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Functional ionic liquids for hydrolysis of lignocellulose

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ABSTRACT

An efficient system for hydrolysis of lignocellulosic materials to prepare reducing sugar in a series of functional acidic ionic liquids with low synthetic cost and excellent dissolved and catalytic activity was established. High yield of reducing sugar was obtained with the use of 1-H-3-methylimidazolium chloride ([HMIM]Cl). The use of ionic liquid under ultrasound irradiation greatly improved the yield of total reducing sugar. The optimum reaction conditions were as follows: ratio of water/sample was 5 (w/w), ratio of IL/sample was 25 (w/w), 70 °C, 120 min and the yield of reducing sugar was up to 53.27 mg from 0.2 g of soybean straw and 50.03 mg from 0.2 g of corn straw.

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1. Introduction

The exhaustion of fossil fuel and the resulting severe environmental consequences from its overuse have necessitated the search for alternative energy sources (Park et al., 2010). Lignocellulosic materials are the major constituent of biomass and the most abundant renewable resource. Extensive studies have been made to convert lignocellulosic materials such as bagasse, corn stover, wheat straw, wood chips into valuable products (Ha, Mai, An, & Koo, 2011; Lever & Ho, 2012; Ma, Xue, Yu, & Wang, 2012). The conversion of lignocellulosic materials into ethanol is increasingly being promoted as a potentially environmentally and economically sustainable fuel (Lever & Ho, 2012). During the process of lignocellulose-to-biofuel, the preparation of reducing sugar is a crucial step. However, because of the compositional features of lignocellulose and the highly crystalline polymer of D-anhydroglucopyranose units, it is hardly processed in common solvents and pretreatment of high temperature or high pressure is required. Low rate and high cost of cellulose enzymes and a large amount of corrosion of inorganic acid are also limits their application for industrial production. It is necessary to develop alternative new techniques.

Ionic liquids (ILs) are environmental friendly molten salts. ILs have the virtues of low melting points, low volatility, excellent solvency and designability as their cations or anions can be introduced into functional groups. The application of ILs in cellulose occurred in 2002. Swatloski, Spear, Holbery, and Rogers (2002) reported the dissolution of cellulose in ILs with the cation of 1-butyl-3-methylimidazolium ([BMIM]) and the anion of Cl^-, Br^- or SCN^- at 100 °C. Following that, ILs with the cation of 1-alkyl-3-methylimidazolium and with the anion of chloride, acetate, or formate appeared effective in dissolving cellulose (Fukaya, Sugimoto, & Ohno, 2006; Kosan, Michels, & Meister, 2008; Luo, Li, & Zhou, 2005). Currently, Li, Wang, and Zhao (2008) reported the hydrolysis of ligocellulosic materials in [BMIM]Cl to prepare reducing sugar with sulfuric acid as a catalyst. Amarasekara and Owereh (2009) reported the hydrolysis of Sigmacell cellulose in 1-(1-propylsulfonic)-3-methylimidazolium chloride. The highest yield of total reducing sugar (62%) was obtained in 1 h of preheating at 70 °C and 30 min of heating at 70 °C after adding water. Xiao, Yin, Xia, and Ma (2012) described enzymatic hydrolysis of cellulose with pretreatment by [BMIM]Cl, [BMIM]COOH or 1-ethyl-3-methylimidazolium acetate. Ma et al. (2012) reported the combined use of ultrasound irradiation and [BMIM]Cl as a potential alternative method in preparation of glutamates using cellulose isolated from sugarcane bagasse.

In many reports, pure cellulose was used. There are very few reports concerning to original lignocellulosic materials. With the aim to produce the ionic liquids with a simply synthetic protocol, low cost, good dissolved and catalytic activity for the preparation of reducing sugar from agricultural lignocellulosic waste, a series of studies were taken. The optimal conditions were also investigated.

2. Materials and methods

2.1. Materials

All chemicals were purchased from Aladin Company (China) and used as received. The corn straw and soybean straw were supplied

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by Northeast Agriculture University (China), and both of them were pulverized by high-speed universal pulverizer and through 40 mesh sieves. KQ-200VDE ultrasound was used. Analysis of reducing sugar was performed on Xinshiji T_6 UV–Vis Spectrophotometer. ^{1}H NMR Spectra was recorded on a Bruker Advance DRX-400 spectrometer at 400 MHz.

