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Supplementary Information

Thermocatalytic depolymerization of Kraft lignin to guaiacols using HZSM-5 in alkaline water-THF co-solvent: A realistic approach

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Effect of stirrer speed

The effect of stirrer speed on lignin depolymerization is shown in Figure S1(a). The reactions were carried out using a combination of HZSM55 (catalyst-to-lignin ratio of 1:10 (w/w)) and NaOH (NaOH-to-lignin ratio of 0.083 (w/w)) at varying stirrer speed (i.e., 600, 800 and 1000 rpm). The stirrer speed had a negligible effect on the lignin depolymerization, but a maximum lignin conversion of 78.2% with 52% selectivity for guaiacols was obtained at a stirrer speed of 800rpm. The FTIR spectra (Figure S1(b)) also clearly showed that the intensity of bands corresponding to characteristic functional groups shifted to a lower intensity at 800 rpm, suggesting that more depolymerization had occurred. This highlights the fact that a stirrer speed of 800 rpm would be suitable for further lignin depolymerization reactions.

Effect of acidification of the reaction mixture on the stability of HZSM-5:

The powder XRD pattern of parent HZSM80 and spent HZSM80 obtained after treating and without treating the reaction mixture with 10% HCl are given in Figure S3(a). The XRD patterns revealed that the fresh HZSM280 and the spent HZSM280 obtained after treating the reaction mixture with 10% HCl exhibits a high crystalline MFI phase. Whereas, the intensity of all diffractions peaks of HZSM280 obtained from the reaction mixture without HCl treatment was decreased significantly. It suggests that the lignin depolymerization reaction followed by acid treatment had a minimal effect on the MFI structure of HZSM280 due to precipitation of unconverted lignin from the reaction mixture. Whereas, the decreased relative crystallinity of the spent HZSM280 obtained without HCl treatment might be due to the deposition of lignin inside the pores of the catalyst. The deposited lignin further transformed to ash during calcination which may interfere during the XRD analysis and imparts amorpohus characteristics to the sample.

Further investigation on the structural properties of the spent HZSM280 obtained from HCl treated and untreated reaction mixture can be derived from the results of N_2 adsorption-desorption meaurement. Table S1 shows the BET surface area and pore volume of sample obtained after HCl treatment and without HCl treatment, which revealed that HZSM280 obtained after acid treatment did not cause significant changes in BET surface area and pore volume. However, the BET surface area and pore volume of spent HZSM280 obtained without acid treatment was remarkably reduced to 303 m^2g^{-1} and 0.17 cm^3g^{-1} when compared to parent HZSM280 (374 m^2g^{-1} and 0.17 cm^3g^{-1}) indicating prominent blockage of pores with ash or may be other inorganics.

The effect of acidification of the reaction mixture on the nature of the acid sites of HZSM280 was then investigated by pyridine absorbed FTIR, as displayed in Figure S3(b). The bands at 1446 and 1546 cm^{-1} correponds to the pyridine adsorbed on the Lewis (L) and Bronsted (B) acid sites[1]. A characteristic band for the combination of Bronsted and Lewis (B+L) acid sites appears at 1490 cm^{-1}. The results showed that the intensity of band at 1546 cm^{-1} (B) and 1490 cm^{-1} (B+L) decreased severely in spent HZSM280 recovered without acidification which might be due to poisioning of Bronsted acid sites after deposition of lignin solution.

Characterization results of HZSM280 recovered after lignin depolymerization reaction in the absence of NaOH:

The XRD pattern of parent and spent HZSM280 recovered after lignin depolymerization reaction in the absence of NaOH is shown in Figure S18(a). Both of the catalyst sample displayed diffraction peaks in the range of $2\theta = 20\text{-}25^0$, reflecting the characteristic MFI topology[2]. A slight decline in the intenstiy of reflection peaks in spent HZSM280 was also observed which might be due to minor morphological changes that might have occurred during the lignin depolmyerization reaction at 533 K or due to occlusion of pores of catayst with ash or other inorganics.

The BET surface area and total pore volume of parent and spent HZSM280 are summarized in Table S7. It can be seen that in the spent HZSM280 recovered after lignin depolmyerization absence of NaOH, there is not any important changes in the total pore volume and BET surface area.

The changes in the structure of zeolites can be followed by IR spectroscopy. The IR spectra of parent and spent HZSM280 were presented in Figure S18(b). The presence of IR band in the region 400-1300 cm^{-1} corresponding to characteristic zeolite phase, 3463 cm^{-1} attributed to ”silanol nests” and at 3663 cm^{-1} ascribed to terminal Si–OH group in spent HZSM280 without NaOH further confirms the preserved structural framework of HZSM280 after lignin depolymerization reaction in the absence of NaOH[3].

The influence on the acid sites of spent HZSM280 were determined by IR studied after pyridine sorption (Figure S18(c)). The presence of band at 1446 and 1546 cm^{-1} correponds to the pyridine adsorbed on the lewis (L) and bronsted acid sites (B)[1]. Whereas, the IR band present in between of these two band at around 1490 cm^{-1} represents a combination of Bronsted and Lewis acid sites (B+L). The pyridine IR pattern of parent and spent HZSM280 was almost similar which indicates the acid sites were also conserved after lignin depolmyerization reaction in the absence of NaOH.

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Table S1 Textural propererties of parent HZSM280 and spent HSM280 with and without acidification process.

Sample	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
Fresh HZSM280	374	0.23
Spent HZSM280_HCl treated	353	0.20
Spent HZSM280_Without HCl treatment	303	0.17

Table S2 Guaiacols yield (%) for the individual runs of the RSM design

	X_1	X_2	X_3	X_4	X_5	X_6	X_7	Y_{GUA} (%)
Run	Time (h)	Temperature (K)	Lignin:Solvent (w/v)	Water:THF (v/v)	NaOH:lignin (w/w)	Catalyst:Lignin (w/w)	Si/Al Ratio	Guaiacols Yield (%)
1	2	533	0.066667	1	0.083	0.1	55	49.08
2	3	533	0.066667	1	0.083	0.1	55	45.19
3	4	533	0.066667	1	0.083	0.1	55	41.20
4	2	493	0.066667	1	0.083	0.1	55	41.32
5	2	513	0.066667	1	0.083	0.1	55	48.63
6	2	533	0.06	1	0.083	0.1	55	45.25
7	2	533	0.075	1	0.083	0.1	55	43.23
8	2	533	0.085714	1	0.083	0.1	55	40.22
9	2	533	0.066667	0	0.083	0.1	55	22.84
10	2	533	0.066667	2	0.083	0.1	55	36.73
11	2	533	0.066667	1.25	0.083	0.1	55	38.71
12	2	533	0.066667	0.8	0.083	0.1	55	49.08
13	2	533	0.066667	1	0.083	0.1	55	50.35
14	2	533	0.066667	0.64	0.083	0.1	55	46.91
15	2	533	0.066667	0.71	0.083	0.1	55	47.08
16	2	533	0.066667	0.50	0.083	0.1	55	43.86
17	2	533	0.066667	1	0	0.1	55	50.37
18	2	533	0.066667	1	0.03	0.1	55	48.92
19	2	533	0.066667	1	0.06	0.1	55	47.69
20	2	533	0.066667	1	0.1	0.1	55	49.86
21	2	533	0.066667	1	0.083	0	55	48.08
22	2	533	0.066667	1	0.083	0.041667	55	48.93
23	2	533	0.066667	1	0.083	0.125	55	51.27
24	2	533	0.066667	1	0.083	0.166667	55	51.45
25	2	533	0.066667	1	0.083	0.1	23	45.20
26	2	533	0.066667	1	0.083	0.1	280	51.64
27	2	523	0.06	0.818182	0.083	0.1	280	56.41
28	2	523	0.06	0.818182	0.066	0.1	280	53.94
29	2	523	0.06	0.818182	0.1	0.1	280	61.35

30	2	523	0.06	0.818182	0.1	0.041667	280	55.28

Table S3 Physiochemical properties of HZSM-5 catalysts.

Catalyst	BET Surface Area (m^2/g)	NH_3-TPD Amount of Acid Sites (mmol/g)			Pyridine FTIR Amount of Acid Sites (μmol/g)		
		Weak	Strong	Total	B	L	B/L
HZSM23	293	1.34	0.31	1.65	0.85	0.49	1.73
HZSM55	295	0.13	0.08	0.21	0.84	0.48	1.75
HZSM280	373	0.01	0.01	0.02	0.80	0.51	1.56

Table S4 Comparative values for the intensity of phenolic –OH($\nu_{phenolic\text{-}OH}$) in residual lignin at different reaction parameters.

Sample	Intensity ($\nu_{phenolic\ -H}$)/3434 cm^{-1}
Effect of Temperature	
RL_493K	0.54
RL_513K	0.59
RL_533K	0.64
Lignin-to-solvent ratio	
RL_1:16.66	0.53
RL_1:15.0	0.64
RL_1:13.33	0.60
RL_1:11.66	0.53
Water-to-THF ratio	
RL_1:2	0.68
RL_0.8:1	0.64
RL_1:1	0.65
RL_1:0.8	0.50
RL_2:1	0.57
RL_1:0	0.46
Effect of catalyst-to-lignin ratio	
RL_1:6	0.59
RL_1:8	0.55
RL_1:10	0.62
RL_1:24	0.52
No catalyst	0.54

Table S5(a) Analysis of variance (ANOVA) results of the quadratic model for guaiacols yield (%) without eliminating the insignificant variables at 95% confidence interval

Source	Degree of Freedom	Sum of Squares	Mean Square	F Value	P Value
Model	17	1220.22	71.778	25.92	0.000
Linear	7	662.13	94.590	34.16	0.000
Time (X_1)	1	46.78	46.782	16.89	0.002
Temperature (X_2)	1	27.56	27.560	9.95	0.010
Lignin:Solvent (X_3)	1	13.57	13.569	4.90	0.051
Water:THF (X_4)	1	586.91	586.905	211.95	0.000
NaOH:lignin (X_5)	1	8.74	8.742	3.16	0.106
Catalyst:Lignin (X_6)	1	16.63	16.628	6.00	0.034
Si/Al Ratio (X_7)	1	20.76	20.760	7.50	0.021
Square	7	175.38	25.054	9.05	0.001
Time*Time	1	0.08	0.080	0.03	0.868
Temperature*Temperature	1	10.63	10.633	3.84	0.078
Lignin:Solvent*Lignin:Solvent	1	19.10	19.105	6.90	0.025
Water:THF*Water:THF	1	110.06	110.061	39.75	0.000
NaOH:lignin*NaOH:lignin	1	7.42	7.420	2.68	0.133
Catalyst:Lignin*Catalyst:Lignin	1	5.00	4.998	1.80	0.209
Si/Al Ratio*Si/Al Ratio	1	6.91	6.914	2.50	0.145
2-Way Interaction	3	23.92	7.974	2.88	0.089
Temperature*Lignin:Solvent	1	9.41	9.409	3.40	0.095
Temperature*NaOH:lignin	1	9.47	9.467	3.42	0.094
Temperature*Catalyst:Lignin	1	12.56	12.560	4.54	0.059
Error	10	27.69	2.769		
Lack-of-Fit	9	26.88	2.987	3.69	0.385
Pure Error	1	0.81	0.809		
Model	17	1220.22	71.778	25.92	0.000
$R^2 = 97.78$, Adj. $R^2 = 94.01$					

Table S5(b) Analysis of variance (ANOVA) results of the quadratic model for guaiacols yield (%) after elimination of insignificant variables at 95% confidence interval

Source	Degree of Freedom	Sum of Squares	Mean Square	F Value	P Value
Model	8	1126.52	140.815	22.04	0.000
Linear	6	935.03	155.838	24.39	0.000
Time	1	60.81	60.809	9.52	0.006
Temperature	1	31.52	31.522	4.93	0.039
Lignin:Solvent	1	76.97	76.973	12.05	0.003
Water:THF	1	644.00	644.002	100.80	0.000
Catalyst:Lignin	1	5.15	5.151	0.81	0.380
Si/Al Ratio	1	85.05	85.049	13.31	0.002
Square	2	151.28	75.641	11.84	0.000
Lignin:Solvent*Lignin:Solvent	1	4.88	4.883	0.76	0.393
Water:THF*Water:THF	1	150.53	150.532	23.56	0.000
Error	19	121.39	6.389		
Lack-of-Fit	18	120.58	6.699	8.28	0.268
Pure Error	1	0.81	0.809		
Total	27	1247.91			
$R^2 = 90.27$, Adj. $R^2 = 86.18$					

Table S6 ^{1}H-NMR chemical shifts and their corresponding functional groups.

Chemical Shift (ppm)	Functional Group	Reference
0.8-1.5	Primary, Secondary and tertiary alkyl groups (Protons on Aliphatic Carbon)	2,3,4,5,9
1.9, 2.1, 2.2, and 2.7	Benzylic proton (Ar-CH_3) or carbonyl group (Ar-CO-CH_3) or ester groups (Ar/R-CH_2-COOR/Ar)	4,8,9
3.1-4.2	Methoxy group (-OCH_3)	4,6,7,8,9
6.5-8	Aromatic protons	1,2,4,6,7,8,9
9.78	Aldehydes (-CHO groups)	4,7,9

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Table S7 Textural properties of parent and spent HZSM280 after lignin depolymerization reaction in the absence of NaOH.

