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Hydrolysis of Soybean By-Products to Prepare Reducing Sugar in Ionic Liquids

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An efficient approach for preparation of reducing sugar from soybean hulls and soybean dregs in a series of ionic liquids was studied. The ionic liquids have excellent dissolved and catalytic ability. High yield was obtained with the use of 1,4-*bis*(3-methylimidazolium)butane hydrogen sulfate ($[MIM]_2C_4[HSO_4]_2$) and pretreatment with 1-allyl-3-methylimidazolium chloride [AMIM]Cl. The effects of several critical factors such as reaction temperature, reaction time and the amount of water and ionic liquid were investigated. At the optimum reaction conditions, the yield of reducing sugar from soybean hulls was up to 68.86 and 119.69 mg from 0.25 g soybean hulls and soybean dregs, respectively.

Keywords: Functional ionic liquids, Soybean hulls, Soybean dregs, Reducing sugar.

INTRODUCTION

Due to energy crisis and global warming, biofuels produced from biomass attracted great interest. Corn and soybean oil has proved the possibility of biomass-to-biofuel, while other problems may arise such as food deficiency. Cellulosic materials have attracted much attention in recent years as it is abundant form of biomass and nonfood source for the bioethanol production. During the process of lignocellulose-to-biofuel, the preparation of reducing sugar is the main obstacle. Generally, there are two widely used approaches to complete this step including inorganic acid method and enzyme method. Both of approaches require a pretreatment at high temperature (180-230 ºC) and high pressure in order to disrupt the hydrogen bond network before hydrolysis. Thus, it is necessary to develop alternative new techniques.

In recent years, ionic liquids (ILs) have gained wide popularity because of their favorable properties such as high thermal stability, low vapor pressure, no flammability and ease of recycling. The properties of ionic liquids can also be changed by easily altering their cation or anion. Thus, ionic liquids are defined as "green" and "designer" solvents. The application of ionic liquids in cellulose occurred in 2002. Rogers group reported the dissolution of cellulose in ionic liquids with the cation of 1-*n*-butyl-3-methylimidazolium ([BMIM]) and the anion of Cl, Br or SCN at 100 °C[1]. Following this successful report, researchers made great effort to study the dissolution and regeneration of cellulose like fabrication into films, gels and composite materials[2]. Others focused on the preparation of cellulose derivatives in ionic liquids like carboxymethyl cellulose and cellulose acetate[3]. Currently, Li *et al*.[4] reported the hydrolysis of sugarcane bagasse or rice straws in an ionic liquid ([BMIM]Cl) to prepare reducing sugar with sulfuric acid as a catalyst. Amarasekara and Owereh[5] reported the hydrolysis of Sigmacell cellulose in 1-(1-propylsulfonic)-3-methylimi-dazolium chloride. We reported the hydrolysis of lignocellulose using 1-H-3-methylimidazloium chloride[6].

Soybean byproducts such as soybean hulls and soybean dregs are rich cellulosic resource from soybean products industry in North China. In this study, an efficient approach to prepare reducing sugar in ionic liquids from soybean by-products was established. In this process, soybean hulls and dregs were "green materials", ionic liquids were "green solvents". A series of ionic liquids with excellent dissolution ability and catalytic ability were studied. The optimal conditions were also investigated.

EXPERIMENTAL

All chemicals were purchased from Aladin Company (China) and used as received. The soybean hulls and dregs were supplied by Harbin Beidahuang soybean product Co. (China), both of which were pulverized through 40 mesh sieves by high-speed universal pulverizer. KQ-500DV ultrasound was used. ^{1}H NMR Spectra was recorded on a Bruker Advance DRX-400 spectrometer at 400 MHz. Analysis of reducing sugar was performed on Xinshiji T6 UV-visible spectrophotometer.

