

Electronic Supplementary Information (ESI)

Transition metal (Ti, Mo, Nb, W) nitride catalysts for lignin depolymerisation

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Experimental section

Materials

Titanium tetrachloride, molybdenum pentachloride, niobium pentachloride, tungsten tetrachloride, urea, titanium nitride were purchased from Sigma Aldrich. Titanium dioxide P25 was purchased from Degussa. Protobind 1000 alkali lignin (sulfur-free lignin with less than 4 wt% carbohydrate and less than 2 wt% ash) was purchased from Greenvalue. Three types of organosolv lignins were supplied by Energy research center of the Netherlands. All chemicals were used without further purification.

Catalyst preparation

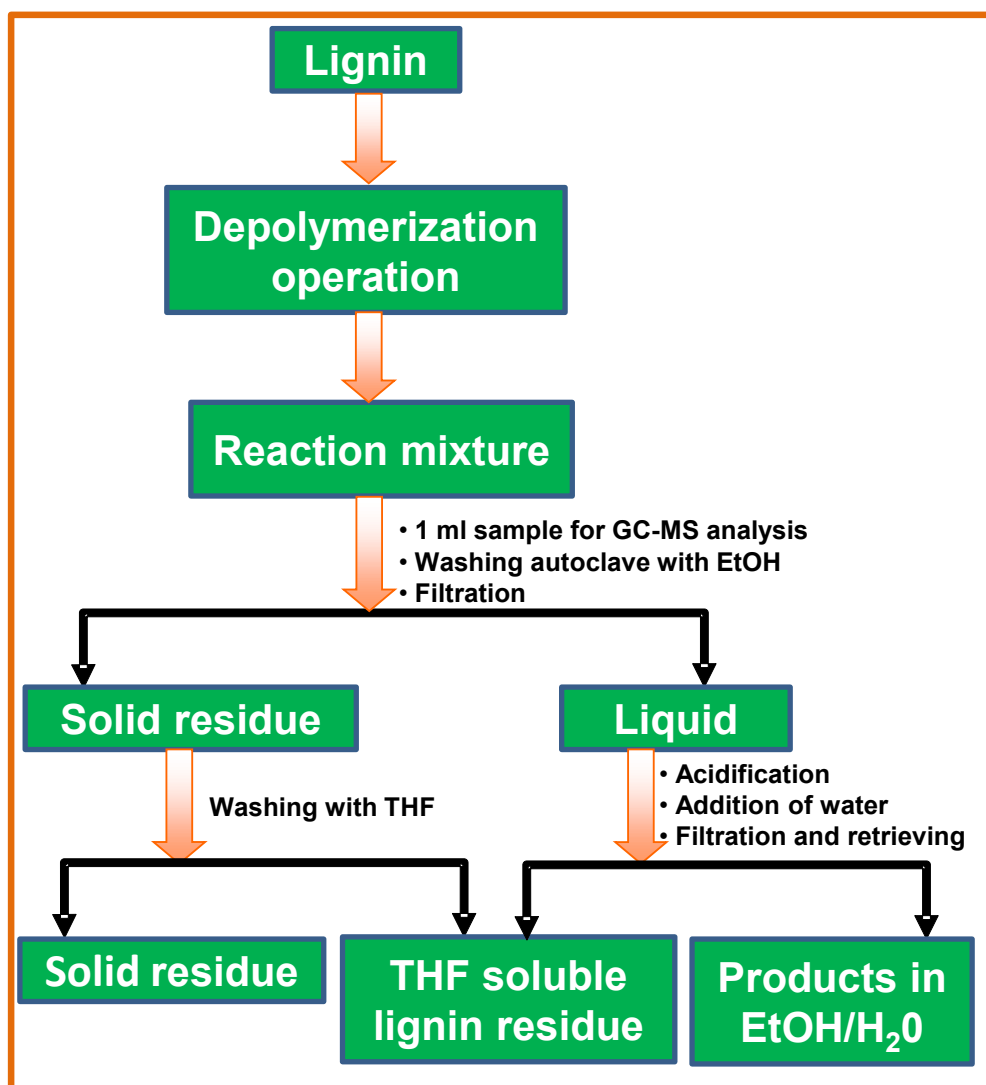
A certain amount of metal chloride was added dropwise to ethanol, until a yellowish solution was observed. Urea was then added slowly to the solution under vigorous stirring for 1 h. The molar ratio of titanium tetrachloride, molybdenum pentachloride, niobium pentachloride and tungsten tetrachloride to urea were 5, 3, 1 and 1, respectively. After this, the solvent was firstly evaporated in nitrogen, followed by drying in an oven at 80 °C overnight to form a gel. The gel was heated under nitrogen flow (heating rate of 2°C/min) up to 750 °C holding the final temperature (750 °C) for 3 hours. The high-surface-area TiN proved to be very pyrophoric. Therefore, the freshly synthesized material was passivated in a flowing 1% O₂/He for 12 h at room temperature.

