

Chemical conversion of cellulose by batch-type and flow-type supercritical water systems

K. Ehara, S. Saka*

Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto, 606-8501, Japan

Tel/Fax: +81-75-753-4738; Shiro Saka, E-mail: saka@energy.kyoto-u.ac.jp

Microcrystalline cellulose (avicel) was treated with supercritical water at 380 °C under three different pressures (25, 40, 100 MPa) using flow-type and batch-type supercritical conversion systems. These conditions gave the different ionic product of water (K_w) ranging from 1.25×10^{-14} to 1.58×10^{-11} , and the yield of glucose increased as the ionic product increases. The higher yield of glucose is obtained the higher pressure condition. This result suggested that the condition in high pressure is better for hydrolysis due to the higher ionic product.

Introduction

Biomass resources will become more important in the future as alternatives to fossil resources which will be exhausted sooner or later and increase the CO₂ in air through its combustion. For the conversion of biomass resources into useful chemicals and biomass-energy, saccharification of cellulosic resources followed by fermentation is one of the directions. There exist two major conversion methods which are hydrolysis by either acid catalyst or enzyme. These methods possess at least the following problems; the former is corrosion of the reactor by acid, and the latter is the high cost of the enzyme. On the other hand, the new development is to focus on the emergence of a noncatalytic supercritical water treatment. Recently, it was reported that woody biomass resources were converted into useful chemicals and fuel [1-3]. However, for the ethanol production from biomass using supercritical water, the treatment condition needs to be optimized. In this paper, therefore, microcrystalline cellulose was treated with supercritical water by batch-type and flow-type systems, and characterization of the obtained samples was performed.

Materials and methods

As biomass samples, avicel was selected for supercritical water treatment. The supercritical water biomass conversion system used in this study was batch-type and flow-type systems employed in a previous work [1-3]. The former type can cover a range of up to 280MPa in pressure and up to 500 °C in temperature, whereas pressure and residence time within 0.1 sec can hardly be controlled. The latter type can cover a range up to 45 MPa and up to 450 °C, and regulate pressure and residence time within 0.1 sec. The obtained reaction mixtures were then analyzed by the high performance liquid chromatography (HPLC) equipped with ULTRON PS-80P column (Shinwa Chem. Ind., Ltd.).

Results and discussion

The reaction conditions and the calculated ionic products were summarized in Table 1. In these treatments, avicel was almost completely solubilized in water. Fig. 1 shows the HPLC chromatograms of the obtained water-soluble portions. In the case of treatment pressure at 25 and 40 MPa for less than 0.3 sec using flow-type systems, the main products were oligosaccharides. Sasaki et al. already have reported that cellosexose, cellopentaose, cellotetraose, cellotriose, cellobiose was derived from cellulose by supercritical water treatment [4]. However, in our experiment, another oligosaccharides, which differ from the results of Sasaki et al., were apparently obtained from cellulose. Identification of these products is not completed, but it is to be inferred that the oligosaccharides in the end of glucopyranose might be transformed such as lactose. These oligosaccharides were diminished, and monosaccharides (glucose and fructose) and its decomposition products (erythrose, levoglucosan, 5-hydroxymethyl furfural and dihydroxyacetone) were increased by prolonged treatment. On the other hand, the glucose with a yield of 22% was main products in the case of treatment pressure at 100 MPa for 5 sec using batch-type system. It is clear that the higher treatment pressure gave the stronger intensity of glucose in HPLC chromatogram. The ionic product during supercritical water treatment was calculated according to Holzappel et al.[5]. The higher treatment pressure at 380 °C gave the higher ionic product. These results, therefore, suggested that higher treatment pressure is better for hydrolysis reaction due to the enhanced effect of acidic catalyst.

Table 1 Summary of experimental conditions.

