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ARTICLE

Solvent Free Depolymerization of Kraft Lignin to Alkyl-phenolics using Supported NiMo and CoMo Catalysts

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The catalytic hydrotreatment of Kraft lignin using sulfided NiMo and CoMo catalysts on different acidic and basic supports (Al₂O₃, ZSM-5, activated carbon (AC) and MgO-La₂O₃) was studied in the absence of a solvent. Experiments were carried out in a batch set-up at a reaction temperature of 350 °C, 4 h and 100 bar initial H₂ pressure. The catalysts before and after reaction were characterized by X-ray diffraction, temperature programmed desorption of ammonia/CO₂, BET surface area and scanning electron microscopy. The liquid products were fractionated and analyzed extensively by different techniques such as GPC, GC-MS-FID, GC-TCD, FT-IR, ¹³C-NMR and elemental analyses. Two dimensional gas chromatography (GCxGC-FID) was applied to identify distinct groups of compounds (aromatics, alkylphenolics, alkanes) after reaction, and product quantification was performed based on this method. Catalyst activity is a function of the support and increased in the order Al₂O₃ < ZSM-5 < AC=MgO-La₂O₃. In addition, the support also largely influenced the extent of depolymerization and monomer yield. The highest lignin oil yields were obtained using the sulfided NiMo supported on activated carbon and MgO-La₂O₃. The highest total monomer yield 26.4 wt.% on lignin intake, which included 15.7 wt.% alkyl-phenolics was obtained using the sulfided NiMo/MgO-La₂O₃ catalyst.

Introduction

Lignin is the second most abundant natural biopolymer on the earth and accounts for about 15-30% of organic carbon within the biosphere.¹ It is an amorphous and complex three dimensional biopolymer with a recalcitrant structure, composed of p-coumaryl, coniferyl, and sinapyl alcohol subunits, which are cross linked *via* aromatic ether as well as various C-C linkages. Therefore the development of methodologies that enable the controlled depolymerization of this challenging structure to defined aromatic monomers, which would serve as interesting building blocks for the sustainable production of bio-based chemicals, is of primary importance.

Kraft lignin is an interesting lignin source for valorization to bio-based chemicals. The production of Kraft lignin in the form of black liquor exceeds 40-50 million tons per year, which is currently only used for combustion in recovery boilers to supply the majority of the energy requirement for the pulp and paper industries.^{2,3} Several approaches have been reported for the valorization of lignin. These include enzymatic methods,^{4,5} thermal treatment in the absence of air (pyrolysis),^{6,7} base catalysed depolymerizations⁸⁻¹¹ and various chemo-catalytic methods like catalytic hydrotreatment in which lignin is reacted with gaseous hydrogen or a hydrogen donor

solvent.^{2,12-14} Oxidative approaches are also known and have also recently been established.^{15,16}

Reductive depolymerization, followed by hydrodeoxygenation of the obtained fragments to low molecular weight products like phenolics and aromatics has emerged as an attractive strategy.^{17,18} During such a catalytic hydrotreatment, a number of reactions may occur, such as hydrocracking leading to depolymerization and hydrodeoxygenation (HDO) to give product mixtures that contain a markedly reduced oxygen content.¹⁹ A bifunctional catalyst suitable to catalyse both these steps is advantageous to achieve high yields of aromatic products.

Usually, catalytic hydrotreatment reactions, either with molecular hydrogen or a hydrogen donor are carried out in a solvent. From a techno-economic perspective, large-scale processes without extensive solvent recovery are advantageous and the development of methods that will in the future enable such processes is highly desired. In addition, solvents are not always inert under hydrotreatment conditions, and may be (partly) incorporated into the products. In this case, the presence of a solvent complicates product work-up and mass balance closures. For instance, it is known that ethanol may react with the depolymerized products leading to substituted aromatics and alkylphenolics, hence resulting in a decrease of product selectivity and impaired mass balances. Solvent free conditions, which mitigate these drawbacks, have been recently introduced and continue showing promise.²⁰⁻²² Thus the development of highly efficient catalysts and understanding structure-activity relationships in the depolymerization of lignin under solvent-free conditions is an important challenge.

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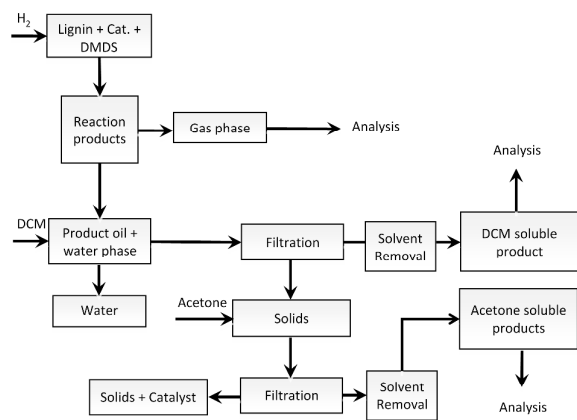


Fig. 1 Hydrotreating of Kraft lignin and reaction workup procedure.

Recently, Meier *et al.* performed the catalytic hydroxypropylation of various lignins including Kraft lignin using NiMo supported on aluminosilica catalysts under solvent free conditions.²⁰ The obtained oil yield was 61.6 wt.% and 1.3 wt.% char was formed. The monomeric yield obtained in the case of organocell lignin was 21.8%. Oasmaa *et al.* reported the catalytic hydrotreatment of different technical lignins under solvent free conditions. The oil yields varied in the range of 49–71 wt.% depending on the lignin feedstock.²¹ The highest oil yield was obtained for organosolv lignin using a NiMo on aluminosilica and Cr₂O₃ catalysts in a 1:1 ratio. The amounts of low molecular weight compounds in the oil were between 14–38 wt.% of the initial lignin. In our previous study, catalytic hydrotreatment of pyrolytic lignins from forestry residue and Alcell lignin in the absence of an external solvent was investigated using Ru/C catalyst. The best results were obtained with forestry residue pyrolytic lignin with > 75 wt.% product oil yield containing 20.5 wt.% of alkyl phenolics and 14.1 wt.% of aromatics.²²

Conventional sulfided Ni/Mo or Co/Mo supported catalysts are known for their excellent HDO activity.^{23,24} Sulfidation of these oxide catalysts generates active sites (sulfur vacant sites) on the edge of the catalysts that act as efficient catalysts for HDO reactions.^{25–27} The experiments of Meier *et al.* already established that higher product yields are obtained when using Kraft lignin instead of organocell lignin (sulfur free), due to sulfidation of the NiMo catalyst, which is known to be more active than its oxidized form.²⁰ This catalyst behaviour is ideal because the sulphur content (2–3%) of Kraft lignin is detrimental for common noble metal hydrotreatment catalyst, which are known to be deactivated by the relatively large S content of Kraft lignin.^{28,29}