Sample	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
Fresh HZSM280	374	0.23
Spent HZSM280_HCl treated	353	0.20

Table S8 IR band assignment in HZSM-5

Wavenumber (cm^{-1})	Assignment
462	T-O bending
533	Double ring vibration
805	External assymmetric stretch
1122	Internal symmetric stretch
3463	Free Si-OH inside the structure
3663	Al-OH groups of extra framework Al of zeolite

Table S9 Textural properties of parent and spent HZSM280.

Catalyst	S_{BET} (m^2/g)	S_{ext}(m^2/g)	S_{micro}(m^2/g)
HZSM80	381	216	157
Spent HZSM280	122	92	30

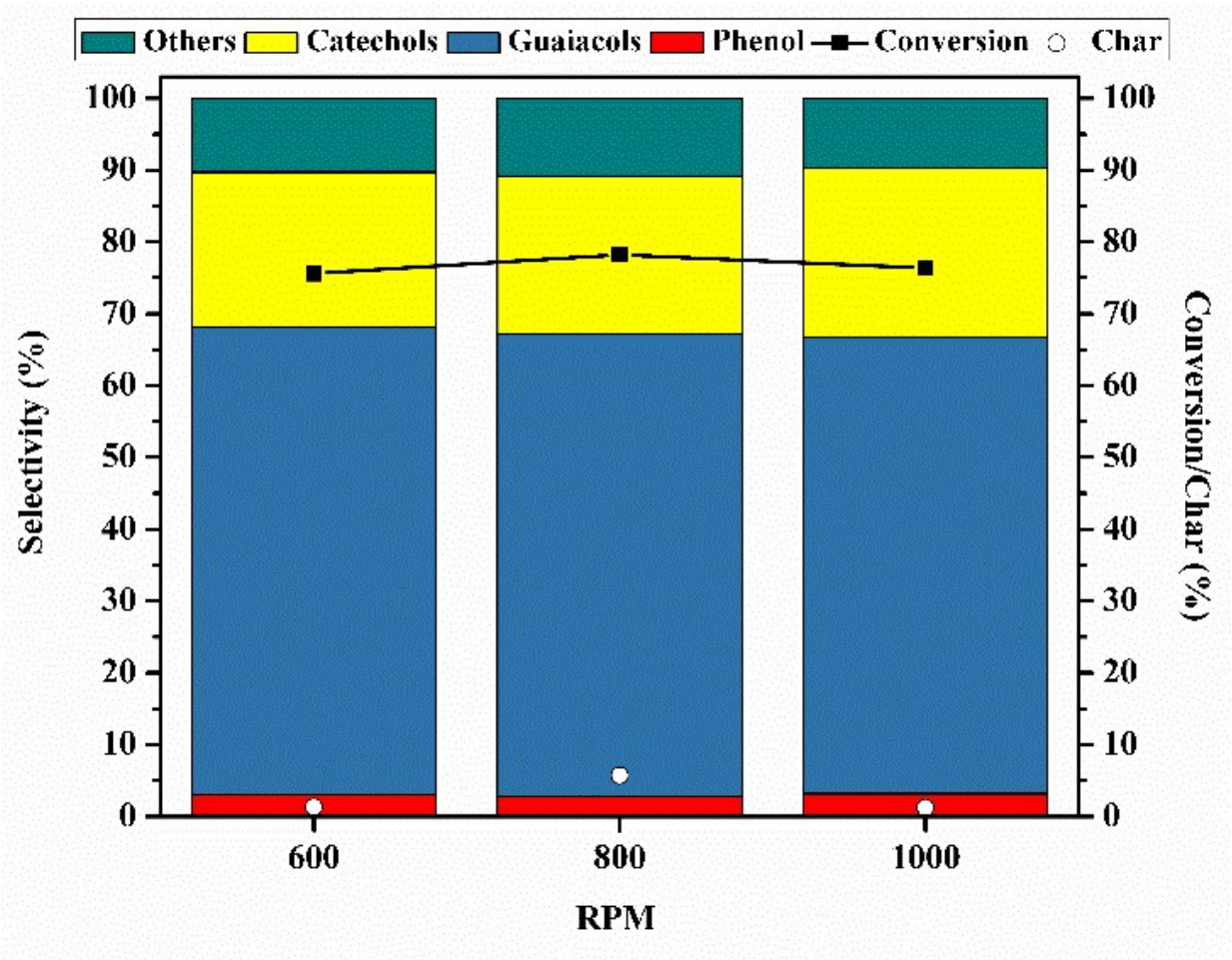


Figure S1(a) Effect of stirrer speed on lignin depolymerization. Reaction conditions: 12g lignin, HZSM55 (1.2g), NaOH (1g), lignin-to-solvent ratio (1:15.0 w/v), water-to-THF ratio (1:1 v/v), Temperature (533 K), Time (2h).

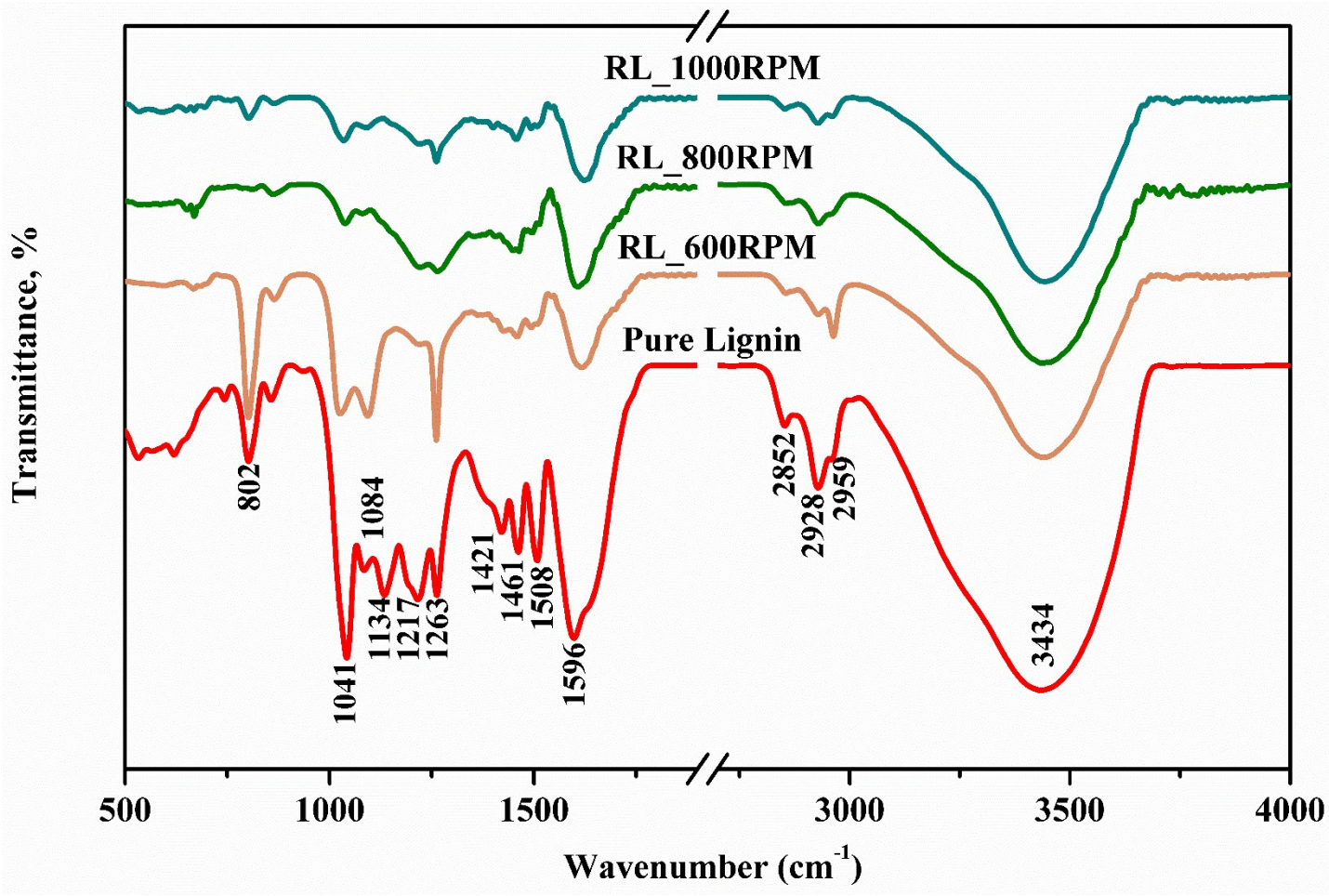


Figure S1(b) FTIR spectra of fresh lignin and resultant residual lignin after depolymerization reaction at different stirrer speed. Reaction conditions: 12g lignin, HZSM5-55 (1.2g), NaOH (1g), lignin-to-solvent ratio (1:15.0 w/v), water-to-THF ratio (1:1 v/v), Temperature (533 K), Time (2h).

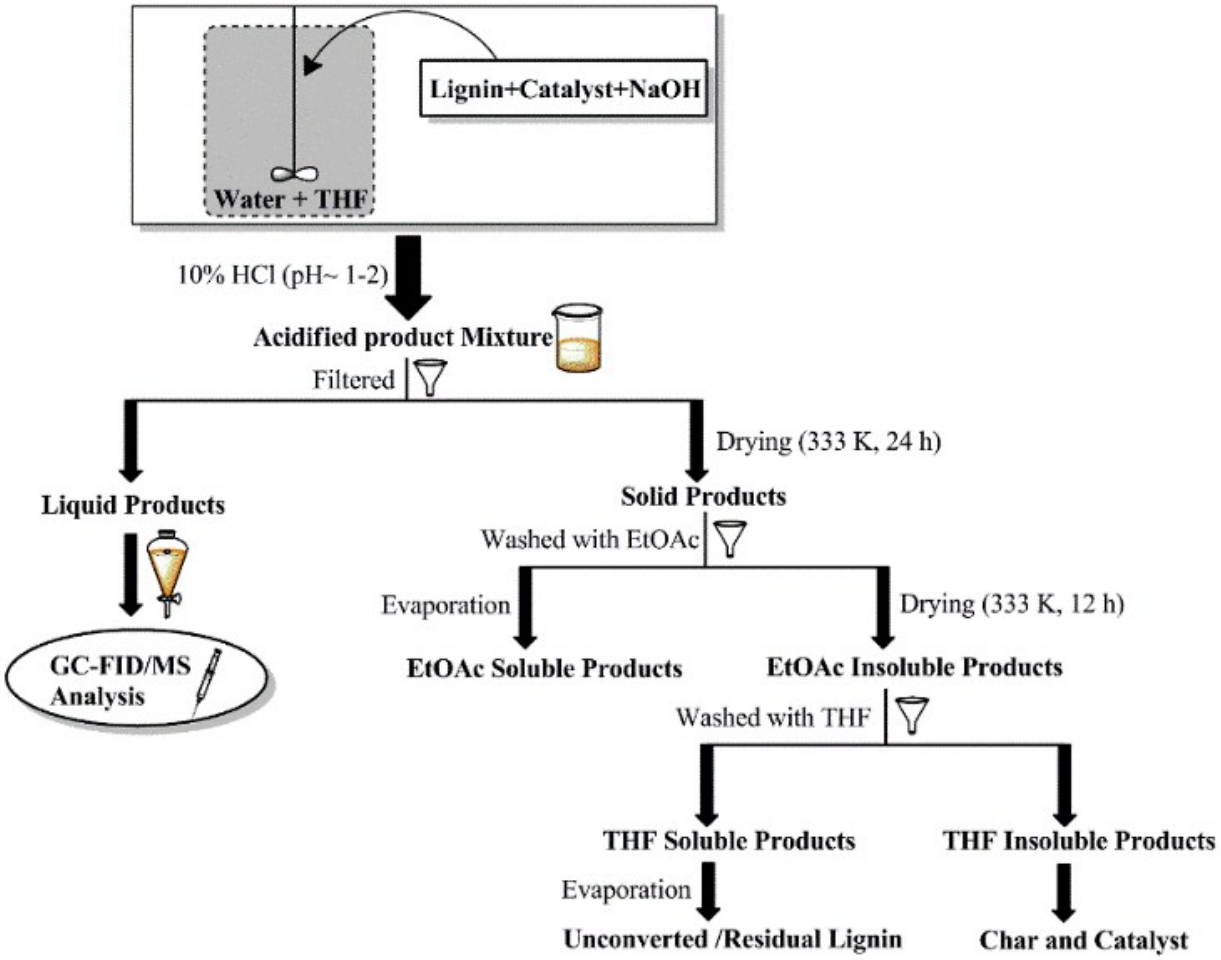


Figure S2 Workup procedure for separation of depolymerized products.

