ISSN 1022-8594
JUJS

Vol. 42, No. 2, pp.79-87

A green technique for non-catalytic solubilization and hydrolysis of crystalline cellulose

Nasrin Jewena[1,*], Mitsuru Sasaki[2], Tsutomu Mashimo[2]
[1]*Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh*
[2]*Institute of Pulsed Power Science, Kumamoto University, Kumamoto 860-8555, Japan*

Abstract

A unique method was established for the decomposition of cellulose using a strong gravitational field at room temperature to recover useful chemical intermediates. Experiments of decomposition of microcrystalline cellulose were conducted at room temperature for 24 hours to a gravitational field of 0.33 x 10^6 G generated by an ultracentrifuge rotating at 80,000 rpm using a specially-designed gravity apparatus. After gravity experiment, we analyzed the compounds by LC-MS spectra and HPLC respectively and showed that strong-gravity treatment of microcrystalline cellulose was successfully hydrolyzed to form cello-oligosaccharides and glucose, and surprisingly phenolic compounds such as guaiacol derivatives.

Keywords: Non-catalytic, hydrolysis, microcrystalline cellulose, strong gravitational field, guaiacol derivatives.

1. Introduction

With increasing environmental awareness worldwide, utilization of biomass from agriculture, industries, and municipalities is becoming increasingly important. Conventional methods for conversion of wastes have serious of shortcomings that limit its applicability. Cellulose is the most cheaply available biomass resource, which can be utilized for the energy production and materials synthesis. Cellulose is the most abundant renewable organic material on earth, with an annual production of over 50 billion tons [1]. It is an essential component of various natural plants, such as wood plants typically consisting of approximately 40-50% cellulose and 20-30% hemicelluloses. This is a kind of renewable resources and is important to solve the current energy problem from the lack of fossil fuels. Cellulose is a β-(1, 4)-linked homopolymer of many anhydro glucose residues and can be easily hydrolyzed by acid catalysts [2] and enzymes [3]

*Author for correspondence e-mail: nasrin28ju@juniv.edu

to cello-oligosaccharides and glucose. A review of Bobleter shows high potential of cellulose conversion in hot water with acid or alkaline catalyst [4]. It was reported that the low temperature (100–120 °C) concentrated acid hydrolysis of cellulose provides glucose yields approaching 100% [5]. Mok and Antal conducted high temperature (190–225 °C) dilute acid hydrolysis of cellulose in higher temperature water, and reported that the glucose yield reached 71% of the theoretical maximum (215 °C, 34.5 MPa and 120 min with 0.05 wt% sulfuric acid) [6]. In case of non-catalyzed hydrothermal degradation of cellulose (215–295 °C), the cellulose hydrolysis rate is much lower than that of acid catalyzed hydrolysis and the glucose yield is also lower (50% even at the optimum condition) [4]. Sasaki *et al*. reported that the products of hydrolysis or 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 [7]. But hydrolysis under supercritical condition has some disadvantages like high energy consumption and also some useful compounds are further decomposed at high temperature and pressure.

In this article, we would like to introduce cellulose decompose by strong gravitational field at room temperature without catalyst. Decomposition of cellulose and isolation of useful compounds under a strong gravitational field (1–10) $\times 10^5$ G (1 G=9.8 m/s^2) still is a new field of research. But micro-gravitational environments are often used in chemistry and life science research. The low gravity can be experienced at the Earth surface, whereas strong acceleration is experienced in case of explosion or impacts. In nature, strong gravity fields of over 10,000 G may exist only at degenerate stars or neutron stars. The 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 one-dimensional displacement of atoms [8, 9]. Mashimo *et al*. had developed high-temperature ultracentrifuge to generate a strong acceleration field of even over 1 million (1×10^6 G) in Kumamoto University [10]. The strong gravity can induce the decomposition reaction through sedimentation [9-14]. The synergism effect of strong gravity state expected to occur that results decomposition of cellulose followed by the formation of new compounds.

2. Experimental

2.1 Sample preparation

Microcrystalline cellulose (Avicel No. 2331; average particle diameter 20-100 µm) was purchased from Merck. Distilled water was obtained from water distillation apparatus (Sibata Co., model PW-16., Japan). Methanol was purchased from Wako Pure Chemicals Industries Ltd. (Japan) and had purity 99.0%. Experimental conditions for the ultracentrifuge are summarized in Table 1.

