for organosolv, kraft and sugarcane bagasse lignin, respectively. The yields of organosolv and kraft HDO reaction products are thus lower than those for the LPR lignin-oils; monomer yields for the bagasse reaction products, however, increased slightly after the HDO reaction. The presence of

more monomers in the HDO product than in the LPR-derived lignin-oil might indicate that the HDO reaction is able to contribute to further depolymerization of the lignin (albeit to a small extent). Notably, the HDO product mixture also contained oxygen-free aromatic products such as benzene, toluene, xylenes and ethylmethylbenzenes. The oxygen-free products consist of 25%, 15% and 20% of the total observed products for organosolv, kraft and sugarcane bagasse lignin, respectively. None of these oxygen-free aromatics were present in the lignin-oils obtained after the LPR reaction, illustrating that the oil was at least partially deoxygenated during the HDO step. As was found for the LPR reaction, the ratio between the mono-, bis- and tris-oxygenated products strongly depended on the lignin source that was used. Indeed, almost 50% of the observed aromatic monomers obtained from organosolv lignin are tris-oxygenated, while the kraft lignin-derived product consisted of 63% of bis-oxygenated compounds. Mono-oxygenated phenolics were the largest fraction (36%) with bagasse. It should be noted that the removal of oxygen leads to a reduction of molecular weight, which partially accounts for the decrease in observed monomer yields. In the organosolv lignin-derived LPR product mixture, 23% of the total observed monomer weight was made up of oxygen atoms in the various products; after HDO this was only 16%. This 7% decrease would result in a 0.7% decrease in the total monomer yield.

The reaction mixtures obtained after Mo_2C/CNF-catalyzed HDO of the lignin-oils generally showed the same product distribution as observed for the $CoMo/Al_2O_3$-catalyzed reactions (Fig. 3 and 4). With 9%, 7% and 6% observed total monomer yields for organosolv, kraft and sugarcane bagasse lignin, respectively, the yields for the Mo_2C/CNF-catalyzed reactions were slightly higher than those for the $CoMo/Al_2O_3$-catalyzed reactions. The 9% overall yield obtained after the HDO of organosolv lignin-oil is the highest obtained; a large fraction of the obtained aromatics (36%) is accounted for by oxygen-free products (cf. 25% in the $CoMo/Al_2O_3$-catalyzed reactions). The reduction in total mass of the products by loss of oxygen in the HDO step again accounted in part for the lower monomer yields obtained in step 2 compared to step 1 (e.g., 0.5% drop for organosolv lignin). The fraction of oxygen-free products observed in the kraft (15%) and sugarcane bagasse-derived product mixtures (16%) were comparable to the amounts obtained with the $CoMo/Al_2O_3$ catalyst. In accordance with the results discussed above for the LPR and the $CoMo/Al_2O_3$-catalyzed reactions, tris-oxygenated products (44%) constituted the largest product fraction for organosolv lignin, bis-oxygenated products (66%) for kraft lignin and mono-oxygenated phenolics (30%) for bagasse.

Somewhat surprisingly, for both the $CoMo/Al_2O_3$ and Mo_2C/CNF catalysts relatively small amounts of mono-oxygenated products were observed in the HDO product mixtures of organosolv and kraft lignin-oils. In contrast, mono-oxygenated phenolics were shown to be the major products in the HDO of lignin model compounds over these catalysts; full HDO to oxygen-free compounds such as benzene, toluene and xylene was only found to occur after all bis-oxygenated model
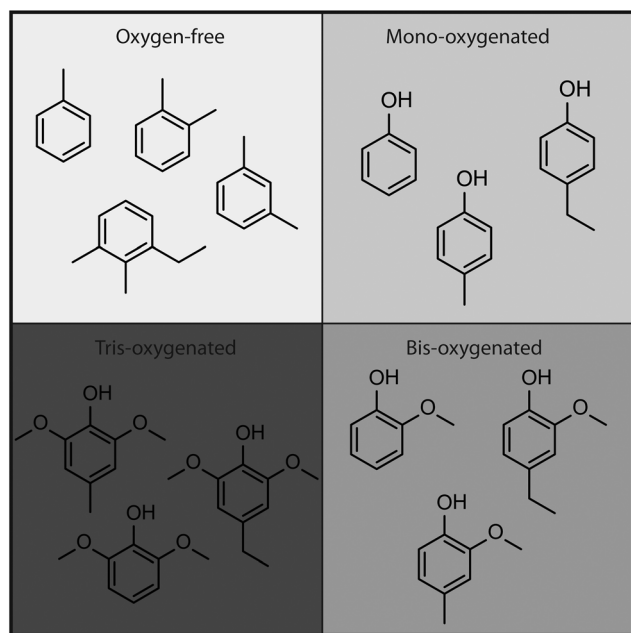

