Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2016

Electronic Supplementary Information

Solid base catalyzed depolymerization of lignin into low molecular weight products

Richa Chaudhary [a,b] and Paresh L. Dhepe ,*[a,b]

[a] Catalysis and Inorganic Chemistry Division, National Chemical Laboratory,
Dr. Homi Bhabha Road, Pune 411008, India
E-mail: pl.dhepe@ncl.res.in

[b] Academy of Scientific and Innovative Research (AcSIR)
New Delhi, India

Table of contents:

List of Figures:

List of Tables:

1. Characterization of lignin:

1.1. Elemental analysis:

Elemental analysis was done using Thermo Finnigan, Italy; model EA1112 Series Flash Elemental Analyzer. This analyzer measures the amount of C, H, N and S in samples by rapid combustion of small amounts (1-2 mg) of the sample in pure O_2 (Dumas or flash combustion method). The analysis of all the elements in the CHNS group was performed simultaneously. From the elemental analysis of lignin and depolymerized products, carbon loss was not observed after the reaction.

1.2. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis:

Samples were analyzed in SPECTRO ARCOS Germany, FHS 12 instrument. Lignin samples were burned in air at 650 °C for 6 h under air, diluted to a known volume with Millipore water and then analyzed. The resultant solution was filtered using 0.22 micron filter and filtered solution was analyzed by ICP-OES. The ICP-OES analysis confirmed the presence of Na in lignin. From elemental analysis it was confirmed that Sulphur is also present in the lignin.

1.3. Fourier Transform Infrared （FT-IR) Spectroscopy:

Functional groups present in lignin were analysed using FT-IR technique. Analysis was done on Bruker Optics ALPHA-E spectrometer, USA; with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm^{-1} region or using a Diamond ATR. Prior to the analysis samples was dried in vacuum over (10^{-4} Mpa) for 3 h.

1.4. Solid state ^{13}C NMR:

This technique was also used for the functional group analysis of lignin. ^{13}C NMR was done in Bruker AV300, Germany; at 10 kHz with a pulse program Cp, av and no. of scans was 8192. Vacuum dried samples was used for the analysis.

1.5. Thermo Gravimetric Analysis-Differential Thermal Analysis (TGA-DTA):

TGA-DTA analysis was carried out using METTLER TOLEDO TGA /SDTA851 series, USA; instrument with a heating rate of 10 °C/min upto 1000 °C to study the complete decomposition. Thermal degradation was studied both in N_2 and air atmosphere.

1.6. X-Ray Diffraction (XRD) analysis:

The morphology of lignin and catalyst was studied using Powder XRD, PANanalytical X'pert Pro, Netherlands; with duel goniometer diffractor. The source of X-ray was Cu Kα (1.5418 Å) radiation with Ni filter and sample scanning was done from a 2θ value of 5 to 90 ° at the rate of 4.3 °/min. Samples were grinded and dried in vacuum over (10^{-4} MPa).

1.7. Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDAX):

The SEM micrographs of the samples were obtained on a Leo Leica Cambridge UK Model Stereoscan 440 scanning electron microscope, with an electron beam of 5-50 eV. The elemental composition of the sample was determined using the EDAX attached with the SEM instrument.

1.8. Ultraviolet-Visible（UV-Vis) Spectroscopy:

Color of wood derives from certain structures of lignin. A **s**tudy was made to identify the contribution of color in the lignin. A compound is colored due to the presence of chromophores. The chromophores were identified by UV-Vis absorption measurements of the sample by VARIAN'S Cary 300 UV-Vis spectrophotometer; Australia. Lignin & products was dissolved in water & methanol respectively and was analyzed in the range of λ= 200-800 nm.

2. Catalyst Synthesis and Characterization:

2.1. Synthesis of NaX:

Hydrothermal crystallization of NaX zeolite was carried out from the Na_2O-SiO_2-Al_2O_3-H_2O system at autogenous pressure. The raw materials used were water–glass solution (28.5% SiO_2, 8.5% Na_2O, 63.0% H_2O), sodium aluminate (43.65% Al_2O_3, 39% Na_2O, 17.35% H_2O), sodium hydroxide (AR, Loba), and distilled water. The initial gel composition expressed in oxide moles was 3.6 Na_2O : 3 SiO_2 : 1 Al_2O_3 : 144 H_2O. The reaction mixture was prepared by controlled addition of a solution prepared by dissolving 29.2 g of sodium aluminate in 125 mL of distilled water to a solution containing 78.94 g of water-glass solution diluted with 65 mL of distilled water with constant stirring. To this mixture was slowly added 14.25 g of NaOH dissolved in 75 mL of distilled water with constant stirring until a homogeneous gel was obtained. The gel was then transferred and sealed in an autoclave and subjected to hydrothermal treatment in an oven maintained at 95 °C. The autoclave was removed after 8 h and quenched to room temperature. The solid product was separated by vacuum filtration. Excess alkali was washed with hot water until filtrate showed a pH in the range 9-11. The product was then dried for 8 h in an oven maintained at 110 °C.

2.2. Synthesis of KLTL:

KLTL was synthesized having oxide molar compositions as 4 K_2O : 10 SiO_2 : 1 Al_2O_3 : 100 H_2O The homogeneous reaction mixture was prepared by adding required amounts of potassium hydroxide and alumina source into deionized water under stirring, optionally, heating the reaction mixture till a clear solution of potassium aluminate is formed. Further solution was cooled to room temperature and compensating the water loss due to boiling, following by the addition of potassium aluminate solution to aqueous suspension of silica source under vigorous stirring and further stirring was done to form homogeneous gel mixture. The final homogeneous reaction mixture thus obtained was transferred into 100 mL stainless steel autoclaves, sealed and then placed in an air-heated oven maintained at 170 °C. The autoclave was then taken out of the oven quenched to room temperature. The solid products were separated by filtration, washed with deionized water till the effluent showed a pH value around 9 and then further dried at 120 °C.

2.3 Characterization of catalysts.

Before using these solid base catalysts in depolymerization of lignin their properties were studied using various physico-chemical techniques.

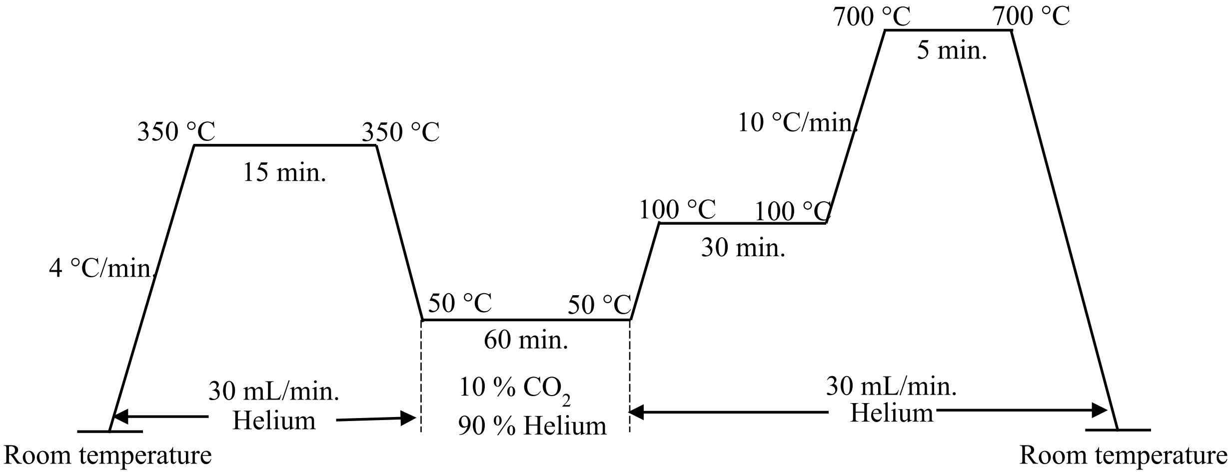
2.3.1. Elemental analysis: same as section 1.1.

2.3.2. ICP-OES: same as section 1.2.

2.3.3. XRD: To determine the morphology of the catalysts on bulk level XRD was done. Please refer section 1.6.

2.3.4. Temperature Programmed Desorption（TPD-CO_2) analysis:

TPD-CO_2 analysis was performed to quantify the total basicity present in the solid base catalysts. Micromeritics AutoChem 2910 instrument was used for the analysis. In this technique, CO_2 was used as acidic probe molecule which is adsorbed on the basic sites of the catalyst. Prior to measurement, samples were activated at 350 °C for 15 min in helium flow (30 mL/min.). Next temperature was allowed to decrease to 50 °C. The adsorption of CO_2 was done at 50 °C and then the sample was kept at 100 °C for 30 min. under helium gas flow (30 mL/min.). Later, at the rate of 10 °C/min. temperature was increased from 100 °C to 700 °C in helium flow (30 mL/min.) and TPD profile was recorded. The amount of CO_2 molecules desorbed corresponds to the amount of basic sites present in the catalyst.



2.3.5. N_2 sorption studies:

Surface area, pore size and pore volume can be determined using nitrogen sorption study. Analysis was done in Autosorb 1C Quantachrome, instrument, USA. Prior to the analysis, samples were activated in vacuum at 200 °C for 3 h. The specific surface area was determined using BET method, pore size data was obtained using BJH & HK method and pore volume using t-plot method.

2.3.6. Solid state ^{29}Si and ^{27}Al-NMR.

The solid state ^{29}Si and ^{27}Al MAS NMR spectra were recorded on a Bruker AV300, Germany. Finely powdered fresh and spent catalyst samples were placed in zirconia rotors and spun at 4 kHz for ^{29}Si (no. of scans 16384) and 6 kHz for ^{27}Al (no. of. scans 16384). The chemical shifts were referenced to TMS (δ = -82.4 ppm from TMS) and $[Al\ (H_2O)\ _6]^{3+}$ (δ = 0.0 ppm) for ^{29}Si and ^{27}Al, respectively.

2.3.7. pH measurement:

To measure the pH of all the solid base catalysts, same quantity similar to reaction mixture was taken. Solution was stirred for 10-15 minutes. After this pH was measured with the help of pH meter and following order was observed:

a) In water (Catalyst = 0.05 g, H_2O = 3 mL, 25 °C)

CaO (pH $\geq$ 13.4) > NaX (pH 11.7) > MgO (pH 11.2) > KLTL (pH 10.9) > HT (pH 10.6) > NaP (pH 9.9) > NaY (pH 9.4) > HAP (pH 6.5)

b) In reaction mixture (Lignin:Catalyst = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 25 °C)
CaO (pH $\geq$ 13.4) > HT (pH 12.5) > MgO (pH 10.5) > KLTL (pH 9.4) > NaX (pH 9.2) > NaY = NaP (pH 8.7) $\approx$ HAP (pH 8.5)

2.3.8. Catalyst recyclable study:

After the reaction, catalyst was separated out from the reaction mixture by centrifugation, washed with ethanol-water (1:2 *v/v*, 30 mL). Further catalyst was dried at 55 ^oC for 16 h and used for the next reaction.

