

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231377380>

Degradation of Cellulose in Dilute Aqueous Solutions of Acidic Ionic Liquid 1-(1-Propylsulfonic)-3-methylimidazolium Chloride, and p-Toluenesulfonic Acid at Moderate Temperatures a...

ARTICLE in INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · OCTOBER 2011

Impact Factor: 2.59 · DOI: 10.1021/ie200938h

CITATIONS

33

READS

174

2 AUTHORS:



Ananda S. Amarasekara

Prairie View A&M University

104 PUBLICATIONS 1,248 CITATIONS

SEE PROFILE



Bernard Wiredu

Prairie View A&M University

23 PUBLICATIONS 142 CITATIONS

SEE PROFILE

Degradation of Cellulose in Dilute Aqueous Solutions of Acidic Ionic Liquid 1-(1-Propylsulfonic)-3-methylimidazolium Chloride, and *p*-Toluenesulfonic Acid at Moderate Temperatures and Pressures

Ananda S. Amarasekara* and Bernard Wiredu

Department of Chemistry, Prairie View A&M University, Prairie View, Texas 77446, United States

ABSTRACT: Dilute aqueous solutions of 1-(1-propylsulfonic)-3-methylimidazolium chloride and *p*-toluenesulfonic acid are shown to be better catalysts than aqueous sulfuric acid of the same H^+ ion concentration for the degradation of cellulose at moderate temperatures and pressures. For example, Sigmacell cellulose ($DP \approx 450$) in aqueous solutions of 1-(1-propylsulfonic)-3-methylimidazolium chloride, *p*-toluenesulfonic acid, and sulfuric acid of the same acid strength ($0.0321 \text{ mol } H^+ \text{ ion/L}$) produced total reducing sugar (TRS) yields of 28.5%, 32.6%, and 22.0%, respectively, after heating at 170°C for 3.0 h. In the same set of experiments, glucose yields of 22.2%, 21.0%, and 16.2% were attained in 1-(1-propylsulfonic)-3-methylimidazolium chloride, *p*-toluenesulfonic acid, and sulfuric acid mediums, respectively.

INTRODUCTION

Cellulose saccharification using dilute aqueous sulfuric acid at high temperature and pressure is the oldest method used in the cellulosic ethanol process. The main disadvantage in this dilute acid hydrolysis of cellulosic biomass is the poor sugar yields and, as a result, low ethanol yield, and the other disadvantage is the high energy cost associated with operating at temperatures above 200°C and at high pressures. With the rapid development of enzyme technologies in the last two decades, the acid hydrolysis process has gradually been replaced by enzymatic hydrolysis. However, an energy-consuming pretreatment of the feedstock is required in the enzymatic method, and the cost of currently available enzyme preparations is a major factor in large-scale industrial cellulosic ethanol production. Although the direct dilute acid saccharification gives lower sugar yields, several research groups have taken an interest recently,^{1–5} giving a second look at this classical method, because of its simplicity and lower cost, when compared to enzymatic saccharification, which requires an energy-consuming pretreatment anyway.

Since the first report in 2002, on the dissolution of cellulose in imidazolium ionic liquids,⁶ there have been numerous attempts to capitalize on this initial discovery, including the use of cellulose-ionic liquid solutions for efficient derivatization of cellulose,^{7–10} fabrication into films and gels,¹¹ as well as conversion to alkylglycosides.¹² In addition, in 2007, Zhang reported^{13,14} the use of a catalytic amount of H_2SO_4 and a small controlled amount of water for the hydrolysis of cellulose dissolved in butylmethylimidazolium chloride, under mild conditions. Later, several reports appeared on the use of solid acid catalysts,^{15–17} as well as an immobilized acidic ionic liquid catalyst,¹⁸ for the hydrolysis of cellulose dissolved in imidazolium ionic liquids. In 2009, we developed the use of Brønsted acidic ionic liquids with a built-in $-SO_3H$ group for the concurrent dissolution and hydrolysis of cellulose under mild conditions.¹⁹ Where we reported that cellulose with $DP \approx 450$ dissolved in Brønsted acidic ionic liquids, 1-(1-propylsulfonic)-3-methylimidazolium chloride and 1-(1-butylsulfonic)-3-methylimidazolium chloride can be hydrolyzed by

the addition of 2.0 equiv of water per glucose unit of cellulose, and heating the solution at 70°C , and at atmospheric pressure, to give glucose, along with other reducing sugars in good yields.