Fig. 4 Typical products obtained after HDO reactions of the various lignin-oils over the Mo_2C/CNF and $CoMo/Al_2O_3$ catalysts.

compounds were converted.[22,23] However, HDO of the lignin-oils led to the formation of oxygen-free products even before all bis- and tris-oxygenated products were consumed. It should be noted that the concentration of oxygenated aromatic molecules in the diluted lignin-oil converted in the second step is lower than the concentration used before for the model compound studies using the same catalysts.[22,23] The lower concentration leads to more limited availability of substrates for the HDO catalyst and possibly explains the differences observed for the model compounds and the lignin-oil. In addition, the products obtained from the HDO of real lignin-oils contained larger amounts of alkylated products compared to the model compound product mixtures. The propyl side chains that are present in the original lignin structure naturally lead to the formation of larger amounts of methyl-, ethyl- and propyl-substituted aromatics. As the model compounds tested previously contained no alkyl substituents, propyl- or ethyl-substituted products were not formed in these reactions.

An HDO experiment with Mo_2C/CNF as the catalyst performed on organosolv lignin directly, *i.e.*, without an LPR pretreatment, confirmed that small amounts of monomeric products can also be formed by HDO alone (Fig. 5). The total amount of monomeric products observed (6%), however, was lower than the 9% observed after the HDO of the LPR-oil from the same lignin. More importantly, the product distribution of this "direct HDO" reaction is more similar to the product distribution of the first LPR step than to the mixture obtained in the second HDO step. Only 3% of the observed products were completely deoxygenated after direct HDO of lignin compared to 36% after LPR followed by HDO, whereas 63% still had three oxygen functionalities after direct HDO. This indicates

that consecutive depolymerization and deoxygenation steps result in a higher deoxygenation degree than a direct HDO reaction alone.

3.3 Reaction optimization

As the highest monomer yields and lowest oxygen content were obtained with the Mo_2C/CNF catalyst and organosolv lignin-oil, additional tests to assess the influence of process parameters on the yield and oxygen content of the product mixture were performed with this lignin–catalyst combination.

The results of the Mo_2C/CNF-catalyzed HDO of the model compound guaiacol showed that by increasing the reaction time and reaction temperature, higher amounts of completely deoxygenated products could be obtained.[23] Increased reaction times possibly also help to increase the total monomer yields by additional cleavage of dimer and oligomer linkages. An HDO reaction of organosolv lignin-oil performed for 15 h rather than 4 h at 300 °C over Mo_2C/CNF showed no increase in the yield of monomeric products, however (Fig. 5). In fact, after a reaction performed overnight the total monomer yield (6%) and the fraction of oxygen-free products (16%) were significantly lower than those after the 4 h reaction. This could be caused by condensation of lignin-derived molecules as was observed before[23] and shows that higher monomer yields of this reaction cannot simply be achieved by increasing the reaction time.

After performing the 4 h HDO of organosolv lignin-oil over Mo_2C/CNF at 350 °C instead of 300 °C (Fig. 5), a total monomer yield of 6% was obtained. This is lower than for the reaction at 300 °C where a total yield of 9% of aromatic monomers could be identified. The oxygen content of the product mixture, however, was reduced to 14%, representing a weight loss of 1%. No tris-oxygenated products could be observed anymore and only 24% of the total observed monomeric products consisted of bis-oxygenated molecules. This is in stark contrast with the results obtained from the reactions at 300 °C, for which the tris-oxygenated products were always the major products. The results thus show that also in the HDO of LPR-derived lignin-oils, products with a lower oxygen content can be obtained at higher temperatures, albeit in lower overall yield. The X-ray diffraction patterns of the spent catalyst recovered after the 350 °C run show that the Mo_2C phase was still present (Fig. 6). This indicates that this catalyst, shown to be stable during the HDO of model compound guaiacol,[23] also remained stable during the HDO of lignin depolymerization oils.

