Experimental Studies on the Hydrotreatment of Kraft Lignin to Aromatics and Alkylphenolics Using Economically Viable Fe-Based Catalysts

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ABSTRACT: Limonite, a low-cost iron ore, was investigated as a potential hydrotreatment catalyst for kraft lignin without the use of an external solvent (batch reactor, initial H₂ pressure of 100 bar, 4 h). The best results were obtained at 450 °C resulting in 34 wt % of liquefied kraft lignin (lignin oil) on lignin intake. The composition of the lignin oil was determined in detail (elemental composition, GC-MS, GC×GC-FID, and GPC). The total GC-detectable monomeric species amounts up to 31 wt % on lignin intake, indicating that 92 wt % of the products in the lignin oil are volatile and thus of low molecular weight. The lignin oil was rich in low-molecular-weight alkylphenolics (17 wt % on lignin) and aromatics (8 wt % on lignin). Performance of the limonite catalyst was compared to other Fe-based catalysts (goethite and iron disulfide) and limonite was shown to give the highest yields of alkylphenolics and aromatics. The limonite catalyst before and after reaction was characterized using XRD, TEM, and nitrogen physisorption to determine changes in structure during reaction. Catalyst recycling tests were performed and show that the catalyst is active after reuse, despite the fact that the morphology changed and that the surface area of the catalyst particles was decreased. Our results clearly reveal that cheap limonite catalysts have the potential to be used for the depolymerization/hydrodeoxygenation of kraft lignin for the production of valuable biobased phenolics and aromatics.

KEYWORDS: Kraft lignin, Hydrotreatment, Iron catalyst, Biobased chemicals, Alkylphenolics

1. INTRODUCTION

Lignin is a major component in lignocellulosic biomass and provides strength and rigidity to the structure. High volumes of lignins are produced within the pulp and paper industry, which are currently underutilized. In addition, the production of second generation biofuels like ethanol from lignocellulosic biomass also leads to the formation of considerable amounts of lignins. As such, there is an incentive to develop valorization routes for leftover lignins into valuable biobased products. Several lignin valorization approaches such as enzymatic conversions, thermal/catalytic pyrolysis, base-assisted/oxidative depolymerization, reductive hydrodeoxygenation, and pyrolysis followed by hydrotreatment have been explored in the past decade. For details related to the various valorization approaches for lignin, the reader is directed to ref 9.

Most of the lignin hydrogenolysis and hydrodeoxygenation studies are performed at high temperature and hydrogen pressure (>300 °C and >50 bar) in combination with transition-metal-based catalysts such as NiMo or CoMo on Al₂O₃ catalysts, originally developed for petroleum processing. The primary function of these hydrotreating catalysts is the removal of sulfur and nitrogen heteroatoms from conventional oil feeds. Interestingly, these catalysts also have proven to be efficient for the removal of bound oxygen along with sulfur and nitrogen from biomass-derived product streams. Usually the hydrotreatment of lignin is performed in the presence of a solvent to avoid recondensation of fragment radicals formed during hydrotreatment, and in some cases, the solvent also acts as a hydrogen donor (tetralin, isopropanol). It must be noted that the solvents under hydrotreatment conditions are usually not inert and may be (partly) incorporated into the final products. Moreover, the use of solvents in large-scale processes should be avoided for economic reasons.

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process economic considerations. Thus, the development of highly efficient, cheap, and environmentally friendly catalysts for the depolymerization of lignin without the use of an external solvent is an important challenge. In addition, the presence of sulfur in the kraft lignin should also be considered when selecting an appropriate catalyst, as it should not be deactivated due to sulfur poisoning.

Meier et al. performed the catalytic hydrotreatment (referred to as hydropyrolysis) of organocell lignin using NiMo supported on aluminosilica catalysts and red mud (iron oxide) under solvent-free conditions. The oil yield obtained using the NiMo catalyst was 61.6 wt %, and the monomeric yield was 21.8%. Furthermore, Oasmaa et al. reported the catalytic hydrotreatment of different technical lignins under solvent-free conditions. The oil yields varied in the range of 49–71 wt %, depending on the type of lignin. The highest oil yield was reported for organosolv lignin using a NiMo on aluminosilica/Cr₂O₃ catalyst. Further research considering the solvent-free approach for lignin depolymerization has been reported by our group using commercial Ru/C catalyst, with monomer yields of up to 21 wt % on lignin intake. The basis of the solvent free approach is that the lignin melts at hydrotreatment reaction conditions and thereby can act as the solvent. Recently, we reported that bimetallic sulfided
NiMo and CoMo catalysts on various supports are also active for the depolymerization of kraft lignin to aromatic monomers under solvent-free conditions.\textsuperscript{20} There is an ongoing interest to identify low-cost, disposable catalyst for the hydrotreatment of lignin.\textsuperscript{31,32} Iron-based catalysts have been extensively explored for coal liquefaction among others due to their low cost.\textsuperscript{34–37} An example is limonite ore, which contains hematite ($\alpha$-Fe$_2$O$_3$) and goethite ($\alpha$-FeOOH).\textsuperscript{38} The hydrotreatment activity of such Fe-based catalysts for coal liquefaction is suggested to be due to the transformation of iron phases ($\alpha$-Fe$_2$O$_3$/$\alpha$-FeOOH) into an active pyrrhotite ($\alpha$-Fe$_{1-x}$S) phase upon sulfidation of the catalyst.\textsuperscript{36,38} It is suggested that hydrogen dissociation occurs on these Fe$_{1-x}$S clusters.\textsuperscript{37}

