

## Effects of Salts on the Decomposition Behavior of Cellulose in Subcritical Water

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In order to obtain the glucose and gluconic acid, noncatalytic decomposition of cellulose in hot-compressed water were performed in a batch reactor. The temperature of water was varied in the range from 523 to 583 K. The cellulose was rapidly converted to water-soluble species (WS) with a relatively high glucose yield in hot-compressed water. As the result of decomposition, the maximum conversion of glucose from cellulose was obtained by the treatment for 40 s in the bath kept at 559 K. Furthermore, effects of salts, such as CaCO<sub>3</sub>, on the decomposition behavior of cellulose in hot compressed water were discussed. The glucose and cellulose were selectively converted to gluconic acid with an addition of salts, such as CaCO<sub>3</sub>. The maximum conversion of gluconic acid from glucose was obtained by the treatment for 40 s at 568 K. The biodegradable polymer was synthesized from the gluconic acid.

### 1. Introduction

Hydrothermal treatments have been attracting much as an effective decomposition method of biomass. Many investigators have reported the decomposition behavior of cellulose in subcritical and supercritical water [1-3]. Most of these studies used cellulose and glucose as the model compound, because of the high content of cellulose-based polymeric materials in the biomass. Sakaki et al.[4] have reported the saccharification of cellulose with hot-compressed water and showed that glucose and fructose could be produced as main components, with yields as high as those reported by Sasaki et al.[3], under a mild condition at around 300 °C by adjusting the reaction time. A saccharification process at lower temperatures would be advantageous compared to a supercritical process from the viewpoint of energy and control. It is difficult to control the hydrolysis process at supercritical temperatures, because of the extremely short reaction time.

On the other hands, the effect of alkali salts as a catalysis on biomass conversion has also been widely known. Accordingly, the additions of the alkali metals accelerate the decomposition rate and suppress the formation of soot and tar[5]. In this work, we discussed the effect of salt on the decomposition behavior in hot-compressed water.

### 2. Experimental Methods

**2.1. Materials** The cellulose used in this study is microcrystalline cellulose prepared from refined pulp for column chromatography (100-120 μm, Funakoshi Co.). The glucose used as model compound for cellulose and CaCO<sub>3</sub> were obtained from Wako Pure Chem. Co. Ltd.

**2.1. Experimental Apparatus** The reactor used for the decomposition of cellulose is shown in Fig. 1, a tube reactor (SUS316, 9.3 mm i.d. x 83 mm length, 6 mL) equipped with a thermocouple and a valve. Dried cellulose powder, 0.5 g, and distilled water, 3.0 g were placed in the reactor. The air in the reactor was replaced with carbon dioxide as an inert gas, and then the reactor was sealed after carbon dioxide was charged at 0.1 MPa. Heating of the reactor was conducted in two steps using two salt baths as shown in Fig. 1. That is, the reactor was immersed in a preheater kept at 250 °C for 3 min and subsequently heated in a main heater for a predetermined time while shaking at ca. 250 times a minute. Then it was immediately cooled in a water bath to terminate the reaction. The reaction conditions are expressed by the bath-heating time in the main heater and the final temperature reached during the reaction period.

**2.3. Analytical Procedure** The analytical procedure after the treatments (preheating, reaction, and cooling) is described in a previous paper [4,6]. After the gas was exhausted, the contents in the reactor were thoroughly washed with hot water of ca. 40 °C and filtered using a glass filter. The

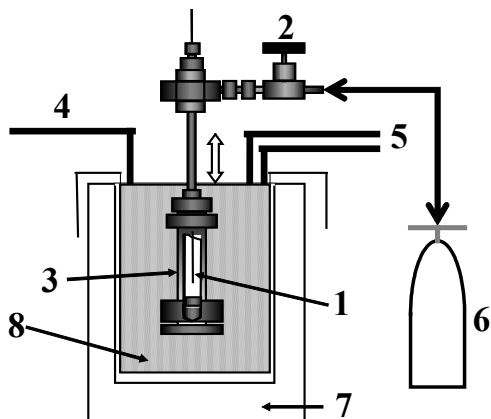


Fig. 1 Schematic diagram of the experimental apparatus for cellulose decomposition. 1, thermocouple; 2, Shut-off valve; 3, Reactor; 4, thermometer; 5, Heater; 6, N<sub>2</sub> gas cylinder; 7, Heater; 8, Salt bath

water in the filtrate was distilled off under vacuum, and the water solubles, WS, were obtained. The filter residue was washed with methanol to examine the formation of water-insoluble fractions: methanol was found to be the best solvent for the decomposed cellulose products among methanol, acetone, benzene, and tetrahydrofuran by supplemental examinations. After thorough washing and filtration, methanol was removed from the filtrate and filter residue, and the methanol soluble, MS, and the methanol insoluble, MI, were obtained. WS, MS, and MI were weighed and each product yield was calculated based on the dry cellulose weight. The weight loss including gaseous products, G, was also obtained by subtracting the yields of WS, MS, and MI from 100.