2.3.9. Catalyst characterization and stability

All the catalysts evaluated for their depolymerization activities in this study were characterized by TPD-CO_2, XRD, ICP, and N_2 sorption techniques (Section 2, ESI) and the details on their properties are summarized in Table S2 (ESI).

Because NaX catalyst has shown best activity and was also used in recycle runs, properties of spent NaX catalyst (250 ^oC, 1 h) were compared with fresh catalyst. The XRD of fresh and spent NaX catalyst showed similar peak pattern (Fig. S12, ESI) although with decrease in the peak intensities in spent catalyst. This indicates that the catalyst underwent slight structural deformations during the reaction, which might be the reason why catalyst showed decline in activity in recycle runs. However, it was seen that the Si/Al ratio in spent catalyst matched well with the fresh catalyst (ICP, Table 2, main text).

From the TPD-CO_2 analysis, total basicity in spent and fresh catalysts was calculated. As seen from Fig. 6 (main text), the TPD profiles for both fresh (0.42 mmol/g) and spent (0.41 mmol/g) catalysts match well and therefore almost similar basicity was calculated. From these characterizations (Table 2 and Fig. 6, main text) it is revealed that the catalyst is mostly stable under reaction conditions. From ICP-OES analysis (Table 2, main text), it is observed that 3.24 mg of additional Na is observed on the spent catalyst as against 17.3 mg Na present on fresh NaX catalyst. The increase of Na may arise from the lignin substrate (Table 2 and S8, ESI).

Early literature reports show that protonated zeolites have lower hydrothermal stability when heated at around 200 ^oC in water[1] during the conversion of hemicellulose. Later many detailed studies are done to show that acidic zeolites are unstable under reaction conditions used in biomass conversions.[1-4] It can also be noted that large volume of literature is available on the stability of zeolites under alkaline conditions used during their synthesis and post-modifications.[5] It is claimed that based on the concentration of the charge-balancing counter cations (CBCC) stability of zeolites can be manipulated. Recent findings show that with an increase in CBCC, better resistance to alkaline conditions is possible. Also, it is mentioned that typically zeolites undergo hydrolysis of ≡Si-O-Si≡ bonds under acidic conditions or even under neutral conditions but when higher temperatures (due to change of ionic product, *Kw*) are used.[6] In basic media the stability of bonds typically follows =Al−O−Si≡ >> ≡Si−O−Si≡ order.[6] Since in this work basic zeolites are used with Si/Al ratio of 1-2.7, it appears that those are more stable than their acidic counterparts since under alkaline conditions, hydrolysis of =Al−O−Si≡ and ≡Si-O-Si≡ bonds is minimized. Nevertheless, it is reported that when highly alkaline solutions are used, base catalyzed hydrolysis of these bonds is also possible. Additionally, literature also reveals that stability of basic zeolites is dependent on size of cation.[7] For instance when Na is used as a cation, stability is better than Li exchanged zeolite. This is because with increase in cation size, diffusion of water or adsorption of water over catalyst is lowered. It is anticipated that in this work, since lower Si/Al ratio zeolites are used having basicity and Na as counter cation, those tend to stabilize the catalyst from hydrothermal degradation. It is postulated that because of presence of Na, even if water has higher *Kw* at elevated temperatures than at ambient temperature, acidity is neutralized. However, a detailed study on this aspect is required to comment further.

3. Lignin Depolymerization reaction:

3.1. Actual lignin with molecular weight to ca. 60,000 Da was taken as substrate. Solid base catalyst (zeolites, clay, metal oxides etc,) was used for the depolymerization of lignin. All the catalysts were activated at 150 ^{o}C for 2 h in vacuum (10^{-4} MPa) prior to catalytic run. Reactions were carried out in a batch mode Parr autoclave. Lignin, catalyst and solvent were charged in the autoclave. EtOH:H_2O (1:2 *v/v,* 30 mL) was used as reaction media for all the reactions. Autoclave was flushed with nitrogen gas at least three times and heating was started under 100 rpm stirring. After attaining the desired reaction temperature stirring was increased to 1000 rpm and this was considered as the starting time of the reaction. After the reaction, reactor was cooled to room temperature and gas was released. Catalyst was separated out by centrifugation, washed thoroughly with ethanol-water (1:2 *v/v*) in order to remove any adsorbed lignin or products on the catalyst. Work procedure followed is mentioned in the main text (Fig. 1).

3.2. For non-catalytic reaction, lignin and solvent (EtOH:H_2O, 1:2 *v/v*, 30 mL) were charged in the autoclave. Autoclave was flushed with nitrogen gas at least three times and heating was started under 100 rpm stirring. After attaining the desired reaction temperature (250 ^oC) stirring was increased to 1000 rpm and this was considered as the starting time of the reaction. After the reaction of 1 h, reactor was cooled to room temperature and in the same reactor without removing the reaction charge, NaP (0.5 g) was added and reaction was started at the same optimized reaction condition (250 ^oC & 1 h). After the reaction, same work up procedure was followed as mention in main text (Fig. 1) and 13% (37% yield) increase in the product yield was observed compared to non-catalytic reaction (24% yield).

4. Extraction of products and yield calculations:

In order to separate the aromatic monomers from the mixture, organic solvents diethyl ether (DEE) and ethyl acetate (EtOAc) were used. The % of organic solvent soluble products was calculated based on the solid recovered after evaporating the respective solvents. Quantification of products was done by calibrating the standards using GC / GC-MS.

$$\text{\% Yield for DEE soluble products} = \frac{\text{Weight of DEE soluble products (g)}}{\text{Weight of lignin (g)}} \text{ X } 100$$

$$\text{\% Yield for EtOAc soluble products} = \frac{\text{Weight of EtOAc soluble products (g)}}{\text{Weight of lignin (g)}} \text{ X } 100$$

5. Analysis of reaction mixture:

Reaction mixture was analyzed using GC-FID, GC-MS, HPLC, LC-MS, ICP-OES, CHNS, NMR and FT-IR analysis.

5.1. Gas Chromatography (GC-FID):

Products formed after the depolymerization of lignin were analyzed by GC using Agilent 7890B model GC, with flame ionization detector (FID). It was equipped with HP-5 capillary column (5 % phenyl 95 % dimethyl polysiloxane) (30 m length, 0.25 mm diameter). N_2 (30 mL/min) is used as a carrier gas, H_2 (25 mL/min) is used for flame and air as oxidizer (300 mL/min). Carrier gas flow was 0.6 mL/min.

Injector temp: 275 °C, Detector temp: 280 °C

The Column oven program used was:

Temperature (°C)	Hold time (min.)	Ramping rate (°C/min.)	Total time (min.)
100	4	-	4
275	20	10	42

However, to confirm the products formed, GC-MS study was also done by using same program.

5.2. Gas Chromatography-mass spectrometry (GC-MS):

The Varian 3800 GC-MS, (Saturn 2000MS) with the VF-5 capillary column (5 % phenyl 95 % dimethyl polysiloxane) (30 m, 0.25 mm) was used to determine the molecular weight of the products identified using GCMS. Helium (0.6 mL/min) is used as a carrier gas; the column oven program used is same as that for GC analysis. From the mass spectrum obtained, m/z value of the compounds and then corresponding M.W is obtained. The GC-MS peaks are matched with the mass spectra in NIST library for compound identification.

5.3. High Performance Liquid Chromatography (HPLC):

Reaction mixture was analysed using Agilent make High Performance Liquid Chromatograph (HPLC) system equipped with autosampler, C18 column (Length: 250 mm, Internal diameter: 4.6 mm, 40 °C) and refractive index (RI) detector (40 °C). CH_3OH: H_2O (1:1 *v/v*) was used as a mobile phase with a flow rate of 1 mL/min. The identification of compounds in the reaction mixture was done by injecting standards.

5.4. Liquid chromatography-mass spectrometry (LC-MS):

Reaction mixture was analysed using Thermo Scientific system (Model no. Q Extractive), C18 column (Length: 150 mm, Internal diameter: 4.6 mm) and mass detector (Orbitrap analyzer). Reverse phase system was used with CH_3OH: H_2O (9:1 *v/v*) as mobile phase and pumped at a flow rate of 0.35 mL/min. Oven temperature was set at 30 °C and an electron source ionization ion source was used for the analysis.

5.5. Nuclear Magnetic resonance (NMR) analysis:

^1H and ^{13}C NMR spectra of alkaline lignin and products were recorded at 200 MHz on Bruker

Ascend- using D_2O and CD_3OD as solvent with TMS as an internal standard. No. of scans used for ^1H, ^{13}C NMR is 16384 and 8192, respectively.

Figures & Tables:

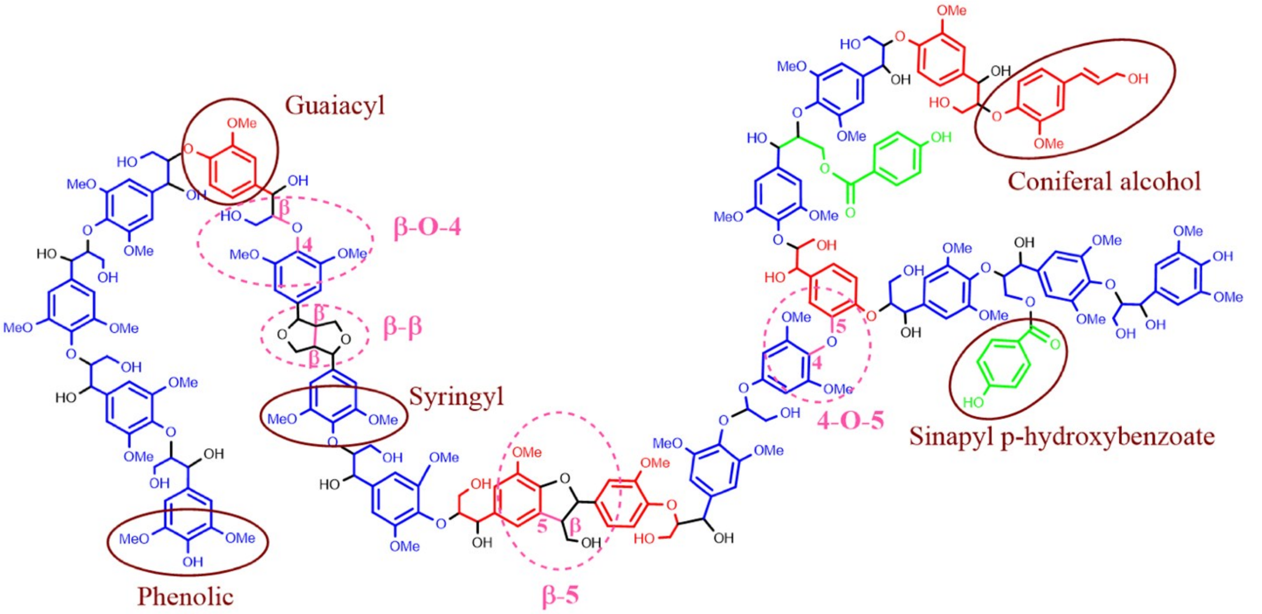


Fig. S1 Schematic representation of lignin showing various linkages and functional groups.