It is well-known that water acts as an antisolvent for the dissolution of cellulose in ionic liquids, and cellulose dissolved in ionic liquids such as butylmethylimidazolium chloride or ethylmethylimidazolium chloride can be easily regenerated via the addition of water. In addition, this regenerated cellulose is shown to have a lower crystallinity²⁰ and seems to undergo relatively facile enzymatic hydrolysis with cellulases; therefore, cellulose regeneration from ionic liquid solution can be used as an alternative pretreatment technique. Since the cellulose–ionic-liquid system has been traditionally studied under anhydrous conditions, and the effect of catalytic amount of ionic liquid in the aqueous phase is unexplored territory. Furthermore, we believe that catalytic effect of water-soluble Brønsted acidic ionic liquids in the aqueous phase is particularly interesting, because these ionic liquids have the sulfonic acid function attached to the imidazolium ionic liquid core structure for acid catalysis process. With this curiosity, we have undertaken to study the effect of catalytic amount of acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride (**1**) (see Figure 1) in the aqueous medium on cellulose at high temperature and pressure. In this publication, we report our results on the degradation of Sigmacell cellulose of $DP \approx 450$ in dilute aqueous solutions of 1-(1-propylsulfonic)-3-methylimidazolium chloride, and comparison with aqueous sulfuric acid, as well as with aqueous *p*-toluenesulfonic acid medium of the same molar H^+ concentration. The acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride was chosen for this preliminary study, because this acidic ionic liquid gave the highest total reducing sugar and glucose yields in our earlier cellulose hydrolysis studies in cellulose–acidic-ionic-liquid

Received: May 2, 2011

Accepted: September 27, 2011

Revised: September 14, 2011

Published: September 27, 2011

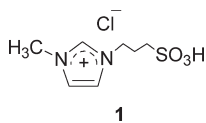


Figure 1. Brønsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride (1).

solutions.¹⁹ *p*-Toluenesulfonic acid was included in this comparison study to see the effect of a neutral aromatic hydrophobic group on the catalytic activity of the $-\text{SO}_3\text{H}$ group.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation. Sigmacell cellulose-type 101 (DP \approx 450, from cotton linters), 1-methylimidazole, 1,3-propanesultone, *p*-toluenesulfonic acid, *o*-dianisidine, glucose oxidase (from *Aspergillus niger*, 181.3 units/mg), peroxidase (from horseradish, 59 units/mg), and dinitrosalicylic acid were purchased from Aldrich Chemical Co. Brønsted acidic ionic liquid 1 was prepared via the condensation of 1-methylimidazole with 1,3-propanesultone and acidification of the resulting salt with concentrated HCl, according to the literature procedure.^{21,22} Cellulose hydrolysis experiments were carried out in 25-mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, purchased from Lonsino Medical Products Co., Ltd. (Jingsu, China). These reaction kettles were heated in a preheated Precision Scientific Model-28 laboratory oven with a temperature accuracy of ± 1 °C. Total reducing sugars (the total glucose and glucose oligomers with reducing groups, abbreviated hereafter as TRS) and glucose concentrations in aqueous solutions were determined using a Carey 50 UV–vis spectrophotometer and 1-cm quartz cells.