From a green chemistry perspective, it is important to reduce the amounts of solvents used in a process and, if solvents are required, to choose ones that are not toxic or environmentally harmful.[34] The use of dichloromethane for the extraction of the lignin-oil after LPR, when also less hazardous solvents such as ethyl acetate are available, is therefore not desirable. The two-step conversion of organosolv lignin was repeated, but now with extraction of the LPR reaction mixture with ethyl acetate. The HDO step was performed with Mo_2C/CNF at 350 °C and the results are shown in Fig. 5. The total
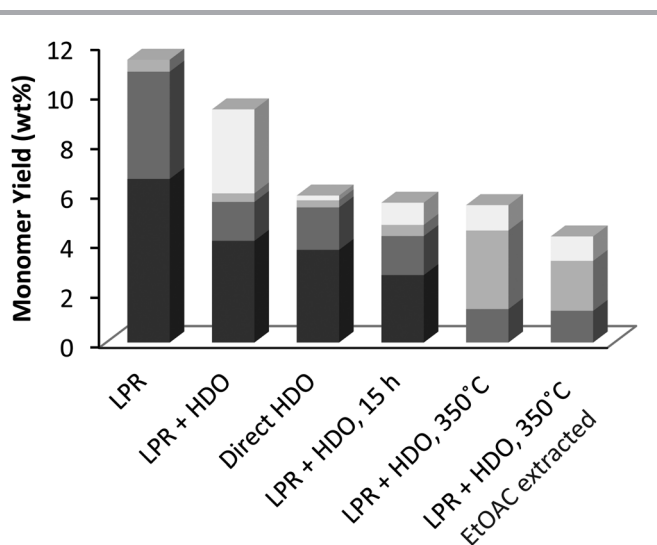

Fig. 5 Yield of monomeric aromatic products after HDO reactions of organosolv lignin-oil over the Mo_2C/CNF catalyst under different conditions: ▢ oxygen-free products, ▨ mono-oxygenated products, ▦ products containing two oxygen functionalities, ■ products with three or more oxygen functionalities. Unless stated otherwise, the reactions were extracted with DCM and performed for 4 h at 300 °C.
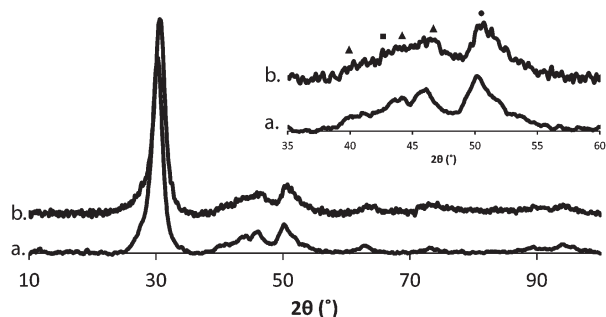
Fig. 6 X-ray diffraction patterns of (a) the fresh Mo$_2$C/CNF catalyst and (b) the Mo$_2$C/CNF catalyst after HDO of organosolv lignin-oil at 350 °C. Reflections are given for graphitic carbon (●), MoO$_2$ (■) and Mo$_2$C (▲).[33]

monomer yield at the end of the second step amounts to only 4%, which is lower than the 6% previously obtained in a DCM-extracted reaction under the same conditions. The oxygen content of the observed products was comparable to the DCM-extracted reaction with no tris-oxygenated compounds and 23% of oxygen-free products. It should be possible to obtain comparable yields and activities after further optimization of the extraction step for a cleaner solvent such as ethyl acetate, however.

The results show that a combination of two appropriate steps can potentially lead to a process for the production of low oxygen-content aromatic chemicals from lignin. Further process optimization is needed for both the LPR and HDO steps to obtain higher yields and selectivities. Higher degrees of depolymerization in the LPR step are, for instance, expected to lead to higher monomer yields in both steps. It is anticipated that the degree of deoxygenation during the HDO step can be optimized by further variation of reaction conditions such as the concentration, temperature and reaction time. The amount of solids that are found after the HDO step can be reduced when lignin-oils with a larger degree of depolymerization are used or when a solvent is used that is able to dissolve also the larger lignin fractions (larger lignin fragments do not dissolve in the dodecane solvent used for the HDO reaction). Furthermore, precipitation of the larger molecules before extraction by changing the ethanol–water ratio of the solvent or separating the smaller from the larger molecules by distillation will probably lead to lower lignin-oil yields but cleaner HDO reaction mixtures. The flexibility of the two-step approach allows replacement of the first LPR step by other processes that produce depolymerized lignins. The product state of lignin-oil obtained by base-catalyzed depolymerization in particular shows great similarity to the products obtained by LPR and has been reported to contain high amounts of monomeric compounds.[14,15,35,36]