As the process objectives and conditions for coal liquefaction resemble those of the hydrotreatment of lignin, the use of iron-based catalyst for the hydrotreatment of lignin is of potential interest. Furthermore, a number of patents and papers reported the use of iron-based salts in the presence of a promoter and solvent for the hydrotreatment of lignin.\textsuperscript{20,22,24,25,39} For instance, in the Noguchi process, an iron(II) sulfide catalyst with a cocatalyst (CuS in most examples) was used in the presence of lignin tar/phenol as a solvent (>50 wt % of lignin) at 250–450 °C at a hydrogen pressure of 150–450 bar. High yields of monophenols (approximately 40%) were reported, which also includes the contribution of the phenolic solvent used in the process.\textsuperscript{20} Later on, Urban et al. reported an improved version of the Noguchi process, claiming 65 and 45% yields of monophenols and cresol, respectively, when using a promoted iron catalyst.\textsuperscript{22} Again, the high monophenolic yields were partly due to the use of the solvents (phenol and methanol). Based on these patents, it is clear that iron-based catalysts are capable of depolymerizing lignin to give substantial yields of phenolics. We here report the use of low-cost iron-based catalysts for the hydrotreatment of kraft lignin without the addition of an external solvent. As such, the molten lignin and the reaction products (in a later stage of the batch reaction) serve as the solvent. A potentially very attractive catalyst is limonite, which is an ore rich in iron (about 50 wt %) and also contains other metals such as Ni, Co, and Cr that can act as a promoters during hydrotreatment. In fact, the use of limonite as a catalyst for coal liquefaction is known.\textsuperscript{39} Performance of the limonite catalyst is compared to that of other iron-based catalysts (Fe$_3$O$_4$, FeOOH, Fe$_2$O$_4$, and Fe$_3$O$_4$–NiO) as well as a commercial CoMo catalyst, a well-known hydrotreatment catalyst. Catalyst stability was probed by performing recycling experiments. Catalyst characterization studies using XRD, TEM, and BET before and after the hydrotreatment reactions are also reported.

2. MATERIALS AND METHODS

2.1. Chemicals. All chemicals used in this study were of analytical grade and used without further purification. Limonite ore was obtained from PT Inco, Soroako, Sulawesi Island, Indonesia. Although limonite composition varies between sources, here we use the term "limonite" to specifically refer to the limonite used in this study. CoMo/Al$_2$O$_3$ (KF-752) catalyst was purchased from Eurecat. Goethite, iron–nickel oxide (Fe$_3$O$_4$–NiO), iron oxide (Fe$_2$O$_3$), and iron disulfide (FeS$_2$) were purchased from Sigma-Aldrich. Dimethylsulfoxide (DMSO) from Sigma-Aldrich was used for sulfiding the catalyst in situ. Tetrahydrofuran (THF), dichloromethane (DCM), and acetone were obtained from Boom B.V. Di-n-butyl ether (DEB) was purchased from Sigma-Aldrich and DMSO (dimethyl sulfoxide) was from J. T. Baker. Hydrogen (>99.9%) and nitrogen gas (>99.8%) were purchased from Hoekloos. Indulin-AT (kraft lignin) was obtained from MWV specialty chemicals and was kindly provided by Dr. R. Gosselink from the Wageningen University and Research Center, The Netherlands. Indulin-AT is a purified form of kraft pine lignin with lignin and ash content of 92.2 and 2.6 wt %, respectively, on dry basis.\textsuperscript{40}

2.2. Catalytic Hydrotreatment Experiments. The catalytic hydrotreatment experiments were performed in a batch Parr reactor system with a maximum operating pressure of 350 bar and 500 °C. It consists of a batch autoclave (100 mL) with electric heating (metal block containing electrical heating elements and channels to flow water for cooling), equipped with an overhead stirrer (Rushton type turbine with a gas induced impeller) and temperature controller. The stirring speed was set at 1200 rpm for all experiments. In a typical experiment, 15 g of kraft lignin, 0.75 g of catalyst (5 wt % on lignin intake), and 0.38 g of DMDS (sulfur source) were loaded in the reactor. The reactor was sealed and subsequently flushed with hydrogen (5 times) followed by pressurizing with hydrogen to 200 bar at room temperature for leak testing. After leak testing, the H$_2$ pressure was reduced to 100 bar, and the reactor was heated at a heating rate of 8 °C/min. The reaction time was set to 0 h when the preset reactor temperature was reached, and the reaction was allowed to proceed for 4 h. The maximum pressure observed during the reaction is dependent on reaction temperature and time due to the formation of gas phase components. At 350, 400, and 450 °C, the maximum pressure after 4 h was 180, 195, and 220 bar, respectively. After 4 h of reaction, the reactor was cooled to room temperature, and the pressure was recorded to determine the amount of gas phase components formed during the reaction. Subsequently, the pressure was released, and the gas phase was collected in a 3 L Tedlar gas bag and was analyzed with gas chromatography. After removing the gas phase, the reactor was opened to collect the other phases (water, oil, and solids). For the experiments at 350 and 400 °C, the organic product was obtained as a highly viscous paste and solvents (like DCM and acetone) were used to collect and extract the product oil (Figure 1a). Interestingly, at 450 °C we observed the formation of an oil phase instead of a paste, and as a result, clear water and oil phases were obtained that were easily separated from the solids by decanting (Figure 1b). For all experiments, the organics absorbed on the solid phase (coke, unconverted lignin, and catalyst) were removed by a solvent-based product separation procedure involving dichloromethane (DCM) followed by acetone (see Figure 1). The DCM and acetone fractions were collected and analyzed. The solid fraction obtained after acetone extraction consists of coke, unconverted lignin, and catalyst and was weighed for mass balance calculations. To determine the amount of unconverted lignin (which is soluble in DMSO), 1 g of solid residue was suspended in 30 mL of DMSO and stirred for 24 h at room temperature. Subsequently, the solution was filtered, and the solids were washed thoroughly with acetone and dried. The difference in the weight of solids before and after the treatment was assumed to be the amount of unconverted lignin.

