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Oleic acid-enhanced dissolution of cellulose in high-temperature water

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Abstract This paper reports, for the first time, the enhanced dissolution of cellulose in subcritical water by addition of a fatty acid. Simply adding oleic acid dramatically promoted the dissolution of cellulose. High-pressure in-situ observation showed that cellulose dissolved in high-temperature water at approximately 500 K, which is 70 K lower than without oleic acid. The yield of oligo and monosaccharides with oleic acid at 473 K was seven times higher than without oleic acid.

Keywords Biomass · Supercritical water · Fatty acid · Co-solvent

Introduction

Bio-ethanol synthesis is a promising biomass conversion method. Biomass is an important resource that can be converted into ethanol for use as fuel. In this case, pretreatment to decompose biomass to compounds that can be easily converted to ethanol with yeast is necessary. In particular, cellulose, which is a major component of the biomass, is expected to decompose to glucose. Thus far, various methods that use acid catalysts, for example sulfuric acid, have been proposed for hydrolysis of cellulose to recover glucose. However, acid-catalyzed reactions require further environmental considerations and post-reaction separation steps.

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Sasaki et al. [1–3] reported that solid cellulose dissolved in supercritical water without any catalyst. They also demonstrated that, after supercritical water treatment, the aqueous cellulose solution could be hydrolyzed to glucose by use of cellulase at a rate approximately 700 times faster than for untreated cellulose particles [1]. This is obviously because of homogeneous phase enzymatic hydrolysis of the cellulose solution. However, this process uses much energy, because this treatment requires temperatures above 573 K. Thus, dissolving cellulose in lower-temperature water is an important objective.

Many methods are used for dissolving cellulose in solvent, even at room temperature [4]. The structure of cellulose has a hydrophilic part that participates in hydrogen bonding and a hydrophobic part that occurs on the surface [5]. To dissolve cellulose, solvents should have affinity for the hydrophobic part and break the hydrogen bonding. A mixture of a polar organic solvent, for example dimethylformamide, and a Lewis acid, for example lithium chloride, has this feature and is a commonly used cellulose-dissolution solvent for scientific research.

Because fatty acids have both hydrophilic and hydrophobic parts, they may have a similar effect on dissolution of cellulose. Furthermore, fatty acids are appropriate for industrial use because they are abundant biomass products and sometimes waste products of the triglyceride oil recovery process. Interestingly, although the solubility of fatty acids in water is poor at ambient temperatures, at higher temperatures and higher pressures fatty acids are soluble in water [6]. Thus, the combined process of cellulose pre-treatment and waste fatty acid treatment in high-temperature water might be both environmentally benign and economical. Further, after the treatment, fatty acids can be separated from water by appropriate reduction of the temperature and pressure.

In this paper, we describe, for the first time, the effect of a fatty acid on promoting the dissolution of cellulose in subcritical water. In-situ observation of cellulose dissolution in subcritical water, with and without the fatty acid, and product analysis were conducted.

Experimental

Experiments were conducted with batch reactors made of Hastelloy-C. The internal reactor volume was 5.0 cm^3. Microcrystalline cellulose was purchased from MERK. Oleic acid (60%, Wako Pure Chemical Industries) and 10% (*w*/*w*) cellulose aqueous slurry were loaded into the reactor. Loaded reactors were heated and shaken for 10 min in an electric furnace with the temperature controlled at 323–523 K. The heat-up time was about 3–5 min. The reactors were then removed from the electric furnace and rapidly quenched in a water bath. Cooling to room temperature required approximately 1 min. After the reactors were cooled, the products in the reactors were recovered with 20 cm^3 of rinsing water. The products were separated from oleic acid by centrifugation. Identification and quantification of the water-soluble products and the precipitates were conducted by high-performance liquid chromatography (HPLC–RI, Shodex KC-811 column, mobile phase; pure water at 1 mL/min) and X-ray diffraction (XRD, Rigaku RINT-2000). Details of the analytical procedures have been reported elsewhere [1–3].

For direct observation of the cellulose in subcritical water with and without oleic acid, a high-temperature and high-pressure optical cell (Taiatsu Techno, TSC-WC-00014) with a Hastelloy-C body and sapphire windows was used. The cell volume was 1.4 cm^3. Cellulose powder was put on the bottom window and oleic acid was loaded into the cell. After capping with an upper window, pure water was introduced to 30 MPa by use of a high-pressure pump (Jasco PU-2086) and a back pressure regulator (Tescom, model 26-1762-24). The temperature was monitored by use of a thermocouple (K type) in the cell and was controlled by four cartridge heaters installed in the cell body. The pressure was kept at 30 MPa by use of a back-pressure regulator while increasing the temperature.

