

## Comparison of catalytic hydrolysis of bagasse cellulose under heterogeneous and homogeneous systems

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**ABSTRACT:** The conversion of cellulose into valuable chemicals has attracted a great deal of interest. In this study, heterogeneous and homogeneous systems in the conversion of bagasse cellulose into the total reducing sugars were investigated. In the heterogeneous system, the effects of several critical factors including types and concentrations of ionic liquid, temperature, and time were all investigated for cellulosic conversion. Parameters considered included temperature, dosage of catalyst, and water in the homogeneous system. It was found that the hydrolysis capacity for cellulose in homogeneous system was better than that in heterogeneous system. In addition, the structure and physicochemical properties of the treated cellulose were characterized by Fourier transform infrared spectroscopy, thermogravimetry, and scanning electron microscopy, and then compared with the native fibers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42228.

**KEYWORDS:** cellulose and other wood products; degradation; ionic liquids; properties and characterization

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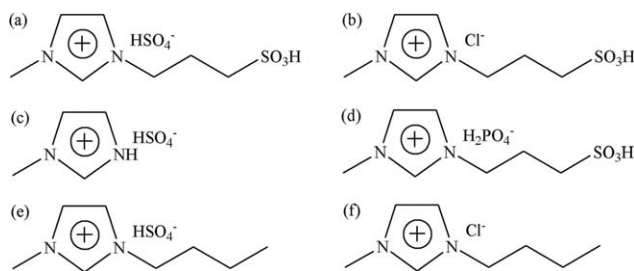
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### INTRODUCTION

As the most abundant renewable biopolymer found on the Earth, cellulose has been widely used due to its fascinating structure and promising properties such as biocompatibility, hydrophilicity, good biodegradability, inexpensive, and low toxicity.<sup>1,2</sup> Many biomass materials contain higher cellulose, like bagasse, which is a rich source of cellulose (45–55%), hemicellulose (20–25%), and lignin (18–24%). It is well known that the high proportion of cellulose in bagasse provides an ideal opportunity for producing value-added products. So far, there is a great deal of methods, mainly including enzymatic hydrolysis,<sup>3,4</sup> acid-catalyzed hydrolysis,<sup>5,6</sup> and hydrolysis in supercritical water,<sup>7</sup> which have been devoted to degradation of cellulose. Enzymatic process is effective and highly selective, but the enzymes are expensive and the system is sensitive to operation conditions such as temperature, pH, and presence of some inhibitors. Mineral acids and solid acids have been used as catalysts for the acid-catalyzed hydrolysis of cellulose. Mineral acid catalysis technologies have been extensively applied in cellulose hydrolysis and are still used at industrial scale.<sup>8</sup> However, it suffers from serious corrosion hazard, energy inefficiency, environmental problems, and the separation of products and catalysts. Recently, solid acid catalysis due to it can be easily separated and recycled from the liquid reaction system; much attention is being attracted in cellulose conversion. Nevertheless, the existing transfer resistance between solid acid and insoluble or partially

soluble cellulose should be taken into account.<sup>9</sup> Cellulose hydrolysis in supercritical water shows some fascinating advantages, such as catalyst requirement and an acceptable high reaction rate, yet it was conducted under rather high pressure and temperature together with special equipments.

In recent years, ionic liquids (ILs) have got a great deal of attention and have been utilized as solvent or catalyst for the conversion of saccharides into valuable chemicals. In 2002, Rogers *et al.*<sup>10</sup> reported that cellulose could be dissolved in ILs at a certain temperature. Since then, the discovery opened a new pathway to deal with cellulose. In 2009, Zhang *et al.* discovered that a pair of metal chlorides (CuCl<sub>2</sub> and CrCl<sub>2</sub>) in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) can efficiently catalyze cellulose to 5-hydroxymethylfurfural (HMF).<sup>11</sup> Then the group<sup>12</sup> investigated the hydrolysis of cellulose in [Emim]Cl combined with CuCl<sub>2</sub>/PdCl<sub>2</sub> catalyst system. Chou and co-workers<sup>13</sup> developed an effective route involving CoSO<sub>4</sub> and the IL 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate ([C<sub>4</sub>SO<sub>3</sub>Hmim]HSO<sub>4</sub>) as catalyst for the hydrolysis of microcrystalline cellulose (MCC). Then the group<sup>14</sup> discussed HMF and furfural produced from MCC in a series of SO<sub>3</sub>H-functionalized acidic ILs, and the result showed that MnCl<sub>2</sub>-containing IL was efficient and selective for the production of HMF. However, to the best of our knowledge, these works always focus on the addition of various kinds of catalysts in IL systems for cellulose hydrolysis; very few papers discussed the effects of reaction



