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Evaluation of kraft and hydrolysis lignin hydroconversion over unsupported NiMoS catalyst

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ABSTRACT

Catalytic hydroconversion of Kraft and hydrolysis lignins was for the first time compared in a batch reactor over an unsupported NiMoS-SBA catalyst. We also report the effect of key reaction parameters on the yields and properties of the products. The results obtained at 20 wt% catalyst loading for hydrolysis lignin showed the highest monomer yield of 76.0 wt%, which consisted of 39 wt% aromatics with the lowest alkylphenolics yield of 10.1 wt%. Identical operating conditions, 400 °C, 80 bar, 5 h at 10 wt% catalyst loading, were used to compare both lignins and the highest monomer yield (64.3 wt%) was found for the hydrolysis lignin, consisting of 16.0 wt % alkylphenolics and 20.1 wt% aromatic compounds. These values are considerably higher than those for Kraft lignin with its 47.0 wt% monomer yield. We suggest that for high yields of monomeric units from hydrolysis lignin is that it is more reactive due to its lower ash and sulfur contents and the chemical structural differences compared to the Kraft lignin. More precisely, the bio-oil from hydrolysis lignin contained higher yields of small molecules, sourced from ring-opening of cellulose in the hydrolysis lignin, which could stabilize the reactive oligomeric groups. These yields were two to seven times higher from kraft and hydrolysis lignin, respectively, compared to those obtained without catalyst. The results showed that the NiMoS-SBA catalyst is a promising catalyst for reductive depolymerization of lignin and in addition that the regenerated catalyst had good stability for multiple reaction cycles.

1. Introduction

The replacement of fossil fuels is of paramount importance. For renewable energy to be sustainable, it must be limitless and provide net-zero CO2 emissions. This demand still depends on several factors including biomass source, regional location and available technologies. Lignin, as a key component of the plant cell wall, has been identified as a major potential source of aromatic renewable resources. From an energy point of view, it has a high C/O ratio and accounts for 40 % of the carbon-based energy content in biomass [1]. However, a vast amount of generated lignin, from paper and bio-ethanol production, is predominantly incinerated and converted into heat or thermal energy and less than 2 % was sold for the production of value-added chemicals [1].

Lignin consists of polymerized three-dimensional monomers, including syringyl (S), p-hydroxyphenyl (H), and guaiacyl (G) units, which have been investigated as model compounds for catalytic hydroconversion [2]. The most common linkages of carbon–oxygen (β-O-4) and carbon–carbon (β-5, 5-5, β-1 and β-β) are formed from these 3D monomers, particularly from S and G monomer units. The β-O-4 bonds are the most abundant interunit linkages, making up almost 50 % of all intermonomer linkages in softwoods and 60 % in hardwoods [3]. The cleavage of two β-O-4 bonds, which are located one on each side of the aromatic unit, is required to produce one monomer unit [4]. Moreover, it has been observed that a higher S/G ratio gives a higher yield of monomers during catalytic depolymerization. It has been reported that during catalytic depolymerization at 250 °C of birch lignin (S/G = 3) a monomer yield of 50 mol % is found, whereas a poplar lignin (S/G = 1.5) produced yields of 44 mol % [5]. Interestingly, Shuai et al. observed a monomer yield of 78 mol % using high-syringyl transgenic poplar lignin (S/G = 38) [6].

With lignin being an integral part of the plant cell wall, its extraction is one of the challenges to achieve a suitable S/G ratio with a high quality. The extraction, depending on its process conditions, may add further structural complexity to the native physicochemical properties of the lignin. The lignin product is often contaminated or not fully extracted with a significant amount of residual carbohydrates or process
Numerous approaches and methodologies have been investigated for Kraft lignin depolymerization. The catalytic reductive depolymerization with hydrogen has been studied extensively as a means to liquify Kraft lignin and selectively produce monomers. Typically, conventional hydrotreating catalysts based on supported molybdenum sulfides (MoS2), promoted by cobalt (Co), nickel (Ni) or iron (Fe) have been studied [9,10]. Recent studies of these transition metal based catalysts showed that they exhibited high activity and selectivity for the C–O bond cleavage [1,11,12]. However, the sulfate pulping process contributes to high ash and sulfur contents in Kraft lignin [15]. The major problem, along with the coke deposition via bimolecular condensation reactions, is that inorganic contaminants can lead to catalyst deactivation during the catalytic depolymerization of Kraft lignin [14].

Compared to Kraft lignin, hydrolysis lignin, containing less ash and sulfur, can be produced from conversion of lignocellulosic biomass during enzymatic hydrolysis, which results in solid lignin (≥60 wt%), and unreacted cellulose [15]. However, limited studies have investigated catalytic reductive depolymerization of enzymatic hydrolysate lignin. Tymchynsh et al. used a MoRu/AC catalyst to depolymerize hydrolysis lignin in acetic solvent and obtained low molecular weight bio-oils (380 g/mol) with high yields of around 85 wt% at 340 °C [15]. It was also reported that an aromatic monomer yield of 12.1 wt% was obtained for hydrolysis lignin over a 5 wt% Ni/Al2O3 catalyst at 240 °C for 4 h with 30 bar H2 in methanol [16]. Bai et al. used 15 wt% Ni/Al2O3 to depolymerize hydrolysis lignin and obtained a yield of 10.3 wt% of aromatic monomers at 320 °C after 7.5 h under 28 bar H2 in ethanol [17]. The effect of reaction conditions on the depolymerization of hydrolysis lignin has been investigated in a semi-continuous process over a sulfided NiMo/γ-Al2O3 catalyst [18]. A full conversion was achieved and the liquid products, mainly aromatics, naphthenes, and phenols increased under the severe reaction conditions of 380 °C and 70 bar H2. Recently, Sang et al. examined the depolymerization of hydrolysis lignin over an unsupported Ni catalyst in supercritical ethanol and achieved complete liquefaction, with the highest monomer yield of 28.9 % at 280 °C for 6 h with 20 bar H2 [19]. Importantly, these unsupported catalysts decrease the mass transfer limitations inherent to supported catalysts, to achieve a more complete liquefaction and prevent char formation during the depolymerization [19]. More recently, the direct conversion of hydrolysate lignin into cycloalkanes over a NiMo/γ-Al2O3 catalyst was carried out in a single step at 320 °C for 7.5 h [20]. The highest obtained overall yield of cycloalkanes was 104 mg/g enzymatic hydrolysate lignin, with an ethyl-cyclohexane selectivity of 44 wt% [20]. However, there are to the best of our knowledge, no published studies where the efficiency of catalytic valorization in reducing conditions have been compared using Kraft and hydrolysis lignin, which is the objective of the current work. In this work, we introduce a facile preparation method for an unsupported NiMoS catalyst that is highly active with a high surface area. This catalyst can be a key factor in enhancing the hydrodeoxygenation and hydrogenation capabilities, and simultaneously decreasing the unwanted repolymerization reactions producing char. In addition, the reaction pathways for both lignins are proposed and discussed to reveal the key steps in their depolymerization and how they differ.

2. Material and methods

2.1. Feedstocks and chemicals

Two different lignins were investigated. Kraft lignin is a three-dimensional polymer that has undergone a hydrolytic degradation process [21,22]. It was supplied by Sigma-Aldrich as a brown dry powder. The enzymatic hydrolysis lignin was kindly provided by Sekab (Sweden). Prior to all experiments, the lignin samples were dried at 80 °C in an oven. The chemicals used were of analytical grade and were not further purified. The reagents used can be found in Supplementary Information (SI).

2.2. Catalyst synthesis

Unsupported NiMoO4 catalysts were synthesized by a nanocasting method using mesostructured silica as a hard template. SBA-16 and MCM-41, consisting of only silica, were used as templates. Hard templating is an important strategy to synthesis crystalline mesoporous materials. The unique structure of the hard template restricts the crystallization or aggregation of the precursors, and a mesoscopic phase having a structure opposite to that of the template can be obtained with the removal of template material by the appropriate method [23]. A mixture of ammonium hexahydride tetrahydrate and nickel nitrate hexahydrate, in a molar ratio of 1:1, was dissolved in ethanol. The aqueous mixture was added to the mesoporous silica and stirred for 2 h at room temperature. Subsequently, ethanol was evaporated gradually using a water bath at 65 °C. The obtained paste was then calcined at 200 °C for 6 h. The resulting solid was re-impregnated again, followed by calcination at 450 °C for 6 h at a heating rate of 6 °C/min. Lastly, the silica template was removed from the mesoporous composite by 0.5 M NaOH using a vacuum filtration process. The solid products were washed with deionized water several times and then dried at 110 °C. Elemental analysis using ICP confirmed the absence of templates and showed the successful removal of the template. The absence of silica was also confirmed with XPS, XRD and TEM-EDS. The oxide forms of the unsupported catalysts will be denoted NiMo-SBA and NiMo-MCM, respectively, according to the mesostructured SBA-16 and MCM-41 templates used in their synthesis.