Catalyst characterization

Transmission electron micrographs (TEM) were recorded on a FEI Tecnai 20 electron microscope, operated 200 kV and equipped with a LaB6 filament. X-ray diffraction (XRD) measurements were performed on a Bruker D4 Endeavor Diffractometer using Cu K α -radiation. N₂ adsorption measurements were carried out Tristar 3000 automated gas adsorption system. Brunauer-Emmett-Teller (BET) method was used to determine the surface area. Prior to analysis, the samples were degassed at 100 °C under vacuum overnight. X-ray Photoelectron Spectroscopy (XPS) was done on a Kratos AXIS Ultra spectrometer, equipped with a monochromatic Al K α X-ray source and a delay-line detector (DLD). Spectra were obtained using an aluminum anode (Al K α = 1486.6 eV) operating at 150 W, with survey scans at constant pass energy of 160 eV and region scans at a constant pass energy of 40 eV. The background pressure was 2×10^{-9} mbar. XP spectra were fitted with the CASA-XPS software. Binding energies (BE) were calibrated using the carbon contamination present (C1s = 284.6 eV).

Lignin depolymerization and guaiacol conversion

50 mL AmAr stirred high-pressure autoclaves were used. Typically, the autoclave was charged with a suspension of 200 mg catalyst and 400 mg lignin or guaiacol in 20 mL solvent. An amount of 10 μ L n-dodecane was added as the internal standard. The reactor was sealed and purged with nitrogen several times to remove oxygen. After leak testing, the pressure was set to 10 bar and the reaction mixture was heated to the desired reaction temperature under continuous stirring at 500 rpm within 1 h. After the reaction, the reactor was rapidly quenched to room temperature in a water bath. A work-up procedure for lignin systems as shown in Scheme S1 was developed. Firstly, 1 mL post-mixture was taken and filtered using 0.45 μ m syringe filter, then analyzed by the GC-MS. The remaining mixture were collected combining with the solution from washing the autoclave with ethanol. The combined mixture was then filtered, forming two fractions which were solid phase and liquid phase. The solid part was then washed using THF. The liquid part was first acidified with diluted HCl solution and then subjected to deionized water to precipitate unconverted lignin and high molecular-weight lignin fragments.



Scheme S1. Schematic diagram of the work up procedure.

¹H-¹³C HSQC NMR analysis of lignin

All NMR spectra were recorded using a Varian 500 MHz spectrometer. Approximately 70 mg of lignin residue (100 mg for P1000) was dissolved in 0.7 mL dimethylsulfoxide-d₆ ([D₆] DMSO). ¹H-¹³C HSQC NMR spectra were obtained using the Crisis gc2HSQC program. The spectral widths were 5000 Hz and 20000 Hz for the ¹H- and ¹³C-dimensions, respectively. Normally, the number of scans was 16, and 256 time increments were always recorded in the ¹³C dimension. Data processing was performed using the MestReNova software.

Gel permeation chromatography (GPC)

GPC analyses were performed by using a SHIMADZU apparatus equipped with two columns connected in series (Mixed-C and Mixed-D, polymer Laboratories) and a UV/Vis detector at 254 nm. The column was calibrated with polystyrene standards. Analyses were carried out at 25 °C using THF as eluent with a flow rate of 1 mL min⁻¹. Samples were dissolved with the concentration of 2 mg mL⁻¹ and filtered using a 0.45 mm filter membrane prior to injection.

