

De-etherification of lignin model compounds and lignins

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Introduction

Lignin is the second most abundant polymer on earth and is found in almost all biomass resources. This inexpensive feedstock is an ideal carbon source that can be used to make fuels and chemicals. However, there are substantial challenges to convert it into a liquid fuel [1]. Lignin is an amorphous polymer consisting of randomly branched phenylpropenyl (C9) groups. The linkages between these groups are primary ether linkages (C-O-C) [1]. The conversion of lignin into a usable product involves cleavage of such linkage, known as de-etherification. In this presentation we discuss our catalytic de-etherification strategies for lignin and lignin model compounds.

Materials and Methods

We used 2-phenylethyl phenyl ether (PPE, with β -O-4 bonding) and benzyl phenyl ether (BPE, with α -O-4 bonding) as lignin model compounds. Organosolv lignin (Acros) and the lignin fraction in bio-oil were also tested. Various catalysts were used including a range of zeolites and solid-phase acids. The experiments were carried out in a semi-batch reactor (Pyroprobe [2]) and continuous fixed-bed reactor system.

Results and Discussion

The Gibbs free energy for conversion of methyl propyl ether (MPE), a model compound of BPE and PPE, was calculated based on available database as shown in Figure 1[3]. The four plausible pathways include de-etherification, hydrolysis, decarbonylation, and hydrogenation. The hydrolysis is thermodynamically unfavorable for whole the temperature range. De-etherification and decarbonylation of MPE are endothermic, and thermodynamically possible at temperatures above 100°C. Hydrogenation is exothermic, and becomes less thermodynamically favorable at higher temperatures. Deoxygenation of phenol, a secondary reaction after de-etherification, is thermodynamic favorable at 450°C and higher (not presented). This suggests that with proper catalysts, de-etherification of lignin is viable.

Figure 2 illustrates the pathways of catalytic PPE conversion. PPE is initially de-etherified to produce phenol and styrene. The phenol and styrene can then undergo further reactions to form benzene or toluene. All reactants and products produce undesired coke. We have previously shown how the reaction conditions can be controlled to produce aromatics with low coke yield from carbohydrate derived feedstocks by catalytic fast pyrolysis [2]. In this presentation we use catalytic fast pyrolysis for conversion of lignin derived compounds. We have obtained aromatics yields of 50% from PPE using amorphous silica alumina catalysts. For ZSM-5, the aromatics yields are about 40%. However, using ZSM-5 as the catalyst produces benzene selectivity up to 63% in the aromatics. In contrast silica alumina produces less than 10 % selectivity of benzene. This suggests shape-selective effect of ZSM-5 may play a major role in product distribution. It is also worth mentioning that phenol selectivity, which supposed to be

equivalent to styrene (shown in Figure 2), is far less than expected, indicating deoxygenation of phenol in this reaction.

Significance

The present study highlights a route for lignin conversion by de-etherification reactions. The effects of catalytic acidity as well as shape selectivity on lignin conversion chemistry are also discussed. The results presented in this paper will allow us a new catalytic route for lignin conversion.

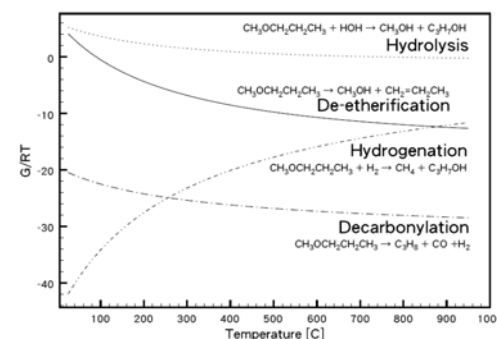


Figure 1. Gibbs free energy of four plausible reaction pathways in MPE conversion.

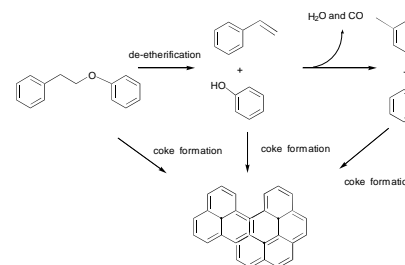


Figure 2. Proposed mechanism of PPE conversion.

References

- Holladay, J. E.; White, J. F.; Bozell, J. J.; Johnson, D. *Top Value-Added Chemicals from Biomass - Volume II Results of Screening for Potential Candidates from Biorefinery Lignin*; PNNL-16983; Other: BM0102070, 2007
- Carlson, T.R., Vispute, T.P., and Huber, G.W. *ChemSusChem* 1, 397 (2008).
- Yaws, C. L. *Chemical Properties Handbook (Physical, Thermodynamic, Environmental, Transport, Safety, and Health Related Properties for Organic and Inorganic Chemicals)*. McGraw-Hill, New York, 1999.