2.3. Catalyst characterizations

 Elemental composition of the catalysts was determined by using an inductively coupled plasma (ICP) and was performed by ALS Scandinavia AB after digestion of the solids in an acid solution. Powder X-ray diffraction (XRD) was used to examine the crystallinity of the catalysts. This was done using a Bruker D8 Advance (40 kV; 40 mA; Cu Kα radiation (λ = 1.542 Å); 20 range of 20-80°; 1°/min scan speed). The textural properties of the samples, such as pore volume, surface area and pore size were determined by nitrogen physisorption using a TriStar 3000 analyzer. Prior to N2-physisorption measurements, approximately 300 mg sample was degassed overnight at 300 °C under a continuous flow of nitrogen gas. After drying, the N2-physisorption isotherms were collected at −195 °C under vacuum. The specific surface area and pore size were determined using the Brunauer-Emmett-Teller equation (BET) and the Barret – Joyner – Halenda equation (BJH), respectively. The lignins and catalysts were thermally characterized by TGA with a TGA/DSC 3+ Star system (Mettler Toledo, Switzerland) featuring automated temperature and weight control as well as data acquisition. The samples were analyzed, without any pre-treatment, from 25 to 800 °C (to 900 °C for catalysts) with a 5 °C/min heating rate. Dry air and nitrogen were used as carrier gases for comparison.

 Scanning electron microscopy (SEM) was used to study the surface structure and morphologies of the sulfided catalyst samples with a JEOL JSM6400, operating at 25 kV. The shape and size of the metal species in the catalysts were examined using transmission electron microscopy (TEM), with a FEI Titan 80–300 microscope (field emission gun; a probe Cs corrector; Gatan image filter Tridium; 300 kV). X-ray photoelectron spectra of the fresh sulfided catalyst was recorded using a PerkinElmer PHI 5000 Versa Probe III scanning XPS Microprobe apparatus equipped with a monochromatic Al Kα source with a binding energy of 1486.6 eV
and the beam size diameter of 100 µm. The reference used is so-called adventitious carbon (AdC) using the C 1 s peak from the surface contamination layer and its binding energy (BE) is set to 284.6 eV.

The NH$_3$ temperature-programmed desorption (NH$_3$-TPD) experiments were conducted in a Differential Scanning Calorimeter (DSC, Setaram Sensys), where the gas flow was regulated with mass flow controllers (MFC, Bronkhorst), and the outlet gases detected with a mass spectrometer (MS, Hiden Analytical HPR 20). 50 mg of NiMoO$_4$ and NiMoS unsupported catalysts were pre-treated at 400 °C for 2 h in an argon flow of 20 mL/min. This was followed by exposing the catalyst to 4 vol% NH$_3$ in Ar (10 mL/min) for 2 h at 120 °C. Thereafter the catalyst was flushed with Ar for 6 h and then the NH$_3$ desorption was studied while increasing the temperature from 120 to 700 °C at a ramp rate of 5 °C/min.

2.4. Analytical methods for products

Elemental analyses (EA) were performed to determine the C, H, N, and S content in the feed lignins, and lignin oils using a vario MICRO cube analyzer. The MICRO cube analyzes the CHNS content of organic compounds in one single run. The amount of oxygen was determined by difference from the CHNS content. All analyses were performed twice and the average value is given.

The water content in organic samples was determined by Karl Fischer (KF) titration using a Metrohm Titriso 807 titration equipment. The sample was added to a glass container with Hydranal® (Riedel de Haen) and the titrations were performed with Karl Fischer titrant Composito 5 K (Riedel de Haen). All analyses were performed twice, and the average value is given.

$^{31}$P NMR technique was used for the characterization and quantification of hydroxyl and carboxylic acid groups in lignin oils using an earlier method involving a prior derivative phosphitylation step [24]. The amount of different hydroxyl groups (mmol OH/g) in lignin oil samples was calculated according to [24]. The $^{13}$C solid-state NMR was conducted on a Bruker Avance III 500 MHz spectrometer equipped with a 4 mm MAS BB/H probe. The rotor was spun at 10 kHz and a cross-polarization time of 1.5 ms was used.

The GC-TCD technique was used to characterize gases formed during lignin hydroconversion. The gas samples were analyzed by a calibrated GC (450-GC, Varian) that was equipped with a TCD detector. A GS-GASPRO column (30 m, 0.32 mm) was used to separate and quantify the light hydrocarbons. The gas samples were collected in a 1 L Tedlar gas bag to determine its composition by using a calibrated GC-TCD technique.

2.5. Reaction experiments and separation protocol

The hydroconversion experiments were carried out in a 450 mL stainless-steel Parr reactor. The influence of catalyst loadings (ranging from 5 to 20 wt% based on a constant 5 g of dry lignin always loaded into reactor), pressures (50–80 bar H$_2$) and temperatures (330–400 °C) have been investigated (Table 1). In a typical experiment, the reactor was loaded with catalyst and lignin (5 g) in 70 mL of hexadecane as a co-processing solvent to reduce the exothermic heat effects. To create a baseline for the study, reaction experiments using only hexadecane with lignin were included in the experimental plan. The sulfidation of the NiMoO$_4$ catalyst was performed in-situ in the liquid phase, with the lignin feedstock and with the addition of (0.25–0.75 mL) dimethyl disulfide (DMDS). In-situ sulfidation of the unsupported NiMoO$_4$-SBA was carried out simultaneously with hydroconversion of Kraft and hydrolysis lignins. The advantage of in-situ activation is the simplification of the startup procedure. The amount of DMDS added depends on the catalyst amount used. During the sulfiding step for all experiments, a mixture of lignin, catalyst, and solvent were blended. Meanwhile, a small amount of DMDS (250, 500 or 750 µL) was added to the corresponding reaction mixture to maintain the sulfidity of the catalyst (5, 10 or 20 wt%, respectively). Under identical operating conditions, some experiments were performed to compare products yields from in-situ sulfided versus pre-sulfided NiMoO$_4$.

After the reactor was closed, it was flushed for 3–5 times with nitrogen to remove the air and thereafter purged three times with hydrogen. After leak testing, the reactor was initially pressurized with 16–25 bar H$_2$ (depending on the target pressure for reaction conditions) and heated up to the designated temperature at an approximate heating rate of 5 °C/min while stirring at 1200 rpm. The time zero was set once the desired reaction temperature and pressure were reached. In the case of our study, duplicate reaction experiments were repeated for many of our experiments and the relative standard deviation (%, RSD) was determined to be within 9.0 %.

After each experiment, different fractions of lignin products were recovered and analyzed. The typical products are gas, liquid bio-oil, unconverted lignin and solid char, as depicted in the product recovery protocol (Fig. S1, Supplementary Information (SI)). The pressure was recorded after the reactor was cooled to room temperature. The hydrogen consumption was determined from the difference in the initial and final pressures at room temperature [25,26]. Hydrogen was considered as an ideal gas and other gases produced during the reaction, were accounted for in the calculation of the hydrogen consumption. The pressure was released to atmospheric pressure and the gas products were collected in a 1 L Tedlar gas bag to determine its composition by using

<table>
<thead>
<tr>
<th>Experiments Notation</th>
<th>Operating Conditions Lt°–r°–P°–t°–W°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft Lignin</td>
<td></td>
</tr>
<tr>
<td>KES$_5$</td>
<td>KL–400–80–5–W$_5$</td>
</tr>
<tr>
<td>KES$_7$</td>
<td>KL–400–50–5–W$_5$</td>
</tr>
<tr>
<td>KES$_8$</td>
<td>KL–400–50–12–W$_8$</td>
</tr>
<tr>
<td>KES$_9$</td>
<td>KL–400–80–5–W$_8$</td>
</tr>
<tr>
<td>Hydrolysé Lignin</td>
<td></td>
</tr>
<tr>
<td>HES$_5$</td>
<td>HL–400–80–5–W$_5$</td>
</tr>
<tr>
<td>HES$_6$</td>
<td>HL–400–80–5–W$_5$</td>
</tr>
<tr>
<td>HES$_7$</td>
<td>HL–400–80–12–W$_7$</td>
</tr>
<tr>
<td>HES$_8$</td>
<td>HL–400–80–12–W$_8$</td>
</tr>
<tr>
<td>HES$_9$</td>
<td>HL–400–80–5–W$_9$</td>
</tr>
</tbody>
</table>

a indicates Lignin type: Kraft (KL), Hydrolysé (HL), b Temperature applied (°C), c Pressure applied (bar), d residence time (hrs.), e wt.% of catalyst loaded based on 5 g of dry lignin.