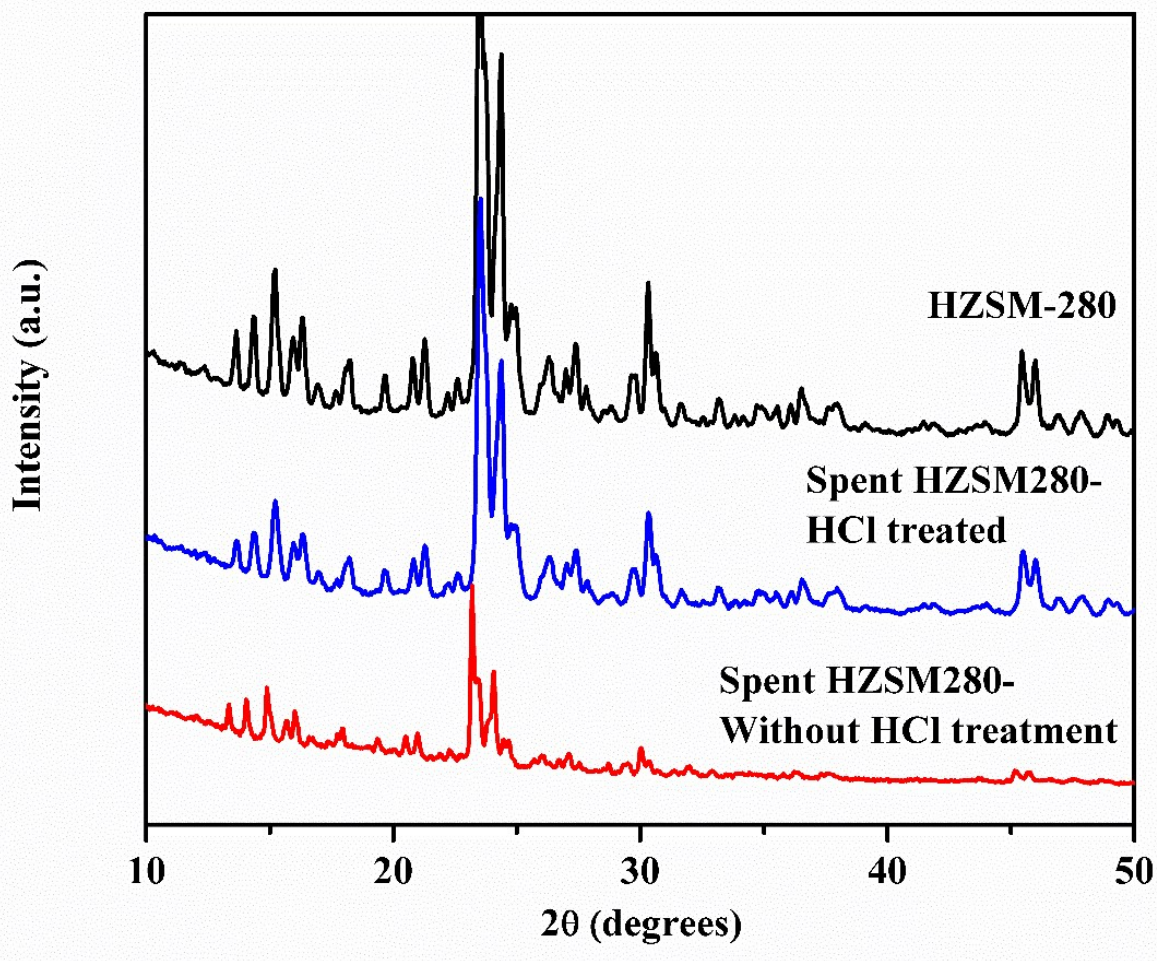


Figure S3(a) XRD pattern of parent and spent HSM280 with and without acidification process.

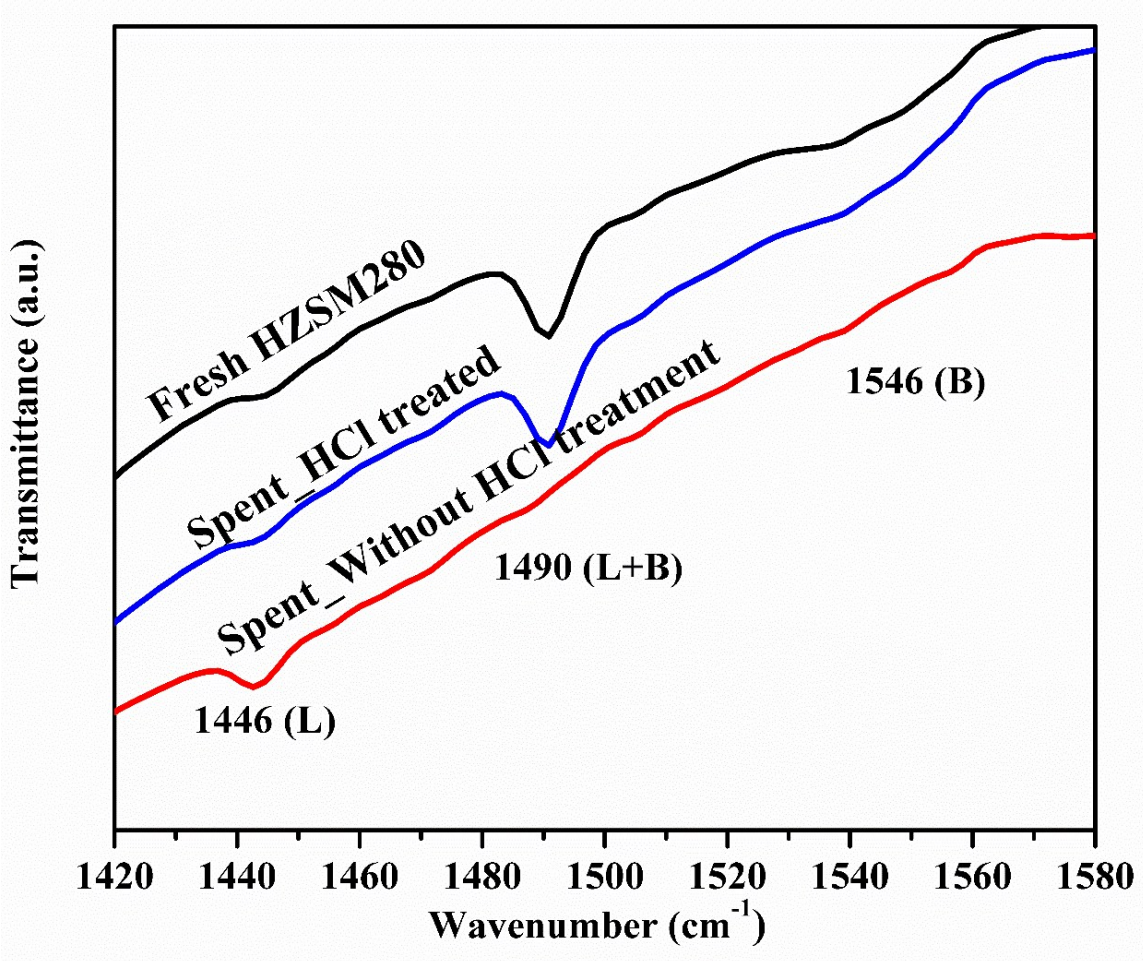


Figure S3(b) Pyridine FTIR spectra of parent HZSM280 and spent HSM280 with and without acidification process.

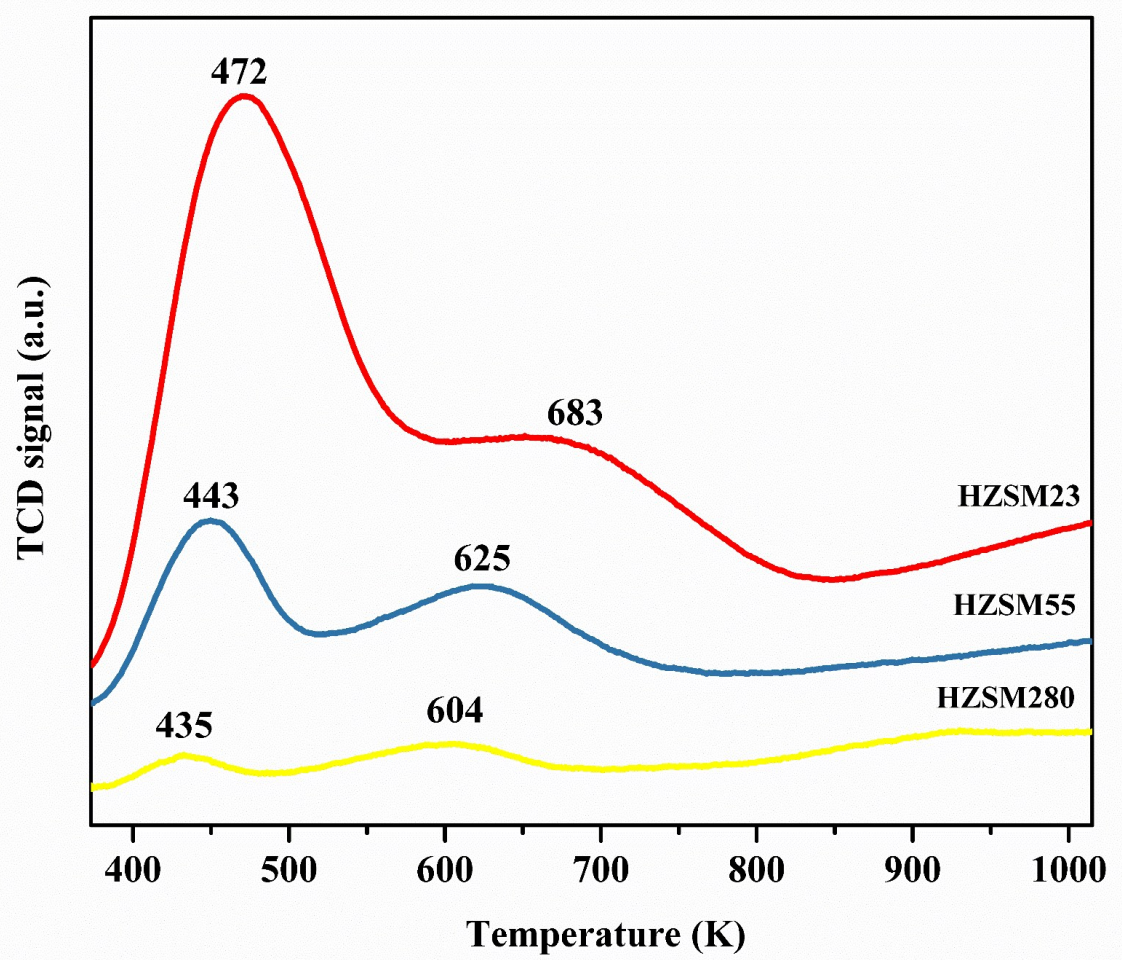


Figure S4 NH_3-TPD profile of HZSM-5.

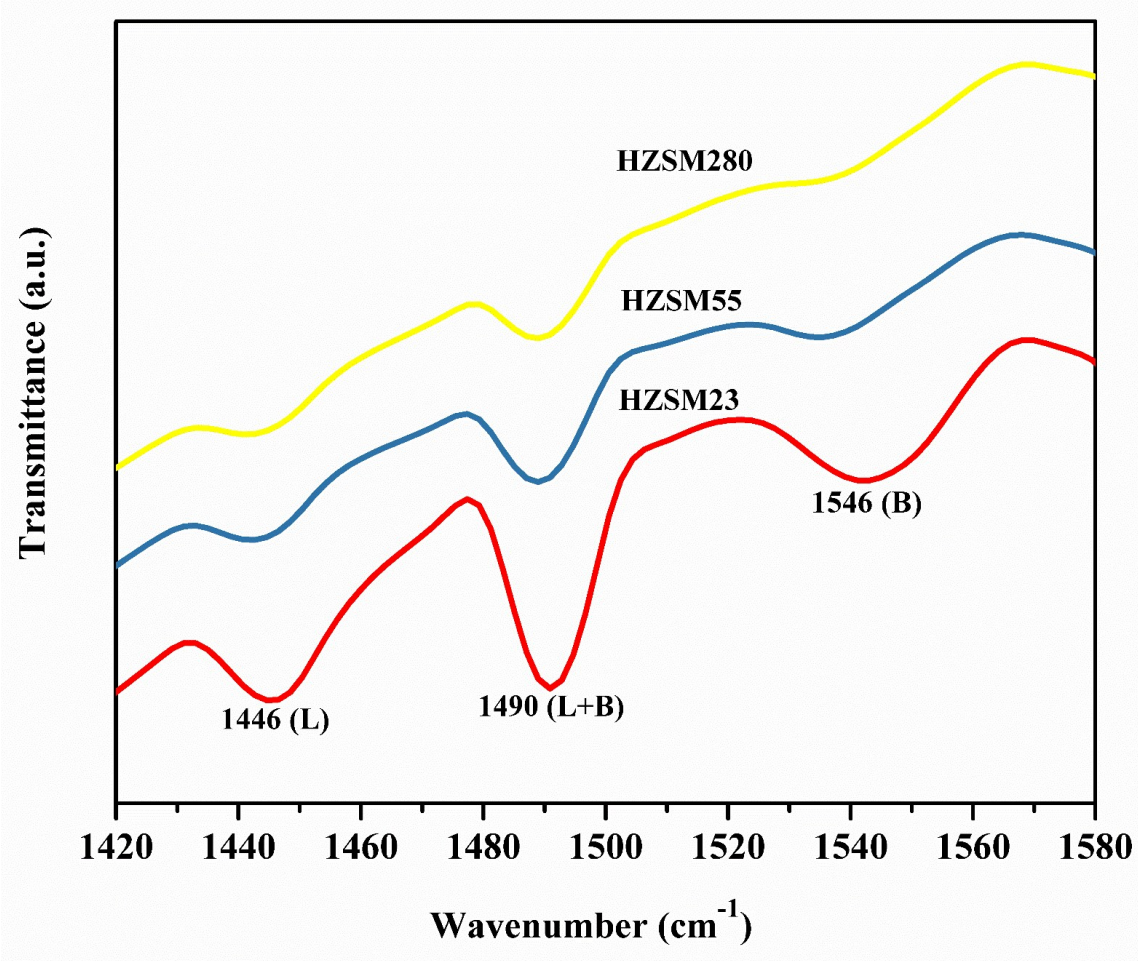


Figure S5 Pyridine FTIR spectra of HZSM-5.