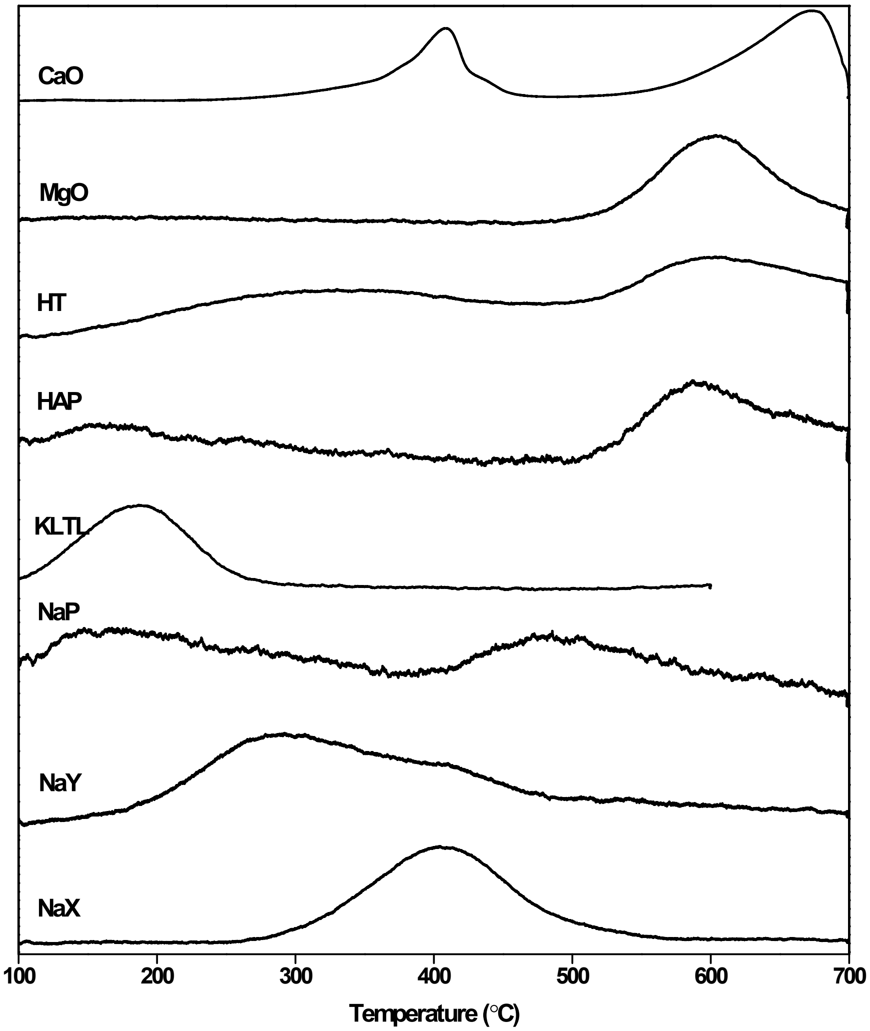


Fig. S2 TPD-CO_2 profile of various solid base catalysts.

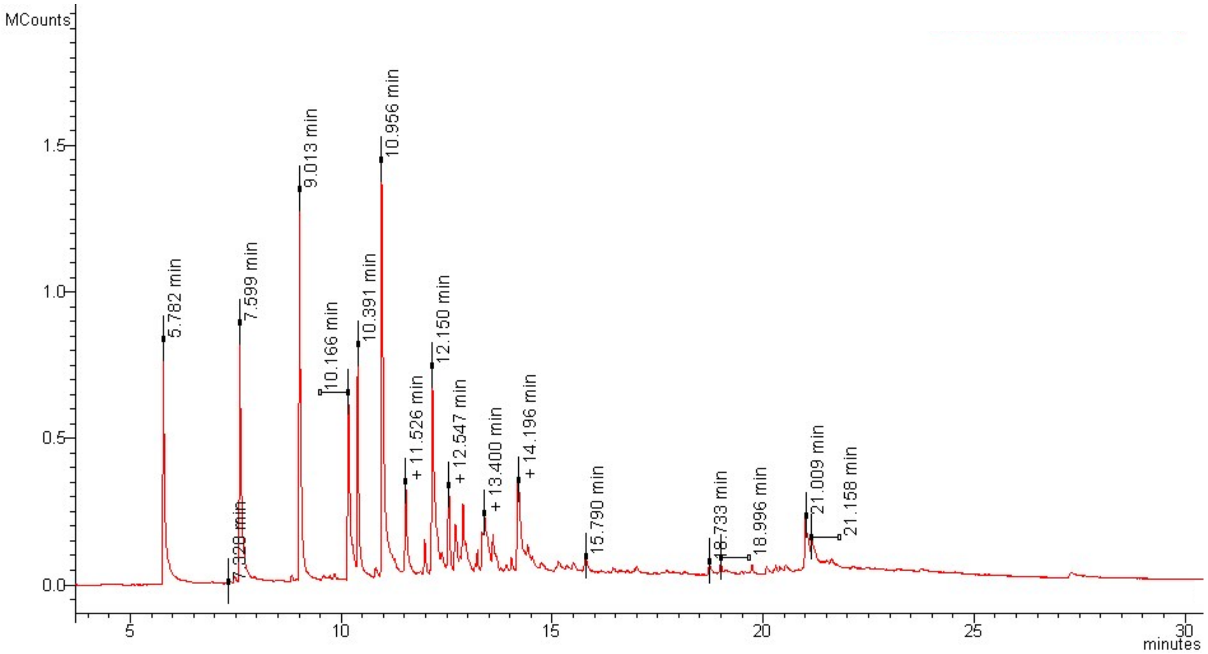


Fig. S3 GC-MS chromatograph of diethyl ether (DEE) soluble products from liquid. Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

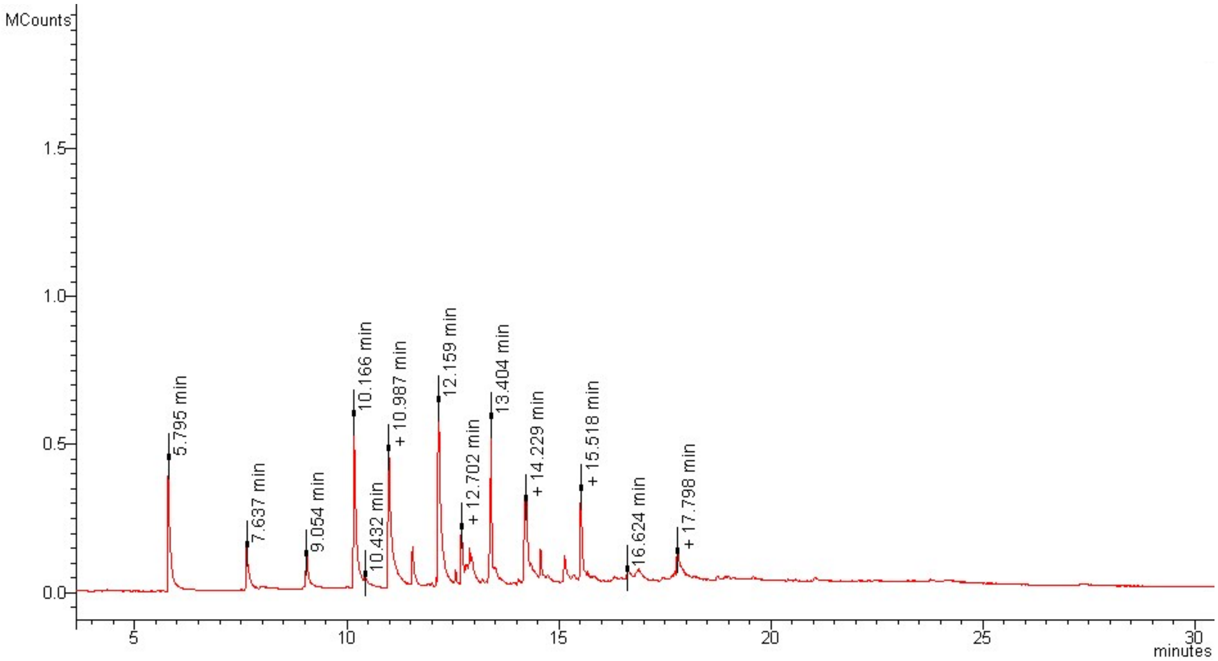


Fig. S4 GC-MS chromatograph of ethyl acetate (EtOAc) soluble products from liquid. Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

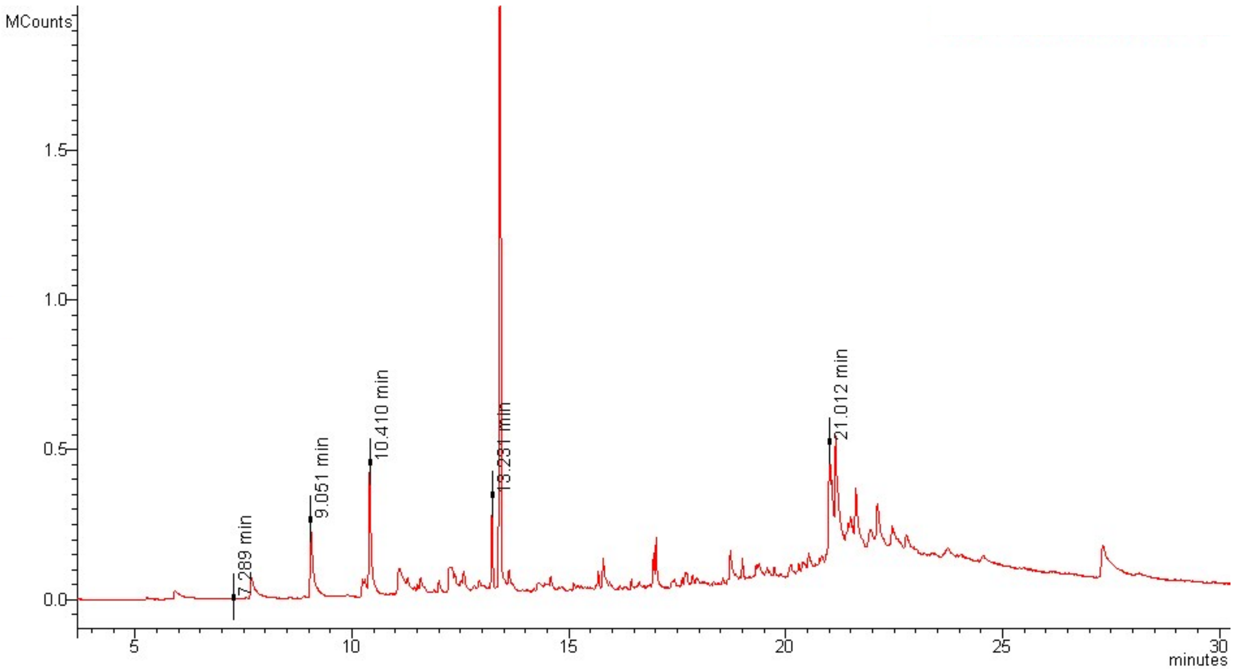


Fig. S5 GC-MS chromatograph of diethyl ether (DEE) soluble products from solid. Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