Table 1

Catalytic hydrotreatment Operational Conditions. In all experiments 5 g of dry lignin was used and 70 mL of hexadecane was added as a solvent.
3. Results and discussions

3.1. Characterisation of the unsupported catalysts

The elemental composition was measured using ICP and the unsupported NiMoO₄-SBA catalyst had a Mo:Ni ratio of 1.08. The pore structural parameters are summarized in Table 2, which displays high surface areas in the range of 155–207 m²/g for none sulfided catalysts. A sulfidation treatment of the unsupported NiMoO₄-SBA leads to an inevitable decrease of the catalyst surface area from 155 to 53 m²/g and a pore volume decreased from 0.19 to 0.08 cm³ g⁻¹, which may be due to the inclusion of sulfur to form NiS₂ and MoS₂ new phases. These catalysts exhibit the type-IV isotherm, confirming their ordered mesostructured morphology. Moreover, the pore size distributions correlate with those of the templates used and exhibited a narrow pore size distribution at around 5 nm for both as prepared and pre-sulfided catalysts. While using MCM-41 as a template, relatively larger cages and mesoporous channels, corresponding to the MCM-41 template, were observed. The pore diameter of the unsupported NiMoO₄-MCM catalyst enlarged to 11.8 nm with a significantly larger pore volume of 0.61 cm³ g⁻¹.

The crystal structures of the unsupported NiMoO₄ were characterized by XRD (Fig. 1). The broad peaks indicate a small crystallite size of the samples. Comparison of the NiMoO₄ fabricated via the two different hard templates, SBA and MCM, reveals that there are distinct differences in the XRD patterns (Fig. 1a). α-NiMoO₄ and β-NiMoO₄ phases have a monoclinic crystal structure (group space C12/m1). The characteristic peak of the β phase is 2θ = 26.4° and for the α phase it is 2θ = 28.7°. From the structural point of view, the relevant important differences between both phases are the molybdenum ion coordination in the crystal structure, being octahedral clusters, [Mo₆O₁₈]₄⁻, for the α-NiMoO₄ and tetrahedral [MoO₄]²⁻, for the β-NiMoO₄ powder [27]. It has been found that for the preparation of highly active unsupported NiMo catalysts, the β-NiMoO₄ phase is most favorable for hydrodesulfurization (HDS) reactions [28–31]. In this work, the unsupported NiMoO₄ fabricated from the SBA hard template which exhibited the β-NiMoO₄ phase was

Table 2
Pore structural parameters of the unsupported catalysts synthesized using different hard templates.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>S BET (m²/g⁻¹)</th>
<th>V孔 (cm³/g⁻¹)</th>
<th>dHHR (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMoO₄-SBA (as prepared)</td>
<td>155</td>
<td>0.19</td>
<td>5.0</td>
</tr>
<tr>
<td>NiMoS-SBA (pre-sulfided)</td>
<td>53</td>
<td>0.08</td>
<td>5.9</td>
</tr>
<tr>
<td>NiMoO₄-MCM (as prepared)</td>
<td>207</td>
<td>0.61</td>
<td>11.8</td>
</tr>
</tbody>
</table>

a Calculated by the BET method.

b The total pore volume was obtained at a relative pressure of 0.99.

c Mesopore diameter was calculated using the BJH method. Pore morphology: NiMo-SBA cubic, NiMo-MCM hexagonal.

NiMoS-SBA pre-sulfided under 330 °C, 20 bar H₂ for 2.5 h.

GC-TCD. The blended organic product was recovered, filtered and labelled as lignin oil. Subsequently, the reactor was rinsed with acetone, filtered, and this product fraction was labelled as the acetone soluble phase. Moreover, the solid phase (char, unconverted lignin, and catalyst) was washed with acetone to remove any adsorbed organics.

The unconverted lignin was determined by suspending 0.5 g of solid residue in 15 mL of DMSO and thereafter stirring for 24 h at room temperature. After filtration of the solution, the solids were washed with acetone and dried. The weight difference between the solids before and after the washings was assumed to be the weight of unconverted lignin.

The conversion, char, and monomer yields were determined using Eqs. (1) to (3).

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

(1)

\[
\text{Char yield (wt. %)} = \frac{(\text{solid fraction (g)}) - (\text{unconverted lignin (g)} + \text{catalyst (g)})}{\text{initial lignin feed (g)}} \times 100
\]

(2)

\[
\text{Monomer yield (wt. %)} = \frac{\text{monomer (g)}}{\text{initial lignin feed (g)}} \times 100
\]

(3)

Fig. 1. XRD of the as-prepared unsupported NiMoO₄ powders using different hard templates MCM and SBA (a) and the pre-sulfided unsupported NiMoO₄-SBA (b).
therefore selected for the catalytic hydroconversion.

The XRD patterns of the pre-sulfided NiMoO₄-SBA are depicted in Fig. 1b. The sulfided NiMoS showed strong diffraction peaks consistent with the relatively good crystalline structure of MoS₂ (JCPDS-ICDD 371492), NiS₂ (JCPDS-ICDD 89–3058), and β-NiS (JCPDS-ICDD 12–0041). The presence of peaks at 20 value of 45.4, 33, 39 and 59 corresponded to the (002), (100), (103) and (110) planes of MoS₂ [32]. As revealed by the XRD patterns, peaks due to NiS₂ and β-NiS species were also detected. Some peaks at 20 value of 27, 31, 35, 38, 45, and 53 were observed, matching well with the NiS₂ [33]. Moreover, the presence of peaks can be clearly indexed to β-NiS at 20 value of 33, 37, 41, 49, 51, and 57 corresponding to (300), (220), (221), (131), (410) and (330) planes [34]. Obvious diffraction peaks from other compounds, such as Ni₃S₄ and NiS₃S₄, were also observed at 20 value of 43.5, and 48 respectively [35,36].

The SEM image of the sulfided NiMoS-SBA catalyst showed two major structural features (Fig. S2a, SI). Small pore sizes can be seen in the material with an average pore size of 5–10 nm (white insert). These smaller pores are the fine intra-aggregate pores of the material. The larger sized pores (>50 nm) may be attributed to the secondary pores formed by the combination of primary particles. The TEM result of the freshly sulfided NiMoS-SBA catalyst is given in Fig. S2b (SI). Areas with black thread-shape fringes that have spacings of about 0.5 nm indicate a freshly sulfided NiMoS-SBA catalyst is given in Fig. S2 b (SI). Areas with black thread-shape fringes that have spacings of about 0.5 nm indicate a freshly sulfided NiMoS-SBA catalyst is given in Fig. S2 b (SI).

The XPS spectra showed that the binding energies of Mo 3d and Ni 2p were located at 228.7 eV and 232.1 eV respectively, owing to the Mo⁴⁺ in MoS₂ [39,40] and there is also a weak peak located at 235.2 eV assigned to Mo⁶⁺ in MoO₃ formed due to oxidation of Mo (Fig. 3b). Another weak peak at the binding energy of 225.9 eV is ascribed to S²⁻ of MoS₂ and NiS₂ [39,40]. Besides, there are two strong peaks at 161.5 and 162.7 eV in the S2p spectrum (Fig. 3c), which are assigned to the S²⁻ of NiS₂. Moreover, there are three peaks present in the Ni 2p spectrum (Fig. 3d) at 853.3, 856.4, and 861.7 eV, which could be assigned to NiS₂.

Fig. 2 displays the TGA and DTG profiles of the pre-sulfided and as-prepared NiMoO₄-SBA catalysts. For the unsulfided NiMoO₄-SBA catalyst, it shows two weight loss areas, totaling about 6.4 wt% up to the reaction temperature of 400 °C, together with corresponding endothermic peaks (Fig. 2b). The first weight loss was about 3.4 wt% from 75 to 170 °C, based on a calculation of the first derivative of the weight loss curve at 70.4 °C and might be attributed to the loss of physically absorbed and chemically bonded water. The following weight loss was about 3.0 wt% from 210 to 415 °C, which can be due to the total phase transformation of α-NiMoO₄ (octahedral MoO₃) to pure β-NiMoO₄ (tetrahedral MoO₃) above 286 °C, which was reported by Pillay et al. by measuring the XRD pattern at high temperature to characterize the α-NiMoO₄ and β-NiMoO₄ phase transitions [38].