The component of WS was measured by HPLC equipped with two columns (SEC W12 + SEC W13, Yakogawa) and two detectors for ultraviolet (UV, 254 nm) and refractive index (RI) in series. HPLC was operated at 40 °C with a 0.8 mL/min flow of mixtures of water and acetonitrile (70/30 by weight) as an eluate. The infrared spectra for MI and WS were obtained with FT-IR using KBr pressed disk technique in which a mixture of 2 mg of sample and 200 mg of KBr was used to form the disk (1 mm thickness x 10 mm diameter).

### 3. Results and Discussion

#### 3.1. Decomposition of Cellulose in Hot Compressed Water

The decomposition products were analyzed

by HPLC equipped with UV and RI as detectors. Figure 2 shows chromatograms decomposition products by 40 s heating from 523 to 583 K. As in the case of supercritical conditions, many kinds of saccharides, products of the hydrolysis, were obtained as shown in Fig. 2(a). On the other hands, oligomers and acids were selectively obtained during the decomposition of cellulose in the near-critical water containing CaCO<sub>3</sub> as shown in Fig. 2(d).

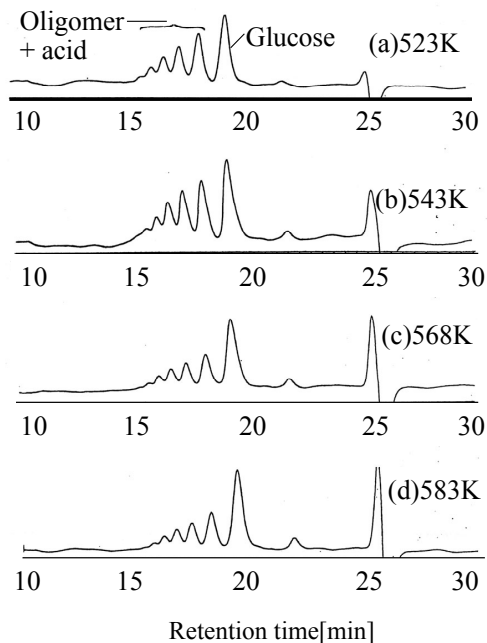


Fig. 2 HPLC chromatograms of recovered liquid samples. Reaction time, 40 s; reaction temperatures, 523 K(a), 543 K(b), 568 K(c), 583 K(d).

The change in the chemical structure of decomposition products was also examined using IR. The spectra for the decomposition products are shown in Fig. 3. The peaks showing double bond (C=O, C=C) appeared at 1700 and 162 cm<sup>-1</sup>, indicating these products are the carbohydrates. Furthermore, decomposition products were analyzed by GC-MS. The obtained products may be considered as the gluconic acid. The glucose, which is the decomposition product of cellulose, is partially oxidized in hot compressed water containing CaCO<sub>3</sub>, and gluconic acid is obtained.

#### 3.2. Effect of Salts on the Decomposition Behavior

In this work, effect of salt on the decomposition

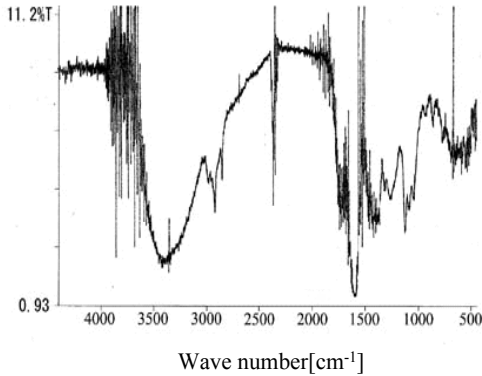


Fig.3 FT-IR spectra of decomposition products in hot compressed water at 573 K. Reaction time, 40 s.

