

Acid functionalized ionic liquid catalyzed transformation of non-food biomass into platform chemical and fuel additive

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ABSTRACT

This paper reports the synthesis of sulfonic acid functionalized Brønsted acidic ionic liquids (BAILs) using *N,N*-dimethyl acetamide [DMA]⁺, *N*-methylpyrrolidone [NMP]⁺ and 1-butyl-3-(4-sulfobutyl)imidazole [BBIM-BuSO₃H]⁺ as cation, and methanesulfonyl [CH₃SO₃]⁻ or (OTf⁻), trifluoromethanesulfonate [CF₃SO₃]⁻ or (OTf⁻), and bis((trifluoromethyl)sulfonyl)amide [(CF₃SO₂)₂N]⁻ or (NTf₂⁻) as anion source. The ionic liquids (ILs) demonstrated excellent catalytic performance in the valorization of waste streams of biomass to 5-hydroxymethylfurfural (HMF) and 5-ethoxymethylfurfural (EMF), a high-value platform chemical and a promising biofuel additive. Catalytic screening indicated that BAILs containing NTf₂⁻ anion exhibits superior performance, giving highest HMF yield. Strong electron withdrawing properties of the trifluoromethyl functionality of [NTf₂]⁻ anion is proposed for this high activity of these BAILs. Detailed studies using NMR reveal the reaction proceeds through the (i) depolymerization of cellulose into glucose, followed by (ii) glucose isomerization to fructose and then the product HMF is formed by (iii) triple dehydration of fructose to HMF. Direct conversion of mushroom to EMF is also observed in one-pot with high yield when ethanol is used as a solvent in excess amount. DFT calculations elucidated that the catalytic performance of the ILs followed the order of their deprotonation energies (DPE) which can be correlated directly to the residual charge on the Brønsted acidic proton. This study of valorization of waste mushroom coupled with DFT calculations, revealing DPE as an important descriptor, is likely the first report of this kind.

1. Introduction

Identification and utilization of alternative energy resource is becoming a significantly important task with the depletion of fossil fuel reserves. Towards this, processes based on fermentation/enzymatic (Ahuja et al., 2004; Alam et al., 2017; Tokiwa and Calabia, 2008), catalytic (De et al., 2015; Kruse et al., 2010), photo-catalytic (Beshkar et al., 2017; Colmenares and Luque, 2014; Zinatloo-Ajabshir et al., 2017, 2016) thermochemical (Alam et al., 2014; De et al., 2011a; Dutta et al., 2012b, 2012a; Ståhlberg et al., 2011; Zakrzewska et al., 2011) and integrated bio-chemo catalytic approaches (Alam et al., 2015; Schwartz et al., 2014) are tried. For the proposed development of a bio-refinery, the Department of Energy at the United States has identified Top-12 biomass-derived platform chemicals from which reaction routes are being developed for the commercial scale synthesis of higher value

fuels and chemicals (Werpy and Petersen, 2004). 5-hydroxymethylfurfural (HMF), obtained from the dehydration of biomass-derived carbohydrates, is one such platform molecule which has been widely studied as the platform chemical to produce specialty chemicals (e.g. levulinic acid), solvents (e.g. alkane diols), bio-gasoline (e.g. 2,5-dimethylfuran (DMF), 5-ethoxymethylfurfural (EMF), ethyl levulinate (EL)) and biopolyester building block (e.g. furandicarboxylic acid, FDCA) (Ahmad et al., 2016; Alam and Saha, 2015; Lanzafame et al., 2011; Pan et al., 2013; Román-Leshkov et al., 2007). However, existing methods of HMF production from edible biomass (e.g., corn and sugarcane) are expected to aggravate the food prices (Bardhan et al., 2015), calling for the identification of non-edible sources to produce HMF (Himmel et al., 2007). In this regard, attempts have been made to produce HMF from untreated raw biomass. This one-pot synthesis of HMF is a difficult process, which generally proceeds in three steps; (i)

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Table 1
Summary of previous results showing the catalytic conversion of untreated biomass into HMF.

