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Short communication

Direct hydrolysis of cellulose to glucose using ultra-high temperature and pressure steam explosion

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ABSTRACT

Hydrolysis of two cellulosic materials, i.e. microcrystalline cellulose powder (MC) and cuprammonium rayon fiber (BEMCOT), to glucose was carried out by steam explosion treatment with ultra-high temperature and pressure steam aiming at an effective usage of unutilized cellulosic materials. 50 g of cellulosic materials were charged in a sealed reactor (2 L) of the steam explosion apparatus kept at steam pressures of 50, 55, 60, and 62 atm for a steaming time of 1 min. The maximum yield of water soluble sugars, 52.8%, was obtained at a steam pressure of 62 atm and a steaming time of 1 min for MC. Furthermore, the maximum yield of water soluble sugars, 67.7%, was obtained at a steam pressure of 60 atm and a steaming time of 1 min for BEMCOT. This water soluble sugars contained 63.1% and 61.0% of glucose, respectively; they are corresponding to 33.3 g and 41.0 g of glucose contained in 100 g of dry steam-exploded cellulosic material.

1. Introduction

In order to produce ethanol and other useful chemicals from unutilized plant materials, it is necessary to hydrolyze cellulose to fermentable sugars, especially glucose (Flores, Fake, Carroll, Hood, & Howard, 2010; Zheng et al., 2007). However, since cellulose molecules have intermolecular and intramolecular hydrogen linkages through the hydroxyl groups and form crystal structure at normal conditions, it is very difficult to hydrolyze cellulose. At present time, main hydrolysis methods of cellulose in plant material are enzymatic method and acid-catalysis method. These methods have many obstacles to overcome, in case of enzymatic method, since cellulose is surrounded by lignin hard network, it is necessary to degrade and/or remove lignin before enzymatic reaction. Furthermore, the enzyme is too expensive to be economically feasible for applications in practical use. In case of acid-catalysis method, corrosion-resistant equipment, acid recovery cycles, and waste water neutralization treatment are required. On the other hand, recently, hydrolysis methods using supercritical, subcritical, and hot compressed water have been widely investigated and developed (Hashaikeh, Fang, Bulter, Hawari, & Kozinski, 2007; Luo et al., 2011; Phaiboonsilpa, Yamauchi, Lu, & Saka, 2010; Sakaki, Shibata, Miki, Hirose, & Hayashi, 1996; Zhao, Lu, Wang, & Yang, 2009). Meanwhile, since most of the equipments used currently are flow type system that cannot treat materials directly, they needs some pretreatment steps and have rapid heating and cooling system for avoiding the degradation of glucose produced from cellulosic materials. Furthermore, due to maintain a high temperature and pressure in the reactor their reactor volume is very small, i.e. tens cubic centimeters. For practical use of the hydrothermal treatment, a large volume reactor to treat samples in large quantities is necessary. Similar to these methods using high temperature and activated water molecule, steam explosion method has been known. The main effect is steam hydrolysis at a high temperature and pressure, followed by the sudden reduction of the pressure which allows to a mechanical treatment of the hydrolyzed product which produces low molecular weight substances from cellulose, hemicellulose, and lignin that are easier to extract (Asada, Kita, Sasaki, & Nakamura, 2011). Though the conventional steam explosion has been operated at a steam pressure of 8–35 atm (i.e. a steam temperature of 170–240 °C), it is difficult to convert cellulose to glucose directly because of such low steam temperatures. Therefore, in this study the steam explosion treatment with ultra-high temperature and pressure steam, i.e. 281 °C and 67 atm, having a reactor (2 L) was used for converting a large amount of cellulose to glucose.

The aim of this study is to estimate the recovery of glucose from two cellulosic materials, i.e. microcrystalline cellulose powder (MC) and cuprammonium rayon fiber (BEMCOT), as model samples of plant biomass and other utilized cellulosic resources (for example, old cotton cloths) using a steam explosion with ultra-high temperature and pressure steam.

