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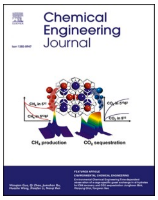

Slurry co-hydroprocessing of Kraft lignin and pyrolysis oil over unsupported NiMoS catalyst: A strategy for char suppression

You Wayne Cheah [a], Rawipa Intakul [a], Muhammad Abdus Salam [a], Joby Sebastian [a], Phuoc Hoang Ho [a], Prakhar Arora [b], Olov Öhrman [b], Derek Creaser [a], Louise Olsson [a], *

[a] *Competence Centre for Catalysis and Chemical Engineering, Chalmers University of Technology, Gothenburg 41296, Sweden*
[b] *Preem AB, Sweden*

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ABSTRACT

Pyrolysis oil (PO) assisted Kraft lignin (KL) liquefaction over an unsupported NiMoS catalyst in a paraffin solvent was explored in this work. A paraffin solvent was used to represent hydrogenated vegetable oil (HVO) which is a biofuel. We have for the first time showed that when co-processing Kraft lignin with pyrolysis oil in a paraffin solvent the char formation could be completely suppressed. The complex composition of PO, containing various compounds with different functional groups, was able to aid the depolymerization pathways of lignin by obstructing the condensation path of reactive lignin derivatives. To further understand the role of different functional groups present in pyrolysis oil during lignin liquefaction, we investigate the co-hydroprocessing of Kraft lignin with various oxygenate monomers using unsupported NiMoS. 4-propylguaiacol (PG) was found to be the most efficient monomer for stabilizing the reactive lignin intermediates, resulting in a low char yield (3.7%), which was 4 times lower than the char production from Kraft lignin hydrotreatment alone. The suppressed rate of lignin fragment repolymerization can be attributed to the synergistic effect of functional groups like hydroxyl (-OH), methoxy (-OCH_3), and propyl (-C_3H_7) groups present in PG. These groups were found to be able to stabilize the lignin depolymerized fragments and blocked the repolymerization routes enabling efficient lignin depolymerization. It was found that the presence of a co-reactant like PG during the heating period of the reactor acted as a blocking agent facilitating further depolymerization routes. Finally, a reaction network is proposed describing multiple routes of lignin hydroconversion to solid char, lignin-derived monomers, dimers, and oligomers, explaining why the co-processing of pyrolysis oil and Kraft lignin completely suppressed the solid char formation.

1. Introduction

Society needs to seek sustainable alternative resources, replacing a fossil-based economy with a bio-based one. Lignocellulosic biomass has gained tremendous interest from the public and has been seen as a potential renewable feedstock to produce renewable carbon-based chemicals, materials, and liquid biofuels. Lignin is, the second most abundant (20–30%) three-dimensional natural polymer found in lignocellulosic biomass. It is constituted of phenylpropane monomer units, such as sinapyl, coniferyl and p-coumaryl alcohol, which are cross-linked by recalcitrant carbon–carbon (C-C) linkages and ether (C-O-C) linkages [1].

Technical lignin like Kraft lignin extracted from black liquor can be a stream from the Kraft pulping process and has an annual global production of 50 Mtons [2,3]. This byproduct is often combusted to produce heat and energy for the pulp and paper mill as a renewable energy source [3]. However, modern pulp and paper mills are increasing their energy efficiency, resulting in less need for energy recovery from lignin combustion during the pulp mill operation [4]. To increase its value and better utilize the Kraft lignin side stream, it can be depolymerized and hydroprocessed to obtain high-value lignin-derived monomers for green chemical and biofuel production. Nonetheless, various hurdles exist such as the low solubility of solid lignin in simple low-cost solvents, repolymerization, and condensation reactions of the depolymerized lignin fragments during hydrotreatment. These difficulties can result in a large amount of insoluble and intransigent solid residue formation during the hydroprocessing, leading to low bio-oil yield, which hampers the implementation of such bio-feedstocks [2].

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* Corresponding author.
E-mail address: louise.olsson@chalmers.se (L. Olsson).

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Several thermochemical methods such as catalytic pyrolysis, gasification, hydrogenolysis, oxidation, and hydrolysis have been explored for the effective depolymerization of lignin sources for the production of lignin-derived bio-oils, gases (CO, CO_2, H_2, and CH_4), and insoluble solid char residues [5]. The bio-oils contain a complex mixture of compounds such as e.g. phenolics, aldehydes, cycloalkanes, aromatics, and aliphatics. During catalytic reductive lignin liquefaction, a combination of depolymerization, hydrogenolysis, and hydrodeoxygenation (HDO) reactions occur in a single step to produce bio-oils with low oxygen content [6,7]. This one-pot lignin conversion process is one of the possible chemical transformations of lignocellulosic biomass or lignin into depolymerized and deoxygenated lignin-derived monomers and oligomers. The process usually involves the liquefaction of solid biomass or lignin in a suitable solvent using an active heterogenous catalyst under hydrogen pressure (up to 100–200 bar) and an appropriate hydrotreatment temperature (300–500 °C) [8]. For instance, organosolv switchgrass lignin was depolymerized and deoxygenated at 350 °C using ethanol as a solvent, and aided by formic acid as a hydrogen source and 20 wt% Pt on carbon catalyst [6]. This resulted in the production of a high yield of depolymerized low molecular weight liquid products and only a small amount of char was produced [6]. During the hydrotreatment of organosolv lignin in supercritical ethanol at 300 °C the addition of a catalyst (5% Ru/γ-alumina) was found to improve the heating value of the bio-oil [7]. Another example is the hydrotreatment of wheat straw soda lignin over a sulfided NiMo catalyst in a hydrogen atmosphere at 350 °C using tetralin as a solvent, which resulted in a liquid product yield of 65 wt% [9]. Common to all of these example studies is the use of solvents that are polar (ethanol) and/or have hydrogen donor properties (tetralin) that can achieve low to no char formation. While it remains a challenge to achieve this using a simple non-polar paraffin solvent. Various previous studies in our group have also shown that the type of catalyst, lignin type, and hydrotreatment parameters play a crucial role in affecting the composition of the bio-oils and also the rate of formation of condensed char residues [10–16].

In term of hydrotreating catalysts, traditional Nickel (Ni) or Cobalt (Co) promoted Molybdenum (Mo) or Tungsten (W) sulfides supported on high surface area porous support or in unsupported form was found to have high deoxygenation activity for lignin conversion to aromatics and naphthenes [17–24]. In this regard, the current work employed an unsupported NiMo sulfide in the co-hydrotreatment of Kraft lignin and pine sawdust-derived pyrolysis oil or oxygenate monomers. The reason for selecting an unsupported NiMoS catalyst in the current work can be justified as follow: (i) Metal sulfides are known to be sulfur resistant, in this work, the sulfur (1–2 wt%) remains in the Kraft lignin after the Kraft pulping process and the sulfur can be seen as advantageous in maintaining the catalytic activity of metal sulphides [25,26]; (ii) Unsupported NiMoS can enhance the accessibility for lignin fragments to the active catalytic sites, continuing the effort from our previous work [13]; (iii) An industrial relevant catalyst, metal sulfides have been employed in the deoxygenation/hydroprocessing of triglycerides feeds and fatty acids derivatives for the production of hydrogenated vegetable oils (HVO) in existing refinery infrastructures [27].

Exploring different approaches that can limit and avoid the condensation and repolymerization reactions that occur under the liquefaction of lignin sources, could provide an opportunity for the production of lignin-derived monomers. Kim et al. have summarized in a mini-review the possible undesired secondary reactions during the liquefaction process of lignin and also efforts to suppress those undesired reactions and in turn maximize the yield of low molecular weight products [5]. Lan et al. presented an overview of different ways to avoid the recondensation of lignin, and these ways can be divided into two major groups, the first group focuses on trapping the reactive lignin intermediates *in situ* and forming a more stable lignin molecule, and the second group focuses on preventing the formation of reactive intermediates by physical or chemical stabilization of lignin linkages [28]. Another review work outlines the strategies aiming to suppress the condensation of reactive intermediates during the defragmentation of biomass by preventing the formation of these intermediates by first functionalizing the native biomass structure or by transforming these unstable intermediates into stable ones [29]. There are also studies suggesting the utilization of phenol as a capping agent in base-catalyzed lignin depolymerisation [30,31]. In addition, hydrothermal liquefaction of lignin showed positive results in terms of achieving high bio-oil yields and also suppressing repolymerization of large lignin fragments [32]. Table 1 presents an overview of a literature survey related to various strategies for suppressing the undesired secondary reactions during lignin valorization using a co-solvent, co-reactant, or capping agent. Tetralin is a very efficient solvent, however, it is quite expensive to use in a large-scale industrial process. The possibility to use other refinery products as solvents would have large economic advantages and could be important to enable large up-scaling of the process. Today hydrogenated vegetable oils (HVO) are very important biofuels, that are produced from e.g. waste cooking oils, tall oils, and waste fats. HVO consists of large amounts of C17 and C18 alkanes. It would therefore be very beneficial to co-process the Kraft lignin with HVO, but that gives challenges in char production since HVO is non-polar.

We have in this work, for the first time in literature, shown that the char formation during Kraft lignin valorization in a non-polar solvent, representing HVO, could be completely suppressed when co-processing with pyrolysis oil. Pyrolysis oil itself is a challenging oil to hydrogenate due to char formation and by co-processing Kraft lignin and pyrolysis oil together large synergies were found. In this work, we used hexadecane as a model component for HVO and studied the catalytic liquefaction of Kraft lignin when simultaneously co-processing with pyrolysis oil. Moreover, for the first time, we also present a study that covered the co-hydroconversion of Kraft lignin with various bio-derived oxygenated monomers (co-reactants) using hexadecane as a non-polar solvent over a hydrothermally synthesized unsupported NiMo sulfide catalyst. To further investigate the role of pyrolysis oil in char suppression we examined multiple model compounds of pyrolysis oil including a wide variety of chemical groups like aldehydes, ketones, carboxylic acids, and phenolics, in terms of their global oil yield (wt%) and also the production of the undesired solid char residues (wt%). We found that the most efficient model compound was 4-propylguaiacol (PG) and further detailed studies were therefore performed on PG. Finally, we propose a reaction network describing the effects of pyrolysis oil/oxygenate monomers on char suppression during co-processing with Kraft lignin.

2. Experimental

2.1. Material

The Kraft lignin used in this study was Indulin AT Kraft lignin purchased from Ingevity Corporation (USA). The Indulin AT is Kraft pine lignin (ash content of 4.05 ± 0.16%, measured by heating in the oven to 800 °C and stayed for 6 h). The fast pyrolysis bio-oil was provided by Preem and was originally produced from pine sawdust. The precursors used for unsupported NiMoS are thiourea (ACS regent $\geq$ 99.0%, Sigma), nickel (II) nitrate hexahydrate (99.999%, Sigma), and ammonium molybdate tetrahydrate (99.98%, Sigma).

2.2. Catalyst synthesis

The unsupported NiMoS catalyst was synthesized using a hydrothermal method with further modification reported in our previous work [11]. Precursors for Ni, S, and Mo were Nickel (II) nitrate hexahydrate, thiourea, and ammonium heptamolybdate tetrahydrate respectively. The metal precursors were weighted according to the molar ratio of Ni:Mo of 1:2 and with 4.25 g of thiourea, they were all dissolved in 180 mL of distilled water. Then 7 mL of HCl (36 wt%) was slowly added into the solution to adjust the pH to approximately pH 1. The sample solution was transferred into a Teflon liner and put into the autoclave before

Table 1
Overview of a literature survey related to various strategies in suppressing char formation during lignin valorization using a co-solvent, co-reactant, or capping agent.

