Lignin depolymerization using HZSM-5 as catalyst: Effect of Methanol-Water as solvent

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Supporting Information

Table of Contents

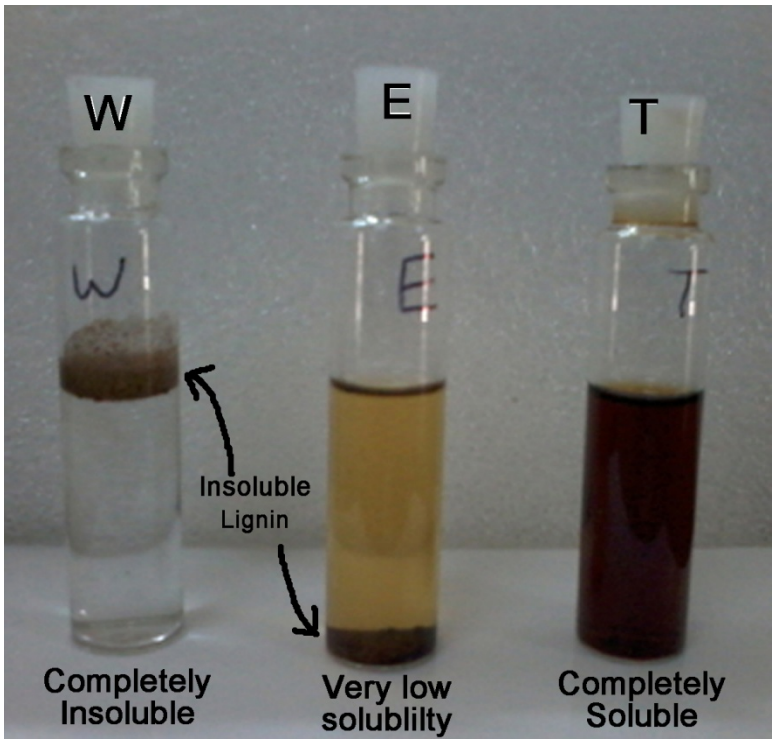

Figure S1 Solubility of 20 mg lignin in 5 ml of each solvent (used for products separation in scheme 1-main paper). W - water, E - ethyl acetate, T – tetrahydrofuran

Table S1 Products yields from reactions performed in only methanol and methanol-water mixture.

Entry	Solvent	Reaction time (Hr)	Catalyst (g)	NaOH (mmol)	% Lignin Conversion	% Water Soluble Products[c]	% EtOAc Soluble Products[c]	% THF Soluble Products[c]	% char	% Gaseous Products[c]
1	Methanol	7	-	-	73.6	10.3	16.4	7.5	18.9	46.9
2	Methanol	15	-	-	68.7	9.5	19.3	14.7	16.5	40.0
3	Methanol	7	-	2	68.5	2.7	18.6	12.5	19.1	47.1
4	Methanol	15	-	2	43.2	3.6	19.0	15.1	41.6	20.7
5	Methanol	7	0.1	-	85.1	4.5	38.5	2.7	12.2	42.1
6	Methanol	15	0.1	-	80.9	4.6	26.5	2.5	16.5	49.9
7	Methanol-Water (1:1)	7	-	-	56.9	9.3	43.6	23.8	19.3	4.0
8	Methanol-Water (1:1)	7	-	2	96.3	16	44.1	3.6	0.1	36.2
9	Methanol-Water (1:1)	15	-	2	86.4	10.9	42.8	13.4	0.2	32.7
10 [20]	Methanol-Water (1:1)	7	0.1	2	98.5	16	44.9	1.2	0.3	37.6
11	Methanol-Water (1:1)	15	0.1	2	88.7	13.4	42	10.7	0.6	33.3

