

Hydrolysis of microcrystalline cellulose using functionalized Bronsted acidic ionic liquids – A comparative study



Firdaus Parveen, Tanmoy Patra, Sreedevi Upadhyayula*

Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

ARTICLE INFO

Article history:

Received 11 June 2015

Received in revised form 14 August 2015

Accepted 17 August 2015

Available online 22 August 2015

Keywords:

Microcrystalline cellulose

Functionalized ionic liquid

Hydrolysis

Hammett function

DFT

Acidity

Catalyst

ABSTRACT

Cellulose conversion to platform chemicals is required to meet the demands of increasing population and modernization of the world. Hydrolysis of microcrystalline cellulose was studied with $-\text{SO}_3\text{H}$, $-\text{COOH}$ and $-\text{OH}$ functionalized imidazole based ionic liquid using 1-butyl-3-methylimidazolium chloride [BMIM]Cl as a solvent. The influence of temperature, time, acidity of ionic liquids and catalyst loading was studied on hydrolysis reaction. The maximum %TRS yield 85%, was obtained at 100°C and 90 min with 0.2 g of $-\text{SO}_3\text{H}$ functionalized ionic liquid. UV–vis spectroscopy using 4-nitro aniline as an indicator was performed to find out the Hammett function of ionic liquid and acidity trends are as follows: $\text{SO}_3\text{H} > -\text{COOH} > -\text{OH}$. Density functional theory (DFT) calculations were performed to optimize the ionic liquid and their conjugate bases at B3LYP 6-311G++ (d, p) level using Gaussian 09 program. Theoretical findings are in agreement with the experimental results.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Depletion of fossil reserves and global climate changes are the outcome of irrational use, increasing population and modernization of the global world. Lignocellulosic biomass is the readily available nonfood based renewable resource (Huber, Iborra, & Corma, 2006). Lignocellulose consists of (40–50%) cellulose, (25–35%) hemicellulose and (15–20%) lignin. Cellulose can be processed and converted into platform chemicals to be used by various sectors such as polymers, fuels, and solvents, etc. (Wyman et al., 2005). Cellulose is the biopolymer of glucose units linked via β -1, 4-glycosidic bond to form a linear molecular chain (Smith, 1937). These chains are stabilized by inter and intramolecular H-bonding, which makes the structure recalcitrant toward the hydrolysis (Remsing, Swatloski, Rogers, & Moyna, 2006; Vitz, Erdmenger, Haensch, & Schubert, 2009).

Dissolution is the crucial step during the hydrolysis of cellulose, 1-butyl-3-methyl imidazolium chloride [BMIM]Cl was found to be the most promising solvent for cellulose dissolution, (Swatloski, Spear, Holbrey, & Rogers, 2002) as it breaks the hydrogen bonding between the cellulose chains via forming H-bond between

cellulose hydroxyl group ($-\text{OH}$) and chloride ion of ionic liquid (Dong & Zhang, 2012). After the dissolution of cellulose, hydrolysis can proceed via mineral acids, solid acids, and enzymes, each have both advantages and disadvantages. The mineral acid is an efficient catalyst, however, its waste neutralization is still a problem, as it produces a large quantity of gypsums and corrodes the reactor (Akpınar, Erdogan, & Bostanci, 2009). The solid acid catalyst does not have these problems, but has the disadvantage of separation of solid residue from the catalyst. The major issue with solid acidic catalysts is high catalyst loading and separation of solid residue from the catalyst. Among all methods, enzyme catalysis is found to be the most promising, as it requires milder reaction conditions and no side products are formed. However, highly pure solvents are required, and the cost of the enzyme is very high (Zhou, Xia, Lin, Tong, & Beltramini, 2011).

Morales et al. reported the hydrolysis of cellulose, using [BMIM]Cl as solvent and organic acids as catalysts, to cellobiose and glucose with high selectivity (Morales-de la Rosa, Campos-Martin, & Fierro, 2012). Recently, acidic ionic liquids attracted the attention of researchers for the conversion of cellulose to glucose (Amarasekara & Owereh, 2009). They reported for the first time the hydrolysis of cellulose using the acidic ionic liquid as solvent as well as catalyst under moderate reaction conditions, to yield 62% total reducing sugar (TRS), after preheating for 1 h without water. Whereas, dilute solution of acidic ionic liquid 1-(1-propyl sulfonic)-3-methylimidazolium chloride $\{(\text{C}_3\text{SO}_3\text{HMIM})\text{Cl}\}$ yield 28.5% TRS at 170°C and 3 h (Amarasekara & Wiredu, 2011).