The present work focuses on hydrotreating of Kraft lignin under solvent free conditions to produce aromatic monomers with particular attention to phenolics. Various NiMo and CoMo catalysts on different acidic and basic supports (Al₂O₃, ZSM-5 zeolite, AC, MgO-La₂O₃) were prepared and the acidity and basicity of the respective catalysts was evaluated. All catalysts were sulfided by an *in-situ* method and tested for the reductive depolymerization of Kraft lignin under solvent free conditions. A suitable fractionation procedure was developed for the treatment of the product mixtures and isolation of the monomeric fraction which was subsequently analysed. The composition of the monomeric product fraction was identified by GC-MS-FID. The formed distinct groups of compounds were in addition analysed by GCxGC and this method also served for quantification of monomer yields based on internal standards. Various spectroscopic methods (¹³C-NMR, FT-IR) and elemental analysis were also used for qualitative analysis of the starting lignin as well as product mixtures. In addition, GPC was

used to confirm lignin depolymerization and the synthesised catalysts were characterized by various techniques.

2 Experimental

2.1 Materials

All the chemicals were of analytical grade and used without further purification. Commercial activated carbon (AC) was purchased from Merck, Germany. Ammonium ZSM-5 (Si/Al ratio of 50:1 and 425 m²/g surface area) was provided by Alfa-Aesar, commercial NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts were purchased from Eurecat, Ni(NO₃)₂·6H₂O (99%), Co(NO₃)₂·6H₂O (>99%), KOH (85%) were purchased from ACROS Organics. Mg(NO₃)₂·6H₂O (98%), La(NO₃)₃·6H₂O (>99%), (NH₄)₆Mo₇O₂₄·4H₂O (>99%), dimethyldisulfide (DMDS), K₂CO₃ (>99%) etc. were purchased from Sigma-Aldrich. Hydrogen (>99.99%) and nitrogen gases (>99.8%) were obtained from Hoekloos. Indulin-AT (Kraft lignin) was from MWV specialty chemicals and was kindly provided by Dr. R. Gosselink from the Wageningen University and Research Center, The Netherlands. Indulin-AT is a purified form of Kraft pine lignin, which is free of hemicellulosic material. The lignin content is 97 wt.% on dry basis.

2.2 Synthesis of the MgO-La₂O₃ support

The MgO-La₂O₃ support was prepared by a co-precipitation method according to a literature procedure.³⁰ The metal precursors (magnesium nitrate and lanthanum nitrate) were dissolved in deionized water (3:1 molar ratio of Mg/La) and these solutions were mixed. The resulting aqueous metal precursor solution was precipitated by the drop wise addition of an aqueous 0.026 M K₂CO₃ solution. During this procedure, the p^H was maintained at about 10 by the addition of an aqueous KOH solution (1 M). The resulting precipitate was filtered and thoroughly washed several times with deionized water. The solid product was dried at 120 °C overnight. Finally, the hydrous MgO-La₂O₃ support was calcined at 650 °C for 6 h.

2.3 Synthesis of the supported NiMo and CoMo catalysts

The NiMo and CoMo supported on AC, MgO-La₂O₃ and ZSM-5 zeolite were prepared by a wet impregnation method. The pre-determined amount of Ni/Co and Mo precursors were dissolved in deionized water. The aqueous precursor solutions were mixed, added drop wise to the support and stirred for 2 h and subsequently the excess of water was removed by evaporation. The resulting solid was dried in an oven overnight and calcined at 450 °C for 2 h. The Ni/Co and Mo contents were kept constant in all the supported catalysts (NiO/Co₂O₃ 5 wt.% and MoO₃ 15 wt.%). In the case of activated carbon support, the catalyst was calcined under an nitrogen flow whereas all other supported catalysts were calcined in air.

Sulfided catalysts were generated *in-situ* by the addition of dimethyldisulphide (DMDS) to the reaction mixture at the start of the reaction.³¹ The sulfided NiMo supported on Al₂O₃, AC, MgO-La₂O₃, ZSM-5 catalysts are designated as S-NiMo/Al₂O₃, S-NiMo/AC, S-NiMo/MgO-La₂O₃, S-NiMo/ZSM-5, respectively. Similarly, sulfided CoMo supported catalysts are abbreviated as S-CoMo/Al₂O₃, S-CoMo/AC, S-CoMo/MgO-La₂O₃, S-CoMo/ZSM-5.

For detailed description of catalyst characterization techniques,

Table 1 Acidity/basicity of the supported NiMo and CoMo catalysts.

Catalyst	NH ₃ uptake (μmol/g)	CO ₂ uptake (μmol/g)
NiMo/Al ₂ O ₃	280.4	-
CoMo/Al ₂ O ₃	339.2	-
NiMo/AC	44.5	0.6
CoMo/AC	77.0	0.7
NiMo/ZSM-5	309.6	-
CoMo/ZSM-5	362.0	-
NiMo/MgO-La ₂ O ₃	-	391.1
CoMo/MgO-La ₂ O ₃	-	337.4

Table 2 Lignin conversion, product yields and mass balances over supported sulfided NiMo and CoMo catalysts.^a

Catalyst	Lignin conv. (%)	DSPs (%)	ASPs (%)	GPs (%)	Water (%)	Residue (%)	Mass balance closure (%)
S-NiMo/Al ₂ O ₃	79	39.7	1.1	6.5	16.8	20.5	89
S-CoMo/Al ₂ O ₃	65	27.5	2.3	6.5	17.9	35.4	90
S-NiMo/AC	91	54.9	2.9	5.7	19.3	9.0	96
S-CoMo/AC	84	46.8	2.7	5.3	19.4	15.9	93
S-NiMo/MgO-La ₂ O ₃	87	48.2	1.8	6.3	12.6	12.7	84
S-CoMo/MgO-La ₂ O ₃	89	48.4	4.2	5.7	12.5	10.7	82
S-NiMo/ZSM-5	81	39.0	4.2	6.3	9.3	19.2	78
S-CoMo/ZSM-5	87	44.5	3.5	6.7	12.7	13.4	83

^a Reaction conditions: lignin, 15 g; catalyst, 0.75 g (5 wt.% on lignin); 350 °C; hydrogen pressure of 100 bar at RT; 4 h; 1200 rpm.

please see Supporting information, Section 1 (Catalyst characterization techniques).

