Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

Ethanol as Capping Agent and Formaldehyde Scavenger for Efficient Depolymerization of Lignin to Aromatics

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1.1 Solvent effect on momomeric product distributions

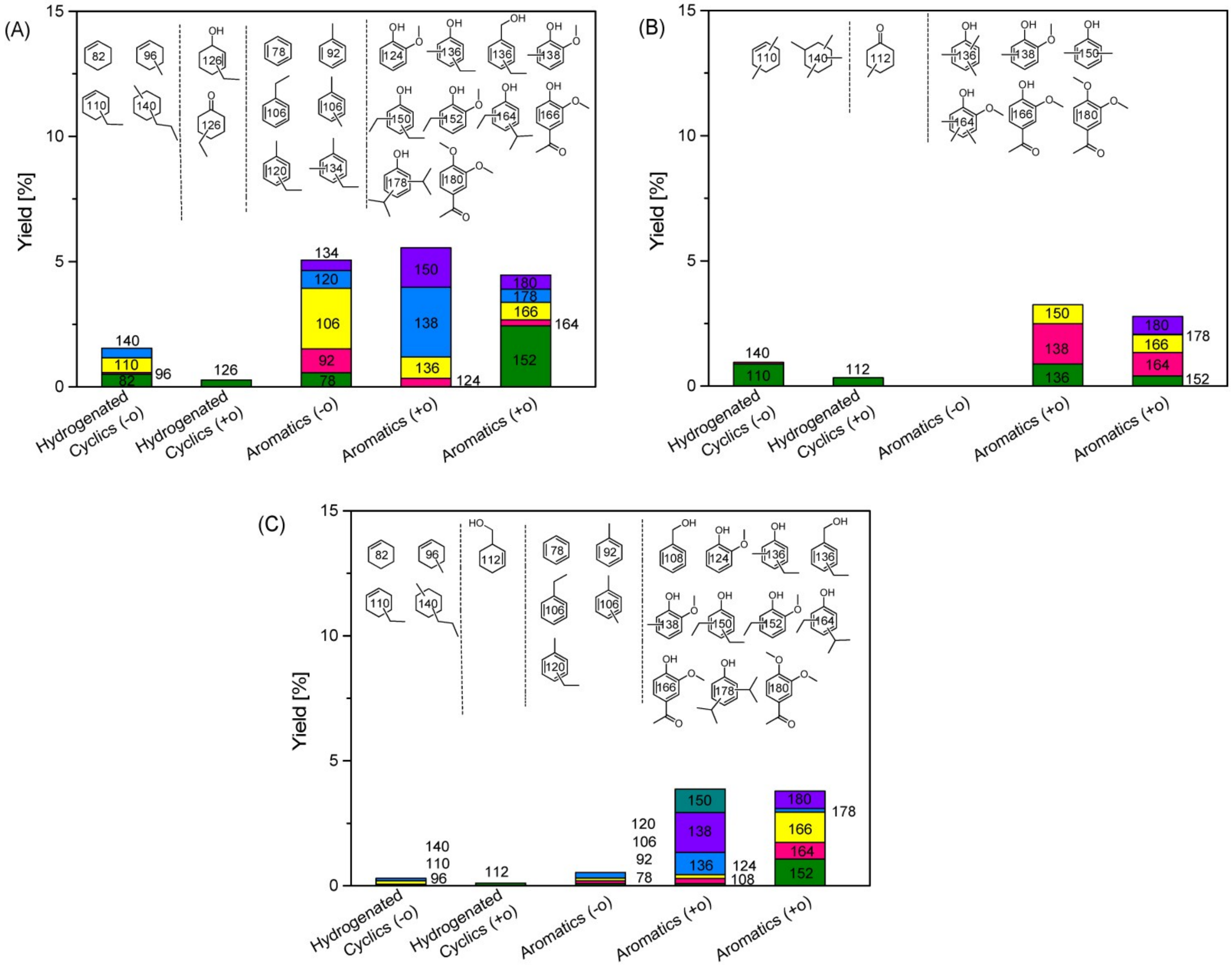


Figure S1. Monomeric product distribution following reaction at 300 °C for 4 h over $CuMgAlO_x$ catalyst in (A) ethanol and (B) methanol, (C) 50%/50% (v/v) methanol/ethanol solvent.