2.2. General Experimental Procedures for the Degradation of Cellulose Samples Using Aqueous 1-(1-Propylsulfonic)-3-methylimidazolium Chloride, *p*-Toluenesulfonic, and Sulfuric Acid Solutions. Stock solutions of the acids, 1-(1-propylsulfonic)-3-methylimidazolium chloride, *p*-toluenesulfonic, and sulfuric acid were prepared by dissolving appropriate amounts of these acids in deionized water to give an acid concentration of 0.0321 mol H^+ /L in each solution. The accuracy of the concentration was checked by titration with a standardized aqueous NaOH solution, using phenolphthalein as the indicator. Sigmacell cellulose-type 101 (DP \approx 450) (0.030 g, 0.185 mmol of glucose unit of cellulose) was suspended in 2.00 mL of aqueous acid solution in a 25-mL high-pressure stainless steel reaction kettle with Teflon inner sleeve. The reaction kettle was firmly closed and heated in a thermostatted oven maintained at the desired temperature for a specified length of time. Then reaction kettle was removed from the oven and immediately cooled under running cold water to quench the reaction. The contents were transferred into a centrifuge tube and diluted to 10.0 mL with deionized water, neutralized via the dropwise addition of 0.5 M aqueous NaOH, and centrifuged at 3500 rpm for 6 min to precipitate the solids before TRS determination, using the 3,4-dinitrosalicylic acid (DNS) method.^{13,23} The glucose formed was measured using glucose oxidase/peroxidase enzymatic assay.^{24,25}

2.3. Analysis of Hydrolyzate. **2.3.1. TRS Assay.** A 1.00 mL of portion of the clear hydrolyzate solution from the centrifuge tube was transferred into a vial and 2.50 mL of deionized water was added. To this was added 0.50 mL of DNS reagent,^{13,23} and the mixture was incubated in a water bath that was maintained at 90 °C for 5 min. The reagent blank sample was prepared with

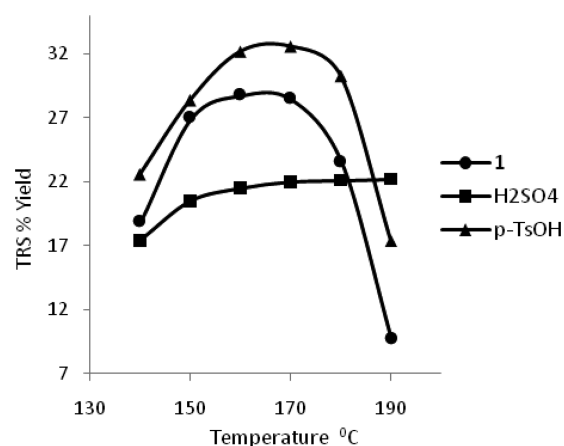


Figure 2. Changes in the yields of total reducing sugars (TRS) produced during the hydrolysis of Sigmacell cellulose (DP \approx 450) in aqueous 1-(1-propylsulfonic)-3-methylimidazolium chloride, aqueous sulfuric acid, and aqueous *p*-toluenesulfonic acid at different temperatures. All acid solutions are used under the following conditions: 0.0321 mol H^+ /L, reaction time = 3.0 h, and 0.030 g of Sigmacell cellulose in 2.00 mL of aqueous acid was used in all experiments. Averages of duplicate experiments are shown.

3.50 mL of deionized water and 0.50 mL of DNS reagent and heated similar to the samples. The absorbance then was measured at 540 nm, against the reagent blank, and TRS concentrations in solutions were calculated by employing a standard curve prepared using glucose.

2.3.2. Preparation of Glucose Oxidase–Peroxidase Assay Reagent. To a solution prepared by dissolving 0.020 g of *o*-dianisidine in 1.0 mL of methanol was added 79.0 mL of a 0.1 M sodium phosphate buffer of pH 6.5. Then, 0.0055 g of glucose oxidase (181.3 units/mg) and 0.0035 g of peroxidase (59 units/mg) enzymes were dissolved in this buffered-*o*-dianisidine solution to prepare the glucose analysis reagent. This reagent was stored in a brown glass bottle, frozen at -20 °C, and was stable for up to 6 months.

2.3.3. Glucose Assay. A quantity of 0.20 mL of the clear hydrolyzate solution from the centrifuge tube was transferred to a vial and diluted with 1.80 mL of deionized water. At zero time, the reaction was started by adding 2.00 mL of glucose oxidase-peroxidase assay reagent to the vial and mixing thoroughly, and the vial was incubated in a water bath at 37 °C for 30 min. The reaction then was quenched by adding 2.00 mL of 6 M HCl to give a pink solution. The reagent blank was prepared by mixing 2.00 mL of deionized water and 2.00 mL of assay reagent and was treated similarly. The absorbance then was immediately measured at 540 nm against the reagent blank, and the glucose concentration in the solution was calculated by employing a standard curve prepared using glucose.