**Figure 1.** Ionic liquids used in this study: (a)  $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4^-$ , (b)  $[\text{C}_3\text{SO}_3\text{Hmim}]\text{Cl}$ , (c)  $[\text{Hmim}]\text{HSO}_4^-$ , (d)  $[\text{C}_3\text{SO}_3\text{Hmim}]\text{H}_2\text{PO}_4^-$ , (e)  $[\text{Bmim}]\text{HSO}_4^-$ , (f)  $[\text{Bmim}]\text{Cl}$ .

conditions and the existence form of cellulose on the conversion efficiency in ILs without other catalyst. In fact, the hydrolysis products still could be produced when using ILs only (no other additives) although the yields were relatively low. This indicates that ILs serve not only as solvent but also as catalyst in these systems. In addition, water displays a negative effect on the dissolution of cellulose in ILs. Therefore, the content of water is closely related to the existence form of cellulose in IL. Consequently, it was believed that the existence form of cellulose in ILs and reaction conditions are very important and fundamental in the initial stage of cellulosic conversion.

In this study, a comparison of catalytic hydrolysis of bagasse cellulose into the total reducing sugars (TRS) under heterogeneous and homogeneous systems was investigated. In the homogeneous system, cellulose dissolves in ILs existed in the form of molecular state. Herein we studied the effects of several critical factors such as reaction temperatures, the dosage of catalyst, and the amount of water on the production of TRS. In contrast, in the heterogeneous system, cellulose exists as the form of its inherent solid state. The main factors influencing the conversion efficiency of cellulose were examined, involving the type and concentrations of ILs, the hydrolysis temperature, and time. This implies meaningful information for the further research and application of ILs in the field of cellulose materials.

## EXPERIMENTAL

### Materials

Sugarcane bagasse investigated in this study was obtained from a local sugar factory. After being dried, it was cut into small pieces (1–3 cm). Then the cut bagasse was dewaxed and ground in a high-speed rotary cutting mill passing through 40 mesh (<0.380-mm-size screen). The passing fraction was selected for subsequent extraction of cellulose. The cellulose used in this study was prepared according to our previous work.<sup>2</sup> The procedure of cellulose preparation was as follows. The dried and ground bagasse was suffered with 7% (w/w) sodium hydroxide solution (fiber-to-liquor ratio of 1 : 40) at 70°C for 8 h. Then the residue was subsequently bleached with sodium hydroxide/hydrogen peroxide mixture to remove residual lignin and hemicelluloses. The resulting cellulosic materials were washed repeatedly with distilled water, dried, and weighed. Then the cellulose fibers were ground in a pulverizing mill and further sieved through a 40–100 mesh sieve. Powdered celluloses (40–100 mesh) were kept at 40°C in a vacuum oven for 24 h.

The structures of ILs used for this study are displayed in Figure 1 and their purities are all above 97%. To remove the coexisting water in the ILs, the ILs have been kept in the vacuum drying oven at 50°C for 24 h before use. All other chemical reagents were analytical grade or higher in purity, purchased from commercial sources in China.

### The Procedure for Hydrolysis of Cellulose into TRS

In the homogeneous catalytic experiment, bagasse cellulose (50 mg) was added into 2.0 g 1-butyl-3-methylimidazolium chloride ( $[\text{Bmim}]\text{Cl}$ ) that was preheated under vigorous stirring at 100°C to form a transparent solution. Followed by the addition of a certain amount of the acidic IL 1-propyl sulfonic acid-3-methylimidazolium hydrogen sulfate ( $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4^-$ ) and water, the mixture was stirred at different temperatures for a certain time. After reaction, the sample was quenched and cooled down immediately by adding some of ultrapure water. The supernatant was subjected to TRS analysis.

Similarly, the cellulose hydrolysis in the heterogeneous system was carried out without the  $[\text{Bmim}]\text{Cl}$  solvent. Typically, bagasse cellulose, acid IL catalyst solution, and 4-methyl-2-pentanone (MIBK) were placed into a vial in sequence. The reaction was then vigorously stirred at a given temperature for a certain time. After the reaction was completed, the reactor was quickly quenched in a cool water bath. Then the mixture was subjected to filtration, and the fraction of aqueous phase was subjected to TRS analysis.