When the reaction was performed in ethanol, the monomeric product mixture contained some hydrogenated cyclics, and mostly aromatic products. Most of these hydrogenated cyclics and aromatic products contained methyl and/or ethyl groups substituents on their rings. This indicates that extensive alkylation has occurred. A significant amount of deoxygenated aromatic products like benzene, toluene, xylenes and ethyl benzene was observed. When the reaction was performed in methanol much less monomeric products were formed. The monomeric products included methylated phenols and guaiacol-type products and a small amount of hydrogenated cyclics. No deoxygenated aromatics were observed in the experiments done in methanol, which is essentially different from the ethanol case.

1.2 Solvent effect on phenol repolymerizaiton (GC-MS analysis).

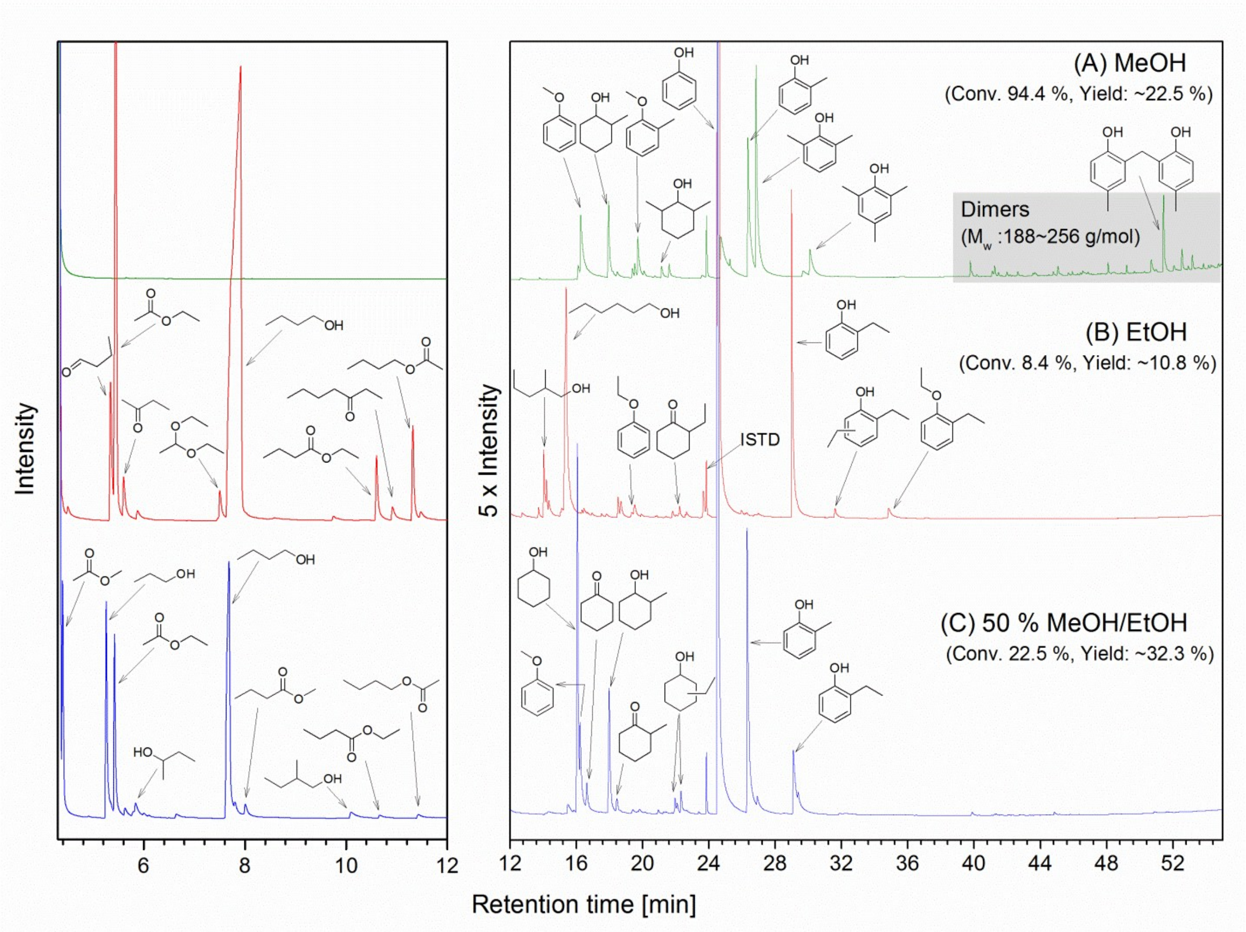
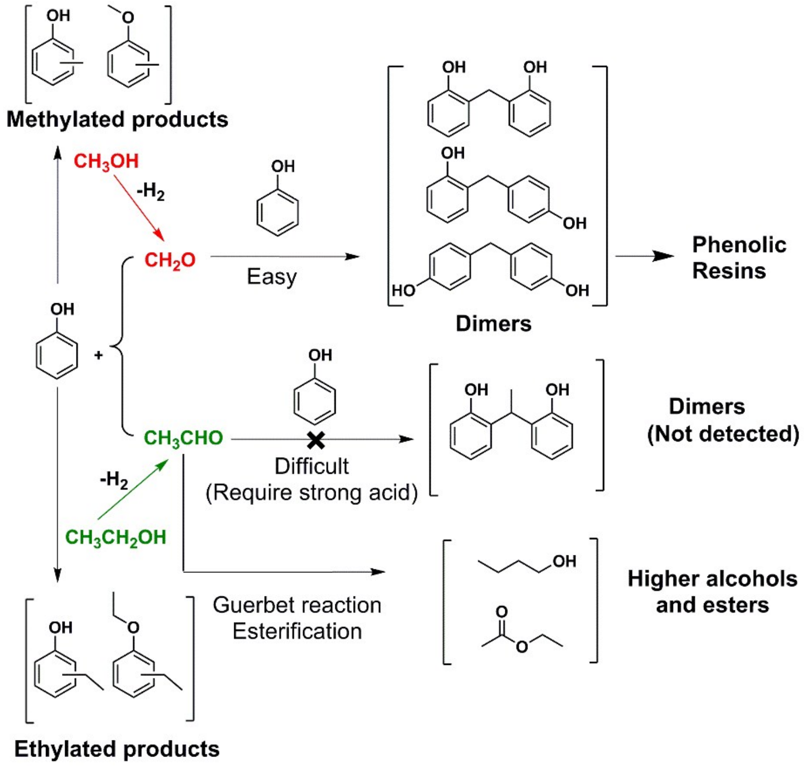


