Electronic Supplementary Information (ESI)

Solid acid catalyzed depolymerization of lignin into value added aromatic monomers

A. K. Deepa, Paresh L. Dhepe*

I. Experimental

1. Depolymerization of lignin

Depolymerization of lignin: Reactions are carried out in the batch mode. Parr autoclaves, USA provided the high pressure, high temperature autoclave. Lignin (0.5 g), catalyst (0.5 g), and solvent (30 ml) were charged in the autoclave. Then, autoclave was flushed with nitrogen gas for at least 3 times and was filled with 0.7 MPa N_2. Afterwards, heating was started under slow stirring (100 rpm). After attaining the desired reaction temperature stirring rate was increased and this time was considered as the starting reaction time. After the reaction the reactor was cooled and gas was released. Initially, reaction mixture (water+methanol) was directly injected in FID-GC after the reaction. Later, solvent was evaporated and solid was recovered. The solid was then dissolved in various organic solvents such as tetrahydrofuran, ethyl acetate for the analysis. The % of aromatic monomer was calculated based on the solid recovered from the above solvents and also by FID-GC calibration curves.

2. Analysis

Reaction mixture was analysed using GC, GC-MS, ICP-OES, MALDI-TOF, CHNS analysis.

2.1. FID-GC, TCD-GC and GC-MS

2.1.1. FID-GC

Reaction mixture is analyzed for the product formation by gas chromatography (GC) using Varian 3800 model GC, Netherland; with flame ionization detector (FID). It was equipped with CPSIL 8CB capillary column (5 % phenyl 95 % dimethyl polysiloxane) (30 m length, 0.25 mm diameter).

N_2 (30 mlmin^{-1}) is used as a carrier gas, H_2 (25 mlmin^{-1}) is used for flame and air as oxidizer (300 mlmin^{-1})

Carrier gas flow =0.6 mlmin^{-1}

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

The Column oven program used was

Temp (°C)	Rate (°Cmin^{-1})	Hold Time (min)
100	___	4
280	10	20

2.1.2 TCD-GC

Gas samples were analyzed by gas chromatography (GC) using Chemito 8610 model GC,with TCD detector. It was equipped with Porapack Q column (9feet, 2mm diameter).

Injector temp: 50°C, Detector temp: 150°C

The Column oven program used was

Temp (°C)	Rate (°Cmin^{-1})	Hold Time (min)
50	___	4
180	10	2

2.1.3. GCMS

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 mlmin^{-1}) 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 GCMS peaks are matched with the mass spectra in NIST library for compound identification

2.2. ICP-OES analysis

It is an analytical technique used for the detection of trace metals. It uses inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelength characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. Argon gas was typically used to create high temperature plasma of 6727°C. Samples were analyzed in SPECTRO ARCOS Germany, FHS 12 instrument. Lignin samples were burned in air at 650°C for 360 min., diluted to a known volume with Millipore water and then analyzed.

Reaction mixture was analysed, to quantify the metal content after the reaction.

2.3. Elemental analysis

Elemental analysis was done in Thermo Finnigan, Italy; model EA1112 Series Flash Elemental Analyzer. This analyzer measures the amount of C, H, N, O and S in samples by rapid combustion of small amounts (1-2 mg) of the sample in pure O_2 (Dumas method or "flash combustion"). The analysis of all elements in the CHNS group was performed simultaneously.

3. Lignin characterization:

Lignin is characterized using following techniques.

3.1. MALDI-TOF mass spectroscopy

MALDI-TOF is a novel spectroscopic technique used for the molecular mass determination of polymer molecules. The charge to mass ratio (m/z) obtained corresponds to the absolute molecular mass of the analyte. MALDI-TOF for lignin samples were obtained using Voyager DE-STR instrument. It was equipped with a N_2 laser (337 nm, 3 ns pulse, 20 Hz maximum firing rate). The matrix compound used was 2, 5-dihydroxy benzoic acid (DHB). Lignin was dissolved in methanol with a concentration of 1mg/ml. Lignin samples (1μl) were overlaid onto the matrix (1μl) placed on the golden MALDI target plate. Plate was then kept for drying until the solvent was evaporated and then subjected for the analysis.

3.2. Elemental analysis.

Same as mentioned above (section 2.3).

3.3. ICP-OES analysis.

Same as mentioned above (section 2.2).

3.4. Thermogravemetric analysis.

The thermal degradation of the sample was studied using METTLER TOLEDO TGA /SDTA851 series, USA; instrument with a heating rate of $10°C min^{-1}$. The sample was heated from room temperature to 1000°C to study the complete decomposition. All the samples were done both in N_2 and air. TGA shows the weight loss of the material with temperature and DTA which is the first derivative of TGA shows the rate of weight loss.

3.5. SEM-EDAX.

Scanning electron microscopy (SEM) is a technique used to study the morphology and particle size of the sample. The SEM micrographs of the samples were obtained on a Leo Leica Cambridge UK Model Stereoscan 440 scanning electron microscope. An electron beam of 5-50 eV was scanned over the sample. The samples were loaded using Carbon tape on the stubs and then analyzed. EDAX is also attached to SEM which helps in the determination of elemental composition of the sample.

4. Catalyst Synthesis and Characterization:

4.1. Synthesis of 10 wt%MoO$_3$/SiO$_2$. 10 wt% MoO_3/SiO_2 was synthesized by sol-gel method (K. Suzuki, T. Hayakawa, M. Shimizu, K. Takehira, *Catalysis Letters* 1995, **30**, 159). The calculated amount of ammonium heptamolybdate was dissolved in ethylene glycol (Merck), to which tetraethyl orthosilicate (Aldrich) was added. The resultant solution was aged under stirring at ca. 80°C for 300 min. Water and a small amount of nitric acid were poured to the solution and kept at 80°C with continuous stirring until it became gel. The gel was then evacuated at 100°C for 300 min. with a rotary evaporator. The resulting powder was

calcined at 650°C for 300 min. in air. Catalyst was characterized with the following techniques.

4.2. Characterization of catalysts.

It is well known in the literature that removal of 'C' from a material can be done by calcining the material/catalyst in air at a temperature of 550-600°C. We calcined the catalyst to remove adsorbed carbon, if any.

4.2.1. XRD.

The morphology of 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 5º to 50° at the rate of $4.3°min^{-1}$.

4.2.2. ICP-OES analysis.

Same as mentioned above (section 2.2).

