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Slurry Hydroconversion of Solid Kraft Lignin to Liquid Products Using Molybdenum- and Iron-Based Catalysts

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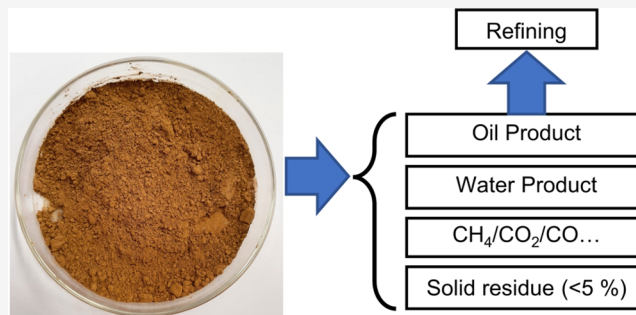


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ABSTRACT: Kraft lignin is an abundantly available and largely underutilized renewable material with potential for production of biobased fuels and chemicals. This study reports the results of a series of slurry hydroprocessing experiments with the aim of converting solid Kraft lignin to liquid products suitable for downstream refining in more conventional reactors. Experiments reported in this study were conducted by feeding a lignin slurry to an already hot, liquid-filled reactor to provide momentaneous heating of the lignin to the reaction temperature. This modified batch procedure provided superior results compared to the regular batch experiments, likely since unwanted repolymerization and condensation reactions of the lignin during the heating phase was avoided, and was therefore used for most of the experiments reported. Experiments were performed using both an unsupported Mo-sulfide catalyst and Fe-based catalysts (bauxite and hematite) at varied reaction temperatures, pressures, and catalyst loadings. The use of Mo-sulfide (0.1% Mo of the entire feed mass) at 425 °C and 50 bar resulted in complete conversion of the Kraft lignin to nonsolid products. Very high conversions (>95%) could also be achieved with both sulfided bauxite or hematite at the same temperature and pressure, but this required much higher catalyst loadings (6.25% bauxite or 4.3% hematite of the total feed mass), and around 99% conversion could be achieved at higher temperatures but at the expense of much higher gas yields. Although requiring much higher loadings, the results in this study suggest that comparatively nonexpensive Fe-based catalysts may be an attractive alternative for a slurry-based process aimed at the hydroconversion of solid lignin to liquid products. Possible implementation strategies for a slurry-based hydroconversion process are proposed and discussed.



1. INTRODUCTION

Replacing fossil transportation fuels with renewable alternatives is a very attractive route to reducing the CO₂ emissions from the transportation sector. Sweden's goal is to reduce the CO₂ emissions from the domestic transport sector (excluding domestic aviation) by 70% in 2030 compared to 2010,¹ which will require great effort. In 2020, biofuels accounted for 23% of the total energy consumption of the transport sector in Sweden, of which hydrogenated vegetable oil (HVO), biogas, and fatty acid methyl esters (FAME) constituted the majority.² To reach the set goals, further increases in the biofuel proportion in the transport fuels will be required.

One abundant and largely underutilized source of renewable material is lignin, which is a complex and water-insoluble aromatic polymer that makes up 15–30% of dry biomass.³ The Kraft pulping process accounts for about 85% of the lignin production in the world.⁴ In this process, lignin is separated from the cellulose, forming black liquor, which is combusted to provide energy for the paper mill as well as heat and power production from the energy surplus. The total annual volume of Kraft lignin from paper production amounts to about 44 TWh in Sweden,⁵ and globally about 130 million tons are generated from the pulp- and paper industry each year.³ There

are some available techniques for separation of lignin as a solid brown powder from black liquor,⁶ where the Lignoboost process is one option.⁷ The separation of lignin from black liquor enables the energy surplus of a paper mill to be utilized in other ways while also reducing the load on the recovery boiler thereby enabling increased pulp production.^{7–9} A future increase in bioethanol production from biomass residues could further increase the availability of lignin. Production of 1 kg ethanol from corn stovers liberates 0.5–1.5 kg lignin, and considering that only 40% of the lignin-rich residue is sufficient to cover the total energy demand of the ethanol production, this could greatly increase the lignin supply.³ Seen from the other perspective, it has also been concluded that for second generation bioethanol production from biomass residues via the organosolv process to be commercially competitive, lignin

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valorization is of great importance.¹⁰ Although being very abundant, only small portions of the industrially generated lignin are separated and converted to more valuable chemicals or fuels today.

Solid materials such as separated lignin cannot be easily processed in traditional oil refinery infrastructure. One way in which solid lignin could be processed along with fossil feedstocks is in a slurry process, where a mixture of liquids and solid catalyst particles are continuously fed and withdrawn from a mixed reactor. This type of process, typically called slurry hydrocracking, is normally considered for processing heavy fossil oils as an alternative to traditional hydrocracking in packed catalyst beds where catalysts quickly become deactivated due to depositions of coke and metal impurities on the catalyst surfaces.^{11,12} Catalysts utilized in the slurry hydrocracking process range from low-cost single-use additives with relatively low catalytic activity to highly active unsupported catalysts.¹¹ The unsupported catalysts can be further divided into two categories, depending on whether they are produced from water-soluble or oil-soluble precursors. The oil-soluble precursors are generally more expensive but show a higher catalytic activity of the activated catalyst.¹³ Slurry hydrocracking of heavy fossil oils with catalysts derived from oil-soluble precursors is normally performed at temperatures of 420–450 °C, H₂ pressures of 70–170 bar, and residence times of 20–180 min.¹³ The most used catalyst for slurry hydrocracking is Mo-sulfide, which has been shown to have high activity in terms of suppressing coke and gas formation.^{14,15} The active Mo-sulfide catalyst particles are formed by sulfidation of the precursors either *in situ* or *ex situ*. An example of a low-cost catalyst considered for slurry hydrocracking of heavy fossil oils is bauxite, which contains Fe-oxide that can easily be converted to catalytically active Fe-sulfide in the reaction with sulfur species present in the feed.¹⁶ Red mud (a waste material from aluminum oxide production from bauxite) has also been studied for slurry hydrocracking of fossil vacuum residue¹⁷ and is utilized in the VEBA combi-cracker system.¹⁸ Studies aimed at coprocessing biobased oils with fossil oils in a slurry hydroprocess have also been conducted,^{19,20} as well as studies on processing only biobased oils.²¹ The Canmet group achieved almost complete deoxygenation of fast pyrolysis bio oil at 320–380 °C and 4.8–9.7 MPa in a slurry reactor using highly dispersed MoS₂ catalysts generated *in situ* from emulsified precursors.²¹ For hydrotreatment of lignin with Fe-based catalysts in slurry-type reactors both limonite²² and Fe(II)-sulfate impregnated on either activated charcoal or directly on the lignin particles²³ have been studied.

A lot of research around lignin valorization has focused on model compounds,²⁴ but it has been demonstrated that conversion of real lignin is a much more difficult task.^{25,26} Ren et al. concluded that, as opposed to model compounds, lignin causes severe catalyst deactivation due to heavy carbonaceous deposits, and even a very small addition of real lignin to a model compound resulted in a clear reduction in conversion of the model compound.²⁶ Studies on real lignin have often achieved relatively low hydrocarbon yields,²⁶ and especially Kraft lignin (as used in this study) produced from the Kraft pulping process is known to be a heterogeneous material that differs significantly from the native lignin it originated from²⁷ and requires harsh hydrotreatment conditions for direct conversion to defunctionalized molecules.²⁴ In one interesting study that gives a very good insight into the reaction pathways

of lignin during hydroconversion, 30 wt % soda lignin in tetraline solvent was reacted with supported NiMo sulfide catalyst at 350 °C and 80 bar in a batch reactor with a ballast of H₂ to prevent lack of H₂ during the reaction.²⁸ The reaction was carried out for 0–28 h, leading to about 10% of the original lignin mass remaining in solid form after the full reaction time. In the reaction, tetraline acted as a H-donor, and replacing tetraline with dodecane gave lower lignin conversion and liquid yield as well as a higher yield of solid residue, and it was concluded that a H-donor solvent was very helpful in depolymerizing the lignin and limiting condensation/polymerization reactions, as has also been noted by Ambursa et al.²⁹ On the basis of these results, it can be concluded that a temperature of 350 °C and a pressure of 80 bar are insufficient to provide complete conversion of lignin within reasonable timespans despite using H-donor solvents. Breunig et al., on the other hand, carried out slurry-phase experiments with lignin and tetraline solvent in batch reactors at up to 500 °C for 1 h and found that reaction at 500 °C resulted in solid residue yields corresponding only to the mass of ash elements in the lignin and the added catalyst but very high gas yields due to formation of primarily C₁–C₄ by cracking of the lignin.²³ A temperature of 435 °C was concluded to provide the best results out of the temperatures investigated in that study (370, 435, and 500 °C) with almost as low solids yield as 500 °C but with much lower gas yield and consequently a higher organic liquid yield.

The focus of this study was to study the direct hydroconversion of solid Kraft-lignin into liquid products in a slurry-based process. The aim was not to produce finished fuels/chemicals from lignin but rather to use the slurry process as a form of pretreatment to transform the lignin, a highly oxygenated solid material, into liquid products with reasonable O contents that could be processed in conventional refinery infrastructure such as fixed bed hydrotreater/hydrocrackers. The effects of temperature, catalyst precursor type (oil-soluble Mo octoate or Fe-based bauxite and hematite), catalyst concentration, reaction pressure, and temperature were studied in a series of screening experiments aiming to evaluate how these parameters can be adjusted to attain as high a lignin conversion as possible, preferably in an as economically feasible and robust process as possible. Fossil vacuum gas oil (VGO) was used as a carrier liquid for the solid lignin particles, although the primary aim of the study was to evaluate the conversion of lignin to nonsolid products and not to study the effect of the process parameter on the VGO processing.

2. EXPERIMENTAL SECTION

2.1. Raw Materials. The properties of the lignin and VGO used in this study are summarized in Table 1. The lignin was used in the experiments at the indicated moisture content without any further drying. Elemental composition was determined by Elemental Microanalysis (UK), using Dumas combustion for C, H, N, and S, and Unterzaucher pyrolysis for O. However, the O content of the lignin was calculated as the difference between 100% and the sum of C, H, N, S, and ash due to unreasonably low analysis value (23.1% O and a total sum of C, H, N, S, and O of only 95.3%). The Mo-octoate used as a catalyst precursor was purchased from Strem Chemicals (15% Mo). The bauxite had an Fe concentration of 12 wt % and the hematite an Fe concentration of 69.4 wt % (pure Fe₂O₃ corresponds to 69.9 wt % Fe). Particle size distribution, determined by wet sieving, was 95.8% < 40 μm for the hematite and 62.5% < 40 μm for the bauxite used. However, the bauxite had a specific surface area (determined by BET) of 253 m²/g, which was drastically higher than

Table 1. Raw Material Properties

elemental composition (wt %)	lignin (as used)	vacuum gas oil
C	64.8	85.4
H	5.8	12.0
N	0.31	0.4
S	1.4	1.3
O	27.4 (by diff)	0.8
moisture (wt %)	3.5	—
ash (wt %)	0.3	—
solubility in THF (%)	91.8	—
boiling point distribution		
residue (% > 524 °C)	—	1.0
VGO (% 343–524 °C)	—	77.9
distillates (% 177–343 °C)	—	20.6
naphtha (% IBP, 177 °C)	—	0.5

hematite ($1 \text{ m}^2/\text{g}$). The porosity of hematite was also very low ($0.003 \text{ cm}^3/\text{g}$) compared to bauxite ($0.21 \text{ cm}^3/\text{g}$), and the hematite is essentially free of pores. The bauxite had a total acidity of $300 \mu\text{mol}/\text{g}$ according to NH_3 -Temperature-Programmed Desorption, whereas the hematite is not expected to possess any acidic properties.

2.2. Experimental Setup. The experimental setup used in this study included two different operational modes termed semi-batch and hot injection semi-batch (HISB), which will be described separately but are represented schematically in Figure 1.

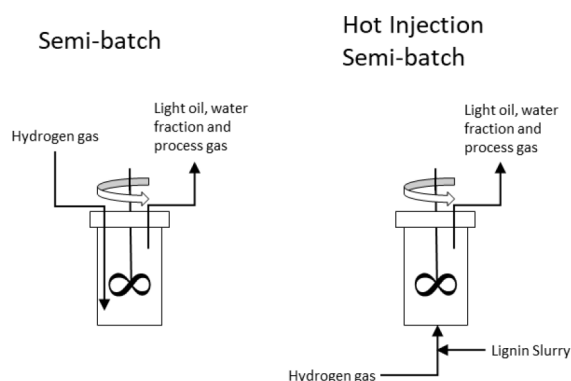


Figure 1. Schematic representation of the semi-batch and hot injection semi-batch setup.