Figure S2. GC-MS chromatograms of reaction mixture obtained from the reactions of phenol at 300 °C for 1 h over CuMgAlO$_x$ in the solvent of (A) methanol, (B) ethanol and (C) 50%/50% (v/v) methanol/ethanol (chromatograms have been normalized by the internal standard (ISTD) peak).

When the reaction was performed in methanol solvent, no linear products were formed. This supports the conclusion that methanol cannot self-couple through the Guerbet reaction. Besides, the phenol conversion was very high (~94.6 wt%), but the monomer yield was only 22.5 wt%. This result shows that the dominant products were dimers, oligomers and polymers. When the reaction was performed in ethanol, only 8.4 wt% phenol was converted and the monomer yield was 10.8 wt%. No dimers were identified in the gas chromatograms. When the reaction was performed in 50%/50% (v/v) methanol/ethanol solvent, the phenol conversion was about 22.5 wt%, yielding 32.3 wt% monomers. Besides, significant amounts of n-propanol and methyl acetate were formed together with some higher alcohols and esters with odd number of carbons. These results point out that significant polymerization of phenol took place in methanol, but not in ethanol. The polymerization reactions were significantly suppressed when mixing the methanol with ethanol.

1.3 Phenol reaction schemes in methanol and ethanol



Scheme S1. Phenol reaction schemes in methanol and ethanol

When the phenol reaction was performed in methanol solvent, serve repolymerization reaction takes place due to the formation of formaldehyde derived from methanol dehydrogenation. Further repolymerimerizaiton will results in formation of phenolic resins. In the ethanol case, the possible dimers from the reaction of phenol and acetaldehyde could not formed, because this reaction requires strong acidic condition. Besides, the acetaldehydes will react with another acetaldehyde or ethanol to form higher alcohols and esters by Guerbet reaction and esterification. These coupling reactions cannot take place between methanol and formaldehyde. In both cases, the O-alkylation and C-alkylation reactions will take place.