The amounts of product oils (wt %) for reactions at 350 and 400 °C were calculated on the basis of the oil recovered after evaporation of the solvent (DCM and acetone). At 450 °C, the reactor content can be weighed accurately, and by subtracting the amount of collected water and solid, the total amount of product oil was calculated. The conversion, product yield (gas, liquid, and solid), and mass and carbon balance closures were calculated based on the initial lignin intake using eqs 1–4.

\[
\text{Conversion} = \frac{\text{lignin intake (g)} - \text{unconverted lignin (g)}}{\text{lignin intake (g)}} \times 100 \text{ wt\%}
\]

\[
\text{Product Yield} = \frac{\text{product (g)}}{\text{lignin intake (g)}} \times 100 \text{ wt\%}
\]
Table 1. Composition of the Limonite Catalyst

<table>
<thead>
<tr>
<th>element</th>
<th>Fe</th>
<th>Al</th>
<th>Ni</th>
<th>Cr</th>
<th>Si</th>
<th>S</th>
<th>Mg</th>
<th>Co</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration</td>
<td>51.5</td>
<td>4.2</td>
<td>1.4</td>
<td>2.0</td>
<td>0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Mass balance closure

\[
\text{Weight of products (oil + water + solid (without catalyst) + gas)} \times 100 \text{ wt\%} = \text{lignin intake (g)}
\]  

Carbon balance closure

\[
\text{C in all the products (oil + water + solid (without catalyst) + gas)} \times 100 \text{ wt\%} = \text{C amount in lignin intake (g)}
\]

2.3. Catalyst Characterization. X-ray diffraction data of the catalysts were recorded on a Broker D8 advance diffractometer operating using Cu Kα radiation (λ = 0.1544 nm) at 40 kV. XRD patterns were measured in reflection geometry in the 2θ range between 2 and 80°, with a step size of 0.04°.

Inductively coupled plasma (ICP) analyzes were performed on a PerkinElmer Optima 7000 DV apparatus using a solid-state CCD array detector. Prior to analysis, the samples were subjected to a microwave treatment in 40% HF to dissolve the samples. Yttrium (10 ppm) and scandium (10 ppm) were used as internal standards, and Ar was used as the purge gas.

BET surface areas of the catalysts were determined with nitrogen physisorption using a Micromeritics ASAP 2420 instrument. The samples were degassed in vacuum at 300 °C (heating rate is 10 °C/min) for 6 h prior to analysis.

Transmission electronic microscopy (TEM) images were obtained using a Philips CM120 operated at an acceleration voltage of 120 kV. Samples for TEM measurements were ultrasonically dispersed in ethanol and subsequently deposited on a mica grid coated with carbon.

2.4. Product Phase Analysis. GC×GC-FID (two-dimensional gas chromatography–flame ionization detector, 2DGC) analysis was performed on product oils using a Trace GC×GC system from Interscience equipped with a cryogenic trap and two columns (30 m × 0.25 mm i.d. and 0.25 μm film RTX-1701 capillary column connected to a 120 cm × 0.15 mm i.d. and 0.15 μm film Rxi-5Sil MS column). A dual-jet modulator was applied using carbon dioxide to trap the samples. The modulation time was set to 6 s. Helium was used as the carrier gas (flow rate of 0.8 mL/min). The injector temperature and FID temperature were set at 280 °C. The oven temperature was kept at 40 °C for 5 min then heated to 250 °C with a rate of 3 °C/min. The pressure was set at 0.7 bar. From the GC×GC-FID spectra, the yields of aromatics, alkylphenolics, ketones, alkanes (linear/cyclic), naphthenes, guaiacols, and catechols in the product oils were calculated based on lignin intake. The identification of the main GC×GC component groups (e.g., alkanes, aromatics, and alkylphenolics) in the lignin oils was done by spiking with representative model compounds for the component groups and GC-MS-FID analysis.

Quantification was performed by using an average relative response factor (RRF) per component group with di-n-butyl ether (DBE) as the internal standard. More details on the GC×GC calibration procedures are given in previous work from our group.

GC/MS spectra were recorded using a Quadrupole Hewlett-Packard 6890 MSD connected to a Hewlett-Packard 5890 gas chromatograph (GC) with a Restek RTX-1701 column (60 m × 0.25 mm i.d. and 0.25 μm film thickness) and a flame ionization detector (FID). Injection and detection were performed at 280 °C, using oven temperature heating profiles from 40 to 250 °C at a heating rate of 3 °C/min. Peak identification was done using the NIST05a mass spectra library. For both the GC×GC-FID and GC/MS-FID analyses, product oils were diluted with tetralydrofuran (THF), and 500 ppm di-n-butyl ether (DBE) was added as an internal standard.

Gas phases were collected in a Tedlar gasbag (SKC Tedlar 3 L sample bag (9.5 in. × 10 in.)) with a polypropylene septum fitting. GC-TCD analysis were performed on a Hewlett-Packard 5890 Series II GC equipped with a Porablot Q Al2O3/Na2SO4 column and a molecular sieve (5 Å) column. The injector temperature was set at 110 °C, and the detector temperature was maintained at 200 °C. The oven temperature was kept at 40 °C for 3 min followed by heating to 90 °C at the rate of 20 °C/min and maintained at this temperature for 7.5 min. A reference gas was used to identify the peaks by retention time and to quantify the products in the gas phase (55.19% H2, 19.70% CH4, 3.00% CO, 18.10% CO2, 0.51% ethylene, 1.49% ethane, 0.51% propylene, and 1.50% propane).