### Analysis Method

The amount of TRS was measured using phenol–sulfuric acid method.<sup>14</sup> A mixture containing 0.2 mL supernatant, 1.8 mL distilled water, 1 mL 5% phenol, and 5 mL 98% concentrated sulfuric acid was prepared. Then the absorbance was measured at 490 nm using UV–vis spectrophotometer. The concentration of TRS was calculated based on the standard curve obtained with glucose.

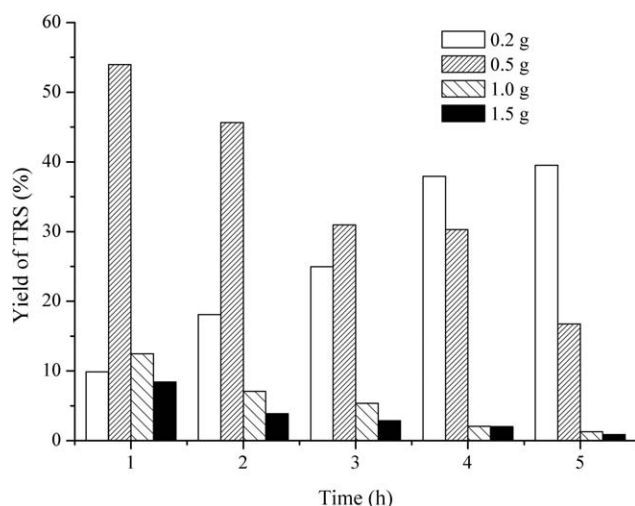
### Cellulose Characterization

The structure and physicochemical properties of the treated cellulose were characterized by L1600300 Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer, USA, KBr disk), 209-F3 thermogravimetric analysis (TG, Tarsus, Germany, ramped up from 30 to 800°C at 10°C/min), and JSM-7500F scanning electron microscopy (SEM, JEOL, Japan, coated with gold).

## RESULTS AND DISCUSSION

### Hydrolysis of Cellulose in Homogeneous System

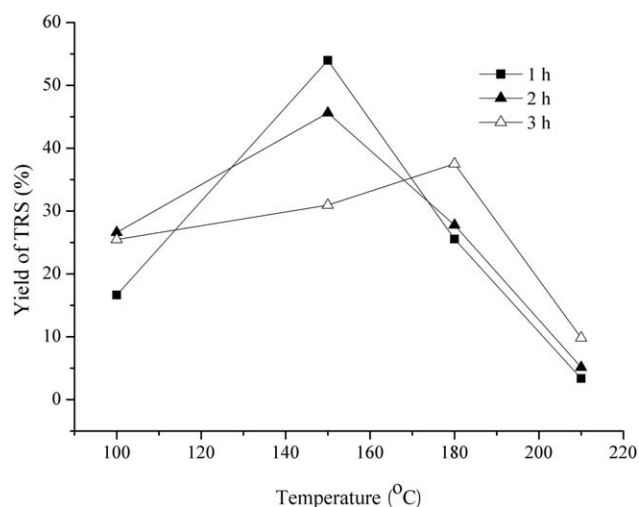
**Effect of the Catalyst Dosage.** The effect of acidic IL dosage on the hydrolysis of cellulose into TRS cannot be ignored. In this study, the influence of catalyst dosage with respect to cellulose conversion into TRS in  $[\text{Bmim}]\text{Cl}$  was investigated and the results are shown in Figure 2. The investigated amounts of catalyst ( $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4^-$ ) were 0.2, 0.5, 1.0, and 1.5 g. It could be seen from Figure 2 that increasing the catalyst loading from 0.2 to 0.5 g led to an obvious increase in yield of TRS, from 9.9 to 54.0% in 1 h. However, when the amount increased from 0.5 to 1.5 g, the TRS yield decreased remarkably. It also displays that with the reaction time getting longer, the difference of TRS yield becomes smaller. This phenomenon could be attributed to



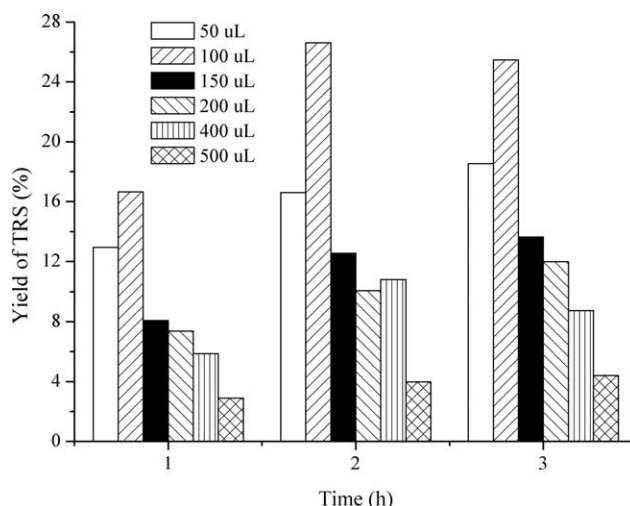
**Figure 2.** Effect of catalyst dosage on the bagasse cellulose conversion into TRS (cellulose 50 mg, [Bmim]Cl 2 g, H<sub>2</sub>O 0.1 mL, temperature 150°C).

that more catalyst accelerated the formation of TRS from cellulose while it also favored the degradation of TRS.<sup>15</sup> Therefore, 0.5 g of catalyst was more reasonable for subsequent experiments.