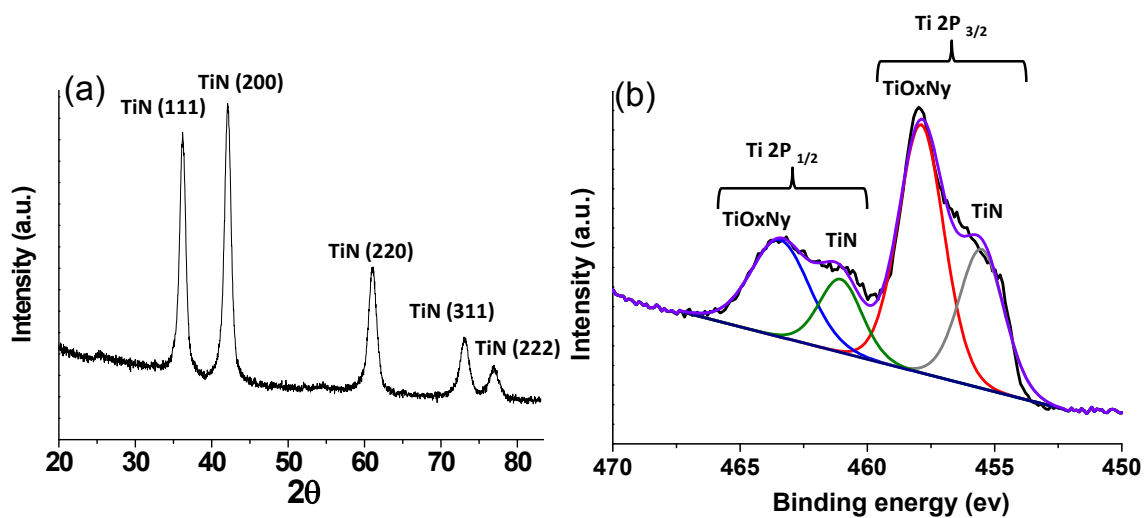


Figure S1. (a) XRD pattern and (b) Ti 2p region of the X-ray photoelectron spectrum of TiN prepared by the urea glass method.

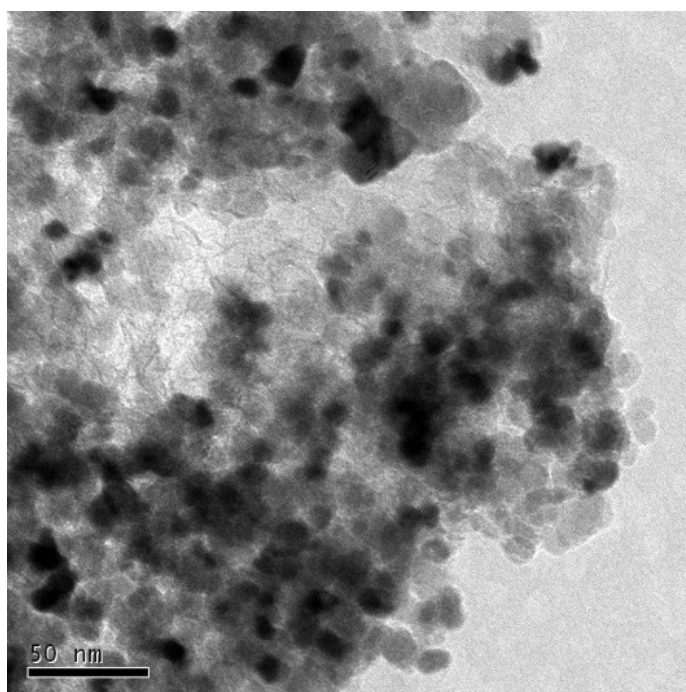


Figure S2. TEM image of TiN (urea glass).