3. RESULTS AND DISCUSSION

Hydrolysis of untreated cellulose in dilute aqueous acid solutions generally requires heating at high temperature under pressure.^{1–5} Therefore, the initial set of experiments was designed to determine the optimum temperature conditions for the degradation of cellulose in these dilute aqueous acids. In these experiments Sigmacell cellulose (DP \approx 450) samples in aqueous 1-(1-propylsulfonic)-3-methylimidazolium chloride, aqueous sulfuric acid, and aqueous *p*-toluenesulfonic acid mediums were

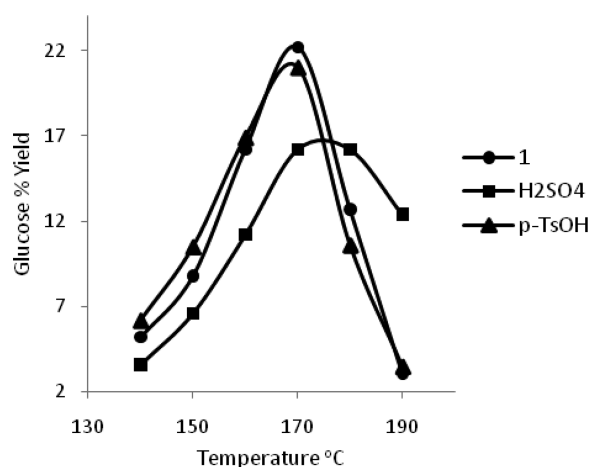


Figure 3. Changes in the yields of total glucose produced during the hydrolysis of Sigmacell cellulose (DP \approx 450) in aqueous 1-(1-propylsulfonic)-3-methylimidazolium chloride, aqueous sulfuric acid, and aqueous *p*-toluene sulfonic acid at different temperatures. All acid solutions are used under the following conditions: 0.0321 mol H⁺/L, reaction time = 3.0 h, and 0.030 g of Sigmacell cellulose in 2.00 mL of aqueous acid was used in all experiments. Averages of duplicate experiments are shown.

heated in stainless steel solvothermal reaction kettles with Teflon inner sleeves in the temperature range of 140–190 °C for 3.0 h, and, after removing the remaining cellulose residue, the hydrolyzate was analyzed for TRS and glucose yields, as described in sections 2.3.1 and 2.3.3. Aryl sulfonic acids, as well as sulfonic-acid-group-attached ionic liquids, are thermally stable²⁶ in the temperature range used in this study. All aqueous acid mediums used in the study were of the same H⁺ ion concentration. According to Oscarson and Izatt's expression regarding the temperature dependence of the first and second dissociation constants of sulfuric acid in an aqueous medium, it is assumed that H₂SO₄ completely dissociates to give two H⁺ ions in the temperature range of 140–190 °C.^{27,28} The average TRS and glucose yields produced in a series of experiments conducted in the temperature range of 140–190 °C are shown in Figures 2 and 3, respectively. These results show that cellulose samples heated in aqueous 1 and aqueous *p*-toluenesulfonic acid mediums in the temperature range of 150–170 °C produce higher TRS yields, compared to the samples heated in aqueous sulfuric acid solutions of the same molar H⁺ ion concentration (see Figure 2). At 170 °C, cellulose heated in aqueous *p*-TsOH and ionic liquid 1 showed TRS yields of 32.6% and 28.5%, respectively, compared to the 22.0% yield of TRS produced in aqueous H₂SO₄, under identical conditions. These are 48% and 30% enhancements of the catalytic activities in the degradation of cellulose, because of the respective tolyl and alkylimidazolium groups attached to the –SO₃H function. This catalytic activity enhancement may be due to an adsorption of *p*-toluenesulfonic acid and 1-(1-propylsulfonic)-3-methylimidazolium chloride on the cellulose surface, which allows the facile disruption of the cellulose structure and hydrolysis of the glycosidic bonds. We believe the protonation of glycosidic oxygen, followed by water attack, is a possible mechanism for hydrolysis of the glycosidic bond. In a recent study on comparison of *Pinaus radiata* bark liquefaction in phenol, using *p*-TsOH and H₂SO₄ as catalysts, Mun found²⁹ that, in *p*-TsOH-catalyzed liquefaction, cellulose residue had a lower crystallinity than in the H₂SO₄ catalyst samples.