Co-solvent or reactant	Reaction system	Finding	Reference
Methanol (MeOH)	Sodium lignosulfonate (SL) depolymerization in continuous mode. Ni on nitrogen-doped carbon was used as a catalyst.	-SL was found to depolymerize thermally, without any catalyst, and independent of the solvent mixture. -The MeOH/water solvent system resulted in higher monomer yield and lower molecular weight products.	[33]
Ethanol/ Methanol	Soda lignin depolymerization. $CuMgAlO_x$ was used as a catalyst.	-The capping effect of ethanol resulted in the stabilization of reactive phenolic intermediates by O-alkylation of OH groups and C-alkylation of aromatic rings. -Ethanol was found to be more efficient than methanol.	[34]
Ethanol/ Methanol	Lignin depolymerization/ hydrogenolysis. $CuMgAlO_x$ was used as a catalyst.	-Ethanol is a better solvent as compared to methanol resulted in a higher monomer yield. -Ethanol scavenges lignin-derived formaldehyde which is known to be involved in undesired repolymerization reactions.	[35]
Phenol/Boric acid	Base-catalyzed lignin depolymerization in water. No solid catalyst was used.	-Boric acid and phenol as a capping agent yielded different products distribution during lignin depolymerization. -Using phenol as a capping agent resulted in higher phenolic compound yield and low char yield.	[30]
Phenol and methanol	Hydrolytic treatment of black liquor using NaOH as a catalyst	-Supplementing phenol reduces the repolymerization and condensation reactions during Kraft lignin depolymerization in black liquor.	[36]
Phenol	Phenol-assisted lignin depolymerization. Catalysts ($ZnCl_2$, H_2SO_4, NaOH, and Ru/C) were used.	-Phenol acts as a solvent for lignin dissolution. -Phenol scavenged the methylene linkages (C-C linkage) in condensed lignin facilitating lignin depolymerization.	[37]
Formaldehyde	Extraction of lignin under acid conditions. Ru on carbon was used as a catalyst.	-Formaldehyde reacts with 1,3 diol structure of β-O-4 linkages to form acetals and prevents the formation of reactive carbocation intermediates inhibiting the condensation reactions.	[38]
Boric acid	Base-catalyzed lignin depolymerization. NaOH was used as a catalyst.	-Boric acid inhibited the addition and condensation reactions by capping the phenolic OH group by forming boric ethers and increasing oil yield.	[39]
Aniline	Oxidative lignin depolymerization. No catalyst was used. NaOH was used as a solvent.	-Aniline can stabilize vanillin by protecting the carbonyl group through the reversible formation of imine.	[40]
Isopropanol	Hydrothermal liquefaction (HTL) of softwood Kraft lignin. Na_2CO_3 was used as a homogeneous catalyst.	-Isopropanol as a co-solvent presented a capping effect such as reduced molar mass of both char and also precipitated solids. -The char-suppressing effect of isopropanol is less effective as compared to phenol under similar reaction conditions.	[41]
Ethylene glycol (EG) and ethanol (EtOH)	Reductive solvolysis of lignosulfonate. Ni-based catalysts were used.	-The depolymerized fragments of lignin oil in EtOH had a lower molecular weight compared to the oil product in EG. -EG inhibited condensation reactions.	[42]
Lignin-derived phenolic oil	Base-catalyzed lignin depolymerization. No catalyst was used.	-The organosolv lignin was depolymerized into phenolic oil and used as a renewable capping agent in base-catalyzed lignin depolymerization. -The usage of a capping agent favored the demethoxylation of guaiacyl units, and reduced the repolymerization reactions and thus the solid char yield.	[31]
p-hydroxybenzyl alcohol (HBA)	Acid-catalyzed lignin depolymerization. H_2SO_4 was used as an acidic homogeneous catalyst.	-HBA is a novel capping agent. -HBA was able to limit condensation reactions resulting in a high yield of depolymerized ethyl acetate soluble lignin with high antioxidant ability.	[43]
Formic acid	Mild catalytic reductive Kraft lignin depolymerization in ethanol/water. Pd/ Al_2O_3 was used as a catalyst.	-Formic acid generates in-situ hydrogen. -The addition of 3.6 vol% formic acid in the process provided smaller depolymerized lignin fragments with more phenolic OH functionalities.	[44]
Glycerol	HTL of kraft lignin. NaOH and Na_2CO_3 were used as alkaline catalysts.	-Glycerol decreases the molecular weight of all product fractions while increasing the char yield.	[45]

(*continued on next page*)

Table 1 (*continued*)

Co-solvent or reactant	Reaction system	Finding	Reference
		-NaOH was beneficial in terms of reducing char yield.	

closing the lid. The oven was set at 200 °C for 12 h. After 12 h, the sample was cooled down, it was filtered, and washed with MilliQ water several times, followed by absolute ethanol. The solid catalyst that was collected on filter paper was covered with aluminum foil and dried in an oven at 50 °C overnight under vacuum. The dried catalyst was ground in a mortar to refine the particles and break any solid clumps, weighted, and stored in a dry cabinet.

2.3. *Catalytic hydrotreatment tests and product analysis*

The catalytic hydrotreatment of Kraft lignin was performed in a 300 mL Parr batch reactor. In a usual experiment, 2.25 g of Kraft lignin, 0.75 g of unsupported NiMoS (without pre-sulfidation step), and 75 mL of hexadecane as a non-polar solvent were loaded in the reactor. Hexadecane was selected as the solvent for all hydrotreatment in this study because it is preferred to perform the liquefaction of lignin in a solvent that does not contain any oxygen moieties which will consume hydrogen due to hydrogenation reactions. It also eased the analytical process as it gave a better separation from oxygenates released from lignin fragments. Moreover, hexadecane can be produced sustainably by combining the fermentation production of isobutene and its further oligomerization and also the deoxygenation of vegetable oils [46–48].

When the reactor was loaded with reactants, the reactor vessel was then mounted and closed using a 35 lb. torque wrench. The batch reactor system was then flushed with N_2 three times to remove any air in the system, followed by H_2 flushing. The reactor system was then pressurized to 35 bar with hydrogen and heated up to the desired reaction temperature (400 °C), requiring 40 min. When the desired temperature was reached, some additional hydrogen was added to ensure the starting pressure was always 75 bar. The stirring rate was set at 1000 rpm and a typical experiment was kept running for 6 h. Reaction parameters like reaction temperature, hydrotreatment time, and catalyst loading were also studied in this work. The catalyst and lignin mass ratio was kept at 1:3. When the hydrotreatment was finished (after 6 h), the reactor system was quenched to room temperature. The products (bio-oils and solid char residues) were collected using a filter crucible and followed by vacuum filtration to separate the liquid and solid products. The liquid product (bio-oil) rich in hexadecane obtained after the hydrotreatment was regarded as bio-oil in this study. The solid residues obtained after the filtration contained char residues, unconverted lignin, and also spent catalysts. The solid residues were washed with acetone several times to remove the residual hexadecane and dried in an oven overnight. The dried solid was thereafter washed with dimethyl sulfoxide (DMSO) to dissolve unconverted lignin. After the DMSO extraction, the solid product was dried overnight in an oven at 80 °C. The yield of lignin-derived char residue was determined based on the initial feed of lignin by subtracting the catalyst weight and the unconverted lignin from the total dried weight of the solid products.

Subsequently, the bio-oil was analyzed using a two-dimensional GC × GC-MS/FID (Agilent 7890-5977A). The modulation time on the modulator was set at 5 s for all samples. For all other settings, see our earlier study [11]. The analysis was done using the GC image software for multidimensional chromatography. The bio-oil yields in this work were measured using external standard calibrations. Dihexyl ether was used as an internal standard. Calibration curves were obtained using different commercially available individual compounds with five known concentrations (wt%) points such as n-butylbenzene, benzene, toluene, ethylbenzene, xylene, propylbenzene, 1,2,3-trimethylbenzene, propylcyclohexane, cyclopentane, cyclohexane, methylcyclohexane, cyclohexanol, propylcyclohexanol, 4-propylphenol, guaiacol, p-cresol, creosol, 2-ethylphenol, 4-propylguaiacol, 4-ethylguaiacol, 1,3-dimethylnaphthalene, propylanisole, butylanisole, methylnaphthalene, 1,5-dimethyltetralin, 2-methyl-1,1′-biphenyl, phenol, biphenyl, and phenanthrene. All detected compounds by GC were accounted for when calculating the total yields of bio-oils and were grouped into deoxygenated cycloalkanes, aromatics like alkylbenzenes, alkylphenolics, and also polyaromatics like indanes and naphthalenes.

For the co-hydrotreatment in which Kraft lignin and pyrolysis oil or oxygenated monomers were used, the bio-oil yield was calculated based on the total initial loaded reactants (both Kraft lignin and pyrolysis oil/monomers). The fraction of bio-oil yield derived from Kraft lignin and monomer after the hydrotreatment was not determined since the oxygenate monomer can also be derived from lignin and pyrolysis oil itself. In the co-hydrotreatment of Kraft lignin (KL) and oxygenated model compounds, different monomers such as 4-propylguaiacol (PG), 4-propylphenol, phenol, methylguaiacol, 4-ethylguaiacol, p-propylanisole, anisole, 4-propylcyclohexanol, benzaldehyde, cyclohexanol, acetic acid, hydroxyacetone, and guaiacol were selected as the co-reactants. The feed mass ratio (KL: PG, w/w) was also varied to study its influence on char and bio-oil yields.

2.4. *Catalyst characterizations*

The catalysts' specific pore volume, pore size and surface area were determined with N_2 physisorption at −196 °C (Tristar 3000). The unsupported NiMoS catalysts (approximately 0.15 g) were degassed at 300 °C overnight in a quartz tube under N_2 flow to remove the moisture. The Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, were used to calculate the specific surface area and pore sizes of the catalysts, respectively. The diffractograms of X-ray diffraction (XRD) were recorded from 5° to 80° (2θ) with a step size of 0.02° (1 s per step) using a D8 Discover (Bruker AXS, Germany) with a Dectris Eiger R 500 K detector. Scanning and high-resolution transmission electron microscopy (SEM and HRTEM) were used to study the morphologies and microstructure of the catalysts. The SEM used was a JEOL 7800F Prime SEM and the TEM was an FEI Titan 80–300 TEM (accelerating voltage: 300 kV). TEM Imaging and Analysis (TIA) software was used and the analysis was made with 15–25 images. The MoS_2 slab length was determined by processing ca. 300–350 MoS_2 slabs using the ImageJ software.

The MoS_2 average slab length (ΔL) and stacking number (Δn) were determined according to [12] :

$$\text{Average } MoS_2 \text{ slab length } (\Delta L) = \frac{\sum_i^n x_i l_i}{\sum_i^n x_i} \tag{1}$$

$$\text{Average stacking number } (\Delta n) = \frac{\sum_i^n x_i N_i}{\sum_i^n x_i} \tag{2}$$

where n is the number of MoS_2 slabs, x_i is the number of MoS_2 slabs with the stacking number N_i that has a length l_i of the MoS_2 slab.

The dispersion of MoS_2 (f_{mo}) of the catalysts was calculated with Eq. (3) expressed in the literature [12] :

$$MoS_2 \text{ dispersion } (f_{mo}) = \frac{Mo_{edge}}{Mo_{total}} = \frac{\sum_i^m 6(n_i - 1)}{\sum_i^m (3n_i^2 - 3n_i + 1)} \tag{3}$$

where Mo_{total} is the number of Molybdenum atoms and the number of Mo atoms placed at the edges are denoted Mo_{edge}. The total number of MoS_2 slabs are denoted m, and for each slab the number of Mo atoms along the edge of the slabs is n_i ($L = 3.2(2\,n_i - 1)$ Å, where L is the length).

The ratio between edges and corners in the MoS_2 slabs was determined according to (4) [49]:

$$\frac{f_{edge}}{f_{corner}} = \frac{5\Delta L}{3.2} - 1.5 \quad (4)$$

2.5. Solid lignin and lignin-derived solid char characterization

Fourier transform infrared spectroscopy (FTIR, Bruker Vertes70v spectrometer) was used to analyze solid residues (from some selected experiments) consisting of the spent catalyst and lignin-derived char resulting from the hydroprocessing. The spectra were recorded in a transmittance mode within the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and 63 scans per sample. Some selected solid residues were also examined using solid-state cross-polarization (CP) ^{13}C NMR measurement using a 4 mm CP MAS probe on the Bruker AVIII 500 MHz spectrometer with the following conditions: ^{13}C CP-MAS at 10 kHz, with Tset = 298 K, a 1H excitation 90°-pulse of P3 = 3.0 μs, a contact time of P15 = 1.5 ms, with CP at 13C 60.0 kHz (PLW1 = 109 W) and 1H optimized ramp 45–90 kHz (SPW0 = 110 W) followed by SPINAL64 decoupling at 83 kHz (PCPD2 = 6.0 μs, PLW12 = 96 W) during acquisition and a relaxation delay of d1 = 2.0 s with 4000 scans.

3. Results and discussion

3.1. Catalyst characterization

The specific surface area of the unsupported NiMoS catalyst was 49.3 m^2g^{-1} as measured from the nitrogen physisorption (Fig. 1a)). The total pore volume was 0.224 cm^3g^{-1} with an average pore size of 131.2 Å. The nitrogen adsorption–desorption isotherm for the NiMoS unsupported catalyst shown in Fig. 1a) depicts type IV isotherm characteristics showing an apparent hysteresis loop in the relative pressure (P/P_0) range of 0.5–1, indicating its mesoporous structure. Fig. 1b) shows the XRD diffraction pattern of the unsupported NiMoS catalyst. The pattern corresponding to the species $(NH_4)_2[Mo_3S_{13}]$ can be observed, which can be attributed to the sulfidation of the ammonium heptamolybdate tetrahydrate (the molybdenum precursor used for the unsupported NiMoS catalysts in this study) [50]. The prominent peaks at 2θ = 14.4°, 32.8°, 39.5°, 49.5° and 58.3° for the NiMoS unsupported catalyst correspond to the (0 0 2), (1 0 0), (1 0 3), (1 0 5), and (1 1 0) planes of MoS_2 indicating the presence of a mixture of 1T and 2H MoS_2 phases [51–53]. Moreover, the diffraction peaks at 27.3°, 31.5°, 35.3°, 38.7°, 45.3°, and 53.6° can be assigned to (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), and (3 1 1) planes of NiS_x [19].

SEM was performed to examine the morphologies and microstructure of the synthesized catalyst. Agglomeration of spherical particles forming a raspberry-like morphology can be observed in the SEM images which are mainly attributed to the MoS_2 particles' laminar growth during the 12 h hydrothermal synthesis (Fig. 1 c-d)). HRTEM was also performed to understand the structural morphology of the synthesized NiMoS unsupported catalyst. The measurement of the MoS_2 fringes (typical tread-like structure) shows an interplanar distance of 0.64 nm that is corresponding to the (0 0 2) MoS_2 basal planes which can be observed in all HRTEM images (Fig. 1e–f)). The spiky edge features can also be seen in all HRTEM images in this study, and according to our previous work, these spiky edges can enhance the specific surface area and also expose more deoxygenation active sites for the hydrodeoxygenation (HDO) reaction [11]. According to the TEM imaging analysis, the average slab length and average stack number of the synthesized NiMoS were found to be 6.34 nm and 3.6, respectively. The calculated MoS_2 dispersion based on analysis of the TEM images was 0.159 and the edge-to-corner ratio was 8.4, which is in line with our previous study [13].