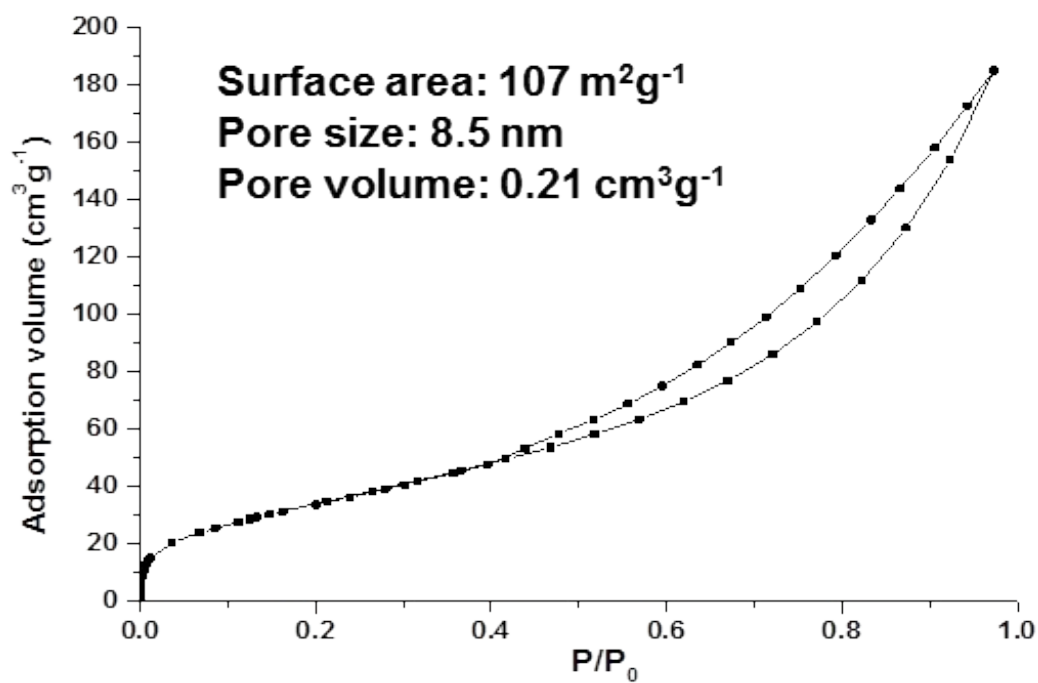


Figure S3. N₂-adsorption/desorption isotherm of TiN (urea glass).

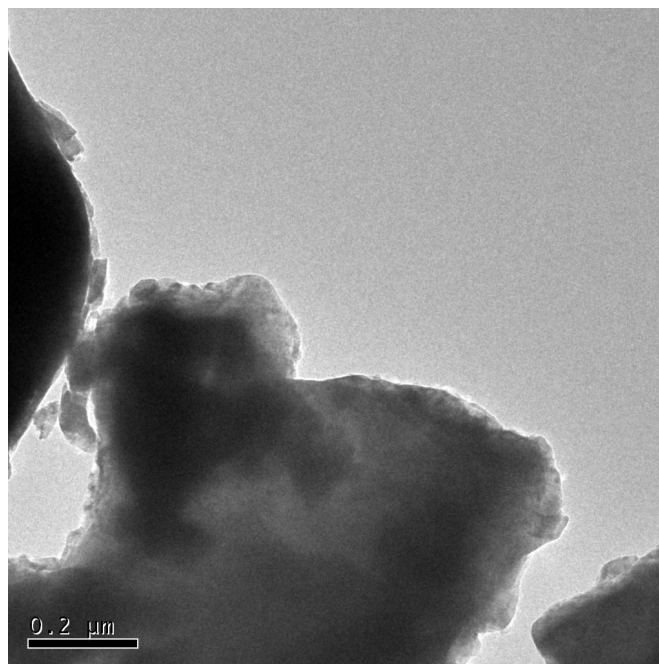


Figure S4. TEM of commercial TiN (Sigma).

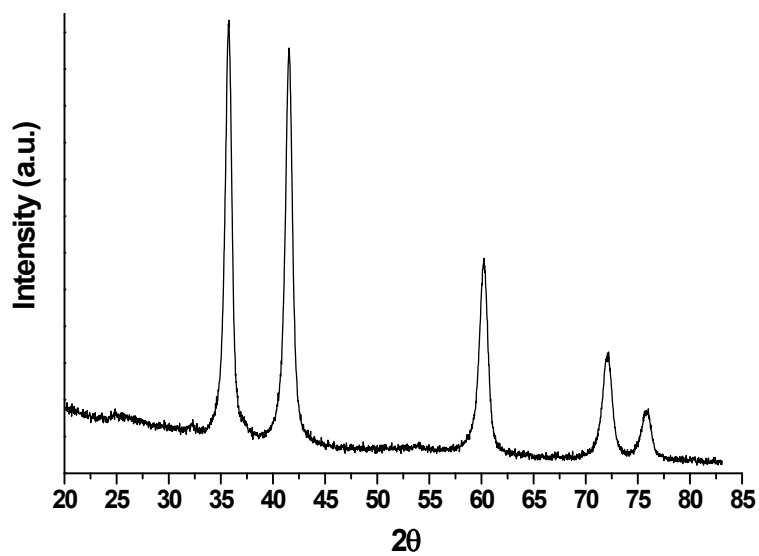


Figure S5. XRD pattern of NbN.

