Useful Products from Lignocellulosics by Supercritical Water Technologies

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Lignocellulosics were treated in supercritical water, and fractionated into water-soluble portion, precipitates, methanol-soluble portion and methanol-insoluble residue. The water-soluble portion contained carbohydrate-derived hydrolyzed products, dehydrated products and fragmented products. The precipitates were found to be glucan which is insoluble in ordinary water but soluble in supercritical water. Methanol-soluble portion was found to be derived from lignin. Based on these results, the supercritical water treatment was concluded to be appropriate to use as a pretreatment for ethanol fermentation, methane fermentation and hydrogen production.

As a result of decomposition behavior of cellulose in previous study, it could be simulated that the saccharides produced from lignocellulosics by supercritical water treatment were converted to ethanol through fermentation. In its ethanol production process, lignocellulosics were converted into 2 parts, water-soluble portion with precipitates and methanol-soluble portion. The former is converted into monosaccharides by enzymatic saccharification or dilute acid hydrolysis, followed by fermentation to ethanol. On the other hand, The latter, methanol-soluble portion, is collected as lignin-derived products.

Lignocellulosics can be also decomposed in supercritical water and converted to various useful products, such as organic acids (formic, acetic, glycolic, lactic and pyruvic acids). Among these, the most predominant organic acid recovered was acetic acid, probably derived from acetyl groups in the hemicellulose of Japanese beech. Furthermore, propyl sidechain of phenylpropane unit of lignin was found to be decomposed to organic acids. In anaerobic fermentation, organic acids are appropriate substrates of methane production. Therefore, an understanding of organic acid production is important for the development of biomass conversion process in supercritical water to methane, which can be further converted to methanol by an enzyme “methane monoxygenase” . In this study, therefore, the production of organic acids from lignocellulosics was studied.

Additional study in this project is on a selective production of formic acid from lignocellulosics by supercritical water treatment. Formic acid is known to be a good substrate to produce hydrogen by *Escherichia coli* genetically engineered with formate hydrogenlyase. However, its yield is lower than other organic acids in supercritical water because of its ease in decomposition. Through our extensive studies, however, we could find a treantment condition to have a higher yield of formic acid with lower yield of other organic acids as treated by subcritical water with hydrogen peroxide (H_2O_2).

Through these lines of study, bioenergy such as ethanol, methane, methanol and hydrogen were found to be achieved from lignocellulosics by applying supercritical water technologies, which can cultivate a new renewable bioenergy field in sustainable energy systems.