3.2. Effect of reaction temperature on hydrotreatment of Kraft lignin

The effect of the reaction temperature (300 °C, 340 °C, and 400 °C) on the yield of undesired char production and the total bio-oil yields (detected by 2D GC × GC-MS) was studied for the Kraft lignin hydrotreatment with an unsupported NiMoS catalyst for 6 h (Fig. 2). One apparent observation that can be obtained by studying the influence of reaction temperature on the hydrotreatment was that the rate of lignin liquefaction increased steadily when elevating the hydrotreatment temperature from 300 °C to 400 °C. This was demonstrated by the increasing bio-oil yields (orange bar in Fig. 2) from 9.4% to 26.9%. Note that this is the yield of mono- and dimeric bio-oil compounds detected by the 2D GC × GC-MS, but there are also larger oligomers present that cannot be detected by 2D GC × GC-MS. At 400 °C, the yield of GC × GC-MS detectable compounds was 26.9%, which consisted of 21.6% deoxygenated cycloalkanes and 3.2% alkylbenzenes. It should also be noted that the formation of polyaromatics like indanes, naphthalenes, and biphenyls was not favored at a higher temperature which could be linked to the lower solid char yield (14.7%) at 400 °C.

When the hydrotreatment temperature is low, only weaker bonds present in the lignin network like the alkyl ether bond will start to cleave and depolymerize and then large lignin fragments could be formed. The large polymeric lignin fragments can then repolymerized and thus resulted in the formation of insoluble solid products indicated by the high solid char yield (47.2%) at 300 °C. The char residue decreased when increasing the hydrotreatment temperature indicating an inhibition of the repolymerization reactions. The inhibition might be due to the saturation of free radicals by hydrogen formed during the depolymerization of lignin, and thus impeding their repolymerization. In addition, with increasing the reaction temperature, the rate of various reactions will increase, such as hydrogenolysis, hydrodeoxygenation, hydrogenation, and decarboxylation, which as a result, increases the bio-oil yields. It is also worth mentioning that the increase in reaction temperature should improve the solubility of lignin in the solvent which in turn can facilitate and enhance the lignin depolymerization reaction [54]. However, a higher reaction temperature can also lead to the higher production of gaseous products, which is undesirable since it will result in less bio-oil production. This is owing to the higher catalytic activity for hydrogenolysis, hydrocracking, and hydrodeoxygenation. This is shown in the study by Heeres et al. where they examined hydrotreatment of pyrolytic lignin (PL) using a series of noble metals supported on carbon catalysts and also the sulfided NiMo and CoMo catalysts [55]. It was found that a higher reaction temperature (350, 375, and 400 °C was examined) resulted in lower organic fraction yields and higher amounts of gaseous and aqueous products. This can be attributed to the higher catalytic activity for hydrodeoxygenation and hydrocracking reactions [55]. A similar observation was obtained in our previous work when increasing the reaction temperature from 425 to 440 °C for the slurry hydroconversion of solid lignin using a bauxite catalyst, which resulted in an increase of gas formation from 10 to 26% [56]. To summarize, our results show that in the examined temperature interval, the bio-liquid yield was the highest and the solid char formation the lowest at 400 °C. Hence, the hydrotreatment temperature was set at 400 °C for the rest of the experiments in this study.

3.3. Pyrolysis oil-assisted Kraft lignin hydrotreatment

Pyrolysis oil (PO), is a liquid product derived from the pyrolysis of lignocellulosic biomass that represents a complex multi-component mixture including furans, furfurals, ketones, aldehydes, alcohol, acids, esters, ethers, sugars, and phenolic compounds [57]. Different capping agents have been examined during lignin depolymerization (Table 1), such as phenols [30,31], ethanol [34], isopropanol [41], and p-hydroxybenzyl alcohol [43]. Since pyrolysis oil includes phenolic compounds as well as alcohols, we have therefore examined the effect of co-processing pyrolysis oil and Kraft lignin with the intention to examine if pyrolysis oil could behave as a capping agent. First, we examined hydrotreatment of pyrolysis oil (PO), without lignin using 2.2 g pyrolysis oil in the presence of unsupported NiMoS at 400 °C, 75 bar total H_2

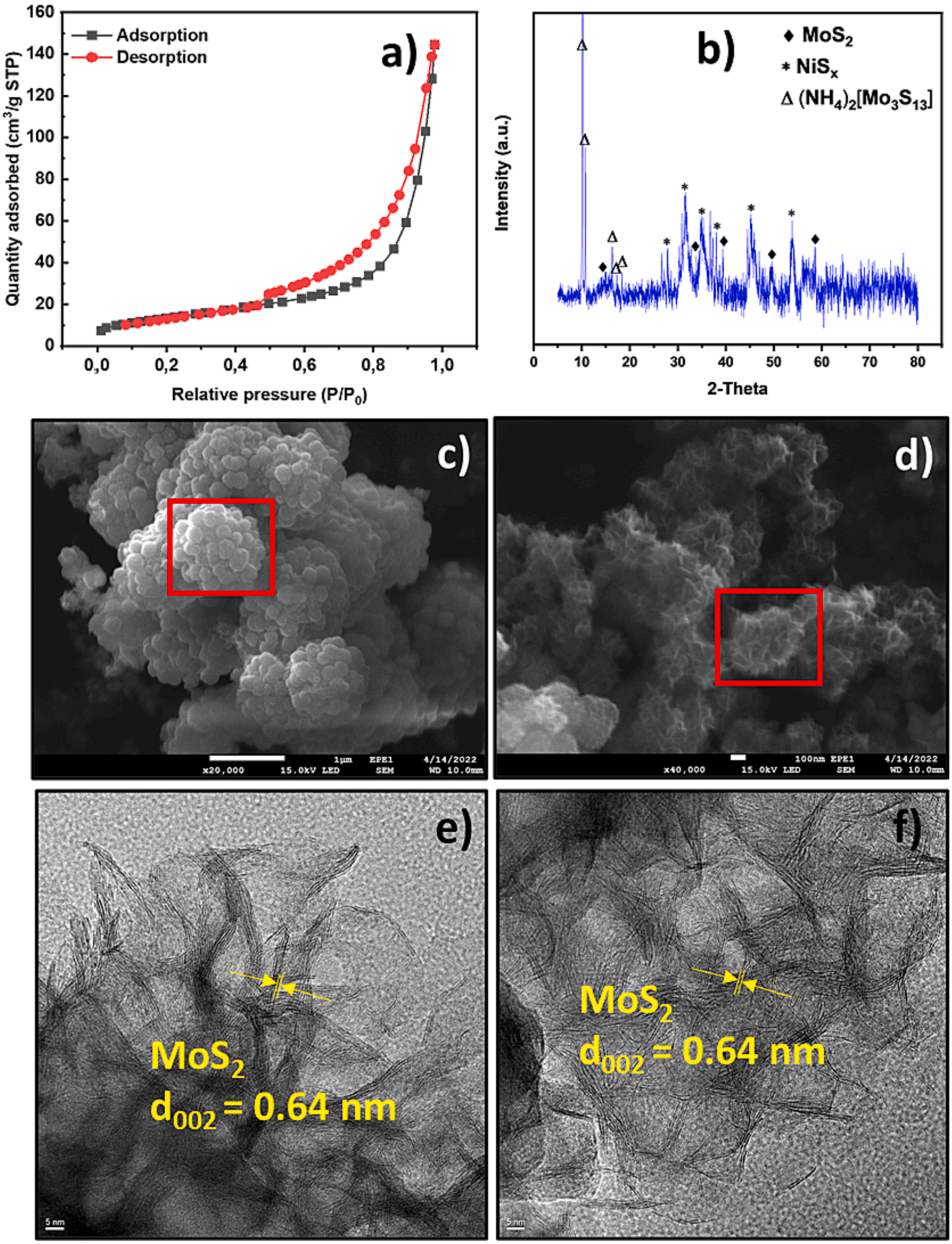


Fig. 1. a) BET adsorption and desorption isotherm b) XRD pattern c-d) SEM images and e-f) HRTEM images of unsupported NiMoS catalyst.

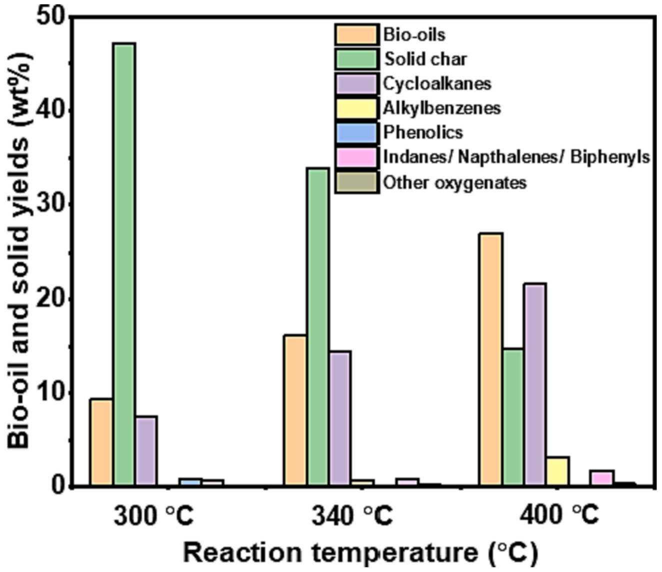


Fig. 2. The influence of reaction temperature on the solid char residue yield (wt%) and the total bio-oil yields (wt%) based on the Kraft lignin hydrotreatment. Reaction conditions: total 75 bar H_2 pressure, 1000 rpm, 6 h, 0.75 g of NiMoS, 2.25 g of Kraft lignin, and 75 mL of hexadecane.

pressure, and 6 h. A total bio-oil yield of 27.9% was achieved after 6 h as shown in Fig. 3. Among the detected compounds, 13.1% of the liquid yield was composed of cycloalkane-derived compounds. Traces of other products from the hydrotreatment of pyrolysis oil included pentanoic acids, sulfurous acids, carbonic acids, hexanoic acids, benzaldehyde-derived compounds, and alcohols like pentanol that amounted up to 9.9% of products, as detected by the 2D GC × GC-MS. Another interesting observation when running only pyrolysis oil hydrotreatment was that there were no solid char products observed at the end of the hydroprocessing. In contrast, for the Kraft lignin hydrotreatment, a char yield of 14.7% was obtained. This result led to further investigation by increasing the amount of pyrolysis oil to 4.4 g. An increase in the liquid product yield detectable by 2D GC × GC-MS to 44.3% was obtained from doubling the amount of pyrolysis oil feed. Similarly, in this experiment, no solid char product was detected when hydrotreating an increased amount of pyrolysis oil (Fig. 3).

The concept of co-hydroprocessing lignin and pyrolysis oil was then implemented. Different ratios of Kraft lignin (KL) and pyrolysis oil (PO) were examined in the co-hydrotreatment, and solid residues and bio-oil liquid product yields are shown in Fig. 3. With a 1:0.1 wt ratio feed of Kraft lignin and pyrolysis oil, 16.8% solid char residues was obtained at the end of the hydrotreatment. A char-suppressing effect of the pyrolysis oil in the Kraft lignin hydrotreatment was not observed, instead, the char yield increased slightly from the reference experiment at 14.7% (only Kraft lignin) to 16.8%. The bio-oil yield obtained in this hydrotreatment (KL:PO ratio of 1:0.1) was 29.6%, of which 27.2% was composed of cycloalkanes and alkylbenzenes. Interestingly, an increased amount of co-processing feed of pyrolysis oil (lignin to pyrolysis oil ratio of 1:0.5) in the co-hydroprocessing decreased the solid yield to approximately 6%. This result shows that co-feeding a suitable amount of pyrolysis oil in the hydrotreatment of Kraft lignin was able to reduce the production of recondensation products indicated by the reduced solid char yield. Even more interestingly, when the lignin to pyrolysis oil feed mass ratio was increased to 1:1, an undetectable level of solid char and an increased bio-oil yield of 42.8% were achieved. This experiment was repeated and indeed, the same results were achieved without detectable solid formation.

These experiments showed excellent results in terms of the apparent ability of co-feeding pyrolysis oil to suppress the formation of solid char products from lignin repolymerization. The result inferred that an optimal amount of pyrolysis oil supplemented in the Kraft lignin hydrotreatment was able, not only to suppress but even completely prevent the solid product formation. The presence of various pyrolysis oil compounds with certain advantageous functional groups at the beginning of the co-hydrotreatment was able to stabilize the lignin-derived intermediates before they repolymerized to condensed solid

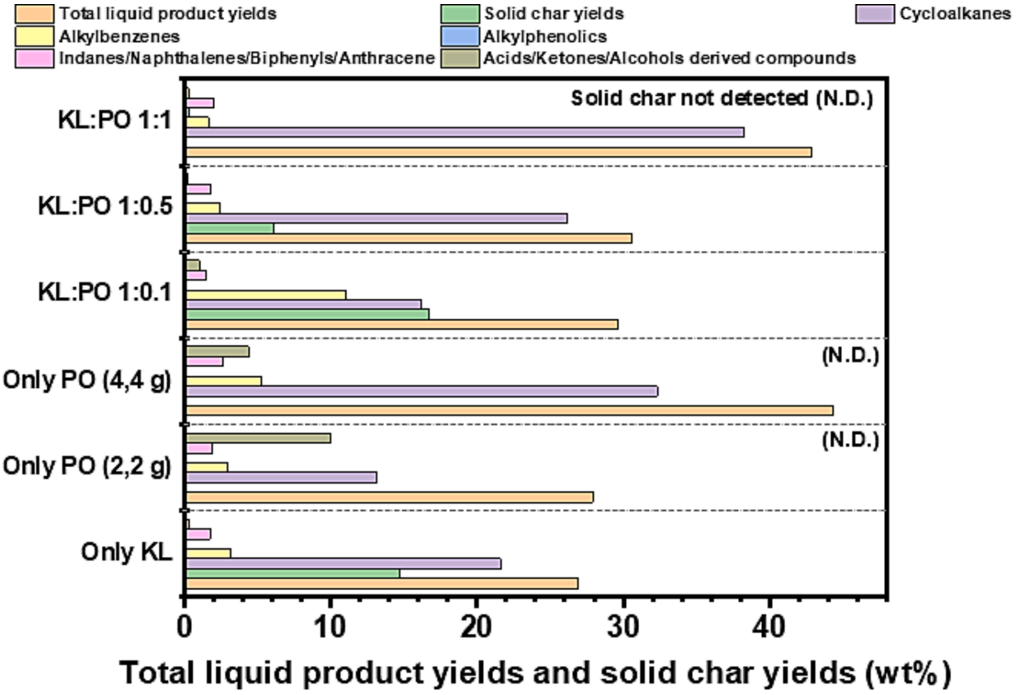


Fig. 3. Co-hydroconversion of Kraft lignin (KL) and pyrolysis oil (PO) over unsupported NiMoS. Operational parameters: 400 °C, 6 h, 75 bar total hydrogen pressure, 1000 rpm, and 75 mL of hexadecane as solvent. The Kraft lignin amount was fixed at 2.25 g and the pyrolysis oil amount was varied. The weight % (wt%) reported was calculated based on the total reactant Kraft lignin and pyrolysis oil feed.

char and also ultimately improved the rate of Kraft lignin liquefaction by facilitating the depolymerization resulting in an improved liquid oil yield.