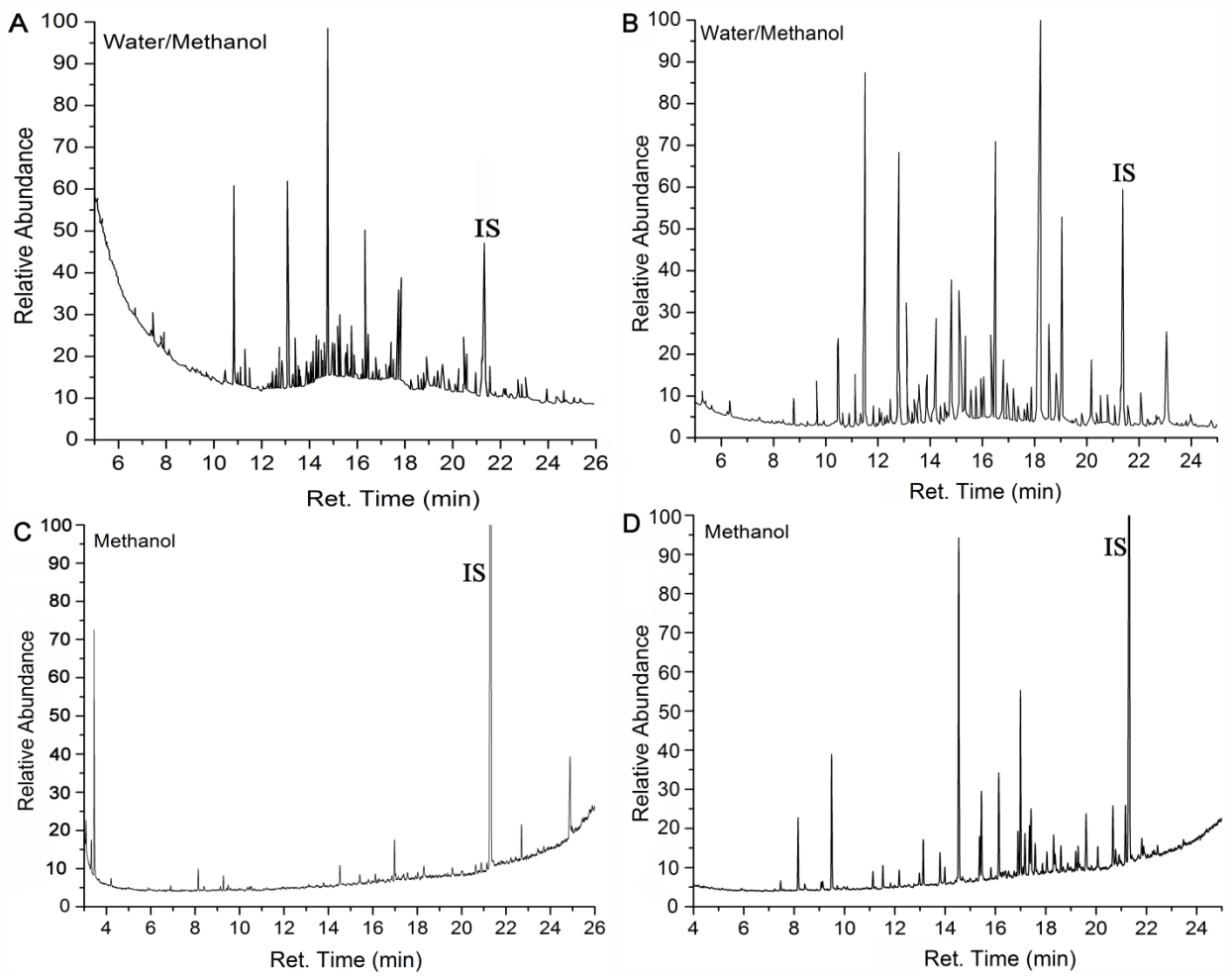

Figure S2 A) EtOAc soluble products B) Water soluble products from the reaction in methanol (Table 3, entry 5), C) EtOAc soluble products D) Water soluble products from the reaction in water-methanol (Table 3, entry 10). *IS-Internal Standard (Phenanthrene)

Table S2 Compound identified in EtOAc soluble products of reaction in methanol (Table 3, entry 5).