**Effect of the Reaction Temperature.** Experiments were conducted at 100, 150, 180, and 210°C to consider the effect of reaction temperature on the hydrolysis of cellulose into TRS. The results are shown in Figure 3. It can be seen that reaction temperature had a great effect on the formation of TRS. As reaction temperature was increased to 150°C, the yield of the TRS increased distinctly in 1 h. It was hypothesized that higher reaction temperature would increase [H<sup>+</sup>] from H<sub>2</sub>O and assist the hydrolysis of cellulose to TRS.<sup>16</sup> With the increasing temperature, the yield of TRS declined, which was due to that higher temperature gives rise to the dehydration of glucose.<sup>15</sup> Thus, there is no doubt that reaction temperature has a great effect



**Figure 3.** Effect of reaction temperature on the bagasse cellulose conversion into TRS (cellulose 50 mg, [Bmim]Cl 2 g, [C<sub>3</sub>SO<sub>3</sub>Hmim]HSO<sub>4</sub> 0.5 g, H<sub>2</sub>O 0.1 mL).



**Figure 4.** Effect of H<sub>2</sub>O on the bagasse cellulose conversion into TRS.

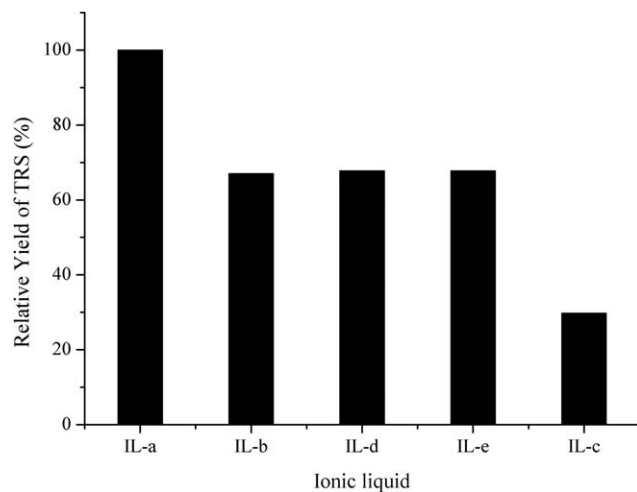
on the hydrolysis of cellulose into TRS and the dehydration of glucose.

**Effect of the Amount of H<sub>2</sub>O.** The amount of water is a critical issue because water acts both as a reactant (for producing monosaccharides) and an inhibitor (for producing HMF) in the overall cellulosic conversion.<sup>16</sup> In fact, it is well known that water displays a negative effect on the dissolution of cellulose in ILs.<sup>17</sup> This indicates that the content of water is closely related to the existence form of cellulose in IL. Consequently, it was believed that the existence form of cellulose in ILs is a very important and fundamental work in the initial stage of cellulosic conversion.

In this study, it was found that the content of water in system had a great effect on the hydrolysis of cellulose. As shown in Figure 4, it is interesting to note that when the amount of water was over 100 μL, the TRS yield declined sharply. It indicated that slight amount of water promoted the hydrolysis of cellulose to TRS. However, with the increasing of water added in [Bmim]Cl, water would impair the cellulose dissolution in [Bmim]Cl by forming competitive hydrogen bonding to the cellulose hydroxyl groups. It could be attributed to the transformation of reaction system from a homogeneous catalytic process to a heterogeneous one. When the amount of water added increased to 500 μL, only 3% TRS yield was obtained. Therefore, the water in reaction system has a significant effect on the hydrolysis of cellulose into TRS.

