

# RAPID AND SELECTIVE CONVERSION OF CELLULOSE TO VALUABLE CHEMICAL INTERMEDIATES WITH SUPERCRITICAL WATER

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## INTRODUCTION

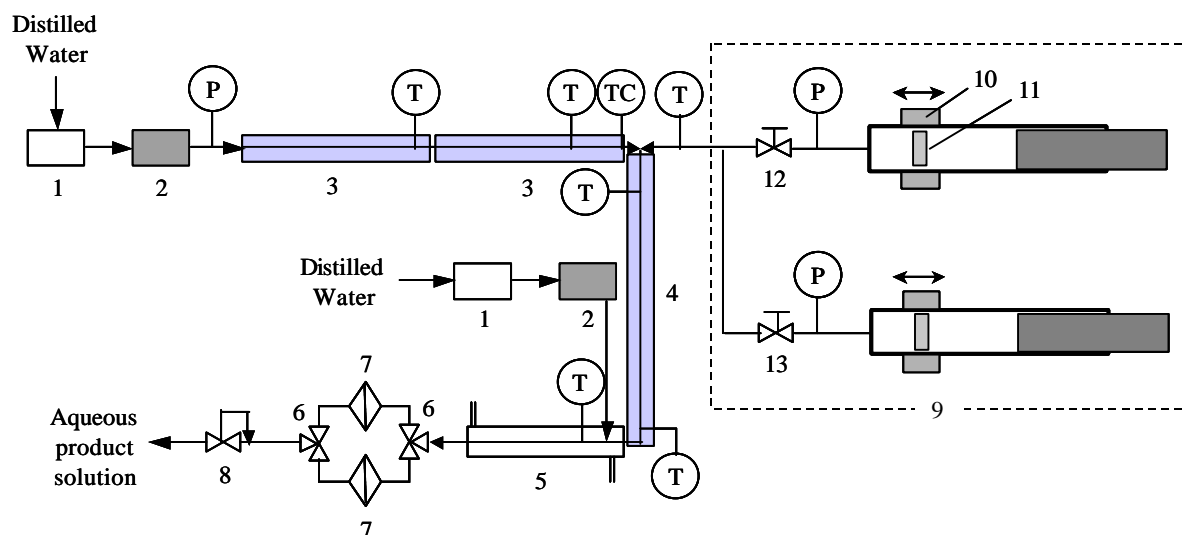
Development of a new environmentally friendly method that valuable chemical intermediates could be recovered from cellulosic biomass in rapid and selective manner using supercritical water has been studied. So far, it was found that microcrystalline cellulose could solubilize with rapidity into near- and supercritical water, followed the rapid hydrolysis to cellooligosaccharides and glucose [1]. Also, in our previous work [2], it was proposed the method for super-rapid enzymatic hydrolysis of microcrystalline cellulose using the solubilization of the cellulose in near- and supercritical water. Further, kinetic studies regarding some carbohydrates in near- and supercritical water were conducted. As a result, the major reaction paths of the carbohydrates and the controllability of each reaction path by the change in temperature and pressure at these conditions were made clear [3-10]. However, few researches regarding the elucidation of the reaction mechanism of microcrystalline cellulose in near- and supercritical water have been reported.

In this study, experiments of microcrystalline cellulose conversion in supercritical water (385-415 °C, 20-40 MPa, and 0.02-4.0 seconds) were conducted and the reaction mechanism of microcrystalline cellulose was estimated based on the detailed product analyses. Next, reaction conditions at which some chemical intermediates could be rapidly and selectively produced from microcrystalline cellulose in supercritical water were elucidated.