4.2.3. NH$_3$ TPD analysis.

Temperature programmed desorption is a technique in which probe molecule like NH$_3$ which is basic in nature, get adsorbed on the acid sites of the catalysts. By increasing the temperature, probe molecule is desorbed and detected using a TCD detector. Analysis was done in Micrometrics Autochem-2910 model, instrument; USA. Catalyst was activated at a temperature of 500°C in Helium gas flow (25 $mlmin^{-1}$). NH$_3$ adsorption (30 $mlmin^{-1}$) was done at 100°C and desorption was started from 100°C to 823°C at the rate of $10°Cmin^{-1}$. From the quantity of NH$_3$ desorbed the density of acid sites can be measured.

4.2.4. Nitrogen sorption studies.

Textural properties like 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 250°C for 180 min. The specific surface area was determined using BET method, pore size data was obtained using BJH method and pore volume using t-plot method.

4.2.5. Elemental analysis.

Same as mentioned above (section 2.3).

4.2.6. Thermo gravemetric analysis.

Same as mentioned above (section 3.4)

5. Yield calculations

Initially, reaction mixture (water+methanol) was directly injected in GC after the reaction. Later, solvent was evaporated and solid was recovered. The solid was then dissolved in various organic solvents such as tetrahydrofuran, chloroform, ethyl acetate for the analysis. The % of aromatic monomer was calculated based on the solid recovered from the above solvents.

$$\text{Aromatic monomers yield}(\%) = \frac{\text{Weight of THF soluble solid}}{\text{Lignin charged}} \times 100$$

For individual aromatic monomers yield was calculated as mentioned in section

6. Mass balance calculation

$$\text{Mass balance}(\%) = \frac{\text{methanol solubles} + \text{solid deposited on the catalyst}}{\text{Lignin charged}} \times 100$$

In the case of dealkaline lignin, it contains 11 % of moisture, as mentioned by the supplier (TCI chemicals, ref. 29 from main text)

So, if 0.5 g dealkaline lignin is charged in the reactor then in fact it contains 0.055 g (11 %) moisture, then the actual lignin charged in the reaction is only 0.4450 g out of 0.5 g (0.5-0.055 g).

To elucidate how mass balance calculations are done following example can be refereed.

Reaction conditions: Dealkaline lignin, Solid acid catalyst, $H_2O:CH_3OH$ (1:5), 250°C, 30 min., 500 rpm, 0.7 MPa N_2 at RT

Total solid charged before the reaction,

Lignin charged= 0.4450 g (actually 0.5 g but contains 0.035 g moisture, from TGA),

Catalyst charged= 0.5000 g

Total solid charged= 0.9450 g (lignin weight + catalyst weight)

After reaction, solids and liquids are separated by centrifugation.

Total solid recovered after the reaction,

Total solid recovered= 0.6159 g (catalyst + solids)

Solid deposited on the catalyst = total solid recovered – catalyst charged = 0.6159-0.5000 = 0.1522 g

The liquids (methanol+water) is then subjected to rotavap (see note below) and solvent is removed to recover the solvent solubles,

Methanol+water soluble= 0.2774 g

Considering above values we can calculate the mass balance for lignin charged,

$$Mass\ balance = \frac{0.2774 + 0.1522}{0.4450} = 97\%$$

This exercise is done for all the reactions carried out and we observed mass balance of 95±10 %.

Note:

To ensure that there is no contribution of solvent in weight of solid we took following precaution:

As we have mentioned in SI (above and in Fig. S1), liquids were subjected to rotavap (rotary evaporator) and solvents were removed. We did not mention in detail over there that after rotavap solids obtained were dried at 60°C in oven for overnight (16 h). Afterwards we kept the solid at 60°C under vacuum for 2 h. We believe that this treatment is sufficient to remove the solvent present in the solid. Then the resulting solid was weighed. So there is an almost no possibility of water or methanol present with the solid. So the weight calculated does not include the solvent weight.

To ensure that no volatile products are escaped during the rotary evaporation we took following precaution:

After the rotavap the solvent (methanol+water) collected in the collection flask was analyzed by GC. We did not find any peak besides methanol in the GC. This helps us to confirm that no products are getting evaporated during the rotavap. Also, typically in our group we use 3 ice traps (in series) while using rotavap to capture any solvents/compounds. This assures us that no volatile compounds are escaping.

7. S/C calculations

Average molecular weight of monomeric lignin unit can be taken as 160 (based on Fig. S3 in SI).

The HUSY (Si/Al=15) catalyst has acid amount of 0.55 mmol/g.

0.5 g (substrate loading)/160 = 3.125 x 10^{-3} mol (3.125 mmol),

0.5 g (catalyst loading) x 0.55 = 0.275 mmol

S/C (mol basis) = 3.125/0.275 = 11.36

II. Results:

Supporting online text

1. Elemental analysis of products in the reaction mixture

CHNS analysis of methanol+water soluble products is done, which showed C=67 % and H=6 %.

2. Formation of gases and stability of solvents

We did blank reactions without any lignin (only solvent and HUSY at 250°C for 30 min). This was done in order to study stability of the solvent under the reaction conditions. We have analysed the reaction mixture (methanol+water) after reaction using GC-FID and we did not find any extra peak besides that for methanol.

Methanol may form CO_2 & H_2 but if this happens then the reaction pressures may increase. This was not observed in our case. Moreover, we have paid careful attention to analyze gas phase of reaction using GC-TCD, which is already mentioned in our manuscript. However we could not see any peaks for CO, CO_2, CH_4, C_2-C_4 and H_2 in the analysis.

3. Stability of catalysts

Zeolites have a proper/definite channel structure and acid sites (active sites for this reaction) can be accessed only if channels are proper/intact. What we observed (by characterizations)

was that zeolites undergo morphological changes (ESI, Figs. S6 and S7; Table S4) after the first run and thus most of the active sites are not accessible any longer (may be buried) by substrates. Moreover, whatever acid sites are accessible can get poisoned by Na and S present in the reaction. Considering this we observed much faster decrease in activity with zeolites as catalysts [HUSY catalyst: 60% (1st run), 25% (2nd run, 59% decrease of 1st run activity)]. On the other hand with SiO_2-Al_2O_3 ca.15% decrease in yield was observed in each consecutive runs (please refer text, recycle study). This explains that compared to SiO_2-Al_2O_3, zeolites undergo quick degradation. We believe this rate of degradation matters as it is easy to prepare SiO_2-Al_2O_3 than zeolites and cost wise also former catalyst is cheaper than the latter.