2.2.1. Semi-batch. The term semi-batch is here used to describe a batch reaction where the reactor (total volume 2 dm^3) was filled with all liquid and solid reactants before sealing. In a typical experiment, the reactor was filled with 634 g vacuum gas oil (VGO), 160 g lignin (corresponding to 20 wt %), and 5.3 g Mo octoate (Strem Chemicals, 15% Mo) as catalyst precursor (corresponding to 0.1% Mo of the total feed). Upon heating, this oil-soluble Mo compound forms catalytically active MoS_2 -species by reacting with sulfur present in the VGO and lignin. After sealing the reactor, it was pressurized with H_2 to 150 bar and then heated to an inner temperature of 425°C , which took a little more than two hours. Once 425°C was reached, this temperature was held for the desired reaction time (0–6 h) before the heating was terminated and the reactor was allowed to cool to room temperature. Throughout the heating of the reactor, during the reaction time, and until the reactor had cooled to 350°C , H_2 was supplied to the reactor (through a dip-tube) at $800 \text{ NL}/\text{h}$. The pressure was maintained at 150 bar throughout the experiments using a pressure regulation valve, and the reactor was stirred at 1340 rpm throughout the experiments. All produced water, and some volatile organic components (total mass of water and organic phase 46–168 g) were collected downstream of the reactor in a gas/liquid separator situated between the reactor and the pressure control valve.

2.2.2. Hot Injection Semi-batch. Contrary to the semi-batches, in the hot injection semi-batches (HISB) no lignin was present in the reactor during the heating to the reaction temperature. In a typical experiment, the reactor (same equipment as with semi-batch) was filled with VGO and the desired amount of catalyst (Mo octoate, bauxite, or hematite). DMDS was also supplied to the reactor at a mass corresponding to five stoichiometric requirements for the sulfidation of Mo to MoS_2 or, in the case of hematite, Fe_2O_3 to FeS. For the bauxite experiments, the addition of DMDS was varied and contributed between 0.5 to 5 stoichiometric requirements.

The reactor was pressurized with H_2 to the intended reaction pressure (50–100 bar) and heated to the desired reaction temperature (400 – 440°C). Once the reaction temperature was reached, feeding of a slurry consisting of either 20 or 40 wt % lignin in VGO was initiated at $8 \text{ mL}/\text{min}$ using a Floxlab BTDP 500–5 syringe pump. (A relatively low feeding rate was chosen to try to minimize the plugging problem associated with feeding of slurry to the reactor. Also, high feeding rates can, from experience, cause a significant drop in reactor temperature due to the cooling effect from the cold slurry fed to the reactor.) A total of 410 mL slurry (with known density to calculate the corresponding mass) was fed to the hot reactor, during about 51 min. To ensure that a correct volume of slurry was fed to the process, all pipes between the pump and a valve near the reactor were filled with slurry and pressurized to the reaction pressure before the valve was opened and feeding commenced. Both H_2 and slurry were supplied to the reactor through the bottom inlet. The H_2 flow was maintained throughout the entire experiment at either $1000 \text{ NL}/\text{h}$ or $1500 \text{ NL}/\text{h}$ when using 20 wt % and 40 wt % lignin in the slurry, respectively. Once feeding was terminated, the reaction temperature of 425°C was maintained for another two hours before heating was stopped and the reactor allowed to cool. The initial amount of VGO present in the reactor during the heating phase varied between 336–396 g and was adjusted to attain a lignin concentration of either 10 or 20 wt % and the desired catalyst loading once all slurry had been fed to the reactor. This setup means that the initial catalyst concentration in the reactor was higher than toward the end of the feeding phase and vice versa for the lignin concentration. All indicated catalyst- and lignin concentrations both refer to the weight proportion of the total mass fed to the reactor, whether present during the heating phase or fed as a slurry. As in the semi-batch setup, produced water and some volatile organic components were collected in the downstream liquid/gas separator throughout the experiments (66–250 g). As in the semi-batch experiments, the reactor was mechanically stirred at 1340 rpm throughout the experiments, and fresh H_2 was supplied after the finished reaction time until the liquid temperature in the reactor had decreased to below 350°C .

2.3. Analysis and Evaluation. **2.3.1. Overall Mass Balance.** After each experiment, the reactor was emptied of its liquid product along with any suspended particles while solid material in the form of lumps (if present) was collected as a separate fraction. In the liquid/gas separator, the liquid fraction consisted of a water phase and organic phase, which were separated gravimetrically. Gas production from the reaction was evaluated as the total mass of gas leaving the reactor, measured by a Coriolis mass flow meter, and subtracting added H_2 . (This approximates that the H_2 consumption was negligible compared to the H_2 added, which was close to the truth due to a relatively high H_2 flow.) The mass of all collected liquid and solid material and the gas yield in relation to the initial liquid and solid mass constituted the mass balance.

When varying the concentration of bauxite and hematite, it was observed that the water phase yield increased linearly with the added amount of these catalysts (an increase is expected since water is formed from the sulfidation of Fe-oxides and in the case with bauxite also from dehydration reactions of aluminum hydroxides to oxides upon heating). Since no relationship between the deoxygenation and the catalyst loading was found, it was concluded that the extra water produced at higher catalyst loadings was primarily from the catalyst itself and not from more deoxygenation of the lignin. The linear trends between the bauxite or hematite addition, and the corresponding water formations could then be used to approximate

the amount of water formed from the bauxite or hematite (26.5% and 19.5% of the initial catalyst mass, respectively). This approximated water formation was then subtracted from the total water formation of each experiment to determine the mass of water formed from the lignin.

2.3.2. Solid Products. Figure 2 describes the evaluation procedure for the lignin product distribution. Three separate slurry samples

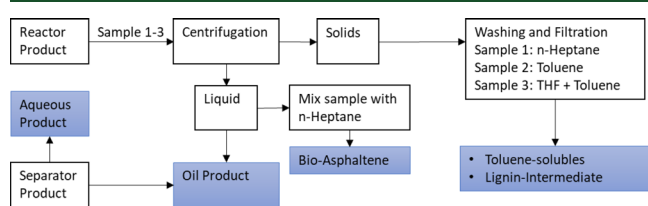


Figure 2. Evaluation procedure for products.

were, after mixing vigorously, withdrawn from the reactor product and were centrifugated for 15 min at 5000 rpm to separate solids and liquids. The solids from each sample were washed with either a mixture of tetrahydrofuran (THF) and toluene, with only toluene, or with *n*-heptane. The samples were thereafter filtered (Whatman GF/B, 1 μ m filter) and dried to constant weight to determine the respective solids concentration in the reactor product slurry. The solubility of any residual lignin decreased in the order THF > toluene > *n*-heptane, and a mixture of THF and toluene were used to dissolve and remove all soluble residue as well as any oil from the solid fraction. The use of these three solvents enabled the expression of the soluble solid residue as a toluene-soluble part and a toluene-insoluble part. Since most of the untreated lignin was soluble in THF but completely insoluble in toluene, the toluene-solubles were considered a highly depolymerized and easily soluble product of the lignin. The solids not soluble in toluene resembled untreated lignin in that it required THF to be dissolved but, as the results will show, is actually a severely depolymerized and deoxygenated product of the lignin. Hence, the solids that could not be dissolved in toluene but required THF to dissolve was defined as lignin-intermediate.

The yields of both the toluene-solubles and the lignin-intermediate are expressed as a proportion of the initial lignin weight. Since reference experiments with only VGO and catalyst showed no presence of these types of residues, it can be concluded that both these solids residues arise exclusively from the lignin. The solids material not soluble in THF (THF-insolubles) include catalyst, inorganics from the lignin, and insoluble organic species. The term coke is in this study used to define the insoluble organic species, and since coke is also produced from the VGO, it is therefore evaluated as a proportion of the total feed mass.

A liquid sample obtained after removing solids by centrifugation was mixed with an excess (2.5 v/v) of *n*-heptane, which caused precipitation of solid material from the liquid. This material was filtered and dried, and the yield of precipitated solids (expressed as a proportion of the initial lignin mass since processing only VGO did not result in any precipitate) was calculated. Material soluble in toluene but insoluble in *n*-heptane is typically defined as asphaltene according to ASTM D6560.³⁰ In this study, the term bio-asphaltene has been used to denote the lignin-derived precipitated material (which does share the solubility characteristics of fossil asphaltene but not necessarily other properties, such as elemental composition and molecular size).

The two solid residue types, toluene-solubles and lignin-intermediate, were isolated by mixing the solid material from an experiment in a stepwise manner first with *n*-heptane (to remove any residual oil), toluene, and finally THF. After the mixing steps using toluene and THF, the solid/liquid mixture was centrifugated to separate liquid from the remaining solid material and the solvent was thereafter evaporated from the obtained liquid fraction. Bio-asphaltene was separated from the liquid reactor product simply by precipitation with *n*-heptane followed by centrifugation, decanting,

and drying of the solid residues. The elemental composition of the residues was analyzed by elemental microanalysis (UK), using Unterzaucher pyrolysis for O and Dumas combustion for C, H, N, and S. Gel permeation chromatography (GPC) was used to evaluate the molecular weights of the residues as well as the untreated lignin. The GPC-analyses were performed using a GPC system (PL-GPC 50 Plus Integrated GPC system, Polymer Laboratories; Varian Inc., Chirch Stretton, UK) equipped with a UV detector operating at 280 nm, two PolarGel-M columns (300 \times 7.5 mm), and one guard column PolarGel-M (50 \times 7.5 mm). The column was calibrated with pullulan standards (Varian PL2090–0100). The analysis was carried out at 50 $^{\circ}$ C, with a flow rate of 0.5 mL/min, and the analyses were performed in duplication. The eluent used was dimethyl sulfoxide (DMSO) with 10 mM LiBr, and the concentration of sample in the eluent was \sim 0.24 mg/mL (filtered at 0.2 μ m before analysis).

The total content of organic matter in the THF-insoluble fractions (consisting of coke, catalyst, and ash) was determined by comparing the weight before and after incineration at 950 $^{\circ}$ C. The sulfur content (determined using a Hitachi TM3030Plus scanning electron microscope with dispersive X-ray) was used to calculate the weight loss due to the oxidation of sulfur upon incineration. Since most of the sulfur was assumed to be associated with the catalyst as MoS₂ or FeS, this weight loss was subtracted from the total weight loss, and the remainder was considered to occur due to incineration of coke. The coke yield from an experiment was thus calculated as the mass yield of THF-insoluble solids multiplied by the proportion of coke in these solids.

2.3.3. Liquid Products. The liquid oil products (from reactor and separator) were analyzed by GC-Simdist (ASTM D2887) to determine the boiling point distribution. Reactor- and separator products were analyzed for O content by elemental microanalysis (UK), using Unterzaucher pyrolysis. The degree of hydrodeoxygenation (HDO) from an experiment was calculated as the difference between the total O mass in the untreated raw materials and the total O mass in the two combined oil products, according to eq 1.

$$\text{HDO} = \frac{\text{feed}_O - \text{oil}_O}{\text{feed}_O} \times 100\% \quad (1)$$

A Mitsubishi NSX-2100 with a vertical furnace (VF-210) and UV-fluorescence detector (SD-210) was used for quantification of S in oil samples. Selected oil samples were also submitted to ALS (Sweden) for determination of metals content using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS).

2.3.4. Gas Products. During all experiments, a μ GC equipped with dual TCD-detectors was used to continually measure C₁–C₃, CO, CO₂, H₂S, and H₂. In addition to this, C₄ and C₅ were measured in gas sample bags with a separate GC instrument equipped with a flame ionization detector (FID). Two gas sample bags were collected at 30 and 90 min after the start of feeding lignin slurry to the reactor in the HISB experiments and the C₄- and C₅-concentration was approximated to follow an identical trend as C₃ but with an offset determined by the ratio of C₄/C₃ and C₅/C₃ at the times the gas sample bags were collected (the ratios at these times were typically quite similar and the average of the two was used). The average gas composition, from started reaction time (semi-batch) or started feeding of lignin slurry (HISB) until heating of the reactor was terminated, along with the summarized gas production was used to calculate the yield of each gas component.

2.4. Performed Experiments. Only three semi-batch experiments were performed, all with Mo-octoate as catalyst precursor at 425 $^{\circ}$ C and 150 bar (Table 2). A total of 17 HISB experiments were performed, which are summarized in Table 3. All experiments were performed not according to a predetermined experimental design but rather in a data driven fashion, where the results of one or a few experiments inspired the next experiments to be performed. The experimental order in Tables 2 and 3 does not reflect the actual order in which the experiments were performed.

It has been shown that Fe-oxides in bauxite easily convert to catalytically active FeS upon contact with H₂S, and a bauxite addition

Table 2. Performed Semi-batch Experiments^a

experiment	lignin (%)	temperature (°C)	pressure (bar)	reaction time (h)
1	20	425	150	0
2	20	425	150	2
3	20	425	150	6

^aAll with Mo octoate as the catalyst precursor at a loading of 0.1% Mo.

