

One-pot catalytic conversion of kraft lignin into value added chemicals over molybdenum carbide catalysts

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Lignin, along with cellulose and hemicellulose, is one of the principal components of the lignocellulosic biomass which constitutes 15–30% of the weight.¹ Currently, there has been an increasing trend to use lignin as raw material for high value added products. Here, we report a strategy for the catalytic conversion of Kraft lignin over a nano molybdenum carbide catalyst ($\text{MoC}_{1-x}/\text{AC}$) in pure ethanol without any gaseous hydrogen consumption. A total yield of 1.64 g/g lignin is achieved, and the 25 most abundant small molecules (LP25) in the products consist of C6 to C10 esters, alcohols, arenes, phenols, and benzyl alcohols.

The products are analyzed with GC-MS and GC-FID. The yields of the main detected liquid products for 6 h reaction over $\text{MoC}_{1-x}/\text{AC}$ are shown in Table 1. In the LP25, Esters and alcohols are found as the major products which contribute over 80% of the total products. The esters consist of ethyl esters with carboxylic acids, which might be generated from the esterification between ethanol and some lignin-derived intermediates such as hexenuronic acid formed in Kraft pulp. The aromatics mainly contain xylol, benzyl alcohol, guaiacol and their derivatives. The monomer products such as 2-methoxyphenol, 4-methyl-2-methoxyphenol, 4-ethyl-2-methoxyphenol, 4-propyl-2-methoxyphenol have been measured. Besides, the high yields of benzyl alcohols and arenes are the first observation in the one-pot heterogeneous catalytic conversion of Kraft lignin.

Figure 1 shows the effects of water concentration in the solvent on the yields of overall liquid products. The yield of the small molecules decreases monotonically with the water content in the range of 0.5 to 50 vol %. Cheng *et al.*² reported that they obtained the the most degraded lignin, with high acetone-methanol soluble fraction yield, when using a 50/50 (v/v) water-ethanol solvent and that this was accompanied by the lowest solid residue; they found that with either pure ethanol or water, higher solid residue were produced. In our present work with the $\alpha\text{-MoC}_{1-x}/\text{AC}$ catalyst and pure ethanol, no tar and char were detected. However, a small amount of char (16 mg/g lignin) was formed here with the same catalyst using a 50/50 water-ethanol mixture and a lower overall LP25 yield (124 mg/g lignin) was obtained.

Significance

Kraft lignin is fully converted to liquid products over $\text{MoC}_{1-x}/\text{AC}$ catalyst in ethanol. The products include C6 monohydric alcohols, C8 to C10 esters, C7 to C10 monohydric phenols, C7 to C10 benzyl alcohols, and C8 to C10 aromatic hydrocarbons. Solvent and catalyst both play key roles, affecting the molecular yields and product composition.³

Table 1. The main liquid products of Kraft lignin valorization reaction at 280 °C for 6 h. (Yield: mg/g lignin)

t (min)	Compound	Yield	t (min)	Compound	Yield
4.32	2-ethyl butanol	96	8.09	2,5-dimethyl ethylbenzene	14
4.47	2-hexenol	46	8.24	2,4-dimethyl ethylbenzene	33
4.57	2-methyl 1-pentenol	79	8.28	2-methoxy phenol	4
4.72	1-hexanol	188	9.04	4-methyl benzyl alcohol	21
4.75	p-xylene	3	9.15	2-methyl benzyl alcohol	14
5.11	o-xylene	56	9.68	3-octenoic acid ethyl ester	32
6.06	3-methyl pentanoic acid ethyl ester	56	9.71	2-methoxy 4-methyl phenol	35
6.18	3-methyl ethylbenzene	12	9.78	2-octenoic acid ethyl ester	106
6.73	hexanoic acid ethyl ester	303	10.48	4-ethyl benzyl alcohol	13
6.87	3-hexene acid ethyl ester	197	11.28	2-methoxy 4-ethyl phenol	16
7.25	3-phenyl propylene	13	12.10	2,4,5-trimethyl benzyl alcohol	10
7.37	benzyl alcohol	13	12.60	2-methoxy 4-propyl phenol	23
7.48	2-hexene acid ethyl ester	253			

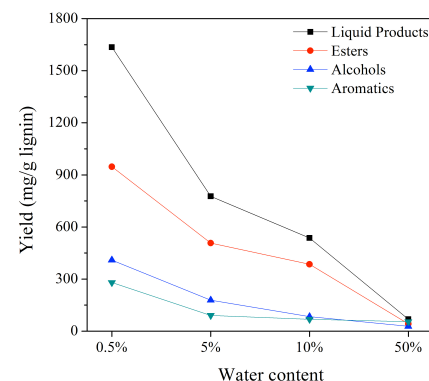


Figure 2 The effects of water concentration on the overall yields of liquid products. (Reaction conditions: 280 oC, 6 h)

References

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