Synthesis and Application of Oxygenated Carbon Catalyst for Cellulose Hydrolysis in a Slurry Process

Abhijit Shrotri[1], Hirokazu Kobayashi[1], Atsushi Fukuoka[1]

[1]*Institute for Catalysis, Hokkaido University, Sapporo, Japan*

*E-mail: fukuoka@cat.hokudai.ac.jp

Heterogeneously catalyzed hydrolysis of cellulose using an easily scalable process is essential for the development of a biorefinery to reduce our dependence on fossil fuels. Our group recently reported that oxygenated carbon catalysts can hydrolyze cellulose to glucose in a batch reactor with high yield [1]. However, costly oxidation methods needed for catalyst preparation prohibit their use in industry. Furthermore, it is necessary to develop a continuous flow process to demonstrate the ability for scale-up of the heterogeneously catalyzed reaction. To overcome these challenges, we report the design and application of a slurry plug-flow process for conversion of cellulose and lignocellulosic biomass to sugar monomers using inexpensive carbon catalyst prepared by simple air-oxidation (Figure 1).

The catalyst was prepared by air-oxidation of activated carbon, which introduced large number of weakly acidic functional groups on the catalyst surface (2.42 mmol g^{-1}) [2]. Mix-milling of the catalyst with cellulose or real biomass (*Eucalyptus*) enhanced the contact between substrate and catalyst, which enabled rapid hydrolysis of β-1,4 glycosidic bonds in cellulose over the acidic functional groups to yield soluble oligomers (DP 2-6) as the main product (Figure 2). Subsequent conversion of oligomers to glucose was slow as the contact was lost when the oligomers dissolved in water. To attain high glucose yield we used dilute HCl as solvent (0.012 wt.% pH=2.5), which quickly hydrolyzed the oligomers resulting in 76 % yield of glucose. We also tested the feasibility of using H_3PO_4 as the acid due to its low corrosive strength. Dilute H_3PO_4 solution (0.043 wt. %) with the same pH also resulted in high yield of glucose. Finally, using biomass as a substrate both hemicellulose and cellulose were hydrolyzed under the same condition yielding 71 wt.% glucose and 73 wt.% xylose (based on the initial cellulose and xylan content in *Eucalyptus*). It is important to note that the residence time of reactant in the slurry reactor was less than 2 minutes, which allows high throughput of products necessary for economic production. This is the first example of a slurry flow process utilizing heterogeneous catalyst for biomass hydrolysis and the simplicity of the design makes is easily scalable for industrial application using existing chemical technology.

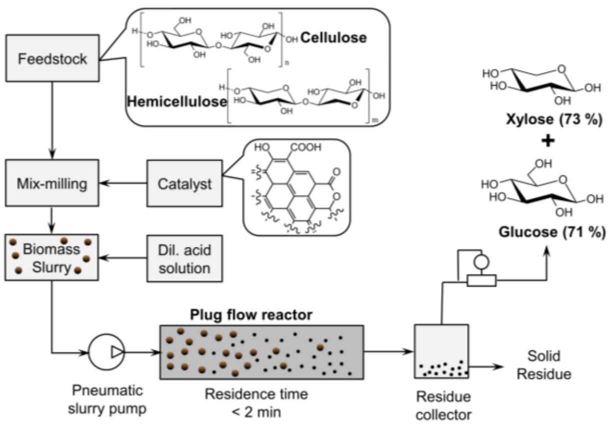

Fig.1 Schematic of the slurry flow process for cellulose hydrolysis.

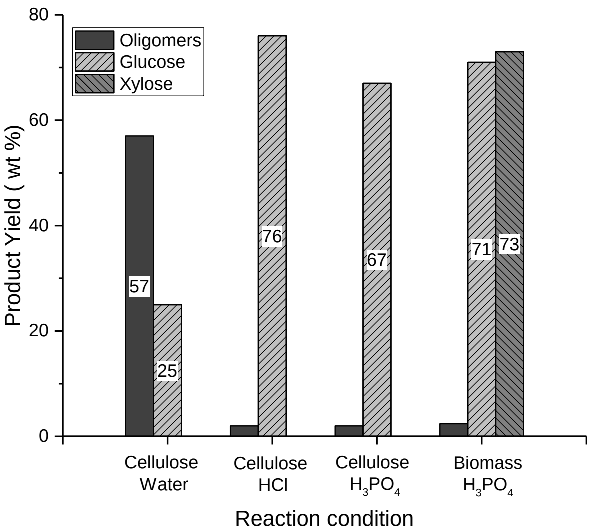

Fig.2 Results for hydrolysis of cellulose and biomass in the flow reactor at steady state.

REFERENCES

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2. A. Shrotri, H. Kobayashi, A. Fukuoka, *ChemSusChem*, 9 (2016) 1299.