The XRD patterns of the pre-sulfided NiMoO₄-SBA catalyst showed two major structural features (Fig. S2a, SI). Small pore sizes can be seen in the material with an average pore size of 5–10 nm (white insert). These smaller pores are the fine intra-aggregate pores of the material. The larger sized pores (>50 nm) may be attributed to the secondary pores formed by the combination of primary particles. The TEM result of the freshly sulfided NiMoS-SBA catalyst is given in Fig. S2b (SI). Areas with black thread-shape fringes that have spacings of about 0.5 nm indicate a high purity of the active components and are characteristic of the (002) basal planes of crystalline MoS₂ (XRD pattern Fig. 1b). This has been confirmed by Yoosuk et al. [37]. As well-known from the intercalation model, slab growth occurs in parallel and perpendicular directions [2]. But for NiMoS in Fig. S2b, the slabs seem curved. These results are in good agreement with the recent study of Yoosuk et al. [37], who also suggested a reduction in the slab length and form when Ni was incorporated into the Mo sulfide. In these directions, the promoting Ni atoms are bonded (in intercalation positions) by Van der Walls forces [36]. It is generally accepted that the best hydrotreating MoS₂ catalysts are promoted with Ni or Co atoms located at the edges of MoS₂ slabs [2], which is discussed later in connection to the lignin depolymerization. In good agreement with the literature data, it can be assumed that the formation of Ni₃S₄ active sites occurred at the rims of MoS₂ sheet crystals.

Fig. 2. (a) Thermogravimetric analysis (TGA) and (b) Derivative thermogravimetric (DTG) curves of the pre-sulfided and as-prepared NiMoO₄-SBA.
oxide and nickel hydroxide, respectively [36,40].

NH$_3$-TPD profiles of NiMoO$_4$-SBA and NiMoS-SBA catalysts are presented in Fig. S3 (SI) to evaluate their surface acidity. Both catalysts exhibited moderate (200–400 °C) and strong (>400 °C) acid sites. The NH$_3$-TPD profile of NiMoO$_4$-SBA displayed a relatively wide peak at 300 °C and a minor peak at 550 °C, which were attributed to moderate and strong acid sites, respectively. Whereas after sulfidation, it can be observed that there is an important decrease in the number of moderate acid sites, while an increase in the acid strength for sulfided NiMoS-SBA.

3.2. Characterization of lignins and product recovery

3.2.1. Lignin characterisation

Chemical structures and thermal characterization of lignins were carried out through thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), elemental analysis (CHONS), and solid state $^{13}$C NMR. TGA curves, under oxidizing atmosphere (Fig. 4), showed that the water content corresponds to the weight loss of about 2.3 wt% for Kraft lignin and 1.5 wt% for hydrolysis lignin at 100 °C, whereas the remaining weight at the end corresponds to the ash content of 3.5 wt% for Kraft lignin and only 0.5 wt% for hydrolysis lignin. Elemental CHONS analyses, ash, water content as well as the H/C and

Fig. 3. XPS spectra of pre-sulfided NiMoS-SBA. (A) full scan spectrum of NiMoS, with high resolution spectra of (B) Mo3d, (C) S2p, and (D) Ni2p.

Table 3

<table>
<thead>
<tr>
<th>Elements</th>
<th>C1s*</th>
<th>O1s**</th>
<th>S2p</th>
<th>Ni2p</th>
<th>Mo3p</th>
<th>Ni/(Ni + Mo)</th>
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<tbody>
<tr>
<td>Atomic %</td>
<td>36.4</td>
<td>34.9</td>
<td>14.6</td>
<td>6.3</td>
<td>7.7</td>
<td>0.45</td>
</tr>
<tr>
<td>Molar</td>
<td>16.9</td>
<td>21.7</td>
<td>18.1</td>
<td>14.4</td>
<td>28.9</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Note: *AdC contamination layer. ** note that the samples were stored in air prior to XPS measurements.

Fig. 4. TGA curves of the kraft (red line) and hydrolysis lignins (blue line) under oxidizing atmosphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Table 4
Elemental analyses, ashes, water, and H/C and O/C ratios and HHV for the lignins.

<table>
<thead>
<tr>
<th></th>
<th>Kraft Lignin</th>
<th>Hydrolysis Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>61.2</td>
<td>55.9</td>
</tr>
<tr>
<td>H (%)</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td>O (%)</td>
<td>30.5</td>
<td>38.1</td>
</tr>
<tr>
<td>N (%)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>S (%)</td>
<td>1.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Ashes (%)</td>
<td>3.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Water (%)</td>
<td>2.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Total (%)</td>
<td>104.8</td>
<td>102.1</td>
</tr>
</tbody>
</table>

Atomic ratio

<table>
<thead>
<tr>
<th></th>
<th>Kraft Lignin</th>
<th>Hydrolysis Lignin</th>
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</thead>
<tbody>
<tr>
<td>H/C</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>O/C</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>HHV (MJ/kg)†</td>
<td>24.7</td>
<td>22.3</td>
</tr>
</tbody>
</table>

† Higher Heating Value.

Fig. 5. Solid state 13C NMR spectrum of Kraft and hydrolysis lignins.

O/C atomic ratios are reported in Table 4.

The chemical structures of Kraft and hydrolysis lignin were analyzed by means of solid-state 13C NMR (Fig. 5). Both lignins showed small signals in the area 200–160 ppm, indicating a low amount of C=O structure, attributed to C=O bonds in Ar-CHO or R-O-CO-CH3 at 177.5 ppm and 181 ppm, respectively [41]. In the Cαm region (110–150 ppm), the intense peak at 150 ppm corresponds to Cαm-O, whereas three weak signals were observed at 115, 123 and 127 ppm corresponding to Cαm-C and Cαm-H [42,43]. The 13C NMR spectrum of hydrolysis lignin showed characteristics of typical lignocellulosic biomass, which is primarily composed of cellulose (62–110 ppm) and lignin [44]. Fu et al. showed that hydrolysis lignin is covalently attached onto cellulosic moieties, indicating that the cellulose from lignocellulosic biomass is not fully isolated [15,45–47]. Note that the high O elemental content result for hydrolysis lignin (38.1 wt%) may be partly due to the presence of cellulosic oxygen content. Moreover, methoxy groups were detected at 58.0 ppm for both lignin types. The CH2, CH3 saturated aliphatic signals (<50 ppm) could not be clearly observed and distinguished. Some identical peaks were observed in both lignins, but the peak intensities were higher for Kraft lignin than the hydrolysis lignin. By comparing these different analytical results, we can observe that both lignins are connected randomly through β-5 linkages, and cellulosic units for hydrolysis lignin showed characteristics of typical lignocellulosic biomass, which is primarily composed of cellulose and lignin [44]. Fu et al. showed that hydrolysis lignin is covalently attached onto cellulosic moieties, indicating that the cellulose from lignocellulosic biomass is not fully isolated [15,45–47].

TGA and DSC curves for hydrolysis and Kraft lignin under inert atmosphere are given in Fig. 6, TGA analysis showed that Kraft and hydrolysis lignins start to decompose in the range of 175–250 °C, the char yields of Kraft (43 wt%) and hydrolysis (31 wt%) were higher than in an oxidizing environment (see Fig. 4 and Fig. 6). These results show that depolymerization of

Table 5
Summary of thermal and catalytic hydrotreatment experiments.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Operating Conditions</th>
<th>Conv. (Wt. %)</th>
<th>Oil Yield (Wt. %)</th>
<th>Gas Yield (Wt. %)</th>
<th>Char Yield (Wt. %)</th>
<th>Water Yield (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft Lignin</td>
<td>KES0</td>
<td>KL–400–80–5–W0</td>
<td>98.9</td>
<td>45.3</td>
<td>0.3</td>
<td>52.9</td>
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<td></td>
<td>KES1</td>
<td>KL–330–50–5–W5</td>
<td>99.5</td>
<td>48.7</td>
<td>0.1</td>
<td>40.5</td>
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<tr>
<td></td>
<td>KES2</td>
<td>KL–400–50–5–W5</td>
<td>91.0</td>
<td>49.7</td>
<td>2.9</td>
<td>30.0</td>
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<tr>
<td></td>
<td>KES3</td>
<td>KL–400–50–12–W5</td>
<td>93.0</td>
<td>59.2</td>
<td>5.6</td>
<td>27.0</td>
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<tr>
<td></td>
<td>KES4</td>
<td>KL–400–80–5–W5</td>
<td>95.3</td>
<td>61.5</td>
<td>2.4</td>
<td>29.0</td>
</tr>
<tr>
<td></td>
<td>KES5</td>
<td>KL–400–80–5–W10</td>
<td>91.4</td>
<td>65.1</td>
<td>2.1</td>
<td>20.6</td>
</tr>
<tr>
<td>Hydrolysis lignin</td>
<td>HES6</td>
<td>HL–400–80–5–W0</td>
<td>96.6</td>
<td>56.4</td>
<td>0.7</td>
<td>38.6</td>
</tr>
<tr>
<td></td>
<td>HES7</td>
<td>HL–400–50–5–W5</td>
<td>97.6</td>
<td>76.4</td>
<td>3.1</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>HES8</td>
<td>HL–400–80–5–W10</td>
<td>94.4</td>
<td>83.7</td>
<td>1.2</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>HES9</td>
<td>HL–400–80–12–W20</td>
<td>95.7</td>
<td>86.8</td>
<td>2.6</td>
<td>3.9</td>
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<tr>
<td></td>
<td>HES10</td>
<td>HL–400–80–5–W20</td>
<td>94.9</td>
<td>87.1</td>
<td>1.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Fig. 6. TGA and derivative curves of (a) Kraft lignin; (b) hydrolysis lignin under N2 atmosphere.
lignin without a catalyst to facilitate hydrogenation and deoxygenation reactions, is likely to yield a high char formation, particularly for Kraft lignin. It can also be seen that the thermal properties of the lignin depend on their source due to their structural variations. However, under catalytic hydroconversion, the conversions of the Kraft and hydrolysis lignins were found to be higher than 90%, which was confirmed by performing DMSO extraction of the unconverted lignin. In the subsequent sections, we examine and discuss in detail the individual product yields of the hydro-treated lignins.