Table 3. Performed HISB Experiments^a

experiment	lignin (%)	temperature (°C)	pressure (bar)	catalyst	catalyst loading (%)
1	20	425	100	Mo octoate	0.1
2	10	425	50	Mo octoate	0.1
3	10	425	50	Mo octoate	0.02
4	10	425	50	bauxite	6.25
5	0	425	50	bauxite	6.25
6	10	440	50	bauxite	3.75
7	0	440	50	bauxite	3.75
8	10	425	100	bauxite	6.25
9	10	425	15	bauxite	6.25
10	10	425	50	bauxite	1.25
11	10	400	50	bauxite	3.75
12	10	425	50	bauxite	3.75
13	10	425	50	bauxite (reused)	6.25
14	10	425	50	hematite	2.15
15	10	425	50	hematite	4.3
16	10	440	50	hematite	4.3
17	10	425	50	hematite (reused)	4.3

^aCatalyst loading is expressed as % Mo, % bauxite, or % hematite of the entire feed mass. All experiments were performed with a 2 h reaction time after the feeding of the lignin slurry finished.

corresponding to 0.4–0.7% Fe for slurry hydrocracking of heavy fossil oils has been proposed as a preferred range.¹⁶ In this study, an initial Fe-loading between 0.15 and 0.75 wt % Fe was chosen for bauxite at a reaction pressure of 50–100 bar and a reaction temperature of 400–440 °C. Hematite has shown lower catalytic activity compared to bauxite with matched Fe-loadings,¹⁶ and therefore, a higher Fe-

loading of 1.5–3.0% was chosen. However, due to the very high Fe concentration in hematite, the solids addition was in the same range for hematite (2.2–4.3%) as for bauxite (1.25–6.25%). All indicated additions of lignin or catalyst are expressed as wt % of the entire feed mass.

3. RESULTS AND DISCUSSION

3.1. Experiments Using Molybdenum Catalyst.

3.1.1. Semi-batches Using Molybdenum Catalyst. Semi-batches conducted for 0 or 2 h resulted in significant amounts of solid material remaining attached to the interior reactor surfaces after finished reactions (Figure S1). After 6 h, only small amounts of solid material attached to reactor surfaces could be observed. The evaluation revealed that the proportion of initial lignin that remained as THF-soluble solids ranged from 56.4% after 0 h to 1% after 6 h (Figure 3). With an additional 3.2% of the lignin remaining as toluene-solubles after the 6 h reaction time the conversion of lignin to nonsolid material reached 95.8%. The yield of THF-insoluble solids (comprised of coke, catalyst, and ash elements) decreased from 1.3% after 0 h to 0.26% after 2 h but did not decrease significantly with further lengthened reaction time, which indicates that most of the THF-insoluble lignin (19.1% of the initial lignin mass) had been converted to more easily soluble components already after 2 h.

During the semi-batches, it was observed that the stirrer started making noise and slowing down due to mechanical resistance at an inner temperature between 230–270 °C. After typically about 2 min this behavior vanished, and the stirrer started behaving completely normal. The tendency for lignin to form solid residue above 250 °C is well-known, which has been attributed to the formation of phenoxyl radicals that have a random tendency for solid residue formation through repolymerization and condensation reactions.³¹ An experiment in which an identical lignin slurry as in the semi-batch experiments was heated in a glass beaker under stirring, and an inert atmosphere showed the formation of large agglomerates around this temperature that quickly grew and eventually engulfed the stirrer. Therefore, it is likely that a similar agglomeration took place in the semi-batch experiments, and these agglomerates either became shattered by the stirrer

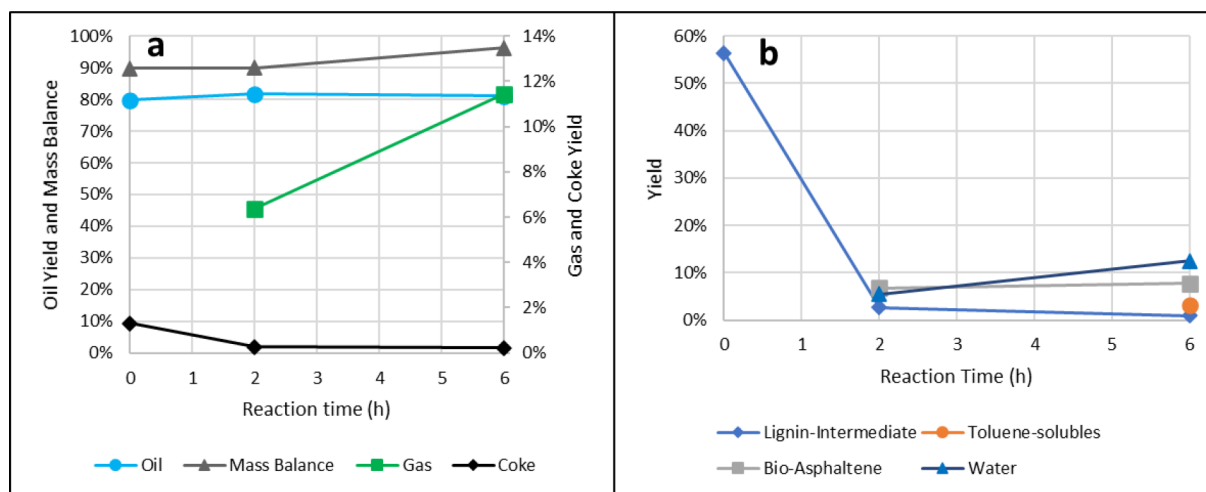


Figure 3. Yield of products from the total feed (a) and yield of lignin-derived products (b) for semi-batch experiments using different reaction times at 425 °C and 150 bar and 0.1% Mo as catalyst loading. Note that toluene-solubles was not determined for semi-batches performed for 0 and 2 h and bio-asphaltene was not determined for the semi-batch performed for 0 h.

(making noise in the process) or became attached to the reactor interiors where it was slowly broken down during the reaction (which would explain the observed decrease in size of the agglomerates attached to the reactor interiors with extended reaction time). An experiment with identical conditions as in Figure 3 (2 h reaction time) was also conducted but with a presulfided catalyst and showed very similar results as when the catalyst was sulfided in situ, which suggests that a presulfided catalyst does not have any positive effect in limiting the agglomerate formation of the lignin at low temperatures.

Due to the undesired reactions occurring at low temperatures during the heating phase, semi-batch experiments suffer from severe limitations and can likely not be used reliably for screening suitable process parameters to implement in a continuous slurry process. To overcome the limitations of semi-batch experiments, the experimental mode termed hot injection semibatch (HISB) was proposed as an alternative, in which the lignin is added to an already hot reactor and therefore is heated extremely fast by mixing with the hot liquid inside the reactor.

3.1.2. Hot Injection Semi-batches Using Molybdenum Catalyst. The HISB experiments overall resulted in a significantly cleaner reactor interior after the reactions (Figure S2). Moreover, the HISB experiment with 0.1% Mo resulted in absolutely no lignin remaining as a solid material and only about 5% of the initial lignin weight could be precipitated as bio-asphaltene by mixing the liquid product with an excess *n*-heptane (Figure 4). Thus, a full conversion of lignin was

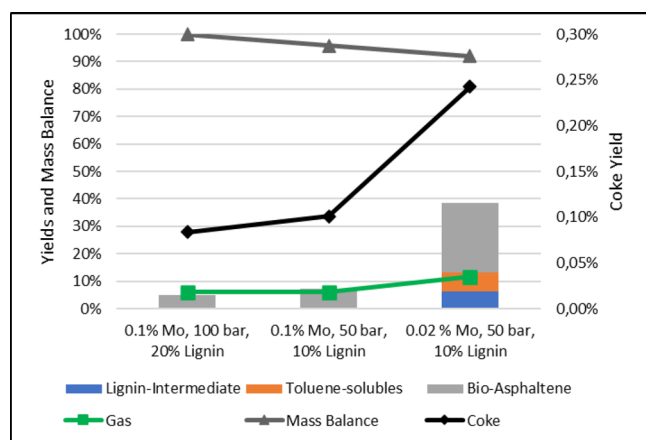


Figure 4. Product yields for HISB experiments performed at 425 °C for 2 h at indicated catalyst loading and pressures. Lignin-intermediate, toluene-solubles, and bio-asphaltene are expressed as proportions of the lignin mass, while the yield of gas and coke is expressed based on the entire feed mass.

achieved. Lowering the reaction pressure to 50 bar, all else being equal, provided nearly identical results with full conversion of lignin to nonsolid products. However, lowering the catalyst loading to only 0.02% Mo at 50 bar showed a very negative effect with nearly 15% of the initial lignin remaining as a solid material (unconverted and toluene-soluble) and another 25% as bio-asphaltene. About a 2-fold increase in gas yield also resulted from lowering the catalyst concentration. The role of the slurry catalyst is to act as a hydrogen transfer agent and deactivate intermediate free radicals thereby preventing excessive gas formation and polymerization reactions.¹³ At the very low catalyst concentration of 0.02%

Mo, the radical deactivation is likely too slow compared to the rate of radical formation, which results in high gas production. The gas yield, besides the lignin conversion, can therefore be used as a good indicator of the catalytic activity in the reactions.

Overall, the HISB experiments showed superior results compared to semi-batches performed with identical settings. However, one aspect to consider is that the catalyst concentration in the HISB experiments was initially double that indicated and then decreased throughout the feeding of lignin slurry to the reactor. Since the catalyst concentration has a clear effect on the outcome, this could have contributed to the superior lignin conversion observed for the HISB experiments with 0.1% Mo compared to the corresponding semi-batch (2 h). Although this may not necessarily apply directly to the feedstock used in this study, for slurry hydrocracking of vacuum residue 0.1% Mo as unsupported MoS₂ formed from oil-soluble precursors that has been shown to be a close to optimal loading without any further positive effect on H₂ uptake at higher loadings.³² A very high loading (0.5%) has been shown to actually increase coke yield.³³ Furthermore, an important observation is that in the semi-batch performed for 2 h, about 75% of the lignin-intermediate was collected as agglomerated material on the reactor surfaces, whereas in the HISB with 0.02% Mo, about 85% of the collected solids were present in slurry form. Thus, there seems to be a clear distinction between semi-batch and HISB in how the reactions proceed. Others have suggested successful three-step approaches to alleviate the problems with catalyst deactivation due to carbon-based deposits in batch reactions with lignin.²⁶ The results presented herein suggest that another way to achieve similar positive effects, without adding extra process steps, may be to simply heat the lignin very rapidly to a sufficiently high temperature in the presence of an adequate amount of catalyst.

3.2. Hot Injection Semi-batches Using Bauxite and Hematite. All experiments using bauxite and hematite were performed as HISB experiments. The effects of varied catalyst loading, pressure, and temperature are presented in the following sections.

3.2.1. Effect of Catalyst Type and Loading. Like the Mo-based catalyst, the catalyst loading with bauxite and hematite had a profound effect on the lignin conversion and gas formation, with increased conversion and reduced gas yield at higher loadings (Figures 5 and 6). The lignin conversion with the Fe-based catalyst did not reach as full conversion as with the Mo-sulfide catalyst (identical temperature and pressure), and even at the highest loadings (6.25% bauxite and 4.3% hematite) about 3.2% of the added lignin still remained as toluene-solubles for both Fe-based catalysts. The gas yields at the highest loadings of bauxite and hematite were practically identical (6.8 and 6.7%), which is slightly higher than the gas yield with Mo-sulfide catalyst (0.1% Mo) at the same temperature and pressure (6%). On the basis of the lignin conversions and the gas yields, the highest loadings of bauxite and hematite used in this study appear to have slightly less catalytic activity than 0.1% Mo.

The bio-asphaltene yields were typically higher in the experiments with hematite (around 20% of the lignin) than in the experiments using bauxite at higher loadings (around 10%). However, significantly lower coke yield was achieved with hematite (0.5% and 0.4% at the lower and higher hematite loading, respectively). With 3.75% bauxite, the coke yield was

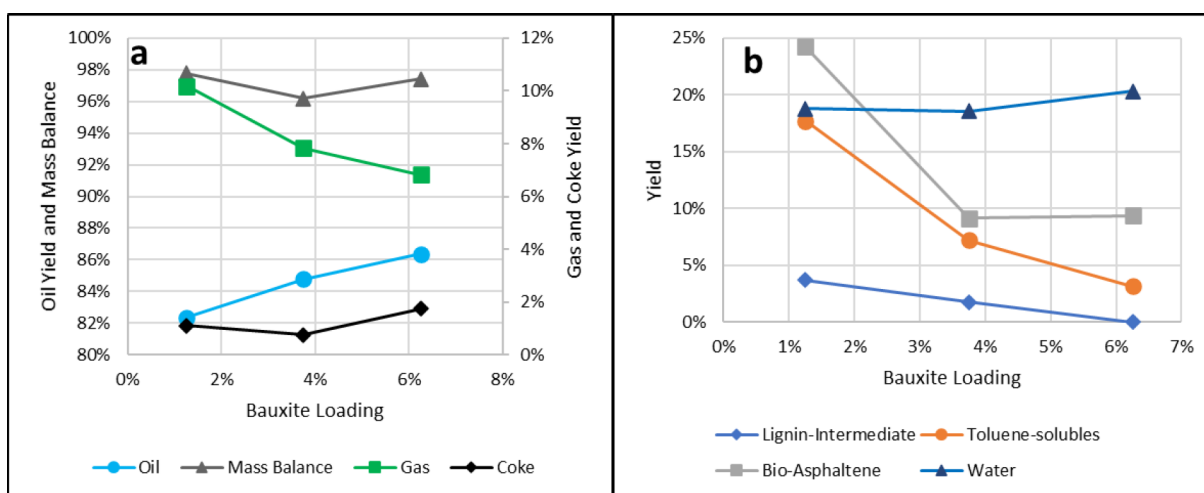


Figure 5. Yield of products from the total feed (a) and yield of lignin-derived products (b) for HISB experiments using different bauxite loadings. All experiments were performed at 425 °C and 50 bar.

