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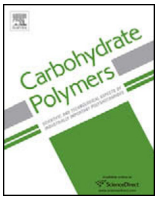

Effects of ionic conduction on hydrothermal hydrolysis of corn starch and crystalline cellulose induced by microwave irradiation

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ABSTRACT

This study investigated the effects of ionic conduction of electrolytes under microwave field to facilitate hydrothermal hydrolysis of corn starch and crystalline cellulose (Avicel), typical model biomass substrates. Addition of 0.1 M NaCl was effective to improve reducing sugar yield by 1.61-fold at unit energy (kJ) level. Although Avicel cellulose was highly recalcitrant to hydrothermal hydrolysis, addition of 0.1 M $MgCl_2$ improved reducing sugar yield by 6.94-fold at unit energy (kJ). Dielectric measurement of the mixture of corn starch/water/electrolyte revealed that ionic conduction of electrolytes were strongly involved in facilitating hydrothermal hydrolysis of polysaccharides.

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1. Introduction

Hydrothermal treatment is one of the effective reaction to loosen and hydrolyze recalcitrant biomass to produce useful chemicals and fuels (Peterson et al., 2008; Sun & Cheng, 2002). Water exhibits unique physicochemical property under subcritical and supercritical conditions. At subcritical condition, the ion product $K_W = [H^+][OH^-]$ of water increases with increase in temperature and induces hydrolysis of substrates without addition of acidic catalysts. In contrast, supercritical water (above 374 °C and 22.1 MPa) shows drastically low ion product. Dielectric constant of water significantly decreases with increase in temperature, and hydrophobic compounds become more soluble in aqueous media without using organic solvents. Hydrothermal reactions are, therefore, applied to chemical synthesis, waste treatment as well as biomass fractionation as green processes (Savage, 2009).

Microwave irradiation is effective for hydrothermal treatment of biomass by direct coupling of microwave with biomass substrates and water medium from within (Tsubaki & Azuma, 2011). Microwave is a kind of electromagnetic wave with frequencies between 300 MHz and 300 GHz and widely used in radar and telecommunication. Since dipolarity and ionic conduction in an oscillating electromagnetic field have been found to provide direct and rapid heating of materials (Gabriel, Gabriel, Grant, Halstead, & Mingos, 1998), microwave heating is widely utilized in various heating process in industries, for instance, vulcanization of rubbers, drying processes, sintering of ceramics and so on. Microwave irradiation is also applied to organic and inorganic synthetic reactions by utilizing advantages in rate enhancement, reduced reaction time, improvement in the product yield and less formation of by-products (Kappe, 2008).We previously characterized the effects of using microwaves for the hydrothermal treatment of biomasses by testing monosaccharides and disaccharides with and without irradiation of microwave. Compared with the conventional heating, microwave heating has an advantage to stabilize glucose by avoiding the unexpected degradation of sugars at the reactor walls (Tsubaki, Oono, Onda, Yanagisawa, & Azuma, 2012, Tsubaki, Oono, Onda, Yanagisawa, & Azuma 2013). In addition, electrolytes such as alkali metal halides in aqueous solution were effective in improving microwave absorption of the reaction system by ionic conduction.

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Electrolytes also exhibited higher saccharification rate of cellobiose at reduced reaction temperatures with lower energy consumption (Tsubaki et al., 2012). Ionic conduction was also important factor for dielectric loss tangent (tan δ) of acidic hydrocolloids in water (Tsubaki et al., 2014; Tsubaki et al., 2015).

This study was designed to characterize the contribution of ionic conduction effects on generation of mono- and oligosaccharides from corn starch and crystalline cellulose by microwave-assisted hydrothermal treatment. First, the effects of ionic conduction of electrolytes were investigated for improving microwave energy efficiency of the hydrothermal hydrolysis of corn starch and crystalline cellulose. The dielectric analyses were then conducted on the mixture of starch/water/electrolyte to reveal the interaction between electromagnetic field and the reaction systems.

2. Materials and methods

2.1. Microwave heating

Microwave heating was performed using a START D multimode microwave oven (frequency; 2.45 GHz, max output; 1,000 W, Milestone Inc. Shelton, CT, USA) and HPR-100 TFM reactor. The reaction temperature was controlled by PID with a thermocouple thermometer. The mixture was stirred with a stirring bar. Briefly, 1 g of corn starch (Wako Pure Chemical Industries, Ltd.) and Avicel cellulose (Merck KGaA) was suspended in 20 mL of distilled water or aqueous solutions of 0.1 M NaCl and $MgCl_2$. The temperature was raised over 4 min and maintained for 10 min. The reactor was immediately cooled in an ice bath (ca. 15 min). Energy consumption was estimated from the oven's microwave output monitor.