3.2.2. Hydrotreatment product distributions

For each lignin, the results of non-catalyzed and catalyzed hydro-treatment reactions are presented in Table 5. The conversions of both lignins were in the range of 91.0–99.5 wt%. The lowest lignin-oil yields were observed for the non-catalyzed experiments (KES50 and HES10), which correlate well with the least water content formed upon the reaction (0.3 and 0.7 wt%) and the highest char formation (52.9 and 38.6 wt%), showing a low degree of deoxygenation without the catalyst.

These results also provide clear evidence that thermal depolymerization reactions play a role. Interestingly, the hydrolysis lignin results in significantly less char for uncatalyzed reactor experiments than Kraft lignin, which is consistent with the TGA results in Fig. 6. When the unsupported NiMoS-SBA catalyst (in situ sulfided) was used under the same conditions, the lignin-oil yield increased to 65.1 and 83.7 wt%, whereas the char yields were repressed to 20.6 and 8.3 wt% for Kraft (KES400 °C, 80 bar H2, 10% catalyst, 5 h) and hydrolysis lignin (HES400 °C, 80 bar H2, 10% catalyst, 5 h), respectively. The characterization results demonstrated that the sulfided catalyst had two separated sulfide phases rather than a trinary Ni-Mo-S phase. Thus, the presence of both phases of MoS2 and NiS2 likely improved the lignin conversion. This is mainly due to a synergism between NiS2 and MoS2, evidently reflected by the major XRD peaks of pre-sulfided NiMoO4-SBA (Fig. 1b). Moreover, the XPS analysis confirms the presence of both phases. It was also reported by Wang et al. that a synthesis of NiS2/MoS2 has higher surface area, resulting in the exposure of more active sites [49]. The hydrodeoxygenation activity is considered enhanced in the presence of both NiS2 and MoS2 which could be described by a Remote Control (RC) model via hydrogen spillover [49]. According to the RC model the two separated sulfide phases of the catalyst are described as a donor phase (promoter, NiS2) and an acceptor phase (active component, MoS2), and thus spillover hydrogen was created on NiS2 which then migrated to MoS2 [49]. It was also reported that a Ni-Mo binary sulfide phase is more active than either of the single Mo or Ni sulfide phases and the maximum (promoter, NiS2 separated sulfide phases of the catalyst are described as a donor phase [37].

A comparison is made between pre-sulfidation and in-situ sulfidation method (see Table S1) and it is found that both methods give similar results. Based on these results, we consider that the DMSD added was adequate to activate both in-situ or pre-sulfided NiMoO4-SBA catalysts.

The influence of temperature, pressure, residence time and catalyst loadings were investigated. The effect of temperature (330 and 400 °C) on the product yield was investigated in experiments KES30 (330 °C, 50 bar H2, 5% catalyst, 5 h) and KES400 (400 °C, 50 bar H2, 5% catalyst, 5 h) using Kraft lignin. Higher temperature led to a slight increase in lignin liquefaction yields from 48.7 to 49.7 wt% and a clear decrease in char residue from 40.5 to 30 wt%. We also observed that both the water and gas contents increased to ~2.0 wt%, indicating that the removal of oxygen functionalities starts above 330 °C. Moreover, a longer residence time of the reaction (KES400 °C, 50 bar H2, 5% catalyst, 12 h) led to further suppression of the char yield to 27 wt%, and large increases in lignin oil, water and gas content were observed. Hydrogen consumption was measured for the 5 and 12 h residence times and it increased from 1.5 to 3.9 mmol per g of Kraft lignin, simultaneously as the water yield increased from 2.3% to 7.9%, due to a higher degree of deoxygenation being achieved.

At a constant temperature of 400 °C, the pressure was increased from 50 to 80 bar (KES2: 400 °C, 50 bar H2, 5% catalyst, 5 h) versus (KES4: 400 °C, 80 bar H2, 5% catalyst, 5 h). This higher pressure ensured a higher solubility of hydrogen in the oil, which resulted in an increase from 49.7 to 61.5 wt% of the oil yield and thereby a higher availability of hydrogen in the vicinity of the catalyst. As seen in Table 5 (KES2 vs KES4), this increases the reaction rate and further decreases the unreacted lignin from 9.0 to 4.7 wt%. Furthermore, higher degrees of deoxygenation are favored by increasing the catalyst loadings from 5 to 10 wt%. Consequently, higher lignin-oil yields of 65.1 and lower char yields of 20.6 wt% were achieved for Kraft lignin (KES4 vs KES5) with increased catalyst loading. Similarly, for hydrolysis lignin (compare HES2, HES4 and HES10), higher loadings of catalyst resulted in increased oil yield and decreased char formation. This could be explained by that when increasing the loading more active sites are available for the adsorption of lignin and in addition, an enhanced hydrogen spillover from NiS2 could occur, resulting in a promotion of the hydrogenation-dehydration reactions.

A comparison of lignin-oil and char yields for Kraft and hydrolysis lignin is presented in Fig. 7. Under identical operating conditions, hydrolysis lignin results display higher lignin oil formation and lower char yields in comparison to Kraft lignin. One of the reasons is that hydrolysis lignin was obtained from enzyme catalytic conditions, making it more active and free from ash and sulfur contents (Table 4), than the lignin materials obtained from chemical processes [20,50]. Generally, additional central factors may be the different chemical structures and compositions of the lignin-types, and in particular their different S/G ratios [51,52]. Moreover, the hydrolysis lignin consisted of both lignin and cellulose (see Fig. 5) and thereby the hydrolysis lignin contains less lignin per mass, and this could also be a factor for producing less char since it is known that lignin often gives large amount of char.

3.2.3. Stability tests

To investigate the stability of the sulfided NiMoO4-SBA catalyst, three consecutive conversions of hydrolysis lignin were conducted using the recycled catalyst (Table S4). Upon completion of the reaction (HES10), the catalyst used was regenerated by calcining the spent catalyst in air at 500 °C for 5 h to burn off any remaining unseparated char or solids. The recycled catalyst was then used for the next reaction cycles as described in the Reaction experiments section 2.5. Table S4 shows that for the experiments with recycled catalyst the conversion and oil yields are similar during repeated cycles. A catalyst weight loss of 10.6 wt% was observed for the first cycle, which is similar to the 8.5 wt% from the TGA thermogram results (Fig. 2a). The second and third cycles were further performed and resulted in negligible weight losses up to 2.0 wt%. Thus, the spent NiMoO4-SBA catalyst was found to have good stability and performance comparable to a duplicated HES10 experiment (Table 5).

