Functional Acidic Ionic Liquids as Effective Solvents for the Fractionation of Lignocelluloses

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There is increasing interest in the application of ionic liquids for the pretreatment and fractionation of lignocelluloses. In this study, a series of functional acidic ionic liquids (ILs) with various heterocyclic organic cations were synthesized. Corn stalks were successfully fractionated into lignin, hemicelluloses, and cellulose when ultrasonically pretreated with ILs at 70 °C for 3 h, and subsequently treated with alkaline extraction. High yields of IL-isolated lignin (18.3% to 19.6%) and (8.3% to 14.6%) were obtained using ILs in the absence and presence of water, respectively. The yield of cellulose ranged from 40.0 to 77.0% from IL treatments, whereas the yield of hemicelluloses ranged from 1.1% to 17.3%. Enzymatic hydrolysis of the isolated cellulose residual produced 89.2% to 94.9% reducing sugar with 77.8% to 86.1% glucose, which corresponded to 80.5% to 91.4% enzymatic conversion of cellulose. Syringol and vanillin were found as the main lignin degradation products.

Keywords: Ionic liquids; Corn stalks; Fractionation; Lignin degradation products

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INTRODUCTION

Issues related to climate change and limited fossil-fuel resources have focused investigators to develop sustainable routes for generating energy and valuable chemical products. Abundant lignocellulosic biomass has been identified as a potential renewable resource to produce biofuels. Lignocelluloses are primarily composed of lignin, hemicelluloses and cellulose (Moniruzzaman and Ono 2013), whereby the lignin constituent contributes to the complex and recalcitrant structure of the biomass. Generally, a pretreatment, such as acid, alkali, steam explosion or ammonia fiber explosion process, is used to degrade the recalcitrant structure of the lignocellulosic biomass (Zhang and Shahbazi 2011).

In recent years, ionic liquids (ILs) have been examined as potential alternative pretreatments for lignocellulosic biomass due to their broad liquidity range, high thermal stability, and low vapor pressure (Mora-Pale *et al.* 2011; Weerachanchai and Lee 2014). Their physical and chemical properties can be directly altered by varying the cation or anion component; hence, ILs can be tailored for specific applications (Hu *et al.* 2013). A variety of ILs have been used for the pretreatment and fractionation of various lignocelluloses. Rice straw has been reported to be pretreated with cholinium argininate for 12 h at 90 °C, which resulted in 46% lignin recovery (based on the starting lignin content). Additionally, 74.6% glucose was produced after 72 h of enzymatic saccharification of the pretreated rice straw solid (An *et al.* 2015). Corn stalks have been pretreated with 1-ethly-3-methylimidazolium acetate ([EMIM]CH_3COO) for 1 h at 125 °C, which resulted in 44% of the original lignin being extracted. 80% glucose and 50% glucose were obtained after enzyme reaction of these pretreated corn stalks at 33% (w/w) and 50% (w/w) biomass loading, respectively (Li *et al.* 2009). Moreover, the use of acidic ILs is potentially a sustainable approach of lignocellulosic biomass conversion, which does not require further acid addition. Fibre sludge hydrolysis using hydroxyalkylimidazolium hydrogensulphate as the IL (30 min at 100 °C) produced 29% reducing sugars (Dong *et al.* 2014). Hydrolysis of switchgrass in 1-(sulfobutyl)-3-methylimidazolium chloride ([HSO_3BuMIM]Cl) resulted in 58.1% reducing sugars under thermal and microwave conditions after 1 h at 70 °C followed by treatment with the addition of water for anther 1 h at 70 °C (Amarasekara and Shanbhag 2012).

