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Hydrothermal decomposition of cellulose using strong gravitational field

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ABSTRACT

We propose a new method for the hydrothermal decomposition of cellulose using a strong gravitational field to recover useful chemical intermediates. Experiments of decomposition of two kinds of cellulose (microcrystalline and low-crystalline) under a hydrothermal condition were conducted at 250 °C for 6 h to a gravitational field of 0.33×10^6 G generated by a ultracentrifuge rotating at 80,000 rpm using a specially-designed gravity apparatus. Results, of our strong-gravity hydrothermal treatment of celluloses showed that both celluloses types successfully hydrolyzed to form cello-oligosaccharides and glucose, and surprisingly phenolic compounds such as guaiacol derivertives, which are applicable for the chemicals and food industries. Due to synergism of strong gravitational field with physical properties of water under hydrothermal condition, this unique method is anticipated as a benign technique to covert cellulose to cello-oligosaccharides and glucose via hydrolysis, and valuable phenolic compounds via any rearrangement or unique reactions of cellulose or its hydrolysis products.

1. Introduction

Cellulose is the most abundant biomass resource which can be used to produce energy, various chemical intermediates and materials. As a renewable resource, it holds potential to remedy problems caused by reliance on fossil fuels. Cellulose is a β-(1,4)-linked homopolymer of many anhydroglucose residues and can be easily hydrolyzed by acid catalysts [1] and enzymes [2] to cello-oligosaccharides and glucose. A review of Bobleter shows high potential of cellulose conversion in hot water with acid or alkaline catalyst [3]. Low temperature (100–120 °C) concentrated acid hydrolysis of cellulose has been to produces glucose yields approaching 100% [4]. Mok and Antal conducted high temperature (190–225 °C) dilute acid hydrolysis of cellulose in water, and reported glucose yields reaching 71% of the theoretical maximum (215 °C, 34.5 MPa and 120 min with 0.05 wt% sulfuric acid) [5]. However, case of non-catalyzed hydrothermal degradation of cellulose (215–295 °C) results in much lower yields of cellulose hydrolysis,with glucose yields also lower (at 50% even at the optimum condition) [3]. While Sasaki et al. reported that the products of hydrolysis, saccharides could be produced with high yields from cellulose in supercritical water temperatures of around 400 °C, however in subcritical water temperatures below 350 °C, the main components were the decomposition products of saccharides [6].

This article details our work to induce cellulose decomposition using strong gravitational field. The gravity at earth surface is 1 G or 9.8 m/s^2. The gravity value on planets is less than several G (1G = 9.8 m/s^2), and even on the sun it is at most 30G. However, gravities stronger than this can be experienced due to accelerations in such cases as explosion or impacts. In nature, strong gravity fields of over 10,000 G may exist only at degenerate stars or neutron stars. We know that sedimentation of macro-particles arises even at earth's gravity (1 G), and that Brownian particles in a liquid can be concentrated by using a conventional ultracentrifuge machine. A strong-gravity field may cause the sedimentation of even atoms, and would be expected to create a metastable crystal state due to their one-dimensional displacement [7,8]. Mashimo et al. had developed a high-temperature ultracentrifuge to generate a strong acceleration field of even over 1 million (1×10^6) G at Kumamoto University [9]. This strong gravity can induced decomposition reaction through sedimentation [8–13]. The synergism effect of the

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Table 1
Experimental condition.

Starting sample	Rotational speed (rev × min^{-1})	Maximum distance (mm)	Maximum acceleration (10^6 G)	Temperature (°C)	Time (h)	Maximum pressure (MPa)
Cellulose, Bemcot®	80,000	46.5	0.33	250	6	4.8