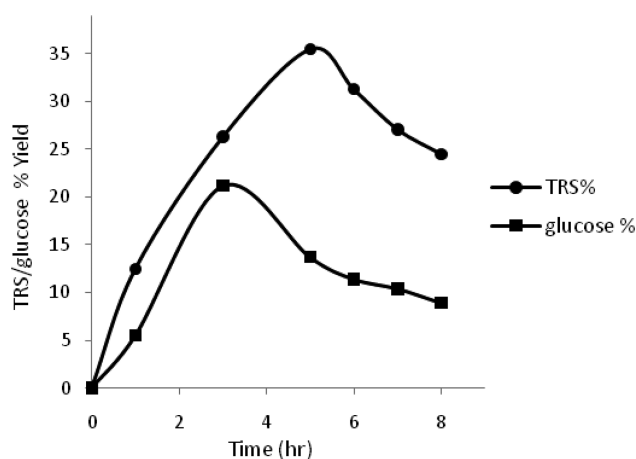


Figure 4. Changes in the yields of TRS and glucose produced during the hydrolysis of Sigmacell cellulose (DP \approx 450) in aqueous 1-(1-propylsulfonic)-3-methylimidazolium chloride (1) (0.0321 mol H⁺/L) at 170 °C. Note that 0.030 g of Sigmacell cellulose in 2.00 mL of aqueous 1 was used in all experiments. Averages of duplicate experiments are shown.

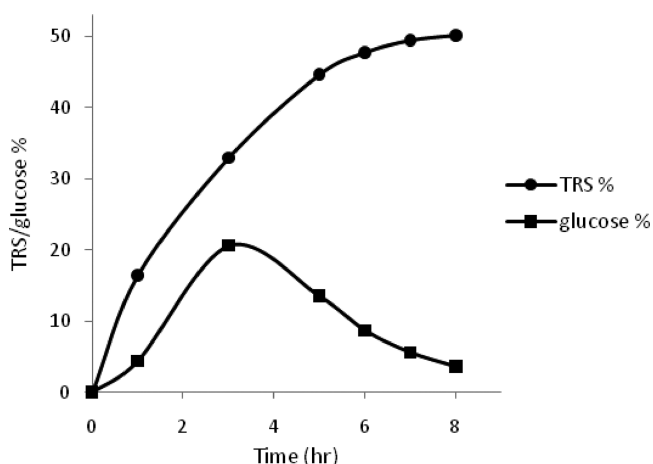


Figure 5. Changes in the yields of TRS and glucose produced during the hydrolysis of Sigmacell cellulose (DP \approx 450) in aqueous *p*-toluenesulfonic acid (0.0321 mol H⁺/L) at 170 °C. Note that 0.030 g of Sigmacell cellulose in 2.00 mL of aqueous *p*-toluenesulfonic acid was used in all experiments. Averages of duplicate experiments are shown.

These results also support our observation of enhanced catalytic activity in the *p*-TsOH catalyzed degradation of cellulose.

It is interesting to note that the TRS yields rapidly decrease at temperatures above 170 °C in *p*-TsOH, and in ionic liquid 1 mediums, whereas the samples heated in aqueous H₂SO₄ continued to give constant TRS yields of \sim 22%. This may be due to the decomposition of glucose and higher oligomers to nonreducing sugar products in *p*-TsOH, and in ionic liquid 1 mediums at higher temperatures. The variation of glucose yields with temperature is shown in Figure 3, which also follows a similar trend to the TRS yields shown in Figure 2. The glucose yields peaks at 170 °C, for *p*-TsOH (21.0%) and ionic liquid 1 (22.2%) mediums, whereas the highest glucose yield in aqueous H₂SO₄ (16.2%) was observed in the 170–180 °C range. As in the case of TRS, a rapid decline was observed in glucose yields in *p*-TsOH, and in ionic liquid 1, at temperatures above 170 °C (see