Molecular weight determinations by GPC were performed using a HP1100 equipped with three 300 × 7.5 mm PLgel 3 μm MIXED-E columns in series using a GBC LC 1240 RI detector. Average molecular weight calculations were carried out with the PSS WinGPC Unity software from Polymer Standards Service. Polystyrene samples were used as calibration standards. For GPC measurements, THF was used as the eluent at a flow rate of 1 mL/min at 140 bar, with an injection volume of 20 μL. TOC (total organic carbon) in aqueous phase was determined with a Shimadzu TOC-5000A TOC analyzer with an OCT-1 sampler port.

The water content in the product oil was determined by Karl Fischer titration using a Metrohm Titirino 758 titration device. A small amount of sample (approximately 0.02–0.06 g) was added to an isolated glass compartment containing Hydralan (KarlFischer 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 values are reported.

Elemental analysis (C, H, N, and S content) of product oil and solid after hydrotreatment were carried out using an automated Euro Vector EA3000 CHNS analyzer with an acetanilide as a calibration reference. The oxygen content was determined by the difference of CHNS. All the samples were analyzed twice, and the average values are reported in this study.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization. The metal composition of the limonite catalyst used in this study is shown in Table 1. The composition is in agreement with literature data.\textsuperscript{27,30,40} In addition to iron (51.5 wt%), the catalyst also contains Ni (1.4 wt%), Cr (2.0 wt%), Al (4.2 wt%), and traces of Co, Mg, Ca, and S. Besides limonite, other iron-based catalysts (goethite and iron disulfide) were also tested, as well as a conventional hydrotreatment catalyst (CoMo/Al2O3). The BET surface areas of limonite, goethite, and CoMo/Al2O3 were determined and are 158, 58, and 140 m²/g, respectively.

Limonite ores contain both hematite (α-Fe2O3) and goethite (α-FeOOH).\textsuperscript{39} XRD analyzes were performed to investigate the types of phases in the limonite catalyst used in this work. As can be seen in Figure 2, the XRD patterns for limonite and goethite catalysts consist predominantly of α-FeOOH, which is in agreement with literature.\textsuperscript{38} For limonite, broader XRD peaks were observed indicating that the average particle size for the limonite catalyst is smaller than that of goethite. To validate this assumption, the catalysts were analyzed using TEM (Figure 3). The limonite sample shows a uniform distribution of rods with a width of 5–10 nm and a length of about 200 nm. Goethite and limonite show similar rod-like particle morphologies (Figure 3), in line with literature data.\textsuperscript{38} However, the average size of the rod-like particles for limonite is significantly smaller than that of goethite (rod width approximately 30–40...
isolated water phase (7.6 wt % at 400 °C). This is con-

firmed by considering the amounts of

gas phase (wt %)\textsuperscript{b}
directly from Tables S1 and S2 for details. In

these cases, the oil yields were considerably lower than those

for the catalytic reactions (approximately 10 wt % of oil at 450 °C). Thus, a catalyst is required for improved product yields as thermal depolymerization mainly yields char as the product with only a limited amount of low molecular weight liquid products.

Some additional experiments were performed to determine whether the sulfur present in the kraft lignin is actually sufficient for catalyst sulfidation and that an external sulfur source is not necessary. The hydrotreatment experiments in the absence of the sulfur source were performed at 350 °C and an oil yield of 26 wt % was obtained. This yield is significantly lower than the oil yield (49%) obtained for experiments with an external sulfur source, indicating incomplete sulfidation of the catalyst when only kraft lignin is used.

The lignin conversion was also determined; see the Materials and Methods section for details on the procedure. For an experiment at 350 °C, the lignin conversion was 90%. Quantitative lignin conversion was observed at 400 °C and higher. The lignin oil yields were between 33 and 49 wt % on lignin intake.

Table 2. Overview of the Catalytic Hydrotreatment Experiments of Kraft Lignin Using Limonite\textsuperscript{a}

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>350</th>
<th>400</th>
<th>450</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic phase (wt %)</td>
<td>49.0</td>
<td>36.3</td>
<td>33.7</td>
</tr>
<tr>
<td>aqueous phase (wt %)</td>
<td>10.6</td>
<td>7.6</td>
<td>21.5</td>
</tr>
<tr>
<td>gas phase (wt %)</td>
<td>6.6</td>
<td>11.0</td>
<td>18.3</td>
</tr>
<tr>
<td>solid phase (wt %)</td>
<td>10.5</td>
<td>25.6</td>
<td>24.7</td>
</tr>
<tr>
<td>total mass balance (wt %)</td>
<td>86.5</td>
<td>78.5</td>
<td>98.1</td>
</tr>
<tr>
<td>total carbon balance (wt %)</td>
<td>98.5</td>
<td>93.5</td>
<td>99.4</td>
</tr>
<tr>
<td>lignin conversion (wt %)</td>
<td>90</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>water content organic phase (wt %)</td>
<td>0.1</td>
<td>0.3</td>
<td>2.3</td>
</tr>
<tr>
<td>carbon content aqueous phase (wt %)</td>
<td>2.5</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
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\textsuperscript{a}Reaction conditions: 4 h, 100 bar H\textsubscript{2} initial pressure, 5 wt % catalyst and 2.5 wt % sulfur source (DMDS). \textsuperscript{b}wt % on lignin intake. Recovery of the water phase was incomplete. \textsuperscript{c}Carbon amount determined by elemental analysis (Table S5). \textsuperscript{d}Water content in the organic phase is the amount of water dissolved in the organic phase as determined by Karl Fischer titrations. \textsuperscript{e}Carbon content in the aqueous phase is the carbon content of the water-soluble components as determined by TOC.