The similar phenomenon of zeolites undergoing morphological changes is presented in our earlier work (on hemicelluloses) published (*ChemSusChem*, 2012, **5**, 751).

III. Tables & Figures

Table S1. Solubility of Dealkaline lignin in various solvents.

Solvent	Polarity index	Solubility (%)[a]
Water	9.0	44
Ethanol	5.2	Insolb.
Methanol	5.1	74
Acetone	5.1	Insolb.
Ethyl acetate	4.4	Insolb.
Chloroform	4.1	Insolb.
Tetrahydrofuran	4.0	Insolb.
Dichloromethane	3.1	Insolb.
Diethyl ether	2.8	Insolb.
Toluene	2.4	Insolb.
Hexane	0.0	Insolb.
Methanol: water (5:1v/v)	—	100

[a] 50 mg lignin solublized in 1ml solvent at RT.

Table S2. Summary on catalyst properties.

Catalyst	Structure	Nitrogen sorption			NH$_3$-TPD		
		BET SA[a] (m^{2}g^{-1})	V[b] (cm^{3}g^{-1})	D[c] (nm)	Weak acid sites[d] (mmolg^{-1})	Stong acid sites[d] (mmolg^{-1})	Total acidity[d] (mmolg^{-1})
H-USY (Si/Al=15)	Micro	873	0.45	0.75	0.06	0.49	0.55
H-ZSM-5 (Si/Al=11.5)	Micro	423	0.22	0.60	0.37	0.61	0.98
H-BEA (Si/Al=19)	Micro	761	0.34	0.60	0.25	0.66	0.91
H-MOR (Si/Al=10)	Micro	528	0.22	0.59	0.5	0.65	1.15
Nb$_2$O$_5$	--	115	--	--	0.30	--	0.30
SO$_4^{2-}$/ZrO$_2$	--	84	0.02	--	nd	nd	Nd
Clay (K10)	Layered	246	0.3	--	0.09	0.33	0.42
Al pillared clay	Layered	Nd	nd	nd	nd	nd	nd
SiO$_2$-Al$_2$O$_3$	Micro-meso	532	0.82	4.90	0.17	0.46	0.63
10%MoO$_3$/SiO$_2$	Nonporous	Nd	nd	nd	nd	nd	nd

[a] Brunauer–Emmett–Teller (BET) surface area, [b] Pore volume, [c] Pore diameter, [d] Acidity measured by NH$_3$-TPD.

Table S3: Quantification of monomers using GC & GCMS Analysis

Compound Code from Fig. S2	Retention time (Minutes)	Compound name	% of monomer present in THF soluble mixture
c)	10.75	BHT	1.8%
d)	11.51	Vanillin	30%
e)	12.20	Eugenol	1%
f)	12.27	Acetoguaiacone	3.3%
g)	12.69	Methyl vanillate	8.2%
h)	12.88	Guaiacyl acteone	24%
i)	13.01	Acetosyringone	2.4%
l)	13.80	Homovanillic acid	9.6%
p)	15.79	Transconiferyl aldehyde	6.2%
			Total=87%

Reaction conditions: Dealkaline lignin, SiO_2-Al_2O_3, H_2O:CH_3OH (1:5 v/v), $250^{\circ}C$, 30 min.500 rpm, 0.7 MPa N_2 at RT.

Note: After reaction separation of the products is done as per the Fig. S1. 87% of THF soluble products are aromatic monomers, which mean that out of 29% of total products obtained by THF extraction, 25% is selectively monomers. Few of the aromatic monomers which are detected (GC-FID, GCMS) in our reaction are commercially not available and hence we could not quantify those (could not calibrate and calculate response factor). However, care has been taken to at least quantify the chemicals which have high intensity peaks. Even with this we could easily say that 87% of THF soluble products are aromatic monomers. Similar method for the quantification of products is reported in the literature [References: W. Xu, S. J. Miller, P. K.Agrawal, C. W. Jones, *ChemSusChem* 2012, **5**, 667; Y. Ye, Y. Zhang, J. Fan, J. Chang, *Ind.Eng. Chem. Res.,* 2012, **51**, 103; N. Yan, C. Zhao, P. J. Dyson, C. Wang, L.–t. Liu, Y. Kou, *ChemSusChem* 2008, **1**, 626 (reference 13 from main text)].

Table S4: Nitrogen sorption study of Fresh & Spent HUSY(Si/Al=15) zeolite

HUSY(Si/Al=15)	BET SA (m^2g^{-1})	V (cm^3g^{-1})	D (nm)
Fresh	873	0.45	0.75
Spent	303	0.14	1.51

Reaction charge

Reaction

RM in MeOH+H$_2$O

Centrifugation

Solution
(CH$_3$OH solb.)

Solid
(Catalyst + Solid)

Rotavap

CH$_3$OH

Solid

Excess THF

*Analyzed in GC & GCMS

Solb.*

Insolb.
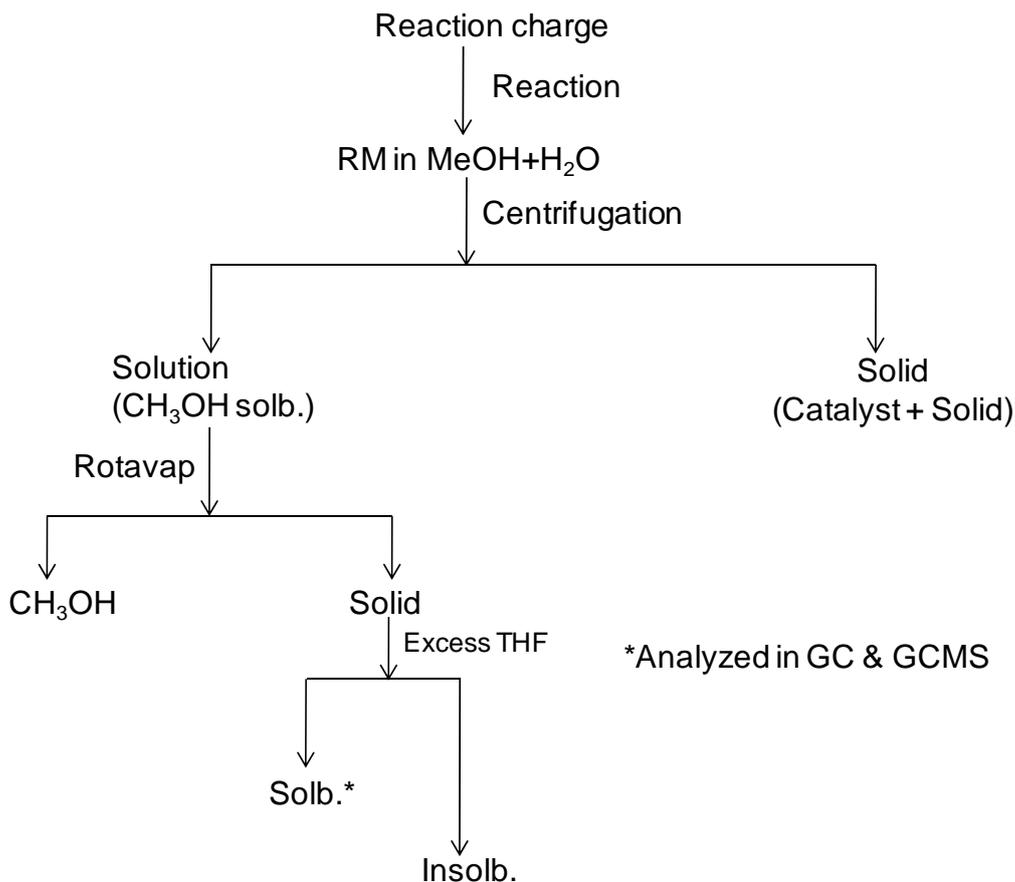
Fig. S1. Scheme for the extraction of organic solvent soluble products in dealkaline lignin reactions.