3.4. Investigating the effect of pyrolysis oil model compounds as co-reactants in Kraft lignin hydrotreatment

Co-processing of pyrolysis oil and Kraft lignin exhibited excellent results and was even able to completely suppress the solid char formation. To deepen our understanding of the co-hydroprocessing of Kraft lignin with pyrolysis oil, we examined the hydrotreatment of Kraft lignin with several model compounds representative of different compounds found in pyrolysis oil. Firstly, different phenols (phenol and propylphenol) and saturated cyclohexanol compounds (cyclohexanol and propylcyclohexanol) were studied in the co-hydrotreatment of Kraft lignin. An increasing trend in terms of bio-oil yields can be observed in the order of: propylphenol (14.7%) < propylcyclohexanol (37.8%) < phenol (44.6%) < cyclohexanol (49.7%). Both saturated molecules, 4-propylcyclohexanol, and cyclohexanol, gave lower char yields of 9% and 6.8%, respectively, compared to their unsaturated ring counterparts. This could be attributed to the saturated rings of both compounds providing hydrogen radicals that react with lignin fragments and radicals, subsequently blocking the radical coupling that otherwise forms C-C bonds.

The effect of a larger pool of model pyrolysis oil compounds was selected for comparison that included: 4-propylguaiacol (hydroxyl, methoxy, and propyl groups), guaiacol (hydroxyl, and methoxy groups), phenol (only hydroxyl group), anisole (only methoxy group), benzaldehyde (only formyl group), acetic acid (only carboxyl group), and hydroxyacetone (only carbonyl group). The effect of the functional groups (hydroxyl, methoxy, alkyl, carbonyl, formyl, and carboxyl) on the yield of bio-oils and solid chars for co-hydrotreatment with Kraft lignin is presented in Fig. 4b). The experiment where only Kraft lignin was used as the sole reactant in the hydrotreatment was taken as a reference for comparison (Fig. 4b)). The condensation rate of large polymeric lignin fragments was found to be extensively suppressed by the presence of three different functional groups (hydroxyl, methoxy, and propyl-) in the case of 4-propylguaiacol (PG), evidently from the scarcely low char yield (3.7%) compared to all other co-reactants. Noteworthy, in the reference experiment where no co-reactant was used, the catalytic Kraft lignin hydrotreatment gives a relatively high char yield of 14.7%, and a bio-oils yield of 26.9% (from 2D GC × GC-MS) in which the yields for cycloalkanes and alkylbenzenes are 21.6% and 3.2%, respectively.

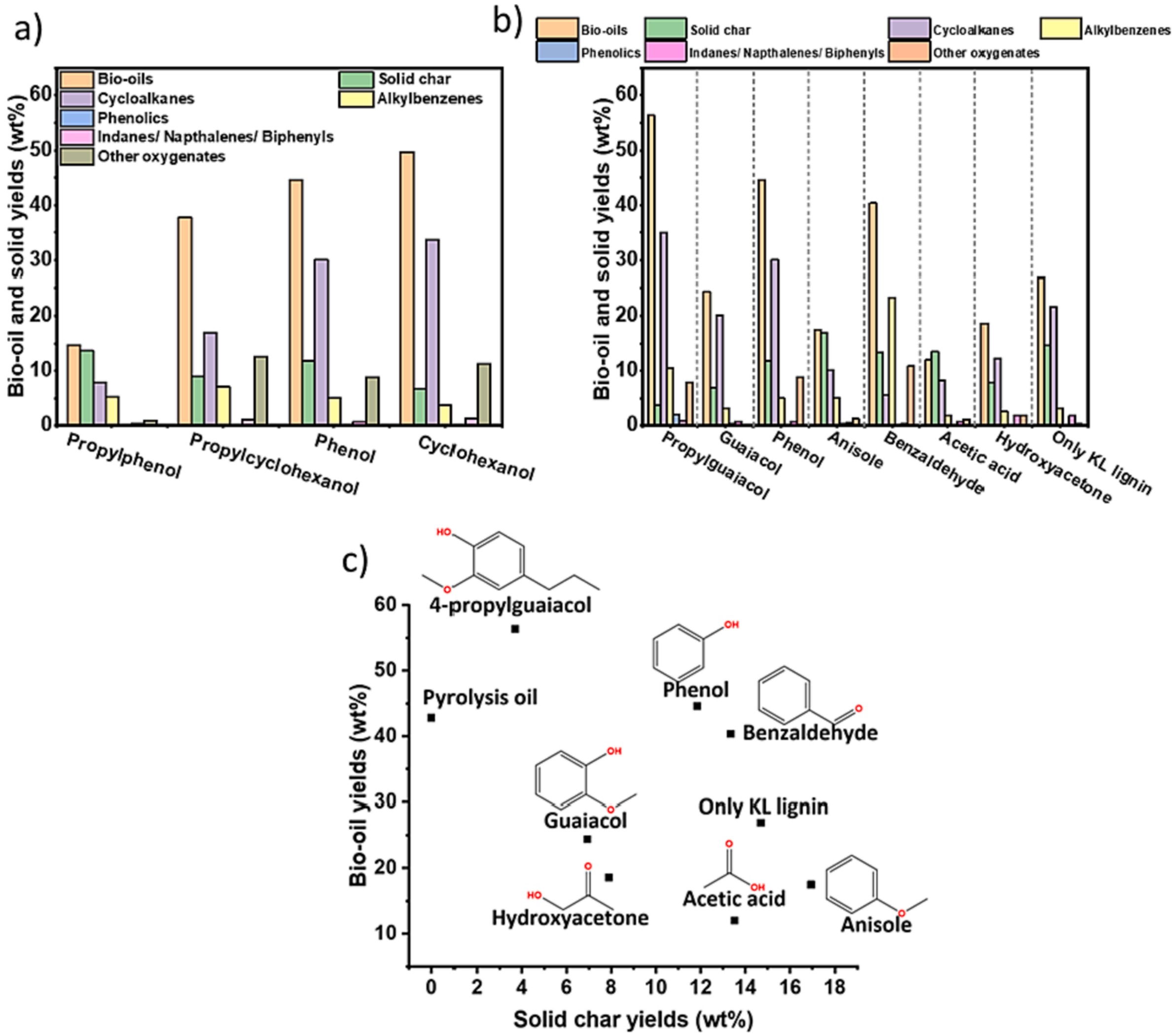


Fig. 4. Co-hydrotreatment of Kraft lignin with different model compounds. a) Effect of ring saturation b) Effect of various functional groups on the bio-oil yields and solid residues. Reaction conditions: 400 °C, 75 bar total H_2 pressure, 1000 rpm, 6 h, and KL:monomer mass feed ratio of 1:1. Monomers included: 4-propylguaiacol, guaiacol, phenol, anisole, benzaldehyde, acetic acid, and hydroxyacetone c) An overview of the ranking of the different molecules with different functional groups in terms of bio-oil yields and solid char yields in the co-hydrotreatment with Kraft lignin.

Apart from PG, co-reactants like phenol and benzaldehyde were also found to enhance the depolymerization of Kraft lignin, resulting in higher bio-oil yields of 44.6% and 40.3%, respectively. Both tests also resulted in a slightly lower solid char production (11.9% for phenol and 13.3% for benzaldehyde) as compared to the reference experiment with only Kraft lignin. Interestingly, for benzaldehyde, a high yield of alkylbenzenes (23.3%, yellow bar in Fig. 4b) was observed, which was not the case for PG and phenol where the major product was cycloalkane-derived compounds. Whereas for guaiacol, anisole, acetic acid, and hydroxyacetone, comparatively low bio-oil yields can be observed compared to the bio-oil yield achieved from only Kraft lignin hydrotreatment (Fig. 4b)). For instance, anisole as a co-reactant in the Kraft lignin co-hydrotreatment gives a poor bio-oil yield of 17.5% and also a higher char yield of 16.9%. These results provide insight into the importance of multiple functional groups of the co-reactant, for instance as in PG, in appearing to have a synergistic effect in limiting the rate of lignin fragment repolymerization during the hydroconversion process over the unsupported NiMoS catalyst.

Fig. 4c) gives an overview of the ranking of the different molecules with different functional groups in terms of bio-oil yields and solid char yields. Several observations can be obtained in Fig. 4c). Firstly, anisole as a co-reactant gives the highest char yield of 17% as compared to all other co-reactants and also only the Kraft lignin hydrotreatment. While other co-reactants like PG, guaiacol, hydroxyacetone, phenol, benzaldehyde, and acetic acid provide a diminished char yield (scattered in Fig. 4c)) as compared to the reference experiment (only Kraft lignin). These reactants were found to be beneficial in terms of reducing the char formation reactions, with PG showing the best char-suppressing capability during co-hydrotreatment with lignin. In terms of the bio-oil yields, PG, phenol, and benzaldehyde show a higher bio-oil yield as compared to the other co-reactants including the reference experiment. A ranking considering the char-reducing potential of the individual compounds with different functional groups is as follows: PG (hydroxyl, -OH, methoxy, $-OCH_3$, and propyl, $-C_3H_7$) > guaiacol (hydroxyl, -OH, methoxy, $-OCH_3$) > hydroxyacetone (carbonyl, $-R_2C = O$) > phenol (hydroxyl, -OH) > benzaldehyde (formyl, $-R-CH = O$) > acetic acid (carboxyl, -COOH) > anisole (methoxy, $-OCH_3$). A summary of the GC × GC-MS detectable yields of bio-oil products and the char yields obtained by the co-hydroprocessing of Kraft lignin and the various oxygenated monomers over the unsupported NiMoS catalyst are shown in Table 2. The other products are the non-detectable compounds by GC such as heavy lignin oligomers, water molecules, and light gaseous products. Since 4-propylguaiacol (PG) was the model compound that gave the lowest char production as well as the highest bio-oil yield, its combination of functional groups under varying conditions was further studied.

3.4.1. Effect of the alkyl chain ($-C_xH_y$), hydroxyl (-OH) group, and methoxy ($-OCH_3$) in the oxygenate monomer co-reactants

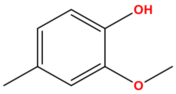
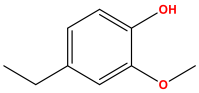
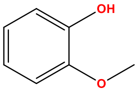
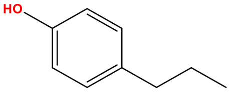
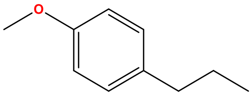
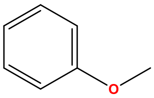
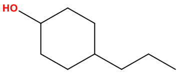
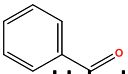
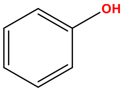
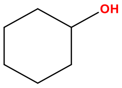
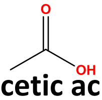
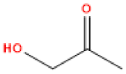
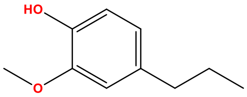
To understand the role of PG in the co-hydrotreatment with Kraft lignin, different oxygenated monomers with its functional groups (-OH, $-OCH_3$, and $-C_nH_{2n-1}$) were co-fed with Kraft lignin to investigate their effect on the bio-oil yields, solid residue yields, and product selectivity. The selected oxygenated compounds for these sets of experiments were guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol (PG), anisole, propylanisole, and 4-propylphenol. The chemical structures for these compounds are shown in Table 2. The respective bio-oils and solid residue yields, and liquid product selectivity for each monomer have been grouped for comparison with PG (Fig. 5). The addition of a methyl, ethyl, and propyl functional group to a guaiacol unit was studied and compared as shown in Fig. 5a). By varying, the substituted alkyl chain length based on guaiacol, there are some changes in terms of the solid residue production, ranging from 6.8% to 3.7%, where PG possesses the lowest char amount. When increasing the chain length from the ethyl (C_2H_5) to propyl (C_3H_7) group of the guaiacol unit, the solid yield reduces by almost half from 6.2% to 3.7%. An increasing trend of bio-oil yields (orange bar in Fig. 5a)) from 15.3% to 56.4%, can be observed for 4-methylguaiacol and 4-propylguaiacol, respectively. It can also be noted that when PG was used as a co-reactant for Kraft lignin hydrotreatment, a significant cycloalkane yield of 35% derived from Kraft lignin and PG was observed (Fig. 5a)).