General procedure for the preparation of functional ionic liquids: A typical procedure for $[MIM]_2C_3[HSO_4]_2$ is given as follows: *N*-methyl imidazole (0.1 mol) and 1,3-dibromobutane (0.05 mol) were added into a three-necked flask. The mixture was refluxed at 70 °C for 24 h under the protection of nitrogen. When the reaction was complete, white solids were formed and further purified by recrystallization in acetonitrile/ethylacetate, dried in vacuum to give the product $[MIM]_2C_3Br_2$. $[MIM]_2C_3Br_2$ (0.01 mol) was dissolved in dichloromethane (20 mL). Sulfuric acid (0.02 mol) was added slowly into the mixture. The mixture was then stirred at room temperature for 16 h. After that, the resulting product was washed with ether. The rest of the solvent was evaporated and the product was dried in vacuum. $[MIM]_2C_4[HSO_4]_2$, $[MIM]_2C_5[H\text{-}SO_4]_2$, $[MIM]_2C_6[HSO_4]_2$ were synthesized with the same procedure as $[MIM]_2C_3[HSO_4]_2$. Other ionic liquid 1-allyl-3-methylimidazolium chloride [AMIM]Cl, 1-butyl-3-methylimidazolium chloride [BMIM]Cl 1,1-butyl-3-methylimidazolium acetate $[BMIM]CH_3COOH$[1] were synthesized according to literatures. $[HSO_3\text{-}pMIM][HSO_4]$ was prepared according to Li *et al.*[4].

$[HSO_3\text{-}p\text{MIM}][HSO_4]$ ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 2.105 (m,2H), 2.507 (t,2H), 3.859 (s,3H), 4.301 (t,2H), 7.720 (s,1H), 7.790 (s,1H), 9.140 (s,1H). IR (KBr, ν_{max}, cm^{-1}): 3152, 2960, 1575, 1228, 1172, 1053.

$[MIM]_2C_3[HSO_4]_2$ ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 2.414 (m, 2H), 3.881 (s, 6H), 4.267 (t, 4H), 7.772 (s, 2H), 7.850 (s, 2H), 9.295 (s, 2H) . IR (KBr, ν_{max}, cm^{-1}): 3110, 2950, 1575, 1456, 1200, 1048.

$[MIM]_2C_4[HSO_4]_2$ ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.783 (m, 4H), 3.864 (s, 6H), 4.233 (t, 4H), 7.740 (s, 2H), 7.805 (s, 2H), 9.220 (s, 2H). IR (KBr, ν_{max}, cm^{-1}) 3068, 2945, 1635, 1489, 1205, 1046.

$[MIM]_2C_5[HSO_4]_2$ ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.228 (m, 2H), 1.832(m, 4H), 3.871 (s, 6H), 4.193 (t, 4H), 7.740 (s, 2H), 7.821 (s, 2H), 9.242 (s, 2H) . IR (KBr, ν_{max}, cm^{-1}) 3114, 2954, 1574, 1457, 1171.

$[MIM]_2C_6[HSO_4]_2$ ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.270 (m, 4H), 1.786 (t, 4H), 3.866 (s, 6H), 4.176 (t, 4H), 7.738 (s, 2H), 7.916 (s, 2H), 9.228 (s, 2H). IR (KBr, ν_{max}, cm^{-1}) 3113, 2947, 1574, 1190.

General procedure for preparation of reducing sugar: Soybean hulls or soybean dregs (0.25 g) was dissolved in 5 g of the ionic liquid. The mixture was treated with ultrasound at 70 °C, 500 W for 1 h. After that, the appropriate amount of functional acidic ionic liquid and water was added into the mixture and the mixture was stirred at an appropriate temperature for a certain time. The entire solids of the mixture were filtered out. The filtrate was cool to room temperature and neutralized by the addition of 2 mol/L NaOH. The total reducing sugar determination using the 3,4-dinitrosalicylic acid (DNS) method[7]. The TRS concentration in the solution was calculated by employing a standard curve prepared using glucose and the absorbance was measured at 540 nm using UV-visible spectrophotometer.

RESULTS AND DISCUSSION

Effect of various ionic liquids as reaction solvents: The hydrolysis of soybean hulls cellulose were first investigated using 5 g of one of the ionic liquid including [AMIM]Cl, [BMIM]Cl or $[BMIM]CH_3COO^-$ as a reaction solvent. The strong hydrogen bond of ionic liquids can disrupt the hydrogen bonds between polysaccharide chains of cellulose and then to dissolve cellulose[8]. As shown in Fig. 1, [AMIM]Cl as reaction media gave better yields of reducing sugars, which due to its lower viscosity compared with [BMIM]Cl and the formation of strong hydrogen bond of Cl^- compared with CH_3COO^-.