The amount of THF-soluble products was quantitatively determined (yields are presented in manuscript), which is mentioned in the text (please refer text). The details on calculation are also mentioned in the supporting information for which reference is mentioned in the text (ESI, Section I.5).

Typically in any lignin conversion papers only solvent soluble product (mainly THF, ethyl acetate) are mentioned as yields (please refer to references: *Fuel* 2003, **82**, 545; *Fuel* 1996, **75**, 795). Also in several other references THF has been used as an extracting solvent (*Energy & Fuels* 2004, **18**, 327; *Bioresource Technology* 2008, **99**, 3424). Besides we have to also choose a solvent in which lignin is not soluble (please refer Table S1) and only products

are soluble. In ethyl acetate the number of monomer products obtained is lesser than compared to THF. Hence we considered THF as a choice of solvent in this study.
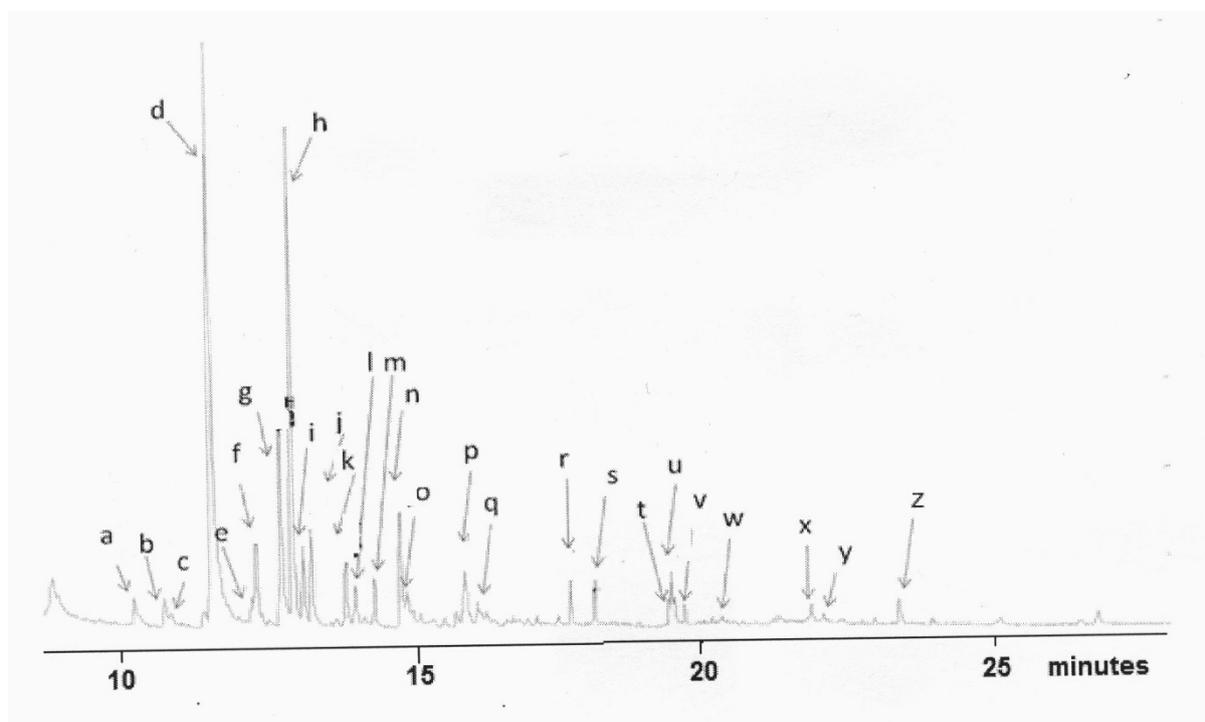