2.2. Chemical analyses of sugars and 5-HMF

The amounts of reducing sugars and glucose were determined by the DNS method and a Wako Glucose CII kit (Wako Pure Chemical Industries Ltd.), respectively. Sugar yields were multiplied by 0.9 to determine conversion to reducing sugars and glucose. A yield of 5-HMF was determined by high-performance liquid chromatography (HPLC), using the LC-2000 plus system (Jasco Co. Tokyo, Japan) equipped with an Aminex HPX-87H column (300 × 7.8 mm, Bio-Rad Laboratories, CA, USA) at 85 °C. The column was eluted with an aqueous solution of 0.008 N sulfuric acid at a flow rate of 0.6 mL/min, with UV detection at 280 nm.

2.3. Dielectric measurements of starch solutions

The relative permittivity (ε') and loss factor (ε'') of distilled water and aqueous solutions of corn starch, corn starch + NaCl and corn starch + $MgCl_2$ were measured by the coaxial probe method using an Agilent Technologies N5242A Network Analyzer and an Agilent high temperature probe in a range of 100 MHz to 20 GHz (Agilent Technologies Inc.) at 25, 40, 50, and 60 °C. The corn starch solution (5 wt%) was prepared by microwaving of corn starch powder in electrolyte solutions (0 ~ 0.2 M of NaCl and $MgCl_2$) at 100 °C for 30 min to obtain gelatinized starch–water system using the same apparatus as shown in the Section 2.1. Tan δ was calculated using the following equation.

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{1}$$

The dielectric property of water was further characterized by the Debye equation (Gabriel et al., 1998):

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \tag{2}$$

where ε^*, ε_s, ε_∞, j, ω, and τ are the relative permittivity and loss factor, the static frequency, the infinite frequency, the imaginary unit, the angular frequency and the relaxation time, respectively. In the case of corn starch solutions, the Cole–Cole equation including the term for conductivity was applied for the better fitting to the results as follows:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}} - j\frac{\sigma}{\omega\varepsilon_0} \tag{3}$$

where, α, σ and ε_0 are the distribution parameter, the conductivity and the permittivity of free space (8.854×10^{-12} F m^{-1}), respectively. The relaxation time for free water (τ) and conductivity (σ) for distilled water and corn starch solutions were obtained from the Eqs. (2) and (3), respectively. The depth of penetration (D_P) was obtained from the following equation:

$$D_P = \frac{\lambda}{4\pi}\left[\frac{2}{\varepsilon'_r\left(\sqrt{1+(\tan\delta)^2}-1\right)}\right]^{\frac{1}{2}} \tag{4}$$

where, λ is the microwave wavelength.

3. Results and discussion

3.1. Effect of ionic conduction of electrolytes on microwave-assisted hydrothermal hydrolysis of corn starch and Avicel cellulose

Electrolyte solutions are well heated by microwave irradiation due to ionic conduction (Gabriel et al., 1998). Since dielectric loss of water at 2.45 GHz decreases with increase in temperature (Okada, Yao, Hiejima, Kohno, & Kajihara, 1999), electrolytes are important for improving dielectric loss of water. Fig. 1A shows yields of reducing sugar after hydrothermal hydrolysis of corn starch with addition of 0.1 M NaCl and $MgCl_2$. Addition of NaCl was effective to increase reducing sugar yield by 1.14- ~ 1.15-fold at -10 ~ -20 °C lower temperatures than the standard hydrothermal hydrolysis in distilled water. $MgCl_2$ was more effective to reduce the reaction temperature by -20 ~ -30 °C, however, the improvement rate of the maximum yield was only 1.06-fold. Glucose yields were also significantly affected by electrolytes. NaCl and $MgCl_2$ decreased the optimized reaction temperature by -10 and -20 °C, respectively, while the maximum glucose yield did not exhibit significant change (56.1 ~ 60.6%, Fig. 1B). Aqueous solution of $MgCl_2$ showed higher hydrolytic activity than NaCl, indicating that the valence of the cation significantly associated with hydrolytic capacity. 5-HMF yield was measured as a representative decomposed material from glucose. Addition of NaCl slightly increased generation of 5-HMF, however, $MgCl_2$ significantly increased the amount of 5-HMF than that by the standard hydrothermal hydrolysis (Fig. 1C). Addition of NaCl was found to exhibit higher selectivity to produce malto-oligosaccharides with less production of 5-HMF. $MgCl_2$, on the other hand, facilitated to produce both glucose and 5-HMF.

The microwave energy consumption required for hydrothermal hydrolysis of corn starch was, then, shown in the Fig. 1D. The standard microwave reaction required $\leq$ 198 kJ, while the addition of NaCl and $MgCl_2$ reduced the energy requirement down to $\leq$ 132 kJ. The reducing sugar yields (%) at unit energy consumption (kJ) were plotted against reaction temperature in the Fig. 1E. The values were significantly improved to 1.61- and 1.54-fold by additions of NaCl and $MgCl_2$, respectively, showing that ionic conduction was effective in improving energy efficiency of microwave-assisted reaction.

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