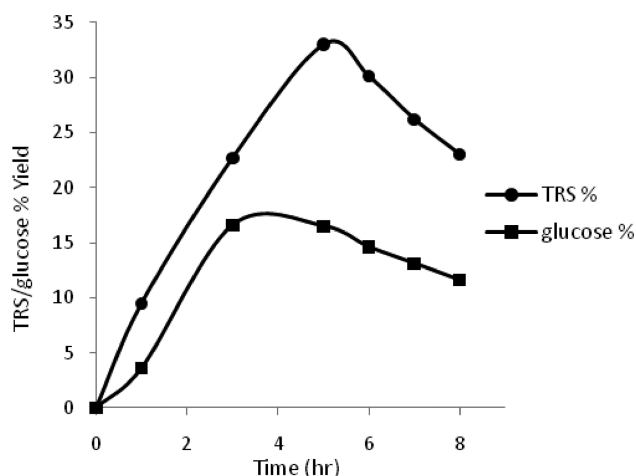


Figure 6. Changes in the yields of TRS and glucose produced during the hydrolysis of Sigmacell cellulose (DP \approx 450) in aqueous sulfuric acid (0.0321 mol H⁺/L) at 170 °C. Note that 0.030 g of Sigmacell cellulose in 2.00 mL of aqueous sulfuric acid was used in all experiments. Averages of duplicate experiments are shown.

Figure 3). Recently, Kupiainen showed²⁷ that glucose decomposition in aqueous acidic media is dependent only on the H⁺ ion concentration and is independent of the acid source. Therefore, in the high-temperature region (170–190 °C), this rapid decline in the glucose yields in **1** and in *p*-TsOH may be due to a decrease in the degradation of cellulose, when compared to the cellulose degradation in aqueous H₂SO₄.

The second set of experiments were conducted to determine the effect of heating time on TRS and glucose yields for samples heated at 170 °C, under isothermal conditions in the three acidic mediums, and results of these experiments are shown in Figures 4, 5, and 6. Cellulose samples heated at 170 °C in aqueous solutions of **1** and H₂SO₄ produced the maximum TRS yields of 35.5% (5 h) and 33.0% (5 h), respectively, whereas in *p*-TsOH medium, a maximum TRS yield of \sim 50% was achieved after 7–8 h. The glucose produced in the hydrolysis of cellulose at 170 °C reached the maximum yields after 3 h, in all three acid mediums. After 3 h, the acidic ionic liquid medium gave the highest glucose yield of 21.6%, whereas an aqueous *p*-toluenesulfonic acid medium produced a yield of 20.6%, and the aqueous H₂SO₄ medium produced the lowest glucose yield (16.6%), confirming the results shown in Figure 3. A rapid decline in glucose yields were seen in **1** and in *p*-TsOH mediums, after 3 h, whereas a slower decrease in glucose yields is observed in an aqueous H₂SO₄ medium, similar to the trend observed in temperature dependence experiments.

The residue left during the hydrolysis experiments was analyzed via infrared (IR) spectroscopy (after drying in a vacuum at 50 °C for 15 h), and was identified as unhydrolyzed cellulose, because there are no significant changes in the IR spectrum, when compared to the original cellulose.

4. CONCLUSION

We have shown that dilute aqueous solutions of 1-(1-propylsulfonic)-3-methylimidazolium chloride and *p*-toluenesulfonic acid are better catalysts than aqueous sulfuric acid of the same molar H⁺ ion concentration for the degradation of cellulose to glucose and higher oligomers at moderate temperature and pressure. The highest catalytic activity enhancements (48% and

30%) were observed in *p*-TsOH and 1-(1-propylsulfonic)-3-methylimidazolium chloride media, respectively, at 170 °C after 3 h. This is a significant enhancement of catalytic activity of the sulfonic acid group by the attached alkylimidazolium cation and the tolyl group, and this can be considered as a lead for understanding the interaction of aqueous sulfuric acid and sulfonic acids with cellulose at moderate to high temperatures and pressures. This finding can be applied to other Brønsted acidic ionic liquids, as well as alkyl/aryl sulfonic acids, to study structure-catalytic activity effects to develop catalysts that are useful in efficient saccharification of lignocellulosic biomass at a lower temperature and pressure for the cellulosic-ethanol process.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +1 936 261 3107. Fax: +1 936 261 3117. E-mail: asamarasekara@pvamu.edu.