Table 1: Experimental condition for the decomposition of cellulose under strong gravity at room temperature

Starting sample	Rotational speed ($rev\times min^{-1}$)	Maximum distance (mm)	Maximum acceleration (10^6 G)	Temperature (°C)	Time (h)	Maximum pressure (MPa)
Cellulose	80,000	46.5	0.33	RT	24	4.8

2.2 Sample characterization

The decomposition experiment of cellulose was carried out in a strong gravitational field in newly developed ultracentrifuge [8]. For this experiment we used microcrystalline cellulose (MCC). We prepared three samples by mixing with different concentration of cellulose and water in methanol mixtures. Samples No. 1, 2 and 3 were prepared by using 4% MCC with water in 50%, 80% and 100% methanol, respectively. After preparing each sample then 0.5 ml of the cellulose mixture was sealed in a stainless-steel capsule and exposed for 24 hours at room temperature to a gravitational field of 0.33×10^6 G generated by a centrifuge rotating at 80,000 rpm.

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. The aqueous products of the reaction products were analyzed by LC/MS and HPLC spectroscopy.

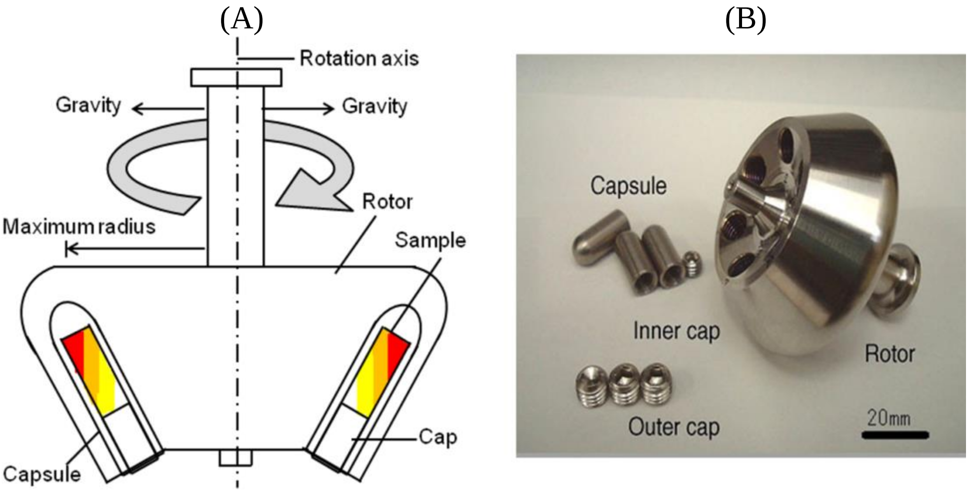

Figure 1: The cellulose mixture sample set up within a rotor (A) and an Inconel alloy rotor (B).

2.3 Analysis

2.3.1 Liquid chromatography mass spectroscopy (LC/MS)

The fractions were analyzed in a LC/MS-ESI Accela composed of a photodiode array detector, an auto sampler, a quaternary pump and a TSQ quantum access. The column was used the BEH C18 column (50mm× 2.1 mm × 1.8 µm) using as purified mobile phases 10 mM ammonium acetate (A) and methanol (B). The mixing ratio of A: B = 80: 20. The flow rate was 0.12 mL/min. The electrospray ionization (ESI) conditions were 0.3 kV and PDA wavelength range were 210- 798 nm.

2.3.2 High performance liquid chromatography (HPLC)

Quantitative analysis of the aqueous phase products was conducted by high performance liquid chromatography (HPLC) with a reflective index (RI) detector, an UV/Vis detector, and a packed column Shodex Sugar SH1011 for the separation of typical sugars and organic acids. The eluents were $HClO_4$ acid solution and BTB solution.

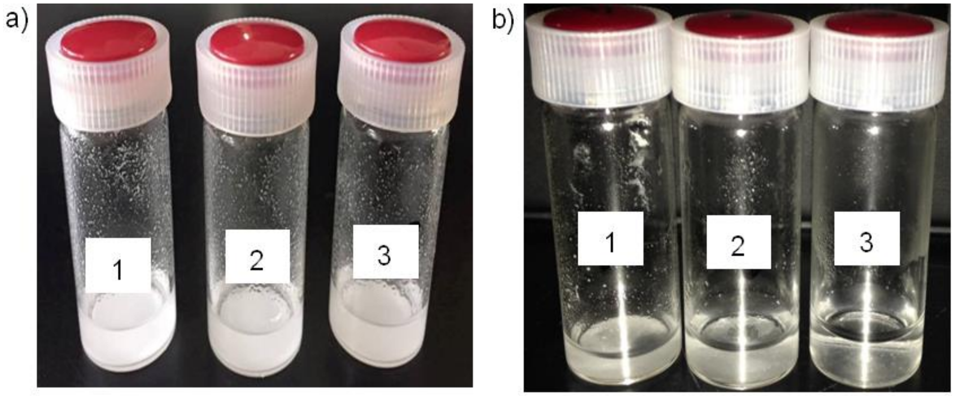

Figure 2: A partial view by all samples before gravity experiment (a) and after gravity experiment (b)