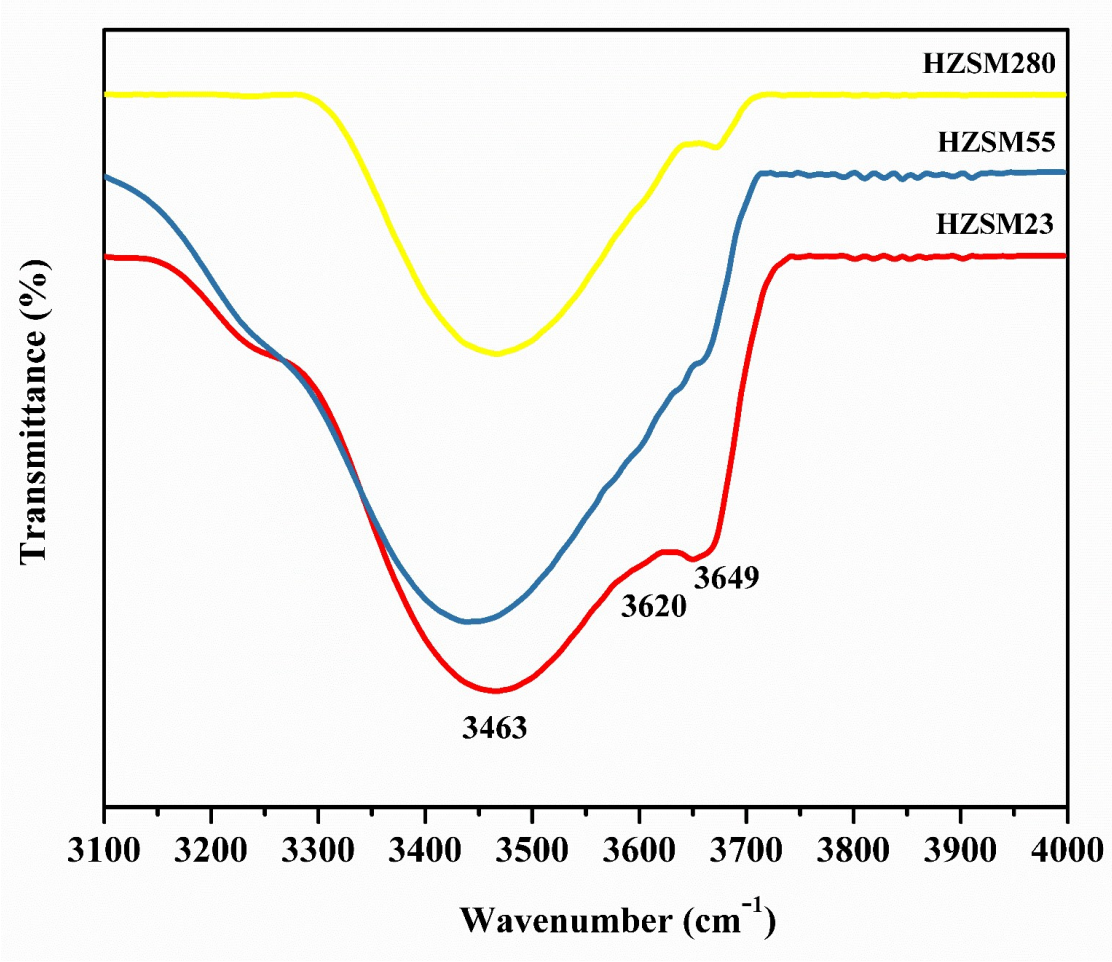


Figure S6 FTIR spectra of HZSM-5 catalyst.

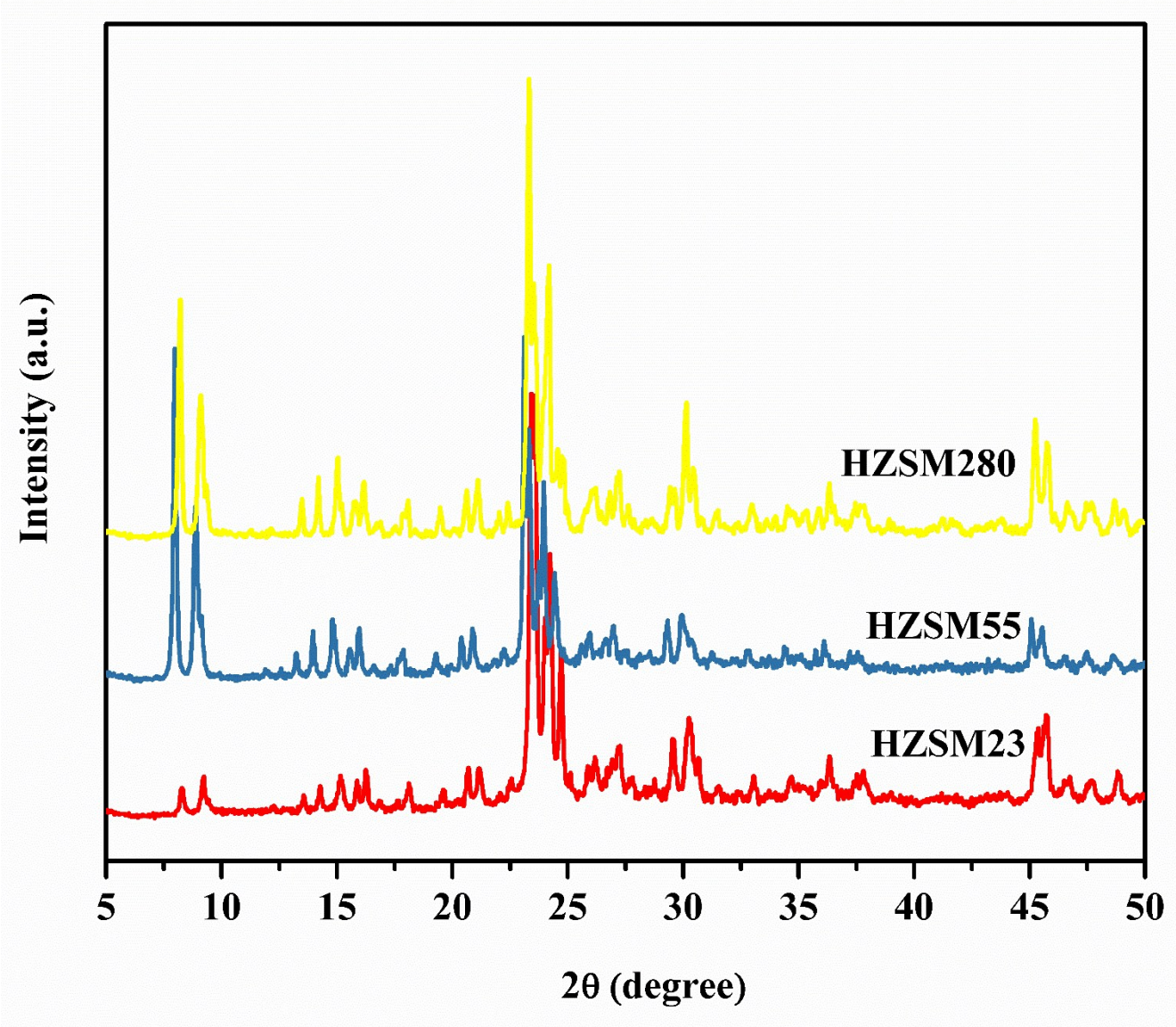


Figure S7 XRD pattern of HZSM-5.

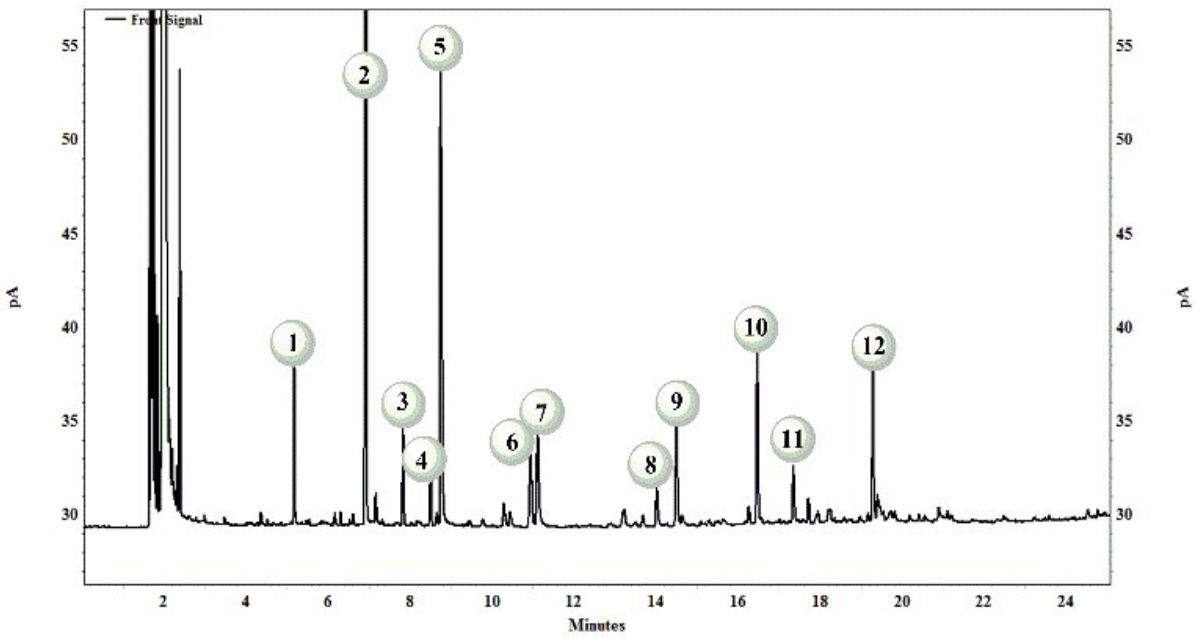


Figure S8 GC-FID chromatogram for EtOAc soluble products. Reaction Conditions: 12g lignin, HZSM280 (1.2g,) NaOH (1g), lignin-to solvent ratio (1:15.0 w/v), water-THF ratio (0.8:1 v/v), Temperature (533 K), Time (2h), RPM (800).

