Hydrolysis of cellulose into reducing sugar via hot-compressed ethanol/water mixture

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ABSTRACT

Hydrolysis of cellulose by hot-compressed ethanol/water mixture is a promising way to obtain reducing sugar (RS) for biofuel production. The purpose of this research is to obtain high RS yield. In this work, the hydrolysis of microcrystalline cellulose by batch hot-compressed ethanol/water mixture was investigated. The influence of the ethanol/water mixture density corresponding to temperature and pressure on the RS yield was further examined. The hydrolysis conditions were optimized for high sugar yield and the crystallinity indexes (CI) of the residue and the original cellulose were analyzed. The RS yield reached as high as 98.22% under the conditions of ethanol mole fraction of 0.22, temperature of 260 °C, pressure of 5.75 MPa, reaction time of 35 s, and stirring speed of 10 Hz. The IR crystallinity index of cellulose was decreased to 0.211 from 0.618. It is shown that the RS can be produced effectively by cellulose hydrolysis in hot-compressed ethanol/water mixture.

1. Introduction

In recent years, renewable energy resources such as biofuels have attracted increasing attention due to the rapid increase of world energy demand and energy consumption [1–4]. Globally, the means to utilize this abundantly available resource in a cost-effective way is a major research focus. Biomass contributes about 12% of the global primary energy supply and up to 40–50% in many developing countries [5]. Cellulose, which is widely present in straw, bagasse, wood and other agricultural and forestry wastes, has been applied in industries of papers, fiber, foods, and chemicals, etc. However, it has not yet been fully utilized. To further utilize cellulose materials, such methods as liquefaction and gasification are essential [6,7]. For the conversion of cellulose into energy and chemical region, saccharification of cellulose and hemi-cellulose followed by fermentation is one of the methods to obtain ethanol which can be used not only as a useful chemical but also as a liquid fuel.

Thus, various methods such as enzymatic hydrolysis and acid hydrolysis as well as combination of both have been proposed and applied to hydrolyze lignocellulosic biomass as a way to recover saccharides [8–13]. In order to further optimize the hydrolysis process, subcritical and supercritical water treatments have also been investigated to obtain saccharides for subsequent fermentation to ethanol [14–21]. Firstly, Bobleter et al. [14] proposed the hydrothermal treatment of lignocellulose in subcritical water without catalyst.

Sakaki et al. [15,16] reported that cellulose was rapidly decomposed to water-soluble compounds in near-critical water by a batch reactor, and yield reached nearly 80%. Sasaki et al. [18] conducted supercritical treatment of cellulose, and found that cellulose can be converted to water-soluble saccharides more effectively in supercritical water (>374 °C, >22.1 MPa) than in subcritical water. Saka and Ueno [22] reported that large amounts of glucose and levoglucosan can be obtained from cellulose in supercritical water. Ando et al. [23] examined the decomposition behavior of plant biomass in hot-compressed water using a semi-batch reactor. The result was that more than 95% of the charged amount of biomass materials could be decomposed by hot-compressed water. However, these hydrolyzed products are further decomposed into various volatile and gaseous compounds in the severe conditions of supercritical water [21].

The above-mentioned researches have made significant breakthroughs in the field of preparing saccharides from cellulose. Nevertheless, the techniques proposed are difficult to be applied in industrial production due to the high reaction temperature and pressure, and low saccharide yield caused by the degradation. Yamazaki et al. [24] reported alcohols with longer alkyl chains could dissolve macromolecules and liquefy lignocellulose rapidly in supercritical region. Thus, we proposed to prepare saccharides from cellulose hydrolysis by hot-compressed alcohol/water mixture. Due to the low critical temperatures and pressures of this conventional alcohols (methanol, T_c: 239.5 °C, P_c: 8.1 MPa; ethanol, T_c: 240.8 °C, P_c: 6.1 MPa; isopropanol, T_c: 235.2 °C, P_c: 4.8 MPa), the critical point and the dielectric constant of the alcohol/water mixture would be lower than that of pure water, which led to milder conditions for the reaction and the increase of the solubility of relatively high molecular weight products from cellulose, hemicelluloses, and lignin. Earlier works [25–28] have reported good conversion of lignocellulosic biomass into liquefied products by supercritical methanol treatment. However, up to now, few studies have been made on saccharides from cellulose hydrolysis by alcohol/water mixture treatment.