3. Results and discussion

Cellulose is a β-(1, 4)-linked homopolymer of many anhydro glucose residues and it is very difficult to breakdown this glycosidic bond without acidic or enzymatic catalysts to convert cello-oligosaccharides and glucose. However, in our gravity experiment the decomposition of cellulose takes place without any catalyst at room temperature. The change in solubility of MCC before and after the ultra-centrifugal experiment is shown Fig. 2 (a) and (b). Different percentages of cellulose water mixtures were insoluble before the gravity experiments but a significant change in solubility were obtained after the experiments.

LC-MS spectra were used for identify the cellulose decomposition products. The main identified compounds from LC-MS analysis were summarized in Table 2. Phenolic compounds were found from samples No. 1 like methylphenol, guaiacol, 4-methylguaiacol, and guaiacylacetone whereas more saccharides and their decompose compound were observed form sample No. 3 like glyceraldehyde, hydroxymethylfurfural-dimer, sucrose, raffinose, cellotriose, levulinic acid and glucose. From the three samples we also got some hydrocarbon related compounds. According to the classical mechanics, dissimilar atoms subjected under centrifugal force experience body forces in the various extend depending on their mass. The lighter element experiences weaker and heavy element experiences stronger force. i.e., $F_M > F_m$; where M > m. Mashimo and Ogata *et al.* [9, 15] reported that, if body force exceeds the existing chemical potential, a relative displacement takes place that allows the atom sedimentation from lighter to heavier. As a consequent, atomic scale graded system is observed under the strong gravitational field.

Table 2: Results of the LC/MS analysis in positive detections

Sample No.	Compound name	m/z
01	2-methylcyclopentenone	95.0497
	Methyl phenol	109.0653
	4-methylguaiacol (or 2-Methoxy-4-methylphenol)	139.0759
	Guaiacylacetone(or 4-Hydroxy-3-methoxyphenyl acetone)	181.0865
	Glucose	181.0712
	Guaiacol (or 2-Methoxyphenol)	125.0603
02	Acetic acid	59.0133
	Levulinic acid	117.0552
	3-hydroxy-4-methoxy mandelic acid	199.0606
	Hydroxymethyl furfural-dimer	235.0606
03	Glyceraldehyde	89.0236
	Hydroxymethyl furfural-dimer	235.0606
	Sucrose	341.1084
	Raffinose	503.1612
	Cellotriose	503.1612
	Levulinic acid	115.0395
	4-methyl guaiacol	139.0759
	Glucose	181.0712

However, the authors have another strategy of the use of methanol-water mixture at room temperature for dissolving and peeling hydrolysis of crystalline cellulose to produce high molecular-weight cellulose molecules in the absence of catalysts. According to Isogai *et al*. [16], crystalline cellulose can be dissolved in specific base conditions (in 8-10 vol% NaOH aqueous solution) at room temperature due to high concentration of OH species around cellulose molecules. In case of the conventional hydrolysis experiments of cellulose using a batch-type reactor, OH and H^+ species can exist anywhere inside the aqueous phase and therefore both acidic and basic effects on cellulose microfibrils. As the result, a part of cellulose might swell or dissolve in methanol-water mixture, but most of cellulose molecules are randomly hydrolyzed by the attack of H^+ to any glycosidic bonds of cellulose to form lower molecular-weight cellulose oligomers, monomers and their degradation products. On the contrary, in this method, OH species, which have larger molecular-weight than H^+, can exist on the outer region (stronger gravity regime) during the high-speed rotation operation [17]. Due to the operation of 80 000 rpm, strong gravitational field is generated along the outward direction from the capsule center and acting on the cellulose sample. Under this strong gravitational field, glucose and its decomposition products exist in the acidic media (lower gravity regime) around the capsule center. The heavy products cellulose and oligomers are deposited in the basic media near the inner surface of the capsule. Thus, crystalline cellulose exists in the water atmosphere having much higher and selective OH , resulting in the occurrence of swelling/dissolving of cellulose molecules with particle peeling hydrolysis. The authors think that this unique distribution of OH and H^+ species under the strong gravitational field is the most important advantage in this method. We conclude from LC-MS analysis that MCC were successfully hydrolyzed to form cello-oligosaccharides, glucose and guaiacol derivatives in methanol-water mixture. These guaiacol derivatives were produced due to sedimentation of atoms under the strong gravitational field. In the conventional method, however guaiacol cannot be obtained from cellulose.