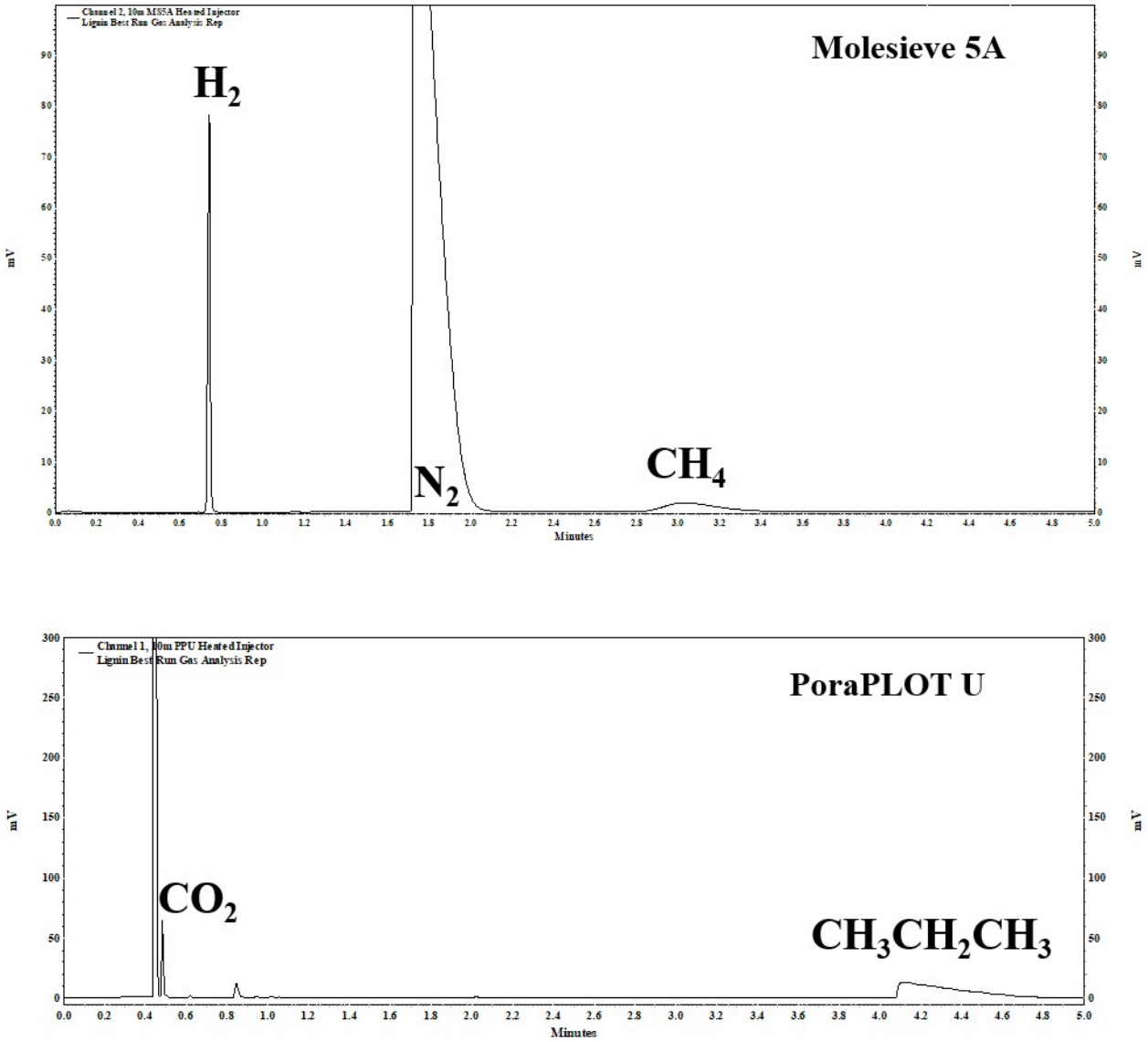


Figure S9 Micro GC- TCD chromatogram of gaseous products generated during lignin depolymerization Reaction conditions: 12g lignin, HZSM280 (1.2g), NaOH (1g), lignin-to-solvent ratio (1:15.0 w/v), water-to-THF ratio (1:1 v/v), Temperature (533K), Time (2h), RPM (800).

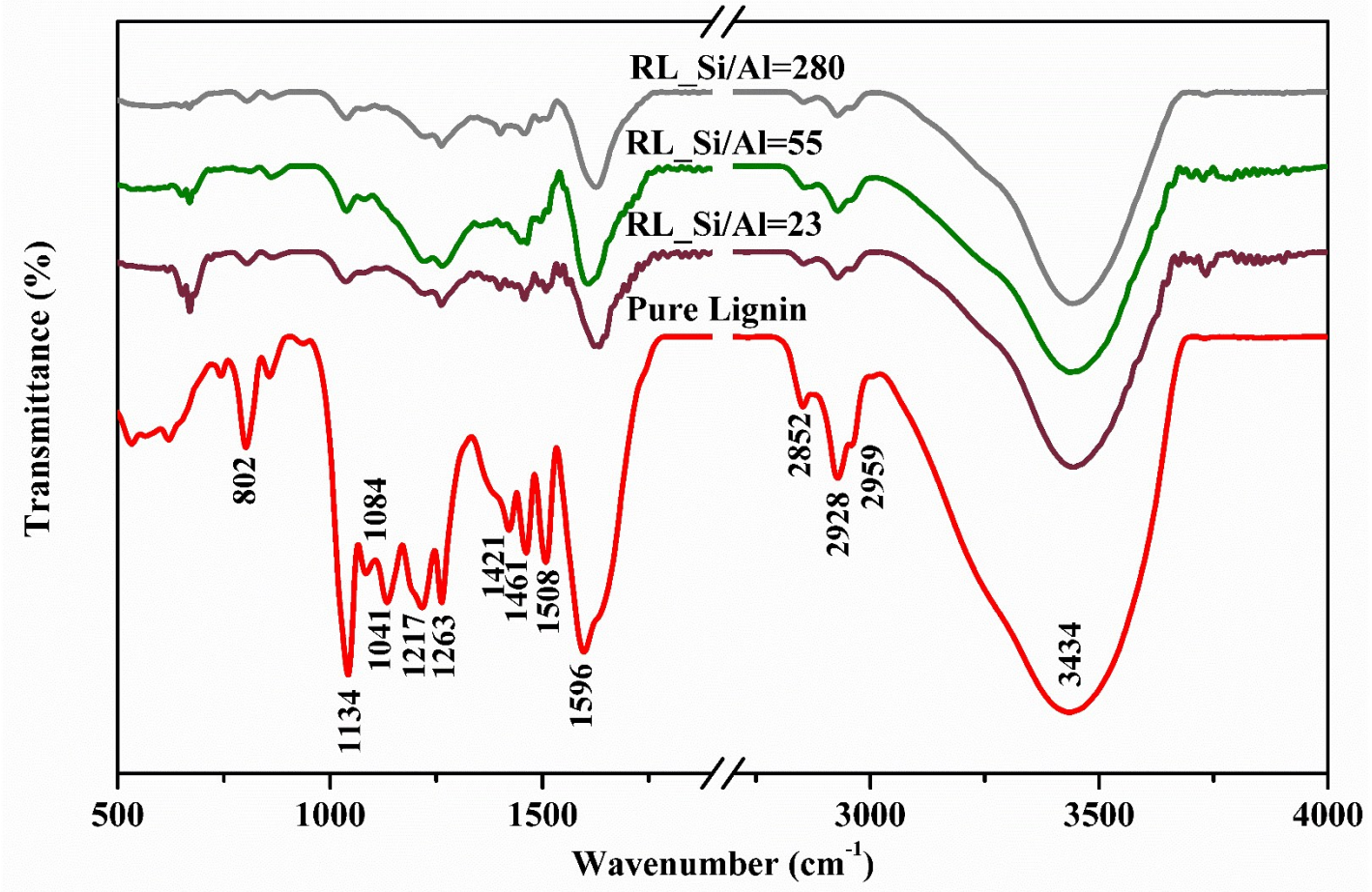


Figure S10 FTIR spectra of fresh lignin and resultant residual lignin after depolymerization reaction at different Si/Al ratio of HZSM-5. Reaction conditions: 12g lignin, HZSM-5 (1.2g), NaOH (1g), lignin-to-solvent ratio (1:15.0 w/v), water-to-THF ratio (1:1 v/v), Temperature (533 K), Time (2h), RPM (800).

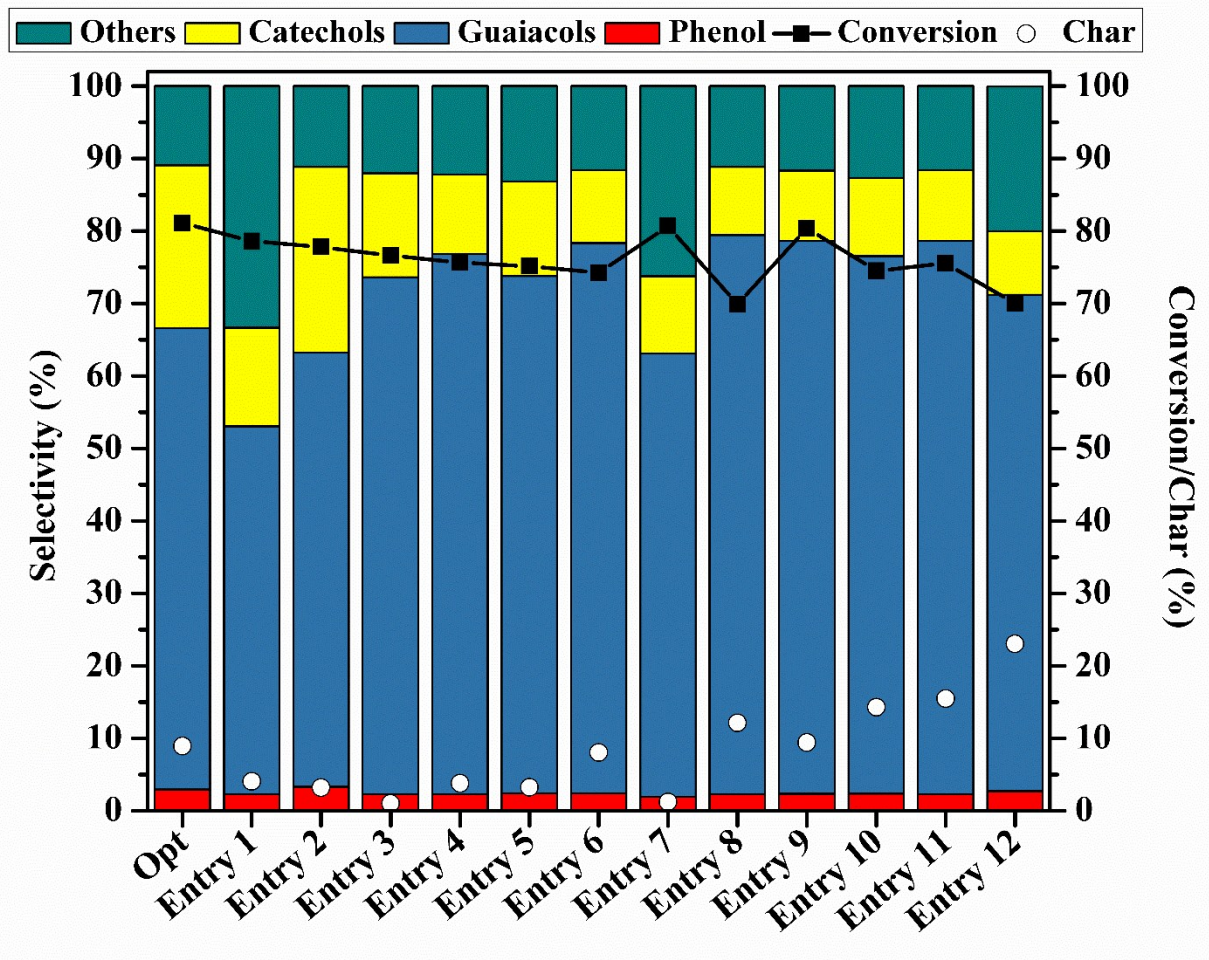
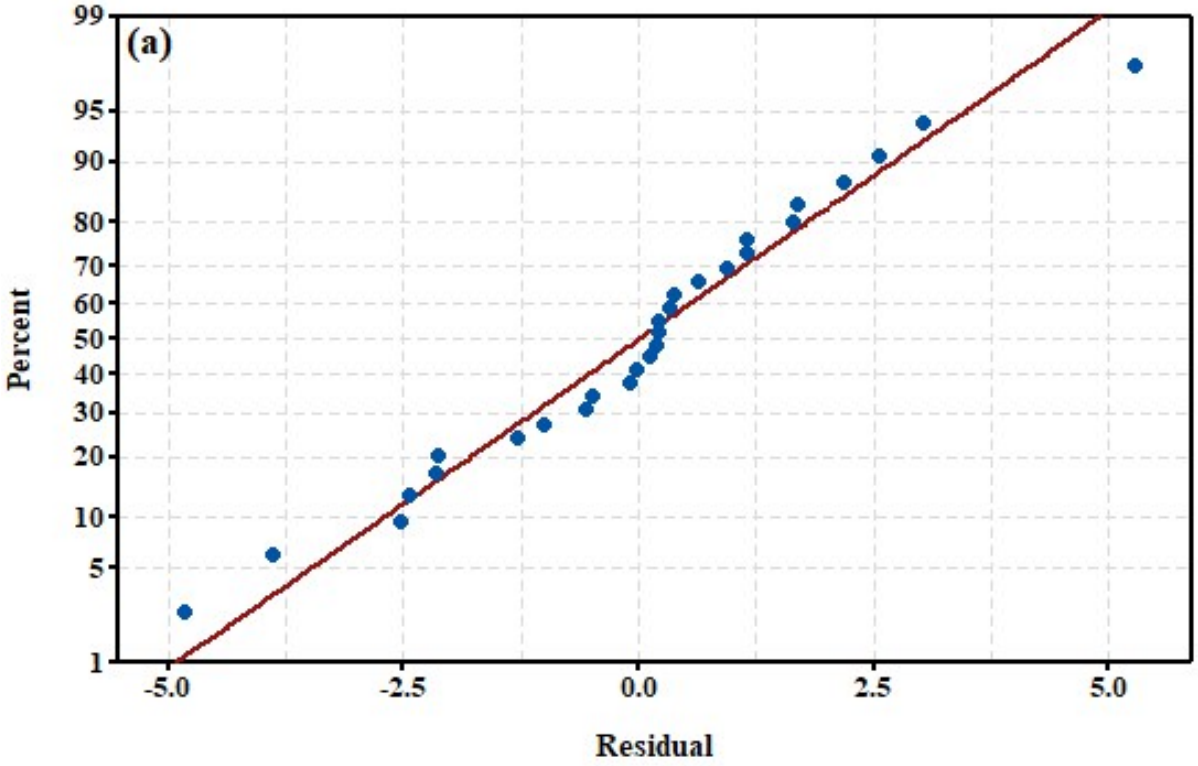


Figure S11 Lignin conversion, product distribution and char formation during sensitivity analysis.