Results and discussion

The HPLC–RI chromatograms of the liquid products at temperatures from 323 to 473 K, with and without oleic acid, are shown in Fig. 1. When oleic acid was added, recovery of hydrolysis products (oligosaccharide, cellobiose, glucose, and fructose) at 473 K increased rapidly, compared with that at 323 and 373 K. Further, the recovery was higher than that for water only at the same temperature. When oleic acid was used, the amounts of oligosaccharide, cellobiose, and monosaccharide obtained were, respectively, 4.5, 15, and 19 times those obtained without oleic acid. The yield of hydrolysis products with oleic acid was, in total, seven times higher than that without oleic acid. These results mean that cellulose dissolution and hydrolysis were accelerated by addition of oleic acid.

From the XRD peaks of precipitates collected after treatment at 503 and 523 K, shown in Fig. 2, when oleic acid was added cellulose II crystals appeared, as reported by Sasaki et al. [2] for supercritical water treatment. These results suggest that cellulose was dissolved by treatment with subcritical water and the fatty acid. The hydrolysis reaction might be promoted by the acidity of the oleic acid.

Fig. 1 Chromatograms obtained from recovered liquid samples

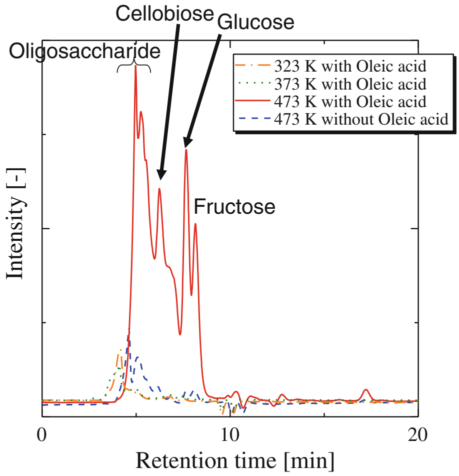
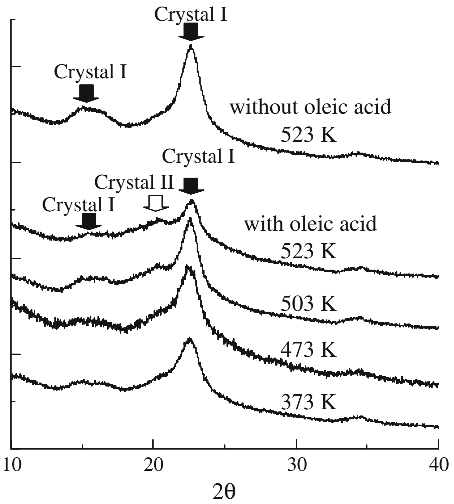


Fig. 2 XRD peaks of collected precipitates



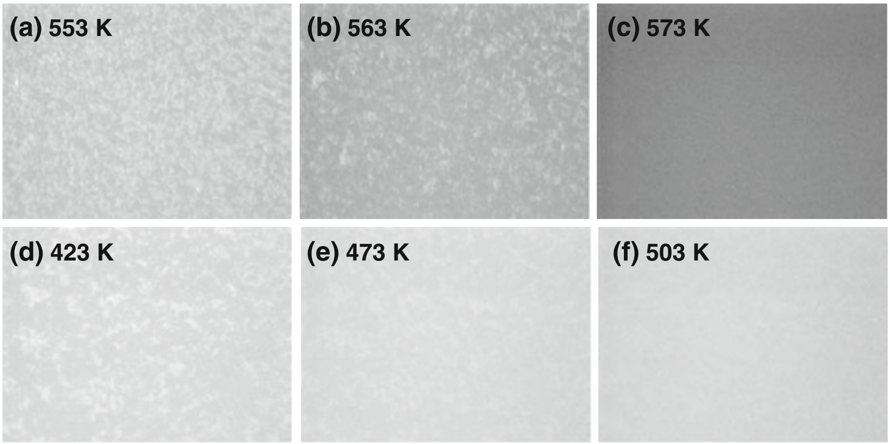


Fig. 3 Direct observation of cellulose in water at 30 MPa: **a**–**c** without oleic acid; **d**–**f** with oleic acid

Direct observation of cellulose at high temperature and high pressure was achieved by use of a Hastelloy cell with sapphire windows. The temperature was increased from room temperature to 573 K in 15 min at a constant rate. Typical examples of the observation results in water without oleic acid are shown in Fig. 3a–c. In these images, the white dots are cellulose particles. At approximately 573 K, the cellulose particles disappeared, which indicates that cellulose dissolves in pure water at approximately 573 K—the same result reported by Sasaki et al. [3] When oleic acid was added, however, the cellulose particles disappeared at temperatures as low as 473–503 K, as shown in Fig. 3d–f.

Because oleic acid has both hydrophilic and hydrophobic parts, it acts as a surfactant. The cellulose structure also has both hydrophilic and hydrophobic parts; the hydrophilic parts are between cellulose molecules and the hydrophobic parts are on the surface of the structure. The dissolution of cellulose was probably promoted by the effect of the oleic acid as a surface-active agent.

In summary, the dissolution and hydrolysis of cellulose in subcritical water was efficiently accelerated in the presence of oleic acid, compared with pure subcritical water, because oleic acid has surface activity and acid catalyst effects.

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