Fig. S2. GCMS of the products obtained in dealkaline lignin reaction. The products are soluble in methanol+water (reaction mixture)
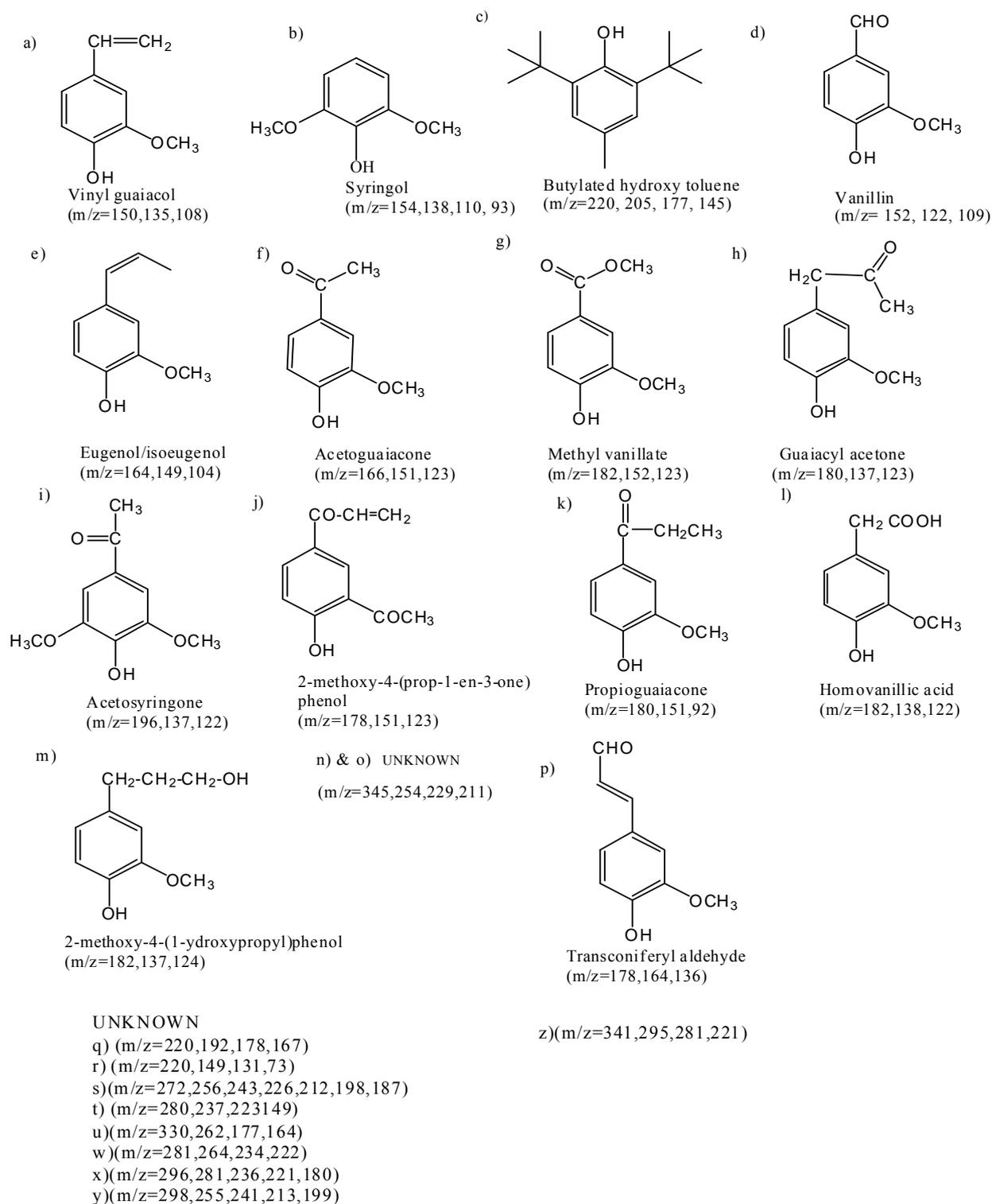
Fig. S3. Products in the reaction mixture identified by GCMS analysis.

There are some unknowns which are very difficult to identify. Moreover, even if those are

unknowns those are aromatics (as m/z mentions, SI) only difficulty is that the structures are

yet to be determined. The aromatics obtained from lignin will certainly be complex as is evident from the earlier works also. Since lignin is a complex polymer made up of several aromatic units and their composition changes as per the plant source, growth conditions etc. until now no firm lignin structure is derived.
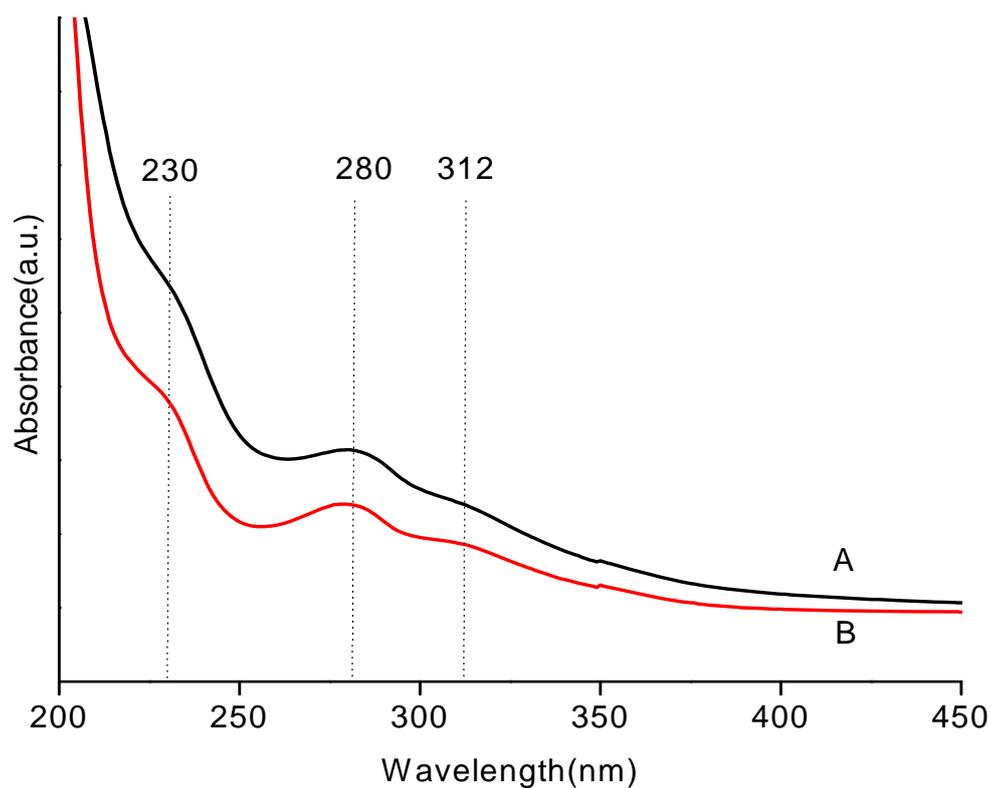
Fig. S4(a). UV-Vis analysis of A) Dealkaline lignin in CH_3OH B) THF soluble products(THF soluble solid was redissolved in CH_3OH
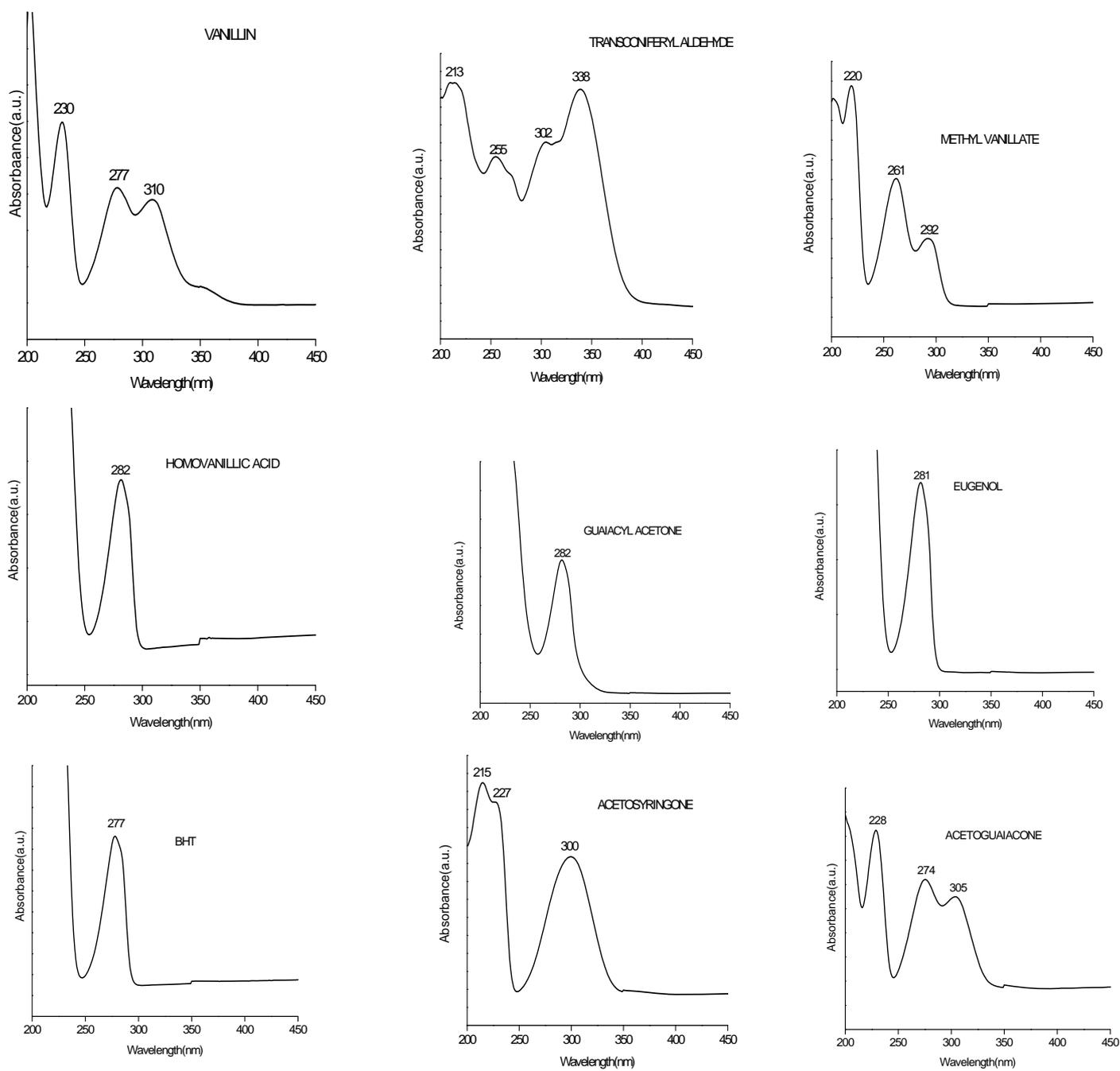
Fig. S4(b). UV analysis of standard compounds of aromatic monomeric products of Dealkaline lignin depolymerization, dissolved in CH₃OH

