Analysis of Hydrolyzates Produced from Cellulose Catalyzed by Carbonaceous Solid Acid in an Ionic Liquid

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The hydrolysis of cellulose using carbonaceous solid acid (CSA) in an ionic liquid was studied. The types and concentrations of products generated during the hydrolysis of the cellulose under different conditions, including temperature, reaction time, water addition, and recycle time, were investigated. The CSA prepared in the study contained 1.45 mmol/g of acidic groups, which was higher than the theoretical amount of sulfonic groups. The highest yields of total reducing sugars (TRS) and glucose were obtained at 5% water content, 6 h of reaction time, and 140 °C. The cellulose was hydrolyzed effectively *via* catalysis of CSA in [AMIM][Cl] with a low water content. Analysis of the products under different conditions in this work provides a strong basis for the full use of hydrolyzed cellulose.

Keywords: Carbonaceous solid acid; Hydrolysis; Cellulose; Ionic liquid

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INTRODUCTION

Biorefineries, which use raw materials including industrial and agricultural waste, urban garbage, and other environmental benign feedstocks instead of fossil fuels, have been receiving increased attention (Cardoen *et al.* 2015; Kamm *et al.* 2016; Papendiek *et al.* 2016). Biorefineries provide fuels and chemicals for use in transportation and various industries, solving some thorny environmental and energy problems at the same time (O'Callaghan 2016; Sadhukhan *et al.* 2016).

Cellulose usually has the dominant content in the lignocellulosic biomass. It is a highly crystalline polymer (Bai *et al.* 2014) connected by β-glycosidic linkages (Rinaldi *et al.* 2008). Suganuma *et al.* (2008) applied a carbon material bearing SO_3H groups to cellulose hydrolysis under hydrothermal conditions, which avoided recovery problems and high energy input of traditional mineral acid catalysts (Namchot *et al.* 2014). The yields of glucose and β-1,4 glucan were 4% and 64%, respectively, while the yields of the experimental group catalyzed by sulfuric acid were 10% and 38% under the same conditions, respectively. Thus, carbon-based solid acid (CSA) can replace mineral acid as the catalyst for the hydrolysis of cellulose; however, further research is needed to enhance the hydrolysis efficiency and yield of desired products.

Glucans consist of more than 30 anhydroglucose units (AGU) and are insoluble in most common solvents (Percival Zhang *et al.* 2006), which hinders cellulose hydrolysis. The ionic liquids can dissolve cellulose effectively due to their anionic and cationic groups. Swatloski *et al.* (2002) firstly reported the dissolution of cellulose in ionic liquid, and consequently, various ionic liquids have been used to depolymerize and hydrolyze cellulose. Hydrolysis of microcrystalline cellulose was examined in an ionic liquid ([BMIM]Cl) with a sulfonated carbon catalyst (Dutta *et al.* 2013; Liu *et al.* 2013; Lian *et al.* 2014). Interesting results were recorded in particular reactions catalyzed by CSA (Guo *et al.* 2012b; Bai *et al.* 2014). Furthermore, the types and contents of chemicals in the hydrolysate should be quantified. There have also been studies producing certain chemicals, especially 5-hydroxymethylfurfural (5-HMF) (Guo *et al.* 2012a; Kang *et al.* 2013); however, different products are generated in the different stages of cellulose hydrolysis, including β-1,4 glucan of a low degree of polymerization (DP), glucose, 5-HMF, formic acid, and levulinic acid (Rinaldi *et al.* 2010). A detailed analysis of the products from different hydrolysis conditions is needed for the full use of hydrolyzed cellulose. Moreover, the ionic liquids are expensive and unrecyclable (Guo *et al.* 2012b). So it makes sense to focus on the hydrolysis of cellulose using CSA in ionic liquids and H_2O.

Based on these reports, the authors have found that the different combinations of CSA and ionic liquid have different effects on cellulose degradation. So the present study analyzed products generated during cellulose hydrolysis catalyzed by CSA in an ionic liquid ([AMIM]Cl) and focused on the variety of products produced under different conditions, including reaction temperature and reaction time. The aim of this work is to analyze the decomposing behaviors of cellulose into cellooligomers, glucose, and 5-HMF which can help to find suitable reaction conditions for various target products. Optimization of 5-HMF and levulinic acid (LA) yield condition in further studies will examine the economic potential of biomass utilization.