The effect of the presence of a hydroxyl (-OH) group was studied by comparing the results for guaiacol, anisole, propylguaiacol, and propylanisole as co-reactants in Kraft lignin co-hydrotreatment (Fig. 5b)). The effect of the presence of a hydroxyl group can be seen by comparing the solid residue yield when using guaiacol and anisole as co-reactants in Kraft lignin co-hydrotreatment. When guaiacol was used, a large reduction in solid yield (green bar in Fig. 5b)) was achieved compared to anisole, from 17% to 6.3%. Similarly, when comparing the char yield achieved while using PG and propylanisole during co-hydrotreatment, a significant solid reduction capability was observed, where PG reduces the production of the undesired repolymerization products to 3.7%. Whereas propylanisole gave a similar solid yield (15.3%) as compared to the reference experiment using only Kraft lignin (14.7%). The effect of the presence of the hydroxyl functional group can also be reflected in the yield of bio-oils detected by 2D GC × GC-MS. The bio-oil yields achieved for guaiacol and propylguaiacol were 24.4% and 56.3%, respectively. These higher bio-oil yields as compared to their counterparts (17.5% for anisole and 15.3% for propylanisole) were mainly attributed to the stabilizing effect of the hydroxyl group and also its ability to suppress the condensation reactions between lignin-derived intermediates forming heavy charring products. These comparisons highlighted the beneficial effect of the presence of the hydroxyl group in suppressing the condensation rates of large lignin polymeric fragments and also capping the radical species resulting in improved bio-oil yields.

The subsequent work then studies the effect of a second functional group (the methoxy group) by selecting phenol and propylphenol as co-reactants for comparison (see Table 2). Fig. 5c) shows the effect of the methoxy group by comparing guaiacol and phenol, and PG and propylphenol. The absence of the methoxy group in phenol resulted in a higher char yield of 11.8% when compared to guaiacol (6.3%). When comparing PG with propylphenol, the absence of a methoxy group in propylphenol also resulted in a higher solid char yield of 13.7%. Interestingly, the co-hydrotreatment of Kraft lignin with anisole (with only one methoxy group) resulted in a higher char yield (17.5%). From these sets of results, it can be concluded that there is a dependency of the benzene ring functionalization on the condensation rate of depolymerized lignin fragments resulting in different char yields. The effect of the presence of a methoxy group with hydroxyl and/or alkyl groups greatly affects the char suppression capability of a co-reactant during co-processing. As discussed above, the presence of hydroxy and methoxy groups in the co-reactant suppresses the char formation reactions. This is shown in the case when PG was used as a co-reactant, where both functional groups are present, revealing a remarkably low char yield of 3.4%. Similarly, when comparing guaiacol (both -OH and $-OCH_3$ groups), phenol (only -OH group), and anisole (only $-OCH_3$ group) with char yields of 6.3%, 11.8%, and 16.9%, respectively, the co-hydrotreatment with guaiacol having the two functional groups gave the lowest char yield.

Other than the hydroxy and methoxy functional groups, the effect of the presence of the alkyl group can also be observed by comparing three pairs (PG versus guaiacol, propylphenol versus phenol, and propylanisole versus anisole) during co-hydrotreatment of Kraft lignin. The general trend that can be observed is that the presence of the alkyl group reduces the formation of repolymerization products. However, one exception is that the char yield was higher for propylphenol than for phenol. Whereas when using guaiacol and anisole as co-reactants, both resulted in higher char yields when compared to using PG and propylanisole, respectively. The favorable effect of the alkyl group could be discussed in connection with a previous study by Huang et al. [34,35]. The authors confirmed the stabilizing effect of ethanol by O-alkylation of the phenolic hydroxyl groups and C-alkylation of the aromatic rings

Table 2
Product yields and char yield (wt% on feed) from co-hydrotreatment of Kraft lignin with different model pyrolytic-derived oxygenates over a hydrothermally synthesized unsupported NiMoS catalyst at 400 °C, 75 bar total hydrogen pressure, a feed mass ratio of KL:monomer of 1:1, 1000 rpm, and 6 h.

		Bio-oil product yield (wt%)					Solid char yield (wt%)
Entry	Co-reactant	Cycloalkanes	Alkylbenzenes	Phenolics	Indanes/Naphthalenes/Biphenyls	Other oxygenates	
1	 **4-methylguaiacol**	12.2	2.2	0.2	0.6	0.2	6.8
2	 **4-ethylguaiacol**	8.4	8.0	1.8	0.8	6.6	10.0
3	 **Guaiacol**	20.2	3.2	0.3	0.8	0.1	6.9
4	 **4-propylphenol**	7.9	5.3	0.1	0.4	1.0	13.7
5	 **P-propylanisole**	7.3	6.9	0.0	0.5	0.6	15.3
6	 **Anisole**	10.2	5.0	0.4	0.6	1.2	16.9
7	 **4-Propylcyclohexanol**	16.9	7.1	0.0	1.0	12.6	9.0
8	 **Benzaldehyde**	5.6	23.3	0.0	0.4	10.8	13.3
9	 **Phenol**	30.0	5.0	0.0	0.7	8.9	11.8
10	 **Cyclohexanol**	33.7	3.7	0.0	1.2	11.2	6.8
11	 **Acetic acid**	8.3	1.9	0.0	0.8	1.1	13.5
12	 **Hydroxyacetone**	12.3	2.6	0.0	1.9	1.9	7.9
13	 **4-propylguaiacol**	35.0	10.5	2.1	0.9	7.9	3.7

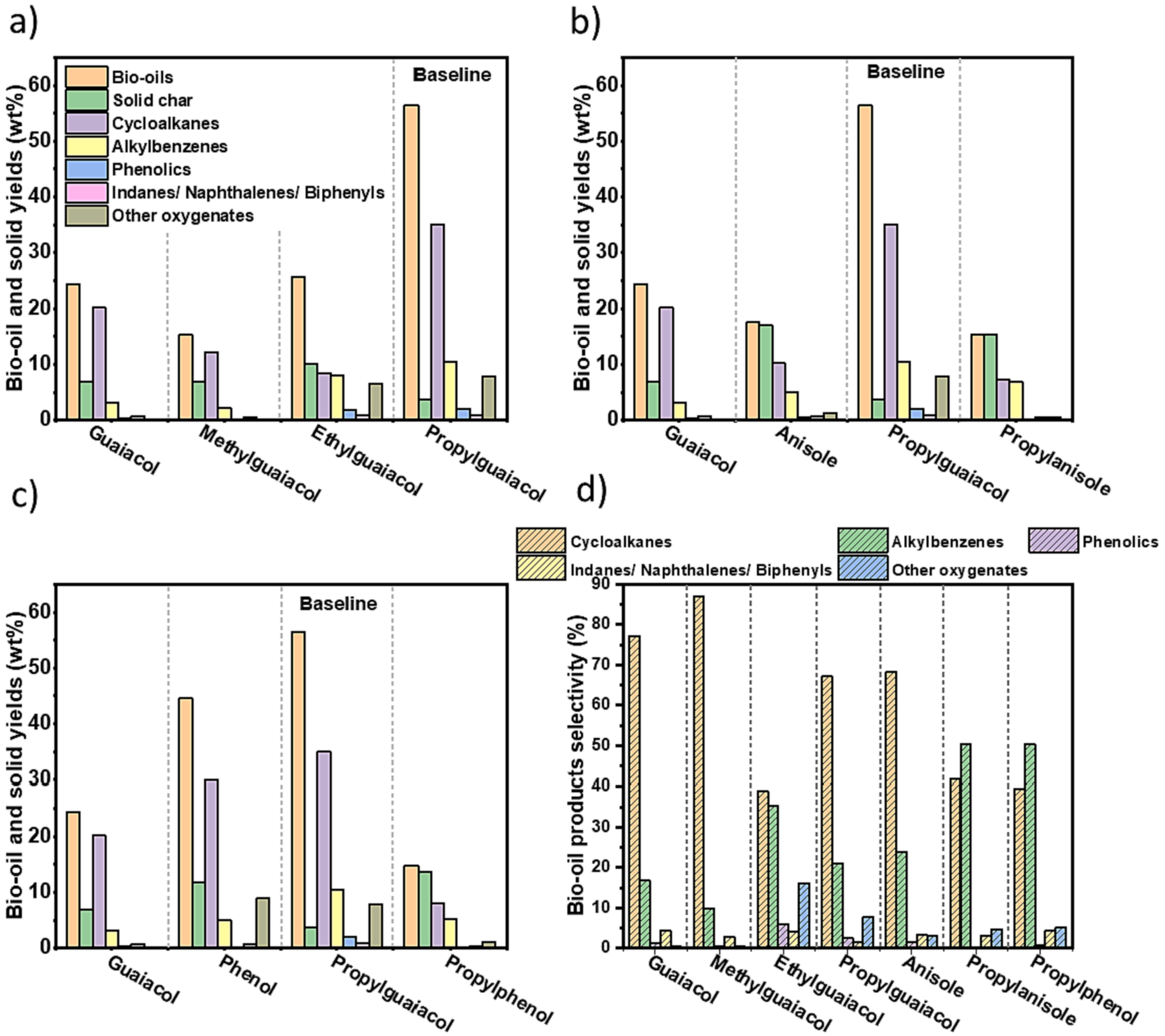


Fig. 5. Co-hydrotreatment of Kraft lignin with different propylguaiacol functional groups. a) Effect of the alkyl chain (-C_xH_y) b) Effect of the hydroxyl (-OH) group c) Effect of the methoxy (-OCH_3) in oxygenated monomers, and d) product selectivity in the co-hydrotreatment of Kraft lignin and monomers. Reaction conditions: 400 °C, 75 bar total H_2 pressure, 1000 rpm, 6 h, and Kraft lignin:monomer mass feed ratio of 1:1. Monomers included: guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, anisole, 4-propylanisole, and 4-propylphenol.

with reactive intermediates [35]. These ‘capping’ reactions by ethanol as a solvent in lignin depolymerization prevented the formation of quinone methide intermediates (precursors of char formation reactions) by subsequently blocking the repolymerization reaction induced by the reactive intermediates [35].

3.4.2. *Influence of mass ratio of Kraft lignin versus 4-propylguaiacol during co-processing*

The influence of the mass ratio between Kraft lignin (KL) and propylguaiacol (PG) was studied using the ratios KL:PG 1:2, 1:1, 1:0.5, and 1:0. The experiments were performed using hexadecane as a solvent over the unsupported NiMoS catalyst at the reaction condition of 400 °C, 75 bar total H_2 pressure for 6 h (Fig. 6a)). Blank experiments, in which the hydrotreatment was performed without catalysts were also conducted as reference experiments. As expected, the undesired repolymerization of the reactive intermediates formed during the non-catalytic depolymerization of lignin resulted in a high solid residue yield of 54.8% and a low bio-oil yield of 17.9% (Fig. 6a), Exp 6). The total bio-oil yield, determined by GC × GC-MS, included cycloalkanes, alkylbenzenes, phenolics, indanes/naphthalenes/biphenyls and other oxygenates such as alcohols and ketones. Interestingly, the solid residue yield (57.9%) is even higher when co-feeding both lignin and PG without catalysts (Fig. 6a), Exp 5), as compared to the experiment in which only lignin was used (evidently shown in the images of solid char residues that remained in the bottom of the autoclave and also around the stirrer in Fig. S1). The higher solid residue yield could be explained by the extensive reactions between the depolymerized lignin fragments and also the added propylguaiacol via repolymerization, radical coupling, and condensation without the activation of hydrogen provided by the presence of a catalyst. The importance of the catalyst for facilitating hydrogenation reactions that stabilize reactive intermediates and eventual hydrodeoxygenation reactions is evident by the high selectivities for phenolics and other oxygenate compounds in the experiments without catalyst and only KL, and then even higher with PG co-reactant (Fig. 6b), Exp 5 and 6).

Further catalytic experiments were performed to understand the influence of adding PG as a co-reactant during lignin hydrotreatment. There was a significant drop in undesired solid product yield when PG

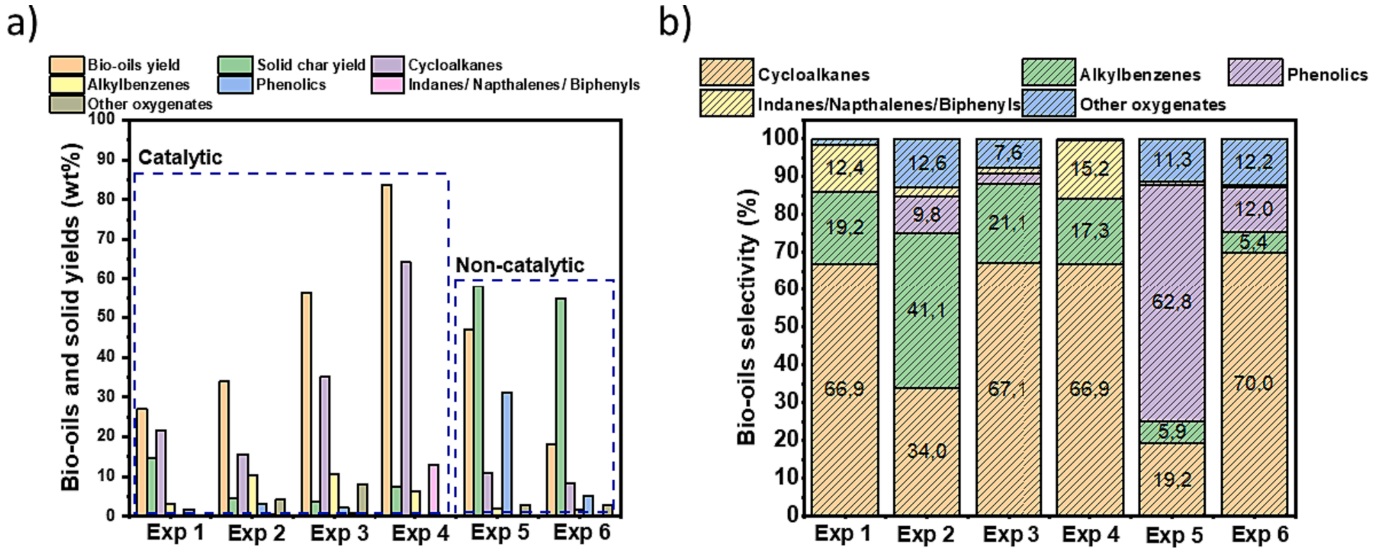


Fig. 6. a) Comparison of bio-oil yield and solid yield from experiments with different feed mass ratios between propylguaiacol (PG) and Kraft lignin (KL) (Catalytic experiments: Exp 1: Only lignin, Exp 2: KL:PG 1:2, Exp 3: KL:PG 1:1, Exp 4: KL:PG 1:0.5, Non-catalytic experiments: Exp 5: KL:PG 1:1 and Exp 6: Only lignin) b) Products selectivity (cycloalkanes, alkylbenzenes, phenolics, indanes, naphthalenes, biphenyls and other oxygenates) comparison for co-hydrotreatment of lignin with PG.

was a co-feed to the catalytic hydrotreatment. A KL:PG feed ratio of 1:1 gave the lowest solid yield (3.7%). Moreover, it gave a notable bio-oil yield (~56.4%). It was worth noting that for the mass ratios of KL:PG of 1:2 and 1:0.5, both co-hydrotreatment tests also gave low solid residue yields of 4.4% and 7.5%, respectively.