* Corresponding author.

E-mail addresses: chz118336@chemical.iitd.ac.in

(F. Parveen), chz118239@chemical.iitd.ac.in (T. Patra), sreedevi@chemical.iitd.ac.in (S. Upadhyayula).

Liu et al. investigated six acidic ionic liquids based on imidazolium, vinyl imidazolium and triethyl amine for the hydrolysis of cellulose and obtained maximum TRS up to 99% at 100 °C (Liu, Xiao, Xia, & Ma, 2013). Amarasekera et al. studied the structure activity relationship of $-\text{SO}_3\text{H}$ functionalized ionic liquid and showed imidazole based ionic liquids have better activity than pyridinium and triethanol ammonium cation (Amarasekera & Wiredu, 2014). Zhuo et al. synthesized novel acidic ionic liquids based on 2-phenyl-2-imidazole to hydrolyze the cellulose to yield 85% TRS (Zhuo et al., 2015).

In this study, the effect of different functional groups $-\text{SO}_3\text{H}$, $-\text{COOH}$ and $-\text{OH}$ was studied on the hydrolysis of cellulose. The effect of temperature, time, catalyst dosage and acidity of ionic liquid on hydrolysis reaction was studied. The minimum energy geometries of ionic liquid and their conjugate bases were obtained by performing density functional theory (DFT) optimization at B3LYP 6-311G++ (d, p) level using Gaussian 09 program to find out the acidity trend and hence, compare their catalytic activity in terms of acidity.

2. Experimental

2.1. Materials

Microcrystalline cellulose, 1-chloro propionic acid were purchased from Merck; 1-methylimidazole, 1,4-butane sultone, were purchased from Sigma–Aldrich; 1-chlorobutane, and 2-bromo ethanol were purchased from Spectrochem.

2.2. Synthesis of [BMIM]Cl ionic liquid

[BMIM]Cl synthesized by using a reported procedure in literature (Dharaskar, Varma, Shende, Yoo, & Wasewar, 2013). ^1H NMR: (300 MHz; D_2O): δ : 0.797(t, 3H), 1.115–1.233(m, 2H), 1.660–1.753(m, 2H), 3.755(s, 1H), 4.059(t, 2H), 7.298–7.346(d, 2H), 8.584(s, 1H).

2.3. Synthesis of acidic ionic liquids

2.3.1. 1-(4-sulfonic acid) butyl-3-methylimidazolium chloride

Acidic ionic liquid containing sulfonic acid was synthesized according to the procedure reported in the literature (Cole et al., 2002). 1,4-butane sultone (0.1 mol, 13.617 g) was taken in 50 mL of toluene and then equimolar amount of 1-methyl imidazole (0.1 mol, 8.21 g) was added dropwise, stirring the solution at 80 °C for 6 h to obtain white zwitterion. The zwitterion was filtered, washed several times with ether and dried under vacuum for 5 h. Ionic liquid afforded after neutralization of zwitterion with an equimolar amount of hydrochloric acid. Yield 92%, ^1H NMR: (300 MHz; D_2O): δ : 1.61–1.66(m, 2H), 1.89–1.94 (m, 2H), 2.84 (t, 2H), 3.78 (s, 3H), 4.14(t, 2H), 7.36(d, 2H), 8.63(s, 1H). ^{13}C NMR: (75 MHz; D_2O): δ : 20.82, 27.99, 35.63, 48.81, 49.91, 122.06, 123.56, 135.81.

2.3.2. 1-propionic acid-3-methylimidazolium chloride

Carboxylic acid containing ionic liquid was synthesized by charging (0.1 mol, 10.85 g) of chloro-propionic acid in 50 mL of anhydrous toluene. Then equimolar amount of 1-methylimidazole (0.1 mol, 8.21 g) was added dropwise with vigorous stirring and refluxed for 5 h under nitrogen atmosphere. After reaction toluene was decanted and the white oil produced was washed three times with ethyl acetate and dried under vacuum at 40 °C for 12 h (Han et al., 2012). Yield 86%, ^1H NMR: (300 MHz; D_2O): δ : 2.92(t, 2H), 3.84(s, 1H), 4.401(t, 2H), 7.397(d, 2H), 8.69(s, 1H). ^{13}C NMR: (75 MHz; D_2O): δ : 33.17, 34.13, 44.92, 122.31, 123.60, 136.49, 174.32.

