

Supplementary Materials: The Promotor and Poison Effects of the Inorganic Elements of Kraft Lignin during Hydrotreatment over NiMoS Catalyst

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Experimental section

S1. Materials

Al₂O₃ spheres of 0.6 mm median diameter and a surface area of 170 m²/g were procured from SASOL, Germany. Ammonium molybdate tetrahydrate [(NH₄)₆Mo₇O₂₄·4H₂O], nickel(II)nitrate hexahydrate [Ni(NO₃)₂·6H₂O], potassium carbonate (K₂CO₃), iron(III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O], hexadecane (C₁₆H₃₄), dimethyl disulfide (CH₃SSCH₃), and kraft lignin (CAS 8068-05-1, Batch no: MKCG9481) were purchased from Sigma Aldrich. Sodium carbonate (Na₂CO₃) was obtained from Merck. Calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) was bought from Alfa Aesar. All chemicals were used without any further purification.

S2. Catalyst synthesis

The catalysts were prepared by the incipient wetness impregnation method. A typical preparation of 5 wt%Ni-15 wt% Mo/Al₂O₃ catalyst was as follows. First, the Al₂O₃ spheres were calcined at 450 °C for 4 h. To 1 g of calcined Al₂O₃, a solution containing 0.2760 g of (NH₄)₆Mo₇O₂₄·4H₂O and 0.2477 g of Ni(NO₃)₂·6 H₂O in 0.5 mL of Milli-Q water (pore volume of Al₂O₃ was 0.53 mL/g) was added, mixed well, covered, and kept at room temperature for 6 h. It was then dried for 12 h at 80 °C. The final calcination was conducted in air at 450 °C (2 °C/min) for 4 h.

The NiMo/Al₂O₃ catalyst with 2.5 wt% of Na, K, Ca, and Fe was prepared by taking the calcined NiMo/Al₂O₃ following the similar incipient wetness impregnation procedure. The precursors used were Na₂CO₃, K₂CO₃, Ca(NO₃)₂·4H₂O, and Fe(NO₃)₃·9H₂O. After the impregnation, the well-mixed catalyst was kept at room temperature for 12 h. It was then dried at 80 °C for 8 h. Finally, it was calcined at 450 °C (2 °C/min) for 4 h.

For the catalyst containing Na, K, Ca, and Fe on NiMo/Al₂O₃ (NaKCaFe/Al₂O₃), a two-step procedure was followed. At first, NiMo/Al₂O₃ was incipient wetness impregnated with solution containing Na and K. It was dried (80 °C for 8 h) and then impregnated with the solution containing Ca and Fe. The final catalyst was dried at 80 °C for 8 h and calcined at 450 °C (2 °C/min) for 4 h.

S3. Catalyst characterization

The elemental composition of the catalysts was analyzed using an inductively coupled plasma (ICP) field mass spectroscopy instrument at ALS Scandinavia AB, Luleå. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the catalyst before and after the reaction with elemental mapping (EDX, energy-dispersive X-ray spectroscopy) were acquired on an FEI-Titan instrument at an operating voltage of 300 kV. The C, H, N, and S contributions in the catalysts were analyzed using an Elementar vario MICRO cube instrument in an oxygen atmosphere.

S4. Lignin and solid residue characterization

The contribution of various inorganic impurities in kraft lignin was quantified by the ICP analysis at ALS Scandinavia AB. The C, H, N, and S contribution in the lignin and the solid residue was determined using an Elementar vario MICRO cube instrument in oxygen atmosphere. The oxygen content was calculated by subtracting the C, H, N, and S contents. Thermogravimetric analysis was performed on a Mettler Toledo TGA/DSC 3+ instrument in air. The ^{23}Na MAS (magic angle spinning) NMR analysis was conducted on Bruker Avance III 500 MHz spectrometer equipped with a 4 mm MAS BB/1H K316701/0001 probe. The spin rate was 13,000 Hz, and the repetition time was 10 s. A single-pulse experiment was used with a radio-frequency pulse with a flip-angle of 10 degrees. The ^1H and 2D NMR analysis of kraft lignin (200 mg) and pretreated kraft lignin (150 mg) in DMSO- d_6 solvent (0.9 mL) was carried out on a Bruker Avance III HD 800 MHz spectrometer equipped with a TXO cryoprobe. The repetition time was 2 s for ^1H and 1 s for the multiplicity edited HSQC.

S5. Catalytic lignin depolymerization

The depolymerization reactions were conducted in a high-pressure Parr-4848 Autoclave (450 mL) with an overhead stirrer and automatic temperature control system. The first step was the sulfidation of the catalyst. Two grams of the catalyst was placed at the bottom of the reactor, to which the sulfiding agent, dimethyl disulfide (2 mL), was added. The reactor was then purged 3 times with 5 bar of N_2 , followed by 3 times with 5 bar of H_2 . It was then pressurized to 20 bar of H_2 and kept for a leak test. After this, the reactor temperature was slowly increased to 340 °C (approximately 7.1 °C/min) and maintained at this temperature for 4 h. At the end of the sulfidation, the heating was stopped, and the reactor pressure was vented out. It was then purged 3 times with 5 bar of N_2 , finally kept at 5 bar of N_2 , and allowed to cool down to room temperature.