Cellulose decomposition products were also identified by HPLC- RI chromatogram. The identified products were cellobiose, fructose, lactic acid, acetic acid, glyceraldehyde, and levulinic acid respectively, from sample No 1, 2, and 3. Retention times of the detected 3 peaks for sample No. 1 were 17.70, 21.10 and 44.50 min for glyceraldehyde, dihydroxyacetone and 5-hydroxymethyl-2-furfural (5-HMF), respectively. The retention times 17.70 and 23.53 min for sample No. 3 were glyceraldehyde and levulinic acid. Glyceraldehyde and dihydroxyacetone are in general formed from fructose, an isomer of glucose, via retro-aldol condensation, and 5-HMF can be obtained by intramolecular dehydration of fructose under hydrothermal conditions [18]. Levulinic acid is a hydrolysis product of 5-HMF under identical conditions. These analytical results clearly indicate that cellulose successfully hydrolyzed at room temperature to glucose and its degradation products by this strong gravity technique.

4. Conclusions

In the current studies, we have demonstrated the hydrolysis of cellulose in methanol- water mixture at room temperature without catalyst. We reported a new method to solubilize crystalline cellulose in methanol-water mixture at room temperature by using strong gravitational field to recover useful chemical intermediates via hydrolysis, methylation and other chemical transformation reactions. Results of our strong-gravity treatment of celluloses at room temperature showed that microcrystalline cellulose was successfully hydrolyzed to form cello-oligosaccharides and glucose, and surprisingly phenolic compounds such as guaiacol derivatives, which are applicable for the chemicals and food industries. Due to synergism of strong gravitational field with physical properties of methanol- water under room temperature, 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. Cellulose decomposition at room temperature under gravity experiment can be used as a green route for the synthesis and recovery of new compounds without organic solvent or additives that adversely affect the environment.

References

[1] He. Chun, Li Xiang-Zhong, VK Sharma, Li Shi-Yu, *Environ. Sci. Tecnol.*2009, 43, 5890-5895.

[2] I. A. Malester, M. Green, G. Shelef, *Ind. Eng. Chem*. 1992, Res 31, 1998.

[3] M. Mandels, L. Hontz, J. Nystrom, *Biotech. Bioeng.* 1974, 16 (2), 1471.

[4] O. Bobleter, *Progr. Polym*. Sci. 1994, 19, 797.

[5] J.W. Dunning, E.C. Lathrop, *Ind. Eng. Chem.*, 1945, 37 (1), 24.

[6] W.S.L. Mok, M.J. AntalJr., *Ind. Eng. Chem*., 1992, Res 31, 94.

[7] M. Sasaki, B. Kabyemela, R. Malauan, S. Hirose, N. Takeda, T. Adschiri, K. Arai, *J of Sup. Fluids*, 1998, 13(1-3), 261-268.

[8] T. Mashimo, *sedimentation, phys. Rev* 1988, 38, 4149-4154.

[9] T. Mashimo, *Philos. Mag.*, 1994, 70, 739-760.

[10] T. Mashimo, X. S. Huang, T. Osakabe, M. Ono, M. Nishihara, H. Ihara, M. Sueyoshi, K.Shibasaki, S. Shibasaki, N. Mori, *Rev. Sci. Instr.*, 74, 2003, 160-163.

[11] T. Mashimo, T. Ikeda, I. Minato, *J. Appl. Phys*., 2001, 90, 741-744.

[12] R. Bagum, A. Yoshiasa, S. Okayasu, Y. Iguchi, M. Ono, M. Okube, T. Mashimo, J. *Appl. Phys*., 2010, 108, 053517.

[13] Y. Abe, T. Sawada, M. Takafuji, T. Mashimo, M. Ono, H. Ihara, *Chem. Lett*., 2010, 39, 174-175.

[14] J. I. Khandaker, M. Tokuda, Y. Ogata, K. Janusko, T. Nishiyama, A. Yoshiasa, T. Mashimo, *J. Appl. Phys*., 2015,117, 185-905.

[15] Y. Ogata, Y. Iguchi, M. Tokuda, K. Januszko, J. I. Khandaker, M. Ono, T.Mashimo, *J. Appl. Phys.*, 2015,117, 125-902.

[16] A. Isogai, R. H. Atalla, *Cellulose*, 1998, 5(4), 309-319.

[17] N. Jewena, R. Miyanomae, M. Sasaki, T. Mashimo, *the Journal of Supercritical Fluids*, 2016,120, 379-383.

[18] B. M. Kabyemela, T. Adschiri , R.M. Malaluan, K. Arai, *Ind. Eng. Chem.*, 1997, Res 36, 2025.