behavior of cellulose in the hot compressed water. The effect of alkali salt as a catalysis on biomass conversion has also been widely known[7-9]. We try to use the 8 salts. As shown in Fig. 4, the maximum gluconic acid yield is obtained by addition of CaCO<sub>3</sub>. The activity is given as CaCO<sub>3</sub> > CaCl<sub>2</sub> > MgSO<sub>4</sub> > CaSO<sub>4</sub> > CH<sub>3</sub>COOK > Na<sub>2</sub>CO<sub>3</sub> > KHCO<sub>3</sub> > HCOONa. The phenomena may be interpreted in terms of the hydration enthalpy of alkali ions. The degree of hydration enthalpy is give as Ca<sup>2+</sup> > Na<sup>+</sup> > K<sup>+</sup>.

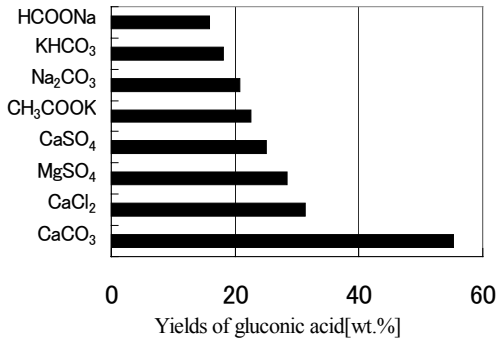


Fig. 4 Effect of salt on the yield of gluconic acid during the decomposition of cellulose in hot compressed water. Temperature, 573 K; reaction time, 40 s; salt concentration, 5 %(wt).

Here we discuss the effect of temperature on decomposition of cellulose in hot compressed water containing CaCO<sub>3</sub>. The gluconic acid yield increases with an increase of temperature, and maximum yields is reached at about 500 K as

shown in Fig. 5. On the other hands, the yields of acids decrease with increasing temperature at temperatures higher than 500 K; the reason is that the gluconic acid is decomposed to 5-hydroxymethyl furfural (HMF). To obtain the gluconic acid with high yield, the control of the decomposition temperature is needed.

The effect of concentration of CaCO<sub>3</sub> on the yields of gluconic acid is shown in Fig. 6. Maximum yields are obtained at 2 %(wt) CaCO<sub>3</sub>.

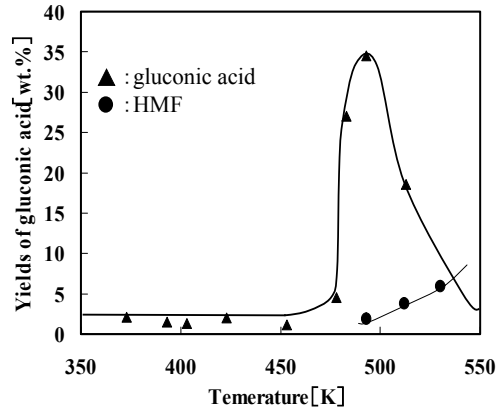


Fig. 5 Effect of temperature on the yield of gluconic acid during the decomposition of cellulose in hot compressed water containing CaCO<sub>3</sub>. Temperature, 573 K; reaction time, 40 s; salt concentration, 5 %(wt).

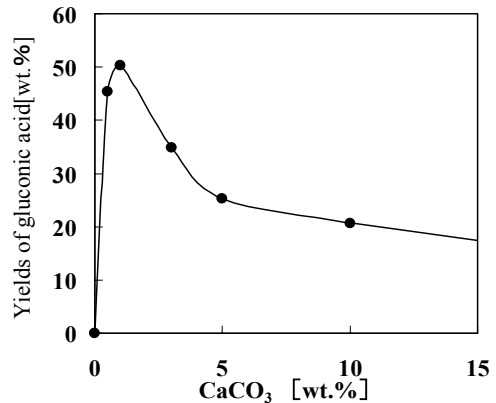


Fig. 6 Effect of CaCO<sub>3</sub> concentration on the yield of gluconic acid during the decomposition of cellulose in hot compressed water. Temperature, 573 K; reaction time, 40 s.

#### 4. Conclusions

Effect of salt, such as  $\text{CaCO}_3$ , on the decomposition of cellulose under hydrothermal condition has been elucidated. We have shown that gluconic acid is obtained by the decomposition of cellulose in hot compressed water containing  $\text{CaCO}_3$ .

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#### References and Notes

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