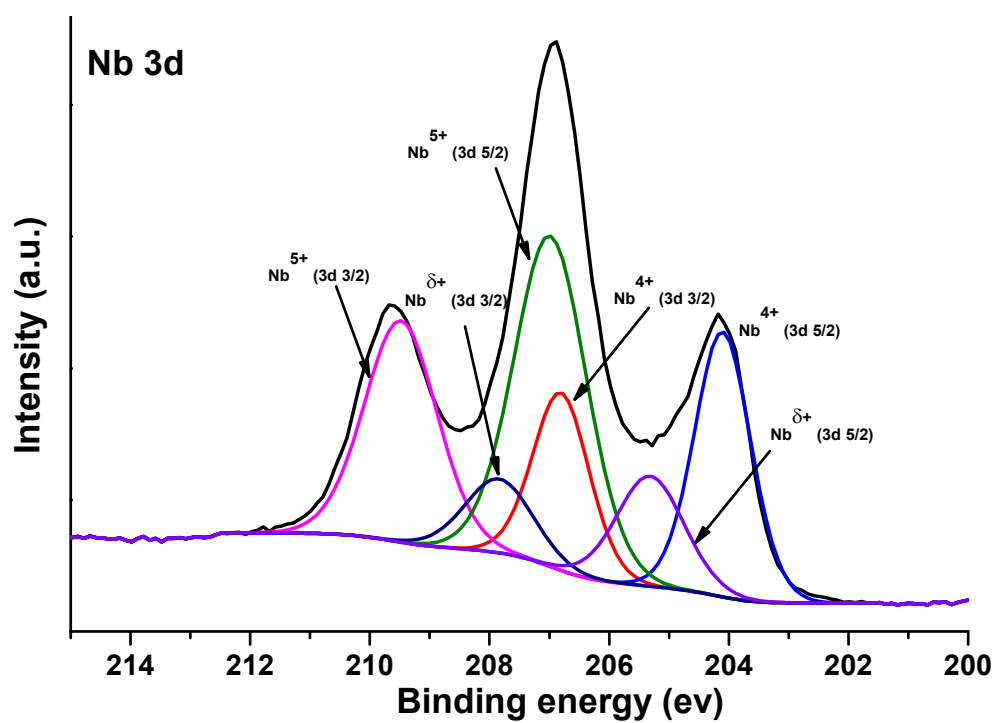


Figure S6. XPS spectrum of Nb 3d region of NbN.

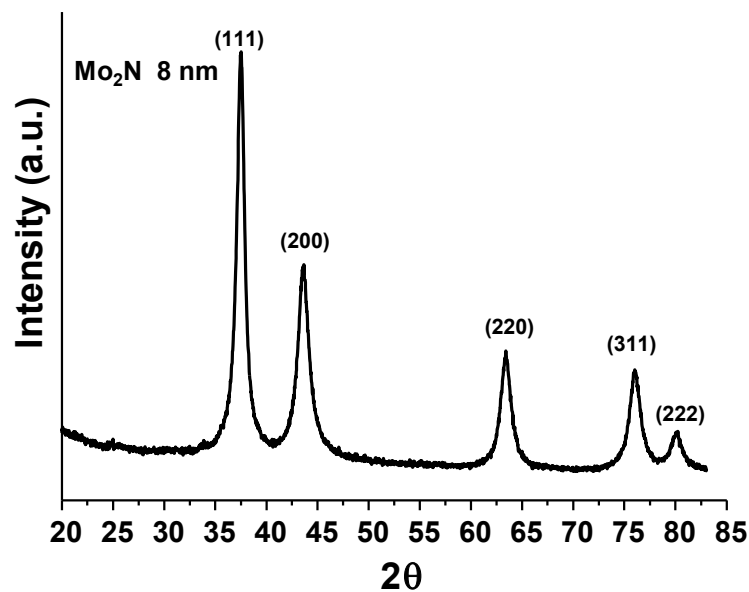


Figure S7. XRD pattern of Mo₂N.