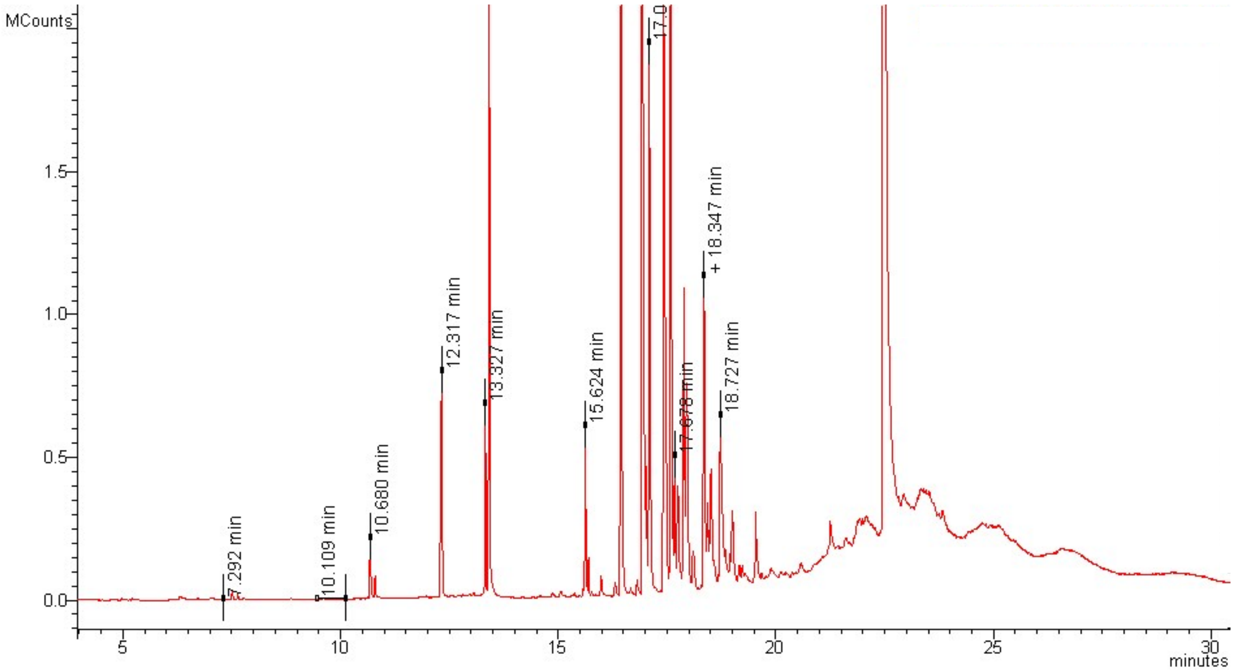


Fig. S6 GC-MS chromatograph of ethyl acetate (EtOAc) soluble products from solid. Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

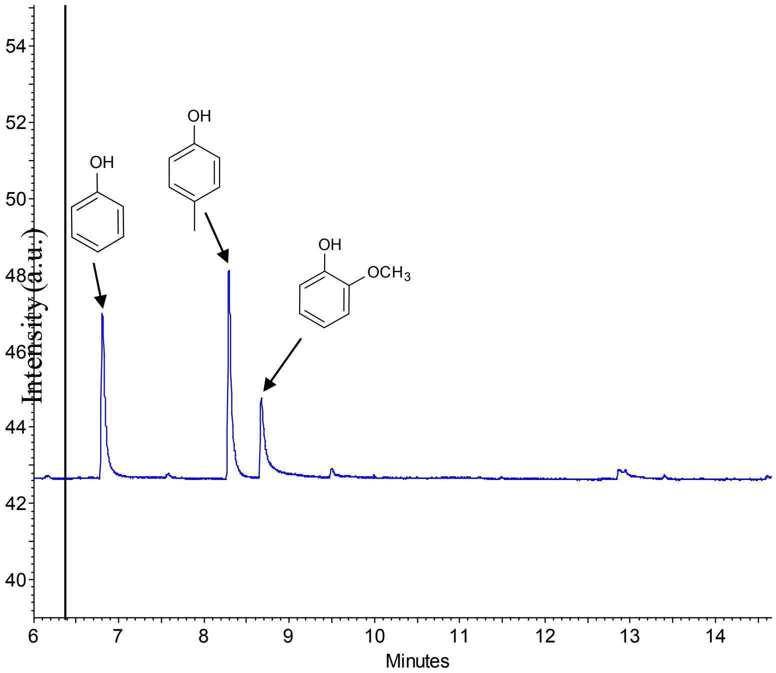


Fig. S7 GC chromatograph of products extracted from catalyst after reaction with CaO at 250 ºC, 1 h.

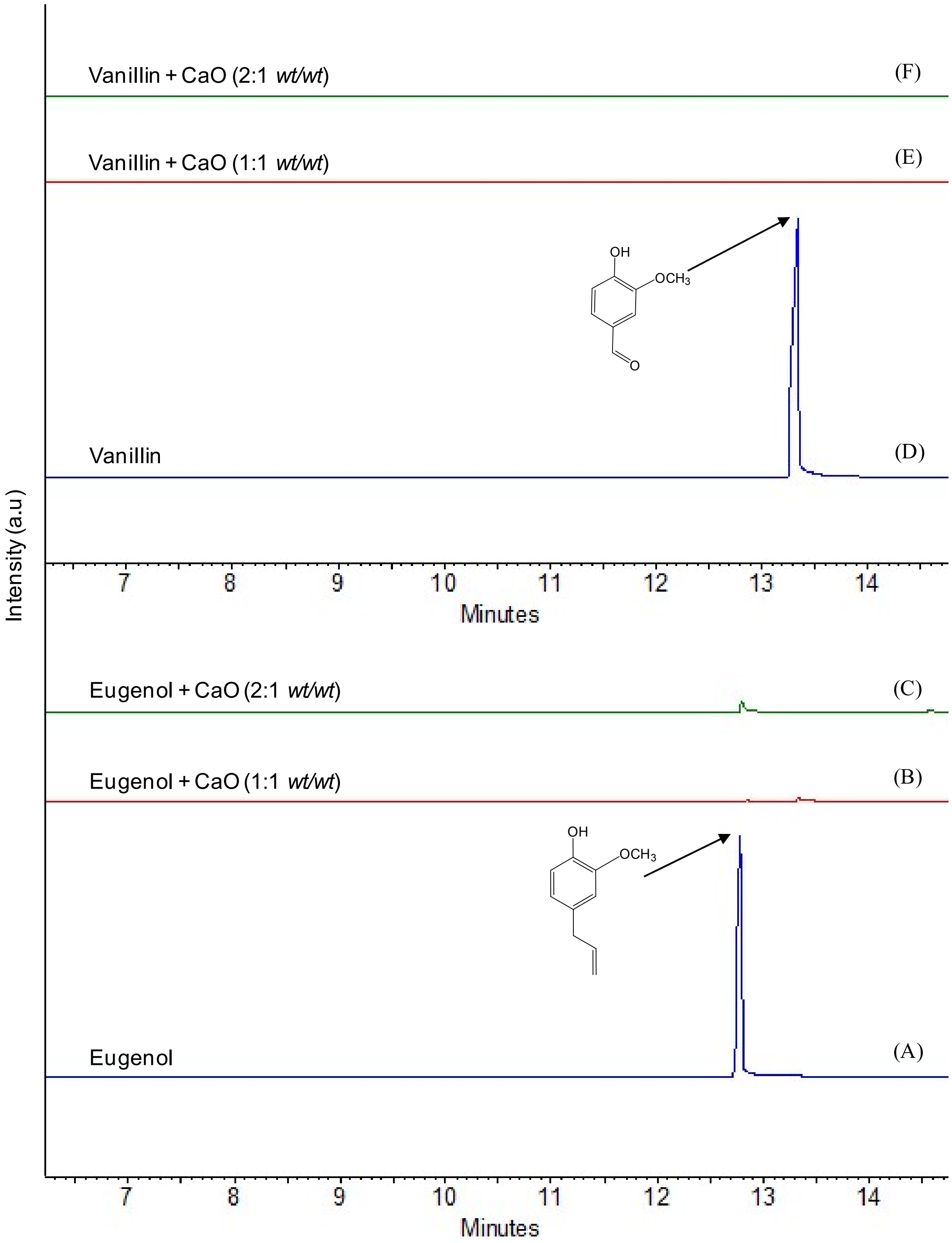


Fig. S8 GC chromatographs of adsorption study with single molecules. (A) Eugenol in EtOH:H_2O (1:2 *v/v*) 6 mL, (B) Eugenol:CaO (1:1 *wt/wt*) in EtOH:H_2O (1:2 *v/v*) 6 mL, (C) Eugenol:CaO (2:1 *wt/wt*) in EtOH:H_2O (1:2 *v/v*) 6 mL, (D) Vanillin in EtOH:H_2O (1:2 *v/v*) 6 mL, (E) Vanillin in EtOH:H_2O (1:2 *v/v*) 6 mL, (F) Vanillin in EtOH:H_2O (1:2 *v/v*) 6 mL.