The production of aromatics with little or no oxygen from lignin has generally proven to be very difficult. Methods reported to date for lignin depolymerization typically lead to the formation of oxygen-rich aromatic monomers with at least two or three oxygen functionalities. Although it has been reported previously that benzene and phenolics could be formed from kraft lignin in processes such as hydrocracking, the harsh reaction conditions employed result in a loss of over 30% of the original lignin by the formation of gases such as CO and methane.[37] Related to the work described here, the hydrodeoxygenation of pyrolysis oil for the production of second generation biofuels has been reported by several groups. Several nickel-based catalysts were used to lower the oxygen content and increase the H/C ratio.[38–40] Although no product compositions were reported, HDO of these pyrolysis oils over nickel catalysts has been shown to result in the formation of mainly ring-hydrogenated products.[41] For the production of BTX and phenol from lignin a two-step process is desired, however, which combines a high depolymerization activity with a HDO catalyst that does not show ring-hydrogenation activity. The combination of an LPR reaction with a sequential HDO step over a CoMo/Al$_2$O$_3$ or Mo$_2$C/CNF catalyst has allowed the production of BTX without loss of aromaticity.

4. Conclusions

A two-step process for the catalytic conversion of lignin into bulk aromatic chemicals is presented. In the first step, the molecular weight of various sources of lignin is reduced *via* the LPR reaction resulting in the formation of monomers, dimers and small oligomers. The lignin-oil obtained after extraction was successfully used as a substrate in a second HDO step. During the HDO of the depolymerized lignin oil, products with a lower oxygen content were obtained and yields of up to 9% monomeric aromatic products of which 24% were oxygen-free products. The oxygen content of the lignin-oil obtained after LPR and of the HDO product greatly depends on the lignin source. Product mixtures from hardwood lignins were shown to have a higher oxygen content than products obtained from softwood or grass type lignins. At increased temperatures of 350 °C the total oxygen content could be lowered even more with complete conversion of all molecules containing three oxygen functionalities even when starting with hardwood lignin. The majority of the products are mono-oxygenated phenolics. The two-step approach proved to be more effective for the production of oxygen-free products than the separate steps. These results show the potential of the approach for the further development and optimization of a practical process for the production of aromatic chemicals from lignin.