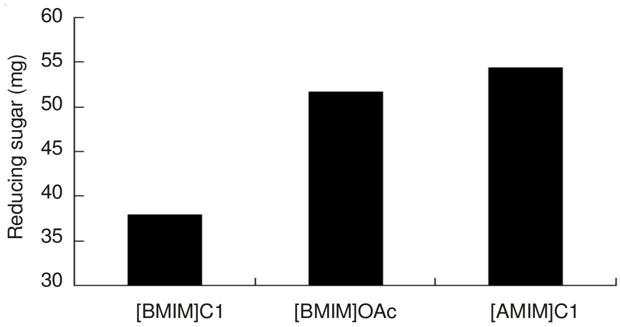

Fig. 1. Yields of products with various reaction solvents. The conditions were fixed as follows: soybean hulls (0.25 g), water (5 g), H_2SO_4 (1.2 g), 95 °C, 80 min

The soybean hull and the ones treated with ionic liquid under ultrasound irradiation were investigated by FTIR spectroscopy in the 4000-400 cm^{-1} region (Fig. 2). The absorption in the range from 3000 to 3500 cm^{-1} is due to stretching vibration of O-H forming among cellulose molecules. It was 3285.95 cm^{-1} in curve a and 3308.36 cm^{-1} in curve b, which may suggests that the intermolecular hydrogen bonds of cellulose are broken greatly[9]. The band (897 cm^{-1}) that was weaker in curve a and stronger in curve b, which means the crystallinity of the cellulose was lower when treated with [AMIM]Cl. Therefore, cellulose was treated with ionic liquid, which can help to disrupt the hydrogen bonds between polysaccharide chains of cellulose and then benefits the preparation of reducing sugar.

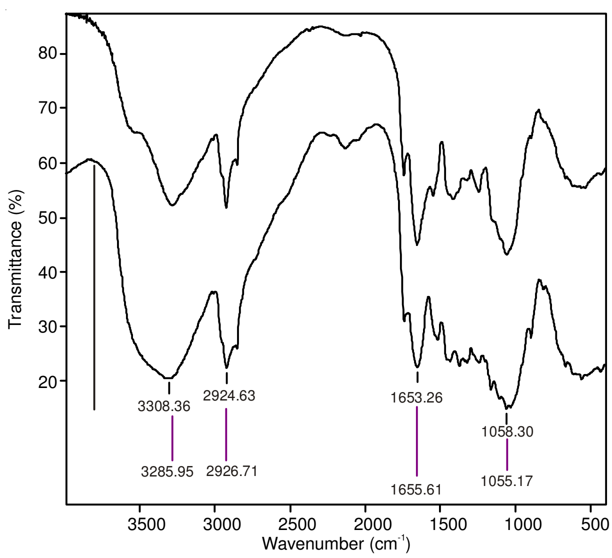

Fig. 2. IR of untreated soybean hull (a) and soybean hull treated with ionic liquid (b)

Effect of various ionic liquids as catalysts: Following the study above, with [AMIM]Cl as reaction solvent, five functional acidic ionic liquids have been investigated for their catalytic activity. The structures of ionic liquids were shown in Fig. 1. According to the report, high yield of reducing sugar was obtained with about 10 % H_2SO_4 in total solvent[10], then 1.2 g of one of the ionic liquids or H_2SO_4 was added in this work. As presented in Fig. 3, all the ionic liquids can catalyze the hydrolysis of soybean hulls cellulose effectively. The catalytic activities of all tested ionic liquids were higher than H_2SO_4 under the same condition. High conversions of cellulose were obtained using $[MIM]_2C_4[HSO_4]_2$. Thus, $[MIM]_2C_4[HSO_4]_2$ was chosen as catalyst for the following reactions.