Fig. 6b) shows the reaction product's selectivity among products from the catalytic and non-catalytic hydrotreatment of Kraft lignin and PG in different mass ratios. The non-catalytic hydrotreatment of Kraft lignin and lignin + PG resulted, as mentioned above, in phenolic selectivities of 12.0% and 52.8%, respectively. Other oxygenates such as alcohol-derived compounds and ketones were in the range of 11–12% for both of these non-catalytic tests. On the other hand, for the catalytic Kraft lignin hydrotreatment, HDO activity was apparent and for the case with the KL:PG ratio of 1:1, no phenolics were detected and 66.9% cycloalkanes and 19.2% alkylbenzenes product selectivities were achieved. For the KL:PG mass ratio of 1:0.5, the product selectivity was similar to that with only Kraft lignin hydrotreatment with 66.9% selectivity for cycloalkanes, as shown in Fig. 6b), while alkylbenzene and polyaromatic product selectivities were 17.3% and 15.2%, respectively. When the feed of PG increased as KL:PG mass ratio decreased from 1:0.5 to 1:2, more phenolics were detected, giving a phenolics selectivity of 9.8% in the case of the KL:PG of 1:2 mass ratio. This could be reasoned by the contribution of derivatives from PG in the co-hydrotreatment as previously discussed and is evident by the comparison of GC × GC spectrums in Fig. 7b) without PG and Fig. 8b) with PG. Since the hydrotreatment with a mass ratio of KL:PG of 1:1 provided the lowest undesired insoluble char products and reasonable total bio-oil yields, this same mass ratio between Kraft lignin and co-reactant model compounds was selected for further experiments.

3.4.3. *Effect of reaction time on co-hydrotreatment of Kraft lignin with 4-propylguaiacol*

The influence of the reaction time on the co-hydroprocessing of Kraft lignin and 4-propylguaiacol (PG) was also investigated by performing the experiments for 0 h, 3 h, 6 h, and 8 h at 400 ℃, with the total H_2 pressure of 75 bars and using the unsupported NiMoS catalyst. It should be noted that the notation of 0 h means the hydrotreatment reaction was stopped once the reaction temperature of 400 ℃ was reached by immediately cooling down (cooling takes 25 mins) to room temperature. The purpose of performing this experiment (0 h) was to understand more about the solid char formation during the heating (takes 40 mins) and cooling of the reactor system. Fig. 9 compares the bio-oil yield calculated based on the identified liquid products from the 2D GC × GC-MS analysis and also solid char yields obtained after different reaction times with and without PG co-processing. The results show that as much as 30.6% (for KL + PG) and 35% (KL) solid char were formed during the heating of the reactor to 400 ℃ (time = 0 h). As expected during the heating period, Kraft lignin was depolymerized and the depolymerized lignin fragments started to undergo coupling reactions at low temperatures which eventually resulted in high solid char formation. These results are in line with the report earlier about lignin pyrolysis. Hosoya et al. reported that the condensation reaction was a major pathway in the early stage of the lignin dimer pyrolysis process and it was effective at a lower pyrolysis temperature [58]. Some of the depolymerized lignin had also further reacted and formed different liquid products. These products included alkylated phenolics, cycloalkanes, aromatics, and polyaromatics as can be seen in the 2D GC × GC spectra shown in Fig. 7a) and Fig. 8a). This can be reasoned by that Kraft lignin starts to decompose thermally at 250 ℃ in which the ether linkages, β-O-4 bonds are cleaved forming monolignols [59]. PG in the co-hydrotreatment was also partially reacted and underwent various reactions, but especially demethoxylation to form propylphenol as is prominent in the 2D GC × GC spectra in Fig. 8a).

As the reaction progresses, the char yields dropped drastically from 0 h to 6 h in both the Kraft lignin hydrotreatment and also co-hydrotreatment of Kraft lignin and PG as shown in Fig. 9. The decrease in the solid char residues can be explained by the formed solids were further depolymerized into oligomers and eventually monomers through reactions like hydrogenolysis, ring hydrogenation, and deoxygenation. The formation of these different oligomers and monomers eventually leads to an increase in the total bio-oil yield as the reaction progresses. For the co-hydrotreatment of Kraft lignin and PG, a maximum bio-oil yield of 56.3% was achieved after 6 h, however, it dropped significantly to 27.5% at 8 h. These results suggest that prolonging the hydrotreatment duration negatively impacted the yield of bio-oils as the monomer units generated might undergo polymerization again and form heavy oligomers and light gases. For the Kraft lignin hydrotreatment, a similar trend of increasing bio-oil yields can also be observed with a maximum bio-oil yield of 27% achieved at 6 h, which slightly dropped to 24%. The decreased bio-oil yields with only a slight

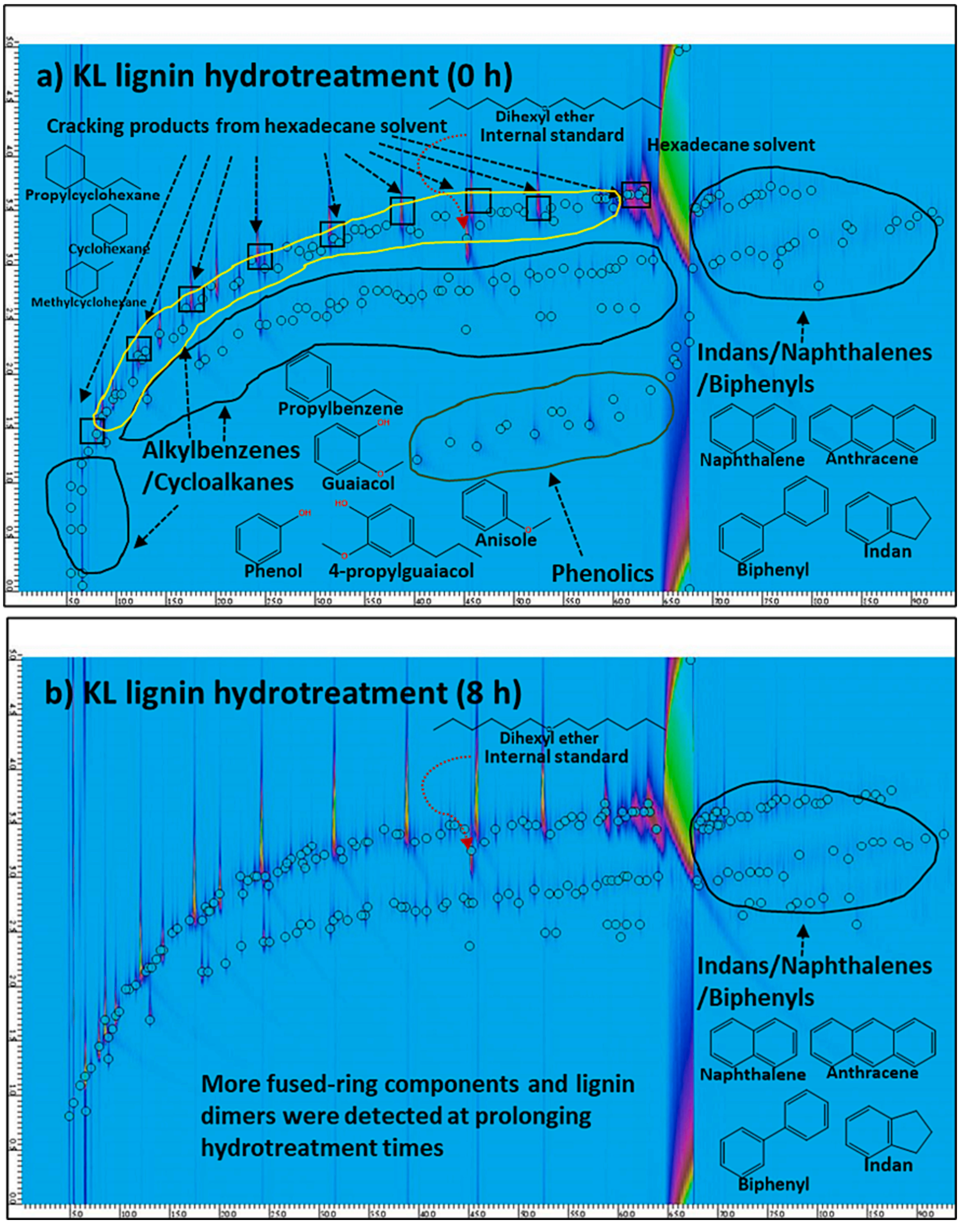


Fig. 7. 2D GC × GC chromatogram of the detectable liquid phase products evolved during different reaction times a) 0 h and b) 8 h from the Kraft lignin hydrotreatment. Reaction conditions: 400 °C, total H_2 pressure of 75 bars, 0.75 g of NiMoS catalyst, 2.25 g of KL lignin, 1000 rpm, and 75 mL of hexadecane solvent.

increase in the char products after 6 h can be reasoned by the possibility that oxygenated monomers undergo oligomerization forming heavy liquid soluble compounds that are non-detectable by the GC. This is evident by the fact that the decrease in bio-oil yield later process is more prominent in the case of co-processing in which oxygenated monomers are present already at the start of the process and remain in high concentrations throughout the process (Fig. 8a) to b)). These available monomers were likely to oligomerize with prolonged reaction times. Besides, the solid residues formed can also undergo further reactions like liquefaction forming heavy oligomers which lead to poorer bio-oil yield.

There are similarities for both cases where Kraft lignin underwent hydrotreatment as a sole reactant and also with PG, such as high production of insoluble solid char products during the early heating stage of the hydrotreatment and that the char production decreased over time. Another interesting observation that can be obtained by comparing both hydrotreatments with and without PG, is that there was a significant reduction in insoluble solid char formation before 6 h in the case when adding PG. The beneficial effect of adding PG in the co-hydrotreatment was most apparent from 0 h to 6 h which might be reasoned that PG plays a crucial role in stabilizing the hydrotreatment intermediates and suppressing the char formation reaction resulting in a low char yield of 3.7%. This can be further demonstrated by the 4-fold higher char yield of 14.7% at 6 h in the case of only Kraft lignin hydrotreatment (absence of PG). It is notable that PG is not as effective during the heating period (before 0 h) in preventing solid formation. This could be connected to the fact that the catalyst is not as effective at enabling hydrogenation reactions at lower temperatures. It was also seen from the non-catalytic experiments that adding PG caused increased solid formation (Fig. 6a), Exp 5 and 6).

These findings further led us to investigate the role of PG in the depolymerization routes of Kraft lignin hydrotreatment. The FTIR spectra of the starting material, i.e. Kraft lignin, and also the lignin-derived char from both Kraft lignin hydrotreatment and co-hydrotreatment with PG for different hydrotreatment times are shown in Fig. 10a-b). A broad band at 3327 cm^{-1}, attributed to the hydroxyl groups in phenolic form, and the band at 2937 cm^{-1} corresponding to