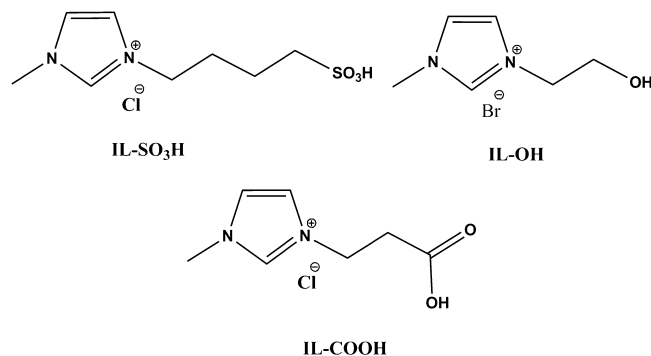


Fig. 1. Functionalized ionic liquid used in this study.

2.3.3. 1-(2-hydroxyethyl)-3-methylimidazolium chloride

Ionic liquid having alcoholic group was synthesized by mixing equimolar amount of 1-methylimidazole (0.1 mol, 8.21 g) and 2-bromoethanol (0.1 mol, 12.964 g) in toluene as solvent. The mixture was refluxed under nitrogen atmosphere for 12 h at 110 °C to obtain pale yellow viscous product. It was purified by washing three times with ethyl acetate and dried under vacuum at 40 °C for 12 h (Lu et al., 2013). Yield 82%, ^1H NMR: (300 MHz; D_2O): δ : 3.853–3.891(6H, m), 4.265(t, 2H), 7.429 (d, 2H), 8.69 (s, 1H). ^{13}C NMR: (75 MHz; D_2O): δ : 35.92, 51.64, 59.88, 122.56, 123.09, 136.43 (Fig. 1).

2.4. Computational method

The minimum energy geometries of $-\text{SO}_3\text{H}$, $-\text{COOH}$ and $-\text{OH}$ functionalized ionic liquids and their conjugate bases were calculated by performing DFT (density functional theory) geometry optimization at B3LYP 6-311G++(d, p) level using Gaussian 09 program (Frisch et al., 2010). A vibrational analysis of each optimized structure was done to ensure the absence of negative frequencies and verify the exact minimum (Kore & Srivastava, 2011, 2012).

The dissociation energy of each ionic liquid (E_{diss} , Eq. (1)) was calculated as the difference between the sum of energies of their corresponding conjugate base (E_{CB}) and the proton (E_{H^+}) and the energy of an acidic ionic liquid (E_{IL});

$$E_{\text{diss}} = [(E_{\text{CB}} + E_{\text{H}^+}) - E_{\text{IL}}] \times 2625.50 \text{ kJ mol}^{-1} \quad (1)$$

2.5. Determination of acidity of ionic liquids using UV–vis spectroscopy

Bronsted acidities of above synthesized ionic liquids were obtained by calculating their Hammett functions, using 4-nitro aniline as indicator to trap the dissociative proton in water using reported procedure (Kondamudi, Elavarasan, Dyson, & Upadhyayula, 2010; Thomazeu, Olivier-Bourbigou, Magna, Luts, & Gilbert, 2003). The Hammett function (H_0 , Eq. (2)) was calculated using the equation below:

$$H_0 = \text{pK}(\text{I})_{\text{aq}} + \log \left(\frac{[\text{I}]}{[\text{IH}^+]_s} \right) \quad (2)$$

where, $\text{pK}(\text{I})_{\text{aq}}$ is pK_a of 4-nitroaniline (0.99), $[\text{I}]_s$, and $[\text{IH}^+]_s$ are the molar concentrations of protonated and unprotonated forms of the indicator. The absorbance of blank (4-nitro aniline) and different concentration of ionic liquid was measured at 380 nm using double beam Dynamica spectrophotometer (Model: Halo DB-20) as shown in Fig. 2.

Download English Version:

<https://daneshyari.com/en/article/1383572>

Download Persian Version:

<https://daneshyari.com/article/1383572>

[Daneshyari.com](https://daneshyari.com)