(a)
Percent
99
95
90
80
70
60
50
40
30
20
10
5
1
-5.0
-2.5
0.0
2.5
5.0
Residual

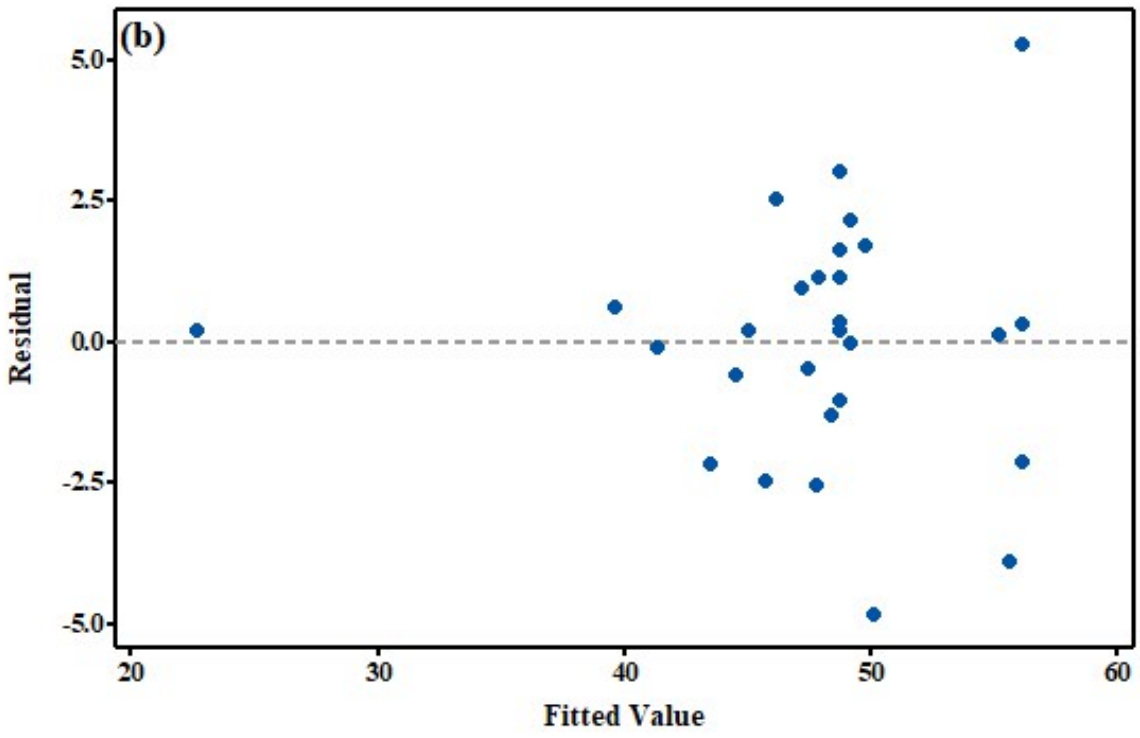

(b)
Residual
5.0
2.5
0.0
-2.5
-5.0
20
30
40
50
60
Fitted Value

Figure S12 Normal probability plot (a) and residuals versus fitted values of the regression for guaiacols yield (%) (b).

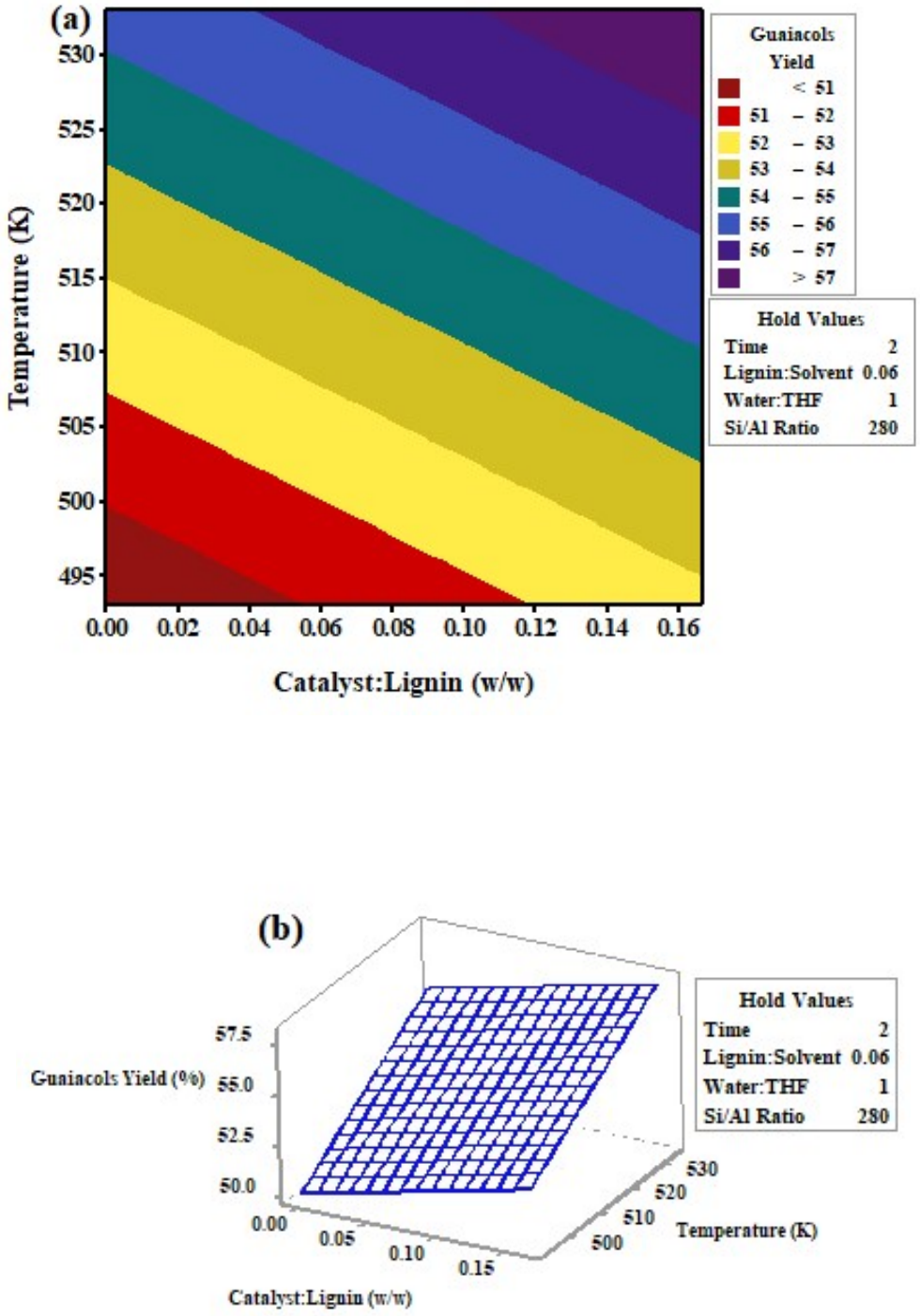
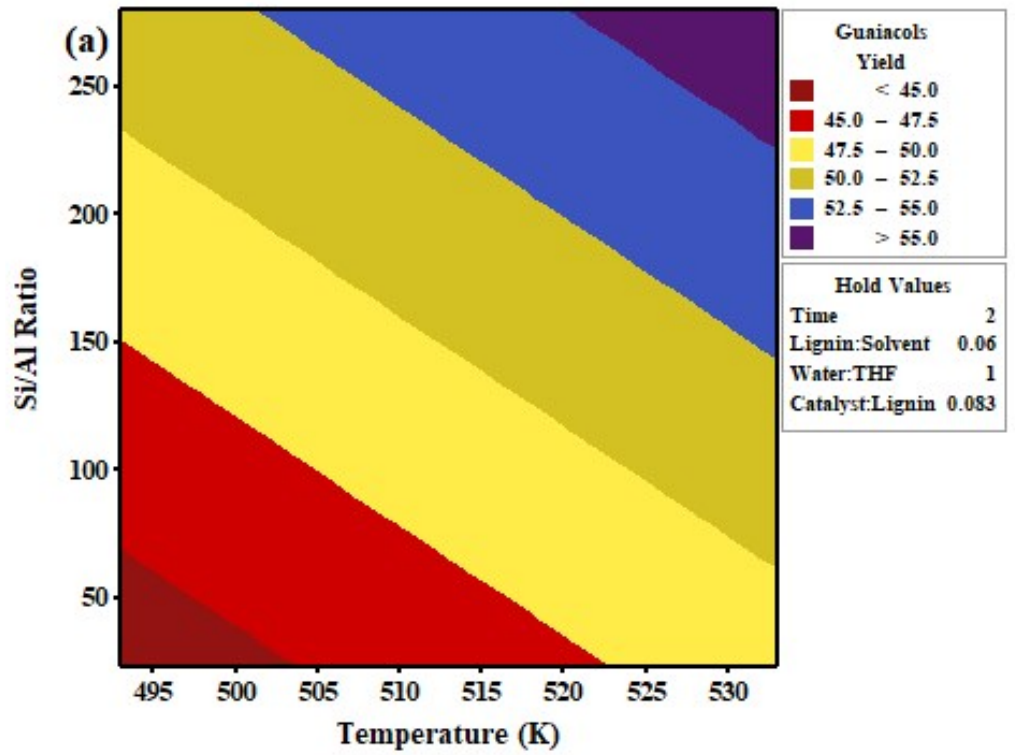


Figure S13 Countours (a) and surface plots (b) representing effect of catalyst-to-lignin (w/w) ratio and Tempratue (K) on guaiacol yield (%).


(a)
Guaiacols Yield
< 45.0
45.0 – 47.5
47.5 – 50.0
50.0 – 52.5
52.5 – 55.0
> 55.0
Hold Values
Time 2
Lignin:Solvent 0.06
Water:THF 1
Catalyst:Lignin 0.083
Si/Al Ratio
250
200
150
100
50
495
500
505
510
515
520
525
530
Temperature (K)

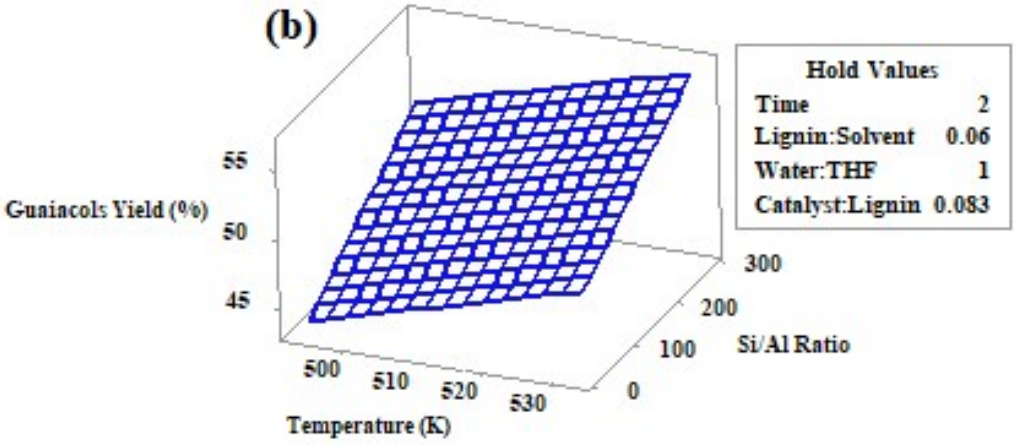
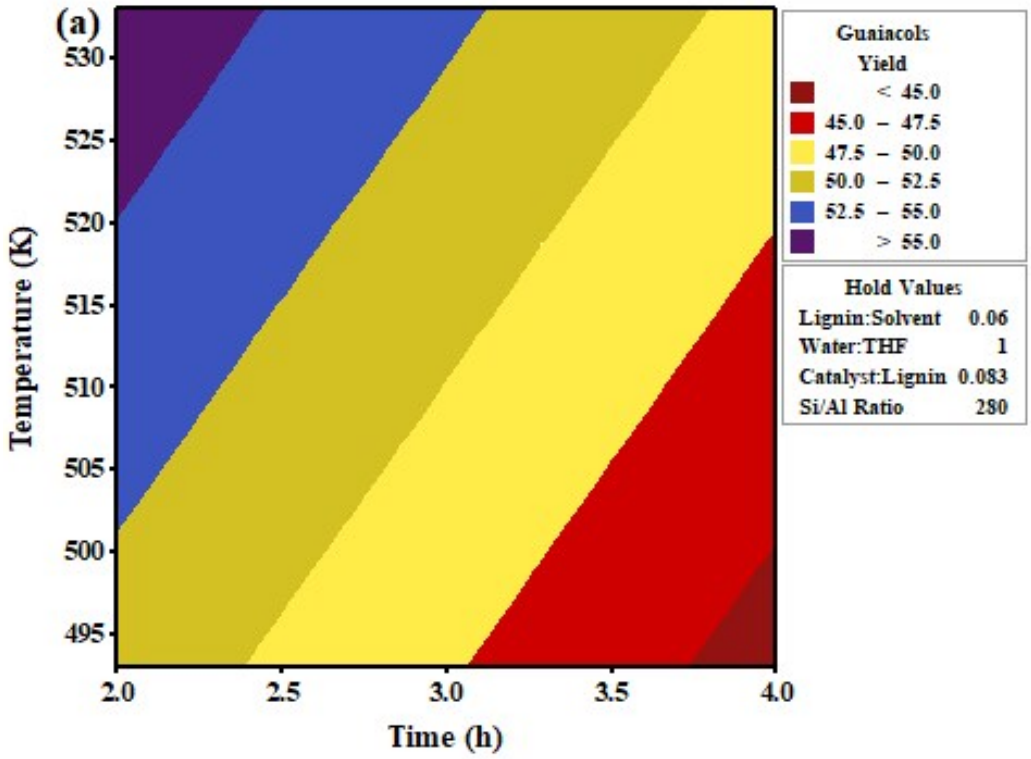