RT	Compound Name	Molecular Weight	Area %
3.081	Cyclopropanepentanoic acid, 2-undecyl-, methyl ester, trans-	124	0.77
3.32	Toluene	92	0.99
3.447	Acetic acid, 2-methylpropyl ester	116	7.55
4.207	Methyl 4-hydroxybutanoate	118	0.3
6.897	1,3,5-Cyclohexanetriol	132	0.23
8.133	1-Pentanol, 2-ethyl-4-methyl-	130	0.8
8.392	3-Octanol, 3-methyl	144	0.17
9.131	3-Pentanol, 2,4-dimethyl-	116	0.15
9.271	Isooctane, (ethenyloxy)-	156	0.5
9.483	1-Hexyne, 6-(1-ethoxyethoxy)-	170	0.23
14.514	Phenol, 2,6-dimethoxy-	154	0.86
15.41	Benzaldehyde, 3-(chloroacetoxy)-4-methoxy-	228	0.41
16.112	o-hydroxy, phenyl acetic acid	152	0.36
16.978	Phenol,2,6-bis(dimethylethyl)-4-methyl	220	1.79
18.298	Benzene acetic acid, 3-methoxy	166	0.58
20.632	1,4-heptadiene,5,6-hydroxy, 6-methyl	142	0.62
20.885	1,4-Cyclohexadiene	80	0.86
21.309*	Phenanthrene	178	76.57
22.694	Hexadecanoic acid, methyl ester	270	1.34
24.852	16-hydroxy, 9-octadecanoic acid, methyl ester	312	1.59
24.884	Cyclopropanepentanoic acid, 2-undecyl-, methyl ester, trans-	310	2.9

*Internal standard

Table S3 Compound identified in water soluble products of reaction in methanol (Table 3, entry 5).

RT	Compound Name	Molecular Weight	Area %
3.445	Acetic acid, 2-methylpropyl ester	116	1.23
8.195	1-Hexanol, 2-ethyl-	130	2.14
9.535	Phenol, 2-methoxy-	124	4.28
11.17	Phenol, 3-ethyl-	122	0.55
11.575	Phenol, 2-methoxy-4-methyl-	138	0.75
12.225	Benzofuran, 2,3-dihydro-	120	0.54
13.02	1,2-Benzenediol, 3-methoxy-	140	0.32
13.17	Phenol, 4-ethyl-2-methoxy-	152	1.49
13.83	2-Methoxy-4-vinylphenol	150	0.93
14.015	Phenol, 4-ethyl-2-methoxy-	152	0.49
14.59	Phenol, 2,6-dimethoxy-	154	11.56
15.4	Benzaldehyde, 3,4-dimethoxy-, methylmonoacetal	198	1.37
15.485	4-Hydroxy-2-methoxybenaldehyde	152	2.8
16.18	Phenol, 2-methoxy-4-(1-propenyl)-	164	3.94
16.945	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	166	1.59
17.04	Butylated Hydroxytoluene	220	5.99
17.215	1,2-Dimethoxy-4-n-propylbenzene	180	1.43
17.38	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	182	1.82
17.45	Benzene, 1,2,3-trimethoxy-5-methyl-	182	2.02
17.61	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	180	1.08
18.075	2-methylphenol	108	0.72
18.345	4-Ethoxy-3-methoxyphenethyl alcohol	196	1.35
18.405	3,4-Dimethoxyphenyllactic acid	226	0.47
18.64	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	194	0.91
19.24	3-methoxy, thiophenol	124	0.73
19.315	1-phenyl, propanol	136	0.79
19.65	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	182	2.2
20.095	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	194	0.64
20.72	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	196	2.41
21.225	Benzoic acid, 4-hydroxy-3,5-dimethoxy-, hydrazide	212	2.25
21.375*	Phenanthrene	178	40.65
21.86	2-Isopropylbenzenethiol	152	0.56

*Internal standard

Table S4 Compound identified in EtOAc soluble products of reaction in water-methanol (Table 3, entry 10).

RT	Compound Name	Molecular Weight	Area %
11.12	2-Naphthalenol, 1,2-dihydro-,acetate	188	0.78
11.31	Dodecane	170	1.34
11.47	à-Irone	206	1.48
12.61	Cyclopropanetetradecanoic acid,2-octyl-, methyl ester	394	4.75
12.72	2-Cyclopenten-1-one, 2-(2-butenyl)-4-hydroxy-3-methyl,(Z)	166	1.46
13.53	2-hydroxy-6-hexadecenoic acid, methyl ester	356	1.91
13.86	Trans-Z-à-Bisabolene epoxide	220	1.11
14.27	1-Hexadecanol,2-methyl-	256	1.67
14.38	Dodecane, 2,6,10-trimethyl-	212	1.47
14.48	à-acorenol	222	0.90
14.75	Tetradecane	198	19.04
15.06	5-Isopropylidene-6-methyl deca-3,6,9-trien-2-one	204	1.33
15.26	Naphthalene, 1,7-dimethyl-	156	5.10
15.33	2H-Cyclohepta[b]furan-2-one, 6-[1-(acetyloxy)-3-oxobutyl]-3,3a, 4,7,8,8a-hexahydro-7-methyl-3-methylene	306	1.26
15.75	Tetradecane, 2,6,10-trimethyl-	240	3.94
15.96	Cyclohexane,1,1,3-trimethyl-2,3-epoxy-2(3-methylcyclobuten-2-yl)-4-acetyloxy-	264	0.76
16.33	Hexadecane	226	5.58
16.47	3-tert-Butyl-4-hydroxyanisole	180	1.65
17.40	1-Dodecanol,3,7,11-trimethyl-	228	3.48
17.52	2-Butenal, 2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	206	1.19
17.72	1-Hexadecanol, acetate	284	8.89
17.83	Nonadecane	268	3.17
18.52	Xanthatin,1'-acetoxy-3-methyl-3-demethylene-1',2'-dihydro-	308	1.18
18.89	8-Octadecanone	268	2.04
20.21	Heptadecane, 3methyl-	254	0.90
20.50	1-Docosene	308	1.74
20.59	Heptacosane	380	2.04
21.32*	Phenanthrene	178	13.56
21.57	2-Myristynoyl pantetheine	484	1.55
23.03	2-Hexadecanol	242	4.73