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2. Materials and methods

2.1. Cellulosic materials

The cellulosic materials used in this study were microcrystalline cellulose powder (MC) purchased from Merck Chemicals and cuprammonium rayon fiber (BEMCOT M3-II) purchased from Asahi Kasei Fibers Corp. BEMCOT was cut into small fragments (2 cm × 2 cm) and used as a sample.

2.2. Degree of crystallinity and crystal structure of cellulosic materials

X-ray diffraction data were obtained using a Rigaku Ultima III X-ray Diffractometer (Rigaku Co. Ltd., Tokyo, Japan). The goniometer scanned a 2θ range between 5° and 50° with a scan rate of 0.5°/min. The crystallinity (%) and crystal structure were determined by the method of Segal's method (Segal, Creely, Martin, & Conrad, 1959) and X-ray diffractograms curve pattern, respectively. BEMCOT samples were prepared by cutting into a powder form and then mounted at the center of the goniometer circle.

2.3. Hydrolysis of cellulose to glucose using steam explosion

Hydrolysis of cellulosic materials was conducted in a steam explosion apparatus NK-2L (Japan Chemical Engineering and Machinery Co. Ltd., Osaka, Japan). The reactor has a reactor capacity of 2.0 L with a maximum pressure of 67 atm and a maximum temperature of 280 °C. The reactor was charged with 50 g (dry matter) of feedstock per batch. Saturated steam from the boiler was then allowed to enter the reactor to heat the cellulosic material at a controlled pressure of 50–62 atm (264–278 °C). Each pressure was maintained for 1 min and then the reactor was suddenly depressurized. The exploded sample was recovered in a cyclone and cooled to a room temperature. Furthermore, the effect of steaming time of 0.5–5 min on glucose production was evaluated at a steam pressure of 60 atm.

2.4. Analysis

Components analysis of the steam-exploded cellulosic material was carried out as follows: 0.2 g (dry matter) of steam-exploded cellulosic material was added to 300 mL of distilled water and extracted for 24 h at a room temperature. The solid and liquid portions were separated by filtration, the solid portion was recovered from the liquid, then concentrated, dried, and weighed. Glucose and cellobiose in the liquid portion were analyzed with the HPLC system with a refractive index detector with a Bio-Rad HPX-87H column at 65 °C temperature. The mobile phase was 5.0 mM H_2SO_4 at a flow rate of 0.6 mL/min. Other water soluble sugars except cellobiose and glucose in the liquid portion were determined by subtracting the amount of cellobiose and glucose from the amount of sugars measured by phenol–sulfuric method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1951). All analytical determinations were performed in triplicate and average results are shown.

3. Results and discussion

3.1. Effect of steam pressure on glucose yield from cellulosic material

In order to treat various unutilized resources that contain cellulose, different forms such as powder and fiber were used as cellulosic materials. The crystallinity and the crystal structure of cellulosic materials were estimated using X-ray diffraction analysis. Table 1 shows the crystallinity and crystal structure of MC and BEMCOT. The crystallinity of MC was 3.3-fold higher than that of BEMCOT. For crystal structure, MC showed the cellulose I and BEMCOT showed the cellulose II, respectively (X-ray diffractograms data not shown). Generally, regenerated cellulose such as BEMCOT showed the crystal structure cellulose II (Saka & Ueno, 1999).

Table 1
Degree of crystallinity and crystal structure of cellulose materials used in this study.

Samples	Forms	Crystallinity (%)	Crystal structure
Microcrystalline cellulose (MC)	Powder	87.2	I
Cuprammonium rayon (BEMCOT)	Fiber	26.5[a]	II

[a] Determined by Asahi Kasei Fibers Corp.