The second step was the hydrotreatment step. To the sulfided catalyst, about 150 mL of hexadecane was added, followed by 4 g of dried kraft lignin (dried at 80 °C for 12 h). The reactor was closed and purged 3 times with 5 bar of N_2 followed by 5 bar of H_2 . Finally, it was pressurized to 45 bar of H_2 and kept for a leak test. Afterward, the reactor temperature was slowly increased to 345 °C (approximately 7.1°C/min) and kept at this temperature for a reaction period of 8 h. At the end of the reaction, the

heating was stopped, the heating furnace was removed from around the reactor cylinder and the internal cooling of the reactor was started. When the reactor temperature reached room temperature, the reactor was depressurized, and the product mixture was filtered through a sintered glass crucible (porosity 4). The filtrate was used for the GC-MS analysis. The solid residue containing catalyst and lignin residue (unconverted lignin, repolymerized lignin, and char) were washed with approximately 150 mL of anhydrous acetone and dried at 100 °C for 12 h for further analysis.

S6. Recycle experiments

The catalyst spheres were separated from the lignin solid residue by sieving. The carbon deposition on the catalyst after a single run was 0.78 wt%, and the reduction in sulfur content was 1.5 wt%. So, before each recycle run, the catalyst was oxidized (450 °C for 4 h, 2 °C/min), and freshly sulfided using DMDS as discussed in Section S5.

S7. Product analysis

The lignin depolymerization products in hexadecane solvent were analyzed by using a GC x GC MS instrument (Agilent Technology 7890B GC and 5977A MSD) using primary 1D and secondary 2D columns (1st column VF-1701ms, 30m x 250 μm x 0.25 μm – 2nd column DB-5MS UI, 1.2 m x 150 μm x 0.15 μm). The modulation period was 10 s, temperature ramp was 1.75 °C/min from 40 to 280 °C, split ratio was 30:1, injection volume = 1 μL, injector temperature = 280 °C, and detector temperature = 250 °C. Random samples were subjected to repeated analysis, and the percentage change in area counts was calculated to be below 7%.

The amount of solid residue formed after the reaction was calculated based on the following equation:

$$\text{Solid residue (wt\%)} = \frac{\text{Total weight of solids after acetone washing} - \text{Weight of catalyst}}{\text{Weight of Kraft lignin taken}} \times 100 \quad (1)$$

The product yield was calculated by the following equation:

$$\text{Yield (wt\%)} = \frac{\text{Total weight of one particular class of compounds (g)}}{\text{Weight of Kraft lignin taken (g)}} \times 100 \quad (2)$$

The GC x GC calibration was done with various classes of compounds (cycloalkanes, aromatics, and oxygenates). The response factors of these compounds are given in Table S1. For compounds outside the table, an average response factor of their respective classes was used for the calculations.

Table S1. Response factors of different compounds were deduced from their five different concentrations.

Compound	Molecular Formula	Response Factor (Peak volume/wt%)
<u>Cycloalkanes:</u>		
Cyclopentane	C ₅ H ₁₀	1.92E+08
Cyclohexane	C ₆ H ₁₂	7.82E+08
Methylcyclohexane	C ₇ H ₁₄	7.18E+08

Propylcyclohexane	C ₉ H ₁₈	1.27E+09
<u>Aromatics:</u>		
Benzene	C ₆ H ₆	9.18E+08
Toluene	C ₇ H ₈	7.82E+08
Ethylbenzene	C ₈ H ₁₀	1.08E+09
o-Xylene	C ₈ H ₁₀	1.15E+09
Propylbenzene	C ₉ H ₁₂	1.20E+09
1,2,4-Trimethylbenzene	C ₉ H ₁₂	1.34E+09
Butylbenzene	C ₁₀ H ₁₄	1.15E+09
1-Methylnaphthalene	C ₁₁ H ₁₀	1.37E+09
1,5-Dimethyltetralin	C ₁₂ H ₁₆	1.31E+09
Biphenyl	C ₁₂ H ₁₀	1.06E+09
1,3-Dimethylnaphthalene	C ₁₂ H ₁₂	1.25E+09
Phenanthrene	C ₁₄ H ₁₀	1.35E+09
<u>Oxygenates:</u>		
Anisole	C ₇ H ₈ O	8.85E+08
Phenol	C ₆ H ₆ O	8.07E+08
Guaiacol	C ₇ H ₈ O ₂	8.34E+08
Propyl anisole	C ₁₀ H ₁₄ O	1.26E+09
m-Cresol	C ₇ H ₈ O	8.48E+08
4-t-Butylanisole	C ₁₁ H ₁₆ O	1.25E+09
Ethylphenol	C ₈ H ₁₀ O	9.87E+08
4-Propylphenol	C ₉ H ₁₂ O	1.02E+09
Propylguaiacol	C ₁₀ H ₁₄ O ₂	9.94E+08

S8. Pretreatment of Kraft lignin

Persson et al.¹ developed a procedure for the pretreatment of biomass prior to pyrolysis, and the same method was applied in the current study for kraft lignin. Five grams of dried kraft lignin was placed in a round-bottom flask attached to a condenser to which 80 mL of 5 vol% glacial acetic acid in Milli-Q water was added and stirred. The pretreatment temperature was set at 85 °C, and the pretreatment time was 1 h. After the pretreatment, the slurry was filtered and washed with 500 mL of Milli-Q. The filter cake was then first dried at a temperature of 60 °C for 2 h and then at 115 °C overnight.