In this study, the chemical conversion of cellulose by hot-compressed alcohol/water mixture treatments was examined. The first goal of this work was to compare the hydrolysis of microcrystalline cellulose in different hot-compressed alcohol/water mixtures treatment, in which RS production was focused on. As a result, it was found that the ethanol/water mixture was the best one. Then an equation expressed the relationship between the RS yield and the density as well as the ethanol mole fraction in ethanol/water mixture system was proposed. Finally, the hydrolysis mechanism of cellulose in ethanol/water mixture was briefly discussed.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose powder (purity ≥ 99.7%; average particle diameter 20–80 μm; Product Number 061208) purchased from Le Tai Chemical Co., Ltd. was used throughout the experiment. Alcohols used in the entire experiment were analytic grade and purchased from the Tianjin Bodi Chemical Holding Co., Ltd.

2.2. Experimental procedures

Fig. 1 shows the experimental setup which consists of a feeding system, a preheating system, a reactor and product collection parts. The alcohol/water mixture in solvent tank were pressurized by a high-pressure pump and preheated in a tin bath heater to the designated temperature. Then, the preheated mixture was fed into an autoclave reactor which contains a certain amount of microcrystalline cellulose powder. Meanwhile, the heater in the reactor was turned on to keep the temperature constant. The thermocouples showed the temperatures of the inlet and interior in the autoclave during the experiment. The reaction time was counted after the inside temperature of the reactor reached the designated temperature. Water-soluble compounds which were produced by hydrolysis left the reactor as aqueous solution and were cooled in a condenser immediately. Samples were then collected. In the present study, the autoclave reactor was preheated to 75–85 °C and alcohol/water mixture at 200–280 °C were supplied.

2.3. Cellulose hydrolysis via hot-compressed alcohol/water mixtures

Microcrystalline cellulose was treated in different hot-compressed alcohol/water mixtures with various mole fractions by using methanol/water, ethanol/water or isopropanol/water as the solvent. Under the concentration of microcrystalline cellulose of 50 kg m^{-3}, mixture volume of 150 mL, reaction time of 35 s, stirring frequency of 10 Hz, and temperatures ranging from 200 to 280 °C, the hydrolysis of cellulose and the yield of RS were investigated. All the experiments were performed in duplicate, with the average value reported.
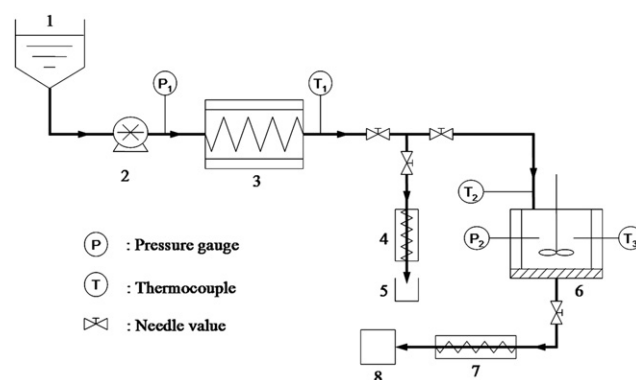

Fig. 1 – Schematic diagram of experimental setup: (1) solvent tank; (2) high-pressure pump; (3) tin bath heater; (4),(7) condenser; (5) waste liquid tank;(6) autoclave reactor; (8) collector.

2.4. Analytical methods

The RS in the liquid samples was determined by DNS color-imetry through an UVmini-1240 UV–visible spectrophotom-eter. The residual solid from the product was separated by filtration (pore size, 15–20 μm), over-dried in an oven at 100 °C, and the original cellulose was dried at 80 °C for 2 h. Then both were analyzed by the US Nicolet 5700 Fourier transform

3. Results and discussion

3.1. Hydrolysis in various alcohol/water mixtures

By selecting methanol, ethanol, and isopropanol as co-solvents, the cellulose hydrolysis in various alcohol/water mixtures were investigated to achieve a high RS yield. The mass fraction yield of RS was calculated with the following Eq. (1):

$$RS\ yield = \frac{the\ concentration\ of\ formed\ glucose \times 0.9 \times the\ dilution\ factor}{the\ concentration\ of\ reactants} \times 100\ \% \tag{1}$$

infrared spectroscopy. The infrared spectra crystallinity index was measured by Nelson and O'Connor (NO'KI) method [29]. $CI = I_{1372\ cm^{-1}}/I_{2900\ cm^{-1}}$, $I_{1372\ cm^{-1}}$ and $I_{2900\ cm^{-1}}$ were the inten-sities of the FT–IR spectrum at wave number of 1372 cm^{-1} and 2900 cm^{-1} respectively, which were determined by a baseline method.