Entry	Substrate	T (°C), t (min)	Catalyst	Solvent	% HMF yield	References
1.	Phragmites communis	120, 120	CrCl ₂ /RuCl ₃	[EMIM]Cl	41	(Kim et al., 2011)
2.	Sugarcane Bagasse	140, 5	Zr(O)Cl ₂ /CrCl ₃ + [BMIM]Cl	DMA–LiCl	42	(Dutta et al., 2012a)
3.	Corn stover	140, 120	CrCl ₃ + [EMIM]Cl	DMA–LiCl	48	(Binder and Raines, 2009)
4.	Rice straw	200, 60	CrCl ₃ ·6H ₂ O	[C ₄ mim]Cl	47	(Zhang and Zhao, 2010)
5.	Wheat Straw	160, 60	FePO ₄ + NaH ₂ PO ₄	Water–NaCl/THF	44	(Xia et al., 2017)
6.	Foxtail grass	120, 2	[DMA][CH ₃ SO ₃]	DMA–LiCl	58	(Alam et al., 2012)
7.	Red nutsedge	120, 2	[DMA][CH ₃ SO ₃]	DMA–LiCl	35	(Alam et al., 2012)
8.	Corn Stover	180, 30	AlCl ₃ ·6H ₂ O	H ₂ O–NaCl/ THF	19	(Yang et al., 2012a)
9.	Pinewood	180, 30	AlCl ₃ ·6H ₂ O	H ₂ O–NaCl/ THF	35	(Yang et al., 2012a)
10.	Poplar	180, 30	AlCl ₃ ·6H ₂ O	H ₂ O–NaCl/ THF	26	(Yang et al., 2012a)
11.	Switch grass	160, 60	AlCl ₃ ·6H ₂ O	H ₂ O–NaCl/ THF	13	(Yang et al., 2012c)
12.	Wood ear mushroom	140, 10	[DMA][CH ₃ SO ₃]	DMA–LiCl	44	This work
13.	Wood ear mushroom	140, 10	[BBIM–SO ₃][NTf ₂]	DMA–LiCl	46	This work

hydrolysis of biomass to monosaccharides (e.g. glucose), (ii) isomerization of the monosaccharide (glucose to fructose) and (iii) dehydration of fructose to HMF. In order to perform this multi-step process, catalyst materials such as HCl (Yemiş and Mazza, 2012), FePO₄ + NaH₂PO₄ (Xia et al., 2017), CrCl₂/RuCl₃ (Kim et al., 2011), CrCl₃ + [EMIM]Cl (Binder et al., 2009), CrCl₃·6H₂O (Zhang and Zhao, 2010), Zr(O)Cl₂/CrCl₃ with [BMIM]Cl (Dutta et al., 2012a), [DMA][CH₃SO₃], [NMP][CH₃SO₃] (Alam et al., 2012; De et al., 2012), and AlCl₃·6H₂O (Yang et al., 2012b, 2012a, 2012c) have been utilized. Table 1 presents a comprehensive overview of biomass sources and catalyst used for direct synthesis of HMF.

