## Extraction of Lignin from Raw Biomass via Organosolv Treatment and Its Conversion to Phenols over Iron-oxide Based Catalyst

<u>Takuya Yoshikawa</u><sup>\*,1</sup>, Yuki Kawamata<sup>1</sup>, Kanta Yamaguchi<sup>1</sup>, Yuta Nakasaka<sup>1</sup>, Teruoki Tago<sup>2</sup>, Shinya Sato<sup>3</sup>, Yoshihito Koyama<sup>4</sup>, Kevin C.-W. Wu<sup>5</sup> and Takao Masuda<sup>1</sup>
<sup>1</sup>Hokkaido University, Sapporo, Japan
<sup>2</sup>Tokyo Institute of Technology, Tokyo, Japan
<sup>3</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan
<sup>4</sup>Idemitsu Kosan Co., Ltd., Sodegaura, Japan
<sup>5</sup>National Taiwan University, Taipei, Taiwan \*E-mail: yoshikawa@eng.hokudai.ac.jp

Valorization of lignocellulosic biomass, which is mainly composed of cellulose, hemicellulose and lignin, has attracted much attention from the viewpoint of sustainable and green technology. Lignin can be an alternative resource of phenol because lignin is a polymer composed of methoxylated alkylphenol units. We have reported a conversion process of reagent lignin, consisting of the following two reaction steps: first, lignin is depolymerized in H<sub>2</sub>O/1-butanol (BuOH) mixed solution using a solid acid catalyst, and next, thus obtained lignin-derived liquid is further reacted over iron-oxide based catalyst to produce phenols [1,2].

In this study, we applied H<sub>2</sub>O/BuOH treatment with a solid acid catalyst to raw biomass for extracting lignin, and carried out catalytic reaction of the lignin-derived liquid. Moreover, we investigated the production of hydroxymethylfurfural (HMF) from the solid product after H<sub>2</sub>O/BuOH treatment, which mainly contained insoluble cellulose.

H<sub>2</sub>O/BuOH treatment of raw biomass was carried out in a batch type reactor using a solid acid catalyst. Wood powder (Japanese cedar) were used as a feedstock, and treatment temperature changed 150–250°C. Fig. 1 shows the yield of liquid and solid products. Composition of cedar is also shown together. Though the yield of liquid product increased with increasing temperature, a considerable decomposition of cellulose also occurred at 250°C. Therefore, we concluded appropriate temperature was 200°C. Then, the molecular weight distribution of BuOH phase after the treatment was analyzed by GPC. Several peaks were observed and the peaks were roughly corresponding to the integral multiple of lignin unit between 2 to 12, that is coniferyl alcohol. Therefore, it was indicate that lignin was extracted from cedar wood and recovered in BuOH phase.

The catalytic cracking of BuOH phase was carried out over iron-oxide based catalyst using a high pressure fixed-bed flow reactor at 673K under 15 MPa of steam atmosphere. Production of phenol was confirmed and total yield of phenols increased to 5.7% after the catalytic reaction. Demethoxylation reaction over the catalyst was previously confirmed using guaiacol (2-methoxyphenol) as a model compound [2,3]. Therefore, it is considered that a similar reaction route proceeded to produce phenol. In addition, the solid product containing insoluble cellulose after H<sub>2</sub>O/BuOH treatment applied was to CrCl<sub>3</sub>.6H<sub>2</sub>O/boric acid catalytic system. resulting in the yield of 45% of HMF [4].





## Acknowledgements

This work was supported in part by the Advanced Low Carbon Technology Research and Development Program (ALCA) from the Japan Science and Technology Agency (JST).

## REFERENCES

[1] T. Yoshikawa et al., Fuel Process. Technol., 108 (2013) 69.

[2] T. Yoshikawa et al., Appl. Catal. B-Environ., 146 (2014) 289.

[3] T. Yoshikawa et al., J. Jpn. Petrol. Inst., 53 (2010) 178.

[4] C.V. Nguyen et al., Nanosci. Nanotechnol. Lett., 8 (2016) 273.