Table S2. Complete elemental analysis of kraft lignin.

Element	Amount (mg/Kg)	Element	Amount (mg/Kg)
Aluminum, Al	18	Manganese, Mn	58
Antimony, Sb	0,06	Molybdenum, Mo	0,7

Arsenic, As	0,08	Sodium, Na	9300
Barium, Ba	2	Neodymium, Nd	0,005
Beryllium, Be	0,013	Niobium, Nb	<0.005
Lead, Pb	0,04	Nickel, Ni	0,4
Boron, B	22	Osmium, Os	<0.005
Bromine, Br	1,2	Palladium, Pd	<0.005
Cerium, Ce	0,012	Platinum, Pt	<0.005
Cesium, Cs	0,13	Praseodymium, Pr	<0.005
Dysprosium, Dy	<0.005	Rhenium, Re	<0.005
Erbium, Er	<0.005	Rhodium, Rh	<0.005
Europium, Eu	<0.005	Rubidium, Rb	4,2
Phosphorus, P	12	Ruthenium, Ru	<0.005
Gadolinium, Gd	<0.005	Samarium, Sm	<0.005
Gallium, Ga	0,15	Selenium, Se	0,09
Germanium, Ge	0,03	Silver, Ag	0,03
Gold, Au	<0.005	Scandium, Sc	<0.005
Hafnium, Hf	<0.005	Strontium, Sr	1
Holmium, Ho	<0.005	Sulphur, S	21000
Iridium, Ir	<0.005	Tantalum, Ta	<0.005
Iodine, I	0,5	Tellurium, Te	<0.005
Iron, Fe	30	Thallium, Tl	0,03
Cadmium, Cd	0,17	Tin, Sn	0,1
Calcium, Ca	200	Terbium, Tb	<0.005
Potassium, K	1100	Titanium, Ti	1,4
Silicon, Si	6000	Thorium, Th	<0.005
Cobalt, Co	0,08	Thulium, Tm	<0.005
Copper, Cu	0,9	Uranium, U	<0.005
Chromium, Cr	0,3	Vanadium, V	19
Mercury, Hg	<0.005	Bismuth, Bi	<0.005
Lanthanum, La	0,007	Tungsten, W	0,3
Lithium, Li	0,07	Ytterbium, Yb	<0.005
Lutetium, Lu	<0.005	Yttrium, Y	0,005
Magnesium, Mg	21	Zinc, Zn	13
		Zirconium, Zr	0,007