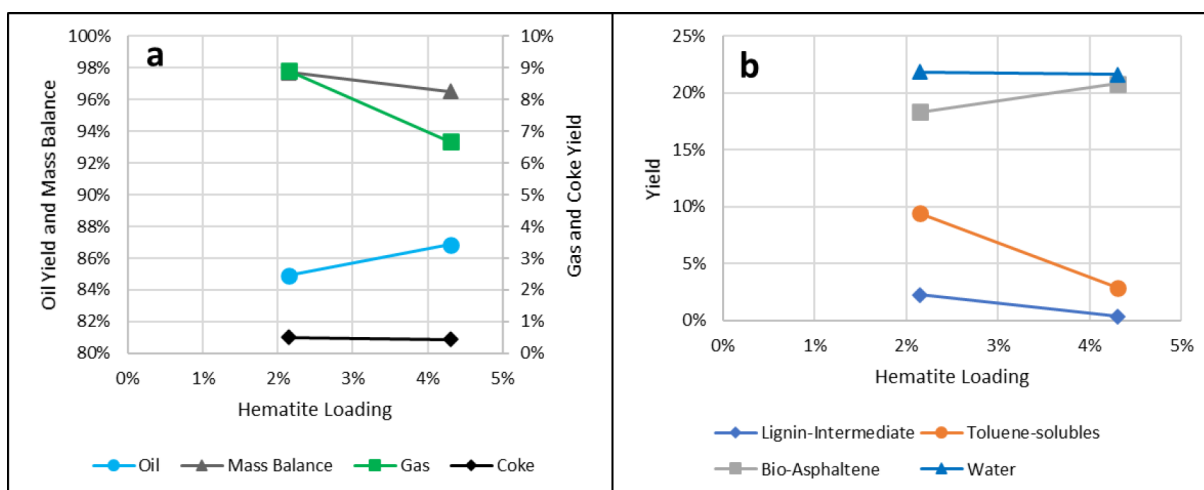


Figure 6. Yield of products from the total feed (a) and yield of lignin-derived products (b) for HISB experiments using different hematite loadings. All experiments were performed at 425 °C and 50 bar.

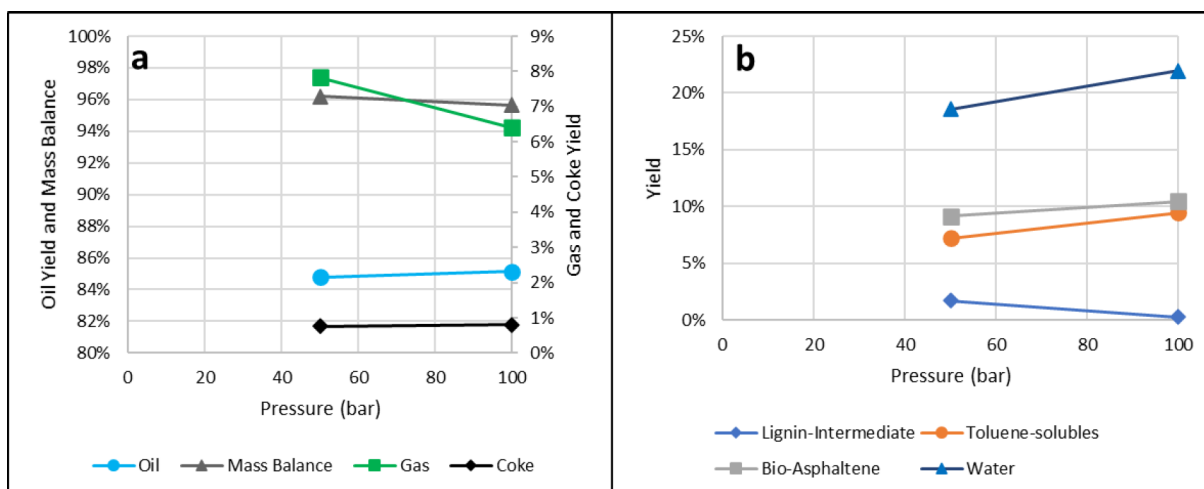


Figure 7. Yield of products from the total feed (a) and yield of lignin-derived products (b) for HISB experiments performed at different pressures. All experiments were performed at 425 °C with a bauxite loading of 3.75%.

0.7% but increased to 1.6% at the highest loading. Aluminum oxide, as present in bauxite, typically possesses some acidic

properties, and acidity has in other studies been linked to increases in coke formation from lignin^{25,29,34} but also higher

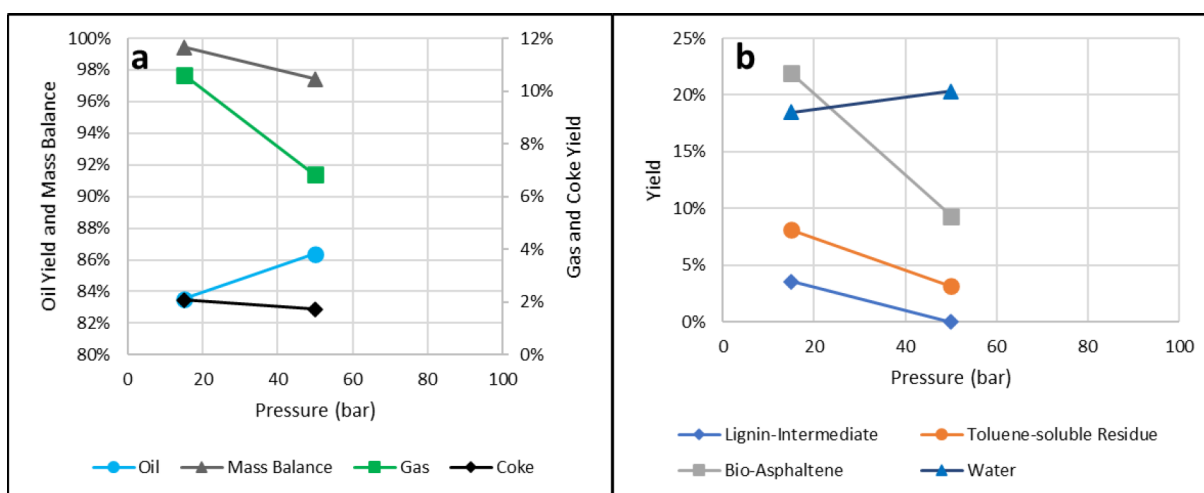


Figure 8. Yield of products from the total feed (a) and yield of lignin-derived products (b) for HISB experiments performed at different pressures. All experiments were performed at 425 °C with a bauxite loading of 6.25%.

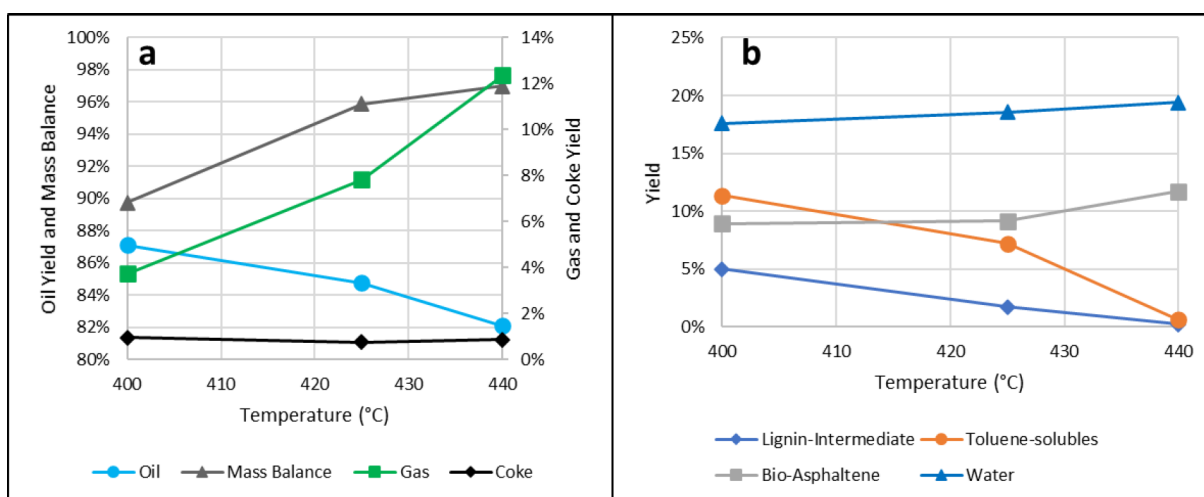


Figure 9. Yield of products from the total feed (a) and yield of lignin-derived products (b) for HISB experiments performed at different temperatures. All experiments were performed at 50 bar with a bauxite loading of 3.75%.

depolymerization rates.³⁴ This suggests that the presence of aluminum oxide in the bauxite, therefore, is responsible for both the higher lignin conversion at identical Fe-loading but also for the increased coke formation. Moreover, since the bio-asphaltene yield was much higher with hematite than with bauxite as a catalyst, this suggests that the bio-asphaltene species formed from the lignin proceeded to form coke to a higher extent when using bauxite as catalyst. This is especially reasonable since asphaltene is a known precursor for coke formation.³⁵ The other major difference between bauxite and hematite is the much higher surface area for bauxite which may also help explain the superior lignin conversion at matched Fe-loadings. However, this does not explain the increased coke formation observed with bauxite, and experiments with increased hematite loading rather suggest that an increase in Fe_2O_3 leads to reduced coke formation. Hence, it can be concluded from the experiments performed in this study that a catalyst consisting of only Fe-based particles (as in the case with hematite) works well as a catalyst, but at matched Fe-loadings, the bauxite is superior in converting the lignin to nonsolid material, although this superiority seems to arise from

the presence of aluminum oxide and comes at the expense of increased coke formation.

3.2.2. Effect of Pressure. Increased pressure from 50 to 100 bar with the Mo-sulfide catalyst has already been shown to have a very minor effect on the lignin conversion and coke formation (Figure 4), but the results were in both cases very good and did not leave much room for improvement. The effects of varied reaction pressures when using bauxite as a catalyst are shown in Figures 7 and 8. Both the bio-asphaltene yield and the solid residue yield at 50 and 100 bar were very similar (Figure 7). A reduction in the lignin-intermediate but an increase in the toluene-solubles was observed, but the sum of these did not change significantly. The only positive effect observed from the higher pressure was a somewhat lower gas yield. The decrease in gas formation observed at higher pressure is likely a result of improved deactivation of free radicals, similarly to what has already been discussed for the effect of catalyst loading on the gas yields. However, a reduction to only 15 bar (Figure 8) resulted in very poor lignin conversion and high gas yield despite the high catalyst loading (6.25% bauxite).

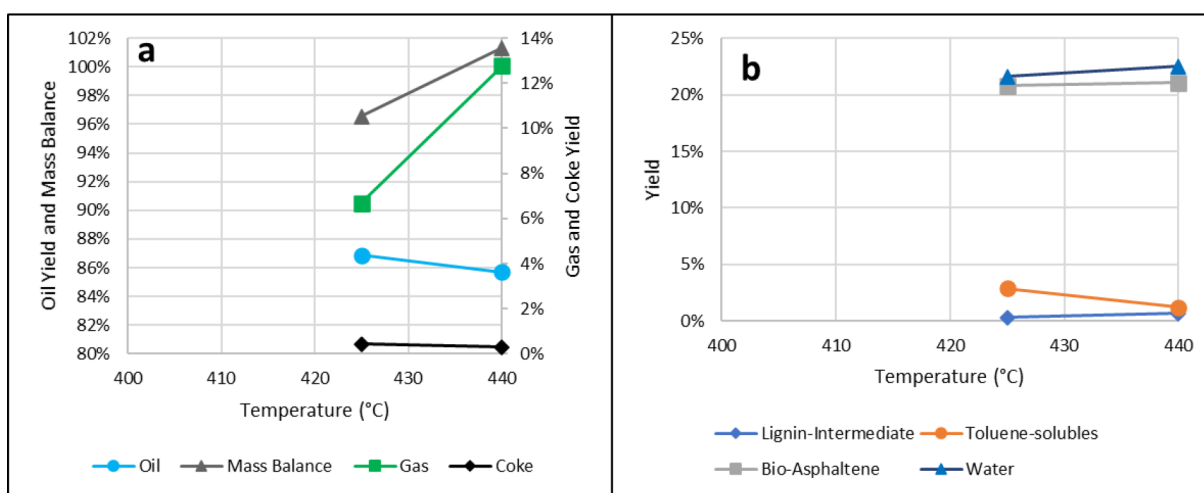


Figure 10. Yield of products from the total feed (a) and yield of lignin-derived products (b) for HISB experiments performed at different temperatures. All experiments were performed at 50 bar with a hematite loading of 4.3%.