2.2. General procedure for the synthesis of ionic liquids

2.2.1. Synthesis of 1-H-3-methylimidazolium chloride ([HMIM]Cl)

1-Methyl imidazole (20 g, 0.244 mol) and hydrochloric acid (30 g, 0.296 mol) were mixed in a round-bottomed flask in ice-water bath and stirred for 24 h at room temperature. The resulting liquid was washed with ether (20 ml ×3). Ether was then removed under rotary evaporation and the product was further dried under vacuum for 10 h to give a colorless liquid. The synthesis of ionic liquids [HMIM][HSO_4], [HMIM][CH_3COO] and [HMIM][H_2PO_4] followed a similar protocol as used for [HMIM]Cl.

[HMIM]Cl: ^{1}H NMR (400 MHz, DMSO-d_6): 3.775 (s, 3H), 7.298 (s, 1H), 7.445 (s, 1H), 8.441(s, 1H).

[HMIM][CH_3COO]: ^{1}H NMR (400 MHz, DMSO-d_6): 1.921 (s, 3H), 3.645 (s, 3H), 6.904 (s, 1H), 7.117 (s, 1H), 7.607 (s, 1H).

[HMIM][H_2PO_4]: ^{1}H NMR (400 MHz, DMSO-d_6): 3.702 (s, 3H), 7.050 (s, 1H), 7.241 (s, 1H), 7.902 (s, 1H), 8.892(s, 3H).

[HMIM][HSO_4]: ^{1}H NMR (400 MHz, DMSO-d_6): 3.874 (s, 3H), 7.607 (s, 1H), 7.675 (s, 1H), 8.990 (s, 1H), 9.123(s, 2H).

2.2.2. Synthesis of 1-allyl-3-methylimidazolium chloride ([AMIM]Cl)

[Amim]Cl was prepared according to a method described in a previous literature (Zhang, Wu, Zhang, & He, 2005). 1-Methylimidazole (22.908 g, 0.275 mol) and ally chloride (25.245 g, 0.33 mol) were added to a round-bottomed flask fitted with a reflux condenser for 7 h at 60 °C with stirring. The resulting liquid was washed with ether (20 ml ×3). Ether was removed under rotary evaporation and the product was further dried under vacuum at 80 °C for 24 h. [AMIM]Cl was obtained as a slightly viscous liquid.

[AMIM]Cl: ^{1}H NMR (400 MHz, DMSO-d_6): 3.901 (s, 3H), 4.911 (d, 2H), 5.330 (m, 2H), 6.045 (m, 1H), 7.822 (d, 2H), 9.464 (s, 1H).

2.3. General procedure for preparation of reducing sugar

Soybean straw or corn straw (0.2 g), an appropriate amount of ionic liquid and water were rapidly added into a vial. The mixture was treated with ultrasound (200 W) or heated with stirring under oil bath at a certain temperature for a matter of minutes. The entire solids of the mixture were filtered out. The filtrate was cooled to room temperature and neutralized by the addition of solid of sodium hydroxide. The amount of reducing sugar was measured using the 3,4-dinitrosalicylic acid (DNS) method (Miller, 1959). The concentration of reducing sugar was calculated by employing a standard curve prepared using glucose and the absorbance was measured at 540 nm using UV–vis spectrophotometer.

3. Results and discussion

3.1. Yield of reducing sugar with different treatments

In recent years, ultrasonic treatment is used widely. The effect of ultrasound is related to cavitation, heating, dynamic agitation, shear stresses, and turbulence (Jambrak et al., 2009; Vilkhu, Mawson, Simons, & Bates, 2008). Liu et al. (2008) reported that the controlled depolymerization of plant cellulose could be achieved by employing suitable ultrasonication. In this work, different treatments were investigated including ultrasound and oil bath or their combination. As presented in Fig. 1, the yield of reducing sugar (RS) was significantly higher when the mixture was treated with ultrasound than with oil bath. The yield of RS was slightly lower with the use of ultrasound and oil bath than with ultrasound. The ultrasonic cavitation might help to increase the reaction interface between cellulose and ionic liquids, enhance the heat transfer and cause a reduction in molecular weight of cellulose. Ultrasound irritation might decrease the IL' viscosity, enhance the movement rate of chloride ions and then accelerate the dissolution of soybean straw cellulose. This work indicated that the combined use of ionic liquid and ultrasound irritation could promote cellulose (net) to the cellulose (chain) process and increase the dissolution of cellulose and then improve the yield of RS. This can be explained from FTIR spectrum either.