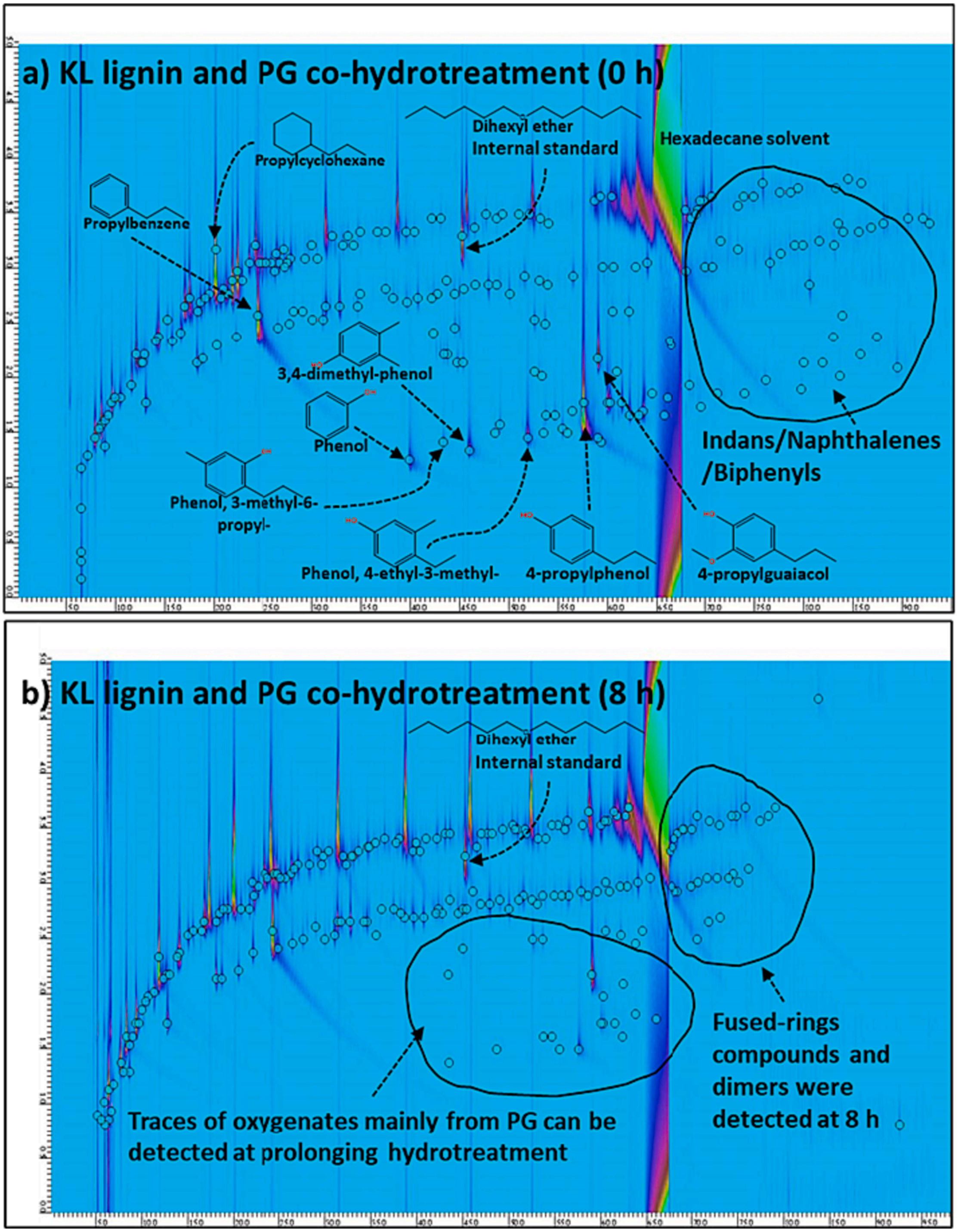


Fig. 8. 2D GC × GC chromatogram of the detectable liquid phase products evolved during different reaction times a) 0 h and b) 8 h from the Kraft lignin and PG (mass feed ratio of KL:PG 1:1) co-hydrotreatment. Reaction conditions: 400 ℃, total H_2 pressure of 75 bars, 0.75 g of NiMoS catalyst, 2.25 g of KL lignin, 1000 rpm, and 75 mL of hexadecane solvent.

the C-H stretching in aromatic methoxy groups can be observed for Kraft lignin starting materials [60]. Moreover, the usual C-H deformation in lignin and the carbonyl stretching conjugated with aromatic ring skeletons at 1454 cm^{-1} and 1593 cm^{-1}, respectively can be observed in the FTIR spectra [61]. The aromatic skeletal vibration of guaiacyl and syringyl units that are present in the lignin aromatic structure can also be identified in the wavenumber range of 1000 cm^{-1} to 1600 cm^{-1} [61]. As the reaction progresses, the absorption peaks of Kraft lignin diminished rapidly from the 0 h to 8 h hydrotreatment, indicating the deconstruction of the complex lignin macromolecule structure. The insoluble char residue for the hydrotreatment shows a similar pattern for all runs and also peaks with weak intensity at 1421 cm^{-1} and 1593 cm^{-1} were observed indicating its aromaticity. A broad peak around 1124 cm^{-1}, representing the C-H plane deformation of the syringyl unit was also observed for the char residue from all hydrotreatment runs. Interestingly, the structure of the Kraft lignin begins to deconstruct as early as during the heating period of the reaction (0 h), and adding PG to the reaction did not affect the lignin deconstruction pathway. It was also worth highlighting that these results are in contrast to the results in a study by Joffres et al. [9]. In their study, the FTIR spectra of the initial

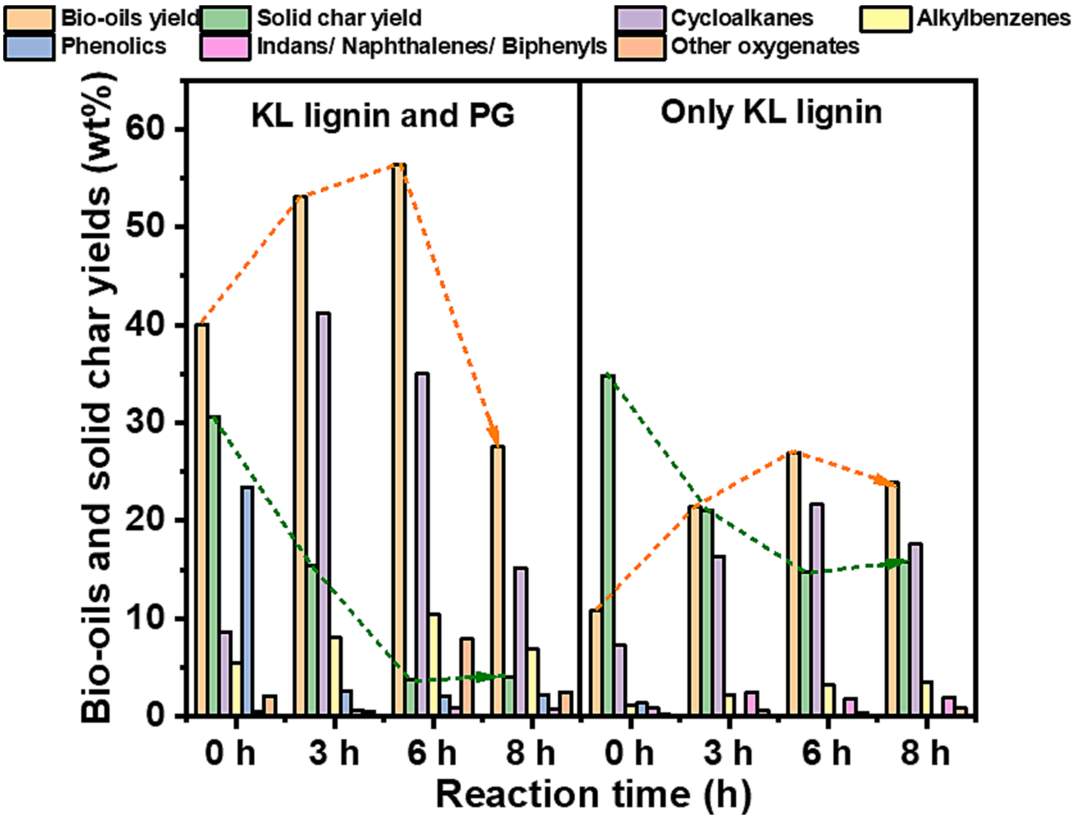


Fig. 9. Effect of different reaction times on the co-hydrotreatment of Kraft lignin (KL) and PG (feed mass ratio of KL:PG is 1:1) at 400 °C, total H_2 pressure of 75 bars, 0.75 g of NiMoS catalyst, 2.25 g of Kraft lignin, 75 mL of hexadecane solvent. The bio-oil yields are calculated based on the total initial intake of reactants.

wheat straw lignin showed a similar pattern as the lignin residue at time zero (at 350 °C after 14 min) [9]. It should be noted that our heating period was significantly longer (40 min) and also that we have used a higher temperature (400 °C). In our study during the heating period of the reactor, the disintegration of the solid Kraft lignin is certainly driven by the increasing temperature regardless of the presence of PG and produces the lignin-derived insoluble char product which further breaks down into smaller lignin fragments for further depolymerization. The high yield of insoluble char at 0 h (after 40 mins of heating) for both cases (with and without PG) can be reasoned by the lower activity of the catalyst for hydrogenation reactions at the low reaction temperatures. PG rather acted as a protecting agent that stabilizes the reactive depolymerized lignin derivatives preventing and limiting repolymerization, but primarily when the catalytic hydrotreatment reactions have reached their full extent. This is further demonstrated in the ^{13}C NMR measurement, as shown in Fig. 10c) and d), where several functional groups present in Kraft lignin were not observed in the solid residues even after the heating period (40 min). Liquid product analysis confirmed the presence of demethoxylated and deoxygenated products like alkylphenols and aromatics. It can be confirmed also from the ^{13}C NMR spectra that the resultant solid residue primarily consists of both aliphatic and aromatic carbon moieties with only small amounts of methoxy groups and C-O-containing groups.

It has been reported in various studies that lignin condensation reactions and lignin intermediate repolymerization are the main reasons for the formation of undesired condensed solid products which have been referred to as solid char in this study [5,6,58,62–64]. These reactions usually involve the formation of quinone methide intermediates which resulted in the generation of recalcitrant condensed interunit C-C linkages on the ortho- and *para*-positions that limit further conversion of lignin oligomers to monomers. Moreover, Liu et al. conducted a real-time experimental observation for pyrolysis of model lignin compounds like Guaiacylglycerol-β-guaiacyl ether and guaiacol with/without HSZM-5 and found that the repolymerization of small lignin oligomers can act as a competitive pathway for the formation of heavy oligomers which thereafter are forming lignin-derived char residues [65]. In addition, Nakamura et al. studied the condensation reactions of lignin model compounds like guaiacol, methylguaiacol, and methylveratrole under pyrolysis conditions (250 ℃, under air atmosphere, and 2 h) and identified the major lignin condensation pathways like vinyl condensation, quinone methide, and radical coupling mechanisms [63]. Okuda et al. studied the depolymerization of lignin in a mixture of water and phenol at 400 ℃ for the production of phenolics [64]. It was also discussed in their study that the cross-linking reactions between the depolymerized lignin fragments and residual lignin can further form heavier molecular weight fragments leading to the formation of char residues [64]. They revealed the addition of phenol as a capping agent in lignin depolymerization was able to capture the reactive species and active sites in larger fragments and suppress the formation of heavier fragments [64]. In this study, when PG was supplemented in the Kraft lignin hydrotreatment, the ‘capping’ effect of PG was demonstrated by the progressively decreasing yield of solid char residues in the early extent of the hydrotreatment, and primarily after a sufficiently high reaction temperature was reached to enable catalytic hydrotreatment. The cross-linking reactions were also suppressed by the entrapment of active lignin fragments and also the stabilization of reactive radical species by PG. As the reaction progresses, and with sufficient rates of catalyzed hydrogenolysis and hydrodeoxygenation reactions, the lower molecular compounds like cycloalkanes, alkylbenzenes, and phenolics increase which eventually contributed to an increased bio-oil yield. It should be noted that the total bio-liquid yields (GC detectable products) for the co-hydrotreatment of Kraft lignin and PG was higher as compared to only Kraft lignin hydrotreatment, which can be explained by the incorporation of reacted products from PG into the bio-oil early during

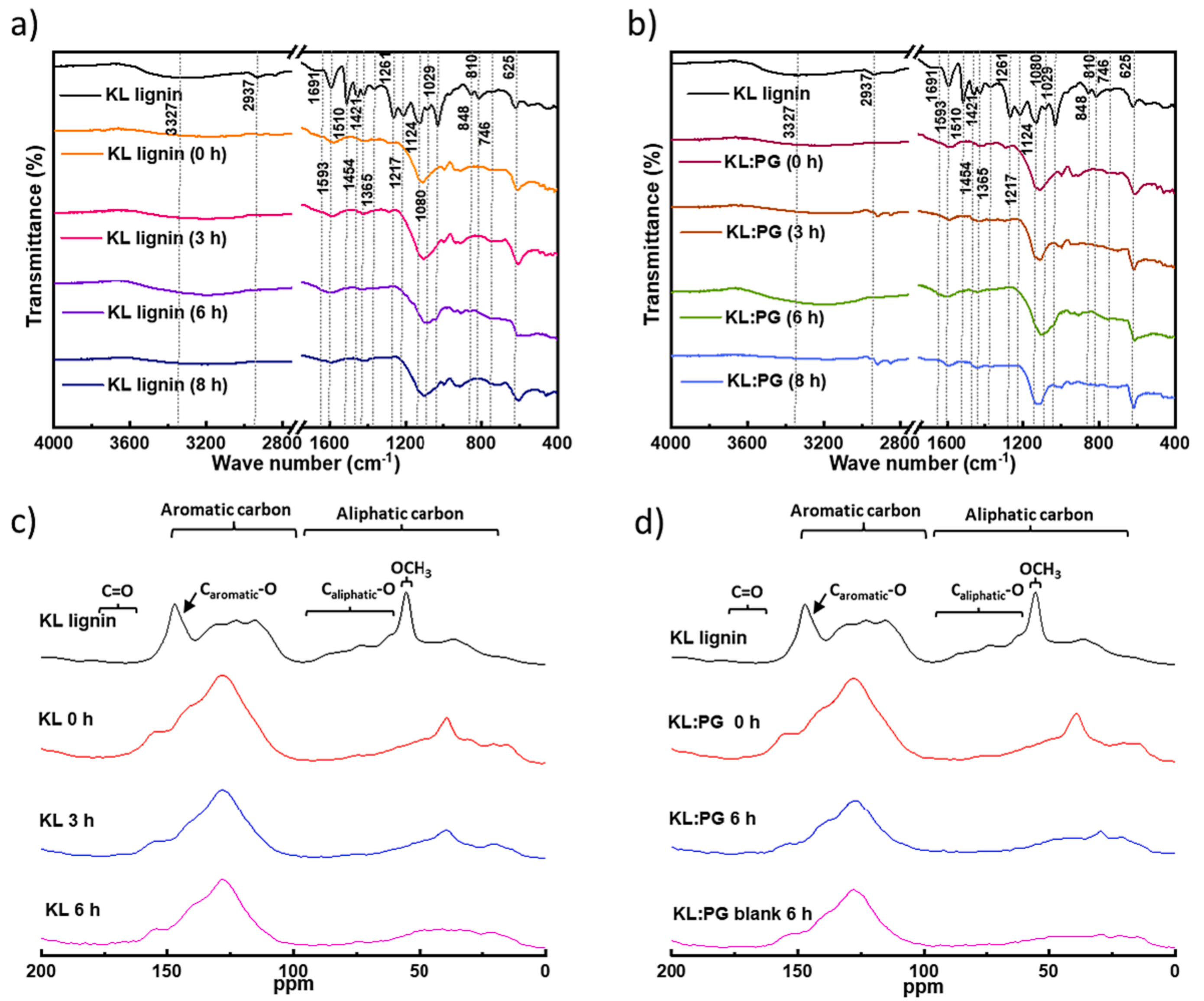


Fig. 10. FTIR spectra (a, b) and ^{13}C NMR spectra (c, d) of starting material Kraft lignin and the lignin-derived solid char products after varying hydrotreatment times for a) and c) Kraft lignin hydrotreatment and b) and d) Kraft lignin and PG co-hydrotreatment.

the liquefaction process.