EXPERIMENTAL

Materials

The ionic liquid (IL) 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) (99%) was purchased from Cheng Jie Chemical Co. Ltd (Shanghai, China). Glucose, microcrystalline cellulose, and other chemicals were obtained from Maolin Company (Guangzhou, China).

Preparation and Characterization of CSA

Typical preparation of a catalyst includes carbonation and sulfonation. First, 3 g of glucose were heated in a tube furnace under N_2 flow. The temperature was increased by 5 °C/min and then maintained at 400 °C for 1 h. After cooling to room temperature, the inadequately carbonized materials were ground into black powder to create a carbon precursor, and 0.8 g of the carbon precursor were heated in 25 mL of sulfuric acid at 100 °C for 12 h to introduce SO_3H groups. The suspension was filtered and washed repeatedly with boiling distilled water until no sulfate ions were detected in the wash water. The black solid was dried at 105 °C overnight and denoted as CSA.

Structural information for the prepared carbon precursor and CSA was obtained by scanning electron microscopy (SEM; S4800, Hitachi, Tokyo, Japan) at 20.0 kV voltage, powder X-ray diffraction (XRD; X'Pert Pro MPD, PANalytical, Amsterdam, Netherlands) with a scanning step length of 4 °/min in the 20 to 80° 2θ range, Fourier transform infrared spectroscopy (FT-IR; TENSOR27, Bruker, Karlsruhe, Germany) using samples mixed with KBr in a full pellet after grinding, and temperature programmed desorption (TPD; ASIQACIV200-2, Quantachrome, Boynton Beach, USA) spectra analyses, and the heating rate of 10 °C/min, the temperature range was 100 to 600 °C . The composition of the samples was determined by the elemental analysis of C, H, N, S, and O using an elemental analyzer (Vario MICRO cube, Elementar, Hanau, Germany), and the sample decomposition temperature was 1000 °C.

Experimental Procedure and Analytical Methods for Cellulose Hydrolysis

The hydrolysis of cellulose was performed in a 35-mL glass pressure vessel by reacting 0.04 g of catalyst, 0.1 g of cellulose, 2 g of [AMIM][Cl], and a given dose of distilled water. The mixture was heated and stirred in an oil bath at a given reaction temperature. The product samples were diluted with 18 g of deionized water and filtered. The solution was analyzed by high-performance liquid chromatography (HPLC) with a UV detector (2695/2489/2414, Waters, Milford, USA), using a Shodex sugar SH-1011 column. The mobile phase was 5 mmol/L H_2SO_4 at a flow rate of 0.5 mL/min. The analysis was performed at a column temperature of 50 °C. The solid was gathered for further analysis and reuse.

RESULTS AND DISCUSSION

Characterization

SEM images of the raw material at different magnification levels revealed that the glucose particles were loose and irregular, with an average particle size of about 200 μm. After carbonation, the typical structure of the carbon precursor became flexible polycyclic carbon sheets (Suganuma *et al.* 2008), and the surface was easily ground and formed into small particles with an average particle size of approximately 500 nm (Fig. 1A). Hence, the surface area of the catalyst and the ratio of the contact between the catalyst and the substrate were both greatly enlarged.

The XRD patterns for the carbon precursor (Fig. 1B-a) exhibited broad diffraction peaks at a 2θ angle of 10° to 30°, with the center at approximately 20°, which is a reflection of the stacking degree of aromatic carbon sheets. After sulfonation, the plane peak of the CSA (Fig. 1B-b) was more symmetrical than that of the carbon precursor; the center moved to a relative higher 2θ angle of approximately 25°, which corresponds to the planes of the micrographites being randomly oriented. Moreover, a new and weaker diffraction peak at 2θ of 35° to 45° appeared, which was due to the plane of the graphite structure. These changes in the XRD pattern suggested that the carbon precursor was further carbonized during sulfonation and that the crystallite growth of the graphite was underway, which introduced amorphous carbon composed of aromatic carbon sheets.