(b)
Hold Values
Time 2
Lignin:Solvent 0.06
Water:THF 1
Catalyst:Lignin 0.083
Guaiacols Yield (%)
55
50
45
500
510
520
530
Temperature (K)
300
200
100
0
Si/Al Ratio

Figure S14 Countours (a) and surface plots (b) representing effect of Temperature (K) and Si/Al ratio of HZSM5 on guaiacol yield (%).



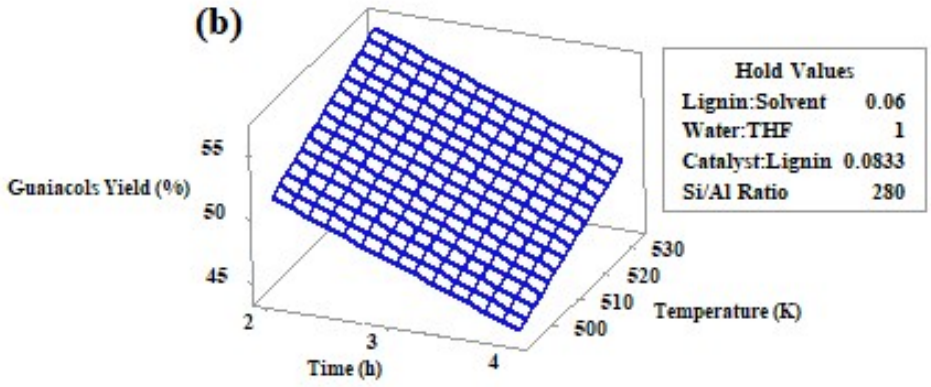


Figure S15 Countours (a) and surface plots (b) representing effect of Time (h) and Temperature (K) on guaiacol yield (%).

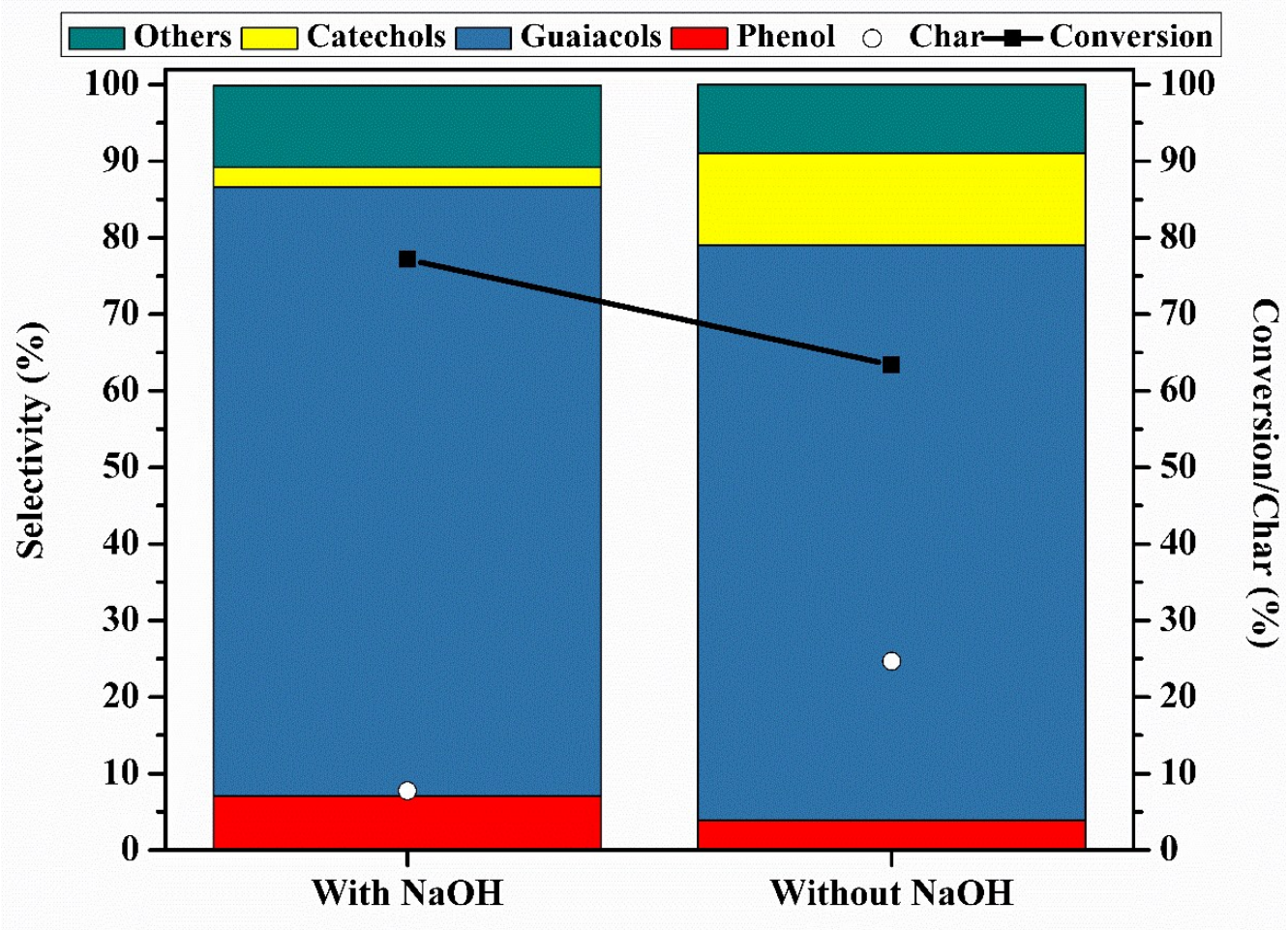


Figure S16 Product distribution obtained during the lignin depolymerization reaction in the presence and absence of NaOH. Reaction conditions (Optimal): 12g lignin, HZSM280 (2g), lignin-to-solvent ratio (1:16.6 w/v), water-to-THF (0.86:1 v/v), NaOH-to-lignin ratio=0.1, Time (2h), Temperature (533 K), RPM (800).

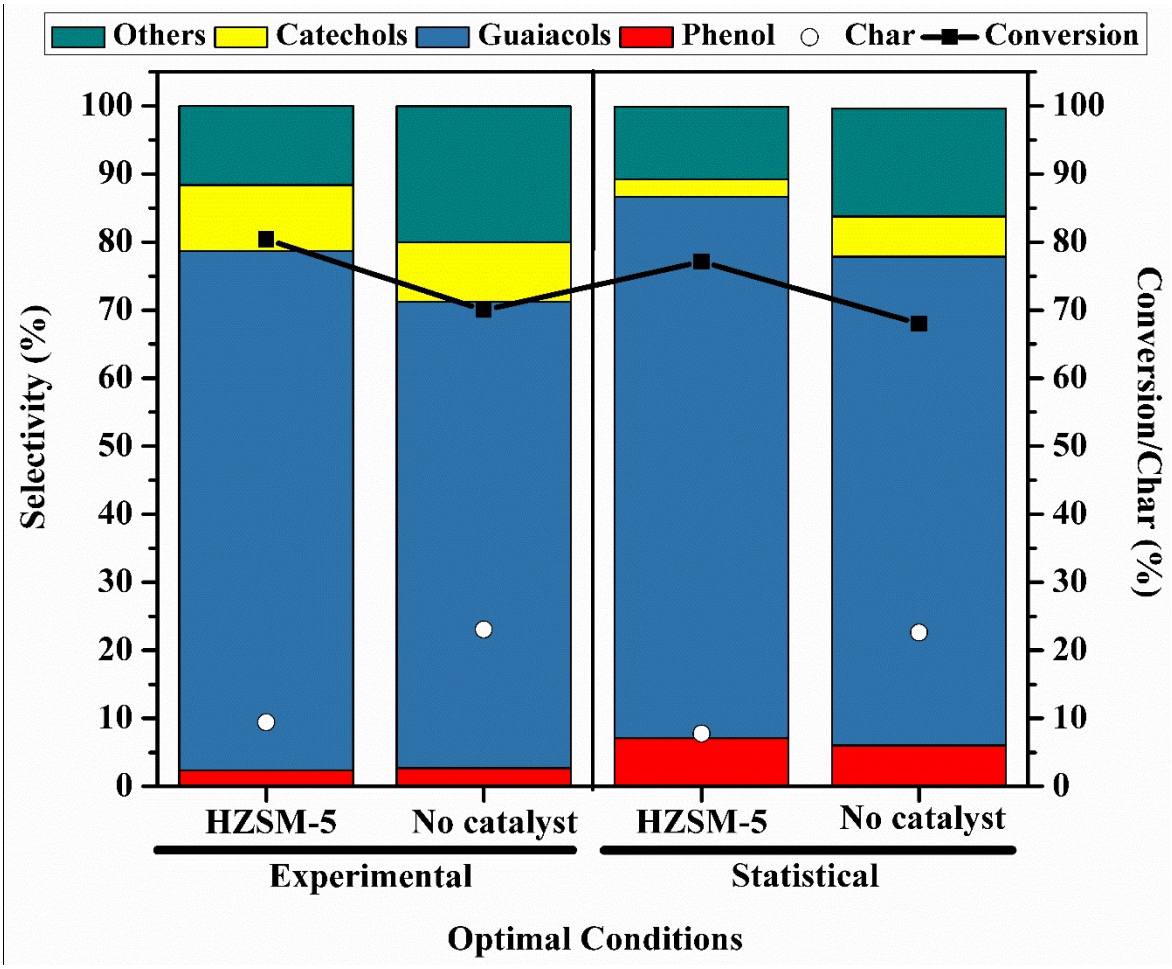


Figure S17 Experimental trails at the optimal condition obtained in experimental and statistical sensitivity analysis in the presence and absence of HZSM-5. Reaction conditions: Statistical Optimal:12g lignin, HZSM280, lignin-to-solvent ratio (1:16.6 w/v), water-to-THF (0.86:1 v/v), NaOH (1.2g), Time (2h), Temperature (533 K), RPM (800). Experimental Optimal: 12g lignin, HZSM280, lignin-to-solvent ratio (1:16.6 w/v), water-to-THF (0.8:1 v/v), Time (2h), Temperature (523 K), RPM (800).