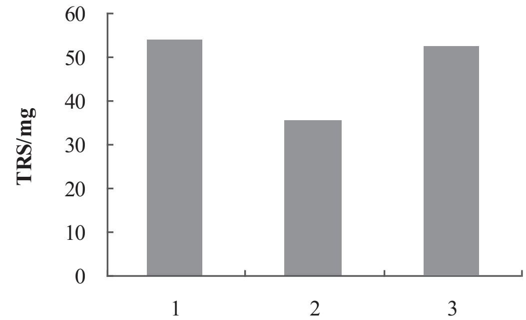

Fig. 1. Yields of reducing sugar with different treatments. Reaction conditions: (1) treatment with ultrasound for 180 min; (2) treatment with oil bath for 180 min; (3) treatment with ultrasound for 60 min, and then oil bath for 120 min. Other conditions were fixed as follows: soybean straw (0.2 g), [HMIM]Cl (5 g), H_2O/soybean straw 15/1 (w/w), reaction temperature (70 °C).

FTIR spectrum of the soybean straw is shown in Fig. 2. In curve a, the peak at 1429 cm^{-1} can be assigned to bending vibration of CH_2. This band is strong in crystalline cellulose, and weak in amorphous cellulose (Nelson & O'Connor, 1964). The CH_2 band is weaker in curve b and weakest in curve c, thus the crystallinity of the cellulose is lower when treated with ultrasound and much lower when treated with IL/ultrasound than the original cellulose. In addition, the broad absorption in the range from 3000 cm^{-1} to 3500 cm^{-1} is due to stretching vibration of inter molecular O–H forming among cellulose molecules. The broad absorption is weaker in curve b and c compared to curve a, which probably indicates the intermolecular hydrogen bonds of cellulose are broken greatly (Xiao et al., 2012). Therefore, the optimal system should be IL/ultrasound that can help to disrupt the hydrogen bonds between polysaccharide chains of cellulose, and thus benefit the preparation of reducing sugar.

3.2. Yields of RS under various reaction media

Various reaction media were studied to identify the optimal one for the preparation of RS. Because [AMIM]Cl was an excellent solvent for the dissolution of cellulose as presented in many reports (Kilpelainen, Xie, King, Heikkinen, & Argyropoulos, 2007), [AMIM]Cl was used as a reaction medium first. With the help of ultrasound, a short yield of RS was produced in [AMIM]Cl as shown in Fig. 3 (No. 1). In addition, an ionic liquid with an acid as a catalyst was described as a good condition for the hydrolysis of lignocellulose (Li & Zhao, 2007; Li et al., 2008). In this work, [AMIM]Cl with an addition of H_2SO_4 was used as a reaction medium and the resulting yield of RS was increased (No. 2). Low yield of RS was obtained when the reaction was carried out in an aqueous H_2SO_4 solution (No. 3).

Theoretically, ILs with the anion of Cl^-, CH_3COO^- have a good dissolved activity and ILs with the anion of HSO_4^-, HPO_4^- can