ACKNOWLEDGMENT

Authors would like to thank Center for Environmentally Beneficial Catalysis (CEBC) at the University of Kansas, the American Chemical Society (through PRF Grant No. UR1-49436), the National Science Foundation (NSF) (through Grant Nos. CBET-0929970 and HRD-1036593), and the U.S. Department of Agriculture (USDA) (through Grant No. CBG-2010-38821-21569) for financial support.

REFERENCES

- (1) Lenihan, P.; Orozco, A. O.; Neill, E.; Ahmad, M. N.; Rooney, D. W.; Walker, G. M. Dilute acid hydrolysis of lignocellulosic biomass. *Chem. Eng. J.* **2010**, *156*, 395–403.
- (2) Sanchez, G.; Pilcher, L.; Roslander, C.; Modig, T.; Galbe, M.; Liden, G. Dilute-acid hydrolysis for fermentation of the Bolivian straw material Paja Brava. *Bioresour. Technol.* **2004**, *93* (3), 249–256.
- (3) Torget, R. W.; Kim, J. S.; Lee, Y. Y. Fundamental Aspects of Dilute Acid Hydrolysis/ Fractionation Kinetics of Hardwood Carbohydrates. 1. Cellulose Hydrolysis. *Ind. Eng. Chem. Res.* **2000**, *39* (8), 2817–2825.
- (4) Kim, J. S.; Lee, Y. Y.; Torget, R. W. Cellulose Hydrolysis Under Extremely Low Sulfuric Acid and High-Temperature Conditions. *Appl. Biochem. Biotechnol.* **2001**, *91*–93, 331–340.
- (5) Xiang, Q.; Lee, Y. Y.; Torget, R. W. Kinetics of Glucose Decomposition During Dilute-Acid Hydrolysis of Lignocellulosic Biomass. *Appl. Biochem. Biotechnol.* **2004**, *113*–116, 1127–1138.
- (6) Swatoski, R. P.; Spear, S. K.; Holbery, J. D.; Rogers, R. D. Dissolution of Cellulose with Ionic Liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.
- (7) Liu, C.-F.; Sun, R.-C.; Zhang, A.-P.; Qin, M.-H.; Ren, J.-L.; Wang, X.-A. Preparation and Characterization of Phthalated Cellulose Derivatives in Room-Temperature Ionic Liquid without Catalysts. *J. Agric. Food Chem.* **2007**, *55*, 2399–2406.
- (8) Cao, Y.; Wu, J.; Meng, T.; Zhang, J.; He, J.; Li, H.; Zhang, Y. Acetone-soluble cellulose acetates prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). *Carbohydr. Polym.* **2007**, *69*, 665–672.
- (9) Liu, C. F.; Sun, R. C.; Zhang, A. P.; Ren, J. L.; Wang, X. A.; Qin, M. H.; Chao, Z. N.; Luo, W. Homogeneous modification of sugarcane bagasse cellulose with succinic anhydride using an ionic liquid as reaction medium. *Carbohydr. Res.* **2007**, *342*, 919–926.
- (10) Liu, C. F.; Sun, R. C.; Zhang, A. P.; Ren, J. L. Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium. *Carbohydr. Polym.* **2007**, *68*, 17–25.