2.4 Catalytic depolymerization of Kraft lignin

The catalytic hydrotreatment reactions were performed in a 100 ml batch autoclave (Parr Instruments Co., stainless steel type 316). The reactor was surrounded by a metal block containing electrical heating elements and channels allowing the flow of cooling water. The reactor content was stirred mechanically using a Rushton type turbine with a gas induced impeller. Temperature and pressure were monitored online and logged on a PC.

The hydrotreatment reaction and workup procedure is shown in Fig. 1. Initially the reactor was loaded with Kraft lignin (15 g), catalyst (0.75 g, 5 wt.% on lignin) and dimethyldisulfide (0.15 g). Subsequently, the reactor was flushed with hydrogen to expel air and pressurized to 120 bar at room temperature for leak testing. After the leak test, the pressure was reduced to 100 bar. Stirring was started (1200 rpm) and the reactor content was heated to 350 °C with a heating rate of about 10 °C min⁻¹. The reaction time was set to zero when the desired temperature was reached. After completion of the reaction, the reactor was cooled to room temperature with a rate of about 40 °C min⁻¹. The pressure at room temperature was recorded to determine the amount of gas phase components produced during the reaction. The produced gas was collected in a 3 L Tedlar gas bag to determine the composition. The reactor consists of products (water and solid organic phase). A solvent based product separation procedure was done with dichloromethane (DCM) and acetone (see Fig. 1). After addition of DCM to both solid and liquid products, the aqueous phase was separated. Extraction of the products was done in two steps: first using DCM followed by acetone as shown in Fig. 1.

The residual solid after the extraction with acetone consists of the catalyst, unconverted/repolymerized lignin and the char (solid residue). Product amounts (wt.%) were calculated on the basis of the solid recovered after evaporation of the solvent. The products after evaporation of DCM and acetone solvents are abbreviated as

DSPs and ASPs, respectively. The conversion of lignin, product yield, residue and mass balances were calculated based on initial lignin intake using the equations (1)–(4).

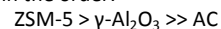
The product monomer mixture was analyzed by GC-MS-FID as well as GCxGC techniques. For a more description see Supporting information, Section 2 (Analytical techniques).

3 Results and discussion

3.1 Catalyst characterization

A series of Ni/Mo and Co/Mo catalysts on a variety of supports were synthesised in order to gain insight into the role of the catalyst composition in the lignin depolymerization process and determine how the composition of the support influences the yields of desired aromatic monomers. The catalysts were characterized in terms of XRD, BET surface area, and SEM analyses (see Supporting information Fig. S1-S3 and Table S1).

The acidity/basicity of the catalysts were measured by temperature programmed desorption experiments using either ammonia or carbon dioxide. The TPD of ammonia profiles are shown in Supplementary information (Fig. S4). The acidity of catalysts was determined from the peak area of the desorbed ammonia and the results are summarized in Table 1. NiMo and CoMo supported on Al₂O₃ catalysts exhibited a high ammonia adsorption capacity (280.4–339.2 μmol_{NH₃}/g_{cat}), with a broad band at low temperatures (120–380 °C, weak/moderate acidic sites) and a low intense desorption peaks at a higher temperature (380–550 °C, strong acidic sites). In the case of NiMo and CoMo supported on ZSM-5 a larger ammonia desorption peak appeared in the temperature range of 100–550 °C, accounting for a total acidity of 309.6 and 362.0 μmol_{NH₃}/g_{cat}, respectively. Instead, with a quite low NH₃ uptake (44.5–77.0 μmol_{NH₃}/g_{cat}), both NiMo as well as CoMo supported on activated carbon showed a low acidity. Based on these results, the supports cover a wide range of total acidity and the acidity decreases in the order:



Moreover, independently of the support, the CoMo-based catalysts display a higher acidity than the corresponding NiMo catalysts.

$$\text{Conversion (\%)} = \frac{\text{Initial lignin wt.} - \text{Residue wt.}}{\text{Initial lignin wt.}} \times 100 \quad \text{--- (1)}$$

$$\text{Product yield (\%)} = \frac{\text{Product wt.}}{\text{Initial lignin wt.}} \times 100 \quad \text{--- (2)}$$

$$\text{Residue (\%)} = \frac{\text{Residue wt.}}{\text{Initial lignin wt.}} \times 100 \quad \text{--- (3)}$$

$$\text{Mass balance (\%)} = \frac{\text{Sum of the wt. of all products}}{\text{Initial lignin wt.}} \times 100 \quad \text{--- (4)}$$

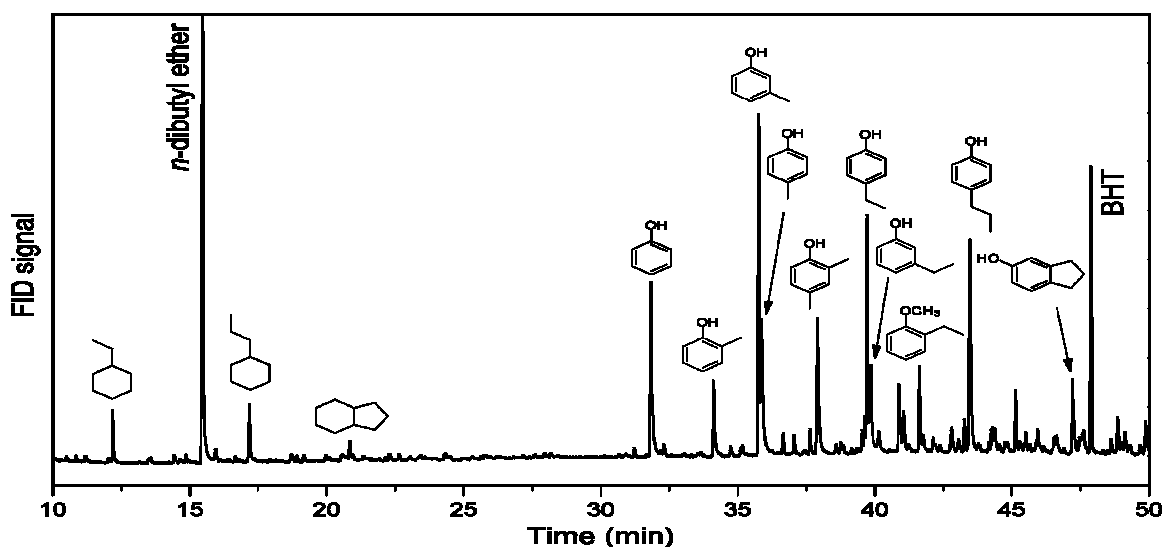


Fig. 3 GC-MS-FID chromatogram of lignin oil obtained for S-NiMo/MgO-La₂O₃ catalyst.