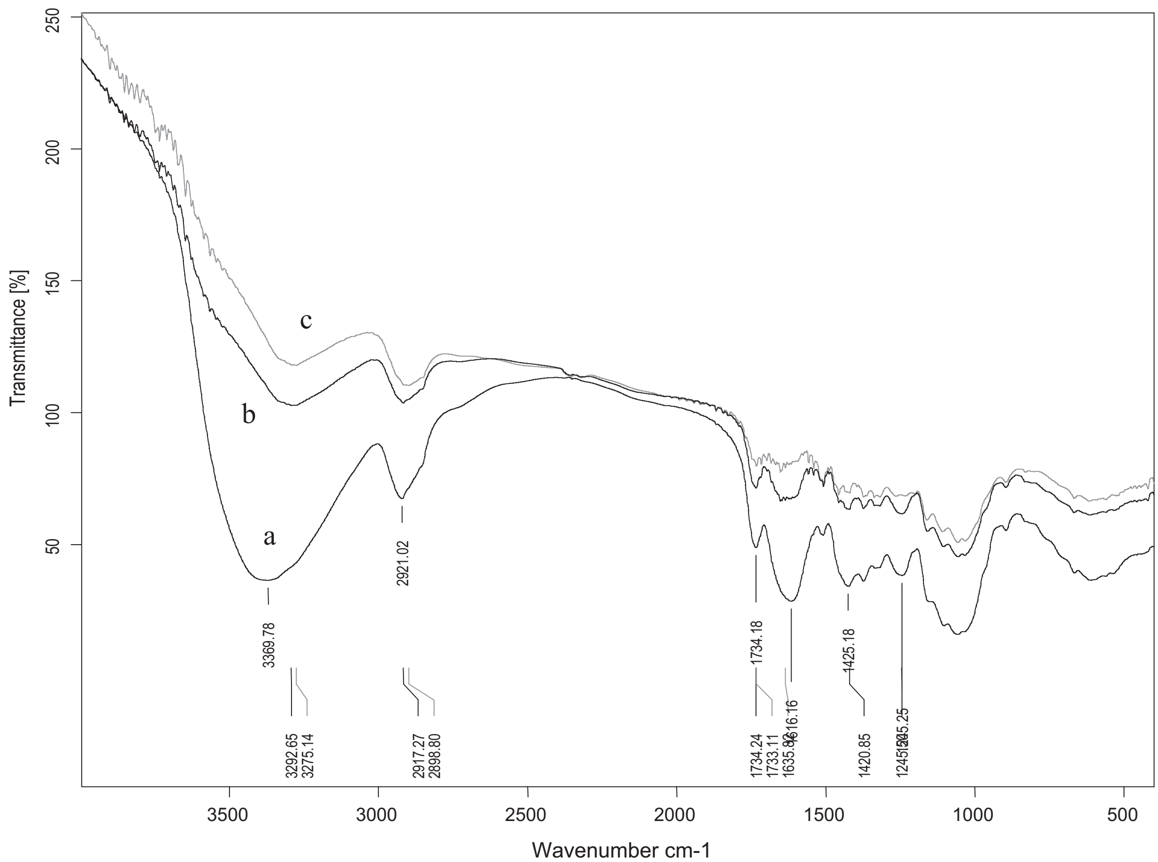

Fig. 2. FT-IR spectra of (a) untreated soybean straw; (b) soybean straw treated with ultrasound for 120 min; (c) soybean straw treated with [HMIM]Cl/ultrasound for 120 min. After treated with (b) or (c), the sample was washed with water (5 ml × 2) and then dried for 24 h.

provide acidic activity for cellulose. Then a series of proton ILs with these anions were synthesized. In their chemical structures, there is an hydrogen in N(1) on the cation that can be dissociated, so all the ILs can provide slight acidity for the hydrolysis of cellulose. Therefore, either of ILs synthesized in this work can act as a solvent and a catalyst. No other inorganic acid is needed. Moreover, high yield of RS was obtained when [HMIM]Cl was used as reaction media (Fig. 3, No. 4), which was due to the formation of strong hydrogen bond of Cl^- compared with [HMIM]HSO_4. The strong hydrogen bond of ILs can disrupt the hydrogen bonds between polysaccharide chains of cellulose and then dissolve cellulose (Mikkola et al., 2007). Therefore, [HMIM]Cl/ultrasound were applied for the following reactions and the optimal conditions were studied.