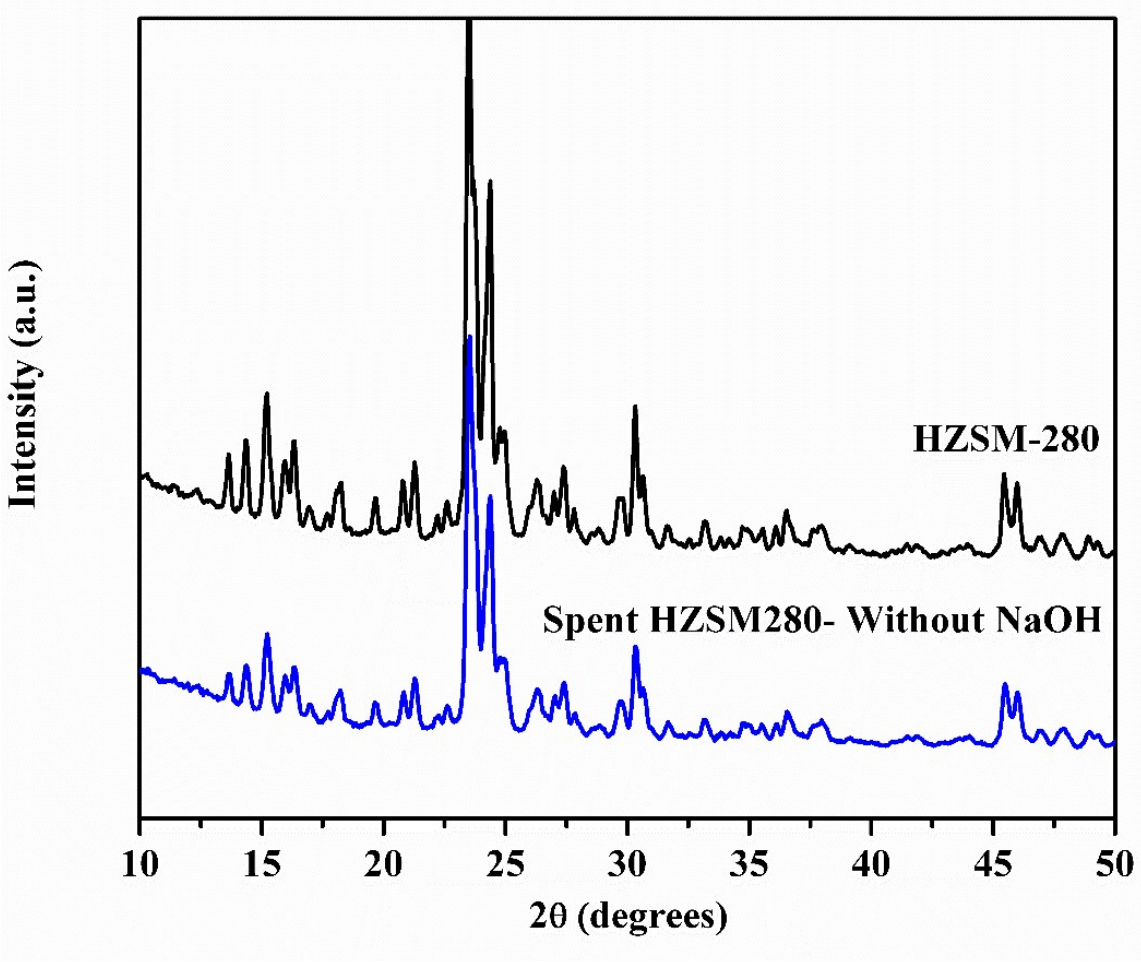


Figure S18(a) XRD pattern of parent and spent HSM280 after lignin depolymerization reaction in the absence of NaOH.

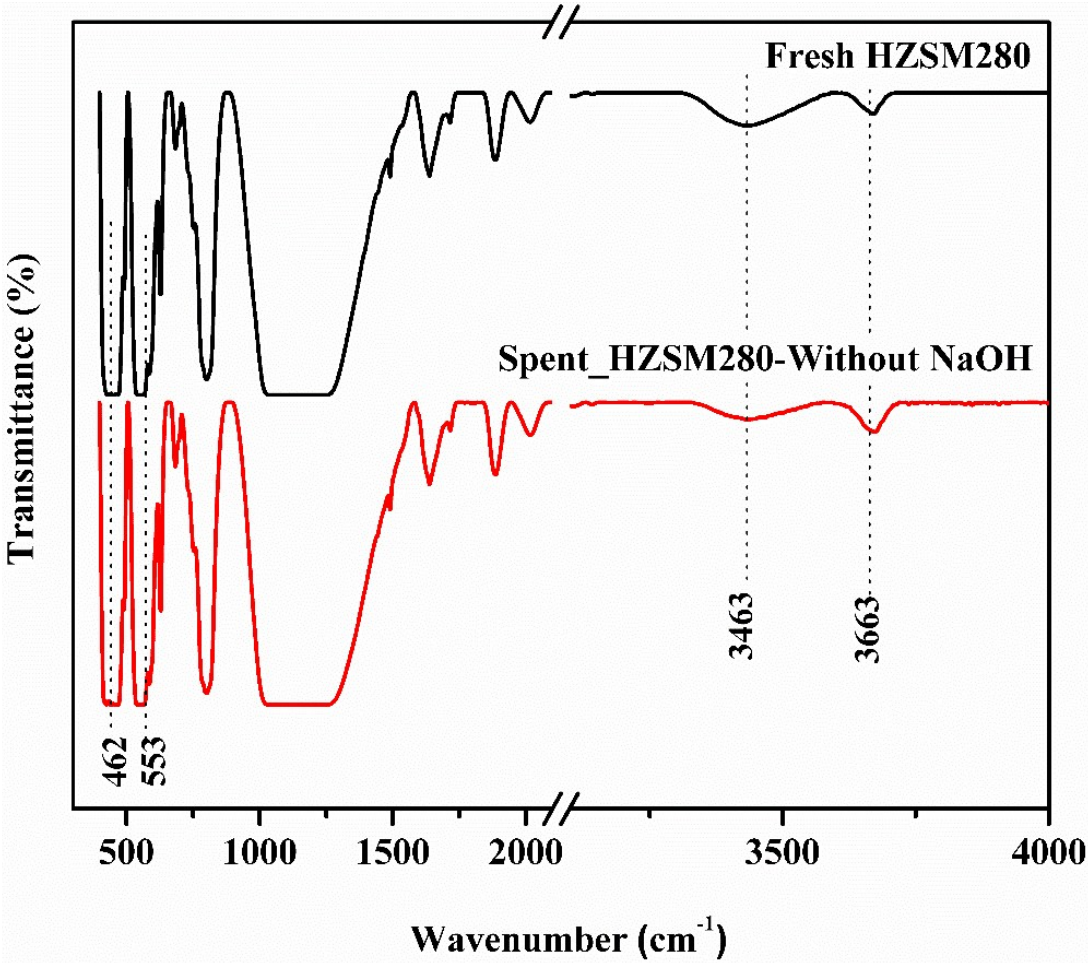


Figure S18(b) FT-IR spectra of parent and spent HZSM280 after lignin depolymerization reaction in the absence of NaOH.

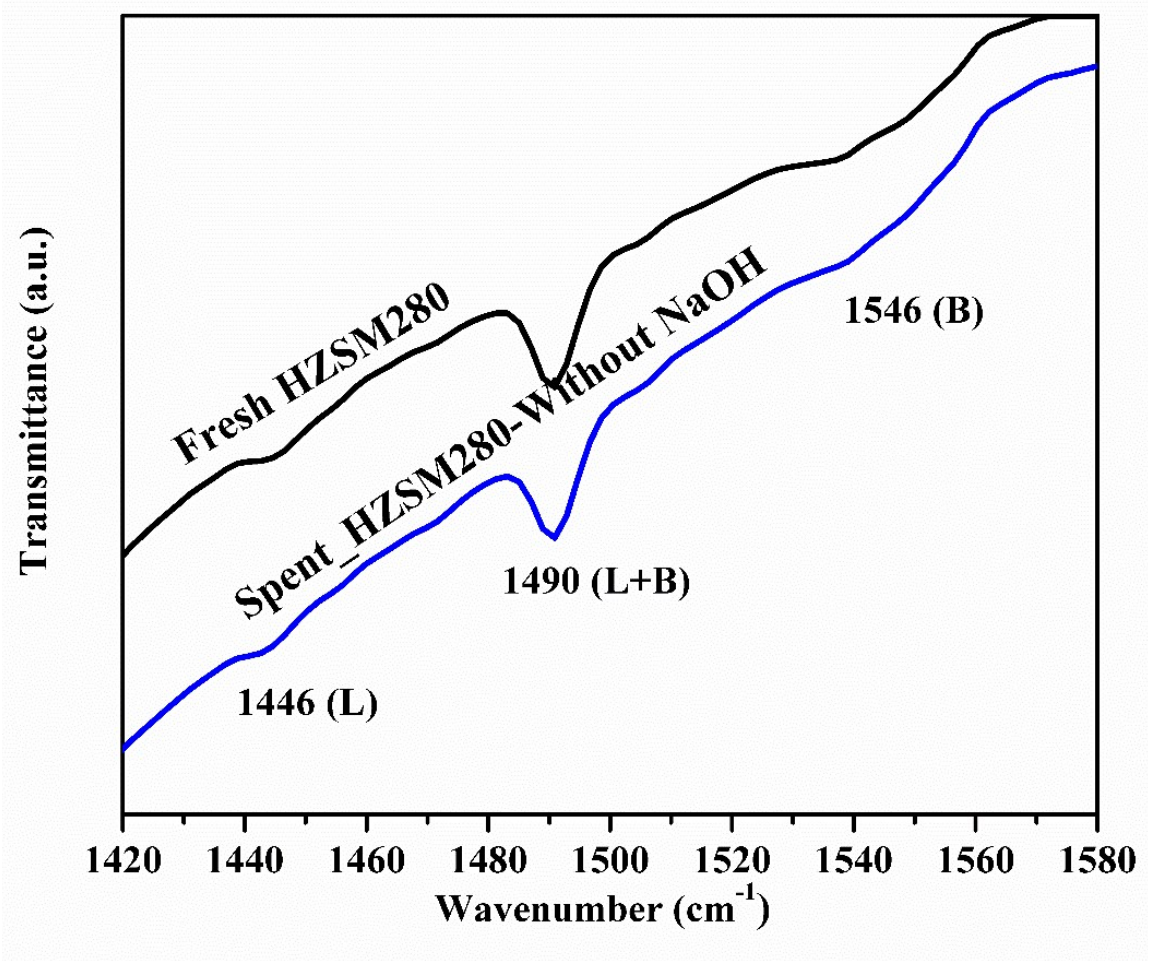


Figure S18(c) Pyridine absorbed FT-IR spectra of parent and spent HZSM280 after lignin depolymerization reaction in the absence of NaOH.

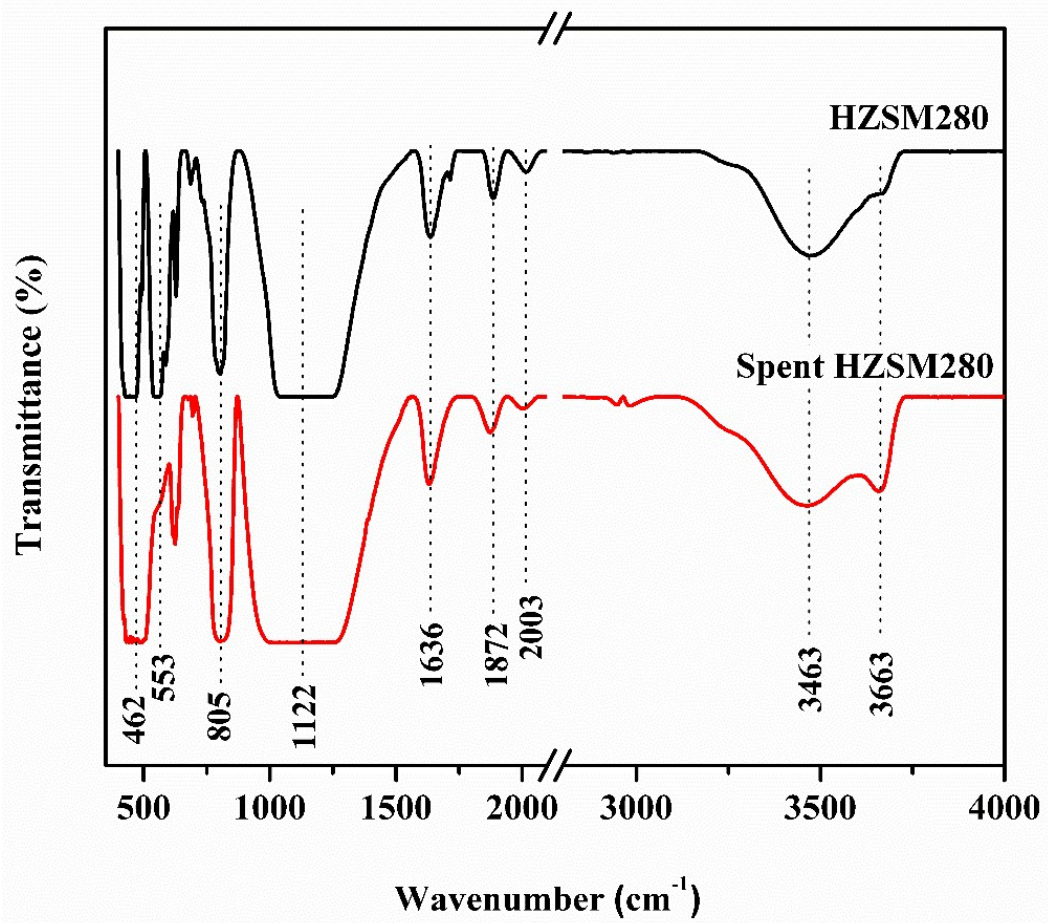


Figure S19. FTIR spectra of fresh and spent HZSM280.