The CO₂ TPD profiles for NiMo and CoMo supported on MgO-La₂O₃ and AC are shown in Fig. S5. No evident desorption peaks were observed for the carbon supported catalysts (NiMo/AC and CoMo/AC) in the investigated temperature range, as is evident from a negligible CO₂ uptake (0.6–0.7 μmol_{CO₂}/g_{cat}). In contrast, NiMo and CoMo supported on MgO-La₂O₃ exhibited a larger desorption band, spanned in the temperature region 250–550 °C, related to CO₂ desorbed from moderate and strong basic sites. The data suggest that the NiMo/MgO-La₂O₃ contains more basic sites (391.1 μmol_{CO₂}/g_{cat}) than the CoMo counterpart.

3.2 Catalytic hydrotreatment experiments using Kraft lignin

Catalytic hydrotreatment reactions were carried out using the supported and sulfided NiMo and CoMo catalysts and the results are presented in Table 2. The conversion of the lignin was in the range of 65–91 % and up to 96% mass balance closure was obtained. Water and gaseous (GPs) products were in the ranges of 9–19 wt.% and 5–7 wt.%, respectively. The catalyst activity, expressed as lignin conversion after 4 h, was clearly influenced by the nature of the support. Acidic supports such as Al₂O₃ and ZSM-5 exhibited lower conversions of lignin compared to neutral (AC) or basic supports (MgO-La₂O₃). The lignin conversion was the lowest (65 %) in the case of S-CoMo/Al₂O₃ catalyst with only 27.5 wt.% of dichloromethane soluble products (DSPs) yield. In the case of S-NiMo/AC, lignin conversion was 91% and the yield of DSPs is about 55 wt.%. Formation of solid residues was more pronounced in the case of acidic supports and found to be highest (35.4 wt.%) in the case of S-CoMo/Al₂O₃ catalyst. This is likely due to re-condensation reactions of reactive intermediates being predominant on acidic supports (see Table 1 and 2). The extent of re-condensation of the lignin depolymerized product can be correlated with the acidity of the support (see Fig. S4). For all catalysts, the acetone soluble product yield, which is the acetone soluble product deposited on the catalyst during reaction, was very low and in the range of 1.1–4.2 wt.%. It can be concluded, that AC and MgO-La₂O₃ are the most suitable supports for the catalytic hydrotreatment of the Kraft lignin based on lignin conversion and dichloromethane soluble products (DSPs) yield.

Fig. 2 shows the GPC chromatograms of the DSPs and ASPs after reaction. The average molecular weight values are presented in the Supporting information (Table S2). GPC chromatograms of the DCM soluble products exhibited sharp peaks in the M_w range of 80–300

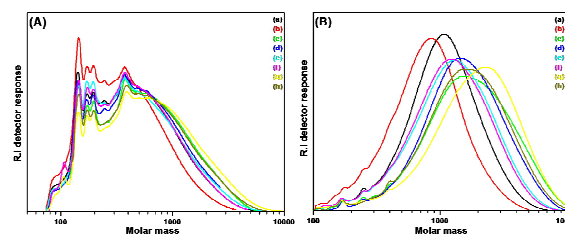


Fig. 2 Gel permeation chromatograms of lignin products (A) DSPs, (B) ASPs, obtained for the various catalysts: (a) S-NiMo/Al₂O₃, (b) S-CoMo/Al₂O₃, (c) S-NiMo/AC, (d) S-CoMo/AC, (e) S-NiMo/MgO-La₂O₃, (f) S-CoMo/MgO-La₂O₃, (g) S-NiMo/ZSM-5, and (h) S-CoMo/ZSM-5.

and a broad peak which is extended to higher M_w values. This is an indication that depolymerization of Kraft lignin to a mixture of monomeric compounds occurred to a significant extent though not quantitative, as is evident from the presence of higher molecular weight compounds. The average molecular weights of lignin oils (DSPs) was in the range of 480–890 g/mol. On the other hand, the acetone soluble products showed a broad, bell shaped peak with M_w values in the range of 950–2380. Thus, the acetone soluble products deposited on the catalyst after reaction are lignin oligomers soluble in acetone. A comparison of the oil yields for S-NiMo on the MgO-La₂O₃ and AC supports reveals a higher DSPs yield for the AC support. However, the average molecular weight of the DSP/ASPs is higher for the AC support. This indicates a more efficient depolymerization of lignin with the more basic MgO-La₂O₃ support than for the AC support.

The Monomeric products present in the dichloromethane fraction were identified by GC-MS-FID analysis and a representative chromatogram is shown in Fig. 3. All major products were identified, and among these alkyl phenolics are the most dominant. Interestingly, the chromatograms of the various products are remarkably similar, the only difference being the intensity of various peaks. A comparison of the GC-MS traces for the various catalysts is provided in the Supporting information (Fig. S7).

Further attention was devoted to the quantification of the products in the dichloromethane soluble fraction. This was carried out by GCxGC-FID analysis using n-dibutylether as the internal