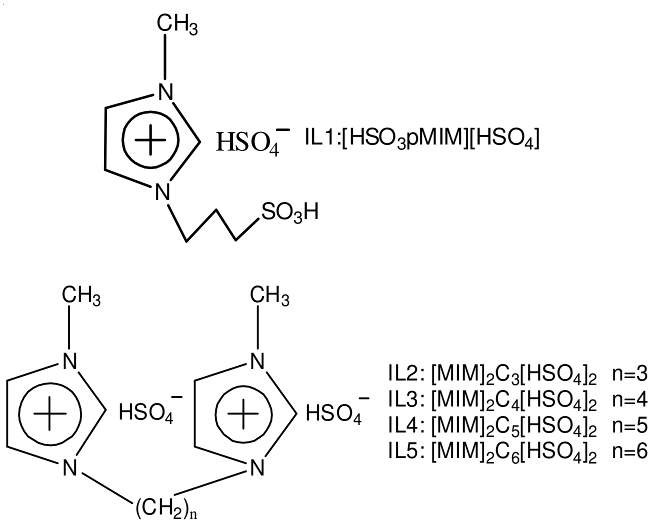

Fig. 3. Structures of functional ionic liquids

Effect of acidic ionic liquid on yield of reducing sugar: In order to investigate the effect of $[MIM]_2C_4[HSO_4]_2$, different amount was investigated. According to Fig. 4, as the ratio of ionic liquids/soybean hull or dreg (w/w) was from 3 to 4.8, either yield of reducing sugar was increased. When the ratio was over than 4.8, the yield was decreased obviously, which was due to strong acidity that caused the further degradation of reducing sugar[4]. Thus the appropriate ratio of ionic liquid/ soybean hull (soybean dreg) should be 4.8.

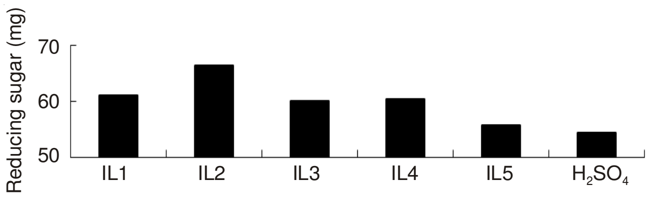

Fig. 4. Yields of products with various acidic catalysts. The conditions were fixed as follows: soybean hulls (0.25 g), water (5 g), [AMIM]Cl (5 g), 95 °C, 80 min

Effect of water on yield of reducing sugar: Water is a reactant in the process of hydrolysis of cellulose. As the amount of water is increased, the hydrolysis reaction will proceed towards the forward reaction. As shown in Fig. 5, when the ratio of water/soybean hull or dreg (w/w) was increased from 10 to 20, either yield of product was increased first, which was due to the appropriate water could improve the hydrolysis rate

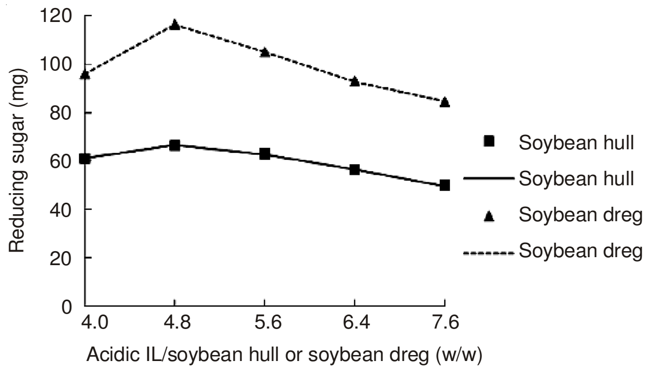

Fig. 5. Yields of products with different amount of acidic ionic liquids. The conditions were fixed as follows: soybean hulls (0.25 g), water (5 g), [AMIM]Cl (5 g), 95 °C, 80 min

and lower the viscosity of the ionic liquid. However, when the ratio was over 20, the yield of products were decreased, which perhaps because the dissolution of cellulose was decreased when more water was added.

Effect of reaction time on reducing sugar: High yield of products and short reaction time always the optimal conditions. In order to find the optimal reaction time, 40, 60, 80, 100, 120 min were studied. Corn straw hydrolysis proceeded significantly faster than RS degradation, but it is important to find an optimal time to maximize the yield of RS[4]. As presented in Fig. 6, the yields of products were enhanced when the time was increased. About 60 min, the yields of reducing sugar reached the highest level and after that, the reducing sugar was further degraded.