3.4.4. *Effect of catalyst loading on co-hydrotreatment*

The effect of the catalyst to reactants (Kraft lignin and PG) ratio is examined using ratios 1:3, 1:6, and 1:12 (Fig. 11). These experiments aim to better understand the interaction between catalytic and non-catalytic reactions and their effect on the overall process. As expected, a higher loading of catalyst results in an increase in the bio-oil yield from 56.4% to 62%, when increasing the ratio from 1:6 to 1:3. The char formation is suppressed and results in a very low char yield of 2.9% when the catalyst loading is doubled. A higher loading of the unsupported NiMoS catalyst leads to a proportionately higher rate of catalytic reactions, which can aid in breaking down the complex lignin framework and improving hydrogenation activity that stabilizes the unstable reactive intermediates. The role of the unsupported NiMoS has also been elucidated in our previous study showing the enhanced accessibility of the NiMoS active sites and further stabilization of the unstable reactive lignin fragment intermediates [13]. The extra loading of NiMoS also allows PG to react forming products such as propylphenol and propylcyclohexanol, creating more ‘capping’ species that could react and stabilize cleaved lignin intermediates and block the repolymerization routes. Interestingly, it can be observed that 5.8% of the dimers, like indanes and naphthalenes, were detected when doubling catalyst loading. Chowdari et al. reported a similar positive effect on monomer yields and also char reduction when increasing the catalysts loading from 5 to 10 wt% [66]. Furthermore, when the amount of catalysts was halved in the case of catalyst:reactants ratio of 1:12 from 1:6, the bio-oil yield decreased even further from 56.4% to 38.5%. Moreover, a solid char yield of 27.4% was obtained in this experiment, this result corroborated with the experiment ran with higher catalyst loading and further demonstrates the apparent synergy between the stabilizing effect of PG (discussed in the previous section) and hydrotreatment reactions promoted by the catalyst.

3.5. *Reaction network for pyrolysis oil-assisted Kraft lignin hydrotreatment*

Findings in this study have prompted us to discuss further ways to avoid and limit the repolymerization and condensation reactions during the degradation and depolymerization of lignin in the context of hydroconversion. For example, Kim et al. summarized various efforts to avoid the undesired reactions that occurred during the fractionation and

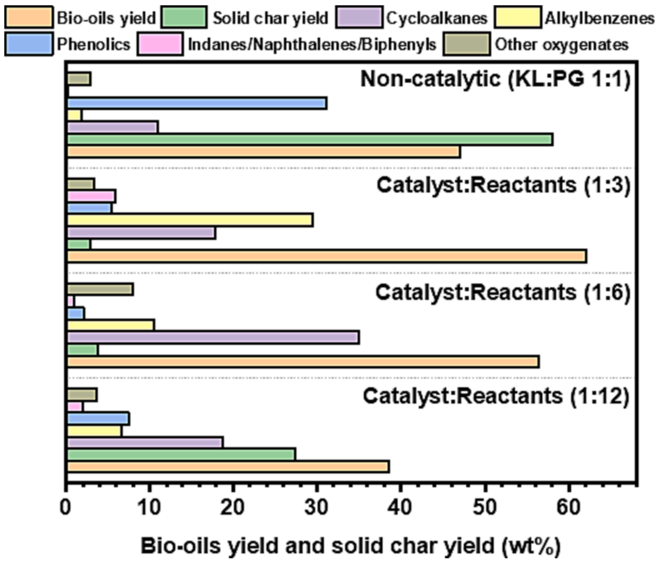
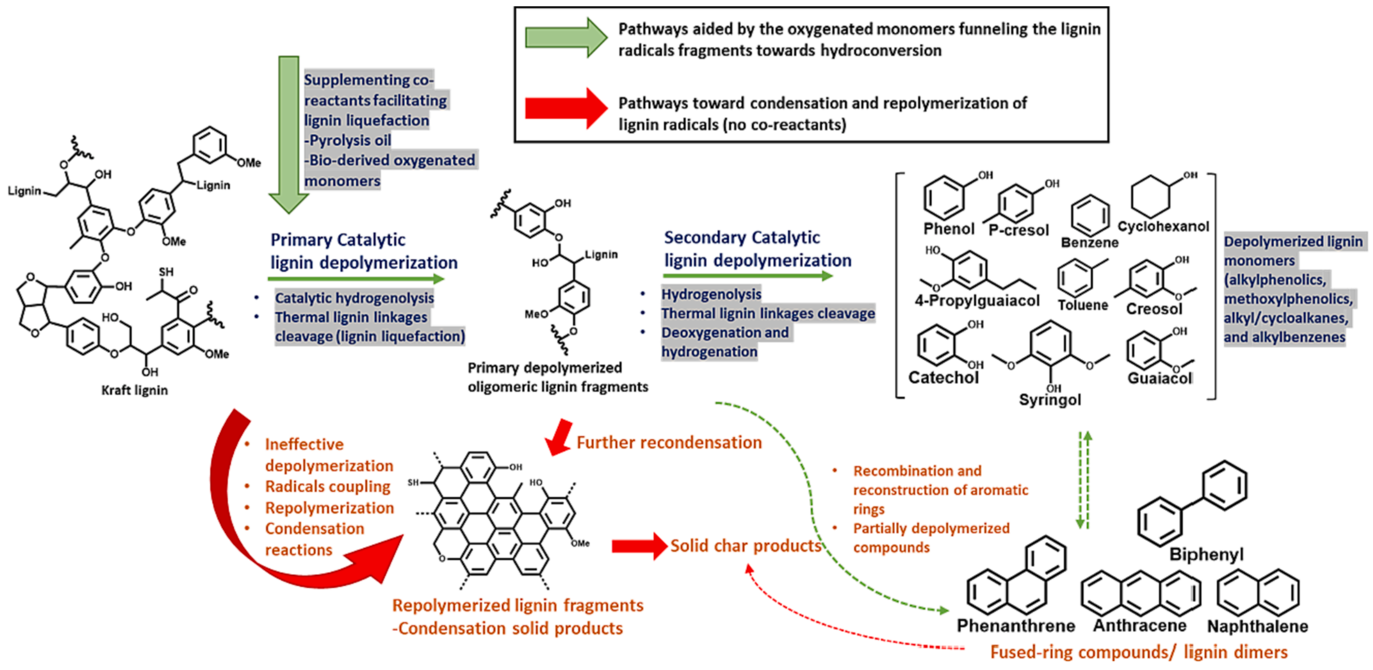


Fig. 11. Effect of the catalyst loading (Catalyst:Reactants (1:3), (1:6), and (1:12)) based on the co-hydrotreatment of Kraft lignin and PG (1:1) at 400 °C, total H_2 pressure of 75 bars, 2.25 g of Kraft lignin, 1000 rpm, 6 h, and 75 mL of hexadecane solvent.

depolymerization of lignin, that in turn affected the yield of low molecular weight products [5]. In one of our previous studies, it was shown that the undesired repolymerization and recondensation reactions can be avoided by injecting a lignin slurry in a pre-heated reactor containing solvent and catalyst, to facilitate swift lignin depolymerisation [56]. This slight alteration of the experimental protocol benefited the deconstruction of lignin by avoiding the undesired repolymerization at the early onset of the reaction during the heating phase of the batch reactor [56]. In a recent study, Lv et al. observed that co-feeding the light fraction of a lignin-derived bio-oil with pine pyrolysis oil resulted in an inhibition of coke formation during pyrolysis oil upgrading [67]. However, they used the light fraction of the lignin bio-oil, which only was about 60% of the initial lignin source. On the other hand, in our current work, the opposite was investigated, where a complex feedstock like pyrolysis oil efficiently blocks and limits the dominant pathway of recondensation and repolymerization and in turn facilitates the depolymerization and liquefaction of Kraft lignin. In our work, we use the whole lignin source as a feedstock together with the pyrolysis oil and can show that the char formation can be strongly suppressed. Another point that can be highlighted here was that the compounds present in the additional feed (PO and oxygenated monomers) used in this study for co-hydrotreatment can also be obtained from the depolymerization of lignin itself which then prevented any further separation process to recover and regenerate the co-feed.

Scheme 1 illustrates the proposed multiple pathways of the catalytic reductive liquefaction of Kraft lignin in hexadecane solvent in the presence of a hydrothermally synthesized NiMoS unsupported catalyst. It is facilitated by the presence of oxygenated monomers funneling the lignin radical fragments to hydroconversion reactions producing deoxygenated monomers instead of condensation and repolymerization reactions forming solid char and lignin dimers. Kraft lignin undergoes primarily depolymerization by the means of hydrogenolysis and the thermal cracking of its condensed linkages, C-C bonds, and ether linkages, C-O-C bonds forming the primary depolymerized lignin oligomers at elevated hydrotreatment temperature. During the heating period, catalytic hydrogenolysis/hydrotreatment reactions are weaker which favors condensation/repolymerization reactions of the reactive lignin oligomeric intermediates forming condensed insoluble solid residues that led to unwanted solid char production. Moreover, the stabilizing effect of PG and pyrolysis oil to reduce solid formation is most beneficial when catalytic hydrogenolysis and other hydrotreatment reactions increase to their full effect. With the presence of an active unsupported NiMoS catalyst, the stabilized lignin oligomers were able to access the catalytic active sites and further undergo secondary depolymerization, yielding monomers such as cyclic compounds, aromatics, and phenolics and lignin dimers like fused-ring compounds via hydrogenation and deoxygenation.



Scheme 1. Proposed multiple routes involving catalytic lignin depolymerization and liquefaction to solid char, lignin dimers, and deoxygenated monomers in hexadecane solvent in the presence of a hydrothermally synthesized NiMoS unsupported catalyst with and without co-reactants.

4. Conclusions

We have in this study, for the first time, explored pyrolysis oil-assisted Kraft lignin reductive liquefaction in a paraffin solvent over an unsupported NiMoS catalyst. We used hexadecane as paraffinic solvent since it has similar properties as HVO. The aim was to use a low-cost renewable solvent that is already produced at the refinery. The co-processing of Kraft lignin and pine sawdust derived fast pyrolysis bio-oil (PO) resulted in an outstanding char reduction potential and improved total bio-oil yield. When using an optimum amount of PO as a co-reactant (KL:PO of 1:1) a complete suppression of char was found, and we propose that the reason for this is the inhibition of the repolymerization routes of reactive lignin intermediates by the various monomers supplied by the co-fed pyrolysis oil.

For further understanding, we examined co-hydroprocessing of Kraft lignin with various oxygenate monomers, as representative for different model compounds for pyrolysis oil, using the same unsupported catalyst. However, the pyrolysis oil was more efficient than all tested monomers. The most efficient model compound was 4-propylguaiacol (PG), which contains hydroxyl, methoxy, and propyl functional groups. The solid char yield decreased from 14.7% (only Kraft lignin) to only 3.4% when adding PG at the same reaction conditions (400 °C, total 75 bar hydrogen pressure, and 6 h). Further oxygenates were tested to investigate the effect of the functional groups of PG. A ranking considering the char-reducing potential of the individual compounds was provided giving the best performance in limiting solid char formation according to: PG (hydroxyl, -OH, methoxy, $-OCH_3$, and propyl, $-C_3H_7$) > guaiacol (hydroxyl, -OH, methoxy, $-OCH_3$) > hydroxylacetone (carbonyl, $-R_2C{=}O$) > phenol (hydroxyl, -OH) > benzaldehyde (formyl, $-R\text{-}CH{=}O$) > acetic acid (carboxyl, -COOH) > anisole (methoxy, $-OCH_3$).

The effect of reaction parameters was examined, including reaction time, temperature, and catalyst loading. When increasing the reaction temperature to 400 °C, a reduction in the solid char yield to 14.7% from 26.9% at 300 °C was found. Moreover, Kraft lignin started to decompose during the heating period and yielded the highest insoluble char yield when the desired temperature was reached. The added 4-propylguaiacol (PG) during the Kraft lignin hydrotreatment did not affect the deconstruction pathway but rather acted as a stabilization agent stabilizing the reactive intermediates. However, for the non-catalytic reaction, the addition of PG instead increased the solid formation. These results show the importance of sufficient rates of catalytic hydrotreatment reactions for PG to be effective in reducing solid formation.

Finally, it was worth highlighting that the strategy of co-feeding pyrolysis oil in the Kraft lignin hydrotreatment shows a large potential for co-processing bio-feedstocks to produce renewable bio-oils. Lignin, well-known for its abundant aromatic functionality will remain an important renewable resource of interest for fine chemical and fuel precursor production.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Prakhar Arora and Olov Öhrman reports financial support was provided by Preem AB. Prakhar Arora and Olov Öhrman report a relationship with Preem AB that includes: employment. Louise Olsson is one of the editors of Chemical Engineering Journal.

Data availability

Data will be made available on request.

Acknowledgments

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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.2023.146056.

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