The RS yield in alcohol/water mixtures with alcohol/water volume ratio of 1:3, 1:2, 1:1 and 2:1 was examined respectively. As shown in Fig. 2, the yield of RS increased with the rising of temperature either treated in methanol/water, ethanol/water or isopropanol/water mixtures at certain temperature range. When treated in methanol/water mixture, the maximum
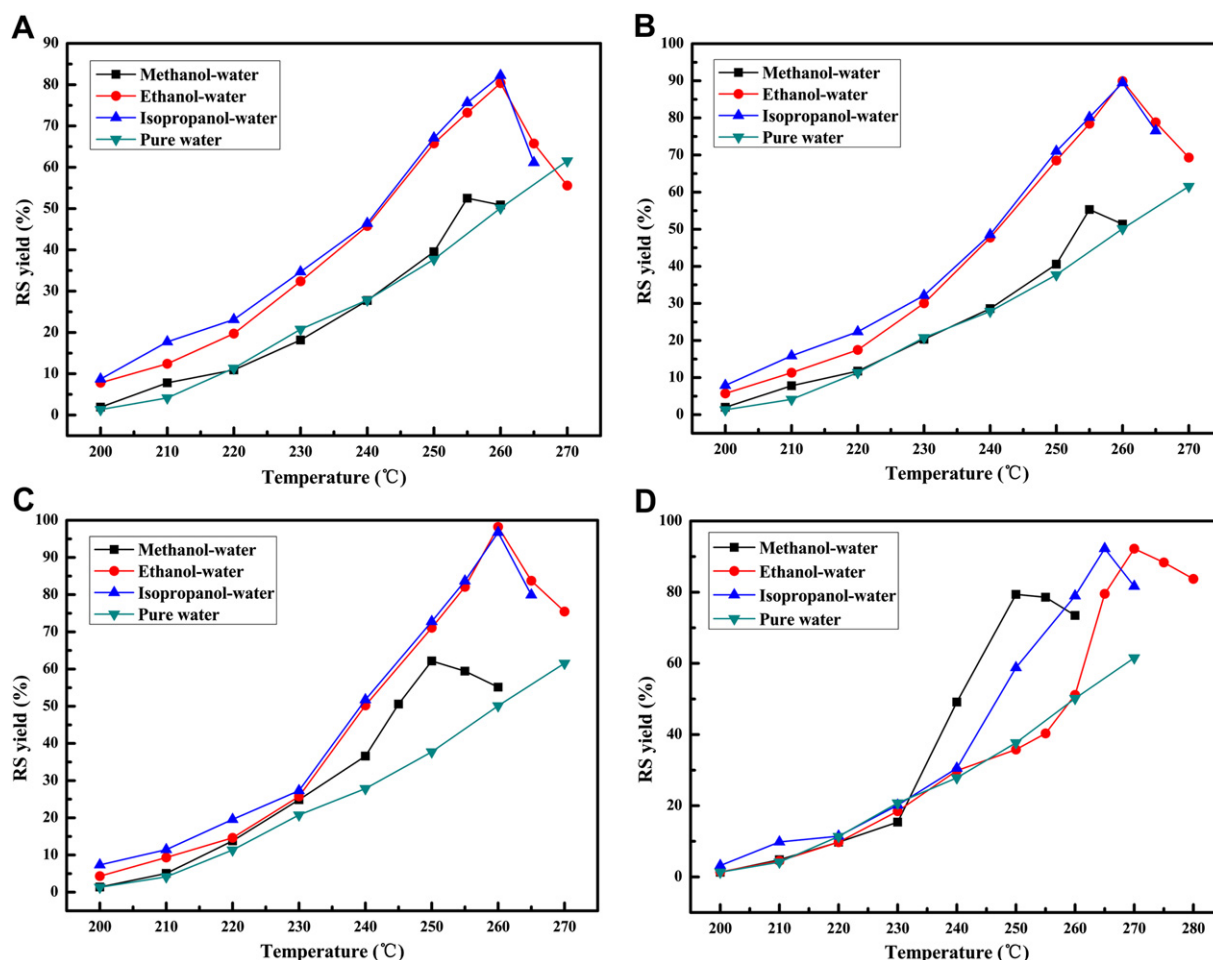

Fig. 2 – Cellulose hydrolysis in different alcohol/water mixtures at various temperatures. (A). Alcohol/water volume ratio of 1:3. The mole fractions were 0.13 (methanol), 0.1 (ethanol) and 0.07 (isopropanol). (B). Alcohol/water volume ratio of 1:2. The mole fractions were 0.18 (methanol), 0.13 (ethanol) and 0.1 (isopropanol). (C). Alcohol/water volume ratio of 1:1. The mole fractions were 0.31 (methanol), 0.22 (ethanol) and 0.19 (isopropanol). (D). Alcohol/water volume ratio of 2:1. The mole fractions were 0.47 (methanol), 0.35 (ethanol) and 0.32 (isopropanol).