## I – EXPERIMENTAL AND ANALYTICAL SECTION

Microcrystalline cellulose (average degree of polymerization ( $DP_{av}$ ): 230) purchased from Merck (Avicel<sup>®</sup>, No. 2331) was used as a starting material. A continuous flow-type reactor with slurry feed pump was employed for the experiment. **Figure 1** shows a schematic diagram of the experimental setup. First, distilled water was fed at a flow rate of 21 g min<sup>-1</sup>

by two HPLC pumps (GL Science Co., Ltd., model PUS-8) into the system, and the pressure in the system controlled to 20-40 MPa by a backpressure regulator (TESCOM, model 26-1721-24). Then, the distilled water was heated up to a desired temperature using an electric furnace (Seiwa Riko Co., Ltd., model FTO-6) and mixed with cellulose-water slurry of 5-10 wt% fed from another line at 3 or 5 g min<sup>-1</sup>, to reach a reaction temperature (385-415 °C) and the reaction was started. After passing through the reactor made from a stainless steel 316 tubing (3.18 mm o.d.; 1.38 mm i.d.), the reaction solution was immediately quenched by using a cooling jacket and the reaction was terminated. At the filtration part (inline filters of 0.5 mm pore size (NUPRO, SS-4TF-05), solid fraction (residue) was continuously trapped for a given period (10-30 minutes) during the experiment. At the same time, aqueous product solution was depressurized by passing through the backpressure regulator and then collected in a sampling bottle for 10-30 minutes. The reaction conditions of the experiments were set to 380-415 °C, 20-40 MPa, and 0.01-4.0 seconds.



**Figure 1.** Schematic diagram of a continuous flow-type reactor for supercritical water experiments of microcrystalline cellulose; 1: Degassing unit; 2: HPLC pump; 3: Preheater; 4: Reactor; 5: Cooling jacket; 6: Three-way valve; 7: Inline filter; 8: Backpressure regulator; 9: Slurry feed pump; 11: Permanent magnet; 12: Static mixer; 13: Needle valve.

The aqueous product solution was decanted for 1-7 days at 20 °C. Then, when white precipitate, that is cellulose II fiber, formed in the solution, it was collected, dried and weighed. Macromolecular properties of the cellulose II fiber were measured by GPC, XRD, FT-IR, and elemental analysis. The aqueous product solution was analyzed by TOF-MS, HPLC and TOC. The solid residue recovered at the inline filter during the experiment was analyzed as with the cellulose II fiber. Conversion of cellulose ( $X$ ) and product yield of component  $i$  ( $Y_i$ ) were calculated by Eqs (1) and (2), respectively.

$$X = 1 - \frac{W_R}{W_o} \quad (1)$$

$$Y_i = \frac{W_i}{W_o} \quad (2)$$

where  $W_o$  [g-carbon] is the ideal carbon weight of untreated cellulose loaded in sampling,  $W_R$  [g-carbon] is the carbon weight of the residue recovered in sampling [g-carbon], and  $W_i$  [g-carbon] is the carbon weight of the product  $i$  collected.

## II – RESULTS AND DISCUSSION

### Analyses results of the residues and products.

**(a) Solid residues.** The FT-IR measurement and elemental analysis of solid residues were conducted. From the FT-IR analysis, no peaks corresponding to the C=O and C=C bond linkages were confirmed in the residues. The elemental composition of the residue was almost the same as that of untreated cellulose. Considered from these results, it was found that intramolecular dehydration of cellulose scarcely occurred on the reactions in supercritical water. Further, from the XRD analysis of the residues recovered from all the supercritical water reactions were found to be mixtures of cellulose I and II, which cellulose II crystal does not exist in native celluloses. This result shows that microcrystalline cellulose actually swells or dissolves in supercritical water.