The catalytic hydrotreatment reactions were performed in a batch reactor using kraft lignin as a feed and limonite as the catalyst (5 wt % on lignin) in the absence of a solvent (initial H\textsubscript{2} pressure of 100 bar at room temperature, 4 h reaction time). After workup (Figure 1), an organic phase, designated as lignin oil, and a water phase were obtained. The organic phase was isolated and analyzed in detail. The results for experiments at three reaction temperatures are presented in Table 2. The carbon balance closures (>93 wt %) for all experiments were good, whereas the mass balance closures (>86 wt %) at 350 and 450 °C were reasonable. The closure at 400 °C was worse due to the formation of a viscous organic/water phase that hampered complete recovery of the water phase from the reactor. This is confirmed by considering the amounts of isolated water phase (7.6 wt % at 400 °C versus >10 wt % for

The lignin oils were analyzed using GCMS-FID to identify the monomeric components in the oil. A representative chromatogram (450 °C) is shown in Figure 4 and reveals

nm and a length of 400 nm). This observation is in line with the BET (larger surface areas for limonite) and XRD data (broader peaks for limonite).

3.2. Catalytic Hydrotreatment at Different Temperatures. The catalytic hydrotreatment reactions were performed in a batch reactor using kraft lignin as a feed and limonite as the catalyst (5 wt % on lignin) in the absence of a solvent (initial H\textsubscript{2} pressure of 100 bar at room temperature, 4 h reaction time). After workup (Figure 1), an organic phase, designated as lignin oil, and a water phase were obtained. The organic phase was isolated and analyzed in detail. The results for experiments at three reaction temperatures are presented in Table 2. The carbon balance closures (>93 wt %) for all experiments were good, whereas the mass balance closures (>86 wt %) at 350 and 450 °C were reasonable. The closure at 400 °C was worse due to the formation of a viscous organic/water phase that hampered complete recovery of the water phase from the reactor. This is confirmed by considering the amounts of isolated water phase (7.6 wt % at 400 °C versus >10 wt % for

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<td>93.5</td>
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<tr>
<td>lignin conversion (wt %)</td>
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<td>100</td>
<td>100</td>
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<tr>
<td>water content organic phase (wt %)</td>
<td>0.1</td>
<td>0.3</td>
<td>2.3</td>
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<tr>
<td>carbon content aqueous phase (wt %)</td>
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these cases, the oil yields were considerably lower than those for the catalytic reactions (approximately 10 wt % of oil at 450 °C). Thus, a catalyst is required for improved product yields as thermal depolymerization mainly yields char as the product with only a limited amount of low molecular weight liquid products.

Some additional experiments were performed to determine whether the sulfur present in the kraft lignin is actually sufficient for catalyst sulfidation and that an external sulfur source is not necessary. The hydrotreatment experiments in the absence of the sulfur source were performed at 350 °C and an oil yield of 26 wt % was obtained. This yield is significantly lower than the oil yield (49%) obtained for experiments with an external sulfur source, indicating incomplete sulfidation of the catalyst when only kraft lignin is used.

The lignin conversion was also determined; see the Materials and Methods section for details on the procedure. For an experiment at 350 °C, the lignin conversion was 90%. Quantitative lignin conversion was observed at 400 °C and higher. The lignin oil yields were between 33 and 49 wt % on lignin, with the highest yield at the lowest temperature. This oil yield is significantly higher than the oil yield (17 wt %) reported using red mud as a catalyst (reaction temperature 380 °C).\textsuperscript{16}

The amounts of solid and gas phase (for product gas phase composition, see Table S4) also show a clear trend with regards to the temperature and both were shown to increase at higher temperature. This observation indicates that both gasification as well as repolymerization of reactive fragments are also prominent at higher temperatures, in agreement with literature data.\textsuperscript{16,17}

The lignin oils were analyzed using GCMS-FID to identify the monomeric components in the oil. A representative chromatogram (450 °C) is shown in Figure 4 and reveals
that the oil contains significant amounts of alkylphenolics, aromatics, and cyclic alkanes.

To quantify the product classes, GC×GC-FID was used. This analysis technique gives a good separation between the various organic compound classes and allows for quantification. A typical GC×GC chromatogram of a product oil obtained at 450 °C using limonite catalyst is shown in Figure 5 (see Figure S1 for chromatograms of oils obtained at 350 and 400 °C).

In the chromatogram, well-separated organic compound classes are visible with highest intensities of peaks in the alkylphenolics and aromatic (including naphthalenes) regions. The quantified GC-detectable product yields at different hydrotreatment temperatures are given in Table 3. The yields of alkylphenolics, aromatics and naphthalenes increase with temperature. Notably, for the lignin oil obtained at 450 °C, 92% of the products are detectable by GC×GC. This implies that the lignin oil obtained with the limonite catalyst at 450 °C mainly consists of low-molecular-weight products.

We believe that the hydrotreatment activity of limonite is due to the transformation of the iron phases (α-Fe₂O₃/α-FeOOH) into an active pyrrhotite (Fe₃₋ₓS) phase upon sulfidation of the catalyst. From the literature, it is clear that the hydrogen dissociation occurs on the Fe₃₋ₓS clusters. Based on the literature and our results, we envision a synergistic effect where the lignin fragments are preferentially adsorbed on an exposed iron surface of Fe₃₋ₓS. The dissociated hydrogen atoms further interacts with the lignin fragments adsorbed on the iron surface, resulting in hydrotreated lignin oil by hydrogenation, hydrocracking, and hydrodeoxygenation reactions. Furthermore, the presence of Ni and Co in the vicinity of Fe further helps in dissociating hydrogen molecules, hence promoting the hydrotreatment activity. Similar synergistic effects of Fe and Ni species on the surface of Ni–Fe particles for the activation of pyridine and dissociation of H₂ have been reported for the hydrodeoxygenation of guaiacol.