sugar yield (79.38%) was obtained with the methanol/water volume ratio being 2:1 (0.47 methanol mole fraction) at 250 °C and thereafter sugar yield decreased with the further increasing of temperature. On the other hand, when treated in ethanol/water mixture, the maximum sugar yield (98.22%) was obtained with the ethanol/water volume ratio being 1:1 (0.22 ethanol mole fraction) at 260 °C and thereafter sugar yield decreased. Similarly, when treated in isopropanol/water mixture, the maximum sugar yield (96.74%) was obtained with the isopropanol/water volume ratio being 1:1 (0.19 isopropanol mole fraction) at 260 °C and thereafter sugar yield decreased. The process of cellulose hydrolysis in pure water was also studied to compare with the corresponding process in alcohol/water mixtures. As indicated in these figures, under the same conditions, the results of cellulose hydrolysis in alcohol/water mixtures were better than that in pure water in terms of the RS yield. The maximum RS yield in ethanol/water mixture was higher than that in methanol/water mixture, and was close to that in isopropanol/water mixture. Since ethanol is cheaper than isopropanol, the former is more suitable as co-solvent for cellulose hydrolysis than the latter, which has

a good agreement with the study of Koell et al. [30] that the highest ratio of lignin/carbohydrate degradation was achieved with ethanol.

As shown in Fig. 2-(D), the curves of three kinds of alcohol/water mixtures parallel-shifted at different temperatures. When treated by three kinds of hot-compressed mixtures with high mole fraction (alcohol/water ratio of 2:1), the increasing of RS yield at low-temperature range was obviously slower than that at high-temperature range due to the decrease of the mixture solubility caused by the increase of alcohol fraction [31–33]. Additionally, the water in these mixtures might be not enough to hydrolyze cellulose because of the abundant alcohol in the mixtures. On the contrary, when the temperature was above 230 °C in methanol/water mixture, above 255 °C in ethanol/water mixture and above 240 °C in isopropanol/water mixture, the RS yield raised rapidly at certain temperature range. Since the raise of the ionization constant of water at high temperature, the hydrogen ions dissociated from water molecules drastically increased, which was conductive to cellulose hydrolysis.
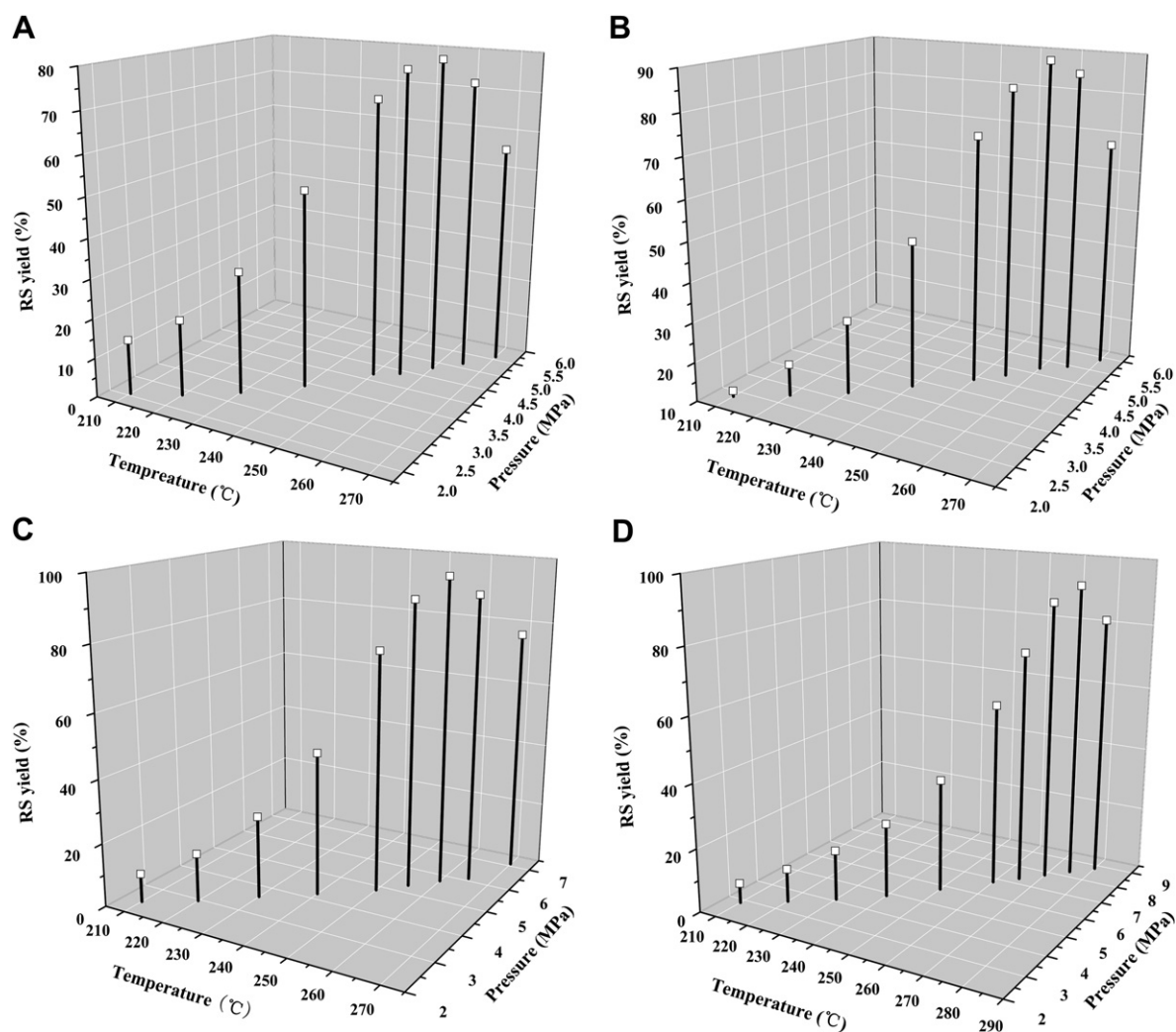