1.4 Identification of peaks in HSQC NMR

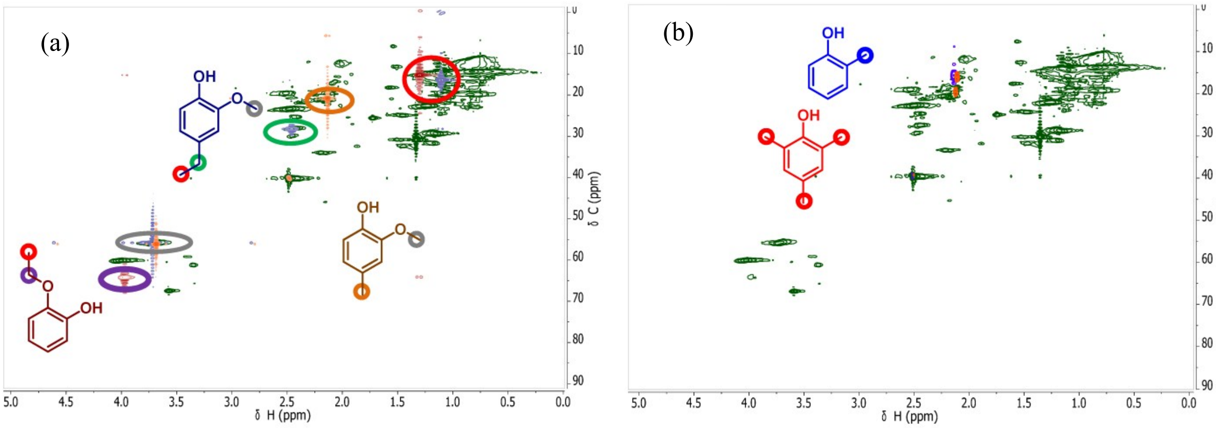


Figure S3. Side-chain region of the of ^{1}H-^{13}C HSQC NMR spectra of the lignin residue (green colour) following catalytic reaction at 300 ºC for 8 h over the CuMgAlO$_x$ catalyst and the standard compounds: (a) 2-ethoxyphenol (red), 4-ethyl guaiacol (blue) and 4-methyl guaiacol (brown); (b) 2-methyl phenol (blue) and 2,4,6-Trimethyl phenol (red).

Standard compounds were used to help to identify the peaks of HSQC NMR spectra. Figure S3 compares the HSQC NMR spectra of lignin residue with some representative standard compounds. It confirms the formation of O-alkylated and C-alkylated products.

1.5 Demethoxylation of lignin

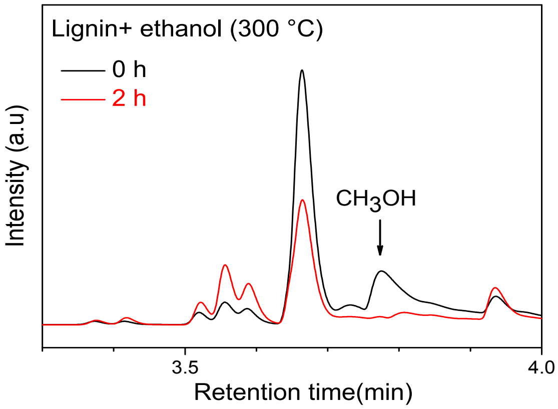


Figure S4. GC-MS results of reaction mixture obtained from lignin reaction at 300°C for heating time and 2 h over the CuMgAlO$_x$ catalyst in ethanol solvent.

The formation of methnaol was detected after reaction at 300°C for heating time. After reaction for 2h, this methanol disapper due to reaction with ethanol and lignin. The HSQC NMR analysis of the THF-soluble lignin residue also proved that the methoxy groups have been significantly decreased after reaction at 300 °C for 8h (ref[1]). After reaction at 380 °C for 8 h, almost all the methoxy groups were removed (Figure 8).The demothoxylation of lignin have also been reported in the literature.