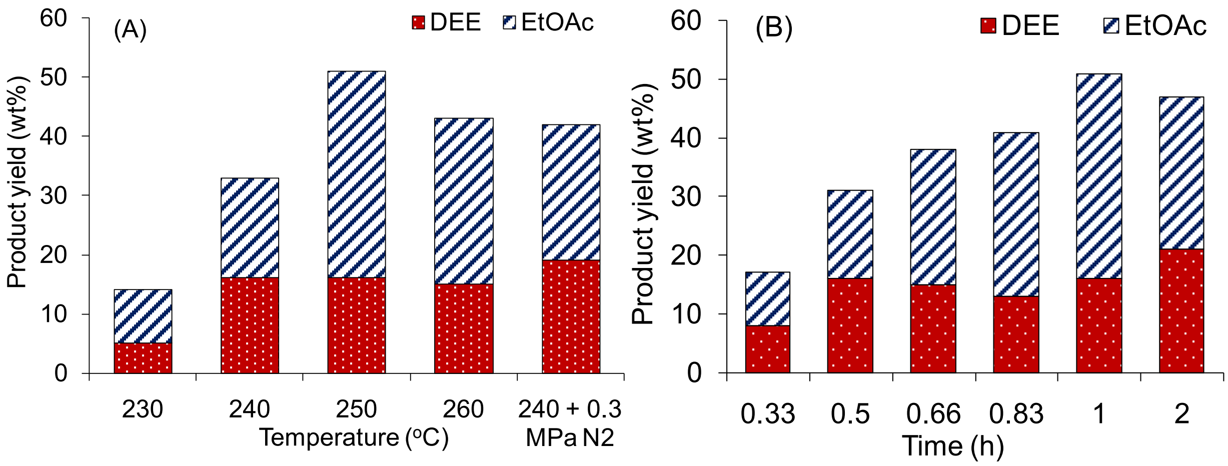


Fig. S9 Depolymerization of lignin. (A) Effect of temperature and (B) Effect of time. Reaction condition: Lignin:NaX = 1:1 *wt/wt*, $EtOH:H_2O$ (1:2 *v/v*) 30 mL.

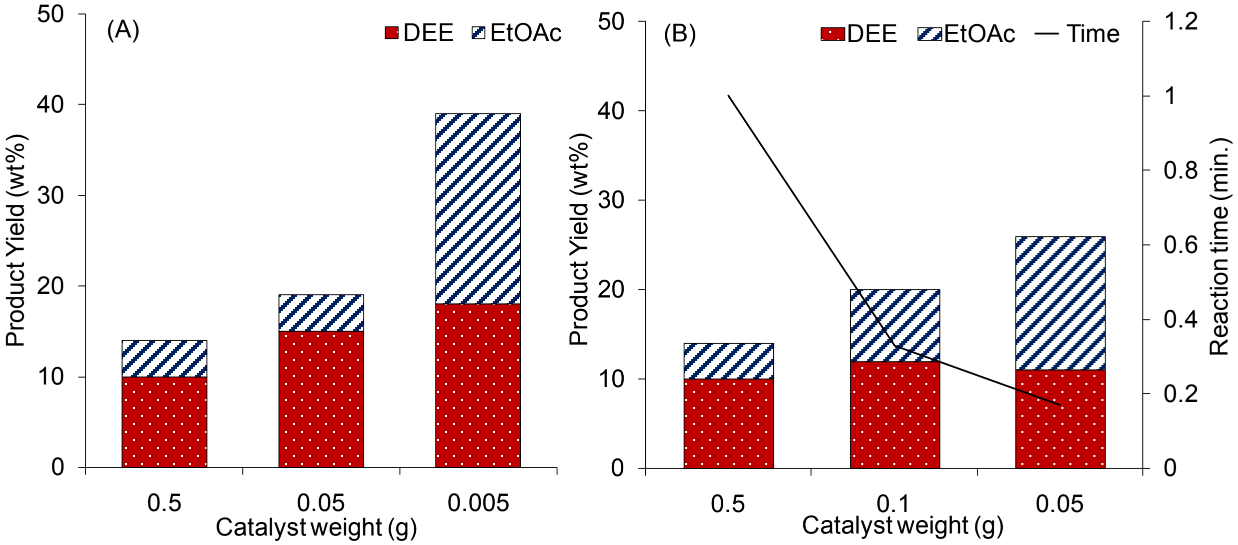


Fig. S10 Depolymerization of lignin using CaO catalyst.
Reaction condition: (A) Lignin (0.5 g), $EtOH:H_2O$ (1:2 *v/v*) 30 mL, 250 °C, 1 h. (B) Lignin (0.5 g), $EtOH:H_2O$ (1:2 *v/v*) 30 mL, 250 °C.

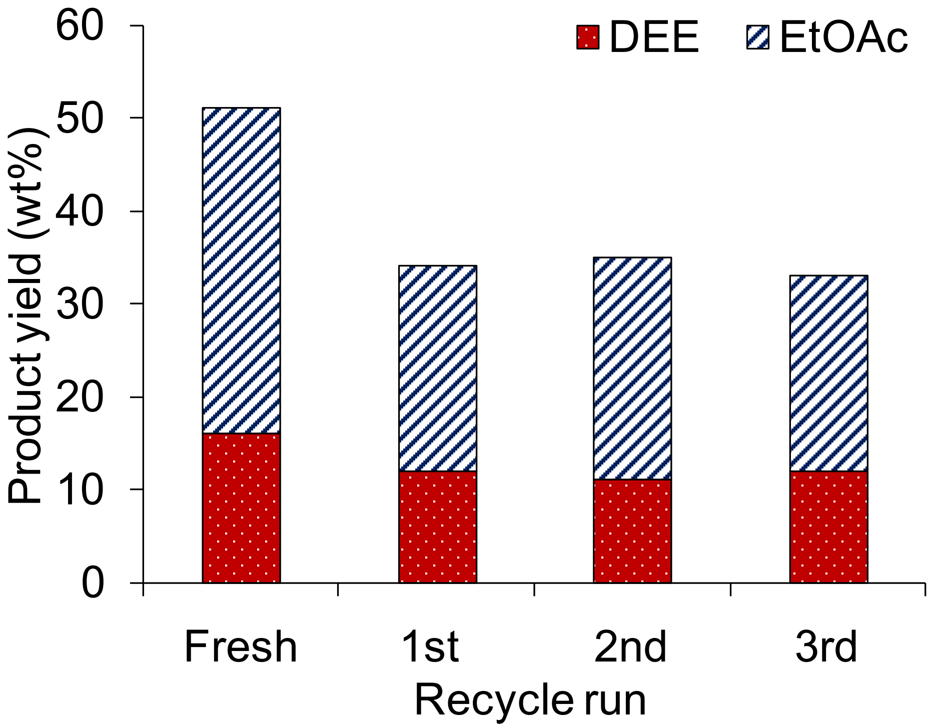


Fig. S11 Recyclability of catalyst (NaX).

Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h

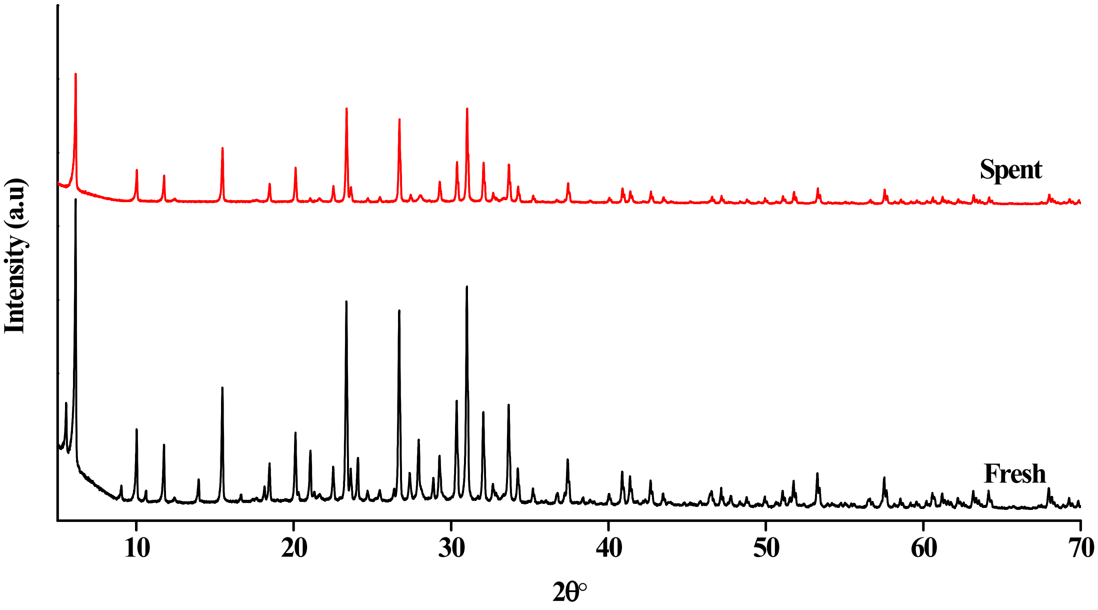


Fig. S12 XRD of fresh and spent NaX catalyst.

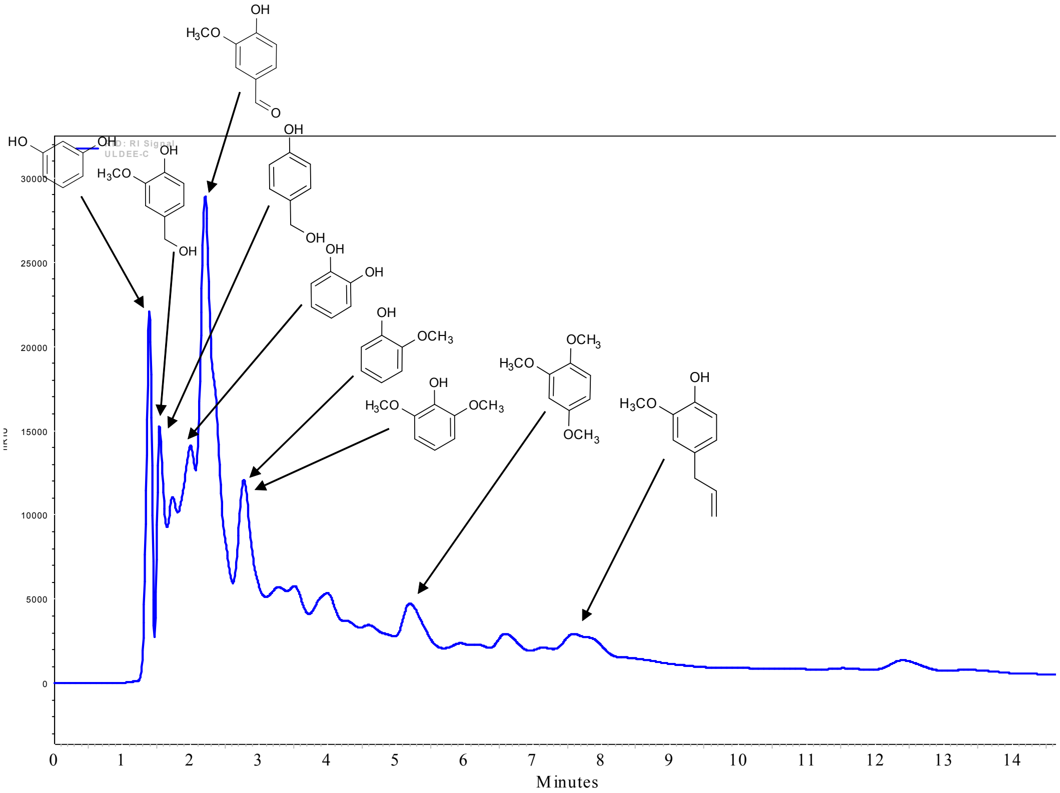


Fig. S13 HPLC chromatograph of lignin depolymerization products.

Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

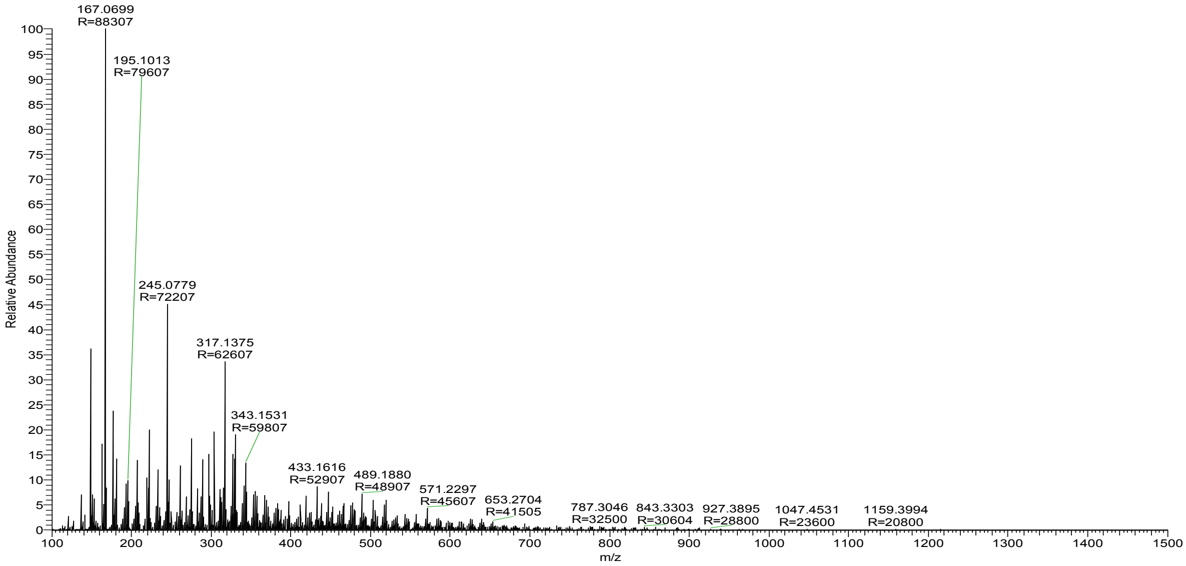


Fig. S14 LC-MS chromatograph of diethyl ether (DEE) soluble products from liquid.

Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

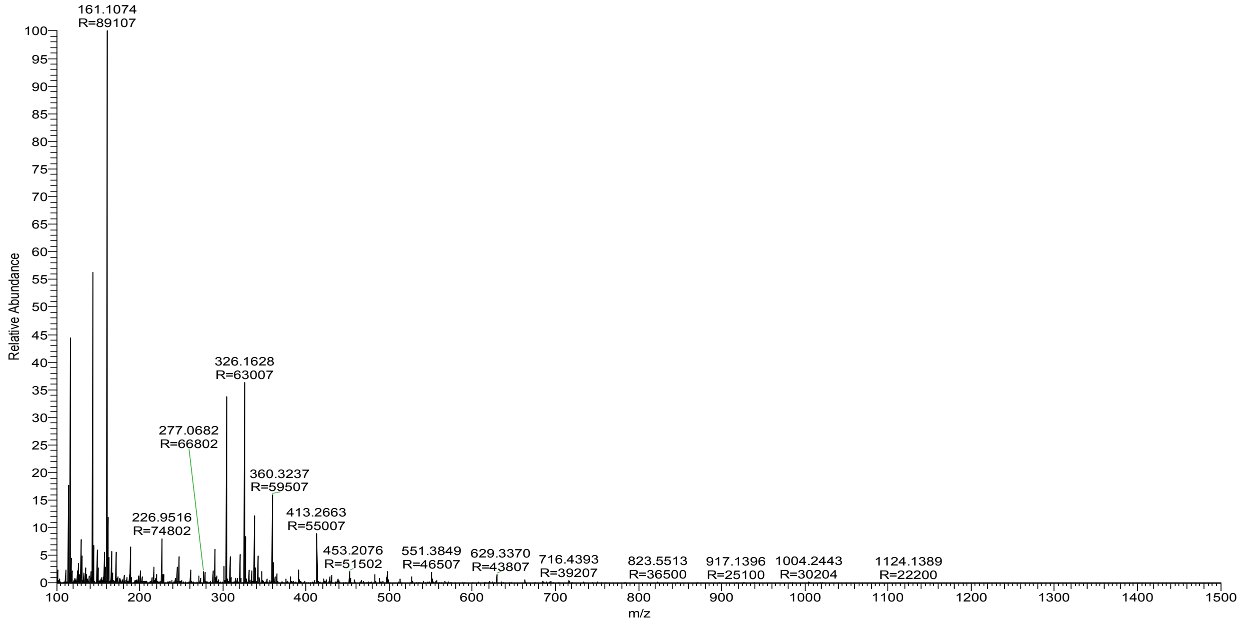


Fig. S15 LC-MS chromatograph of ethyl acetate (EtOAC) soluble products from liquid. Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

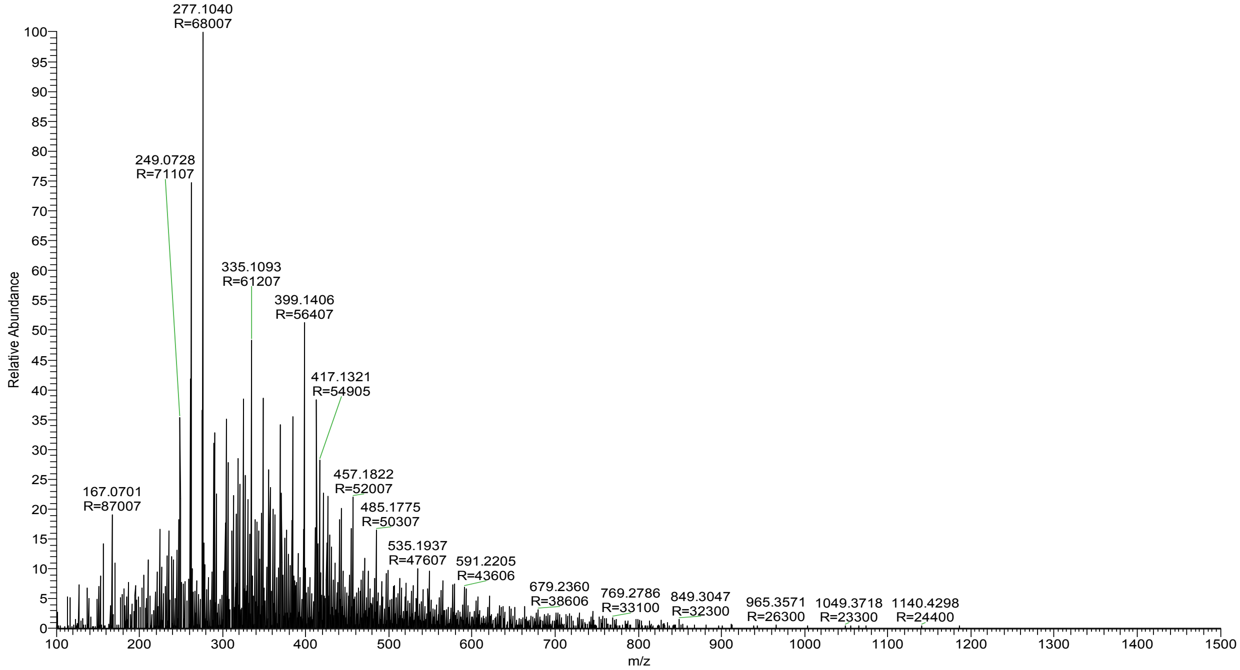


Fig. S16 LC-MS chromatograph of diethyl ether (DEE) soluble products from solid. Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

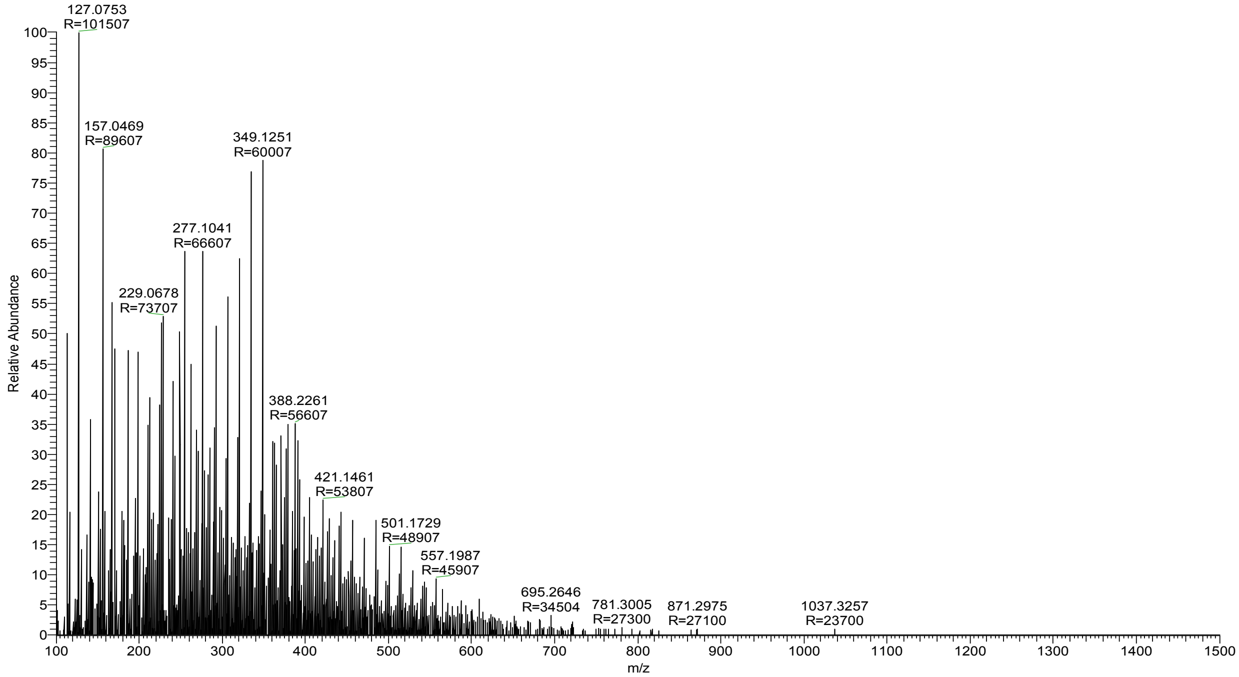


Fig. S17 LC-MS chromatograph of ethyl acetate (EtOAC) soluble products from solid. Reaction condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