3.2.4. Gas and lignin oil compositions

The gaseous phase composition was quantified, and the results are given in Table 6. The results show a maximum of 5.6 wt% gas product yield measured at room temperature after the reaction. The dominant gas products were CH4 (0.1–3 wt% on lignin), and CO2 (0.1–2.4 wt%), with small quantities of olefins C2-C4 (<0.7 wt%). The gas-phase formation may be explained by reactions occurring during lignin hydroconversion, along with gas phase reactions. The olefins are derived from the C–C cleavage of alkyl chains or via dehydration of intermediate small alcohols derived from the cleavage of the β-O-4 ether linkage. The formation of CH4 can be explained by demethylation, which is favored under our conditions. Another possible pathway for methane formation is the reaction of the released CO2 and CO with H2. This was also demonstrated for model compounds such as formic and acetic acid over a Ru/TiO2 catalyst [53,54]. Moreover, the formation of CO2 and traces of CO can result from decarboxylation and water gas shift reactions. The decarboxylation of –COOH to form larger amounts of CO2 product was observed for the catalytic hydroconversion at 400 °C (KES2), but not at
These results are consistent with those reported previously, suggesting that decarboxylation of carboxylic acids occur at a temperature higher than 350 °C \([52,55]\). When increasing the temperature (KES\(_1\) versus KES\(_2\)) and residence time (KES\(_2\) versus KES\(_3\)) for Kraft lignin over the NiMoS-SBA catalyst, the yields of CH\(_4\) and CO\(_2\) increased, whereas it was similar when increasing the pressure (KES\(_1\) versus KES\(_4\)). With increasing catalyst content from 5 wt% (KES\(_5\)) to 10 wt% (KES\(_6\)), the yields of CH\(_4\) and CO\(_2\) were similar. However, a significant decrease in gas yield was observed for hydrolysis lignin while increasing the catalyst loadings from 5, 10 and up to 20 wt% (HES\(_7\), HES\(_8\), and HES\(_{10}\)). In contrast to our results, Chowdari et al. \([56]\) found that the total yield of gases slightly increased when increasing the catalyst loading for a 20NiMoP/AC from 5 wt% to 10 wt%, respectively from 8.6 to 9.4 % at 400 °C \([56]\). This can be due to several differences, such as much higher selectivity for the decarboxylation and demethylation with their supported 20NiMoP/AC catalyst and the conditions under which it was used.

The oxygen and hydrogen contents in the lignin-oils are displayed in the form of Van Krevelen diagrams (Fig. 8). The hydrolysis lignin used in this study has a relatively high O/C ratio of 0.51, while that of Kraft lignin is considerably lower, 0.39. This is likely due to differences in the extraction methods, feedstock origins and their different compositions (e.g. cellulose in hydrolysis lignin). Based on the Van Krevelen diagrams, the lignin oils show significantly lower O/C ratios (0.02–0.11) and an increase in H/C ratios (1.97–2.26), suggesting that the hydroconversion reactions have occurred to a large extent. It is interesting to note that the estimated Higher Heating Values (HHV) (Tables S1 and S2) are high and similar to those of traditional petroleum-based fuels \([57]\). Despite the higher starting O/C ratio, hydrolysis lignin showed overall lower oxygen contents in the oils, which possibly can allow easier conversion into high-quality fuels compared to the oil from Kraft lignin. Also, the presence of hydrogen and catalyst resulted in a reduction in sulfur content in the lignin-oils (<0.02 wt%), showing the efficiency of the catalyst for

### Table 6

The effect of NiMoS-SBA unsupported catalyst on the gas product yield and distributions during lignin hydroconversion. See Table 1 for operating conditions.

<table>
<thead>
<tr>
<th>Entries</th>
<th>Operating Conditions</th>
<th>Gas Yield (wt.%)</th>
<th>CH(_4) (wt.%)</th>
<th>CO(_2) (wt.%)</th>
<th>C(_2)H(_x) (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kraft Lignin</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KES(_0)</td>
<td>KL–400–80–5–W(_0)</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>KES(_1)</td>
<td>KL–330–50–5–W(_5)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>KES(_2)</td>
<td>KL–400–50–5–W(_5)</td>
<td>3.1</td>
<td>1.5</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>KES(_3)</td>
<td>KL–400–50–12–W(_1)</td>
<td>5.6</td>
<td>3.0</td>
<td>2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>KES(_4)</td>
<td>KL–400–80–5–W(_1)</td>
<td>2.4</td>
<td>1.3</td>
<td>1.2</td>
<td>0.2</td>
</tr>
<tr>
<td>KES(_5)</td>
<td>KL–400–80–5–W(_10)</td>
<td>2.1</td>
<td>1.2</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Hydrolysis Lignin</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HES(_6)</td>
<td>HL–400–80–5–W(_1)</td>
<td>0.7</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>HES(_7)</td>
<td>HL–400–80–5–W(_5)</td>
<td>3.1</td>
<td>1.7</td>
<td>1.1</td>
<td>0.5</td>
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<tr>
<td>HES(_8)</td>
<td>HL–400–80–5–W(_1)</td>
<td>1.2</td>
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</tr>
<tr>
<td>HES(_9)</td>
<td>HL–400–80–5–W(_10)</td>
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<td>1.1</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>HES(_10)</td>
<td>HL–400–80–5–W(_20)</td>
<td>1.0</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Fig. 7. Comparison of lignin-type, Kraft and hydrolysis, for their conversion, lignin-oil, and char yields (a) 5 wt%; (b) 10 wt% catalyst loading. Conditions: 400 °C, 80 bar H\(_2\), 5 h, and 1200 rpm.

Fig. 8. Van Krevelen diagram of lignin-oils for Kraft and hydrolysis lignins. See Table 1 for operating conditions.
HDS reactions (see Tables S1 and S2). In the absence of catalyst (KES₀ and HES₉), the values of oxygen were higher (8.3–11.6 wt%) than for all experiments with unsupported NiMoS-SBA catalyst (1.9–6.3 wt%), which clearly demonstrates the beneficial effect of the catalyst. The above results suggest that NiMoS-SBA is an effective catalyst for hydrogenation, deoxygenation and desulfurization of lignin under the selected conditions. At high temperature and pressure (KES₅), the H/C ratio increases, and it can further increase with extended reaction time as was evident for KES₅ versus KES₂. For reactions performed at 400 °C and 80 bar, an increase in catalyst loading (KES₅ versus KES₂) leads to a decrease in the O/C ratio, which results in that >87 % of the oxygen was removed, compared with the initial feedstocks used.

³¹P NMR analysis on the lignin-oils was performed to help elucidate the changes that occurred during the reaction. This offers the unique ability to distinguish hydroxyl groups attached to p-hydroxyphenyl, guaiacyl, and syringyl units. Fig. 9 shows ³¹P NMR spectrums of lignin-oils obtained under the selected conditions. A compressed compilation of hydroxyl groups in lignin oils and their typical chemical integration ranges are summarized in Fig. 9 along with the quantitative data (Table 7) clearly shows that Kraft and hydrolysis lignin oils were rich in p-hydroxyphenyl and guaiacyl OH groups, while syringyl and condensed OH groups (C₅-substituted OH) were observed in small amounts for the highly catalyzed Kraft lignin (10 wt% loaded, KES₅) and less catalyzed (5 wt% loaded, HES₇) and uncatalyzed hydrolysis lignin (HES₈ and HES₉). Small amounts of carboxylic acid (133.6–136 ppm) and aliphatic OH (145–150 ppm) can be distinguished for Kraft and hydrolysis lignin oils as well.

The total quantity of monomer in the lignin-oils is of high interest to indicate the effect of the unsupported catalyst and various operating conditions on the target product classes in this study. Therefore, all lignin-oils were subjected to GCxGC analysis, with a correction for the hexadecane solvent contribution (Fig. 10). The lignin-oil phase product comprises a complex mixture of monomeric compounds. The monomer composition detected by GCxGC is quite similar for both lignins when other variables are kept constant (listed in Fig. 10). For noncatalyzed reactions shown in the ³¹P NMR spectrum, the total OH content (Fig. 9, uncatalyzed) in the lignin-oils was lower and dominated by p-hydroxyphenyl (phenolic OH groups). This implies that hydrogenolytic cleavage of aryl-O-aryl and aryl-O-aliphatic linkages in the lignin only partially occurred. A series of operating conditions were examined with the presence of the unsupported NiMoS-SBA catalyst and exhibited an important impact on lignin depolymerization, namely enhanced cleavage of C–O–C linkages between lignin units. ³¹P NMR spectrums showed the presence of a larger amount of p-hydroxyphenyl and guaiacyl in the area 138–140 ppm (Fig. 9, catalyzed). By increasing the temperature to 400 °C for Kraft lignin, the methoxylphenol were converted to alkylphenolics by O-demethylation reactions, as confirmed by GCxGC analysis (KES₂ to KES₅, Fig. 10). This suggests that most of the O-demethylation (–OCH₃) and hence higher CH₄, CO₂ and water yields (Table 5 and Table 6) resulted from cleavage of guaiacol, syringyl and C₅-substituted OH groups occurring at the higher temperature.