3.3. Catalytic Hydrotreatment Using Other Fe-Based Catalysts. The hydrotreatment activity of the limonite catalyst

Table 3. Product Distribution of Lignin Oils Obtained at Different Hydrotreatment Temperatures Using Limonite Catalyst

<table>
<thead>
<tr>
<th>compound class</th>
<th>yield (wt %) 350 °C</th>
<th>yield (wt %) 400 °C</th>
<th>yield (wt %) 450 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkylphenolics</td>
<td>11.7</td>
<td>12.1</td>
<td>16.7</td>
</tr>
<tr>
<td>aromatics</td>
<td>1.8</td>
<td>1.8</td>
<td>4.1</td>
</tr>
<tr>
<td>naphthalenes</td>
<td>0.7</td>
<td>1.8</td>
<td>3.2</td>
</tr>
<tr>
<td>ketones</td>
<td>1.7</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>cyclic/linear alkanes</td>
<td>0.9</td>
<td>0.7</td>
<td>5.0</td>
</tr>
<tr>
<td>catecholics</td>
<td>0.4</td>
<td>0.2</td>
<td>1.6</td>
</tr>
<tr>
<td>guaiacolics</td>
<td>0.01</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>total yield</td>
<td>(wt % lignin)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.3</td>
<td>17.5</td>
<td>30.9</td>
</tr>
</tbody>
</table>

*Yields are in wt % based on lignin intake.

Figure 4. GC×GC chromatogram for the lignin oil obtained at 450 °C using the limonite catalyst.

Figure 5. GC×GC-FID chromatogram for the lignin oil obtained at 450 °C using limonite.

Figure 6. GPC analysis on the product oils (Figure 6). The average molecular weight (Mₜ) reported for kraft lignin is approximately 4000 g/mol. The molecular weight distribution for the product oils significantly shifts toward lower molecular weight for oils obtained at higher hydrotreatment temperatures (Table 4). The Mₜ values for both the oil and acetone fraction at 450 °C is very low (140−175 g/mol), which correlates well with the GC×GC results.

We believe that the distillation of the iron phases (α-Fe₂O₃/α-FeOOH) into an active pyrrhotite (Fe₃₋ₓS) phase upon sulfidation of the catalyst. From the literature, it is clear that the hydrogen dissociation occurs on the Fe₃₋ₓS clusters. Based on the literature and our results, we envision a synergistic effect where the lignin fragments are preferentially adsorbed on an exposed iron surface of Fe₃₋ₓS. The dissociated hydrogen atoms further interacts with the lignin fragments adsorbed on the iron surface, resulting in hydrotreated lignin oil by hydrogenation, hydrocracking, and hydrodeoxygenation reactions. Furthermore, the presence of Ni and Co in the vicinity of Fe further helps in dissociating hydrogen molecules, hence promoting the hydrotreatment activity. Similar synergistic effects of Fe and Ni species on the surface of Ni–Fe particles for the activation of pyridine and dissociation of H₂ have been reported for the hydrodeoxygenation of guaiacol.
was compared with other iron-based catalyst (goethite and iron disulfide) as well as with a commercial CoMo catalyst. The reactions were carried out at 450 °C for a reaction time of 4 h using kraft lignin (as feed), catalyst (5 wt % on lignin), DMDS (as sulfur source, 2.5 wt % on lignin), and an initial H2 pressure of 100 bar. The kraft lignin conversion, mass balance closures, and product yields are presented in Table 5. Good mass balance closure was observed for all the experiments (>91 wt %) and (>93 wt %) for the carbon balance. At these conditions, quantitative lignin conversion was observed. Solids yield was the highest for the disulfide catalyst, indicating that it is not a very active hydrotreatment catalyst, leading to considerable repolymerization of reactive fragments instead of hydro(deoxy-)genation to more stable, lower-molecular-weight components.

The limonite catalyst gives the highest oil and monomeric yield in comparison to all other iron-based catalysts. This observation indicates that the activity of limonite is not only due to the presence of the goethite (α-FeOOH) and/or pyrrhotite (Fe1−xS) phase but also due to the presence of other elements (Ni, Co, etc.). The presence of other metals in the limonite catalysts indeed has reported to have a promotional effect on the liquefaction activity when using coal as the feed.49 These catalysts may also influence the hydrotreatment activity and are the subject of follow up studies.

The hydrotreatment performance of the limonite catalyst in terms of oil and total monomer yield is rather comparable with that for the conventional hydrotreatment catalyst (CoMo/Al2O3); see Table 5 for details. For CoMo/Al2O3, 34 wt % oil yield was obtained with 88% of the product being GC-detectable. These values may be compared to earlier research by Meier et al. and Oasmaa et al.16,17 These authors report an oil yield of approximately 60 wt % for kraft lignin, though

Figure 6. Molecular weight distribution of product oils obtained at different hydrotreatment temperatures using limonite (a) lignin product oil and (b) acetone soluble organics.

Table 4. Molecular Weight (Mw) of Product Oils Obtained at Different Hydrotreatment Temperatures Using Limonite

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>DCM soluble/oil (g/mol)</th>
<th>Acetone soluble (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>520</td>
<td>1280</td>
</tr>
<tr>
<td>400</td>
<td>265</td>
<td>430</td>
</tr>
<tr>
<td>450</td>
<td>140</td>
<td>175</td>
</tr>
</tbody>
</table>

*DCM soluble organics (350 and 400 °C) or lignin oil (450 °C).