3.3. Effect of reaction temperature

Generally, when the temperature is increased, the reaction rate will be improved. As the temperature was from 40 °C to 80 °C, the hydrolysis rate of cellulose should be increased and then the resulting yield of RS was improved as shown in Fig. 4. Another reason for the increasing yield of RS was perhaps due to ILs' viscosity. As reported by Remsing, Swatloski, Rogers, and Moyna (2006), cellulose was dissolved into ILs, because the chloride ions in IL could go into the interspaces of 1,4-linked β-D-glucose units and disrupt intermolecular hydrogen bonds between the units. It was supposed that when the temperature was increased, [HMIM]Cl became less viscous, which would enhance the movement rate of chloride ions

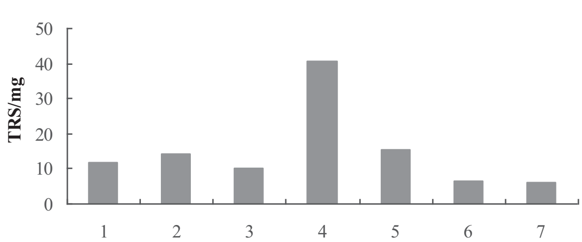

Fig. 3. Yields of reducing sugar under various reaction systems. Reaction conditions: (1) [AMIM]Cl (5 g) and water (2 ml); (2) [AMIM]Cl (5 g) and H_2SO_4 (1 M, 2 ml); (3) H_2SO_4 (1 M, 7 ml); (4) [HMIM]Cl (5.00 g) and water (2 ml); (5) [HMIM][HSO_4] (5 g) and water (2 ml); (6) [HMIM][CH_3COO] (5 g) and water (2 ml); (7) [HMIM][HPO_4] (5 g) and water (2 ml). Other conditions were fixed as follows: soybean straw (0.2 g), H_2O/soybean straw 15/1 (w/w), reaction temperature (70 °C), ultrasound for 120 min.

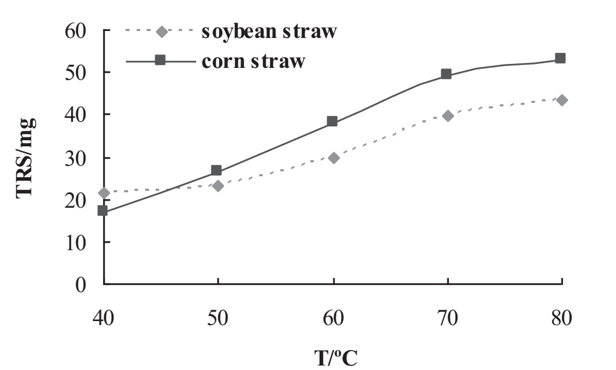

Fig. 4. Yields of reducing sugar under various reaction temperatures. The conditions were fixed as follows: straw (0.2 g), [HMIM]Cl (5 g) and water (3 ml), ultrasound for 120 min.

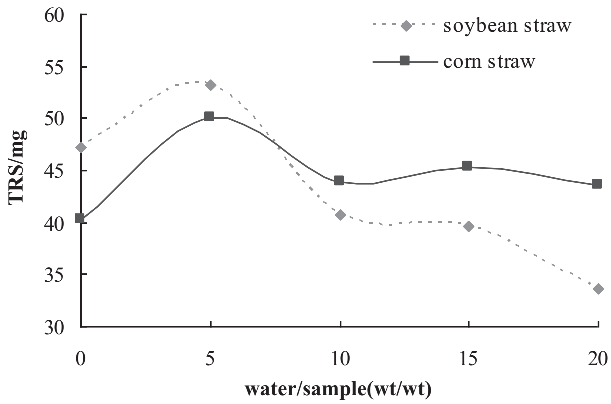

Fig. 5. Yields of reducing sugar under different ratio of water/sample (w/w). The conditions were fixed as follows: straw (0.2 g), [HMIM]Cl (5 g), reaction temperature (70 °C), ultrasound for 120 min.

and then accelerate the dissolution of cellulose and improve the yield of RS. As presented in Fig. 4, when the temperature was from 70 °C to 80 °C, the increasing rate of the yield of RS was slow down. High temperature might cause the degradation of RS and consumed more energy. Therefore, 70 °C was chosen for the following reactions.