Typical differences were observed when comparing the two FT-IR spectra of the carbon precursor (Fig. 1C-a) and its corresponding CSA (Fig. 1C-b). First, the relative intensity of the bands near 3300 cm^{-1}, which were assigned to the stretching vibration of O-H, increased appreciably and reflected a large number of residual hydroxyl groups on the CSA after sulfonation. Second, the peaks in the range of 2800 to 3000 cm^{-1}, assigned to C–H stretching, were weakened considerably. A broad band centered at approximately 1600 cm^{-1}, which was assigned to C=O vibration, was also weakened, which further confirmed that the carbonization of glucose had taken place during sulfonation. Interestingly, after sulfonation, some new peaks appeared. The peaks near 1225 and 1042 cm^{-1} were assigned to O=S=O symmetric stretching and $–SO_3H$ stretching, respectively, which suggested that sulfonation had occurred.

After carbonization, both the hydrogen (4.16%) and the oxygen (16.06%) content decreased noticeably compared with glucose; this result indicated that dehydration was the main reaction that occurred. After sulfonation, the sulfur content increased to 3.55% compared with that of the carbon precursor. As the sulfonic group is the only moiety in CSA that contains sulfur, the amount of sulfonic groups was calculated as 1.11 mmol/g. The increase in oxygen (31.37%) content and decrease in hydrogen (3.55%) and carbon (61.53%) contents in the CSA compared with the carbon precursor was attributed to the sulfonation.

Temperature-programmed desorption (TPD) of ammonia showed that the CSA (Fig. 1D) contained 1.45 mmol/g of acidic groups, which was higher than the theoretical amount of sulfonic groups. This result suggested that there were other acidic groups present in the CSA in addition to the sulfonic groups. The TPD profile exhibited peaks at the desorption temperatures of 200 and 400 °C, implying that there were two different acidic groups (sulfonic and carboxyl group) in the CSA (Suganuma *et al.* 2008). Compared with conventional catalysts, which have only one kind of reactive group, a variety of reactive groups in the CSA intensified the contact with the substrate and strengthened the binding. With these physico-chemical properties, the CSA had high catalytic activity for the high yield conversion of cello-oligosaccharides into glucosides.