Based on the above review of current studies, more practical investigations regarding the pretreatment of lignocelluloses with functional ILs are necessary. A more efficient protocol is necessary to isolate lignin and to increase carbohydrate saccharification efficiency using low pretreatment temperature (Li *et al.* 2010; Haykir *et al.* 2013). The aim of this work was to develop functional acidic ILs as fractionation and pretreatment solvents for lignocellulosic biomass. In a previous investigation, a series of imidazolium salts with various anions were tested; promising results were obtained using 1-methylimidazolium chloride ([HMIM]Cl), with Cl^- as the anion for the IL (Zhang *et al.* 2015). Hence, in this work, a series of ionic liquids that are based on different heterocyclic organic cations paired with the Cl^- anion were prepared. These ILs were investigated as pretreatments for corn stock biomass in order to fractionate its constituents. Furthermore, there is limited information concerning lignin degradation products resulting from the IL-pretreatment process. In this work, the lignin degradation products were characterized and their relative quantities were analyzed.

EXPERIMENTAL

Materials

Chemical reagents and cellulase powder from *Aspergillus niger* (10,000 U/g) were obtained from Aladdin Company (Shanghai, China). High-performance liquid chromatography (HPLC) was conducted using an Agilent 1100 HPLC instrument equipped with an Agilent ZORBAX carbohydrate column (Agilent Technologies; Santa Clara, CA, USA). An AV-III 400 MHz NMR spectrometer (Bruker AXS, Inc.; Madison, WI, USA) was used to record ^1H NMR and ^{13}C NMR. Reducing sugars and IL acidities were measured using ultraviolet-visible (UV-Vis) spectroscopy with an UV-mini-1240 spectrometer (Shimadzu Corp.; Tokyo, Japan). The constituents of the raw corn stalks (22.47% lignin, 19.33% hemicelluloses, 43.21% cellulose and 0.74% ash) were determined in accordance to the National Renewable Energy Laboratory (NREL) method (Sluiter *et al.* 2011). Pyridinium chloride ([HPY]Cl), *N*-methylpyrrolidinium-2-one chloride ([HNMP]Cl) and 1-methylimidazolium chloride ([HMIM]Cl) were synthesized in accordance to (Zhang *et al.* 2015).

Synthesis of Ionic Liquids

1-(3-Sulfopropyl)-3-methylimidazolium chloride ([MIM(CH_2)$_3$$SO_3$H]Cl)

1,3-Propanesultone (0.4 mol; 99% purity) was dissolved in ethyl acetate (200 mL; 99.5% purity). 1-Methylimidazoline (0.4 mol; 99% purity) was added dropwise into the mixture. The mixture was reacted at room temperature for 24 h. The product was obtained by the evaporation of the ethyl acetate solvent at reduced pressure; the residue was further vacuum-dried at 60 °C for 24 h. The intermediate product (0.2 mol) was then treated with concentrated hydrochloric acid (0.2 mol) at room temperature for 24 h. The resulting product was washed with 20 mL of diethyl ether and was then dried at 60 °C for 24 h. ^{1}H-NMR (400 MHz, DMSO-d_6) : 2.08 (*t*, 2H), 2.44 (*t*, 2H), 3.84 (*s*, 3H), 4.29 (*t*, 2H), 7.70 (*s*, 1H), 7.78 (*s*, 1H), and 9.16 (*s*, 1H).

1-(2-Carboxyethyl)-3-methylimidazolium chloride ([MIM(CH_2)$_2$COOH]Cl)

3-Chloropropionic acid (0.4 mol; 98% purity) and 1-methylimidazole (0.4 mol; 99% purity) were added into ethyl acetate ((200 mL; 99.5% purity). The reaction mixture was stirred at 70 °C for 24 h. The product was obtained by the evaporation of the ethyl acetate solvent at reduced pressure; the residual was further vacuum-dried at 60 °C for 24 h. ^{1}H-NMR (400 MHz; DMSO-d_6) : 2.93 (*t*, 2H), 3.86 (*s*, 3H), 4.36 (*t*, 2H), 7.77 (*s*, 1H), 7.86 (*s*, 1H), 9.43 (*s*, 1H), and 12.87 (*s*, 1H).