1.5 Monomeric product distribution when using Alcell lignin and Kraft lignin as feedstock

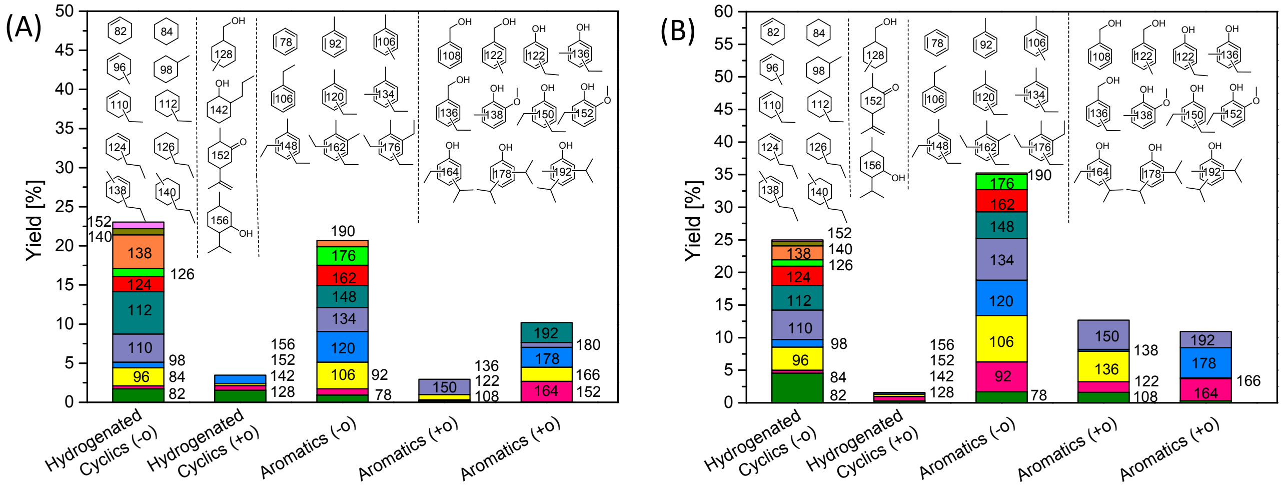


Figure S5. Monomeric product distribution following reaction at 380 °C for 8 h over $CuMgAlO_x$ catalyst in (A) Alcell lignin and (B) Kraft lignin.

1.6 Gas phase products anslysis.

Table S1. Analysis of gas phase products after reaction under varying conditions over the $CuMgAlO_x$.

Entry	Lignin	Solvent	Temp. (ºC)	Time (h)	Gas compositions [mmol]								Sum [mmol]	Sum [mg]
					CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	CO_2	H_2	CO		
					Reactions in 50 ml autoclave[a]									
1	P1000	EtOH	300	4	0.62	0.50	0.30	0.03	0.13	0.61	9.12	0.38	11.70	96.1
2	P1000	MeOH	300	4	1.24	0.04	0.02	0.01	0.01	0.73	2.57	0.58	5.19	76.0
3	P1000	50% MeOH/EtOH	300	4	0.85	0.13	0.10	0.01	0.03	0.68	4.60	0.45	6.83	73.3
					Reactions in 100 ml autoclave[b]									
4	P1000	EtOH	380	8	12.13	10.34	7.91	1.34	1.43	8.14	54.87	11.78	107.94	1648.0
5	THF-soluble LR[c]	EtOH	380	8	4.74	4.90	4.10	1.17	0.96	5.78	34.72	6.20	62.56	931.0
6	Alcell	EtOH	380	8	10.52	11.04	8.79	1.71	1.26	11.64	56.47	14.18	115.62	1902.0
7	Kraft	EtOH	380	8	14.38	14.66	10.29	2.29	2.25	13.58	74.16	7.62	139.24	2121.8

[a] 50 ml autoclave conditions: 1 g lignin, 0.5 g catalyst, 20 ml solvent. [b] 100 ml autoclave conditions: 1 g lignin, 0.5 g catalyst, 40 ml solvent. [c] 1.07 g THF-soluble LR obtained from a reaction of 2 g lignin, 1 g catalyst, 40 ml ethanol at 380 ºC for 8 h.

Reference

1. X. Huang, T. I. Korányi, M. D. Boot and E. J. M. Hensen, *ChemSusChem*, 2014, **7**, 2276-2288.