The effect of steam pressure of steam explosion on the glucose yield from these two cellulosic materials was studied using steam pressures of 50, 55, 60, and 62 atm for a steaming time of 1 min. Fig. 1 shows the mass balance of steam-exploded cellulosic materials at different steam pressures. The maximum amount of water soluble sugars (glucose, cellobiose, and other water soluble sugars) produced was observed at a steam pressure of 62 atm for MC (52.8%, Fig. 1(a)) and 60 atm for BEMCOT (67.7%, Fig. 1(b)) for steaming time of 1 min. Furthermore, glucose contained in the water soluble sugars was 63.1% and 61.0%, respectively. Furthermore, they are corresponding to 33.3 g and 41.0 g of glucose in 100 g of dry steam-exploded cellulosic material. Sakaki et al. (1996) reported that the highest yield of glucose (40%) from cellulose powder was obtained at 355 °C and 15 s using a reactor with near-critical water (6 cm^3). Zhao et al. (2009) reported that the highest yield of fermentable hexoses from corn stalks (27.4% of raw material) was obtained at 280 °C and 27 s, and from wheat straw (6.7% of raw material) at 280 °C and 54 s using a reactor with subcritical water (5 cm^3). In this work, since 30–40% of glucose yield was obtained, it seems that the ultra-high temperature and pressure steam explosion can be used as an alternative method of near-critical and subcritical water treatments. However, since in the case of BEMCOT the yields of water soluble sugars and glucose are 52.2 and 31.1%, respectively, a higher pressure could not increase their yields. It indicated that decomposition of hydrolyzed sugars occurred at a higher pressure condition. Liquid hot water, steam explosion, and acidic treatments of cellulosic materials at elevated temperatures generate water soluble materials which act as an inhibitor for yeast growth (Kim, Ximenes, Mosier, & Ladisch, 2011; Larsson et al., 1999; Palmqvist, Hahn, Galbe, & Zacchi, 1996). 5-Hydroxymethylfurfural is a product from the degradation of hexose, i.e. glucose (Cara, Ruiz, Ballesteros, Negro, & Castro, 2006). Moreover, it was found that higher yields of water soluble sugars and glucose were obtained using BEMCOT compared to MC. Saka and Ueno (1999) also reported that two cellulosic materials, i.e. avicel (cellulose I) and Lyocell (one of the regenerated cellulose, cellulose II), were liquefied by supercritical treatment (500 °C) at about 10 s, glucose yields of cellulose I and cellulose II were 32 and 48%, respectively. And they mentioned that the degree of crystallinity is not an important factor for hydrolysis rate.

3.2. Effect of steaming time on the glucose yield from cellulosic material

The effect of steaming time of steam explosion at a steam pressure of 60 atm on the glucose yield from cellulosic materials was investigated using a steaming time of 0.5, 1, 3, and 5 min. Fig. 2 shows the mass balance of steam-exploded cellulosic materials at different steaming times. The maximum amount of water soluble sugars produced was observed at a steaming time of 1 min for MC (47.6%, Fig. 2(a)) and BEMCOT (67.7%, Fig. 2(b)). Furthermore, the amounts of glucose contained in the water soluble sugars were 62.0

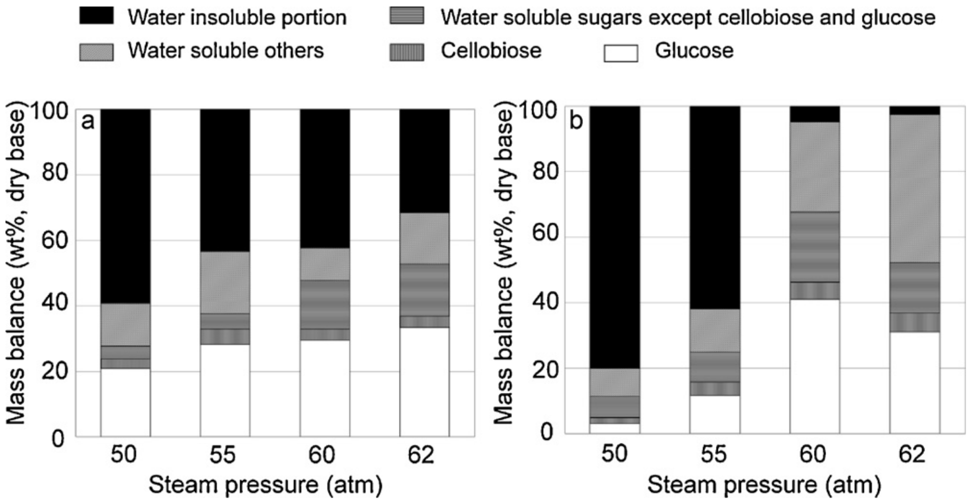

Fig. 1. Mass balance of steam-exploded cellulosic materials at various steam pressures for a steaming time of 1 min. (a) Microcrystalline cellulose powder (MC), and (b) cuprammonium rayon fiber (BEMCOT).