1-Hydroxypropyl -3-methylimidazolium chloride ([MIM(CH_2)$_3$OH]Cl)

The synthesis of [MIM(CH_2)$_3$OH]Cl followed a similar protocol as that of [MIM(CH_2)$_2$COOH]Cl. 3-Chloro-1-propanol (0.2 mol; 98% purity) was reacted with 1-methylimidazole at 70 °C for 24 h. ^{1}H-NMR (400 MHz; DMSO-d_6): 1.89 (*quint*, 2H), 3.31(*s*, 2H), 3.88 (*s*, 3H), 4.26 (*t*, 2H), 5.23 (*s*, 1H), 7.81 (*s*, 1H), 7.98 (*s*, 1H), 9.62 (*s*, 1H).

Determination of ILs Acidity

The Hammett method was used to characterize the acidity of ILs at room temperature (Duan *et al.* 2006; Zhang *et al.* 2012). The acidity was measured with 4-nitroaniline as an indicator (*i.e.*, I) by evaluating the extent of its protonation (*i.e.*, HI^+) as a ratio of the concentrations of the acid-base pair (*i.e.*, [I]/[HI^+]),

$$H_0 = \quad pK_{\mathrm{aq}}(\mathrm{I}) + \log([\mathrm{I}]_s/[\mathrm{HI}^+]_s) \qquad (1)$$

where H_0 is the Hammett acidity function of the IL, pK_{aq}(I) is that for the indicator (which is 0.99 for 4-nitroaniline), and $[\mathrm{I}]_s$ and $[\mathrm{HI}^+]_s$ are the molar concentrations of the unprotonated and the protonated form of the indicator in solution, respectively.

Fractionation of Corn Stalk

The fractionation of corn stalk constituents is schematically shown in Fig. 1. Corn stalk powder (1 g) was added into one of the ionic liquids (20 g) along with water (4 mL). The mixture was heated to 70 °C for 3 h in an ultrasonicator operating at a 400 W power level (Zhang *et al.* 2015). An acetone/water solution (100 mL; 1/1 v/v) was then poured into the IL solution, and the mixture was vigorously agitated. The resulting solid residue, which contained the cellulose-rich fraction, was separated by filtration; the solid was washed with an acetone/water solution (1/1 v/v). The dissolved lignin in the ILs was obtained by evaporating the acetone from Filtrate 1 (Fig. 1); the resulting solid was further washed with water. Filtrate 2 (Fig. 1) was neutralized by the addition of sodium hydroxide. The amount of reducing sugars in the neutralized filtrate was determined by the colorimetric method as described by Miller (1959) that used 3,4-dinitrosalicylic acid (DNS).

The cellulose-rich solid was treated with 50 mL aqueous NaOH solution (3% w/w) at 80 °C for 3 h (Fig. 1). The insoluble residue was separated by filtration, and the solid was washed with water to obtain the purified cellulose fraction. The pH of Filtrate 3 (Fig. 1) was adjusted to 6.80 with an HCl solution (30%,w/w). Three volumes of 95% ethanol were added to the pH-adjusted solution to precipitate the hemicelluloses. Filtrate 4 (Fig. 1) was concentrated under reduced pressure to remove the ethanol. The resulting residual was acidified to pH 2 to precipitate the alkaline lignin (Yang *et al.* 2012; da Costa Lopes *et al.* 2013a). All isolated residues were vacuum-dried for 24 h at 60 °C. All samples were performed for three replicates and their yields were calculated in reference to the untreated corn stock powder:

$$\text{Residue}(\%) = \frac{\text{Residue (mg)}}{\text{Untreated corn stalk (mg)}} \times 100 \qquad (2)$$