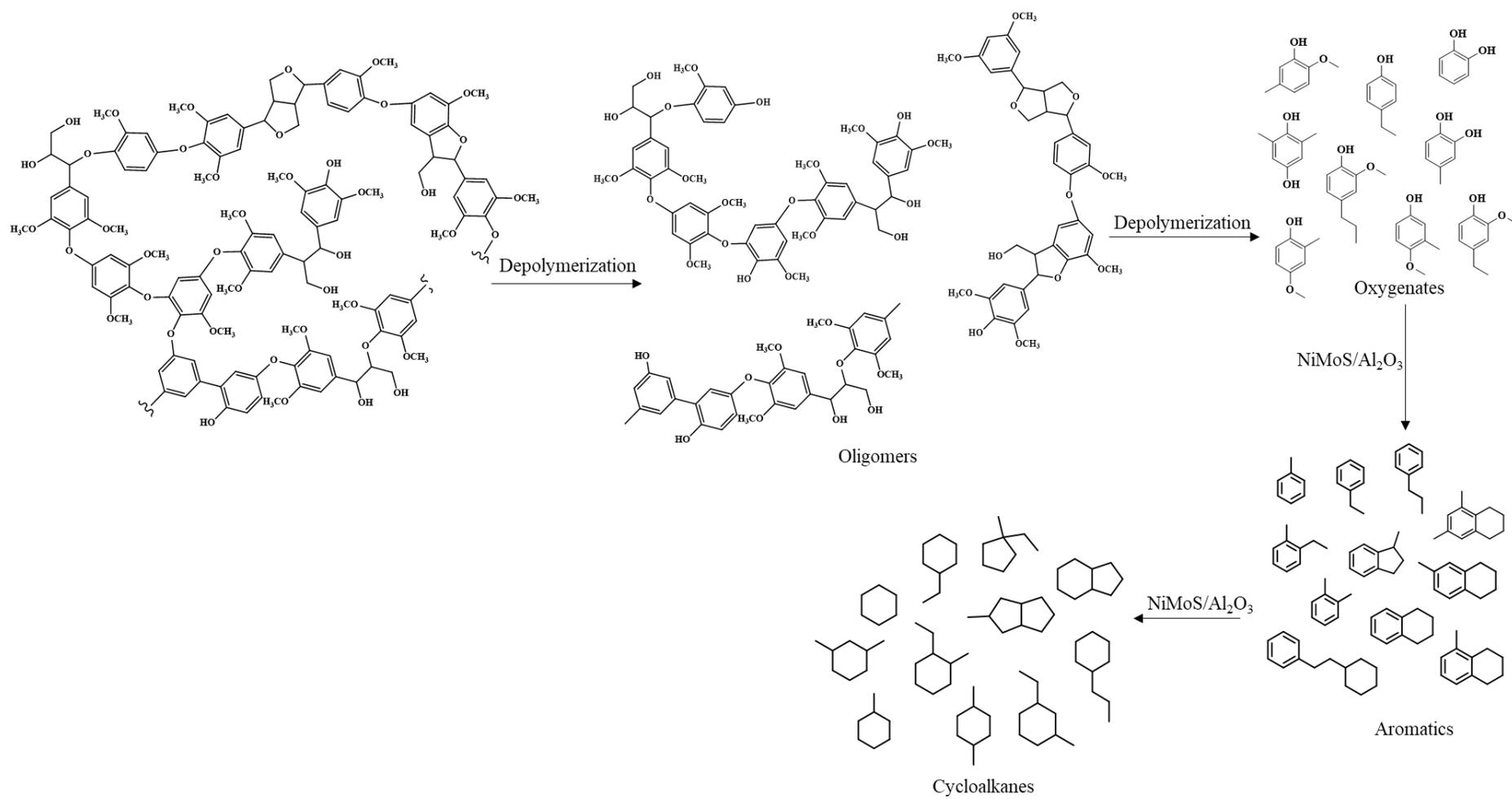


Figure S1. Tentative reaction pathway of lignin depolymerization to aromatics and cycloalkanes.

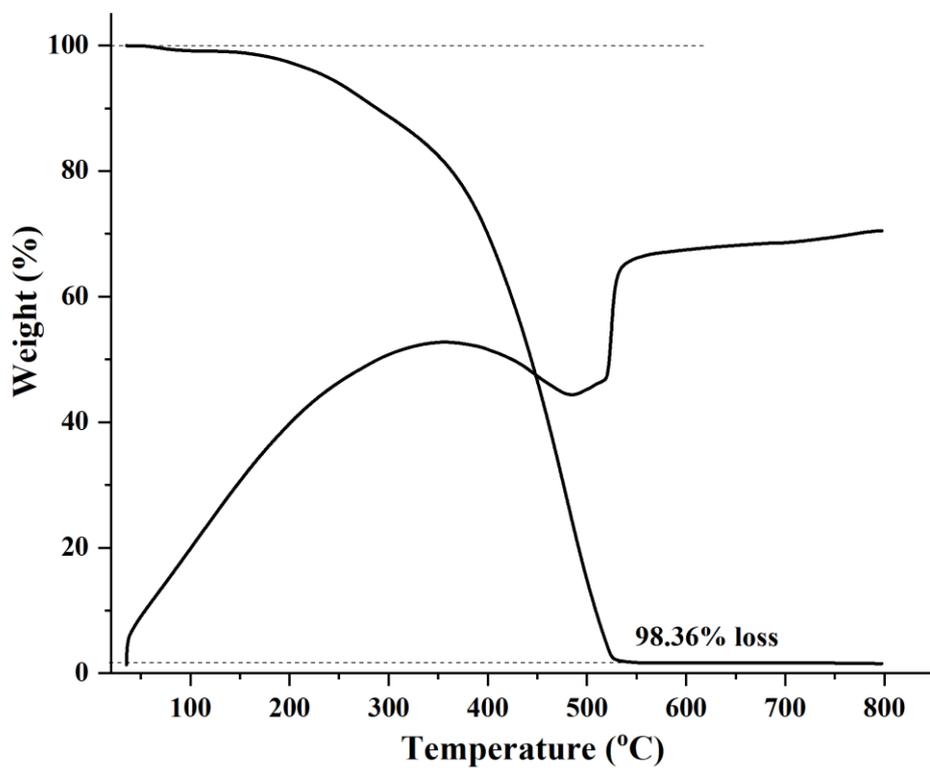


Figure S2. TGA/DSC analysis of dried kraft lignin showing 1.64 wt% of ash content.