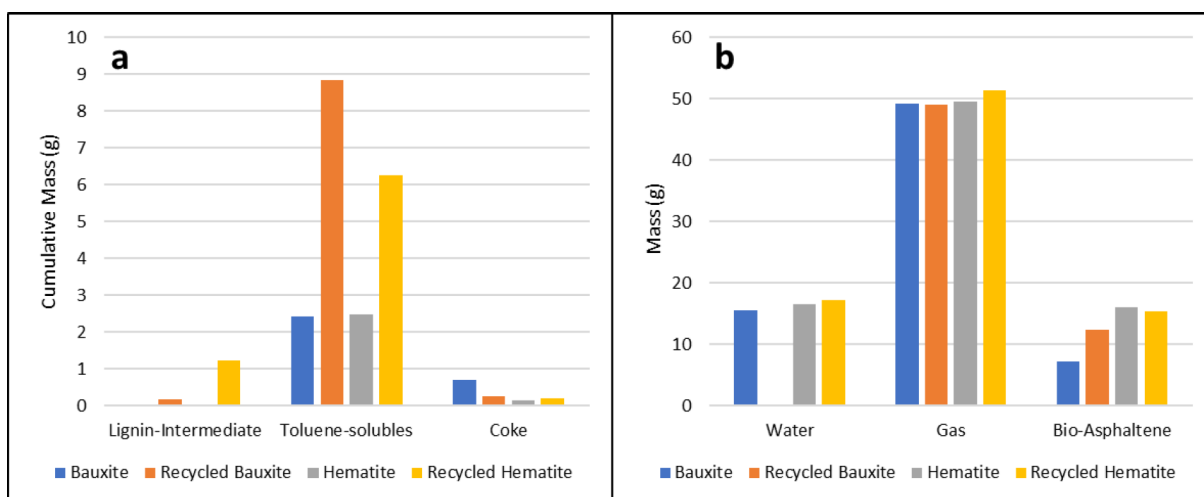


Figure 11. Cumulative mass of recycled products (a) and yields of nonrecycled products (b). Experiments using bauxite for HISB experiments performed at different temperatures. All experiments were performed at 50 bar and 425 °C with 6.25% bauxite or 4.3%. The water phase product from the experiment using recycled bauxite was accidentally spilled before weighing and can not be presented.

Since no major positive effect was observed with increased pressure from 50 to 100 bar (at a bauxite loading of 3.75%), it was decided not to pursue a higher reaction pressure than 50 bar any further as this is logically associated with significantly increased investment and operational costs for a hypothetical process. However, decreasing the pressure too low, as illustrated by the HISB with only 15 bar, had a clear negative impact.

3.2.3. Effect of Temperature. The reaction temperature had a very profound effect on the lignin conversion, and only about 1% of the initial lignin mass remained as solid material after reaction at 440 °C with both bauxite and hematite (Figures 9 and 10). Conversely, using only 400 °C resulted in 5% lignin-intermediate and another 12% toluene-solubles (Figure 9). The high conversion at the highest temperature was accompanied by higher gas yields compared to at 425 °C, which could be expected since the gas-forming cracking reactions are thermally controlled.³³ The coke yield did not differ significantly between the different temperatures for neither bauxite nor hematite. A bit surprisingly, the bio-asphaltene yields were not reduced at 440 °C compared to

425 °C. It could be expected that the high temperature would result in enhanced breakdown of these components as well, as is typically the case with slurry hydrocracking of asphaltene-containing fossil feedstocks.^{32,36} However, with the high lignin conversion observed, a higher generation of bio-asphaltene from the raw lignin might also be expected, which might mask the bio-asphaltene reduction. Such an observation was made by Pu et al. when hydroprocessing lignin, where the yield of the heptane-precipitated product increased as the reaction proceeded, while the yield of solids products decreased.³⁷

3.2.4. Effect of Catalyst Reuse. To study the effects of catalyst recirculation, all solid material (including the lignin-intermediate and toluene-solubles) from one experiment with 6.25% bauxite and one experiment with 4.3% hematite was separated by centrifugation and recycled back to the reactor for the next experiment using an identical setup (about 5% of the THF-insoluble solids, i.e., coke, catalyst, and ash, were removed for analytical purposes and replaced with fresh catalyst). In the recycling experiment with bauxite, the collected mass of lignin-intermediate plus toluene-solubles increased from 2.4 g in the first batch to 9 g in the second

batch (an increase of 3.74 times). For hematite, the corresponding mass increase was 3 times, from 2.5 to 7.5 g (Figure 11). One could hypothesize that by recycling the solid organic products back to the reactor, these would be broken-down and possibly be replaced with new solid products from the fresh lignin. This, however, does not seem to be the case as the mass increase of solid products is at least 3 times, whereas the amount of processed lignin after the second run is only twice the amount. Hence, it appears not possible with neither bauxite nor hematite to avoid an accumulation of solid lignin products in the product mixture when recycling the catalyst (along with lignin-intermediate and toluene-solubles) with the process parameters used. This indicates that more severe reaction conditions may be needed or some form of washing step for the solid material if recycling of the Fe-based catalysts is desired. The gas yields were practically identical in the first and second experiment for both bauxite and hematite, which suggests similar catalytic performance in both experiments. Also the bio-asphaltene and water phase yields were similar in both runs for hematite.

Bio-asphaltene, which is not present as solid material was therefore not recycled, but the yield increased by 1.74 times between the first and second catalyst use with bauxite. The coke yield was lower in the second run with the bauxite catalyst, which might have been affected to some extent by the incomplete recovery of the solid material from the first experiment. However, also the concentration of organic matter in the THF-insoluble fraction was lower after the second use (27% compared to 31%), which indicates greatly reduced coke formation in the second experiment. As has already been discussed, the higher coke yields but lower bio-asphaltene yields with bauxite compared to hematite suggests that a large part of the coke is formed from the bio-asphaltene. The results from the experiments with recycled bauxite strengthen this reasoning. With recycled bauxite it seems that coke deposits hinders both of these effects from the aluminum oxide, and the bio-asphaltene yield, therefore, approaches that observed with hematite (which of course completely lacks aluminum oxide).

It should be noted that full recovery of all catalyst from the first experiment was difficult. Incineration of a sample of THF-insoluble solids from the first experiment with bauxite revealed that the catalyst recovery was only 77.4%, and thus, the catalyst concentration in the recycle experiment might have been a lower percentage. In the recycling experiment with hematite, the catalyst recovery was determined before the second experiment by incineration of a sample of the THF-insolubles, and fresh hematite (23.5% of the initial amount) was added to compensate for any losses.

3.2.5. Comparison with Reference Experiments. As also the VGO produces gas, coke, and liquid products, the exact amount of the products from the lignin cannot be determined unless experiments with identical process parameters but without lignin have been conducted. Such reference experiments were performed for two of the lignin experiments, and the product distribution from the lignin was estimated by comparing the obtained yields with and without lignin present and assuming that the VGO reacted identically in both cases (Table 4). (It should be noted that there is no evidence presented here that the reactions of the VGO are completely unaffected by the presence of lignin in the feed. If the VGO actually reacts differently with the presence of lignin, the product distributions presented may to some extent be skewed.) The results demonstrate that the higher temperature

Table 4. Distribution of Lignin Products Based on Comparison with Reference Experiments without Lignin^a

	425 °C, 6.25% bauxite	440 °C, 3.75% bauxite
oil product yield	52.5%	49.6%
>524 °C	0.0%	0.0%
343–524 °C	50.9%	0.1%
177–343 °C	−1.5%	43.5%
<177 °C	3.0%	5.9%
water phase yield	20.3%	19.4%
gas yield	9.9%	26.3%
soluble solid residue	3.1%	0.8%
coke	10.2%	5.0%
total sum	96.1%	101.0%

^aAll experiments were performed with 50 bar pressure.

(440 °C) resulted in a significant gas formation from the lignin (26.3%), which was a drastic increase compared to results obtained at 425 °C (9.9%). The higher temperature (and lower catalyst concentration) also resulted in more lignin products in a boiling point range of 177–343 °C (corresponding roughly to diesel), while at 425 °C nearly all of the liquid product formed from the lignin remained in a higher than diesel boiling point range (>343 °C).

As has already been discussed, in the experiments with lignin in the feed, a higher bauxite loading resulted in a higher coke yield than when less bauxite was used. This was true also when comparing the coke yield from the two experiments without lignin (coke yields 0.38% and 0.67%) at the lower and higher catalyst loading, respectively. Comparing experiments with and without lignin, the coke yields from lignin were determined to be 9.6% and 4.8%, and the lignin is hence much more prone to formation of coke than the VGO. Since no reference experiments with hematite or Mo-sulfide catalyst were performed, the coke yield from lignin in these experiments cannot be assessed in detail. However, assuming that no coke was formed from the VGO, the coke yield from lignin would be about 1% with Mo-sulfide and 3–4% with hematite, which is lower than that determined for the bauxite experiments in Table 4. Moreover, since the VGO likely produced some amounts of coke with Mo-sulfide and hematite as well, these numbers are likely exaggerated.

3.2.6. Characterization of Solid Residues. The three fractions lignin-intermediate, toluene-solubles, and bio-asphaltene were separated as individual fractions from the reactor product obtained from the HISB with 1.25% bauxite (this experiment provided plenty of available material, whereas many experiments yielded very low amounts of solid residue). The separated bio-asphaltene and lignin-intermediate were solids at room temperature but melted when the residual solvents were evaporated at 100 °C. The toluene-solubles, on the other hand, remained as a dark and viscous liquid at room temperature. The elemental compositions of the three solid fractions are illustrated in a Van Krevelen diagram in Figure 12. All the residue fractions share similar characteristics and are very nonpolar (low O/C ratio) and aromatic (low H/C ratio). Some solid residues from other experiments were also analyzed for their elemental composition but showed overall similar results (Table S1). Analysis of the residues with GPC showed average molecular weights of 198 g/mol for the toluene-solubles, 343 g/mol for bio-asphaltene, and 596 g/mol for the lignin-intermediate. In comparison, the untreated lignin had an average molecular weight of 12,080 g/mol (Figure S3). As the

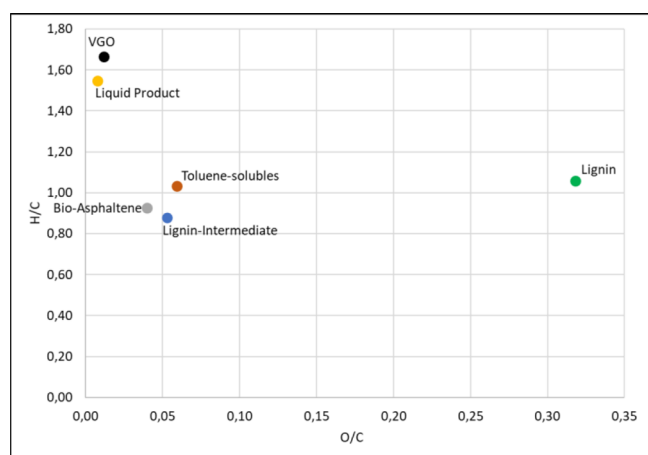


Figure 12. Van Krevelen diagram, showing atomic ratios, of bio-asphaltene, lignin-intermediate, and toluene-solubles from the experiment with 1.25% bauxite. Untreated lignin, VGO, and liquid product (pooled from reactor and separator) are also shown as references.

characterized residues originated from the experiment with only 1.25% bauxite, which showed low conversion of lignin to nonsolid material, this implies that the solid residues obtained in all experiments are severely depolymerized and deoxygenated residual fragments of the lignin.

The precipitation procedure with *n*-heptane used in this study has clear similarities to ASTM D6560,³⁰ by which the asphaltene content is determined. Asphaltene is a complex polyaromatic compound group found in fossil oil, which is defined by its insolubility in *n*-alkanes but solubility in toluene. In fossil oil, the asphaltene is typically present as colloidal particles,¹² and the addition of an excess of *n*-alkanes, such as heptane, causes flocculation, which facilitates separation through filtration and determination of the asphaltene mass proportion in the sample. The method of precipitating lignin-derived products with *n*-heptane after catalytic hydroconversion has also been previously used by Joffres et al.³⁸ The authors concluded that the product fraction precipitated with *n*-heptane was relatively similar in composition to the THF-soluble solid lignin residue obtained in their experiments but consisted of somewhat smaller oligomeric fragments (average

1300 g/mol for the “bio-asphaltene” compared to 2300 g/mol for their THF-solubles, which is both significantly higher than observed molecular weights in this work, likely due to milder conditions used by Joffres et al.). The composition of the liquid cofeed or product will of course have a strong influence on the solubility of the heavy fragments, where highly aromatic cofeeds are preferred, and very saturated cofeeds increase the risk of flocculation of the colloidal particles with possible deposit and plugging problems as consequences. These issues are well-known from handling of asphaltene-containing fossil oils^{39,40} and might be an issue also when hydrotreating the liquid product derived from lignin, although this needs to be studied further.