Enzymatic Reaction

Enzymatic hydrolysis of the isolated cellulose (0.05g) was carried out in a sodium citrate buffer solution (5 mL; 0.1 M), which was mixed with cellulase (0.02 g) and 2% (w/w) sodium azide aqueous solution (100 µL) at a pH of 4.8. The reaction mixture was shaken at 150 rpm for 72 h at 50 °C. The hydrolyzed solution was quenched for 5 min at 100 °C. The yield of monosaccharide (*i.e.*, glucose) was measured using HPLC (Sluiter *et al.* 2011). All samples were performed for three replicates. The enzymatic cellulose conversion was calculated:

$$\text{Conversion of cellulose}(\%) = \frac{\text{glucose (mg)} \times \frac{162}{180} + \text{cellobiose(mg)}\,\frac{324}{342}}{\text{cellulose(mg)}} \times 100 \qquad (3)$$

Analysis of Lignin Products

Corn stalk powder (100 mg) was added into one of the ionic liquids (2 g) with the addition of water (0.4 mL), which was then heated to 70 °C for 3 h in an ultrasonicator operating at a 400 W power level. Benzene (5 mL) was then added to the mixture to extract all the non-polar compounds. This procedure was repeated three times. The benzene extracts were collected, combined, and concentrated to 1 mL in volume to achieve the sample. The concentrated extracts were analyzed using gas chromatography-mass spectrometry (GC-MS) with an Agilent 7890 GC plus 4789 MS (Agilent Technologies; Santa Clara, CA, USA) equipped with a HP-5MS chromatographic column (30 m length, 0.25 mm ID, and 0.25 µm packing). A total of 10 µL of the sample was injected into the GC at an inlet temperature of 220 °C. Anthracene-d_{10} was used as the internal standard, and helium was used as a carried gas. Standards were used for each compound to calculate the individual GC response factors.

RESULTS AND DISCUSSION

A series of functional ionic liquids (ILs) that were based on different heterocyclic organic cations were synthesized with Cl^- as the anion. Their chemical structures are depicted in Fig. 1.

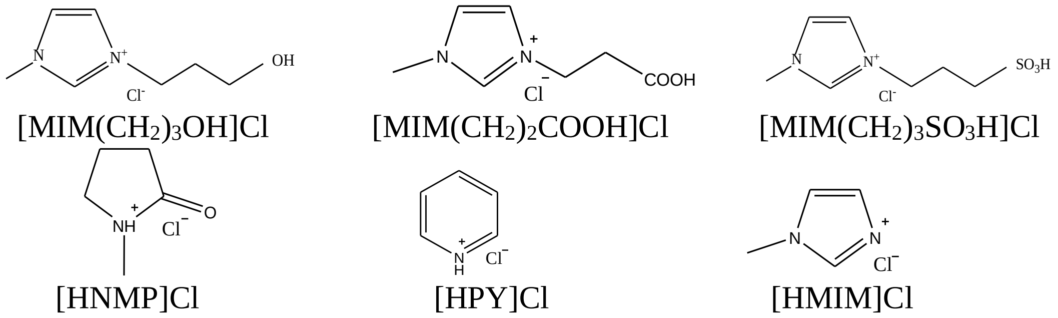

Fig. 1. Chemical structures of ionic liquids

The values of the Hammett acidity function (H_0) for the various ILs are listed in Table 1. Different IL activities (Amax) were derived from their Brønsted acidities.

Table 1. Acidity of Ionic Liquids

Ionic liquid (IL)	A_{max}	I (%)	HI^+ (%)	H_0
blank	1.5068	100.00	0.00	-
[MIM(CH$_2$)$_3$OH]Cl	1.5068	100.00	0.00	-
[MIM(CH$_2$)$_2$COOH]Cl	1.2524	83.12	16.88	1.75
[MIM(CH$_2$)$_3$SO$_3$H]Cl	1.4015	93.01	6.99	2.11
[HMIM]Cl	1.4819	98.35	1.65	2.77
[HPY]Cl	1.4569	96.69	3.31	2.46
[HNMP]Cl	1.1351	75.33	24.67	1.47