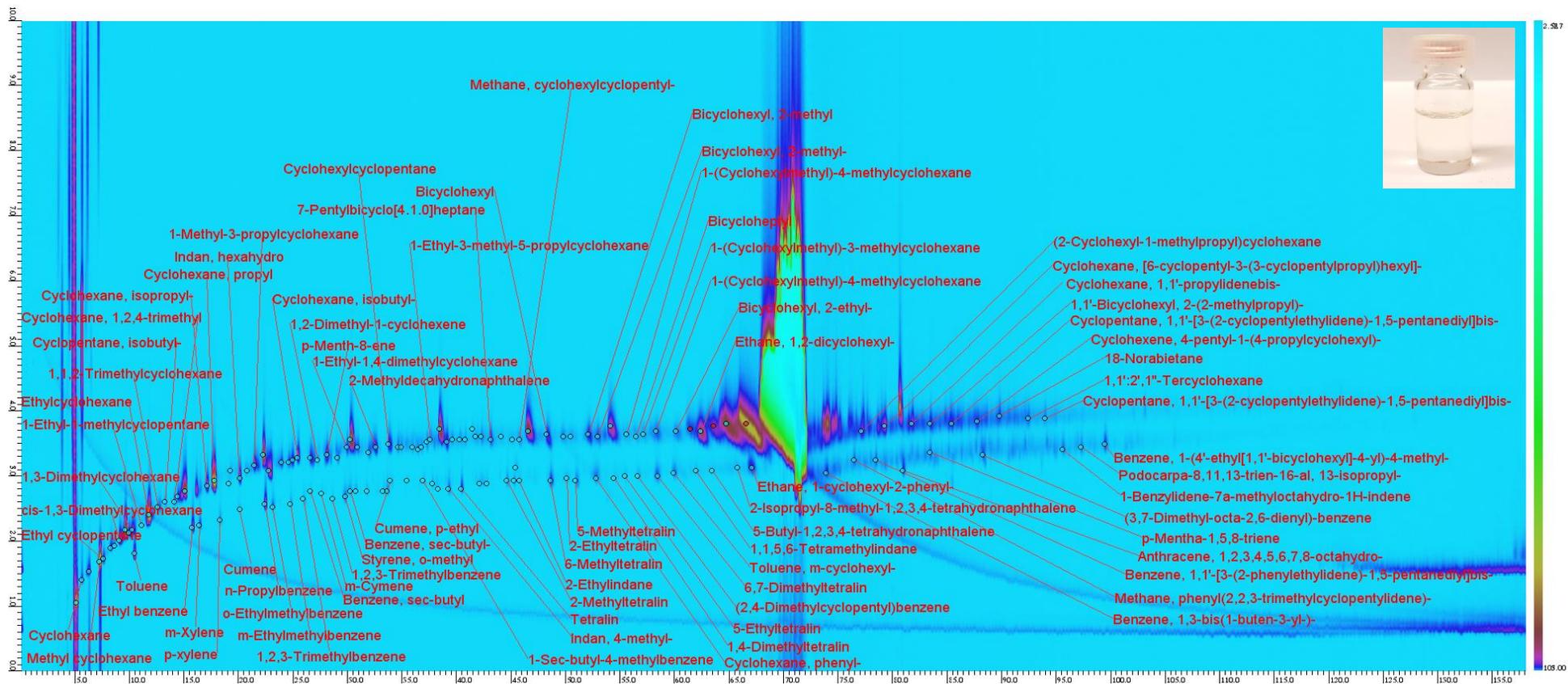


Figure S3. GC x GC chromatogram of reaction product (inset) obtained over the NiMoS/Al₂O₃ catalyst.