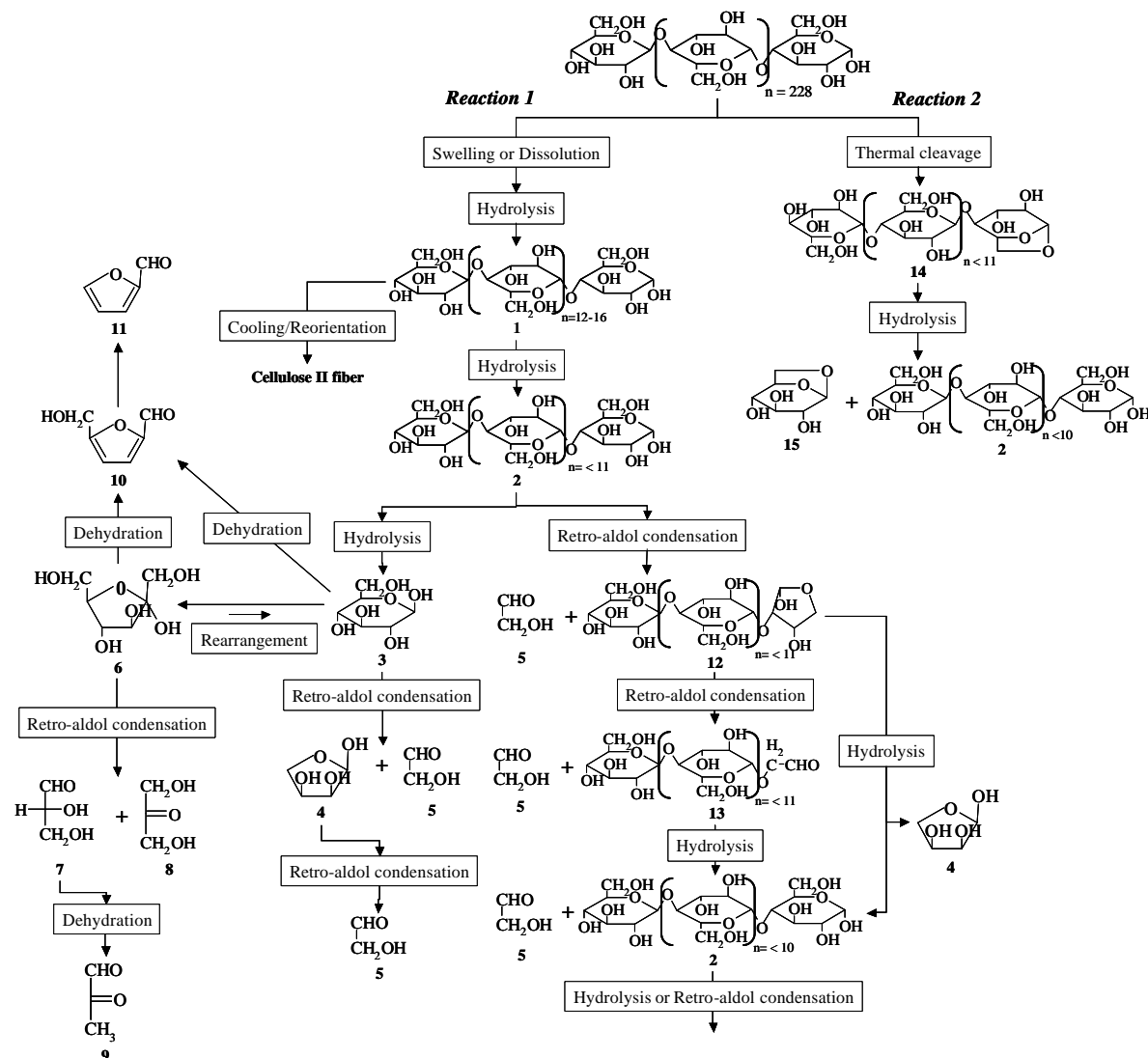
**(b) Precipitates.** Next, the XRD and GPC analyses of each precipitate obtained were carried out. As a result, it was found that the precipitate had pure cellulose II crystal form with high crystallinity and relative high  $DPs$  [11,12].

**(c) Water-soluble products.** The TOF-MS and HPLC analyses of water-soluble products were conducted. The main products were hydrolysis products (precipitate, water-soluble celooligosaccharides, glucose, levoglucosan, and aqueous degradation products of glucose such as glycolaldehyde). As the result of the TOF-MS analysis, it was found that some kinds of celooligosaccharides that had glycolaldehyde, erythrose, or anhydroglucose residues at the reducing ends were formed during the supercritical water reaction and their  $DPs$  ranged from 2 to 13 [12].