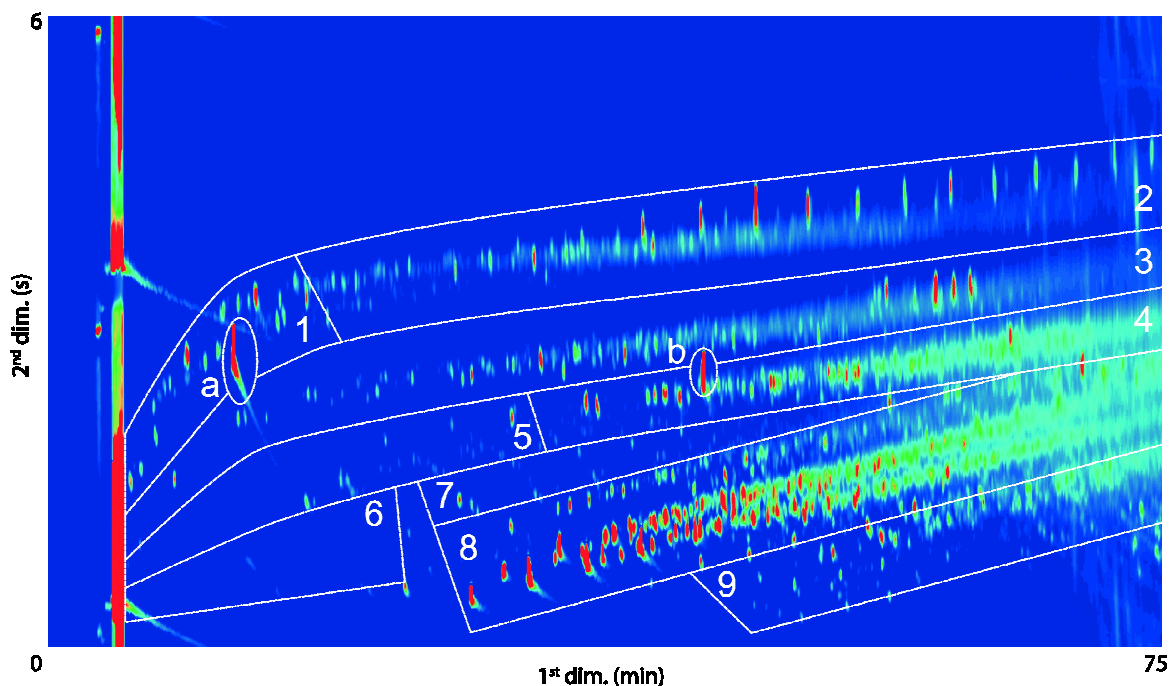


Fig. 4 GCxGC-FID chromatogram of the lignin oil (DSPs) obtained for S-NiMo/MgO-La₂O₃. 1) cyclic alkanes, 2) linear/branched alkanes, 3) aromatics, 4) polycyclic aromatics, 5) ketones/alcohols, 6) acids, 7) guaiacols, 8) alkyl phenolics, 9) catechols, a) internal standard (di-n-butylether), and b) 2,5-di-t-butylhydroxytoluene (stabilizer in THF).

standard and extensive calibration curves (see Supplementary information). The advantage of this analysis method is that it allows for improved separation of main product component classes (like aromatics, alkylphenolics), as they are clustered in specific regions based on chemical similarity. Fig. 4 show a typical GCxGC chromatogram of the DSPs obtained using S-NiMo/MgO-La₂O₃ as the catalyst. This chromatogram clearly shows the different monomeric product regions with good separation. From the GCxGC chromatogram it is also clear that the amount and intensity of the peaks in the alkyl phenolics region is most dominant. Quantification of the product yields for all catalysts is presented in Table 3. Clearly, the main GCxGC detectable products in the DSPs obtained from various catalysts are alkyl phenolics and aromatics. The highest amount of monomeric products was found in the case of S-NiMo/MgO-La₂O₃ catalyst (26.4 wt.%), with 15.7 wt.% of phenolics and 5.9 wt.% of aromatics on lignin intake. In contrast, the total monomer yield was considerably lower (10.8 wt.%) for S-CoMo/Al₂O₃.

Fig. 5 shows the lignin conversion and monomer yields (alkyl phenolics and other aromatics) for the various supported catalysts. The lignin conversions and monomer yields were low in the case of NiMo, CoMo supported on acidic supports (Al₂O₃ and ZSM-5) and were best for AC and MgO-La₂O₃ supports. Lignin conversion increases in the order Al₂O₃ < ZSM-5 < AC = MgO-La₂O₃. Although, AC and MgO-La₂O₃ showed almost similar lignin conversion, the highest monomer yield was obtained in the case of S-NiMo/MgO-La₂O₃ catalyst.

The most active catalyst (NiMo/MgO-La₂O₃ fresh and used) was subjected to BET, SEM, and XRD analysis. Relevant textural properties are given in Table S1 (Supplementary information) and reveal that the surface area of the fresh and used catalysts are 29.5 and 23.1 m²/g, respectively. The reduction in surface area after reaction is ascribed to limited agglomeration and/or some coke deposition, without a significant modification in terms of porosity (from 0.16 to 0.14 cm³g⁻¹).

Table 3 Monomeric product yield (%) distribution for the various supported sulfided NiMo and CoMo catalysts.

Compound	S-NiMo/ Al ₂ O ₃	S-CoMo/ Al ₂ O ₃	S-NiMo/ AC	S-CoMo/ AC	S-NiMo/ MgO-La ₂ O ₃	S-CoMo/ MgO-La ₂ O ₃	S-NiMo/ ZSM-5	S-CoMo/ ZSM-5
Alkyl phenolics	10.5	7.1	13.3	12.6	15.7	12.5	10.5	12.3
Aromatics/Naphthalenes	3.0	3.0	4.3	5.3	5.9	3.1	3.2	3.6
Catecholics	-	-	-	-	0.2	0.1	-	0.1
Guaiacolics	0.1	0.1	0.2	0.2	0.1	0.3	0.1	0.2
Linear /Branched alkanes	0.6	0.2	1.3	2.2	2.9	0.8	0.6	0.8
Ketones/alcohols	-	0.1	0.1	0.1	0.5	0.3	0.1	0.1
Cyclic ring alkanes	0.6	0.3	1.2	1.1	1.1	0.9	1.0	1.1
Total yield* (%)	14.8	10.8	20.4	21.5	26.4	18.1	15.5	18.2

* Yields are quantified from GCxGC analysis and based on lignin intake (wt.%).

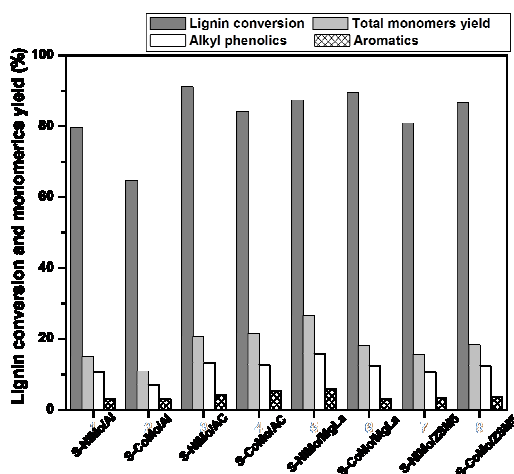


Fig. 5 Comparison of lignin conversion and monomeric product distribution for the various catalysts.

XRD patterns of the NiMo/MgO-La₂O₃ (fresh) and S-NiMo/MgO-La₂O₃ (used) are shown in Supplementary information (Fig. S2). XRD patterns of the fresh NiMo/MgO-La₂O₃ catalyst showed only diffraction lines related to lanthanum and magnesium oxides.^{32,33} Characteristic peaks related to NiMoO₄ were not observed in the sample due to overlap with the support. In the case of the used catalyst, crystalline phases corresponding to NiS, Ni₃S₄ and MoS clusters are clearly visible,^{34,35} an indication for the formation of a sulfided NiMo/MgO-La₂O₃ catalyst during reaction. The metal cluster size of the fresh and used catalysts was calculated using the Scherrer equation (Table S1). The cluster size of the fresh catalysts was about 4.3 nm, whereas it is higher for the used catalyst (15.7 nm). This increase in particle size during reaction suggest the occurrence of agglomeration of the active metal clusters during reaction.

