Reaction pathways of catalytic lignin conversion in ethanol

<u>Yongdan Li*</u>¹, Yushuai Sang²,

¹ Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, Espoo, P.O. Box 16100, FI-00076, Finland ² School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

*E-mail: yongdan.li@aalto.fi (Y. Li)

Lignocellulose, mainly composed of cellulose, hemicellulose and lignin, is a sustainable feedstock for producing the commodity chemicals and fuels. For hundreds of years, cellulose has been utilized in paper production. Recently, cellulose and hemicellulose are converted into bio-ethanol in 2G biorefineries. Nevertheless, Kraft lignin from paper industry and enzymatic hydrolysis lignin (EHL) from 2G bioethanol productions are not fully utilized and are regarded as large volume solid wastes.

Our previous works focused on the depolymerization of Kraft lignin in ethanol. Mo-based catalysts (MoC_{1-x}, MoN₂ and Mo/Al₂O₃) were employed, yielding small molecules without formation of char [1, 2]. There was evidence that Kraft lignin was firstly fractured into smaller segments through non-catalytic ethanolysis, and then these segments are further converted into monomers with catalyst. Recently, EHL in 2G ethanol production was explored and phenolic monomers are obtained with different catalysts, e.g., WO₃/Al₂O₃, NiMo/Al₂O₃ and Ni catalysts [3-5]. The cleavage of lignin linkages and the role of different catalytic sites in EHL conversion are clarified. The ether linkages are cleaved through homolysis without the participation of a catalyst. The metal sites play the role for suppressing repolymerization through hydrogenation of active bonds. The acid and base sites convert phenolic monomers into complex alkylated and etherification, but also promote repolymerization steps.

These works, including those published by colleagues in similar period, provide an efficient strategy for Kraft lignin and EHL utilization and also give a deep understanding of the mechanism of lignin depolymerization reaction.

^[1] R. Ma, W. Hao, X. Ma, Y. Tian, Y. Li, Angew. Chem., Int. Ed., 2014, 53, 7310-7315.

^[2] X. Ma, R. Ma, W. Hao, M. Chen, F. Iran, K. Cui, Y. Tian, Y. Li, ACS Catal., 2015, 5, 4803-4813.

^[3] Y. Bai, K. Cui, Y. Sang, K. Wu, F. Yan, F. Mai, Z. Ma, Z. Wen, H. Chen, M. Chen, Y. Li, *Energy Fuels*, **2019**, *33*, 8657-8665.

^[4] F. Mai, Z. Wen, Y. Bai, Z. Ma, K. Cui, K. Wu, F. Yan, H. Chen, Y. Li, *Ind. Eng. Chem. Res.*, **2019**, 58, 10255-10263.

^[5] Y. Sang, M. Chen, F. Yan, K. Wu, Y. Bai, Q. Liu, H. Chen, Y. Li, *Ind. Eng. Chem. Res.*, **2020**, *59*, 7466-7474.