

Organic Acid Production from Japanese Beech by Supercritical Water Treatment

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1. INTRODUCTION

Lignocellulosics can be decomposed in supercritical water ($>374^{\circ}\text{C}$, $>22.1\text{MPa}$) and converted to various useful products such as saccharides and organic acids. Organic acids are appropriate substrates of methane production in anaerobic fermentation. Therefore, an understanding of organic acid production in hydrothermal condition is important for the development of biomass conversion to methane.

It was reported that the organic acids could be produced from Japanese beech (*Fagus crenata*) in supercritical water. During a relatively short supercritical water treatment (5sec, 380°C , 100MPa), cellulose and hemicellulose were decomposed to formic, pyruvic, glycolic, acetic and lactic acids, but there was little in production of organic acids from lignin. However, during the prolonged treatment (4min, 380°C , 100MPa), propyl side-chains of phenylpropane unit of lignin were found to be decomposed to organic acids. Thus, reaction time affects the decomposition of lignocellulosics. The effect of reaction pressure on organic acid production and its pathway, however, remains unknown. In this study, therefore, the effect of reaction pressure on the production of organic acids from Japanese beech was investigated in supercritical water condition.

2. MATERIALS AND METHODS

Japanese beech (*Fagus crenata* Blume) was used as a sample of lignocellulosics. Supercritical water treatment was conducted by using the biomass conversion system with a batch-type reaction vessel. Distilled water was fed with the sample to a 5ml reaction vessel made of Inconel-625. The sample was then treated in supercritical water (380°C , $25\sim 100\text{MPa}$, $1\text{min}\sim 4\text{min}$). The flow-type system was also used in this study, under the conditions of 380°C , 25 and 40MPa .

The obtained reaction mixture was filtrated to separate the supercritical water-soluble portion from the supercritical water-insoluble residue. The supercritical water-insoluble residue was then extracted with methanol to separate the methanol-soluble portion from the methanol-insoluble residue. The methanol-insoluble residue was dried and weighed. The water-soluble portion obtained from supercritical water-soluble portion was analyzed by high performance liquid chromatography and capillary electrophoresis.

3. RESULTS AND DISCUSSION

We investigated the relationship between the density (pressure) of water under various pressures and yields of organic acids as Japanese beech was treated in supercritical water at 380°C for 1min and 4min. For each organic acid, formic acid was found to be low in its yield under all conditions tested but higher yields were resulted at lower treatment densities. On glycolic acid, its yield was maximal at 40MPa (0.59g/ml), while acetic acid reached a maximum in a yield at the highest pressure tested (100MPa , 0.72g/ml). For the total organic acids, the maximum yield was resulted at 30MPa (0.53g/ml), over the critical pressure of water. These results suggest that the amounts of organic acids produced in supercritical water might be manipulated by controlling the density of supercritical water, and that the reaction condition under comparatively lower pressure ($30\text{-}40\text{MPa}$) is more suitable to produce organic acids than higher pressure (100MPa). In addition, organic acids were found to be produced more efficiently from carbohydrate (cellulose and hemicellulose) than from lignin.