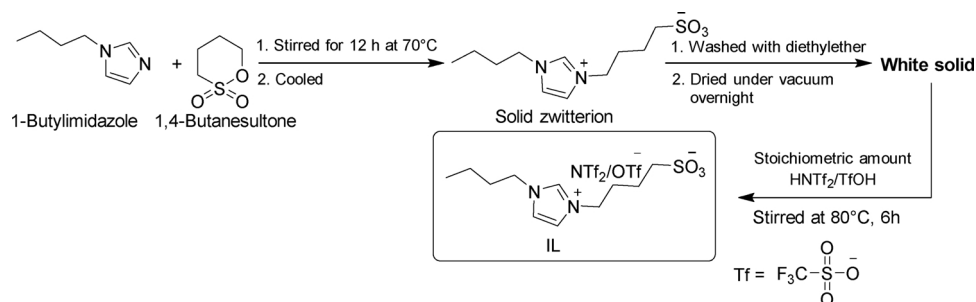
In this study, wild mushrooms were tried as an alternative biomass source, other than the ones studied before (Table 1), to synthesize HMF. The choice of mushrooms as the biomass-source was motivated from its high carbohydrate content (Beluhan and Ranogajec, 2011; Berna and Jaworska, 2010; Kalac, 2009; Yong-jun et al., 2012), rapid cultivation rate, and non-edible value (Kalac, 2009), which may be beneficial for commercial scale economic production of HMF. In addition, a variety of ionic liquids (ILs) were studied as a catalyst in reactions for the direct transformation of mushroom samples to the HMF. Brønsted acidic ionic liquids (BAILs) possess ability to donate protons which is helpful in deconstructing the complex structure of lignocellulosic biomass, containing H-bonds and glycosidic linkages. The protons in BAILs reside at a number of locations in the structure, among which the N or O in the anion, and the acidic moieties (e.g. COOH and SO₃H) attached to the cations are the most common locations (Amarasekara, 2016). Thus, the catalytic activity of a BAIL depends on its structure and ionic components. A comprehensive study by Roger and co-workers had shown a significant improvement in the HMF yield on using ILs (Swatloski et al., 2002). In subsequent studies, several other ILs with acidic hydrogen on anion (e.g. 1-butyl-3-methylimidazolium hydrogensulfate), cation (e.g. N-methyl-2-pyrrolidonium methyl sulfonate [NMP]⁺[CH₃SO₃][−]) and acidic functional groups have been used for HMF production (Ding et al., 2012; Tao et al., 2011b, 2011a; Zakrzewska et al., 2011).

In addition to the use of various varieties of mushrooms and

different types of BAILs, this study is focused on studying the effect of the solvent environment, for example in producing HMF in the N,N-dimethylacetamide-Lithium chloride (DMA–LiCl) medium, and its counterpart ethoxymethylfurfural (EMF) in ethanol. Non-edible mushrooms were thus subjected to an etherification reaction in presence of ILs in one pot to produce EMF, which is receiving wider attention as a fuel with energy densities comparable to gasoline and diesel. (Gruter and Dautzenberg, 2012). Earlier, our group had reported, one pot transformation of sugarcane bagasse and foxtail weed biomass to EMF with Zr(O)Cl₂/CrCl₃ and [DMA][CH₃SO₃] catalysts, respectively (Alam et al., 2012; Dutta et al., 2012a).

An array of sulphonic acid functionalized BAILs were synthesized and used to valorize the waste streams of mushroom biomass into HMF and EMF. Since the acidity of ILs plays a critical role in HMF formation, many techniques have been used to measure the acidity. However, the accuracy of the results depended on the measurement procedure (Johnson et al., 2007; Mihichuk et al., 2011). In addition, the results were observed to be sensitive to impurities by using a UV–vis probe (Mihichuk et al., 2011). Iglesia and co-workers have reported a method based on DFT simulations to calculate the deprotonation energy (DPE) of the polyoxometallates (POM). Their results showed a trend between the activity of the POM catalysts and DPE in acid catalyzed reactions, which was consistent with the experimental results observed between the activity and acidity (Macht et al., 2008, 2007). Lower DPE of the POM was suggested to be higher acidic, which resulted in high activity of the catalysts.

In order to study the role of Brønsted acidity of the ILs in HMF and EMF formation, in this study, the values of DPEs were theoretically calculated using DFT, for IL compositions prepared from 3 different cations (DMA⁺, NMP⁺ and BBIM–BuSO₃H⁺) and 4 different anions [(CH₃SO₃[−]) (OTf[−])], [(CF₃SO₃[−]) (OTf[−])], [(CH₃SO₃)₂N[−] (NTh₂[−])] and [(CF₃SO₃)₂N[−] (NTf₂[−])]. Based on the predicted DPE values, –SO₃H functionalized ILs (Schemes 1 and 2) containing 1-butylimidazolium, DMA and NMP as cation and/or OTf[−] and NTf₂[−] counter ions with varying DPE values were chosen for the transformation of waste



Scheme 1. Schematics showing the preparation routes for Brønsted acidic ionic liquids, [(BBIM–SO₃)[OTf] and [(BBIM–SO₃)[NTf₂] from 1-butyl imidazole and 1,4-butanedisulfonate.

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