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References

1 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552.
2 H. Werhan, J. M. Mir, T. Voitl and P. R. von Rohr, *Holzforschung*, 2011, **65**, 703.
3 K. Stärk, N. Taccardi, A. Bösmann and P. Wasserscheid, *ChemSusChem*, 2010, **3**, 719.
4 http://www.borregaard.com
5 Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu and J. Xu, *Energy Environ. Sci.*, 2013, **6**, 904.
6 C. Li, M. Zheng, A. Wang and T. Zhang, *Energy Environ. Sci.*, 2012, **5**, 6383.
7 W. Xu, S. J. Miller, P. K. Agrawal and C. W. Jones, *ChemSusChem*, 2012, **5**, 667.
8 P. T. Patil, U. Armbruster, M. Richter and A. Martin, *Energy Fuels*, 2011, **25**, 4713.
9 K. Barta, T. D. Matson, M. L. Fettig, S. L. Scott, A. V. Iretskii and P. C. Ford, *Green Chem.*, 2010, **12**, 1640.
10 R. Y. Nsimba, C. A. Mullen, N. M. West and A. A. Boateng, *ACS Sustainable Chem. Eng.*, 2013, **1**, 260.
11 P. R. Patwardhan, R. C. Brown and B. H. Shanks, *ChemSusChem*, 2011, **4**, 1629.
12 H. Ben and A. J. Ragauskas, *ACS Sustainable Chem. Eng.*, 2013, **1**, 316.
13 M. P. Pandey and C. S. Kim, *Chem. Eng. Technol.*, 2011, **34**, 29.
14 V. M. Roberts, V. Stein, T. Reiner and A. Lemonidou, *Chem.–Eur. J.*, 2011, **17**, 5939.
15 J. M. Lavoie, W. Baré and M. Bilodeau, *Bioresour. Technol.*, 2011, **102**, 4917.
16 E. Furimsky, *Appl. Catal., A*, 2000, **199**, 147.
17 J. S. Shabtai, W. W. Zmierczak and E. Chornet, *WO Patent*, 9910450, 1999.
18 Q. Bu, H. Lei, A. H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wie, Y. Liu, J. Tang, Q. Zhang and R. Ruan, *Bioresour. Technol.*, 2012, **124**, 470.
19 J. C. Hicks, *J. Phys. Chem. Lett.*, 2011, **2**, 2280.
20 H. Ben, W. Mu, Y. Deng and A. J. Ragauskas, *Fuel*, 2013, **103**, 1148.
21 J. Zakzeski, A. L. Jongerius, P. C. A. Bruijnincx and B. M. Weckhuysen, *ChemSusChem*, 2012, **5**, 1602.
22 A. L. Jongerius, R. Jastrzebski, P. C. A. Bruijnincx and B. M. Weckhuysen, *J. Catal.*, 2012, **285**, 315.
23 A. L. Jongerius, R. W. Gosselink, J. Dijkstra, J. H. Bitter, P. C. A. Bruijnincx and B. M. Weckhuysen, *ChemCatChem*, 2013, DOI: 10.1002/cctc.201300280.
24 A. Pandey, C. R. Soccol, P. Nigam and V. T. Soccol, *Bioresour. Technol.*, 2000, **74**, 69–80.
25 R. J. A. Gosselink, J. E. G. Van Dam, E. De Jong, E. L. Scott, J. P. M. Sanders, J. Li and G. Gellerstedt, *Holzforschung*, 2010, **64**, 193.
26 B. Kamm, P. R. Gruber and M. Kamm, *Biorefineries – Industrial Processes and Products*, Wiley-VHC Verlag, 2006, vol. 2, pp. 151–163.
27 C. Heitner, D. R. Dimmel and J. A. Schmidt, *Lignin and Lignans*, CRC Press, 2010, pp. 14–18.
28 C. R. Lee, J. S. Yoon, Y.-W. Suh, J.-W. Choi, J.-M. Ha, D. J. Suh and Y.-K. Park, *Catal. Commun.*, 2012, **17**, 54.
29 Y. Want, T. He, K. Liu, J. Wu and Y. Fang, *Bioresour. Technol.*, 2012, **108**, 280.
30 R. W. Gosselink, D. R. Stellwagen and J. H. Bitter, *Angew. Chem., Int. Ed.*, 2013, **52**, 5089.
31 J. Han, J. Duan, P. Chen, H. Lou, X. Zheng and H. Hong, *Green Chem.*, 2013, **13**, 2561.
32 H. Ren, W. Yu, M. Salciccioli, Y. Chen, Y. Huang, K. Xiong, D. G. Vlachos and J. G. Chen, *ChemSusChem*, 2013, **6**, 798.
33 ICDD PDF-2 database package http://www.icdd.com/products/pdf2.htm
34 T. Laird, *Org. Process Res. Dev.*, 2012, **16**, 1.
35 A. Vigneault, D. K. Johnson and E. Chornet, *Can. J. Chem. Eng.*, 2007, **85**, 906.
36 A. Toledano, L. Serrano and J. Labidi, *J. Chem. Technol. Biotechnol.*, 2012, **87**, 1593.
37 D. T. A. Huibers and H. Jonson, *DE Patent*, 3228897, 1983.
38 A. R. Ardiyanti, S. A. Khromova, R. H. Venderbosch, V. A. Yakovlev, I. V. Melián-Cabrera and H. J. Heeres, *Appl. Catal., A*, 2012, **449**, 121.
39 N. Joshi and A. Lawal, *Chem. Eng. Sci.*, 2012, **74**, 1.
40 I. Graça, J. M. Lopes, H. S. Cerqueira and M. F. Ribeiro, *Ind. Eng. Chem. Res.*, 2013, **52**, 275.
41 C. Zhao and J. A. Lercher, *Angew. Chem., Int. Ed.*, 2012, **51**, 5935.