By increasing the residence time (KES₂ to KES₅), both alkylated phenolic and aliphatic OH were increased for Kraft lignin (Table 7 and Fig. 10), whereas the carboxylic acid (COOH) was significantly suppressed, leading to the enhancement of CO₂ formation (Table 6). This is
probably due to the reduction of the carboxylic acids accompanied by an increase in solubility of the Kraft lignin in the fluid phase [58]. A similar effect on content of carboxylic acid was observed for hydrolysis lignin while increasing the residence time from 5 to 12 h at 400 °C (HES₅ to HES₉), however; this resulted in slightly decreased phenolic and aliphatic OH contents according to NMR results (Table 7). It is noteworthy to mention that part of the phenolic OH detected by ³¹P NMR includes those in oligomeric compounds which are not detected by GCxGC analysis. Thus, the enhancement of alkenolic and aromatic compounds when increasing the residence time from 5 h to 12 h, as shown in the GCxGC results (HES₅ to HES₉, Fig. 10), can be explained by a deep cleavage of the oligomeric compounds (Table 7). As can be seen in Fig. 9, the C₅-substituted OH units for uncatalyzed (0 wt%, KES₀) and less catalyzed Kraft lignin (5 wt%, KES₅) were not observed, whereas it was observed for the highly catalyzed Kraft lignin (10 wt%, KES₁₀). For hydrolysis lignin, the uncatalyzed (0 wt%, HES₀) and less catalyzed (5 wt%, HES₅) lignin showed small amounts of C₅-substituted OH units, however; none were observed at the higher catalyst loading (10 wt% HES₁₀). Although the reaction conditions were nearly identical, the depolymerization and cleavage of C–O bonds differed to a certain extent between the lignins.

Upon increasing the catalyst loading from 10 wt% (HES₅) to 20 wt% (HES₁₀) for hydrolysis lignin, all hydroxylic groups and particularly the phenolic OH content decreased by eightfold (Table 7), which was accompanied by a significant reduction in the char yield and an enhancement in lignin-oil yields (HES₅, Table 5). These changes also resulted in an increase in aromatic, and a decrease in alkenolic phenolics and aliphatic OH/Ketones yields (HES₁₀, Table 5). As shown by comparison between the Kraft and hydrolysis lignins in Fig. 9, the high correlation between alkenolic phenolics and aromatics is strongly dependent on the composition and structural complexity of the lignins which influences their hydroconversion reactivity.

The total monomer yield ranged from 25.1 to 47.0 wt% for Kraft lignin (KES₀ to KES₅, Fig. 10) and from 32.7 to 76.0 wt% for hydrolysis lignin (HES₀ to HES₁₀) under the various reaction conditions. Alkenolic phenolics are the dominant chemical group from Kraft (7.0–22.7 wt%) and hydrolysis (11.9–24.8 wt%) lignin oil, except at higher than 10 wt% of catalyst loading for both the Kraft and hydrolysis lignins in which case the aromatics were the major compound from Kraft (18.3 wt%) and hydrolysis lignin oil (39.4 wt%). However, the proportion of the oil products composed of aromatics/naphthalenes varies between the lignin oils, where higher aromatic yields of 14.7 wt% were obtained for hydrolysis lignin (HES₅) compared to 7.3 wt% for Kraft lignin oil (KES₄) at the same operating conditions. When comparing the 10 wt% loading of catalyst at the same conditions (HES₀ vs KES₀), it is apparent that hydrolysis lignin produces higher lignin-oil yields of 83.7 wt% compared to Kraft lignin-oil of 65.1 wt% (Table 5), corresponding to 64.3 and 47.0 wt% of monomer yields respectively (Fig. 10). This has been previously confirmed using model compounds over NiS₂/MoS₂ [50]. It was reported that only an appropriate proportion of donor phase (NiS₂) to acceptor phase (MoS₂) could produce the maximum HDO activity. More specifically, the hydrogenation activity was enhanced in the presence of NiS₂, leading to an increase in cyclohexane derivative selectivity and deoxygenation degree. The authors claimed that an optimal Ni/(Ni + Mo) molar ratio of 0.3 was important to achieve the highest activity with 99.8 % deoxygenation degree [50]. In our study, this ratio, determined from XPS analysis, was about 0.33, which is in good agreement with the reported optimum.

In a recent study, Chowdari et al. [56] reported a total monomer yield of 45.7 wt% over 10 wt% bimetallic 20NiMoP/AC for Kraft lignin at 400 °C and 100 bar with no added solvents. These findings are in line with our results for Kraft lignin, with monomer yields in the range of 42.3–47.0 wt%. However, the aromatics were reported to be lower (8.7 wt%) for the 20NiMoP/AC catalyst in comparison to the unsupported NiMoS-SBA (18.3 wt%), whereas opposite levels in the yields of alkenolic phenolics resulted (25.0 wt% for 20NiMoP/AC and 16.1 wt% for NiMoS-SBA). A higher solid yield was obtained for our operating conditions, but notably at lower pressures of 50–80 bar. The adjustment of pressure, residence time (from 5 to 12 h) and catalyst loadings can likely further reduce the char formation and significantly increase lignin-oil and monomeric yields. Interestingly by increasing the catalyst loading from 5 % to 10 % (KES₅ to KES₁₀), the degree of deoxygenation is strongly increased from about 46.0 to 60.5 % and therefore resulted in an increment of aromatics from 7.3 to 18.3 wt% respectively for Kraft lignin oil. This was also evident by a reduction of the calculated oxygen content of the oils (Tables S2 and S3) and indicating that the unsupported catalyst exhibits better selectivity for deoxygenated products under nearly identical conditions.

In the case of hydrolysis lignin, the effect of catalyst loading (from 5 to 20 wt%) on lignin oil yields and composition was investigated at 400 °C using the same unsupported NiMoS-SBA catalyst. By increasing the catalyst loading from 5 to 10 wt%, the monomer yield was
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significantly enhanced from 46.6 to 64.3 wt% with a suppression of char to 8.3 wt% (HES8). While increasing the residence time (from 5 to 12 h), the monomer yield was further enhanced from 64.3 to 70.6 wt% with a suppression of char from 8.3 down to 3.9 wt% for HES8 and HES9 respectively. Upon increasing the catalyst loading to 20 wt%, the total monomer yield was still further increased to 76.0 wt%. The char formation was suppressed considerably at the highest catalyst loading from 8.3 to 4.6 wt% (HES10) due to the depolymerization reactions involving the bimetallic NiMoS-SBA catalyst. These results are also in agreement with data reported by Chowdari et al. [56], suggesting that the repolymerization reactions leading to char are likely thermal and not catalytic, while the depolymerization reactions are catalytic. However, Chowdari et al. found that higher temperature (>400 °C) leads to the formation of more char and less oil yield [56]. In our study, the main objective was to explore reaction conditions that are favorable using an unsupported NiMoS-SBA catalyst. The results obtained at 20 wt% loading of catalyst for hydrolysis lignin showed that over 87 wt% of lignin can be depolymerized, which consists of 39 wt% of aromatics/naphthalenes with the lowest alkylphenolic yield of 10.1 wt%.

Like a previously published work [59], TGA analysis was used to evaluate the volatility of lignin-oils resulting from biomass conversion. Comparison of the volatilities of Kraft (KES5) and hydrolysis (HES8) lignin-oils were performed with oils produced under the same operating conditions (400 °C, 80 bar, 5 h). Fig. 11 shows that a complete weight loss for both lignin-oils was observed when increasing the temperature to 500 °C under N2 flow. The hydrolysis lignin oil contains less thermally stable compounds, as indicated by its higher volatilization rate at 200 °C. In addition, it requires more energy (higher temperature) to completely volatilize the produced Kraft lignin-oil (>300 °C). This difference may be due to the influence of the origin of the lignins and their extraction processes. More importantly, both lignin-oils followed the TGA curve of diesel oil, particularly for hydrolysis lignin-oil [59]. This implies that the hydrolysis lignin-oil contains a higher share of low boiling point compounds than the Kraft lignin-oil.

3.2.5. Reaction mechanisms

Based on the above analysis and discussion, lignin hydroconversion to produce lignin-oils, gas and residual solids involves various reaction pathways depending on the lignin composition, and operating conditions. Numerous studies have proposed and summarized schemes for the conversion of Kraft lignin by depolymerization [56,60–63]. In contrast to Kraft lignin, limited studies have investigated reaction pathways of the depolymerization of enzymatic hydrolysis lignin. Chudakov et al. and Pikovskoi et al. [64,65] proposed a unique macrostructural composition of hydrolysis lignin consisting of about 7000 peaks of deprotonated molecules [M—H]−. The largest detected molecules were decamers with molecular weights up to 1600 Da, containing up to 10 aromatic units with an average molecular weight of 150 Da per structural unit [64,65]. Pikovskoi et al. also claimed that depolymerization of hydrolysis lignin released coniferous lignin corresponding to the abundant guaiacyl structural unit of about 196 Da. In addition to Chudakov and Pikovskoi’s suggestions, the hydrolysis lignin in this work showed the presence of cellulolic units by means of solid-state 13C NMR (Fig. 5), as depicted in Scheme 1.