- (11) Kadokawa, J.; Murakami, M.; Kaneko, Y. A facile preparation of gel materials from a solution of cellulose in ionic liquid. *Carbohydr. Res.* **2008**, *43*, 769–772.
- (12) Ignatyev, I. A.; Mertens, P. G. N.; VanDoorslaer, C.; Binnemans, K.; deVos, D. E. Cellulose conversion into alkylglycosides in the ionic liquid 1-butyl-3-methylimidazolium chloride. *Green Chem.* **2010**, *12* (10), 1790–1795.
- (13) Li, C.; Zhao, Z. K. Efficient Acid-Catalyzed Hydrolysis of Cellulose in Ionic Liquid. *Adv. Synth. Catal.* **2007**, *349*, 1847–1850.
- (14) Li, C.; Wang, Q.; Zhao, Z. K. Acid in ionic liquid: An efficient system for hydrolysis of lignocellulose. *Green Chem.* **2008**, *2*, 177–182.
- (15) Rinaldi, R.; Palkovits, R.; Schüth, F. Depolymerization of cellulose using solid acid catalysts in ionic liquids. *Angew. Chem., Int. Ed.* **2008**, *47*, 8047–8050.
- (16) Zhang, Z.; Zhao, Z. K. Solid acid and microwave-assisted hydrolysis of cellulose in ionic liquid. *Carbohydr. Res.* **2009**, *344* (15), 2069–2072.
- (17) Kim, S. J.; Dwiatmoko, A. A.; Choi, J. W.; Suh, Y. W.; Suh, D. J.; Oh, M. Cellulose pretreatment with 1-*n*-butyl-3-methylimidazolium chloride for solid acid-catalyzed hydrolysis. *Bioresour. Technol.* **2010**, *101* (21), 8273–8279.
- (18) Amarasekara, A. S.; Owereh, O. S. Synthesis of a sulfonic acid functionalized acidic ionic liquid modified silica catalyst and applications in the hydrolysis of cellulose. *Catal. Commun.* **2010**, *11*, 1072–1075.
- (19) Amarasekara, A. S.; Owereh, O. S. Hydrolysis and Decomposition of Cellulose in Brønsted Acidic Ionic Liquids Under Mild Conditions. *Ind. Eng. Chem. Res.* **2009**, *48*, 10152–10155.
- (20) Dadi, A. P.; Varanasi, S.; Schall, C. A. Enhancement of Cellulose Saccharification Kinetics Using an Ionic liquid Pretreatment Step. *Biotechnol. Bioeng.* **2006**, *95* (5), 904–910.
- (21) Yang, Q.; Wei, Z.; Xing, H.; Ren, Q. Brønsted acidic ionic liquids as novel catalysts for the hydrolyzation of soybean isoflavone glycosides. *Catal. Commun.* **2008**, *9*, 1307–1311.
- (22) Zhu, G. Y.; Wang, R.; Liu, G. H.; Xu, L. Q.; Zhang, B.; Wu, X. Q. Synthesis of multi-hydroxyl and sulfonyl dual-functionalized room temperature ionic liquids. *Chin. Chem. Lett.* **2007**, *18*, 633–635.
- (23) Breuil, C.; Saddler, J. N. Comparison of the 3,5-dinitrosalicylic acid and Nelson-Somogyi methods of assaying for reducing sugars and determining cellulase activity. *Enzyme Microb. Technol.* **1985**, *7*, 327–332.
- (24) Bergmeyer, H. U.; Bernt, E. In *Methods of Enzymatic Analysis*; Bergmeyer, H. U., Eds.; Academic Press: New York, 1974; pp 1205–1212.
- (25) Southgate, D. A. T. *Determination of Food Carbohydrates*; Applied Science Publishers, Ltd.: London, 1961.
- (26) Amarasekara, A. S.; Owereh, O. S. Thermal properties of sulfonic acid group functionalized Brønsted acidic ionic liquids. *J. Therm. Anal. Calorim.* **2011**, *103*, 1027–1030.
- (27) Kupiainen, L.; Ahola, J.; Tanskanen, J. Comparison of Formic and Sulfuric Acids as a Glucose Decomposition Catalyst. *Ind. Eng. Chem. Res.* **2010**, *49*, 8444–8449.
- (28) Oscarson, J. L.; Izatt, R. M.; Brown, P. R.; Pawlak, Z.; Gillespie, S. E.; Christensen, J. J. Thermodynamic quantities for the interaction of SO_4^{2-} with H^+ and Na^+ in aqueous solution from 150 to 320 °C. *J. Solution Chem.* **1988**, *17*, 841–863.
- (29) Mun, S. P.; Jang, J. P. Liquefaction of cellulose in the presence of phenol using *p*-toluenesulfonic acid as a catalyst. *J. Ind. Eng. Chem. Res.* **2009**, *15*, 743–747.