The morphology of the NiMo/MgO-La₂O₃ (fresh) and S-NiMo/MgO-La₂O₃ (used) catalysts were studied by scanning electron microscopy and the SEM images are shown in the Supplementary information (Fig. S3). The SEM images showed that the fresh sample consists of small particles with a uniform distribution. For the used catalyst, larger non-uniformly distributed particles were observed. This might be due to agglomeration of the particles in the used catalyst, as previous deduced from BET measurements.

Table S3 shows the elemental analysis results of the DSPs and the ASPs products. The Kraft lignin feed contains 30.6 % of oxygen,

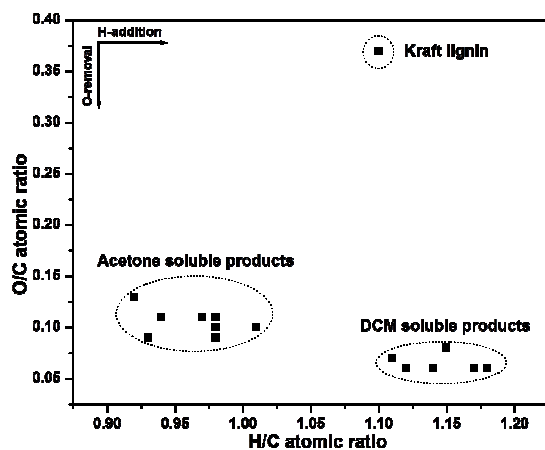


Fig. 6 van Krevelen plot for Kraft lignin, DSPs, and ASPs.

61.1 % of carbon, 5.6 % hydrogen and 1.6 % sulfur. The oxygen level for the DSPs and ASPs is in the range of 6.4-8.9 and 9.8-13.2%, respectively, which is considerably lower than the Kraft lignin feed. Further information from these elemental composition data is obtained by a van Krevelen diagram, which shows the atomic O/C ratio as a function of the H/C atomic ratio (Fig. 6). The O/C ratio of Kraft lignin is about 0.37, which is decreased to 0.07-0.08 for the DSPs and 0.09-0.13 for ASPs. These results indicate the occurrence of hydrodeoxygenation reactions. The H/C ratio of the Kraft lignin is 1.1, for the DSPs, H/C ratios are in the range of 1.11-1.18. As such, the H/C ratio for the all DSPs is comparable to the parent lignin. The population and intensity of the peaks in the cyclic alkanes region (Fig. 4, box 1) is low which is also in agreement with the observed lower H/C ratios for DSPs. This finding suggests that hydrogenation of aromatic rings to the saturated analogs does not occur to a significant extent, as this would lead to higher H/C ratio's for the products.

To gain insights in the molecular transformations, FT-IR analysis was performed for both the lignin feed and a representative example of a DCM soluble product oil (Fig. 7). An extended comparison for all product oils is shown in the Supplementary information (Fig. S8). Kraft lignin shows a broad hydroxyl signal in the range of 3100-3500 cm⁻¹. The peaks at 2940 and 2840 cm⁻¹ are due to symmetric and asymmetric stretching of the C-H bonds. The C-H deformation vibrations are observed at 1454 cm⁻¹ (-CH₂-) and 1367 cm⁻¹ (-CH₃). The peak at 1740 cm⁻¹ attributed to the unconjugated carbonyl group.^{36,37} Peaks at 1593, 1514, and 1420 cm⁻¹ are corresponding to C-H stretching vibrations in aromatic rings. Peaks in the range of 1100-1350 cm⁻¹ are stretching vibration of C-O and C-O-C bonds, indicating the presence of -OCH₃ and C-O-C bonds.³⁶

In the case of DSPs, the intensity of the peak related to the -OH group (3365 cm⁻¹) increased, indicative for the presence of phenolics in the products. The stretching frequency (2927, 2854 cm⁻¹) and bending mode (700-850 cm⁻¹) of the C-H bonds in the products are similar to that of the feed. However, the intensity of these peaks is higher than for the lignin feed, this might be due to depolymerization of lignin. Peaks in the range of 1030-1120 cm⁻¹ are absent in all products and imply cleavage of methoxy (C-O) and ether (C-O-C) bonds during reaction. From these results (increase in the signal intensities of -OH, C-H bonds and absence of the peak related to ether and alkoxy group), it can be concluded that lignin depolymerization occurs to a significant extent, which is in agreement with the product portfolio identified by GC-MS, GCxGC measurements (Fig. 3 and Table 3) and the GPC data.

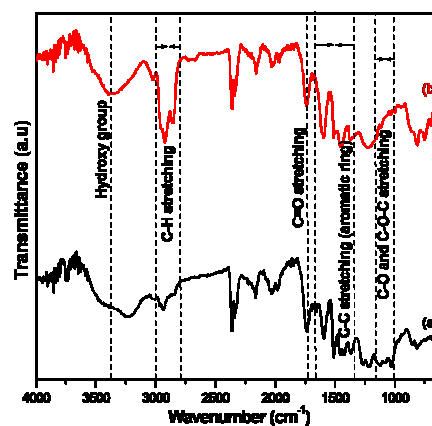


Fig. 7 FT-IR spectra of Kraft lignin and lignin oil (DSPs) obtained over the S-NiMo/MgO-La₂O₃ catalyst.