The contents in THF soluble and ethyl acetate soluble are different. With a consecutive extraction method of aromatic compounds obtained by depolymerization over H-USY it was found that the compounds like acetoguaiacone(product code, f) and homovanillic acid (product code, l) was not extracted by the solvent EtOAc from the THF soluble product mixture. This was clearly understood by the GC & GCMS analysis as shown in the figure below
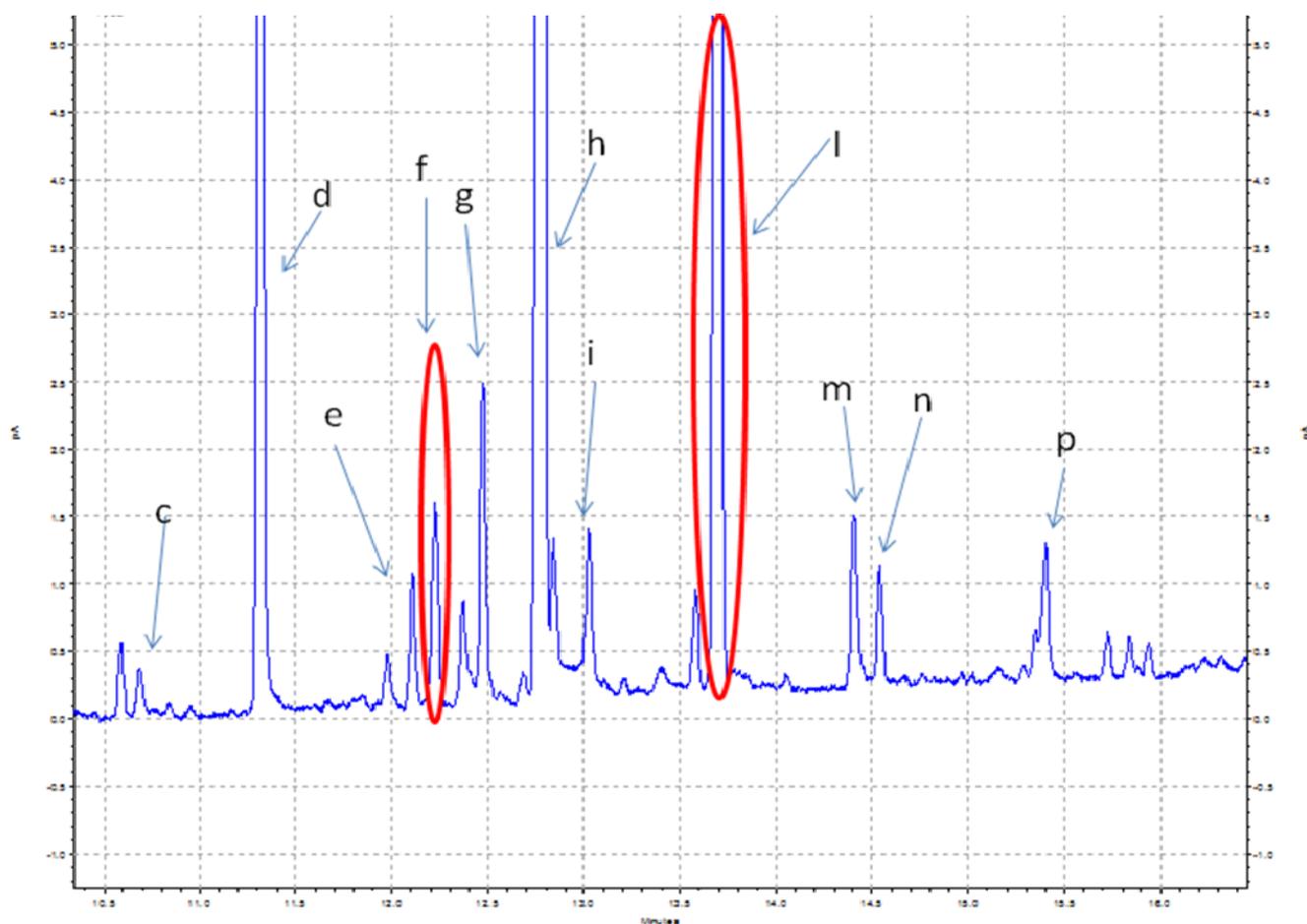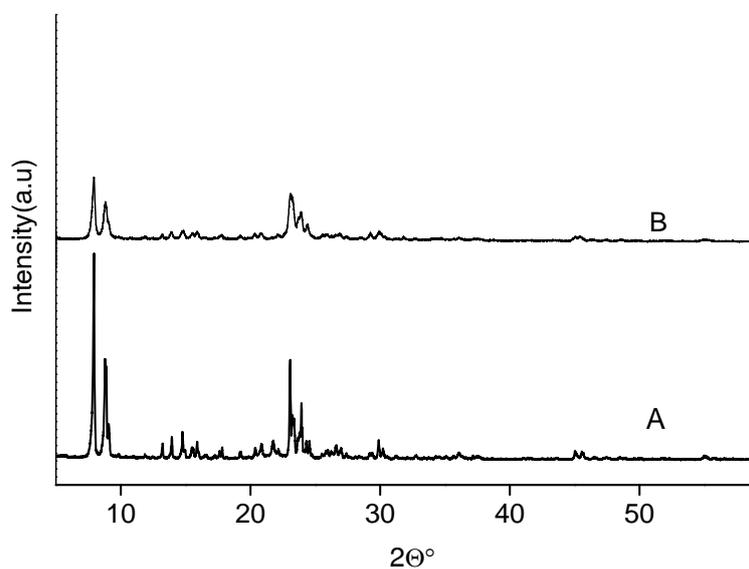