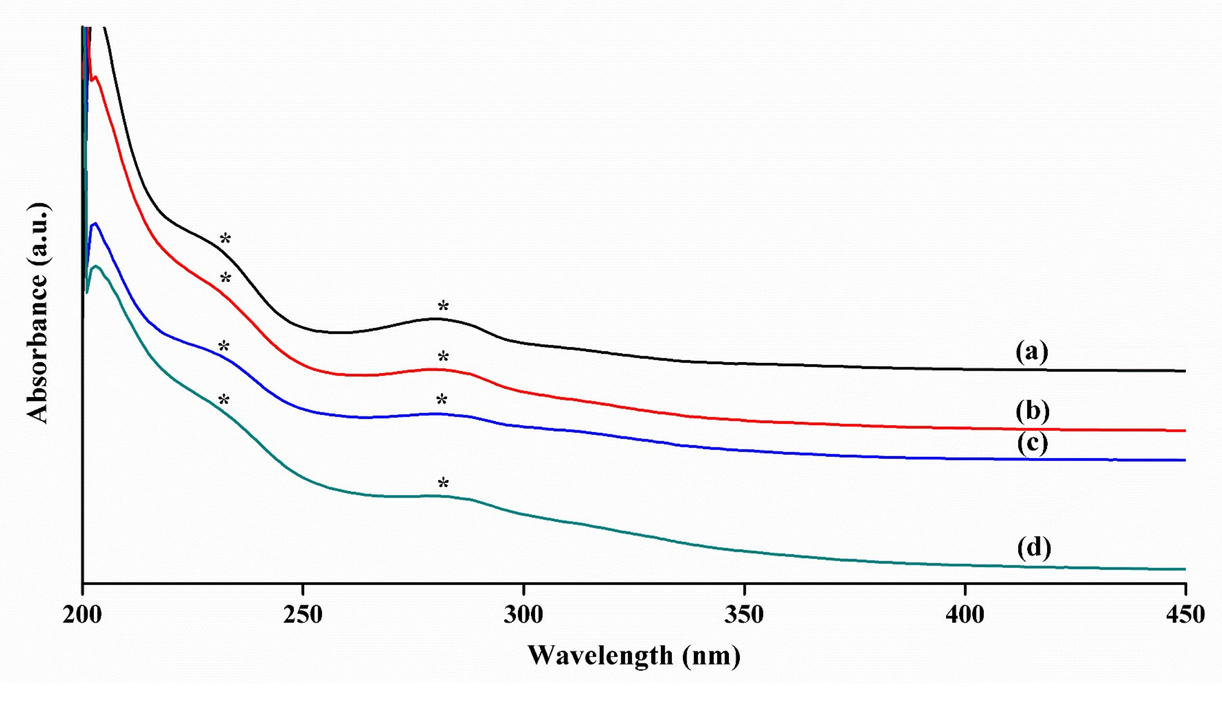


Fig. S18 UV analysis of products (a) DEE soluble products from liquid, (b) EtOAc soluble products from liquid, (c) DEE soluble products from solid, (d) EtOAc soluble products from solid. Reaction Condition: Lignin:NaX = 1:1 *wt/wt*, EtOH:H_2O (1:2 *v/v*) 30 mL, 250 °C, 1 h.

* Characteristics peak for aromatics

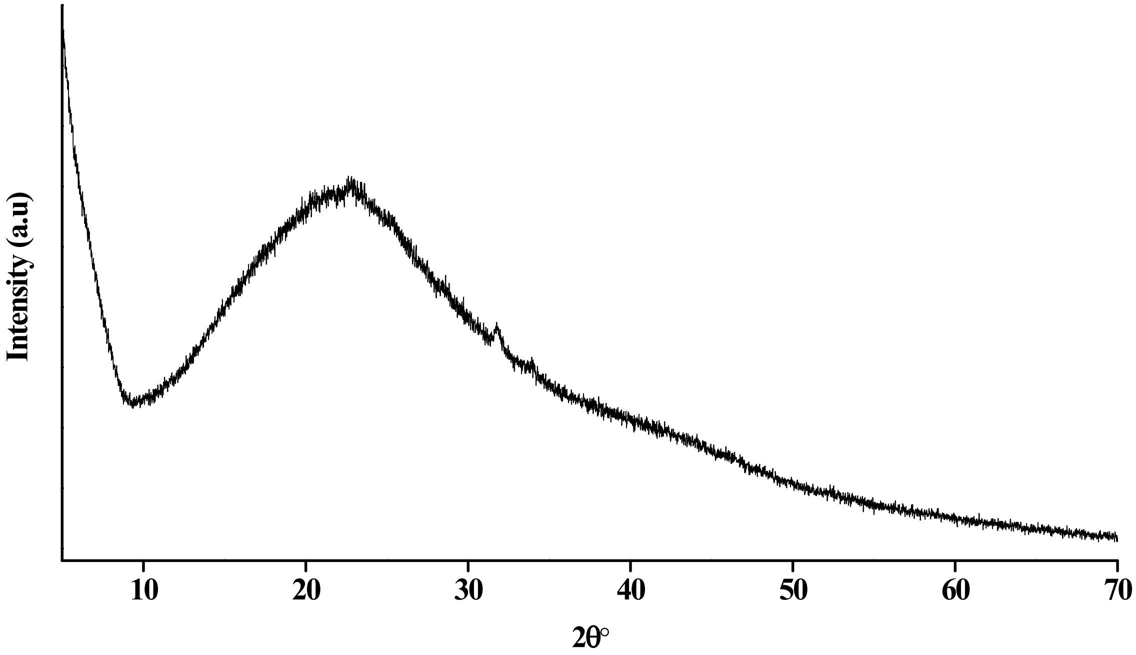


Fig. S19 XRD of alkaline lignin.

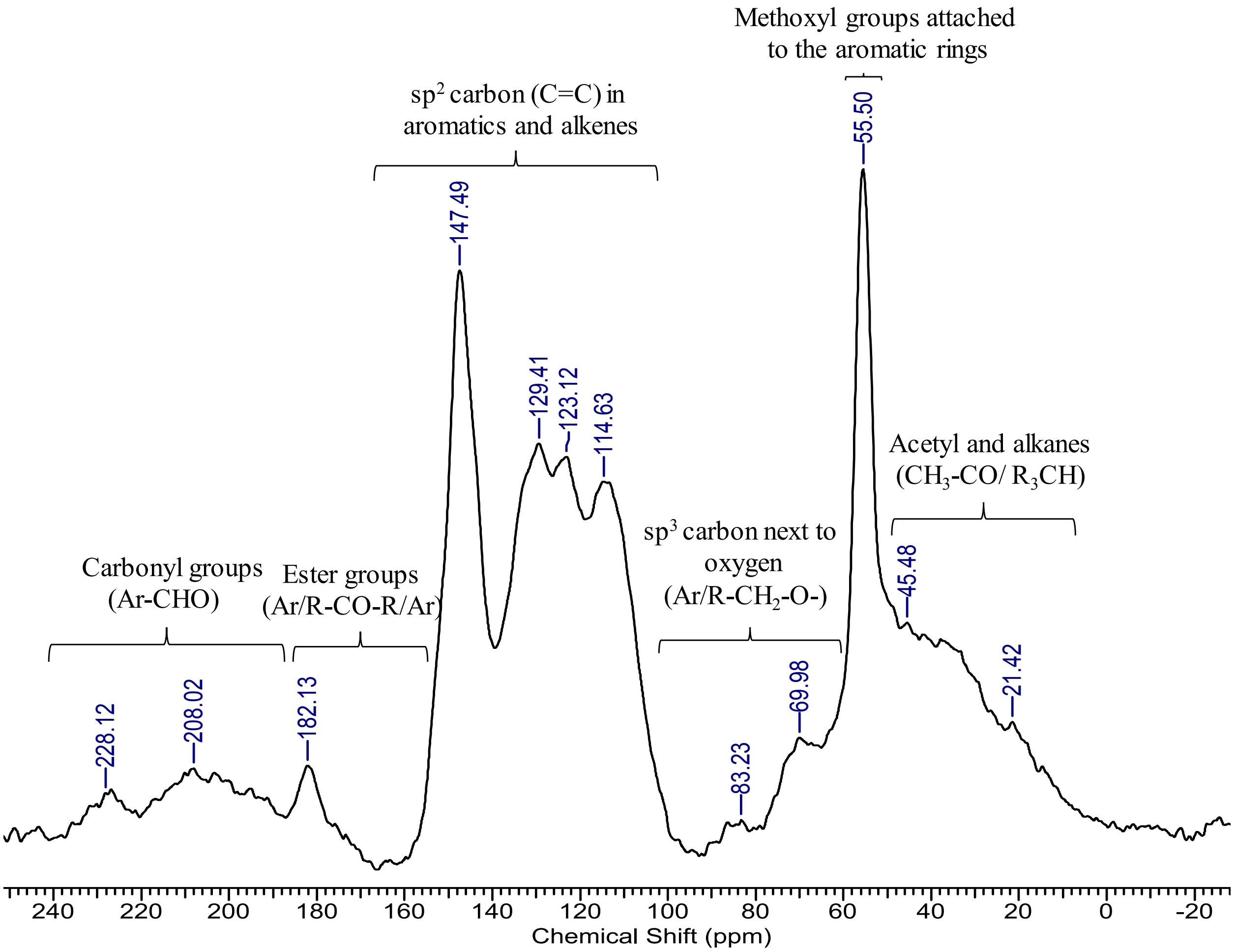


Fig. S20 Solid state ^{13}C NMR of alkaline lignin.