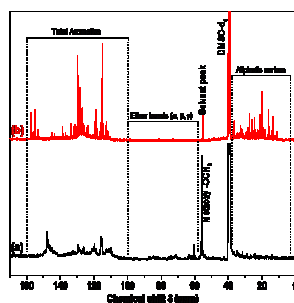


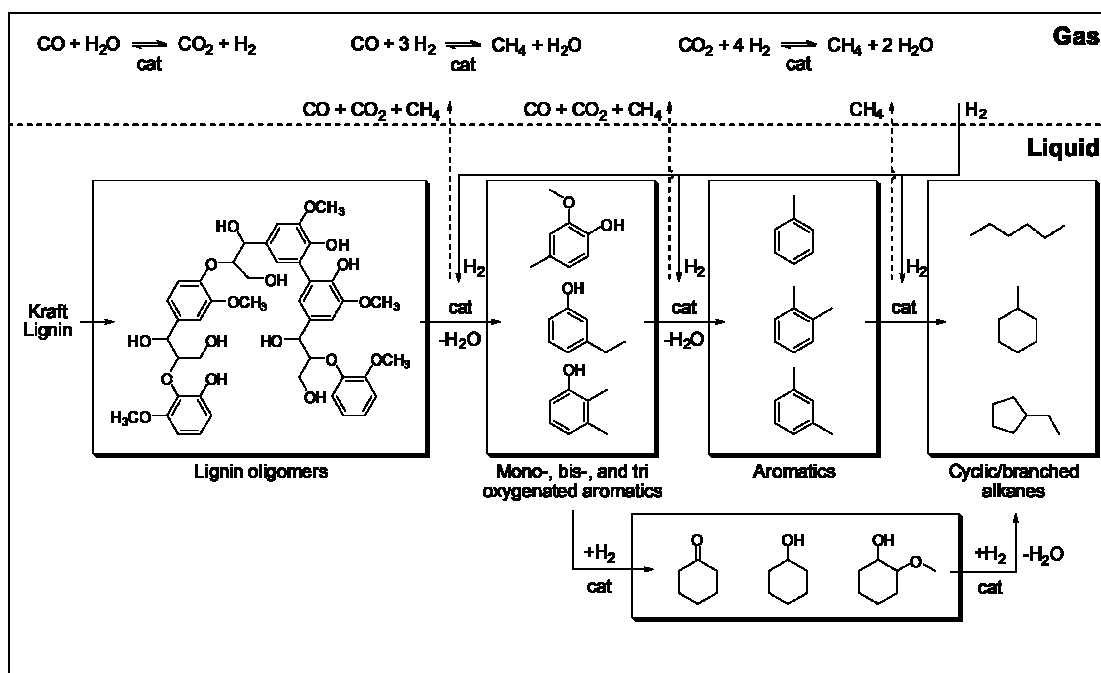
Fig. 8 ^{13}C -NMR spectra of (a) Kraft lignin and (b) lignin oil (DSPs) obtained over the S-NiMo/MgO-La₂O₃ catalyst.

A ^{13}C -NMR spectrum of Kraft lignin along with a representative example of a DCM soluble product are shown in Fig. 8. ^{13}C -NMR spectra for all lignin oils are given in the supplementary data (Fig. S9). The peak at δ 55.3 ppm in all DSPs is due to presence of minor amount of solvent (DCM). The peaks appearing at δ 56.1 ppm and δ 60.4 ppm in the lignin sample, corresponding to -OCH₃ and C-O-C (ether) bonds, respectively are absent in all DSPs, indicating that the O-C ether bonds are largely cleaved during the catalytic hydrotreatment reaction. This finding is supported by the FT-IR spectra of the DSPs, which also did not reveal any peaks related to methoxy or ether bonds (Fig. 7 and Fig. S8). Elemental analysis of DSPs are also in agreement with these results, as the DSPs contain only 6.5-8.9% of oxygen which is low compared to Kraft lignin (30.6%). The intensities of the peaks in the aliphatic region (δ 0-36

ppm) for all DSPs is higher than for the Kraft lignin feed, also implying that depolymerization of lignin and/or minor hydrogenation of some of the depolymerized products occurs. The peaks in the aliphatic region are from alkyl substituents (-CH₃, -C₂H₅ etc.) on the phenolics and of the over hydrogenated products such as ethyl and propyl cyclohexane (GCxGC analysis). The lack of signal corresponding to methoxy carbon (-OCH₃) in ^{13}C NMR for DSPs is in consistent with GC-MS-FID analysis results, the majority of the products are alkyl phenolics only (Figure 3). Intensities of the peaks in the aromatic region (δ 100-160 ppm) are higher in all DSPs samples in comparison to the parent lignin implying that the aromatic structure in the depolymerized products (DSPs) is retained. These results are in agreement with the monomeric product yields as obtained from GCxGC analysis.

3.3 Reaction network

On the basis of the results discussed in the previous sections (GC-MS, ^{13}C -NMR, FT-IR, GPC and GCxGC) and available literature data, a reaction network is proposed for the catalytic hydrotreatment of Kraft lignin with NiMo and CoMo supported on acidic and basic supports (Scheme 1). Within the experimental conditions (high H₂ pressures of 100 bar, 350 °C, reaction time up to 4 h) lignin is converted by a number of parallel and consecutive reaction pathways. During the hydrotreatment reaction, the Kraft lignin melts and starts to depolymerize thermally and/or catalytically by cleavage of the C-O-C and C-C bonds between the aromatic nuclei to lower weight lignin oligomers. It is expected that the catalyst also plays a role and for instance is active for the cleavage of ether bonds, as is evident from model component studies with supported NiMo and CoMo catalysts. Depolymerization is a relatively slow process and after 4 h reaction time, GPC data indicate that oligomers are still present (likely linked by C-C linkages, which are more difficult to cleave) and the maximum monomeric products yield is far from quantitative (GCxGC data, e.g. 26.4 wt.% for NiMo and CoMo supported catalysts). The support plays a major role in lignin depolymerization. For acidic supports, the amount of solids after



Scheme 1 Proposed reaction network for the catalytic hydrotreatment of Kraft lignin.

reaction is by far higher than for the neutral and basic supports (Table 2). However, the average molecular weight of DSPs is lower than for the neutral and basic supports (Table S2). These findings suggest that the acid supports result in higher depolymerization rates (lower M_w), though that the rate of undesirable re-polymerization (leading to solid residues) is also much higher,^{10,38} overall leading to a lower performance (lower DSPs and monomeric yields). Similar observations were made for the NiMo and CoMo catalysts supported on acidic and basic supports.

The lignin oligomers react further to lower molecular weight oxygenated aromatics (mainly alkylphenolics) with the concomitant formation of water and methane. The alkylphenolics may react in two parallel pathways to alkanes, viz. i) hydrogenation of the aromatic C-C double bonds to form saturated cyclic ketones and alcohols followed by subsequent hydrogenations and ii) the hydrodeoxygenation of the oxygenated aromatics to aromatics, followed by over hydrogenation to alkanes. To achieve high yields of alkylphenolics and aromatics, the hydrogenation of the aromatic rings should be avoided. From the data in Table 3, it is clear that the yields of over hydrogenation products like aliphatic alkanes and cyclic ring alkanes are low. This is also consistent with the van Krevelen plot, which shows a limited increase in H/C ratio during the catalytic hydrotreatment reaction.

4 Conclusions

A highly efficient, solvent free approach was developed for the depolymerization of Kraft lignin to aromatic monomers using a series of bimetallic sulfided NiMo and CoMo catalysts on various supports. Sulfided NiMo and CoMo catalysts were generated by an in-situ method and sulfidation was confirmed by XRD analysis of the catalysts after reaction. It was shown, that the nature of the support plays a major role and has a profound effect on both the product yield and composition. Catalysts on the basic MgO-La₂O₃ support gave the highest monomeric product yield and lowest solid residue after reaction. The catalytic activity of the various supports increased in the following order: Al₂O₃ < ZSM-5 < AC=MgO-La₂O₃. In depth analysis of the lignin oils by various techniques (GC, FT-IR, ¹³C-NMR, GPC) revealed that Kraft lignin can be depolymerized under solvent free conditions to low molecular weight phenolics in satisfactory yields. The best results were obtained with the sulfided NiMo/MgO-La₂O₃ catalyst, giving 87% lignin conversion and 26.4 wt.% of monomers of which 15.7 wt.% were phenolics and 5.9 wt.% aromatics.