*Internal Standard

Table S5 Compound identified in water soluble products of reaction in water-methanol (Table 3, entry 10).

RT	Compound Name	Molecular Weight	Area %
9.64	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	138	0.90
10.46	1,4-Benzenediol, 2,5-dimethyl-	138	1.93
11.12	1-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-	152	0.93
11.50	Phenol, 2,4,6-trimethyl-	136	10.37
12.62	2-Cyclopenten1one, 2-(2-butenyl)- 4-hydroxy-3-methyl-,(Z)	166	0.77
12.74	Benzene, 1-ethoxy-2-methoxy-4-methyl-	166	2.08
12.80	1,4-Benzenediol, 2,3,5-trimethyl-	152	5.17
13.07	Phenol, 2-ethyl-4,5-dimethyl-	150	3.08
13.58	2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-1-methoxy-	180	1.41
13.87	Phenol, 3-methoxy-2,5,6-trimethyl-	166	1.57
14.21	Phenol, 2,3,5,6-tetramethyl-	150	2.59
15.11	2,5-Heptadienoic anhydride, 2,3,4,5,6-pentamethyl, Z,Z-	208	2.47
15.21	3-Buten-2-one,3-methyl-4-(1,3,3-trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl)-	222	0.98
15.33	Phenol, 5-methoxy-2,3,4-trimethyl-	166	1.58
15.55	1,4-Benzenediol, 2,3,5-trimethyl-	152	1.36
15.76	2-Oxabicyclo[3.3.0] oct-7-en-3-one, 7-(-1- hydroxypentyl)-	210	0.70
15.93	5,6,7,8-Tetramethylbicyclo[4.1.0]Hept-4-en-3-one	164	1.53
16.03	Carbofurane	221	0.99
16.49	Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	180	5.53
16.69	Phenol, 5-methoxy-2,3-dimethyl-	152	0.69
16.79	Phenol, 4-methoxy-2,3,6-trimethyl-	166	1.22
16.94	Phenol, 2-(1,1-dimethylethyl)-3-methyl-	164	0.68
17.26	àTetralol, 2-amino-5,6-dimethoxy-	223	0.74
17.34	Benzene, 1,4-dimethoxy-2,3,5,6-tetramethyl-	194	0.65
18.24	Durohydroquinone	166	19.05
18.53	Phenol, 2-methoxy-4-methyl-6-[propenyl]-	178	1.86
18.81	Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	180	1.08
19.03	4’,6’-Dihydroxy-2’,3’-dimethylacetophenone	180	4.11
20.17	2-Hydroxy-4,5-methylene dioxypropiophenone	194	1.28
20.51	3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl) cyclohex-2-enone	206	0.75
20.59	4(3,3-Dimethylbut-1-ynyl) 4-hydroxy-2,6,6-trimethylcyclohex-2-enone	234	0.68

20.78	4,7-Dimethoxy-2-methyl indan-1-one	206	0.73
21.29*	Phenanthrene	178	16.65
21.35	Phenol, 2,5-bis(1,1-dimethylethyl)-	206	0.79
22.06	Trimethyl-3,4-methylene dioxychromane	220	0.69
23.05	7,9-Ditert-butyl-1-oxaspiro-[4,5]-deca-6,9-dien-8-one	262	2.41

*Internal Standard