3.2.7. Characterization of Gas Products. Lignin has been shown to produce mainly CO, CO₂, and CH₄ at an early stage of reaction at 350 °C.³⁷ This is in agreement with the gas production profiles obtained in this study (shown in Figure 13 for semi-batch and Figure 14 for HISB). In the semi-batches, an increase in CO₂ and CO was observed well before the reaction temperature of 425 °C was reached and an increase in CH₄ just before reaching 425 °C. However, as there is a delay between the formation of gas in the reactor and this gas reaching the μ GC, this gas formation should not in detail be ascribed to any certain temperature. The gas production in the HISB experiments was characterized by a sharp increase in primarily CH₄, CO, and CO₂ shortly after the lignin slurry feed to the reactor was initiated, and once the feeding was stopped the concentration of CO and CO₂ in the gas soon dropped to zero and the concentration of CH₄ fell sharply, to begin with, and then slowly decreased throughout the reaction period. The yields of CO and CO₂ were very stable throughout all experiments and not even an increased reaction temperature to 440 °C led to any increased yields of these, even though the yield of C₁–C₅ increased significantly. The formation of carbon oxides is clearly associated with decarbonylation and decarboxylation of lignin, and no detectable levels were observed in the experiments without lignin.

Comparison with reference experiments without lignin for two reaction settings show that the gas production rates become identical relatively soon after the feeding of fresh lignin has stopped (Figure 14), which indicates that the gas production rate from lignin has become identical to that

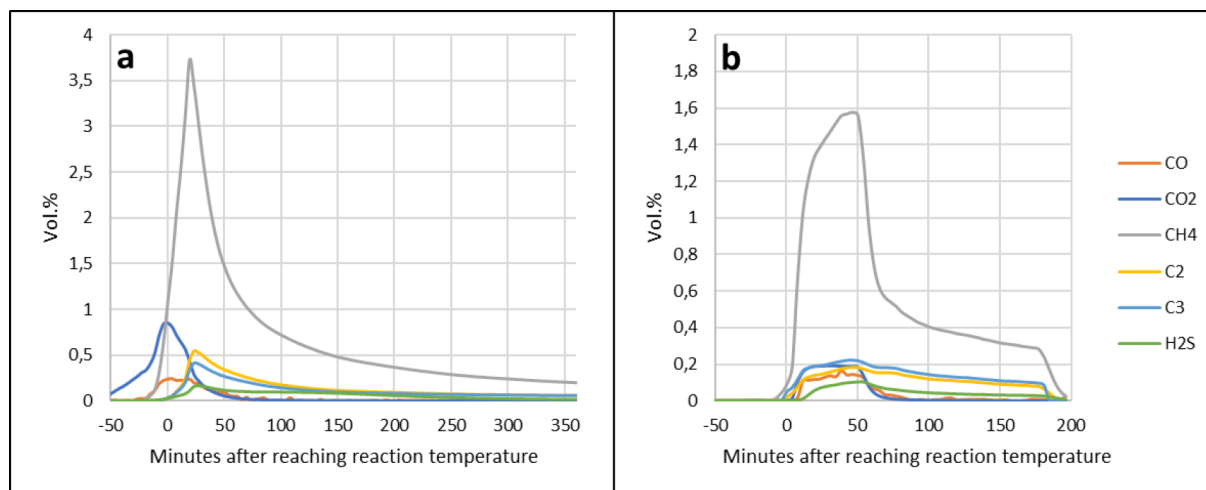


Figure 13. Gas production profile for semi-batch with 0.1% Mo at 425 °C and 150 bar (a) and HISB with 3.75% bauxite at 425 °C and 50 bar (b). The feed of lignin slurry was stopped at 51 min after reaching reaction temperature (and start of slurry feed).

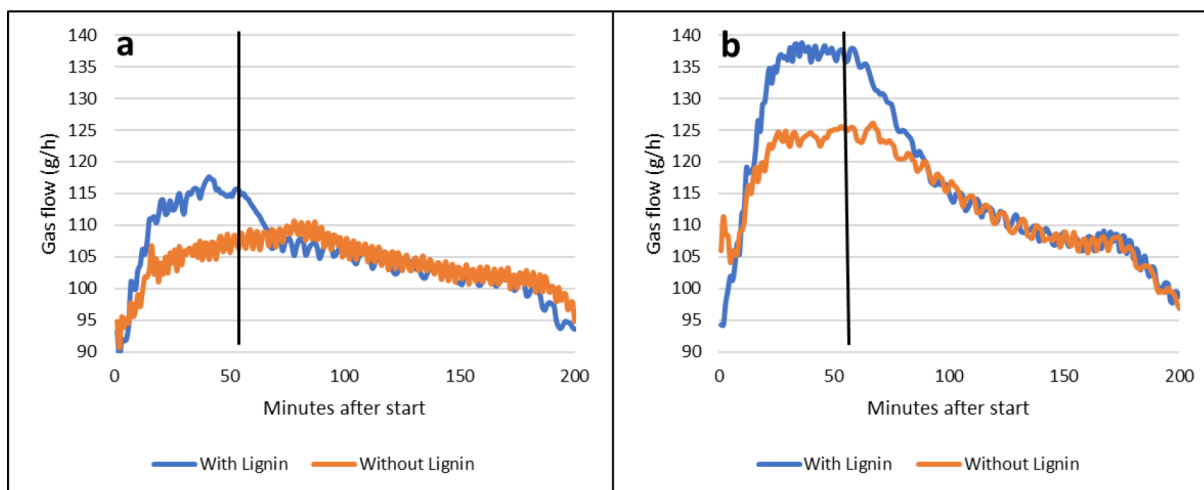


Figure 14. Comparison of gas production for HISB experiments performed with or without lignin using 6.25% bauxite and 425 °C (a) or 3.75% bauxite and 440 °C (b). Feeding of the lignin slurry was initiated at the start of the graph and was stopped at the vertical line.

from the VGO. This might indicate that the gas formation at this point occurs through identical mechanisms (mainly C–C bond cleavage) since all the functionalities in the lignin that are responsible for easily formed gaseous species (CH_4 from methoxy groups, CO from carbonyls, and CO_2 from acids or esters³⁷) are already gone. Moreover, the gas formation was maintained at a relatively high level throughout the entire reaction time at 440 °C and a significant part of the total gas production took place well after the feeding of lignin slurry had ended. Possibly, the high lignin conversion observed at 440 °C could be maintained while reducing the gas formation (from lignin as well as the cofeed) by decreasing the reaction time at this high temperature, although this was not investigated any further.

A large part of the increase in gas yield from lignin observed at 440 °C compared to at 425 °C constituted of CH_4 , which increased from 8.5% to 14.4%, while the rest of the increase came from C_2 – C_5 (Figure 15). Calculations for the 425 °C

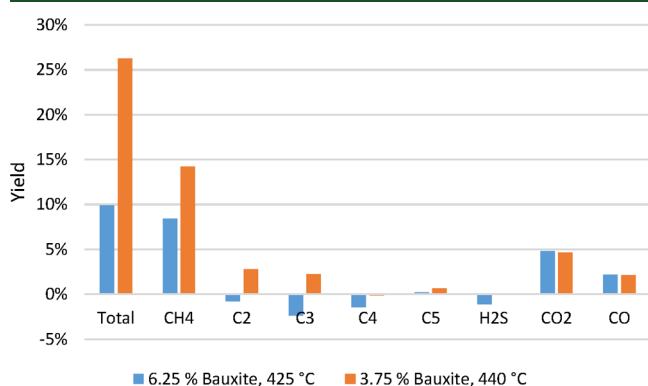


Figure 15. Gas yield from lignin-based on comparison with reference experiments with only VGO.

experiment resulted in negative yields of C_2 – C_4 and H_2S , but it cannot be concluded, based on only these experiments, if the presence of lignin has an actual lowering effect on the formation of these gas species at these settings or if the reason is simply measurement errors (no similar effect from the lignin addition was observed at 440 °C). Since the difference in feed composition between the two corresponding experiments was

only 10%, sometimes small differences in yields will be significantly amplified, and experimental or analysis-related errors can have an unproportionally large effect on the outcome. Others have reported yields of about 12, 7, 2, and 1% of CH_4 , CO_2 , C_2 – C_5 , and CO, respectively,³⁷ which overall agree well with the results in this study, but the gas yields of course depend on the exact composition of the lignin used as well as reaction conditions.

3.2.8. Characterization of Liquid Products. The liquid products were collected from the reactor (95% boiling above 220–250 °C) and the liquid/gas separator (95% boiling below 200–280 °C). The combined liquid product boiling point distribution (Figure S4) says very little about the liquid products formed from lignin as the liquid fraction is completely dominated by the VGO products. One thing that can be noted is that there is a clear correlation between the gas formation and boiling point range of the liquid product (Figure 16). This agrees well with the observations already made for lignin in

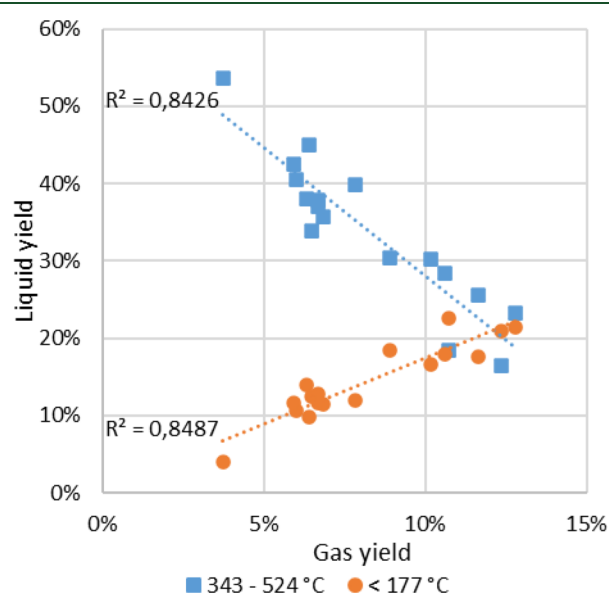


Figure 16. Relationship between the yields of light (boiling point < 177 °C) and heavy (343–524 °C) liquid components at different gas yields.

Table 4, but as VGO-derived products dominate the liquid composition, the same trend appears true also for the VGO. The gas yield is therefore a very good indicator of the extent of cracking reactions in general, which seem to affect the VGO and lignin similarly. Furthermore, selectively cracking lignin species to desired boiling point range components without producing excessive amounts of gas may prove difficult.

The degree of hydrodeoxygenation (HDO), expressed as a percentage of the entire feed oxygen content, varied between 66–83% in all experiments (Figure S6). Typical O concentrations in the oil product from the reactor and gas/liquid-separator were 1–1.5% and 1.3–1.8%, respectively, compared to 0.4–0.5% for both products when no lignin was added to the reaction. (The oil product collected in the gas/liquid separator would likely have been deoxygenated to a higher degree if not evaporated from the reactor.) Noteworthy is that the four experiments with the highest HDO were sent to the external laboratory for oxygen analysis in the same delivery and were analyzed on the same occasion. Since the parameters in these four experiments gave otherwise rather poor results, this might indicate some analytical error. Subtracting the amount of oxygen removed from the VGO based on an average of the two reference experiments results in calculated HDO-values for the lignin of 69–91%. However, neglecting the four best HDO-values for the reasons mentioned above reduces this range to 69–79%, which is likely more correct. The calculated water phase yields from the lignin were 17.6–21.8%. On average, water formation was responsible for 78% of the total observed deoxygenation of the lignin, while the rest can be attributed to CO and CO₂ formation (6% and 16%, respectively).

Hydrodesulfurization (HDS) of around 60% was achieved with a Mo-sulfide catalyst at 0.1% Mo-loading (Figure S6). For the experiments using bauxite and hematite, it was observed that when a large amount of DMDS was added as a sulfiding agent, some of the DMDS evaporated from the reactor before it could be converted to H₂S and CH₄. The accumulation of DMDS in the separator resulted in negative calculated HDS-values, which are of course incorrect. The HDS-values using a recycled Fe-based catalyst, in which no DMDS (with bauxite) or very little (with hematite) was added, and for experiments with bauxite, where comparatively small amounts of DMDS were added to the feed, resulted in around 40% HDS at best. (The amount of added DMDS was varied between 0.5–5 stoichiometric S requirements when using bauxite, but no correlation between sulfidation, which was determined by SEM-EDS and DMDS addition could be observed, Figure S5.) The Mo-sulfide catalyst, therefore, seems to have higher activity in terms of HDS than bauxite and hematite, but no similar difference could be observed for the HDO.