Fig. S5(a). GC analysis of THF soluble products, Reaction conditions: Dealkaline lignin, HUSY(S/Al=15), H_2O:CH_3OH (1:5 v/v), $250^{\circ}C$, 30 min., 500 rpm, 0.7 MPa N_2 at RT.
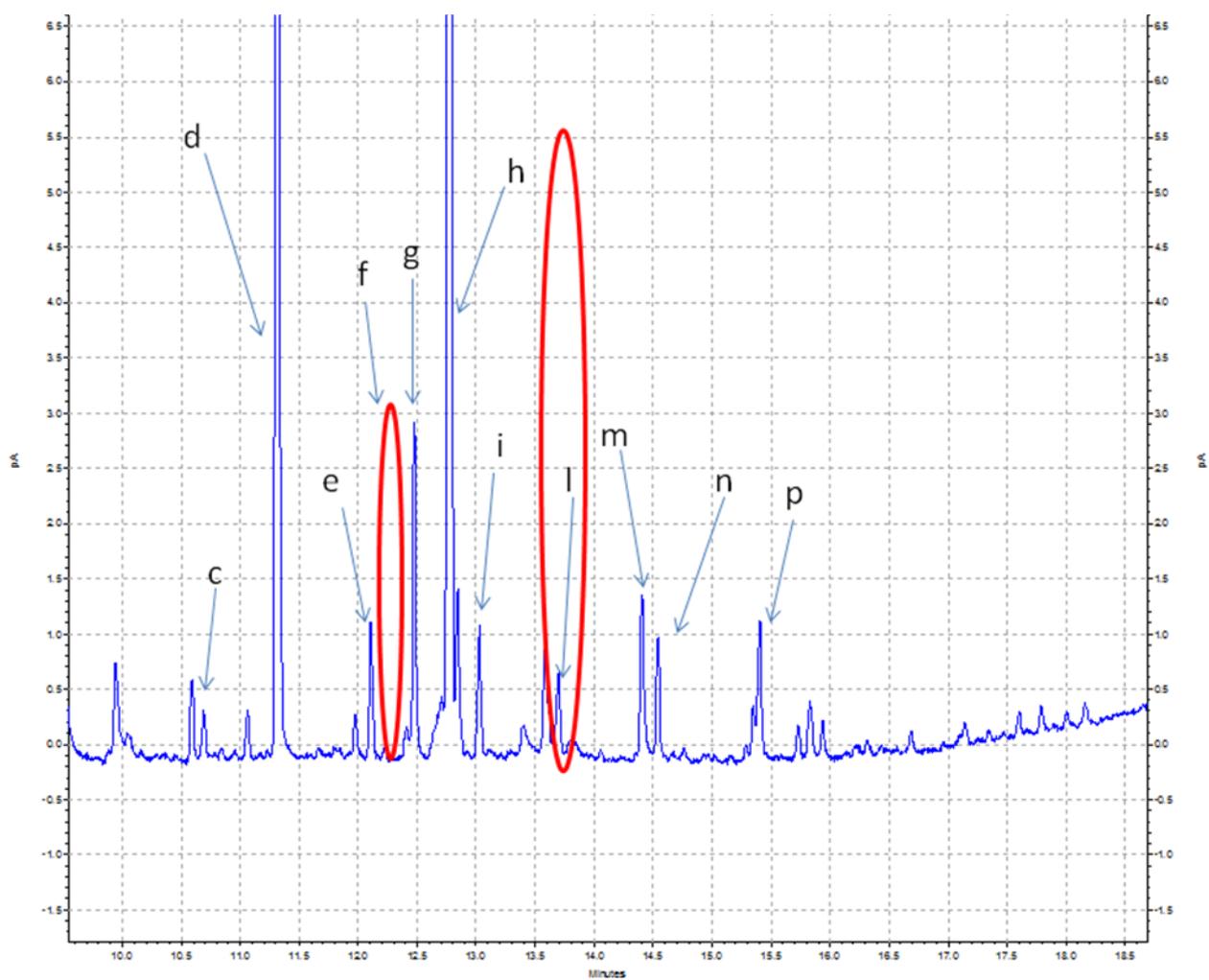
Fig S5(b). GC analysis of EtOAc soluble products, Reaction conditions: Dealkaline lignin, HUSY(S/Al=15), H_2O:CH_3OH (1:5 v/v), $250^\circ C$, 30 min., 500 rpm, 0.7 MPa N_2 at RT.
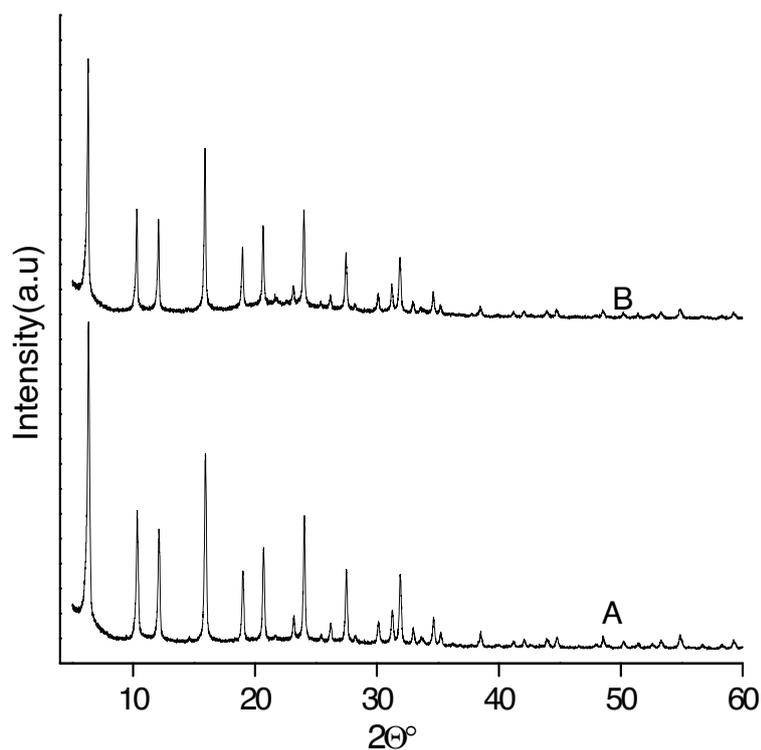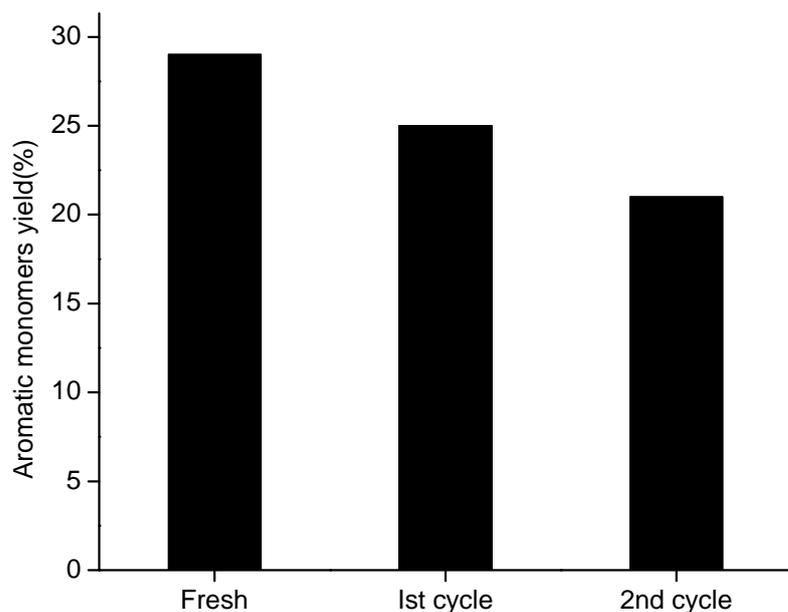
**Fig. S6.** XRD pattern of HUSY(Si/Al=15) catalyst, A) Fresh B) Spent-calcined.