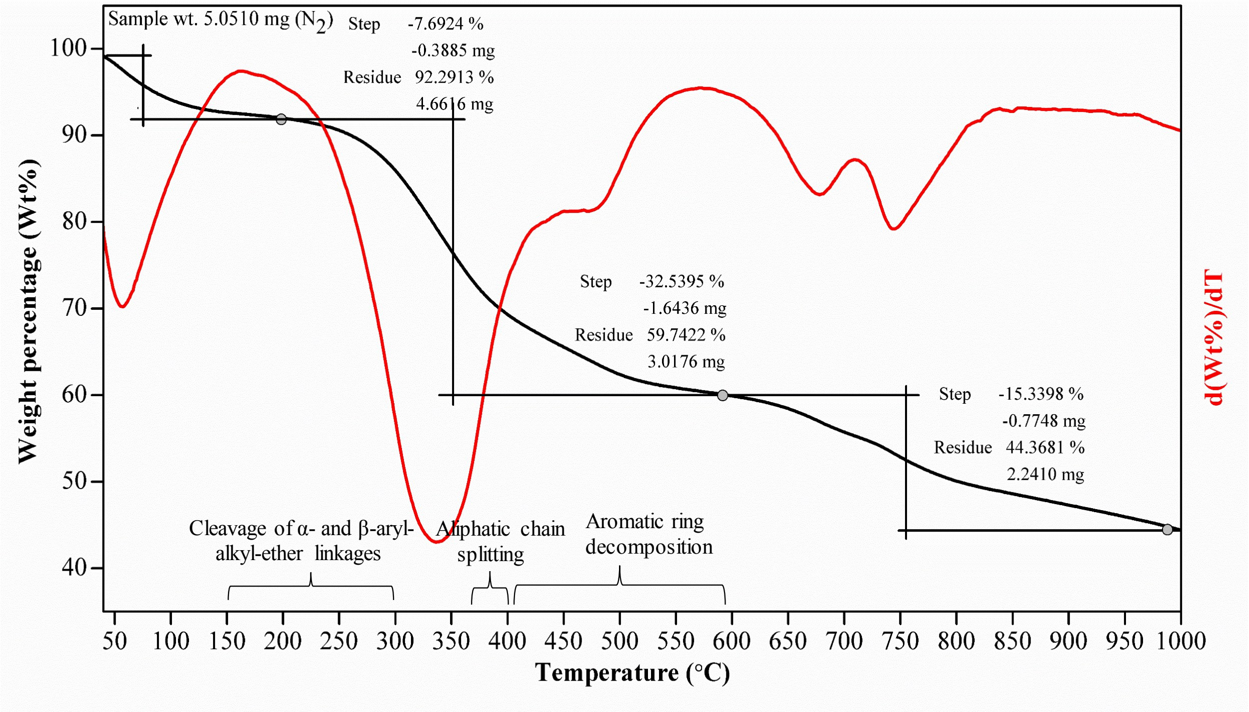


Fig. S21 TGA-DTA study of alkaline lignin.

Table S1 Solubility of alkaline lignin in various solvents.

Solvent	**Solubility (%)***
Water	100
Ethanol	4.1
Methanol	11.8
Acetone	1.3
Ethyl acetate	1.0
Chloroform	1.7
Tetrahydrofuran	2.4
Dichloromethane	2.7
Diethyl ether	0.3
Toluene	nd
Hexane	nd
Methanol:water (5:1 *v/v*)	85.5
Ethanol:water (1:2 *v/v*)	100

*0.5 g lignin dissolved in 30 mL of solvent.

Table S2 Summary of catalyst characterization.

Catalyst	**N_2 sorption**			**TPD-CO_2**	
	BET Surface area (m^2/g)	**Pore volume (cm^3/g)**	**Pore diameter (nm)**	**Total Basicity (mmol/g)**	**Peak maxima (°C)**
NaX	586	0.32	1.10	0.42	404
NaY	575	0.33	1.15	0.34	292
NaP	14	0.10	1.8	0.09	171 & 486
KLTL	220	0.13	nd	0.14	188
HT	207	0.95	9.2	0.40	294 & 603
HAP	39	0.18	9.08	0.12	166 & 587
CaO	12.4	0.05	8.2	1.96	408 & 673
MgO	9.2	0.02	4.8	0.24	604

Table S3 Summary on fresh and recovered catalyst weight.

Catalyst	**Fresh catalyst weight (g)**	**Recovered solid weight (g)**	**Solid other than catalyst (g) (Recovered - Fresh)**	**After extraction of adsorbed products weight of solid (g)***
NaX	0.5	0.49	-	-
HT	0.5	0.6349	0.1349	0.6304
HAP	0.5	0.5384	0.0384	0.5145
MgO	0.5	0.7583	0.2583	0.7095
CaO	0.5	0.9178	0.4178	0.8929
MgO	0.03	0.0412	0.0112	0.0378
CaO	0.0055	0.0122	0.0067	0.010

* After extraction of adsorbed products in mixture of DEE and EtOAc (1:1 *v/v*, 30 mL), dried at 55 °C for 16 h.

Table S4 Details on carbon analysis of fresh and spent catalysts and adsorbed products.

Catalyst (0.5 g each)		**HT**	**HAP**	**CaO**	**MgO**
Weight of Spent catalyst (g)		0.6349	0.5384	0.9178	0.7583
Weight of solid adsorbed on spent catalyst (g)		0.1349	0.0384	0.4178	0.2583
Elemental analysis of fresh catalyst (%)	**C**	1.59	-	-	-
	H	2.46	-	-	-
	O	-	-	-	-
Elemental analysis of spent catalyst (%)	**C**	13.07	3.27	16.32	7.63
	H	3.47	0.34	2.05	3.23
	O	-	-	-	-
Increase of 'C' on spent catalyst (%)		11.8	3.27	16.32	7.63
Increase of C, H and O (g)	**C**	0.073	0.018	0.15	0.058
	H	0.008	0.002	0.015	0.004
	O	0.029	0.007	0.06	0.023

Weight of solid on spent catalyst based on elemental analysis (g)	0.11	0.027	0.225	0.085

Table S5 Adsorption study with single molecules.

Aromatic monomers	**CaO fresh weight (g)**	**Recovered solid weight (g)**
Vanillin (0.1 g)	0.1	0.16
Vanillin (0.1 g)	0.05	0.073
Eugenol (0.1 g)	0.1	0.1841
Eugenol (0.1 g)	0.05	0.1216

Table S6 Catalyst charge in the reactor to maintain the particular pH.

Catalyst	**Weight of the catalyst (g)**	**pH**
NaX	0.5	9.2
NaX	0.08	8.7
NaY	0.5	8.7
NaP	0.5	8.7
MgO	0.5	10.5
MgO	0.03	9.2
CaO	0.5	≥ 13.4
CaO	0.0055	9.2

Table S7 Solubility of Catalysts in water at different temperatures.

Catalyst	**Solubility in water (g/100 mL)**		**Solubility (g/30 mL)***
	25°C	**100 °C**	
CaO	0.120	0.054	
$Ca(OH)_2$	0.159	0.070	0.021
MgO	0.086	-	
$Mg(OH)_2$	0.0009	0.004	0.0012

* Calculated in 30 mL of water (this volume is used in reaction) by considering solubility of hydroxides at 100 °C in 100 mL.

Calculation on percentage (%) catalyst in heterogeneous phase

MgO (Mw. = 40 g/mol)	$\xrightarrow{H_2O}$	$Mg(OH)_2$ (Mw. = 58 g/mol)	
0.5 g of MgO taken for reaction	$\longrightarrow$	0.725g of $Mg(OH)_2$	(formation considering 100% conversion of MgO into $Mg(OH)_2$)
If 0.725g	$\longrightarrow$	100%	
0.0012g (solubility of $Mg(OH)_2$ in 30 mL water) – please see Table 2	$\longrightarrow$	(100 x 0.0012) / 0.725	
		= 0.1655 % $Mg(OH)_2$ is only soluble in 30 mL water	

Hence, only 0.1655% catalyst is soluble in water considering 100% formation of $Mg(OH)_2$ under reaction conditions from MgO.

Thus, expected heterogeneous form of catalyst = total MgO taken –solution of $Mg(OH)_2$ in H_2O

= 0.5 g – 0.0012g

= 0.4988 g which is 99.76% of total catalyst taken.

Thus, 99.76% catalyst remains as heterogeneous.

Similar to MgO, calculations are also done for CaO,

$CaO \xrightarrow{H_2O} Ca(OH)_2$

(Mw. = 56 g/mol) (Mw. = 74 g/mol)

0.5 g of CaO taken for reaction $\longrightarrow$ 0.6607g of $Ca(OH)_2$ Considering 100% conversion of CaO into $Ca(OH)_2$

If 0.6607 g $\longrightarrow$ 100%

0.021 g (solubility of $Ca(OH)_2$ in 30 mL water) – Please refer Table 2 $\longrightarrow$ (100 x 0.021) / 0.6607

= 3.17 % of $Ca(OH)_2$ is soluble in 30 mL water

Hence, only 3.17 % catalyst is soluble in 30 mL water considering 100% conversion of CaO into $Ca(OH)_2$.

Expected heterogeneous form of catalyst = total CaO taken –solution of $Mg(OH)_2$ in H_2O

= 0.5 g – 0.021g

= 0.479 g of catalyst remains as heterogeneous (95.80%)

Thus, 95.80% catalyst remains as heterogeneous.

From above calculations, it is clear that almost all the catalyst is heterogeneous under reaction conditions.

Table S8 Summary on lignin characterization.

Substrate	M. Wt. (Da)	Elemental analysis (%)			TGA-DTA (Residue %)		EDAX (element)	Monomer molecular formula
		C	H	S	N_2	Air		
Alkaline Lignin	60,000	52	5	2.05	44	17	C, O, Na, S	$C_{8.7}H_{9.1}O_{5.1}S_{0.13}$

References:

1. R. Sahu and P. L. Dhepe, *ChemSusChem*, 2012, **5**, 751-761.
2. F. S. b. Ryan M. Ravenelle, Andrew D'Amico, Nadiya Danilina, Jeroen A. van Bokhoven, Johannes A. Lercher, Christopher W. Jones, and Carsten Sievers, *J. Phys. Chem. C*, 2010, **114**, 19582-19595.
3. H. Xiong, H. N. Pham and A. K. Datye, *Green Chem.*, 2014, **16**, 4627-4643.
4. L. Zhang, K. Chen, B. Chen, J. L. White and D. E. Resasco, *J Am Chem Soc*, 2015, **137**, 11810-11819.
5. J. V. A. Thijs Ennaert , Jan Dijkmans , Rik De Clercq , Wouter Schutyser , Michiel Dusselier , Danny Verboekend and Bert F. Sels *Chem. Soc. Rev.*, 2016, **45**, 584-611.
6. D. Verboekend, M. Milina and J. Pérez-Ramírez, *Chemistry of Materials*, 2014, **26**, 4552-4562.
7. J. P. B. J.C. Moise, A. Methivier, *Microporous and Mesoporous Materials*, 2001, **43**, 91-101.