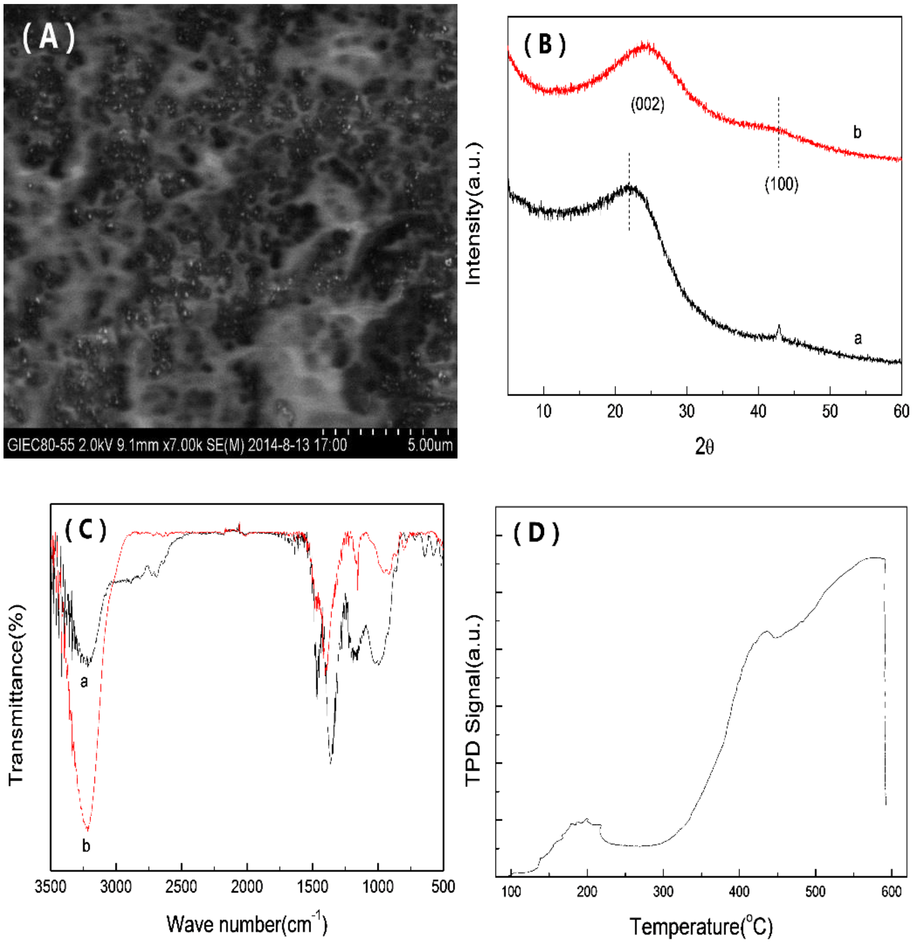

Fig. 1. SEM images, XRD patterns, FT-IR spectrum, and TPD images of the CSA

Stability of CSA and Cellulose in the IL

An experiment was carried out to determine whether the cellulose and the CAS were separately degraded in the ionic liquid *via* a typical hydrolysis reaction at different water contents. The results are shown in Table 1. In the ionic liquid, the CSA was extremely stable, as no small molecular sugars, acids, or other breakdown products were detected. The major product generated from cellulose degradation was 5-HMF at 2.02%, which demonstrated that the ionic liquid itself had little catalytic effect on the degradation of the cellulose; however, the hydrolyzate is commonly glucose (Bai *et al.* 2014). The presence of only 5-HMF, which dehydrated from glucose, reflected that the reaction conditions were a little too severe for cellulose hydrolysis. Thus, the CSA catalytic reaction conditions were further optimized.

Table 1. Hydrolysis of Cellulose in [AMIM][Cl]*

Water Content (wt.%)	5-HMF (mg/mL)	5-HMF Yield (%)
0	0.101	2.02
10%	0.106	2.12
30%	0.124	2.48

*0.1 g cellulose and 2 g of [AMIM][Cl] were reacted at140 °C for 9 h

Effect of Water Addition on TRS Yield

The relationship between reducing sugar yields and water content was investigated (Table 2). The water content of the IL ranged from 0 to 10 wt.%. This range was selected considering the stability of the IL and the solubility of cellulose. A 5% addition of water (based on the mass of IL) gave the highest yield of TRS and glucose. The added water also affected cellulose hydrolysis. Because the hydrolysis products were most likely oligosaccharides and more soluble in aqueous solutions, almost no glucose degradation products were observed. Formation of degraded glucose products during hydrolysis was inhibited by the water addition. The reaction system almost stopped when the water content increased to 10%; therefore, a water content of 5% was used in subsequent experiments.

Table 2. Effect of Water Addition on TRS Yield Obtained by Cellulose Hydrolysis Catalyzed with CSA in [AMIM][Cl]*

Water Content (wt.%)	Cellobiose (mg/mL)	Glucose (mg/mL)
1%	0.114	0.107
3%	0.041	0.017
5%	0.169	0.214
7%	0.101	0.111
10%	0.038	0.012

*0.1 g of cellulose, 2 g of [AMIM][Cl] and 0.04 g of CSA were reacted at 140 °C for 9 h

Effect of Catalyst Dosage on TRS Yield

Table 3 shows the effect of catalyst dosage on the TRS and glucose yields at the optimum temperature (140 °C). A certain amount of catalyst was needed to facilitate the formation of the reducing sugar (glucose). The yield of cellobiose increased from 0.183 to 0.199% as the catalyst dosage increased from 4:5 to 12:5. The increase in catalyst dosage decreased the yield of glucose from 0.215 to 0.171 mg/mL, which may reflect accelerated degradation of formed glucose caused by excess active sites in the catalytic reaction. Therefore, the ratio of 4:5 of catalyst/cellulose was used in subsequent experiments.

Table 3. Effect of Catalyst Dosage on TRS Yield Obtained by Cellulose Hydrolysis Catalyzed with CSA in [AMIM][Cl]*

CSA/Cellulose	Cellobiose (mg/mL)	Glucose (mg/mL)
4:5	0.183	0.215
6:5	0.176	0.203
8:5	0.188	0.182
2:1	0.187	0.183
12:5	0.199	0.171

*0.1 g of cellulose, 0.01 g of water, and 2 g of [AMIM][Cl]

Effect of Reaction Time

The effect of reaction time on cellulose hydrolysis was studied at the duration of 3 h, 4 h, 5 h, 6 h, and 7 h for the different test groups. As shown in Fig. 2a, cellobiose had a lower concentration than glucose in the hydrolysis solution. The cellobiose content increased until a reaction time of 5 h, and then decreased gradually.