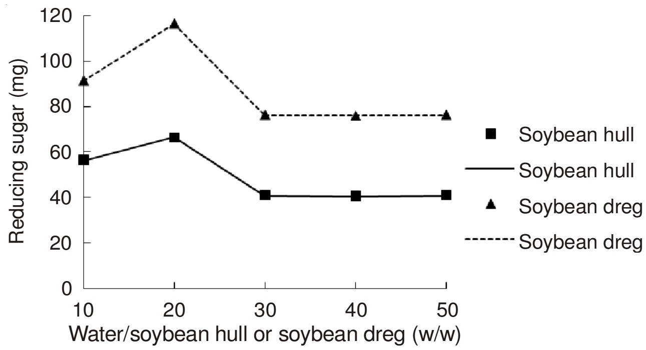

Fig. 6. Yields of products with different amount of water. The conditions were fixed as follows: soybean hulls (0.25 g), H_2SO_4 (1.2 g), [AMIM]Cl (5 g), 95 °C, 80 min

Effect of reaction temperature on reducing sugar: Cellulose was dissolved into ionic liquids, because the chloride ions in ionic liquid 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, ionic liquids became less viscous, which would enhance the movement rate of chloride ions and then accelerate the dissolution of cellulose and improve the yield of reducing sugar. The highest yields of reducing sugar for both of the soybean hull or dreg were observed at 95 °C (Figs. 7 and 8). However, when the temperature was over 95 °C, it may cause the change of some monosaccharides into other derivates and then lead to the decrease of the yield of reducing sugar.

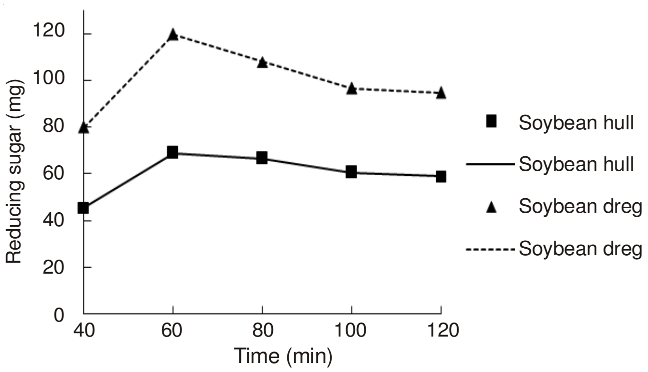

Fig. 7. Yields of products after different reaction time. The conditions were fixed as follows: soybean hulls (0.25 g), water (5 g), H_2SO_4 (1.2 g), [AMIM]Cl (5 g), 95 °C

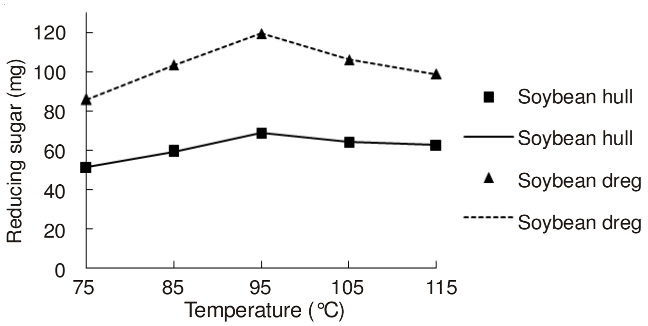

Fig. 8. Yields of products at different reaction temperature. The conditions were fixed as follows: soybean hulls (0.25 g), water (5 g), H_2SO_4 (1.2 g), [AMIM]Cl (5 g), 60 min

Conclusion

In conclusion, an efficient, green and economical method of reducing sugar for cellulose-ethanol production was established. Five functional acidic ionic liquids were prepared. High yield was obtained with the combined use of $[MIM]_2C_4[HSO_4]_2$ and [AMIM]Cl. The optimal condition for soybean hull and dregs was consistent and that is 95 °C, 60 min, ionic liquid/soybean hull was 4.8/1 (wt/wt), water/soybean hull was 20/1 (wt/wt) in 5 g of [AMIM]Cl and the yield of reducing sugar was up to 68.86 and 119.69 mg from 0.25 g of soybean hulls and soybean dregs, respectively. This approach has great potential for the preparation of cellulose-ethanol for industrial production.

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