According to the reported data in Table 5, Table 6 and Fig. 10 the non-catalytic experiments favored the formation of solid-char. We suggest that the highly reactive intermediates (oxygenated compounds) formed during the thermal decomposition of lignin results in condensation (Scheme 1A) and large char formation. Generally, the alkylation reactions predominantly have a significant role to restrain the condensation reaction by multiple substitutions of the abundantly formed positively charged species (e.g., R—O—Ar) with electron-rich active species (negatively charged Ar, Ar—O—Ar that jointly affect the electron distribution of both lignins [67,68]. Without the presence of catalyst (Scheme 1A), a negatively charged aromatic, ring rich in electrons, is mostly formed (Ar—O—Ar) and subjected to substitution of phenol-ether and/or alkylphenolic (Ar—O—OH and Ar—O—OH). In addition to the resonance effect, the inductive effect of the positively charged moieties (R—O—Ar) leads to higher electron densities, which are involved in lignin condensation by forming benzylic carbonations and thereby enhance char formation [67,68]. This suggestion is supported by the fact that the formed alcohols/ketones, olefins and CH4 were present in the lowest amounts and only account respectively for less than 0.2 and 0.3 wt% of products for both lignins during uncatalyzed reactions (KES8 and HES8).

In the presence of the unsupported NiMoS-SBA catalyst (Scheme 1B–E), the hydrotreatment of both lignins becomes relevant and contributes to heterogeneous catalyzed processes at higher temperatures. Due to the difference in structural and chemical composition of hydrolysis lignin, a higher yield of small ketone and aliphatic alcohols in hydrolysis lignin-oils (13.2 wt%) were obtained due to the depolymerization and ring opening of cellulose and furan units present in hydrolysis lignin, as was evident from the 13C NMR spectrum and GCxGC results (Fig. 5 and Fig. 10). According to Shuai and Saha [69] alcohols, ketones and aldehydes can block the electron-rich sites on the aromatic ring and the benzylic cation on the side chain, which would reduce the lignin condensation. The larger amount of alcohols and ketones formed in hydrolysis lignin (Fig. 9) could be one reason for the lower char amount and enhanced monomeric yields in the liquid phase (Scheme 1B). Huang et al. [68] examined lignin depolymerization in the presence of ethanol and suggested that the C-alkylation and O-alkylation reactions are important reactions for decreasing the condensation and thereby the char formation. We therefore suggest that during the depolymerization of hydrolysis lignin, higher stability of the aromatics (negatively charged moieties) via C- and O-alkylation reactions mainly come from cleaved and dehydration of the aliphatic OH and ketones. Additionally, these small ketones/alcohols derived from lignin can be hydrogenated to small alkenes via cracking dehydration (Scheme 1C).

The primary stable monomers obtained from lignin (Scheme 1D) may undergo secondary hydrogenation reactions of oxygenates to form more stable monomer products (Scheme 1E).

Generality across different mechanisms can be accepted considering the complexity of the types of lignin depolymerized and may play a role in the identification of effective catalysts. In this study, evidence suggests that a combination of mechanisms hinders the formation of oligomeric C=C linkages and thus blocks the re-condensation reactions. From our set of experiments and the literature [6,66–68], Scheme 2...
summarizes the most important aspects hindering the repolymerization over the unsupported NiMoS-SBA catalyst. We suggest that the condensation reaction rate was slowed down by blockage of the electron-rich sites (aromatic ring) via hydrogen spillover generated on Ni$_x$S$_y$, which prevented the formation of benzylic cations. Thereafter, the negatively charged aryl molecules either undergo hydrogenolysis interactions in series or in parallel reactions with the supplied hydrogen (H$^+$) and/or with alkylated species present in the lignin-oils. These
alkylated species are present in greater quantities from hydrolysis lignin (13.2 wt%) and thus serve as promoters for depolymerization compared to the lower quantities of alkylated species from Kraft lignin (6.8 wt%).

We also suggest that the stabilization of aromatic rings is enhanced by a combination of interunit C(aryl)—C(alkyl) linkages and the supplied hydrogen species as shown for hydrolysis lignin (Scheme 2B), whereas these factors are less dominant in the case of Kraft lignin (Scheme 2A). This accounts for the higher resulting monomeric yields and lower char formation from hydrolysis lignin compared to Kraft lignin. In this study, our hypothesis is built on the importance of the inductive effect that provides higher electron densities on methoxy groups (R—O—CH₃) due to the formation of interunit C(aryl)—C(alkyl) linkages, which create higher electron densities on the aromatic ring to further stabilize it and block the reactive benzylic positions. Based on literature, our proposal agrees with that of by Shuai et al. [6,69] that found that formaldehyde acted as a lignin stabilizer by blocking the reactive benzylic positions of intermediates [6]. Also in agreement with our results, Huang et al. [68] suggested that ethanol is a capping agent acting as a scavenger for formaldehyde formed by removal of methoxy groups from the lignin, that thereby suppresses repolymerization reactions involving formaldehyde [68].

To summarize, lignin valorization is more efficient with hydrolysis lignin compared to Kraft lignin, which could be seen by a significantly higher amount of monomer bio-oil produced and lower char formation. This is be explained by (i) differences in the structure of hydrolysis lignin, which facilitates thermal decomposition, (ii) less lignin per mass unit in hydrolysis lignin, due to the presence of cellulose (iii) less inorganic ash in the hydrolysis lignin which could negatively affect the catalytic reactions and (iv) suppressing the repolymerization reactions with components formed from the cellulose.

4. Conclusions

In this study, we have for the first time according to our knowledge compared the reductive catalytic lignin depolymerization using Kraft and hydrolysis lignin and we found large differences. We have synthesized a highly active unsupported NiMoS catalyst that was used in this work. The use of the unsupported NiMoS-SBA demonstrated a potentially promising approach to obtain bio-oils with a high proportion of aromatic and alkylphenolic compounds. The influence of the operating conditions (temperatures, pressure and time) with various catalyst loadings of 5–20 wt%, were evaluated in terms of product yields and composition.

Catalytic hydrotreatment experiments with hydrolysis lignin exhibited deeper deoxygenation performance in comparison to Kraft lignin. The increase in the reaction temperature, between 330 and 400 °C, dramatically enhanced the cleavage of C—O—C bonds, especially increasing alkylated phenolics from 7.0 to 20.1 wt% yield respectively. On the other hand, it was observed that as the pressure increased from 50 to 80 bar and residence time increased, the yields in oil and monomeric compounds also increased, and char formation could be suppressed to a certain extent. Interestingly, the monomers yield was the highest and the char was the lowest for hydrolysis lignin at comparable reaction conditions. In addition, the NMR and GCxGC analysis demonstrated that with an increase in catalyst loading, the phenolic OH groups were decreased in the product oil which resulted in an increment in the aromatics yield. Comparing the volatilities, lignin-oils from Kraft and hydrolysis lignin showed a complete volatilization which indicates a high content of low boiling compounds, particularly for hydrolysis lignin-oil.

The unsupported NiMoS catalyst displayed notable deoxygenation activity, with 87 wt% lignin-oil yield from hydrolysis lignin, with less than 5 wt% char yield. Remarkably the significant reduction of char from hydrolysis lignin compared to Kraft lignin led to an increase in water and lignin-oil yields, resulting in higher selectivity and yield of aromatics. These results highlighted the importance of the chemical stability and the nature of processed lignins that arise directly from the oligomer composition of the lignin, and their correlation between depolymerization yields and the ratio of C—O—C and C—C linkages in the lignins. From the experimental results, the higher monomeric yield from hydrolysis lignin can be explained by that the hydrolysis lignin more easily depolymerizes. Moreover, the hydrolysis lignin also contains less lignin (since it contains both lignin and cellulose) and less ash, which also are important reasons for the lower char production and higher bio-oil yield when using hydrolysis lignin. In addition, the molecular binding mechanism of hydrolysis lignin is a key to generate higher-value small molecules through depolymerization. Results suggested that the high electron densities of the formed small molecules from cellulose decomposition could interact with the aromatic ring and influence the reactivity of the benzylic carbocations formation. Apart
from effective hydrotreating cleavage, the catalyst demonstrates a good activity and stability over multiple regeneration cycles; however, long testing will be required in a pilot scale reactor to assess its total lifetime in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2022.139829.

References

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