Fig. 3 – The RS yield in ethanol/water mixture. (A) 0.1 mol fraction of ethanol; (B) 0.13 mol fraction of ethanol; (C) 0.22 mol fraction of ethanol; (D) 0.35 mol fraction of ethanol.

The RS could dissolve into alcohol [31,34,35] and the solubility of the as-prepared RS in alcohol was increased with the increasing of temperature. In previous works, our research group has studied the stabilities of glucose in super/subcritical alcohol/water system to lower the requirements of reaction conditions and reduce the degradation of fermentable sugar. We found that the stability of glucose in ethanol/water mixture was better than that in methanol/water mixture and in water, and we also found pressure had little effect on the stability of glucose [36]. Thus the degradation of the as-prepared RS in the alcohol/water mixture could be substantially restrained. When the concentration of alcohol is relatively low, decomposition of RS cannot be avoided as much as possible owing to the insufficient protection of alcohol for the RS molecule. On the other hand, when the concentration of alcohol is high, the solubility of RS in alcohol will decrease, leading to a high degradation.
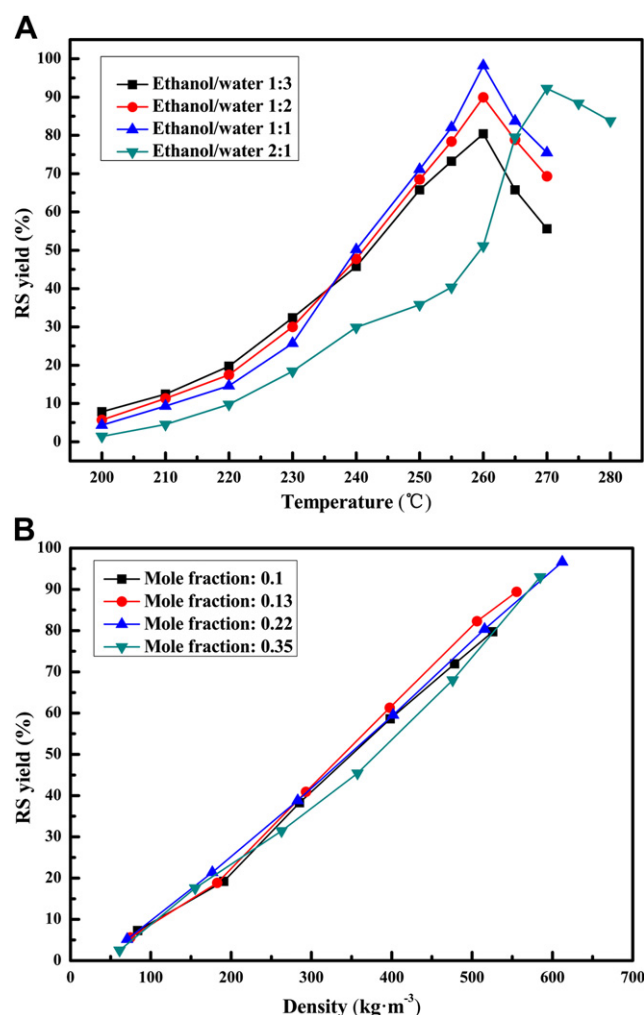
3.2. Hydrolysis of cellulose via hot-compressed ethanol/water mixture