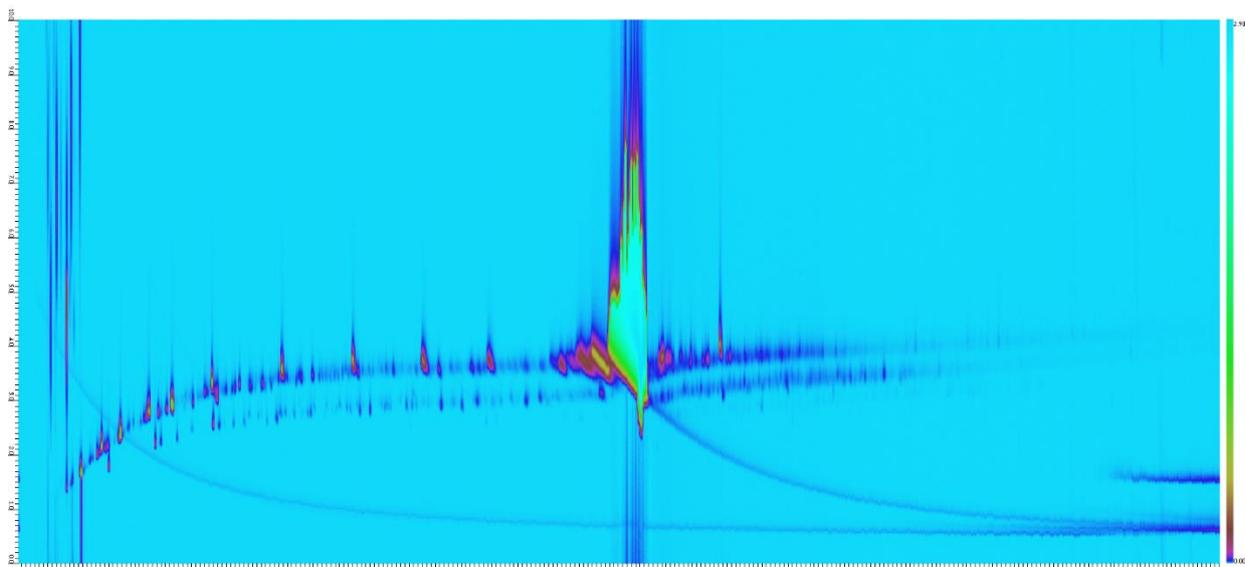


Figure S4. GC × GC chromatogram of the reaction product obtained after the 3rd consecutive run of the Ni-MoS/Al₂O₃ catalyst showing the absence of oxygenates. Figure 1a in the manuscript guides to the region where the oxygenates were observed.

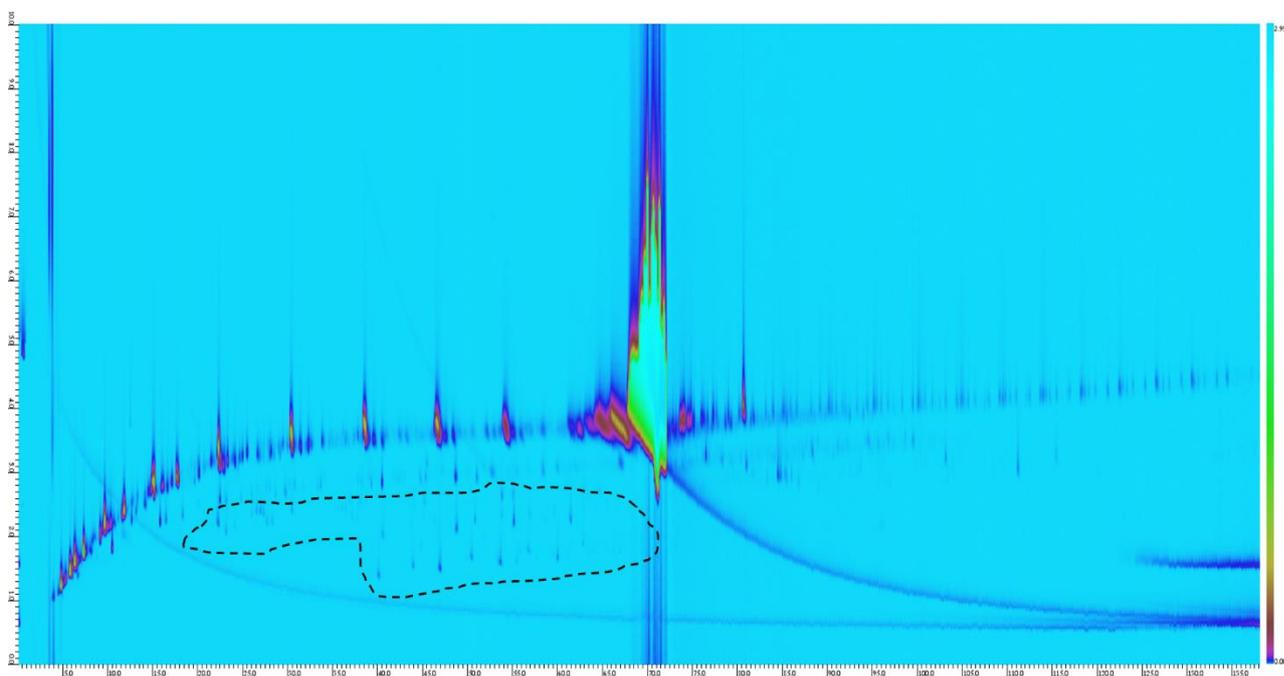


Figure S5. GC × GC chromatogram of the reaction product obtained over the 2.5wt%Na- NiMoS/Al₂O₃ catalyst showing the presence of oxygenates (enclosed dotted region).