#### Hydrolysis of Cellulose in Heterogeneous System

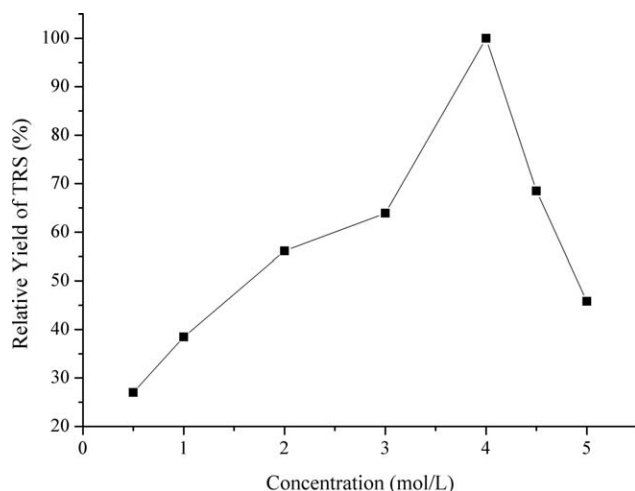
**Effect of the Types of IL.** In this study, the performance of the heterogeneous reaction system was first conducted to compare the reactivity with the previous homogeneous system. As a result, it is obvious that the hydrolysis in heterogeneous reaction system without [Bmim]Cl showed a remarkably poor activity. However, the acidity and structure of ILs are among the most important factors in the hydrolysis of cellulose. The acidic liquids used in the heterogeneous reaction system involved three kinds of cations and three kinds of anions. The performance of the selected ILs was compared under the same conditions. As seen in Figure 5, [C<sub>3</sub>SO<sub>3</sub>Hmim]HSO<sub>4</sub> performed steadily well



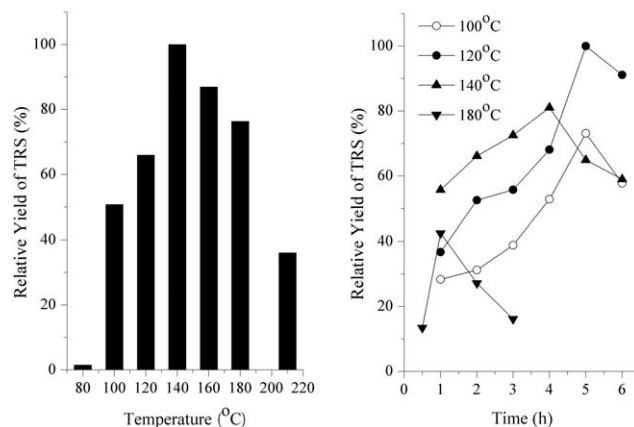
**Figure 5.** The effect of ionic liquids type on the bagasse cellulose conversion into TRS (relative to the base peak taken as 100%).

among these ILs. However, the IL [Hmim]HSO<sub>4</sub> showed a remarkably poor activity perhaps because of its relatively weak acidity. Moreover, compared with other anions (Cl<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>), HSO<sub>4</sub><sup>-</sup> could achieve a better performance. It was attributed to more active acid sites accelerating the fracture of glycosidic bonds. Collectively, for the acidic ILs used in our study, the results suggest that strong acidity and structure of ILs are important in promoting the fracture of glycosidic bond of cellulose.<sup>18</sup>

**Effect of the Concentration of IL.** In order to investigate the impact of the concentration of IL in cellulose hydrolysis, IL concentrations were set in the range of 0.5–5 mol/L. Figure 6 illustrates that the yield of TRS increased clearly when the concentration changed from 0.5 to 4 mol/L. However, it decreased when the concentration went up to 5 mol/L. A low concentration could lead to a slow hydrolysis rate and low yield of TRS, and higher concentration could increase the viscosity of reaction, thus, affect the yield of TRS due to the increasing mass



**Figure 6.** The effect of ionic liquid concentration on the bagasse cellulose conversion into TRS (relative to the base peak taken as 100%).



**Figure 7.** The effect of temperature and time on the bagasse cellulose conversion into TRS (relative to the base peak taken as 100%).

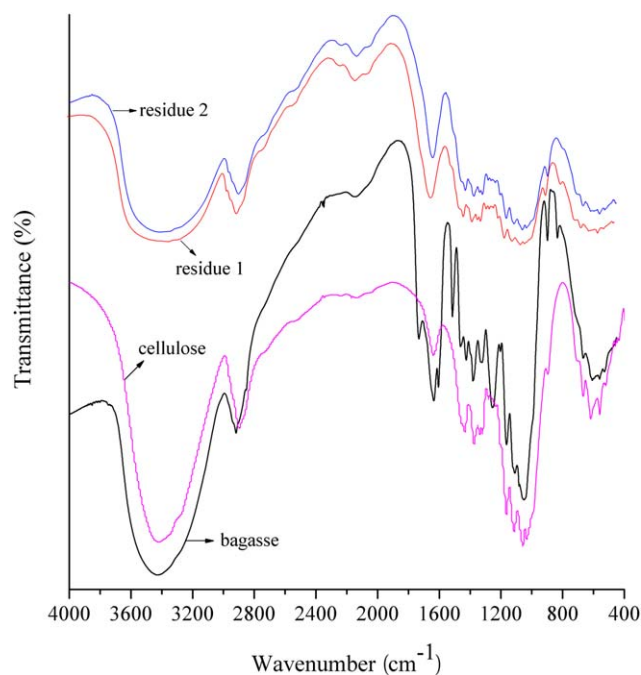
transfer resistance. Therefore, there is no doubt that IL concentration has a great effect on the hydrolysis of cellulose.