The three-dimensional charts were developed with temperature and pressure as the abscissas and the RS yield as the vertical axis, as shown in the Fig. 3. Then, the effects of temperature and pressure on hydrolysis process in ethanol/water mixture with different mole fractions were investigated. Fig. 3 shows that, with the rising of temperature and pressure, the RS yield increased gradually, and ultimately reached a maximum value. When the temperature continued to rise, the RS yield declined due to the side reactions that RS was decomposed in the high temperature and pressure conditions. The optimal temperature of cellulose hydrolysis in ethanol/water mixture was about 260 °C. 79.56%, 89.40%, 98.22%, 92.70% were the maximum yields of RS in Fig. 3(A)—(D) respectively. Therefore, under the ethanol mole fraction of 0.22, reaction temperature of 260 °C and pressure of 5.75 MPa, the RS yield reached as high as 98.22%, which was higher than the yield of 80% from other reports [15,16].

In the process of cellulose hydrolysis, the changes of solvent property have a significant influence on the RS yield. Density and dielectric constant of the alcohol/water mixtures play a major role in soubilizing organic compounds in alcohol/water treatment. In this experiment, the pressure was changed through temperature controlling. It is well known that each temperature corresponds to a pressure. Meanwhile, a fixed group of pressure and temperature also corresponds to a density. Therefore, density was chosen as a factor, and then, the RS yield from hot-compressed ethanol/water mixture treatment with different density values was researched.

In super/subcritical region, density has a great influence on the solubility of the solvents to the solute. The greater the density of the solvent is, the greater the solubility of the solute will be. In super/subcritical ethanol/water mixture system, small changes of temperature and pressure have influence on the density of the mixture. Bazaev et al. [37] have investigated the density value of ethanol/water mixture with different

Fig. 4 — The effects of mole fraction and density. (A) The yield in ethanol/water mixtures with various volume ratios: 1:3 (0.1 mol fraction), 1:2 (0.13 mol fraction), 1:1 (0.22 mol fraction), 2:1 (0.35 mol fraction); (B) The effect of density on the RS yield in ethanol/water mixture.
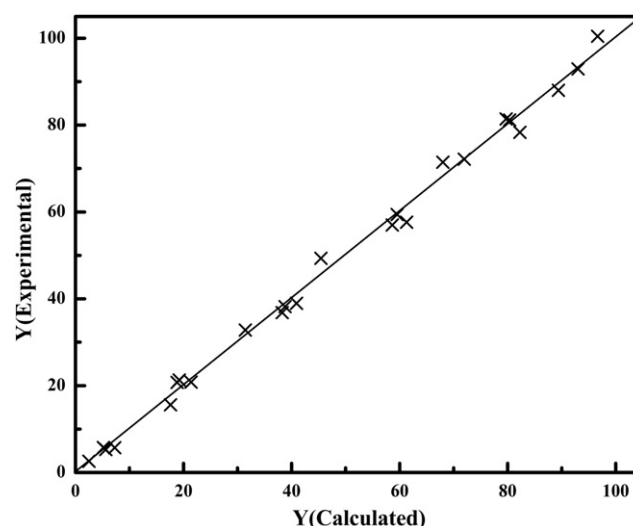