Cellulose Fraction

The recovery yields of the cellulose-rich fraction ranged from 51.1% to 77.0%, depending upon which IL that was used (Table 2). A high yield of the cellulose-rich fraction was obtained with [MIM(CH$_2$)$_3$OH]Cl as the IL pretreatment. On the other hand, pretreatment with [MIM(CH$_2$)$_3$SO$_3$H]Cl as the IL resulted in a low yield of the cellulose-rich fraction, which could be attributed to the effectiveness of this IL to remove lignin and hemicelluloses from the recalcitrant biomass. After IL-treatment, the cellulose-rich fraction was extracted with alkali, and resulted in about 39 to 41% cellulose being recovered from the starting biomass material.

Table 2. Yields of Cellulose and Hemicelluloses

Carbohydrate component	[MIM(CH$_2$)$_3$OH]Cl		[MIM(CH$_2$)$_2$COOH]Cl		[MIM(CH$_2$)$_3$SO$_3$H]Cl	
	Ave. yield (%)	SD	Ave. yield (%)	SD	Ave. yield (%)	SD
Cellulose-rich fraction	76.98	0.4	75.16	0.8	51.10	1.2
Cellulose	41.88	0.7	39.59	0.8	35.08	0.2
Hemicellulose	17.33	0.4	16.76	0.3	3.31	0.2

Lignin Fraction

As was expected, effective lignin removal (8.34%) was observed when [MIM(CH$_2$)$_3$SO$_3$H]Cl was used as the IL-treatment (Table 3). It has been reported that 8.0%

lignin was recovered when wheat straw was pretreated with [EMIM]CH_3COO and subsequently alkali extracted, which was based on the original mass of the wheat straw (da Costa Lopes *et al.* 2013b). It has been described that 55.6%, 47.8%, and 14.6% of the lignin content was extracted from rice straw when [EMIM]H_2PO_2, [EMIM]CH_3COO, and [EMIM]Cl were used as the IL for pretreatment at 110 °C for 24 h, which was based on the mass of lignin in the rice straw (Xu *et al.* 2015). In this work, a low IL pretreatment temperature and a short processing time was employed. Most of the original lignin in the corn straw was dissolved when [MIM$(CH_2)_3SO_3H$]Cl was used as the IL, which resulted in a high lignin extraction (8.34%). Thus, a low yield of alkaline lignin (4.81%) was remaining with the cellulose-rich fraction (Table 3).

Table 3. Average Yields of Lignin and Reducing Sugars

Component	[MIM$(CH_2)_3$OH]Cl		[MIM$(CH_2)_2$COOH]Cl		[MIM$(CH_2)_3SO_3H$]Cl	
	Ave. yield (%)	SD	Ave. yield (%)	SD	Ave. yield (%)	SD
IL-isolated lignin	2.86	1.1	3.16	0.2	8.34	0.8
Alkaline lignin	7.52	0.4	8.92	0.2	4.81	0.6
Reducing sugars	6.89	0.5	14.41	0.5	25.25	0.7

Hemicelluloses Fraction

Specifically, 3.3% of the hemicelluloses were extracted when the corn stalks were pretreated with [MIM$(CH_2)_3SO_3H$]Cl (Table 2), whereas 17.3% of the hemicelluloses were extracted with [MIM$(CH_2)_3$OH]Cl treatment. It is possible that the hemicelluloses were hydrolyzed during IL pretreatment due to their acidic nature of these ionic liquids.

The strong acidity of [MIM$(CH_2)_3SO_3H$]Cl resulted in the increased hydrolysis of the hemicelluloses, as well as effective lignin removal, from the corn stalks. Hence, high yields of reducing sugars (25.2%) were obtained when [MIM$(CH_2)_3SO_3H$]Cl was used as the pretreatment IL (Table 3), whereas low yields (6.9%) were obtained when [MIM$(CH_2)_3$OH]Cl was used.