**Effect of the Reaction Temperature and Reaction Time.** The effects of process parameters such as reaction temperature and time were also intensively investigated. The results, listed in Figure 7, show that the hydrolysis process is very temperature dependent. The yield of TRS increased sharply when the reaction temperature was elevated from 80 to 140°C. It then decreased rapidly when the temperature was further increased to 210°C. Higher reaction temperature would increase [H<sup>+</sup>] from H<sub>2</sub>O and assist the hydrolysis of cellulose to TRS.<sup>16</sup> Chen and co-workers have also reported that the temperature influenced the *K<sub>w</sub>* in the [Emim]Cl/H<sub>2</sub>O system.<sup>19</sup> Nevertheless, too high temperature gives rise to the decomposition of TRS. Therefore, exploration of an optimal reaction temperature is highly demanded.

The same trend can also be observed by varying the reaction time. As time increased, it was found that the TRS yield reached a peak and then started to fall. It is reasonable that the increase of TRS within a short time was resulted from the degradation of cellulose. However, TRS yield also decreased with prolonged time. We supposed that this was due to the decomposition of TRS to other byproducts. It was examined about the possible byproducts such as furfural and 5-hydroxymethylfurfural. Figure 7 also shows that a decreased TRS yield appeared earlier at higher temperature. Conclusively, the decrease in TRS yield with elevated temperature and prolonged time can be attributed to the decomposition of TRS.

### Characterization of the Cellulose

**FTIR Analysis.** In the FTIR analysis, the spectra of sugarcane bagasse, native cellulose, and treated cellulose—i.e., homogeneous catalytic hydrolyzed cellulose (residue 1) and heterogeneous catalytic hydrolyzed cellulose (residue 2)—are shown in Figure 8. The peaks centered at 1732 cm<sup>-1</sup> in the FT-IR spectrum of ground sugarcane bagasse is associated with the C=O stretching vibration of hemicelluloses.<sup>20</sup> Peaks at 1601, 1515, and 1461 cm<sup>-1</sup> are predominantly attributed to the aromatic skeleton vibrations of lignin. The peak at 1256 cm<sup>-1</sup> that is present only in the spectrum of bagasse indicates the C—O out-of-plane



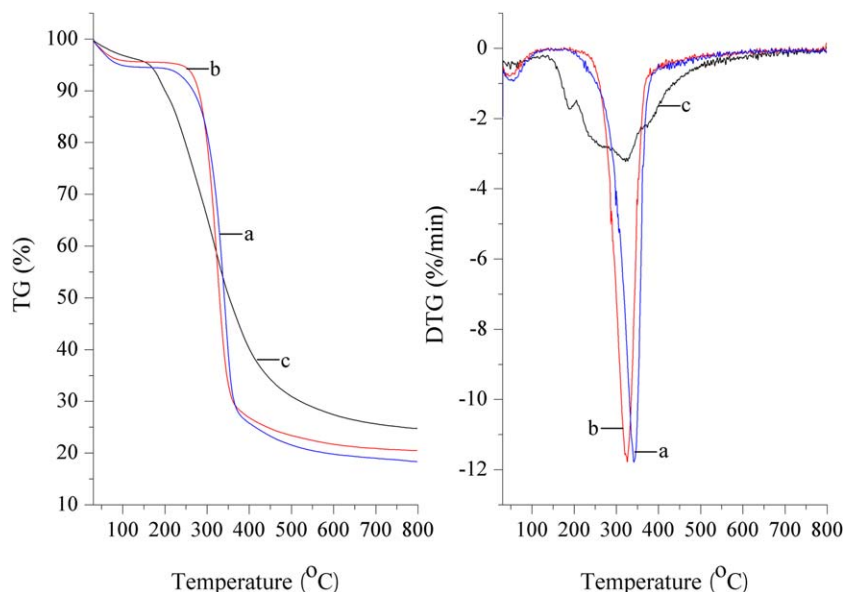
**Figure 8.** FTIR spectra of untreated bagasse, cellulose, and residues. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