Fig. 5 — Comparison of values between experimental with calculated.
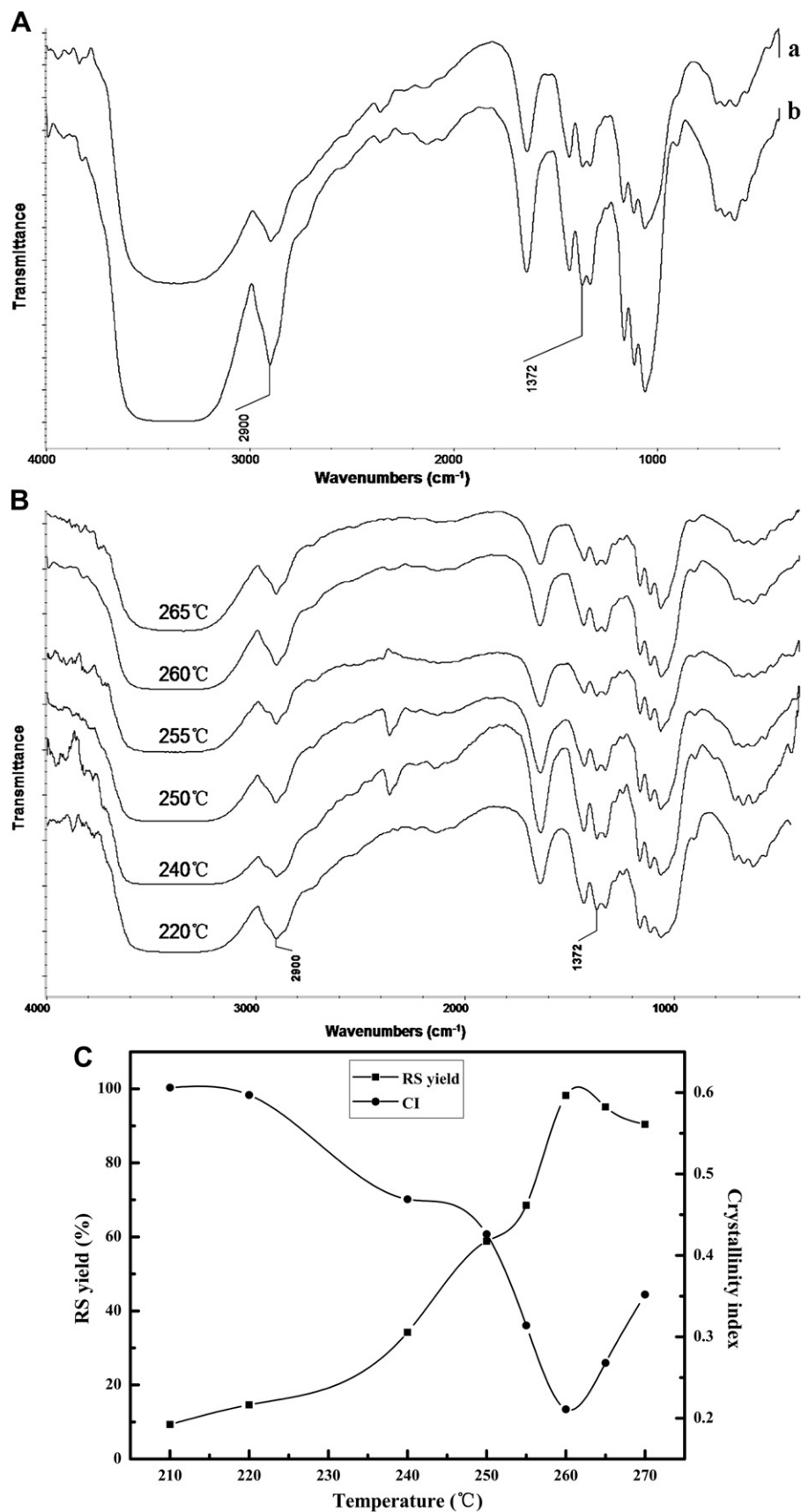
Fig. 6 — The IR results. (A) IR spectra of the original cellulose (a) and the residue (b) treated in ethanol/water of 1:1 (at 260 °C, 5.75 MPa, 35 s, and 10 Hz); (B) FT–IR spectra of the residues as treated by hot-compressed ethanol/water mixture; (C) The relationship between the RS yield and the crystallinity index (CI) of cellulose at various temperatures.

mole fraction at different temperatures and pressures. In this experiment, microcrystalline cellulose was treated in hot-compressed ethanol/water mixture at density range of $60-570$ kg m^{-3}. On the basis of the experimental density values, the other density values have been obtained by regression and simulation, and the effects of the mole fraction and the density on the RS yield have been obtained, as shown in Fig. 4.

From Fig. 4, the influence of the ethanol mole fraction on the RS yield (Fig. 4(A)) was much less than that of the density (Fig. 4(B)), while the density is a function of the mole fraction. Thus, the effect of density on the sugar yield was examined emphatically. Fig. 4(B) shows the density of the ethanol/water mixture in subcritical region has a certain linear relationship with the RS yield from cellulose hydrolysis at a certain mole fraction extent. The greater the density of the solvent mixture is, the greater the extent of cellulose hydrolysis will be, and the higher the yield of RS will be. Based on the above results, a higher density of the ethanol/water mixture would be more conducive to cellulose hydrolysis. As shown in Fig. 4(B), when the mole fraction of ethanol was $0.1-0.35$, the data of RS yield rise almost on an approximated straight line with the increasing of density at the range of $60-570$ kg m^{-3}. Using all the integrated values from our experiments, the regression equation was obtained by least-squares approximation which expresses the relationship between the RS yield and the density as well as the ethanol mole fraction in ethanol/water mixture system.

$$Y = -7.3489 + 52.5791x - 118.9355x^2 + 0.0402\rho^{1.2216} \quad (2)$$

where Y (%) is the RS yield, ρ (kg m^{-3}) is the density of ethanol/water mixture, and x is the amount of ethanol mole fraction in ethanol/water system. The average absolute relative deviation of this equation is 5.346%. Once the equation is determined, the values of the RS yield at each density and mole fraction can be calculated from Eq. (2).