Fig. S7. XRD pattern of HZSM-5(Si/Al=11.5) catalyst, A) Fresh B) Spent-calcined.

There was a decrease in the intensity of peaks in XRD pattern of spent HUSY (Si/Al=15) and HZSM-5 (Si/Al=11.5) catalyst after the reaction, which indicates the structural deformation of this catalyst.

Fig. S8. Recycle study Reaction conditions: Dealkaline lignin, SiO_2-Al_2O_3, H_2O:CH_3OH (1:5 v/v), 250°C, 30 min., 500 rpm, 0.7 MPa N_2 at RT.
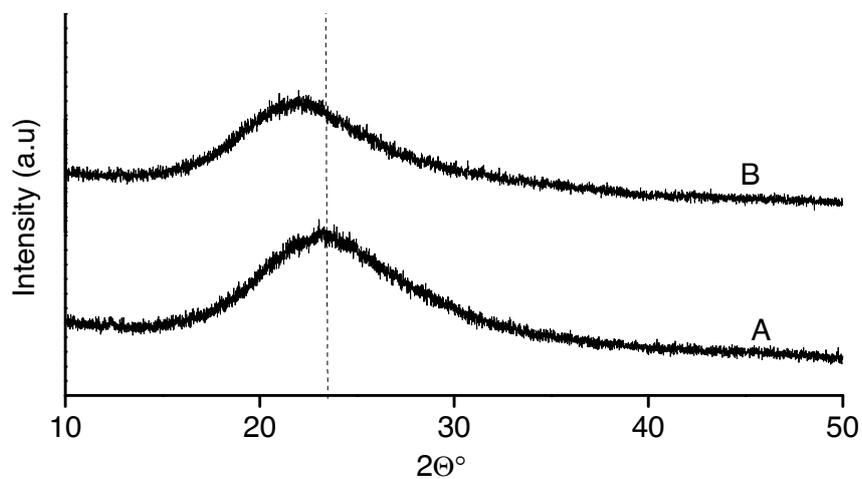
Fig. S9. XRD pattern of SiO_2-Al_2O_3 catalyst, A) Fresh B) Spent-calcined sample.

The calcination step did not change the morphology of the catalyst, since XRD of spent uncalcined catalyst and spent calcined catalysts have showed the similar patterns.

Refer main text.