### Proposed reaction mechanism of microcrystalline cellulose in supercritical water.

Based on the detailed analyses of the residues and products, reaction mechanism of microcrystalline cellulose in supercritical water was estimated as shown in **Figure 2**. The major reaction paths are hydrolysis via swelling or dissolution of microcrystalline cellulose (**Reaction 1**) and thermal cleavage of the glycosidic bond linkage in the crystalline region (**Reaction 2**). In the **Reaction 1**, the intermediate (**1**) is formed and then recrystallizes to cellulose II fiber or hydrolyzes to lower  $DP$  saccharides (**2**). Further, **2** hydrolyzes to glucose (**3**) or converts to some products (**4, 5, 12, and 13**) via retro-aldol condensation. On

the contrary, in the **Reaction 2**, various DPs cellooligosaccharides (**14**), each of which has a 1,6-anhydroglucose residue, are formed by thermal cleavage of microcrystalline cellulose and subsequently levoglucosan (**15**) can be formed by thermal cleavage or hydrolysis of **14**.



**Figure 2.** Proposed reaction mechanism of microcrystalline cellulose in supercritical water. **1:** Swelled (or Dissolved) cellulose; **2:** cellooligosaccharides; **3:** Glucose; **4:** Erythrose; **5:** Glycolaldehyde; **6:** Fructose; **7:** Glyceraldehyde; **8:** Dihydroxyacetone; **9:** Pyruvaldehyde; **10:** 5-HMF; **11:** 2-Furfural; **12:** Glucopyranosyl-erythrose; **13:** Glucopyranosyl-glycolaldehyde; **14:** Anhydro-cellooligosaccharides; **15:** levoglucosan.

### Effects of temperature and pressure on the major reactions of microcrystalline cellulose.

Effects of the temperature and pressure on the major reactions of microcrystalline cellulose were evaluated from the experimental and analytical findings. As a result, it was found that the degree of swelling or dissolution of microcrystalline cellulose could be related to the conversion of cellulose regardless of the temperature and pressure in supercritical water. As

regards hydrolysis, it was clarified that the contribution of hydrolysis to the overall conversion rate of cellulose increased with increasing the pressure and temperature. Further, effect of temperature and pressure on thermal cleavage of the glycosidic bond linkage of cellulose molecules in the crystalline regions was evaluated by examining the formation rates and yields of levoglucosan, a typical product formed by thermal cleavage [13], at all the reaction conditions. The formation rate of levoglucosan became fast and its yield increased with increasing the temperature and decreasing the pressure in supercritical water. In other words, it was shown that the contribution of thermal cleavage of cellulose was promoted as the density of water decreased at this condition.

**Preparation of some chemical intermediates in supercritical water.** Reaction conditions for selective production of water-soluble celooligosaccharides and glucose were explored at 385-415 °C, 20-40 MPa. The yield of the hydrolysates increased with an increase of the pressure, and reached about 80 % at 400 °C, 35 MPa and 0.05 second [12]. In this case, the yield of aqueous degradation products of glucose was less than 10 % [12]. Conditions for producing the cellulose II fiber from microcrystalline cellulose were also explored. As a result, it was found that the cellulose II fiber could be obtained in relatively high yield at 400 °C [11,12]. This experimental finding suggests that this method has high potential as an alternative process for the conventional production processes that have used aqueous alkaline solution and hazardous additives during the swelling or dissolution and regeneration of microcrystalline cellulose.

## CONCLUSIONS

Elucidation of the reaction mechanism of microcrystalline cellulose in supercritical water was carried out through the cellulose conversion experiments of using a flow-type reactor and detailed analyses of residues and products. Also, it was found that some valuable chemical intermediates could be rapidly produced from microcrystalline cellulose by manipulating the temperature and pressure in supercritical water without any catalyst. From these experimental findings, it was suggested that this cellulose upgrading method using supercritical water was applicable to a new chemical recovery process without organic solvents and additives that have high impact to the environment.

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