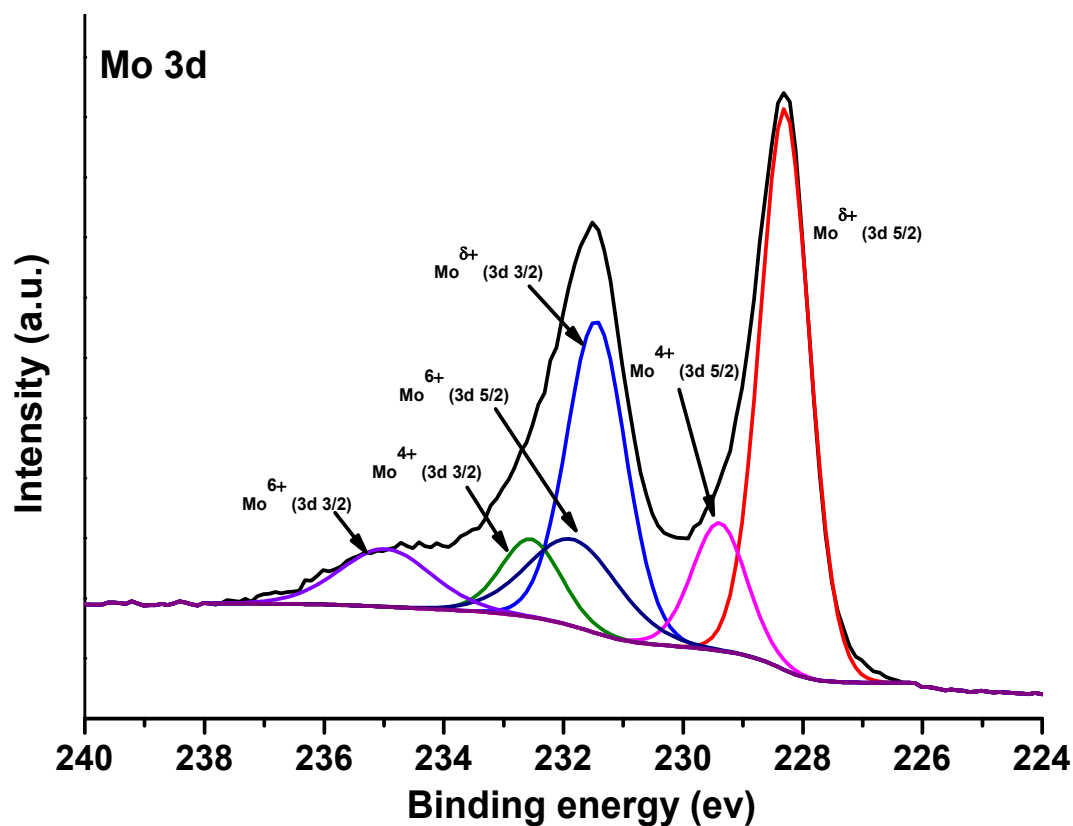


Figure S8. XPS spectrum of Mo 3d region of Mo₂N.

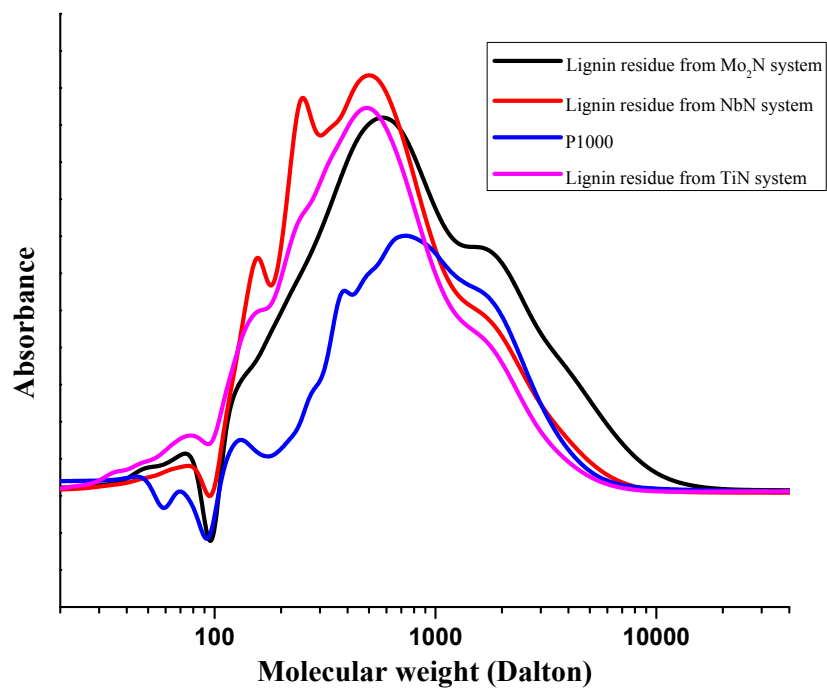


Figure S9. GPC of lignin residues from different catalytic systems compared with native fractionated lignin.