Table 5. Overview of the Catalytic Hydrotreatment Experiments of Kraft Lignin Using Various Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Limonite</th>
<th>Goethite</th>
<th>Iron disulfide</th>
<th>CoMo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic phase (%)</td>
<td>33.7</td>
<td>28.9</td>
<td>27.0</td>
<td>34.2</td>
</tr>
<tr>
<td>Aqueous phase (%)</td>
<td>21.5</td>
<td>21.8</td>
<td>12.6</td>
<td>22.8</td>
</tr>
<tr>
<td>Gas phase (%)</td>
<td>18.3</td>
<td>15.7</td>
<td>17.7</td>
<td>13.8</td>
</tr>
<tr>
<td>Solid phase (%)</td>
<td>24.7</td>
<td>28.7</td>
<td>33.6</td>
<td>23.3</td>
</tr>
<tr>
<td>Total mass balance (%)</td>
<td>98.1</td>
<td>95</td>
<td>91.1</td>
<td>94.0</td>
</tr>
<tr>
<td>Total carbon balance (%)</td>
<td>99.4</td>
<td>95.6</td>
<td>105</td>
<td>93.4</td>
</tr>
<tr>
<td>Lignin conversion (%)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Water content organic phase (%)</td>
<td>2.3</td>
<td>2.4</td>
<td>0.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Carbon content aqueous phase (%)</td>
<td>1.3</td>
<td>1.4</td>
<td>1.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**Table 5. Overview of the Catalytic Hydrotreatment Experiments of Kraft Lignin Using Various Catalysts**

- **catalyst**: limonite, goethite, iron disulfide, CoMo
- **organic phase (%)**: 33.7, 28.9, 27.0, 34.2
- **aqueous phase (%)**: 21.5, 21.8, 12.6, 22.8
- **gas phase (%)**: 18.3, 15.7, 17.7, 13.8
- **solid phase (%)**: 24.7, 28.7, 33.6, 23.3
- **total mass balance (%)**: 98.1, 95, 91.1, 94.0
- **total carbon balance (%)**: 99.4, 95.6, 105, 93.4
- **lignin conversion (%)**: 100, 100, 100, 100
- **water content organic phase (%)**: 2.3, 2.4, 0.8, 1.7
- **carbon content aqueous phase (%)**: 1.3, 1.4, 1.4, 0.8

- **Monomer Product Yield (wt %)**: 16.7, 14.6, 15.0, 12.0
- **alkylphenolics**: 16.7, 14.6, 15.0, 12.0
- **aromatics**: 4.1, 3.2, 1.1, 8.0
- **napthenes**: 3.2, 2.6, 5.5, 4.1
- **ketones**: 0.4, 0.6, 0.3, 0.1
- **cyclic/linear alkanes**: 5.0, 1.4, 0.1, 4.0
- **catecholics**: 1.6, 1.1, 1.7, 1.1
- **guaiacylics**: 0.1, 0.1, 0.0, 0.2
- **total yield (%)**: 30.9, 23.5, 23.6, 29.4

**Elemental Composition Organic Phase (wt % dry basis)**

- **carbon**: 84.6, 83.6, 83.7, 82.4
- **hydrogen**: 7.7, 7.8, 7.1, 7.5
- **oxygen**: 7, 7.9, 6.9, 9.7
- **sulfur**: 0.1, 0.2, 1.9, 0.0

- **Reaction conditions**: 450 °C, 4 h, 100 bar H2, initial pressure, 5 wt % catalyst and 2.5 wt % sulfur source (DMDS), 2 wt % on lignin intake.
- **Product oil recovered using DCM**.
- **Elemental composition of kraft lignin (wt % dry basis)**: carbon = 61.1, hydrogen = 5.6, oxygen = 30.6, and sulfur = 1.6. Water content in the organic phase is the amount of water dissolved in the organic phase as determined by Karl Fischer titrations. **Carbon content in the aqueous phase is the carbon content of the water-soluble components as determined by TOC.**

The hydrotreatment performance of the limonite catalyst in terms of oil and total monomer yield is rather comparable with that for the conventional hydrotreatment catalyst (CoMo/Al2O3).
between 50 and 300 g/mol $M_w$ range. This indicates that the depolymerization of kraft lignin into a mixture of monomeric compounds occurred to a significant extent, correlating well with GC×GC data showing that >80% of the compounds are GC-detectable.

In addition, the elemental composition of the kraft lignin and the lignin oils were determined (Table 5), and the results are presented in a van Krevelen diagram (Figure 8). The kraft lignin feed consists of 61.1 wt % carbon, 5.6 wt % hydrogen, 30.6 wt % oxygen, and 1.6 wt % sulfur. The carbon and hydrogen contents of the lignin oils are considerably higher and observed in the ranges of 82−85 and 7.1−7.8 wt %, respectively (Table 5). Notably, the oxygen content for the lignin oils is between 6.9 and 9.7 wt %, which is considerably lower than that of the starting feed. These findings are clearly visible in the van Krevelen plot (Figure 8). The O/C ratio is reduced considerably from 0.38 to 0.06−0.09, whereas the H/C ratio of the products oils is between 1.01 and 1.1. These results further confirm the occurrence of hydrodeoxygenation of alkylphenolics to aromatics reactions. Interestingly, the H/C and O/C ratios for product oils were between the alkylphenolic and aromatic range. This observation compares well with GC×GC results where the product oil was indeed found to consist mainly of alkylphenolics and aromatics.

3.4. Catalyst Recycling Studies for the Limonite Catalyst. The possibility for reuse of the limonite catalyst was tested by reperforming reactions with a catalyst isolated after the first batch reaction. This spent catalyst was not directly used for a second reaction but first subjected to an oxidative treatment (500 °C for 4 h in air) to remove any carbon deposits. A significant decrease in the BET surface area from 158 (fresh catalyst) to 10 m$^2$/g was observed for the regenerated catalyst. Furthermore, TEM images (Figure 9) clearly indicate a change in the morphology of the catalyst. A thin rod-like morphology was observed for the fresh limonite catalyst (Figure 3a,b), whereas the spent catalyst (Figure 9) shows a distinct different morphology and appears to be sintered. The sintering of catalyst particles is in line with the decrease in the surface area after regeneration. It must be noted that sintering of the limonite catalyst particles occurs during the hydrotreatment reaction and not during regeneration (see TEM images and BET values in Figure S2, where no change in particle size or BET value were observed when fresh limonite was calcined). These observations are in agreement with coal liquefaction literature where the agglomeration of active pyrrhotite (Fe$_{1-x}$S) is observed under liquefaction conditions resulting in crystal growth and loss of surface area of the catalyst.$^{33,37}$