Fig. 5 shows the errors between the experimental RS yield (Y(Experimental)) and the calculated RS yield (Y(Calculated)) obtained from Eq. (2). A 45° auxiliary line was added in the axis to facilitate comparison. If an experimental value was exactly the same with a calculated value, the point would appear on the 45° auxiliary line. From Fig. 5, the errors were relatively small, which indicated that the above regression equation (Eq. (2)) has a high reliability on the result of cellulose hydrolysis in ethanol/water mixture. Eq. (2) also revealed that, when the density of ethanol/water mixture was determined, the equation was a quadratic equation about x.

3.3. Analysis of residue

As shown in Fig. 6(A), the IR spectrum of the residue was more or less the same as that of the original cellulose. The FT—IR graph of the residue (Fig. 6(B)) has shown that the peak intensity in characteristic peaks (1372 cm^{-1}, C—H deformation in cellulose; 2900 cm^{-1}, C—H stretching vibration) almost had not changed with the increasing of temperature at the range of $220-265$ °C. The peak (2335 cm^{-1}) was aroused from the interference of CO_2 in air, which can be ignored. This indicated that, there were no other functional groups formed in the

process of cellulose hydrolysis. Crystallinity index of cellulose at different temperatures was obtained by calculation with a baseline method. As shown in Fig. 6(C), the relationship between the RS yield and the cellulose crystallinity index was correlated. The minimum crystallinity index was 0.211, which indicated that the crystallinity index of cellulose was significantly lower as compare to that of original cellulose (0.618).

Fig. 6(C) shows that there is a certain correspondence between the yield of RS and cellulose crystallinity index, which revealed that the higher the sugar yield is, the higher the degree of cellulose hydrolysis is, and the lower the cellulose crystallinity index is, the higher the degree of decrystallization is.

As treated by hot-compressed ethanol/water mixture, the crystallinity index of cellulose decreased with temperature when the temperature was lower than 260 °C. The minimum crystallinity index of cellulose obtained at 260 °C was 0.211, while the corresponding RS yield (98.22%) was the maximum value, which indicated that 260 °C was the optimal temperature to hydrolyze the cellulose, and the majority of cellulose was decomposed and converted into RS. When the temperature increased over 260 °C, the crystallinity index increased and the RS yield decreased. The reasons of these changes can be speculated into two possibilities. One is that, the char or other possible repolymerization products were formed at higher temperature. The other is that, the surface structure of cellulose particles were changed with the temperature rising and the continuous hydrolyzing even formed a protective cover on the surface to prevent continued hydrolysis of the inside. According to the above possible causes, the reaction temperature was controlled at about 260 °C. Different with other report which indicated that higher temperature about 270 °C was needed to hydrolyze cellulose [38], 260 °C was high enough to hydrolyze cellulose into RS when treated in hot-compressed ethanol/water mixture, which was not only concluded from RS yield but latter FT—IR analysis of residue after treatments. Therefore, a group of lower temperature (260 °C) and pressure (5.75 MPa) was enough to hydrolyzed cellulose efficiently in hot-compressed ethanol/water mixture.

4. Conclusions

In this paper, we conducted the hydrolysis of microcrystalline cellulose in hot-compressed alcohol-water mixtures. Among three kinds of alcohol/water mixtures, the hot-compressed ethanol/water mixture was the most appropriate system to hydrolyze cellulose into RS. The RS yield of cellulose hydrolysis was reached as high as 98.22%, under the optimal conditions of ethanol mole fraction of 0.22, temperature of 260 °C, and pressure of 5.75 MPa. The equation expressed the relationship between the RS yield and the density as well as the ethanol mole fraction in ethanol/water mixture system was proposed. The greater the density of the ethanol/water mixture, the higher the yield of the RS. Hydrolysis of cellulose by ethanol/water mixture cannot only obtain a high yield of RS but also reduce energy consumption, without pollution. This work proposed a green and efficient RS production method.

Acknowledgment

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