stretching vibration of the aryl group in lignin.<sup>21</sup> Aromatic C—H out of bending occurs at  $824\text{ cm}^{-1}$ .<sup>20</sup> All these characteristic peaks of hemicellulose and lignin have thoroughly disappeared in the spectrum of isolated cellulose. These peaks are also absent in the homogeneous and heterogeneous catalytic hydrolyzed cellulose (residue 1 and residue 2). The spectra of residue 1 and residue 2 resemble that of native cellulose. However, compared to the native cellulose, residue 1 and residue 2 have obvious shrinking at peak  $1060\text{ cm}^{-1}$  (C—O—C pyranose

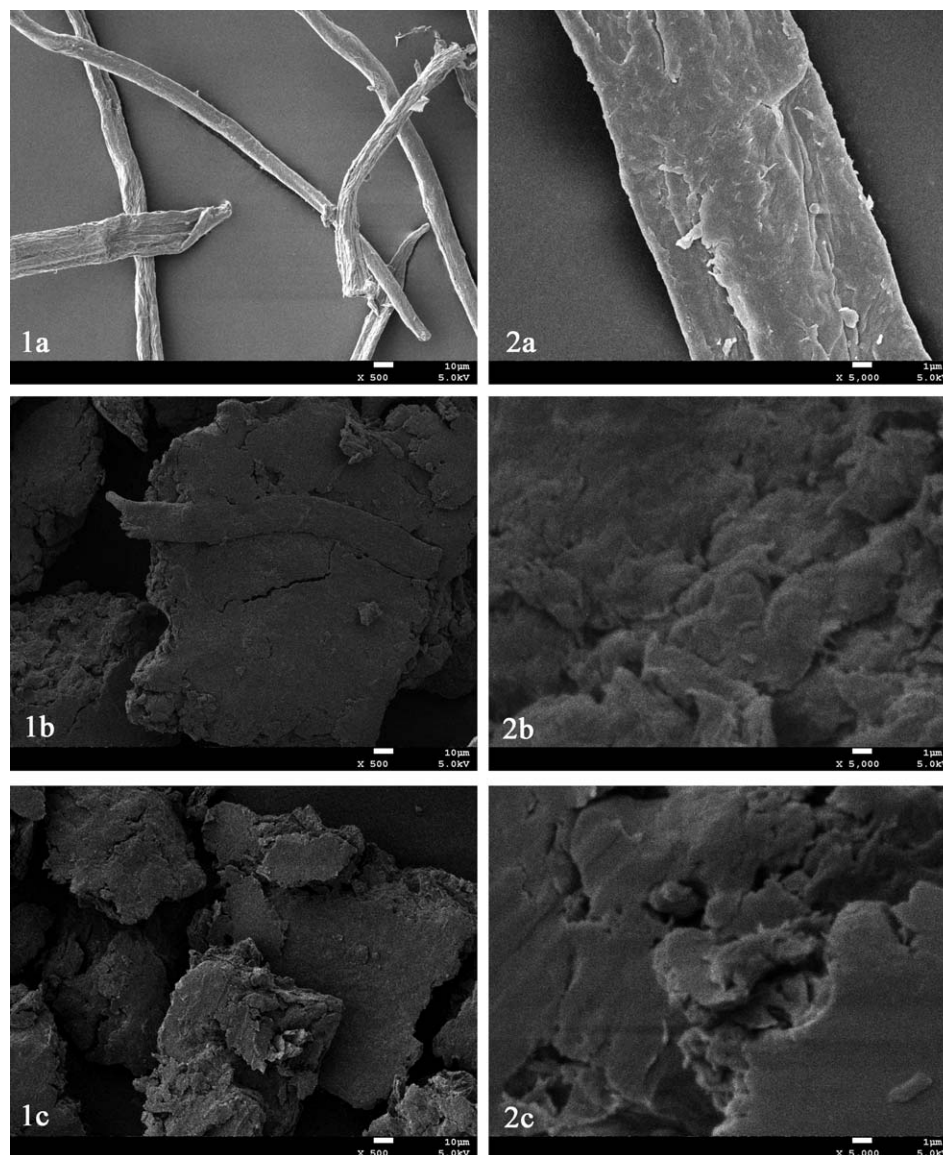
ring stretching vibration). These results indicate that the reaction has successfully hydrolyzed cellulose. However, there is no significant difference in chemical structure between residue 1 and residue 2. The TG was further applied to compare their structure.