The C content in the water fractions was analyzed for three HISB experiments and showed 2.0, 2.2, and 2.5%, which corresponds to 1.0–1.4% of the C from lignin.

Metal analysis (Table S2) of the reactor- and separator product from the experiment with 6.25% bauxite at 425 °C and 50 bar showed no detectable levels of Na or K (<5 ppm), which constituted 434 and 92 ppm of the untreated lignin, respectively. Si, another major ash element found in the lignin at 278 ppm, was not detected either, but the limit of detection was likely too high (100 ppm) to detect any Si if present. Analysis of the THF-insoluble solids from experiments using Mo-sulfide catalyst with SEM-EDS showed the presence of Na, K, and Si, but quantification with SEM-EDS at low levels

cannot be considered reliable and is not presented. No ash elements could be observed in the THF-insolubles when using bauxite or hematite as a catalyst, likely due to severe dilution with the catalyst. Although further investigations are needed, the absence of ash elements in the oil products indicates no, or at least low, transfer of ash elements found in lignin to the oil products. That practically all ash elements in the lignin are retained in the insoluble fraction has been observed in another study, although no metal analysis of the liquid products was performed in that case, and the complete absence of ash elements in the liquid product was therefore not confirmed.³⁷

3.3. Economic Evaluation. The raw material prices for the three different catalysts studied differ very much, with Mo-oxide being significantly more expensive than bauxite and hematite. The cost of the catalyst raw material, as well as sulfidation to MoS₂ or FeS, is compared in Figure 17, based on

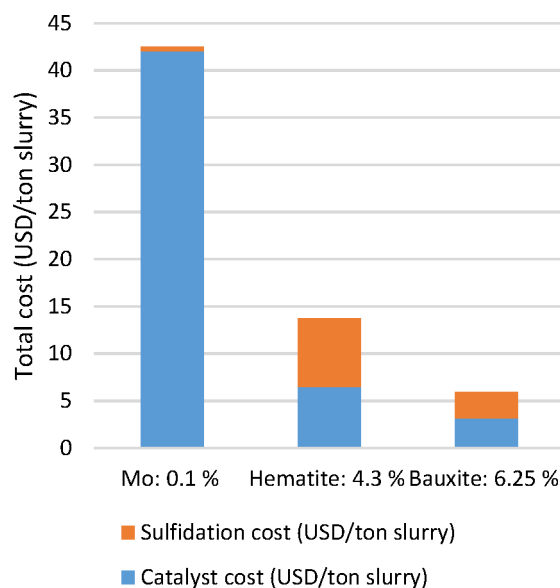


Figure 17. Raw material cost of catalyst and sulfidation, assuming no catalyst recycle. Assumed catalyst raw material costs: 42,000 USD/ton Mo as oxide,⁴² 50 USD/ton bauxite,⁴³ and 150 USD/ton hematite.⁴⁴ Sulfidation cost is calculated from the required H₂ to convert SO₂ from the combustion of the used catalyst back to H₂S and a price of 3 USD/kg H₂.

a scenario where no recirculation of the catalyst or liquid product takes place, and the spent catalyst is combusted to oxide after use. Mo-oxide has been used as an assumed raw material for the production of the Mo-based catalyst but any cost of converting this to an oil-soluble catalyst precursor has not been included as this is very hard to estimate. The sulfidation cost is calculated by assuming that after combustion of the sulfur present in the catalyst to SO₂ it is converted with H₂ to H₂S, which is used to sulfide fresh catalyst over again. (This may of course occur first by reduction to elemental S and later using this for sulfidation of catalyst by further reduction to H₂S.) The H₂ consumption for this reaction, along with an assumed price of 3 USD/kg for H₂ imposes the sulfidation cost of the catalyst in Figure 17. If electrolysis is used as a source of renewable H₂ for the process, the price will on the other hand be significantly higher, at least in the short term.⁴¹ Three USD/kg H₂ was thus chosen as a middle ground to illustrate the cost of the catalyst sulfidation.

Bauxite results in the lowest overall cost, despite a very high required loading (6.25%). Hematite has a generally higher price per mass than bauxite and requires more sulfur for the sulfidation process. (The observed water formation from hematite suggests that only 64% of the Fe-oxide was converted to sulfide, likely due to low available surface area. The S demand in Figure 17 is presented based on this actual requirement.) The sulfur present in the lignin can be estimated to contribute with 25% of the required sulfur to sulfide all Fe-oxide in hematite. This has not been considered for either bauxite or hematite in Figure 17. CH₄ produced from lignin in the process could also be used as a source of cheap H₂ through steam reforming, and estimations show that a CH₄ yield of 8.6% from the lignin is required to cover the theoretical H₂ demand to fully deoxygenate the lignin. (This number assumes that all O forms water, which provides an overestimation of the H₂ demand for deoxygenation, but the saturation of aromatics, etc. is on the other hand not considered.) Approximately this CH₄ yield from lignin was observed in this study at a temperature of 425 °C, but at a higher temperature, significantly more CH₄ was produced. Hence, the process has the possibility to supply the H₂ demand by itself if this is desired.

The calculations in Figure 17 assume that the spent catalyst offers no value. This is of course not true, and the extent to which the catalyst can be recycled, possibility for purification/reactivation, and rest value or disposal cost of spent catalyst are important factors that influence the total cost associated with using a certain catalyst and will need to be assessed in future work.

3.4. Future Perspectives. The process described in this study could be considered a pretreatment of lignin that converts it from a highly oxygenated, ash-containing solid material into a liquid product with reasonable oxygen content (~5%) and no detectable ash elements, which make it (or at least parts of it) suitable for further refinement in fixed bed hydrotreaters/hydrocrackers. However, investigating in what type of downstream process (or combination of processes) the lignin products may be refined is, although very important, out of the scope of this study.

For a continuous (continuous feeding and withdrawal of catalyst, gas and liquid to/from reactor) slurry hydro-conversion process for lignin, two hypothetical implementation options are proposed in Table 5. Option A uses a relatively high temperature, which has been shown in this study to result in a high conversion but also a relatively high gas yield from the lignin. This effect can likely be reduced by having a

relatively high catalyst loading and high LHSV (short residence time in the reactor). Downstream of the reactor, the product is distilled to a desired cutoff and the high boiling point (heavy) components, along with catalyst and solid residue, are recycled back to the reactor along with fresh feedstock. To prevent any excessive accumulation of ash, coke, or solid lignin residue in the process, some part of the heavy fraction needs to be purged and fresh catalyst added to the feedstock to compensate for purged catalyst (this concept is similar to the ENI slurry process⁴⁵). The required amount of purge, or possible washing/separation steps will be dictated by the process tolerance for solid material, possible deactivation of the catalyst, and similar aspects. As the LHSV is high in option A, the fresh lignin concentration in the feed to the reactor can be kept at a moderate level and still attain a high throughput. In the most radical implementation, there is even a theoretical possibility to mix only lignin with the recycled heavy fraction and completely omit any fossil or biobased fresh liquid cofeed. Although some heat-insensitive liquid will be required in the start-up, this concept would eventually lead to a completely lignin-based process.

Option B uses no recycling of any catalyst, solid lignin residue, or high boiling point components and is inherently a very simple and robust process concept as there is no possibility for any buildup of solids or bio-asphaltene in the system. Since there is no recycling, the liquid product and its different distillation fractions would in this case be refined directly in downstream processes such as fixed bed hydrotreaters/hydrocrackers and fluid catalytic crackers or other suitable equipment. For this option to be viable, the catalyst concentration must be optimized to minimize the catalyst-associated costs but at the same time reach a high lignin conversion to nonsolid material as any solid lignin will not be recycled to the process but rather combusted along with all solid material. Since there is no catalyst recycling, only hematite and bauxite are considered as options in this case due to their lower cost compared to Mo-sulfide. The lignin concentration of the feed in option B would ideally have to be higher than in option A to reduce the cost per processed ton of lignin and the required amount of suitable cofeed. The LHSV and temperature also need to be optimized to enable high lignin conversion along with reasonable gas yields and residence time in the reactor.

Both the presented options of course need to be investigated further. Some parts of the lignin are hard to break down (indicated by the presence of some remaining toluene-solubles and bio-asphaltene for all experiments using Fe-based catalysts), but at the same time, other parts of the lignin seem to break down very easily. By using a short reaction time, overcracking and subsequent gas formation of the easily converted components could be minimized. In option A, the resilient (high boiling point) lignin components would be recycled back to the process, providing increased time at reaction temperature and hopefully increased conversion of these species to liquid products. Especially a high temperature in the reactor could lead to a very high total conversion. In option B, which does not use any recycling of lignin-intermediate, a similar optimization could be achieved by two reactors in series and a separation of low boiling point components in between. The first reactor would in this case use a moderate temperature to provide conversion of easily converted parts of the lignin, while the second reactor would use a high temperature to ensure full conversion. This concept

Table 5. Proposed Implementation Options for a Lignin Hydroconversion Process

	option A	option B
catalyst type	Fe- or Mo-based	Fe-based
catalyst/solids recycling to process	yes	No
temperature	high (425–440 °C)	moderate (about 425 °C)
catalyst loading	high (4.3% hematite, 6.25% bauxite, or 0.1% Mo)	moderate
liquid hourly space velocity (LHSV)	high	moderate
fresh lignin concentration in the feed	moderate (20–40%)	high (≥40%)

would increase the cost and complexity of a hypothetical hydroconversion unit and would require careful consideration.

A clear downside with the hematite used in this study is the very low surface area of 1 m²/g, which likely contributes to the high requirement of catalyst to achieve desired results. The water produced from the hematite corresponded only to about 64% of that theoretically expected if all Fe would have been sulfided, which indicates that the rest of the Fe-oxide is likely not accessible on the particle surfaces and therefore does not become sulfided. Simply utilizing hematite with a very fine particle size distribution, and thereby a high surface area, may be a simple factor that could improve its catalytic performance and enable decreased catalyst loading with maintained results. Other results with Fe-based catalyst impregnated on activated charcoal have shown similar performance as in this study at significantly lower loading,²³ which further suggests that strategies to improve the surface area of the Fe-sulfide catalyst may be beneficial in reducing the required amount of catalyst. Overall, Fe-based catalysts have great potential as nonexpensive and robust catalysts for hydroconversion of lignin, and the bauxite and hematite used in this study are only two options.

4. CONCLUSIONS

In this work, the hydroconversion of solid Kraft lignin to nonsolid products in a slurry-based process using both unsupported MoS₂ and Fe-based catalysts (bauxite and hematite) has been investigated. The conclusions to be drawn from this study are as follows. (i) During heating to reaction temperature, lignin produces agglomerated material by repolymerization and condensation reactions that start to occur around 250 °C. This material can slowly be broken down, given sufficient time at a temperature of 425 °C and in the presence of sufficient amounts of catalyst. Therefore, slow heating, such as in batch experiments, has clear limitations for studying lignin hydroconversion. Contrary to this, the hot injection semi-batch (HISB) protocol used in this study, where lignin slurry was fed to a hot reactor, resulted in a momentaneous heat-up, and lignin repolymerization/condensation reactions occurring at low temperatures could effectively be prevented. (ii) Using the HISB protocol, complete conversion of solid lignin to oil-soluble products, water fraction, and gas could be achieved with an unsupported Mo-sulfide catalyst supplied at 0.1% Mo of the total feed and a reaction time of 2 h. These results were superior to those achieved with a semi-batch at corresponding settings. (iii) Both bauxite and hematite could be used as catalysts for achieving very high conversions (up to around 99%) of lignin to nonsolid and deoxygenated products (around 75% of the oxygen removed) but required much higher loadings than the Mo-sulfide catalysts (6.25% bauxite and 4.3% hematite based on the entire feed mass was found to be suitable loadings). (iv) For all studied catalysts (Mo-sulfide, bauxite, and hematite), the catalyst loading was a very important parameter and too low addition resulted in reduced lignin conversion and increased gas formation. (v) When using bauxite or hematite, a high reaction temperature was very beneficial for reaching a high lignin conversion to nonsolid products. This was accompanied by an increased gas formation, and at a temperature increase from 425 to 440 °C, the gas formed increased from 10 to 26% of the lignin mass. At a reaction temperature of 440 °C, lignin formed liquid products mainly in the diesel boiling point range, while this changed to higher than diesel range at 425 °C. (vi) A reaction pressure of 100 bar

showed only minor improvements compared to 50 bar. A further reduction to only 15 bar provided clearly worse results. (vii) Although showing similar results at appropriate loadings, using bauxite resulted in higher coke (insoluble organic solid) yields than when using hematite as a catalyst. Hematite resulted in very low coke yields but instead higher yields of bio-asphaltene (determined by precipitation from the liquid product by mixing with *n*-heptane). It was suggested that the extra coke produced with bauxite was formed from the bio-asphaltene species due to the presence of acidic aluminum oxide in the bauxite. (viii) Experiments with previously used Fe-based (both hematite and bauxite) catalyst indicated low catalyst deactivation (especially using hematite) but an accumulation of unconverted solid lignin (which was also recycled along with the catalyst) in the process. (ix) An economic evaluation suggests that bauxite appears to be the most nonexpensive alternative of the studied catalysts. Possible implementation strategies for a slurry-based hydroconversion process for lignin were proposed and discussed. However, further research is required for realizing such a process concept, but the possibility of converting solid Kraft lignin to a liquid product suitable for downstream refining is very attractive.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c01664>.