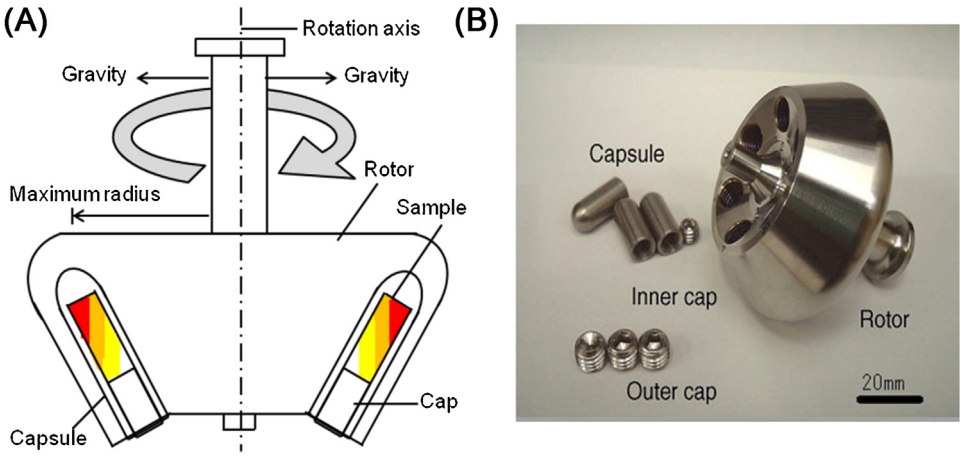

Fig. 1. The thin-plate type sample set up within a rotor (A) and an inconel alloy rotor (B).

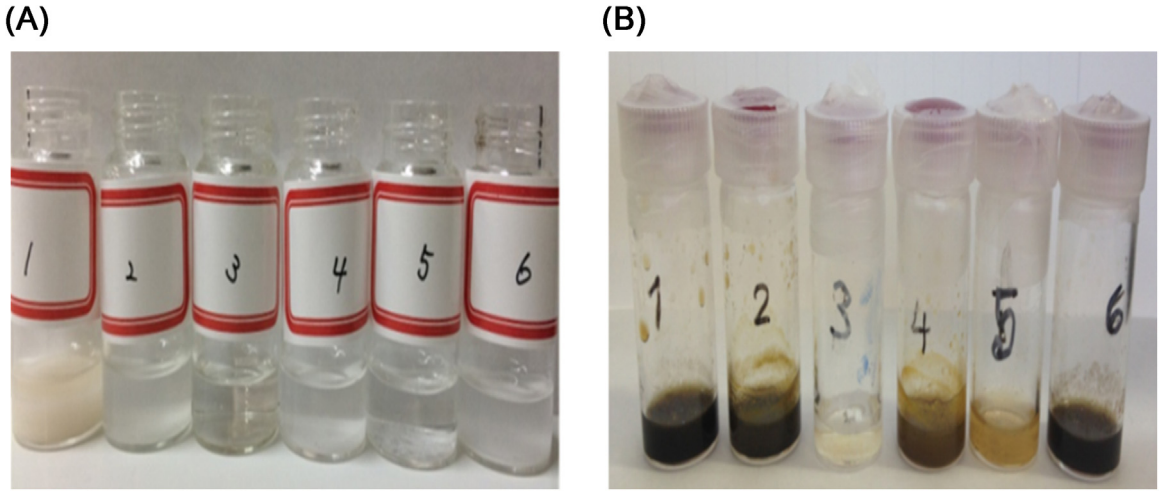

Fig. 2. A partial view by all samples before gravity experiment (A) and after gravity experiment (B).

strong gravity with a hydrothermal state results in decomposition of cellulose followed by the formation of new compounds.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (Avicel No. 2331; average particle diameter 20–100 μm) was purchased from Merck. Bemcot®, a brand of clean room wiper produced by Asahi Kasei from cotton linter and is pure cellulose, was purchased from local market and used as a model cellulose with low crystallinity.

2.2. Experimental apparatus and procedure

The decomposition experiment of cellulose was carried out using a strong gravitational field created by a newly developed ultracentrifuge [7]. This experiment we used two different types of celluloses (MCC and Bemcot®), the latter of which has lower crystallinity. Six samples were prepared by mixing different concentrations of cellulose and water in sulfuric acid mixtures. The first three samples were prepared using Bemcot®. Samples Nos. 1 and 2 were prepared using, respectively, 6% and 0.6% Bemcot® with water in dilute sulfuric acid. Sample No. 3 was prepared by mixing 0.6% Bemcot® and water only. The remaining three samples were prepared in the same way using MCC. After preparation 0.5 mL of each sample was sealed in a stainless steel capsule and exposed for 6 h at 250 °C to a gravitational field of 0.33×10^6 G generated by a centrifuge rotating at 80,000 rpm. Experimental conditions for the ultracentrifuge are summarized in Table 1. The entire capsule was fixed tightly with the outer cap into an Inconel alloy rotor shown in Fig. 1(A) of outer diameter 110 mm by the bulk type sample setup, where the specimen was preferentially set perpendicular to the centrifugal force called thin-plate type sample set up shown in Fig. 1(B) the maximum distance of the specimen was 46.5 mm from the rotor axis. The rotor was heated by radiation from the surround carbon cylinder which is heated by a high frequency heating system. After exposure to the centrifuge, reaction products were

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