In addition, the regenerated limonite sample was analyzed using ICP to determine the elemental composition (Table 6). Based on the ICP results, it is clear that the composition of the fresh limonite is considerably different from that of the regenerated one. The Fe content decreased considerably from 51.5 to 33.4 wt %, whereas the sulfur and Na contents increased significantly. It must be noted the Ni and Cr are still present.
though show a subtle decrease. The overall decrease in Fe amount along with the other metal elements in comparison to the fresh limonite sample is likely due to the significant increase in sulfur and Na amounts, which likely stem from the sulfur source and kraft lignin, respectively.

XRD analysis was further performed to determine the various iron phases in the regenerated limonite catalyst. As can be seen in Figure 10, the XRD patterns for limonite and regenerated limonite catalyst differ significantly. The limonite catalyst consists predominantly of α-FeOOH (section 3.1). However, after hydrotreatment followed by regeneration, the limonite catalyst reveals an XRD reflection pattern for a typical hematite phase (α-Fe₂O₃).

As the limonite catalyst after regeneration differs from the fresh one, we further tested the hydrotreatment activity of the regenerated catalyst at 450 °C (Figure 11). Interestingly, the regenerated catalyst demonstrated significant activity, irrespective of sintering and loss of surface area after regeneration. Similar findings were also reported for iron-based catalysts such as pyrite and iron oxide used for coal liquefaction. In addition, it is clear that the transformation of α-Fe₂O₃/α-FeOOH phases to the active pyrrhotite (Fe₁₋ₓS) phase under hydrotreatment conditions in the presence of sulfur source is reversible, which is in agreement with the literature. In comparison to the fresh limonite catalyst, a small but significant decrease in oil yield and a significant decrease in the total monomer yield (25 wt %) was observed for the regenerated catalyst. In line with this observation, the amount of GC detectables for the fresh limonite catalyst (92%) is by far higher than that for the regenerated limonite catalyst (77%). This indicates that the lignin oil obtained with the regenerated limonite catalyst consists not only of monomeric species (GC-detectables) but also higher-molecular-weight compounds (oligomers). This was confirmed by GPC (Figure 12). From our results, it is clear that the hydrotreatment activity of limonite catalyst decreases after regeneration which is possibly due to the sintering, decrease in metal composition, and decline in surface area of the catalyst particles.

From our findings, it is clear that the limonite, a low-cost iron ore, has potential to be used as a hydrotreatment catalyst for kraft lignin, which is expected to have a positive effect on the process economics. The costs of the use of an external sulfur source (here DMDS) must be also considered in the total costs of the process. A possibility to reduce the cost associated with

<table>
<thead>
<tr>
<th>element</th>
<th>Fe</th>
<th>Al</th>
<th>Ni</th>
<th>Cr</th>
<th>Si</th>
<th>S</th>
<th>Na</th>
<th>Co</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration</td>
<td>33.4</td>
<td>3.1</td>
<td>1.0</td>
<td>1.4</td>
<td>1.1</td>
<td>8.5</td>
<td>6.5</td>
<td>0.1</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 6. Composition of the Regenerated Limonite Catalyst (ICP)

Figure 10. XRD peak pattern of the fresh and regenerated limonite catalyst.

Figure 11. Comparison of monomeric product distribution of lignin oils obtained after the catalytic hydrotreatment of kraft lignin with limonite and regenerated limonite catalyst (450 °C, 4 h, 100 bar H₂ initial pressure, 5 wt % catalyst).
sulfur addition is to use hydrogen sulfide as a sulfur source, which is a cheap alternative and already used in large-scale hydrodesulfurization processes for fossil feeds. When considering the large monomeric yields (which can be up to 31 wt % on kraft lignin), the limonite catalyst has good potential to be used for the valorization of lignin to valuable bulk chemicals.

4. CONCLUSIONS

Various iron-based catalysts were screened for the hydrotreatment of kraft lignin with the incentive to depolymerize the lignin to a product oil enriched in low-molecular-weight monophenolics and aromatics. The best results were obtained for a limonite catalyst at 450 °C, giving 34 wt % of a lignin oil on lignin intake. Notably, 92 wt % of the components in this oil are detectable by GC. GPC confirms that the oil consists mainly of low-molecular-weight products. Additionally, the performance of the limonite catalyst in terms of oil and total monomer yield was found to be comparable with those of conventional CoMo/Al₂O₃ hydrotreatment catalyst. The lignin oil hydrotreated with limonite was rich in alkylphenolics (17 wt % versus 12 wt % for CoMo), whereas the aromatics yield (4 wt % versus 8 wt % for CoMo) was lower. Furthermore, the limonite catalyst may be reused after an oxidative treatment and still show substantial activity for the hydrotreatment of kraft lignin. To the best of our knowledge, we are the first to demonstrate limonite as a hydrotreatment catalyst for (kraft) lignin. From our findings, it is clear that the limonite, a low-cost iron ore, has the potential to be used as a hydrotreatment catalyst for kraft lignin, which is expected to have a positive effect on the process economics. When considering the large monomeric yields (which can be up to 31 wt % on kraft lignin), the limonite catalyst has good potential to be used for the valorization of lignin to valuable bulk chemicals.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b03012.

Tables with the oil yields, mass balances and monomer yields for experiments in the absence of a catalyst, and an overview of experimental data with other Fe-based catalysts; figures including a GC×GC chromatogram for a representative oil and TEM images of the limonite catalyst before and after calcination (PDF)

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Notes

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