(Figure S1) Reactor stirrer and cooling coil after various reaction times at 425 °C and 150 bar with a catalyst loading of 0.1% Mo; (Figure S2) reactor stirrer and cooling coil after HISB at 100 bar and 425 °C for 2 h (after finished feeding slurry), using a Mo loading of 0.1% Mo; (Figure S3) molecular weight distribution of solid residues and untreated lignin, as determined by GPC; (Figure S4) boiling point distributions of liquid products from HISB experiments; (Figure S5) iron sulfidation at different stoichiometric additions of sulfur in the form of DMDS; (Figure S6) hydrodeoxygenation (HDO) and hydrodesulfurization (HDS); (Table S1) elemental composition of lignin residues, raw materials, and liquid product; (Table S2) metal concentration in reactor and separator product from experiment with 6.25% bauxite at 425 °C (PDF)

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Notes

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■ REFERENCES

- (1) "Government Offices of Sweden," [Online]. Available: <https://www.government.se/articles/2021/03/swedens-climate-policy-framework/> (accessed 2022-05-04).
- (2) The Swedish Energy Agency, "Drivmedel 2020: Redovisning av rapporterade uppgifter enligt drivmedelslagen, hållbarhetslagen och reduktionsplikten," 2021. [Online]. Available: <https://energimyndigheten.a-w2m.se/Home.mvc?ResourceId=203063> (accessed 2022-10-07).
- (3) Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijninx, P. C.; Weckhuysen, B. M. "Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis," *Angew. Chem., Int. Ed.* **2016**, *55*, 8164–8215.
- (4) Chen, H. Lignocellulose Biorefinery Feedstock Engineering. In *Lignocellulose Biorefinery Engineering*, Chen, H., Ed.; Woodhead Publishing: Cambridge, UK, 2015; pp 37–86.
- (5) Furusjö, E.; Jafri, Y.; Wetterlund, E.; Anheden, M.; Kulander, I.; Wallinder, J.; Håkansson, Å. *Techno-economics of long and short term technology pathways for renewable transportation fuel production - detailed report*; f3 2018:09; Göteborg, **2018**.
- (6) Ház, A.; Jablonský, M.; Šurina, I.; Kačík, F.; Bubeníková, T.; Đurković, J. "Chemical Composition and Thermal Behavior of Kraft Lignins," *Forests* **2019**, *10*, 483.
- (7) Tomani, P. THE LIGNOBOOST PROCESS. *Cellulose Chemistry and Technology* **2010**, *44* (1), 53–58.
- (8) Di Francesco, D.; Dahlstrand, C.; Löfstedt, J.; Orebom, A.; Verendel, J.; Carrick, C.; Håkansson, Å.; Eriksson, S.; Rådborg, H.; Wallmo, H.; Wimby, M.; Huber, F.; Federsel, C.; Backmark, M.; Samec, J. "Debottlenecking a Pulp Mill by Producing Biofuels from Black Liquor in Three Steps," *ChemSusChem* **2021**, *14*, 2414–2425.
- (9) Valmet, 2021. [Online]. Available: <https://www.valmet.com/media/articles/up-and-running/new-technology/PEERS1stLignoBoostPlants/> (accessed 2021-09-06).
- (10) Kautto, J.; Realff, M.; Ragauskas, A.; Kässi, T. Economic analysis of an organosolv process for bioethanol production. *BioResources* **2014**, *9*, 6041–6072.
- (11) Zhang, S.; Liu, D.; Deng, W.; Que, G. "A Review of Slurry-Phase Hydrocracking Heavy Oil Technology," *Energy Fuels* **2007**, *21* (6), 3057–3062.
- (12) Sahu, R.; Song, B. J.; Im, J. S.; Jeon, Y. P.; Lee, C. W. "A review of recent advances in catalytic hydrocracking of heavy residues," *Journal of Industrial and Engineering Chemistry* **2015**, *27*, 12–24.
- (13) Nguyen, M. T.; Nguyen, N. T.; Cho, J.; Park, C.; Park, S.; Jung, J.; Lee, C. W. "A review on the oil-soluble dispersed catalyst for slurry-phase," *Journal of Industrial and Engineering Chemistry* **2016**, *43*, 1–12.
- (14) Panariti, N.; Del Bianco, A.; Del Piero, G.; Marchionna, M. "Petroleum residue upgrading with dispersed catalysts: Part 1. Catalysts activity and selectivity," *Applied Catalysis A: General* **2000**, *204* (2), 203–213.
- (15) Kim, S.-H.; Kim, K.-D.; Lee, D.; Lee, Y.-K. Structure and activity of dispersed Co, Ni, or Mo sulfides for slurry phase. *J. Catal.* **2018**, *364*, 131–140.
- (16) Alakananda, B.; Ellyn, G.; Mezza, B. Process for using catalyst with rapid formation of iron sulfide in slurry hydrocracking. U.S. Patent 8,277,638 B2, 2012.
- (17) Nguyen-Huy, C.; Kweon, H.; Kim, H.; Kim, D.; Kim, D.; Oh, S.; Shin, E. W. Slurry-phase hydrocracking of vacuum residue with a disposable red mud catalyst. *Applied Catalysis A: General* **2012**, *447–448*, 186–192.
- (18) Zhang, S.; Liu, D.; Deng, W.; Que, G. A Review of Slurry-Phase Hydrocracking Heavy Oil Technology. *Energy&Fuels* **2007**, *21* (6), 3057–3062.
- (19) Bergvall, N.; Molinder, R.; Johansson, A.-C.; Sandström, L. "Continuous Slurry Hydrocracking of Biobased Fast Pyrolysis Oil," *Energy Fuels* **2021**, *35* (3), 2303–2312.
- (20) Bergvall, N.; Sandström, L.; Weiland, F.; Öhrman, O. G. "Corefining of Fast Pyrolysis Bio-Oil with Vacuum Residue and Vacuum Gas Oil in a Continuous Slurry Hydrocracking Process," *Energy Fuels* **2020**, *34* (7), 8452–8465.
- (21) Zhang, Y.; Monnier, J.; Ikura, M. "Bio-oil upgrading using dispersed unsupported MoS₂ catalyst," *Fuel Process. Technol.* **2020**, *206*, 106403.
- (22) Hita, I.; Heeres, H. J.; Deuss, P. J. Insight into structure-reactivity relationship for the iron-catalyzed hydrotreatment of technical lignins. *Bioresour. Technol.* **2018**, *267*, 93–101.
- (23) Breunig, M.; Gebhart, P.; Hornung, U.; Kruse, A.; Dinjus, E. "Direct liquefaction of lignin and lignin rich biomasses by heterogeniccatalytic hydrogenolysis," *Biomass and Bioenergy* **2018**, *111*, 352–360.
- (24) Zakzeski, J.; Bruijninx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* **2010**, *110*, 3552–3599.
- (25) Leal, G. F.; Lima, S.; Graça, I.; Carrer, H.; Barrett, D. H.; Teixeira-Neto, E.; Curvelo, A. A. S.; Rodella, C. B.; Rinaldi, R. "Design of Nickel Supported on Water-Tolerant Nb₂O₅ Catalysts for the Hydrotreating of Lignin Streams Obtained from Lignin-First Biorefining," *iScience* **2019**, *15*, 467–488.
- (26) Ren, T.; You, S.; Zhang, M.; Wang, Y.; Qi, W.; Su, R.; He, Z. "Improved conversion efficiency of Lignin-to-Fuel conversion by limiting catalyst deactivation," *Chemical Engineering Journal* **2021**, *410*, 128270.
- (27) Crestini, C.; Lange, H.; Sette, M.; Argyropoulos, D. "On the Structure of Softwood Kraft Lignin," *Green Chem.* **2017**, *19*, 4104–4121.
- (28) Joffres, B.; Nguyen, M.; Laurenti, D.; Lorentz, C.; Souchon, V.; Charon, N.; Daudin, A.; Quignard, A.; Geantet, C. "Lignin hydroconversion on MoS₂-based supported catalyst: Comprehensive analysis of products and reaction scheme," *Applied Catalysis B: Environmental* **2016**, *184*, 153–162.
- (29) Ambursa, M.; Juan, J.; Yahaya, Y.; Taufiq-Yap, Y.; Lin, Y.-C.; Lee, H. "A review on catalytic hydrodeoxygenation of lignin to transportation fuels by using nickel-based catalysts," *Renewable and Sustainable Energy Reviews* **2021**, *138*, 110667.
- (30) ASTM D6560-17 *Standard Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products*, 2017.
- (31) Demirbas, A. "Effect of lignin content on aqueous liquefaction products of biomass," *Energy Conversion and Management* **2000**, *41* (15), 1601–1607.
- (32) Rezaei, H.; Ardakani, S. J.; Smith, K. J. Comparison of MoS₂ Catalysts Prepared from Mo-Micelle and Mo-. *Energy Fuels* **2012**, *26*, 2768–2778.
- (33) Panariti, N.; Del Bianco, A.; Del Piero, G.; Marchionna, M.; Carniti, P. "Petroleum residue upgrading with dispersed catalysts Part 2. Effect of operating conditions," *Applied Catalysis A: General* **2000**, *204*, 215–222.
- (34) Kumar, C. R.; Anand, N.; Kloekhorst, A.; Cannilla, C.; Bonura, G.; Frusteri, F.; Barta, K.; Heeres, H. J. Solvent free depolymerization of Kraft lignin to alkyl-phenolics using supported NiMo and CoMo catalysts. *Green Chem.* **2015**, *17*, 4921–4930.
- (35) Nguyen, N. T.; Park, S.; Jung, J.; Cho, J.; Lee, C. W.; Park, Y.-K. "Comparative reactivity between thermal and catalytic hydrocracking of vacuum residue: Effect of asphaltenes," *Journal of Industrial and Engineering Chemistry* **2018**, *61*, 32–38.

- (36) Lim, S.; Go, K.; Nho, N.; Lee, J. "Effect of reaction temperature and time on the products and asphaltene dispersion stability in slurry-phase hydrocracking of vacuum residue,". *Fuel* **2018**, 234, 305–311.
- (37) Pu, J.; Nguyen, T.-S.; Leclerc, E.; Lorentz, C.; Laurenti, D.; Pitault, I.; Tayakout-Fayolle, M.; Geantet, C. Lignin catalytic hydroconversion in a semi-continuous reactor: An experimental study. *Applied Catalysis B: Environmental* **2019**, 256, 117769.
- (38) Joffres, B.; Lorentz, C.; Vidalie, M.; Laurenti, D.; Quoineaud, A.-A.; Charon, N.; Daudin, A.; Quignard, A.; Geantet, C. "Catalytic hydroconversion of a wheat straw soda lignin: Characterization of the products, the lignin residue,". *Applied Catalysis B: Environmental* **2014**, 145, 167–176.
- (39) Gharbi, K.; Benyounes, K.; Khodja, M. "Removal and prevention of asphaltene deposition during oil production: A literature review,". *J. Pet. Sci. Eng.* **2017**, 158, 351–360.
- (40) Gawel, I.; Bociarska, D.; Biskupski, P. "Effect of asphaltenes on hydroprocessing of heavy oils and residua,". *Applied Catalysis A: General* **2005**, 295, 89–94.
- (41) International Energy Agency "Energy Technology Perspectives 2020," 2020. [Online]. Available: <https://www.iea.org/reports/ccus-in-clean-energy-transitions> (accessed 2022-11-07).
- (42) "news.molybdenum.com.cn," Molybdenum News Center, [Online]. Available: <http://news.molybdenum.com.cn/en/molybdenum-news/19364-mn-2787> (accessed 2022-07-27).
- (43) "ise-metal-quotes.com," Institut für seltene Erden und Metalle AG, [Online]. Available: <https://ise-metal-quotes.com/> (accessed 2022-03-29).
- (44) "www.marketindex.com.au," Market Index, [Online]. Available: <https://www.marketindex.com.au/iron-ore> (accessed 2022-03-29).
- (45) Bellussi, G.; Rispoli, G.; Landoni, A.; Millini, R.; Molinari, D.; Montanari, E.; Moscotti, D.; Pollesel, P. "Hydroconversion of heavy residues in slurry reactors: Developments and perspectives,". *J. Catal.* **2013**, 308, 189–200 December.

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