3.4. Effect of the ratio of water/sample

Water is a reactant in the process of hydrolysis of cellulose. As the amount of water is increased, the hydrolysis reaction will proceed toward the forward reaction. As shown in Fig. 5, when the ratio of water was increased from 0 to 5, the yield of product was increased, because the appropriate water could improve the hydrolysis rate and lower the viscosity of the IL. However, when the ratio was more than 5, the yield of product was decreased, probably because the dissolution of cellulose was reduced when more water was added. The highest yield of reducing sugar was observed with the ratio of water/sample was 5/1(w/w).

3.5. Effect of the ratio of IL/sample

In order to investigate the effect of the amount of ionic liquids, the reaction was carried out at 70 °C for 120 min. According to Fig. 6, as the ratio of [HMIM]Cl/sample was from 15 to 25, the hydrolysis rate was improved and the yield of reducing sugar was increased. While when the ratio of mass was more than 25, the yield was decreased. The overuse of IL was also a waste of resources for production. In order to save the production cost, the appropriate ratio of [HMIM]Cl/sample (w/w) should be 25/1.

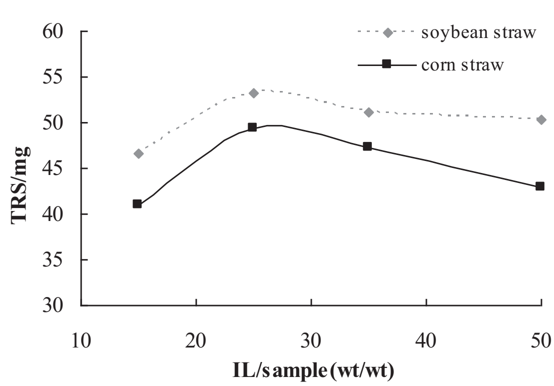

Fig. 6. Yields of reducing sugar under different ratio of [HMIM]Cl/sample (w/w).The conditions were fixed as follows: straw (0.2 g), water (1 ml), reaction temperature (70 °C), ultrasound for 120 min.

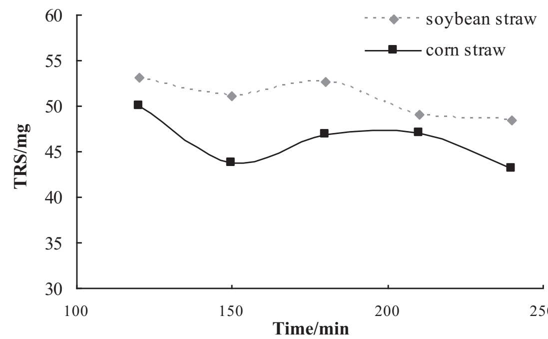

Fig. 7. Yields of reducing sugar under various reaction times. The conditions were fixed as follows: straw (0.2 g), [HMIM]Cl (5 g) and water (1 ml), reaction temperature (70 °C).

3.6. Effect of reaction time

Reaction time has an effect on the industrial production of RS. High yield of RS and short reaction time are always the optimal conditions. As presented in Fig. 7, longer reaction time would lead to the low yield of the product. Corn straw hydrolysis proceeded significantly faster than RS degradation, but it is important to find an optimal time to maximize the yield of RS (Li et al., 2008). It was supposed that the hydrolysis of cellulose and degradation of monosaccarides into other derivates coexist. In order to improve the efficiency of production and save the energy, the appropriate reaction time should be 120 min.

4. Conclusion

In conclusion, an efficient and economical approach to prepare reducing sugar in ionic liquids under mild conditions with low consumption of energy for the cellulose-ethanol production from agricultural waste was established. Ultrasound assisted [HMIM]Cl was proved as the most efficient system. The optimum reaction conditions were as follows: ratio of water/sample was 5 (w/w), ratio of IL/sample was 25 (w/w), reaction temperature was 70 °C with ultrasound for 120 min and the yield of RS was up to 53.27 mg and 50.03 mg from 0.2 g of soybean straw and corn straw respectively. In this process, soybean straw and corn straw are “green materials”, ionic liquids are “green solvents”. [HMIM]Cl has the lowest synthetic cost compared with ILs that have been successfully reported. This simple and environmentally acceptable method has a great potential for the preparation of bioethanol for industrial production.

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