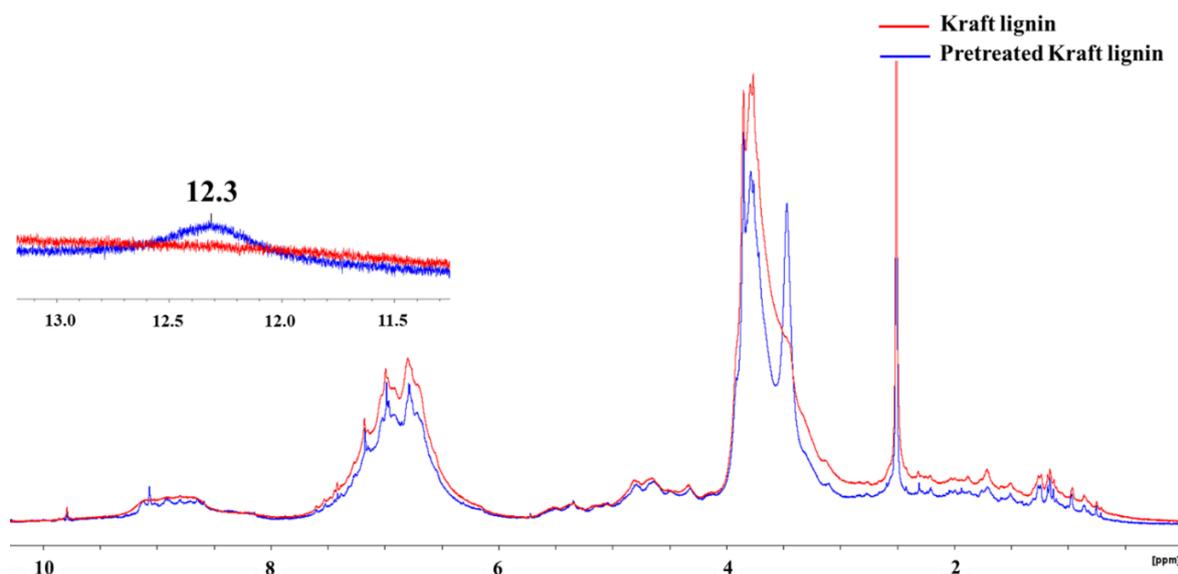


Figure S6 ^1H NMR spectra of the Kraft lignin and the pretreated Kraft lignin in DMSO-d_6 .

Figure S6 shows the ^1H NMR spectra of the kraft lignin and the pretreated kraft lignin in DMSO-d_6 solvent. The most distinguishable regions of the spectra were ^{2,3} the 6–8 ppm corresponding to the aromatic region, the 3.0–4.1 ppm corresponding to the methoxy groups, and the 0.5–1.5 ppm region corresponding to the aliphatic hydrogens. The signal at 9.78 ppm is indicative of H in the benzaldehyde units, and the signal at 3.46 ppm was due to the residual moisture. Since Na was removed to its negligible level after the acid washing, most of the carboxylic acid groups which were ionized by Na ($-\text{COONa}$) were regenerated back to their acid hydroxide form ($-\text{COOH}$). This is observable as a small hump at around 12.3 ppm in the NMR spectrum of pretreated kraft lignin (Figure S6, inset). This observation further confirms that Na cations in kraft lignin exist as a single-site ionic form as deduced from the ^{23}Na MAS NMR.

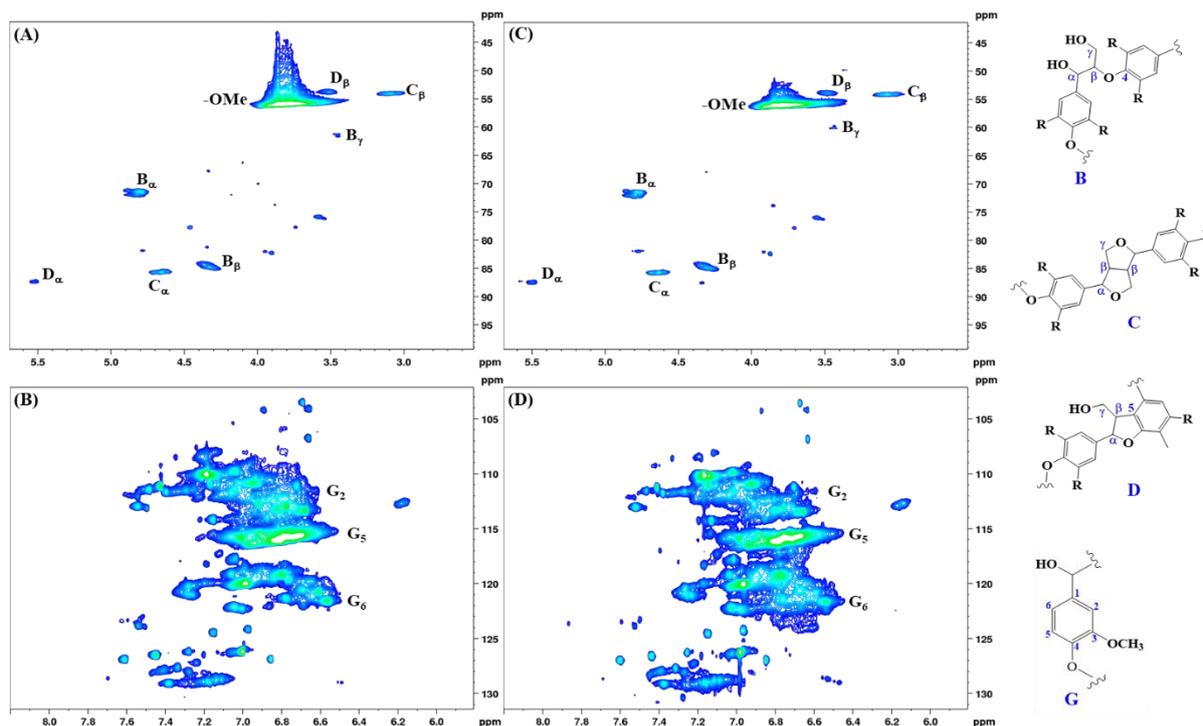


Figure S7 2D HSQC NMR spectra of (A) & (B) Kraft lignin, and (C) & (D) pretreated Kraft lignin.