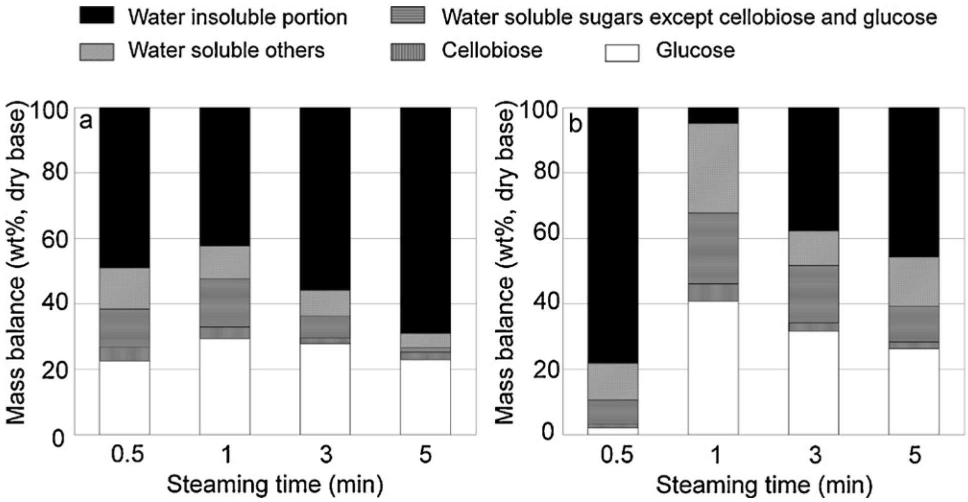

Fig. 2. Mass balance of steam-exploded cellulosic materials at various steaming times under a steam pressure of 60 atm. (a) Microcrystalline cellulose powder (MC), and (b) cuprammonium rayon fiber (BEMCOT).

and 41.0%, respectively. 62.0% of MC is corresponding to 29.5 g of glucose from 100 g of dry steam-exploded cellulose. In this figure, no increasing effect of longer steaming time on the yields of water soluble sugars and glucose was observed.

As a result, in the range of steam pressures (50–62 atm) and steaming times (0.5–5 min) the optimal steam explosion conditions were determined as follows: a steam pressure of 62 atm (278 °C) and a steaming time of 1 min for MC, and a steam pressure of 60 atm (276 °C) and a steaming time of 1 min for BEMCOT. It was found that a significant higher pressure steam explosion (about 60 atm) compared with conventional steam explosion (steam pressure of 8–35 atm) is necessary for the direct conversion of MC and BEMCOT to glucose.

4. Conclusions

This study presents an attempt to evaluate the feasibility of hydrolysis of two kinds of cellulosic materials, i.e. microcrystalline cellulose powder (MC) and cuprammonium rayon fiber (BEMCOT), to obtain fermentable glucose directly using a steam explosion with a large volume of reactor. It was found that the steam explosion with ultra-high temperature and pressure steam could produce 30–40 g of glucose from 100 g of cellulosic materials. This finding obtained in this work suggests that the ultra-high temperature and pressure steam explosion are very effective for direct hydrolysis of cellulose to glucose because the scale-up of steam explosion seems to be possible. Future study will be focused on the determination of optimal condition by steam explosion experiments under various steam pressures and steaming times, and the application to not only cellulosic materials, i.e. old cotton cloths and paper sludge, but also plant biomass, i.e. woods, straws, and barks.

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