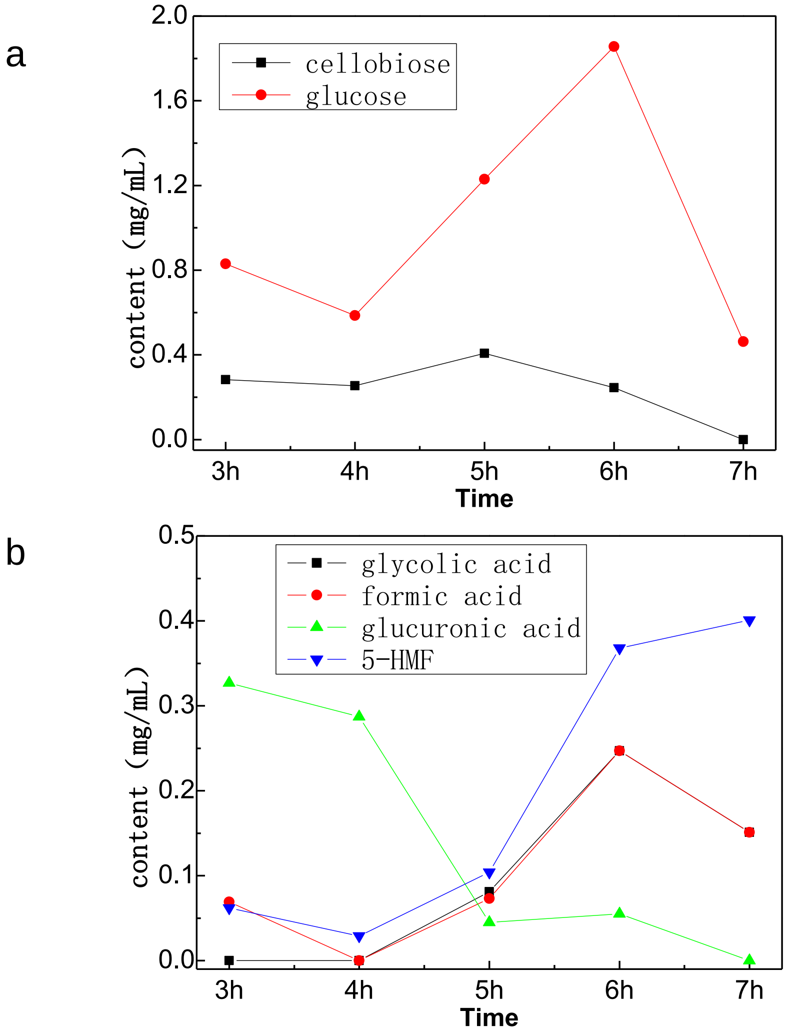

Fig. 2. The effect of reaction time on the products of cellulose hydrolysis catalyzed with CSA in [AMIM][Cl] (0.1 g cellulose, 0.01 g water, 2 g [AMIM][Cl], and 0.04 g CSA). a) trends in sugar content; b) trends in 5-HMF and other small molecule products

The concentration of glucose decreased from 3 h to 4 h and then increased until a peak at 6 h. For the glucose degradation by-products, glucuronic acid was the only product that decreased with reaction time. The contents of 5-HMF, glycolic acid, and formic acid had remarkable increases after 5 h. Glycolic acid and formic acid reached a peak at 6 h, while 5-HMF continued to increase until 7 h (Fig. 2b).

The main reason for the observed changes in glucose concentration was the fact that during the first 3 h the main reaction taking place was the rapid degradation of the short chain polysaccharides in the substrate. Thereafter, the cellulose, which is more stable and has a high degree of polymerization, began to degrade at 5 h, obscuring the trend of monosaccharide degradation. Thus, glucuronic acid, being a direct heterogeneous product from glucose, was generated at a relatively high concentration at the beginning of the reaction. As hydrolysis continued, further heterogeneous hydrolyzates were formed, including 5-HMF and small molecular weight acids, mainly formic acid and glycolic acid. In the early stage of the reaction, the reaction equilibrium favored the production of glucuronic acid. At the midpoint of the reaction at about 4 h, with early glucose being exhausted by decomposition, the glucuronic acid was converted to small molecule metabolites and accounted for a noticeable amount in the solution. In the latter part of the reaction from 5 h to 6 h, only 5-HMF and small molecular weight acids showed markedly increased concentration, while the initial hydrolyzates of the cellulose showed a noticeable reduction.