Run no.	System type	Condition			Density (Kg/m ³)	Ionic product logK _w *
		Temperature (°C)	Pressure (MPa)	Residence time (s)		
1	Batch	380	100	5.00	724.1	-10.8
2	Flow	380	40	0.48	604.2	-12.1
3	Flow	380	40	0.24	604.2	-12.1
4	Flow	380	25	0.48	459.4	-13.9
5	Flow	380	25	0.29	459.4	-13.9

*Ionic product K_w was calculated in the following formula;[4]

$\log K_w(\rho, T) = 2[7.2 + 2.5(\rho/\rho_0)] \log(\rho/\rho_0) + \log K_w(\rho_0, T)$, where $\rho_0 = 1 \text{ g/cm}^3$. The temperature dependence of the ionic product at $\rho_0 = 1 \text{ g/cm}^3$ may be approximated by the relation $\log K_w(\rho_0, T) = -(3108/T) - 3.55$, where T is in °K and K_w in (mol/liter)².

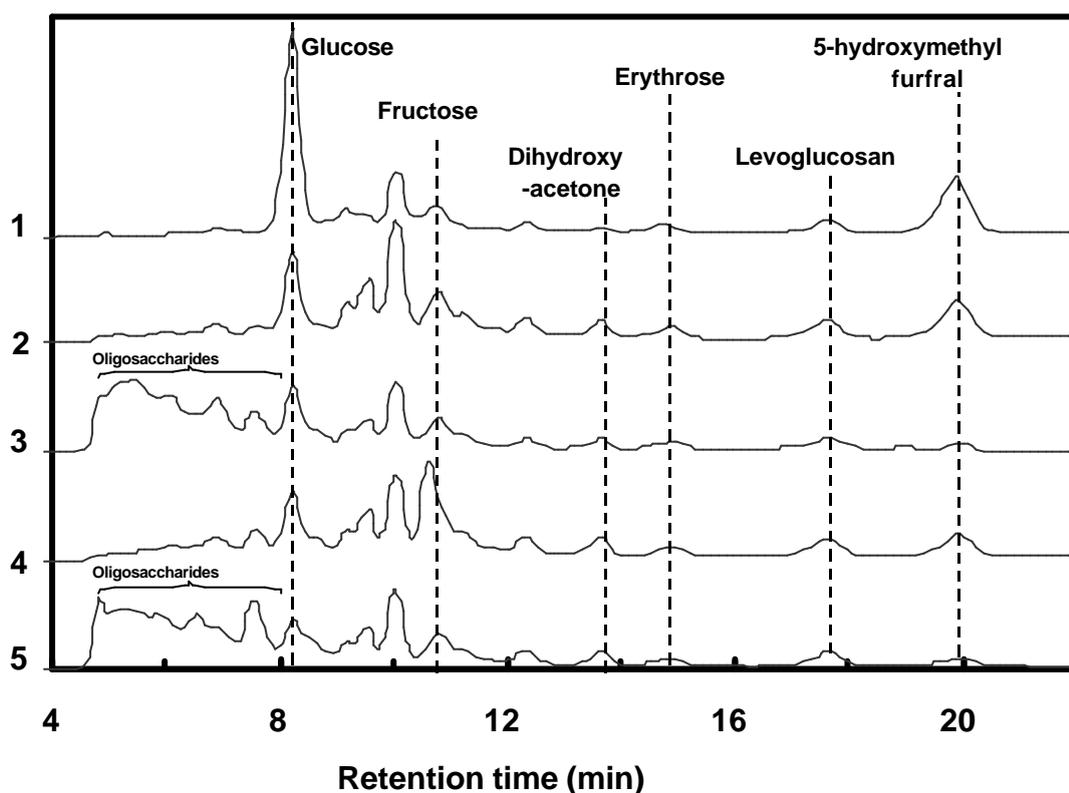


Fig. 1 HPLC chromatograms of obtained reaction mixtures as treated with supercritical water. The number 1 to 5 refers to those in Table 1.

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