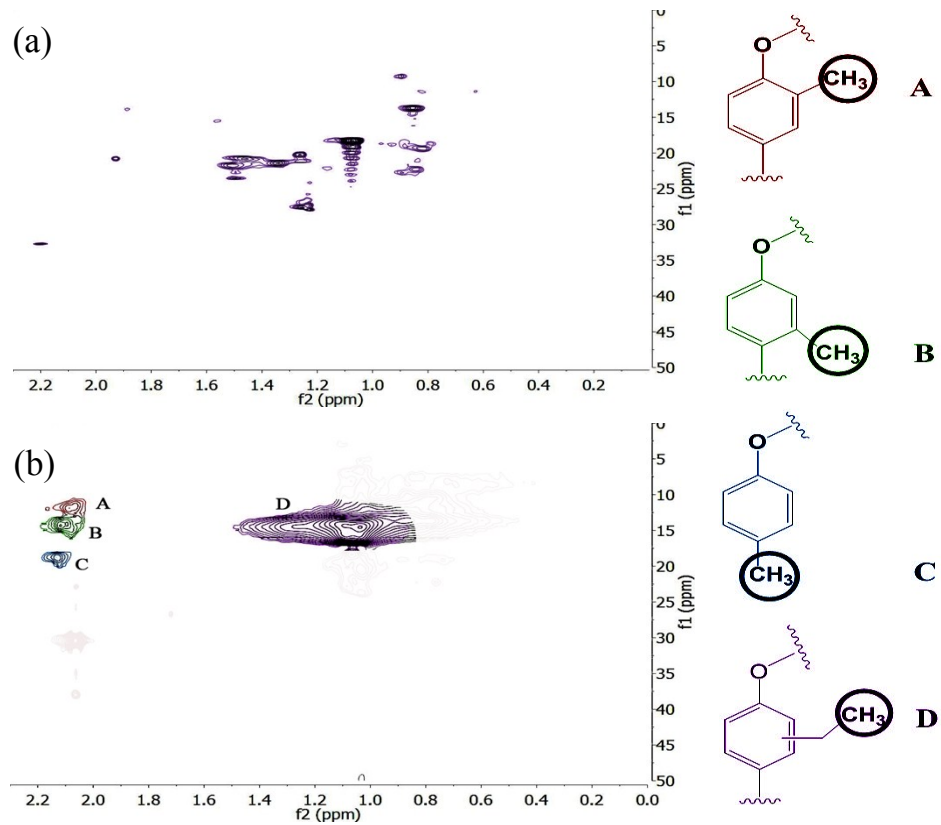
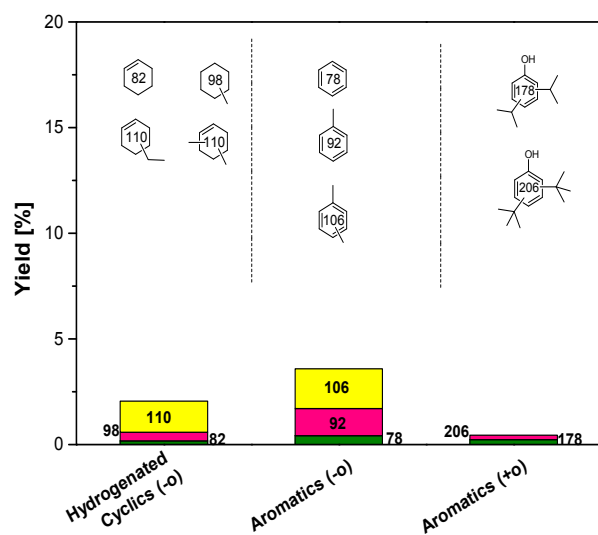
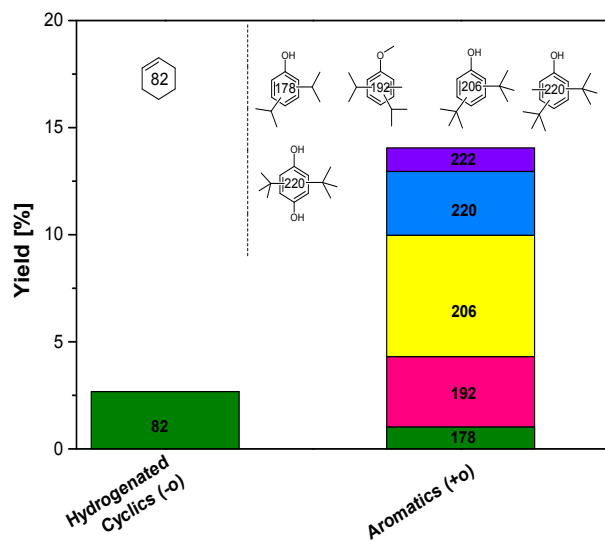