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References

- 1 A.J. Ragauskas, G.T. Beckham, M.J. Bidy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.N. Naskar, J.N. Saddler, T.J. Tschaplinski, G.A. Tuskan and C.E. Wyman, *Science*, 2014, **344**, 1246843.
- 2 J. Zakzeski, P.C.A. Bruijninx, A.L. Jongerius and B.M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552.
- 3 G.W. Huber, S. Iborra and A. Corma, *Chem.Rev.*, 2006, **106**, 4044.
- 4 M.E. Brown, M.C. Walker, T.G. Nakashige, A.T. Lavarone and M.C.Y. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 18006.
- 5 J. Reiter, H. Strittmatter, L.O. Wiemann, D. Schieder and V. Sieber, *Green Chem.*, 2013, **15**, 1373.

- 6 R.N. Olcese, G. Lardier, M. Bettahar, J. Ghanbaja, S. Fontana, V. Carre, F. Aubriet, D. Petitjean and A. Dufour, *ChemSusChem*, 2013, **6**, 1490.
- 7 X. Li, L. Su, Y. Wang, Y. Yu, C. Wang, X. Li and Z. Wang, *Front. Environ. Sci. Eng.*, 2012, **6**(3), 295.
- 8 V.M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li and J.A. Lercher, *Chem. Eur. J.*, 2011, **17**, 5939.
- 9 R. Beauchet, F.M. Rivera and J. M. Lavoie, *Bioresour. Technol.*, 2012, **121**, 328.
- 10 J.E. Miller, L. Evans, A. Littlewolf and D.E. Trudell, *Fuel*, 1999, **78**, 1363.
- 11 A. Toledano, L. Serrano and J. Labidi, *J. Chem. Technol. Biotechnol.*, 2012, **87**, 1593.
- 12 S.K. Singh and J.D. Ekhe, *Catal. Sci. Technol.*, 2015, **5**, 2117.
- 13 A.K. Deepa and P.L. Dhepe, *ACS Catal.*, 2015, **5**, 365.
- 14 T. Parsell, S. Yohe, J. Degenstein, T. Jarrell, I. Klein, E. Gencer, B. Hewetson, M. Hurt, J.I. Kim, H. Choudhari, B. Saha, R. Meilan, N. Mosier, F. Ribeiro, W.N. Delgass, C. Chapple, H.I. Kenttamaa, R. Agrawal and M.M.A. Omar, *Green Chem.*, 2015, **17**, 1492.
- 15 A. Rahimi, A. Ulbrich, J.J. Coon and S.S. Stahl, *Nature*, 2014, **515**, 249.
- 16 H. Zhu, Y. Chen, T. Qin, L. Wang, Y. Tang, Y. Sun and P. Wan, *RSC Adv.*, 2014, **4**, 6232.
- 17 A. Vigneault, D.K. Johnson and E. Chornet, *Can. J. Chem. Eng.*, 2007, **85**, 906.
- 18 M.P. Pandey and C.S. Kim, *Chem. Eng. Technol.*, 2011, **34**, 29.
- 19 E. Furimsky, *Appl. Catal. A*, 2000, **199**, 147.
- 20 D. Meier, R. Ante and O. Faix, *Bioresour. Technol.*, 1992, **40**, 171.
- 21 A. Oasmaa, R. Alen and D. Meier, *Bioresour. Technol.*, 1993, **45**, 189.
- 22 A. Kloekhorst, J. Wildschut and H.J. Heeres, *Catal. Sci. Technol.*, 2014, **4**, 2367.
- 23 A.L. Jongerius, R. Jastrzebski, P.C.A. Bruijninx and B.M. Weckhuysen, *J. Catal.*, 2012, **285**, 315.
- 24 Y.C. Lin, C.L. Li, H.P. Wan, H.T. Lee and C.F. Liu, *Energy Fuels*, 2011, **25**, 890.
- 25 C. Wang, D. Wang, Z. Wu, Z. Wang, C. Tang and P. Zhou, *Appl. Catal. A*, 2014, **476**, 61.
- 26 M. Grilc, G. Vervasov, B. Likozar, A. Jesih and J. Levec, *Appl. Catal. B*, 2015, **163**, 467.
- 27 Y. Wang, H. Lin and Y. Zheng, *Catal. Sci. Technol.*, 2014, **4**, 109.
- 28 C. Zhao, Y. Kou, A.A. Lemonidou, X. Li and J.A. Lercher, *Angew. Chem., Int. Ed.*, 2009, **48**, 3987.
- 29 M. Osada, N. Hiyoshi, O. Sato, K. Arai and M. Shirai, *Energy Fuels*, 2007, **21**(4), 1854.
- 30 R. Kishore, M. Lakshmi Kantam, J. Yadav, M. Sudhakar, S. Laha and A. Venugopal, *J. Mol. Catal. A*, 2013, **379**, 213.
- 31 T. Kabe, A. Ishihara and W. Qian, in *Hydrodesulfurization and Hydrodenitrogenation: Chemistry and Engineering*, Wiley-VCH, Weinheim, 1999, 14p.
- 32 F.S.H. Simanjuntak, V.T. Widyaya, C.S. Kim, B.S. Ahn, Y.J. Kim and H. Lee, *Chem. Eng. Sci.*, 2013, **94**, 265.
- 33 M. Lakshmi Kantam, R. Kishore, J. Yadav, M. Sudhakar and A. Venugopal, *Adv. Synth. Catal.*, 2012, **354**, 663.
- 34 B. Yoosuk, D. Tumnantong and P. Prasassarakich, *Fuel*, 2012, **91**, 246.
- 35 B. Yoosuk, C. Song, J.H. Kim, C. Ngamcharussrivichai and P. Prasassarakich, *Catal. Today*, 2010, **149**, 52.
- 36 S.K. Singh and J.D. Ekhe, *RSC Adv.*, 2014, **4**, 53220.
- 37 A. Tejado, C. Pena, J. Labidi, J.M. Echeverria, I. Mondragon, *Bioresour. Technol.* 2007, **98**, 1655.
- 38 S. Karagoz, T. Bhaskar, A. Muto and Y. Sakata, *Fuel*, 2004, **83**, 2293.