The structural changes in pretreated kraft lignin were analyzed by 2D heteronuclear single-quantum coherence nuclear magnetic resonance (HSQC NMR) analysis (Figure S7). The signal assignments were performed based on the literature.^{2,4-7} The spectra represent two regions: the oxygenates region ($\delta_C/\delta_H = 45\text{--}95/2.5\text{--}5.5$, Figure S7A,C) and the aromatics region ($\delta_C/\delta_H = 105\text{--}130/6.0\text{--}8.0$, Figure S7B,D). In general, all types of linkages are present in the pretreated kraft lignin even after the acid washing, however, with different intensities. For a better comparison, the ratio of relative integral intensities of different linkages within a spectrum was compared.^{2,8} The relative integral intensities should be seen as an indicator since the set parameters were not optimized for being quantitative. At first, the methoxy (-OMe , $\delta_C/\delta_H = 56.0/3.8$) to aromatic integral ($G_2 + G_5 + G_6$) ($\delta_C/\delta_H = 110.8\text{--}119.3/6.5\text{--}7.1$) ratio was considered. It was 0.65 for the kraft lignin and 1.57 for the pretreated kraft lignin. The higher ratio in pretreated lignin indicates that the C_2 , C_5 , and C_6 (G_2 , G_5 , and G_6 in Figure S7B,D) contribution has significantly reduced, alluding to their consumption by condensation reactions during the pretreatment. Similarly, the ratio of $\beta\text{-O-4}$ (B_β , $\delta_C/\delta_H = 84.5/4.3$) to the sum of C-C linkages ($C_\beta + D_\beta$, for C_β , $\delta_C/\delta_H = 54.0/3.1$, and for D_β , $\delta_C/\delta_H = 53.7/3.5$) was also compared (Figure S7A,C). The ratio was 0.88 for the kraft lignin and 0.73 for the pretreated kraft lignin. The slight decrease in the ratio indicates a higher contribution of the C-C bonds after the pretreatment. Such behavior of the condensation/polymerization of the kraft lignin leading to a small increase in molecular weight was expected during the batch pretreatment process.⁹

The increase in C–C bonds would affect the degree of depolymerization of the lignin and would increase the amount of lignin solid residue as the C–C bonds are more difficult to cleave than the C–O bonds.

Table S3 Complete elemental analysis of pretreated Kraft lignin.

Element	Amount (mg/Kg)	Element	Amount (mg/Kg)
Aluminum, Al	125	Manganese, Mn	1,7
Antimony, Sb	0,03	Molybdenum, Mo	0,6
Arsenic, As	0,03	Sodium, Na	28
Barium, Ba	0,5	Neodymium, Nd	0,01
Beryllium, Be	<0.005	Niobium, Nb	0,01
Lead, Pb	0,06	Nickel, Ni	0,35
Boron, B	4	Osmium, Os	<0.005
Bromine, Br	3	Palladium, Pd	<0.005
Cerium, Ce	0,02	Platinum, Pt	<0.005
Cesium, Cs	0,02	Praseodymium, Pr	<0.005
Dysprosium, Dy	<0.005	Rhenium, Re	<0.005
Erbium, Er	<0.005	Rhodium, Rh	<0.005
Europium, Eu	<0.005	Rubidium, Rb	0,09
Phosphorus, P	3	Ruthenium, Ru	<0.005
Gadolinium, Gd	<0.005	Samarium, Sm	<0.005
Gallium, Ga	0,12	Selenium, Se	0,07
Germanium, Ge	0,03	Silver, Ag	0,08
Gold, Au	<0.005	Scandium, Sc	0,006
Hafnium, Hf	<0.005	Strontium, Sr	0,05
Holmium, Ho	<0.005	Sulphur, S	9000
Iridium, Ir	<0.005	Tantalum, Ta	<0.005
Iodine, I	<0.1	Tellurium, Te	<0.005
Iron, Fe	24	Thallium, Tl	0,005
Cadmium, Cd	0,15	Tin, Sn	0,14
Calcium, Ca	7	Terbium, Tb	<0.005
Potassium, K	5	Titanium, Ti	4
Silicon, Si	<100	Thorium, Th	<0.005
Cobalt, Co	0,03	Thulium, Tm	<0.005
Copper, Cu	1	Uranium, U	0,007
Chromium, Cr	0,6	Vanadium, V	13
Mercury, Hg	0,04	Bismuth, Bi	<0.005
Lanthanum, La	0,01	Tungsten, W	0,15

Lithium, Li	0,03	Ytterbium, Yb	<0.005
Lutetium, Lu	<0.005	Yttrium, Y	0,009
Magnesium, Mg	9	Zinc, Zn	10
		Zirconium, Zr	0,03

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