As shown in Figure 8, the broadly stretched intense at  $3420\text{ cm}^{-1}$  and the peak at  $1370\text{ cm}^{-1}$  are related to the characteristic vibrations of O—H in cellulose molecules. In addition, the relatively strong absorbance peak at  $1640\text{ cm}^{-1}$  was contributed to the O—H bending vibration of the adsorbed water.<sup>21</sup> Moreover, the absorption at  $898\text{ cm}^{-1}$  was corresponded to the  $\beta$ -glycosidic linkages between glucose units in cellulose.

**TG Analysis.** TG was used to characterize the thermochemical properties and kinetics of thermal degradation of pure cellulose (Figure 9), the residue produced by homogeneous catalytic hydrolysis of pure cellulose (residue 1), and the residue produced by heterogeneous catalytic hydrolysis of pure cellulose (residue 2). It is quite interesting to note that the decomposition of pure cellulose and residue 1 follows almost identical mechanism, while the decomposition of the residue 2 is associated with an additional small shoulder around  $188^\circ\text{C}$ . The thermal decomposition of pure cellulose begins at  $302^\circ\text{C}$  and its DTG curve exhibits a single weight loss peaking at  $341^\circ\text{C}$ . The residue 1 sets to decomposition at  $298^\circ\text{C}$  and the peak rate of decomposition is reached at  $326^\circ\text{C}$  as revealed by DTG curve. The decomposition of residue 2 occurs at  $199^\circ\text{C}$  and the rate of decomposition reaching its peak at  $322^\circ\text{C}$ . In the case of residue 1, it could be found about the reduction in the onset temperature of decomposition with respect to the pure cellulose. The relatively lower initial temperature of decomposition at  $298^\circ\text{C}$  should result from the rearrangement and reorientation of the crystals in cellulose. In the residue 2, the sample exhibits a lower onset temperature for decomposition, but gives a higher char yield (nonvolatile carbonaceous material, 25%) on pyrolysis, indicated by the residual masses after the



**Figure 9.** TG and DTG curve of (a) untreated cellulose, (b) homogeneous catalytic hydrolyzed cellulose (i.e., residue 1), and (c) heterogeneous catalytic hydrolyzed cellulose (i.e., residue 2). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10.** SEM images of (a) untreated cellulose, (b) homogeneous catalytic hydrolyzed cellulose (i.e., residue 1), and (c) heterogeneous catalytic hydrolyzed cellulose (i.e., residue 2) (1a, 1b, 1c: 500 $\times$ ; 2a, 2b, 2c: 5000 $\times$ ).

decomposition step. The decomposition of residue 2 appearing to follow a different mechanism was also manifested by the presence of two humps in other investigation.<sup>21</sup> The higher yield of remnant after decomposition can be ascribed to sulfated amorphous and crystalline regions of cellulose which are intrinsically flame resistant.<sup>22</sup>

**SEM Analysis.** SEM is usually used to intuitively investigate the surface structure of the solid. In this study, it was employed to examine the surface structures of untreated cellulose, the residue produced by homogeneous catalytic hydrolysis of pure cellulose, and the residue produced by heterogeneous catalytic hydrolysis of pure cellulose, which could estimate the influence of hydrolysis process on the fibers morphology. The results are illustrated in Figure 10.

It could be easily observed that the surface of the native cellulose prior to hydrolysis is smooth and plump (a), and the fiber bundle was observed clearly. After hydrolysis, the morphology

of the fiber was significantly changed. It is easy to know that the whole framework of the cellulose fiber was destroyed (b and c), leaving a rough and loose but conglomerate texture.

## CONCLUSION

In this study, homogeneous and heterogeneous systems in the conversion of bagasse cellulose into TRS were investigated and compared. It is obvious that the hydrolysis in homogeneous reaction system with [Bmim]Cl showed a remarkably favorable activity. In the homogeneous system, the amount of catalyst has great effect on the hydrolysis of cellulose. When the dosage of acidic catalyst is higher, the degradation of TRS increased. In addition, it should be noted that the presence of water in [Bmim]Cl has conspicuous influence on the hydrolysis of cellulose. This is because the content of water is closely related with the existence form of cellulose in IL. Moreover, the acidity and

structure of ILs are important aspects in cellulose hydrolysis as revealed by the results of heterogeneous reaction. Furthermore, the structure and physicochemical properties of the treated cellulose underwent great changes compared with that of the pure cellulose. Thus, the obtained information would be a beneficial reference for further studies on the cellulosic conversion.

#### ACKNOWLEDGMENTS

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