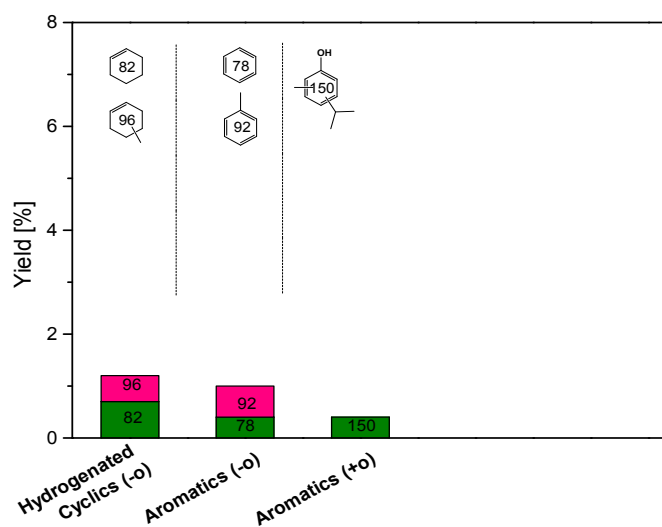
Figure S10. (a) Aliphatic region of HSQC of parent lignin, (b) Aliphatic region of HSQC of lignin residue recovered from entry 8 (Table 1) experiment.



Mo₂N system



NbN system



W₂N system

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Figure S11. Products distribution in the monomers obtained from P1000 depolymerisation catalysed by Mo₂N, NbN and W₂N at 340 °C.

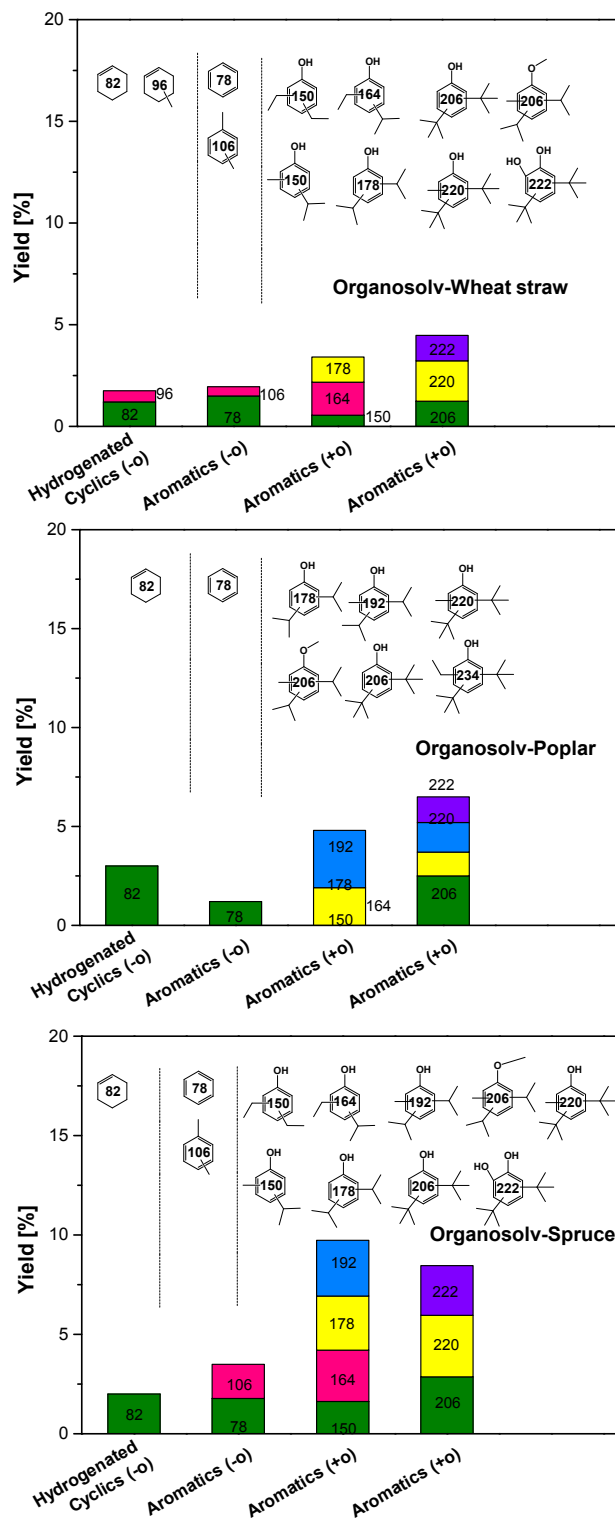


Figure S12. Products distribution in the monomers obtained from three types of organosolv lignin depolymerisation catalysed by TiN at 340 °C.