Table 4. Effect of Reaction Temperature Obtained by Cellulose Hydrolysis Catalyzed with CSA in [AMIM][Cl]*

T (°C)	Cellobiose (mg/mL)	Glucose (mg/mL)	Glucuronic Acid (mg/mL)	5-HMF (mg/mL)	Glycolic Acid (mg/mL)	Formic Acid (mg/mL)
120	0.125	0.222	-	-	-	-
140	0.402	1.735	0.055	0.095	0.186	0.102
160	-	0.496	-	-	0.146	0.251

*0.1 g of cellulose, 0.01 g of water, 2 g of [AMIM][Cl], 0.04 g of CSA

Effect of Reaction Temperature

The experiments were conducted at 80 °C to 160 °C. When the temperature was maintained at 80 °C to 100 °C, no hydrolyzed cellulose product was detected. With increased temperature, there was enhanced hydrolysis, and a glucose yield of 46.02% was attained at 140 °C. As the temperature continued to increase, the rate of glucose decomposition increased, and its content in the solution reduced remarkably. This result illustrated that in the present reaction system, 140 °C is the ideal reaction temperature for glucose production *via* cellulose hydrolysis.

Recycling of the Catalyst

The recyclability of a catalyst is important in industrial applications. After the first reaction in the oil bath, the mixture was cooled to room temperature and centrifuged to separate the lipid phase from the IL. The solid residue, which contained the catalyst and the cellulose, was recovered from the hydrolytic solution by filtration and then washed with hot water. After drying, the catalyst was used in the next experiment under identical conditions. As shown in Fig. 2, the recycling process was repeated three times. The reducing sugar yield was about 72.2%, 65.7%, and 53.7% in the first, second, and third recycling cycles, respectively. The yield of glucose products was 21.8%, 21.2%, and 18.5% in the three cycles, respectively. The decrease in reducing sugar (glucose) yield was probably due to the reduction of $–SO_3H$ groups during filtration and washing. Compared with many other solid acid catalysts, the recyclability of the catalyst used in this work was relatively low (Table 5).

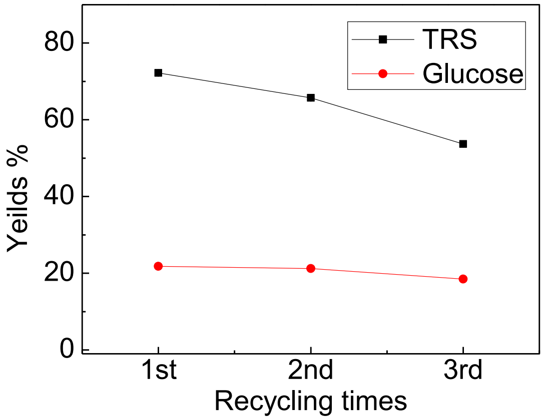

Fig. 3. The effect of water addition on TRS yield obtained by cellulose hydrolysis catalyzed with CSA in [AMIM][Cl] (0.1 g of cellulose, 0.01 g of water, 2 g of [AMIM][Cl], and 0.04 g of CSA)

Table 5. Effect of Recycling time Obtained by Cellulose Hydrolysis Catalyzed with various Solid Acid Catalysts

Catalysts	Solvent	TRS yield (%)			References
		Fresh catalyst	First recycling	Second recycling	
$GC-SO_3H$	[BMIM]Cl	72.7%	61.0%	58.5%	Guo *et al.* 2012b
$SC-SO_3H$	[BMIM]Cl	80.0%	72.0%	-	Liu *et al.* 2013
$CoFe_2O_4/SiO_2-SO_3H$	H_2O	63.0%	59.0%	50.0%	Takagaki *et al.* 2012
CSA	[AMIM][Cl]/H_2O	72.2%	65.7%	53.7%	This work

CONCLUSIONS

1. Cellulose and carbonaceous solid acid (CSA) prepared by carbonization and sulfonation of glucose were both stable in ionic liquid, with or without water. Cellulose was hydrolyzed and effectively catalyzed by CSA in [AMIM][Cl] with a low water content. The best conditions for hydrolysis reaction were 5% water content, 6 h of reaction time and 140 °C as reaction temperature.
2. The catalyst dosage positively affected the hydrolysis of glucose, but at a certain level, it reduced the yields of TRS and glucose. The ratio of 4:5 of catalyst/cellulose was the optimum condition in experiments.

3. The reaction temperature and duration time had great effects on the yields of different products, depending on the equilibrium between cellulose hydrolysis and glucose decomposition.

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