Sample Fractionation by Protic ILs

On the basis of previous work (Zhang *et al.* 2015) and experimental results reported in this study, protic ILs seemed more effective; hence, these ILs were further evaluated for their ability to fractionate lignocelluloses. The yields of the fractionated samples are presented in Table 4. Yields of 40.4% and 42.8% cellulose-rich materials were obtained when the corn stalks were treated with [HNMP]Cl and [HPY]Cl, respectively. This observation indicated that most lignin and hemicelluloses were removed during the IL pretreatment.

Lignin acts as a physical barrier for enzymatic hydrolysis of lignocellulosic materials. In this work, 14.6% lignin (based on the original corn stalk powder) was isolated when using [HNMP]Cl as the pretreatment (70 °C for 3 h), as shown in Table 4. Isolation of 8.5% lignin (based on the original corn stalk powder) was obtained when using [HPY]Cl as the pretreatment. Isolation of 13.6% lignin (based on the original corn stalk powder) was reported in our previous work with [HMIM]Cl pretreatment (Zhang *et al.* 2015). [HNMP]Cl is considered to be a promising IL solvent to fractionate lignin from lignocellulosics.

Moreover, when corn stalks were pretreated by [HNMP]Cl and [HPY]Cl, 1.98% and 1.09% hemicelluloses were obtained, respectively (Table 4). Most of the hemicelluloses were hydrolyzed during the IL pretreatment, which resulted in high yields of reducing sugars (Table 4). This observation is attributed to the strong acidity of these ILs as noted in Table 1.

Interestingly, higher IL acidity is noted with [HNMP]Cl than with [HPY]Cl and [MIM(CH_2)$_3$$SO_3$H]Cl on the basis of the Hammett method (Duan *et al.* 2006; Zhang *et al.* 2012). However, a lower yield of reducing sugars was observed with [HNMP]Cl (Table 4), which could be due to its strong acidity causing further degradation of the sugars. HPLC analysis showed that 9.4% xylose and 8.0% glucose were isolated with [HPY]Cl treatment, whereas 5.0% xylose and 4.9% glucose were isolated with [HNMP]Cl treatment.

Furthermore, it is expected that residual water assisted the hydrolysis of the hemicelluloses, which helped to provide good yields of lignin as the corn stock was decomposed. However, the highest yield of IL-isolated lignin (19.6%) was obtained with [HNMP]Cl treatment in the absence of water. It has been reported that [BMIM]MeSO_4 is most effective IL to extract lignin (18.8%) from apple tree prunings when microwaved (Prado *et al.* 2012). Higher yields of IL-isolated lignin (18.9% and 18.3%) were also observed with [HMIM]Cl and [HPY]Cl treatments without water. In this study, water could compete with the anions of the ionic liquids to form hydrogen bonds with lignin (Shill *et al.* 2011). Therefore, high yields of lignin were observed with ILs treatment in the absence of water.

Table 4. Yields of Cellulose, Hemicelluloses, Lignin, and Reducing Sugars

	[HPY]Cl		[HNMP]Cl		[HMIM]Cl [a]
Biomass fraction	Ave. (%)	SD	Ave. (%)	SD	Ave. (%)
Cellulose-rich material	42.8	1.2	40.44	1.4	39.99
Cellulose	33.36	0.2	30.07	0.9	31.21
Hemicellulose	1.09	0.2	1.98	0.2	2.23
IL-isolated lignin	8.48	0.5	14.63	0.8	13.59
Alkaline lignin	2.44	0.4	2.31	0.2	4.81
Reducing sugars	28.24	0.4	17.98	1.1	25.37

[a] [Hmim]Cl data were reported in a previous study (Zhang *et al.* 2015).

Lignin Degradation Products

The acidic or basic conditions of the treatment may influence the monomeric degradation products of lignin. It has been reported that vanillin is obtained from alkaline treatment (Varanasi *et al.* 2013). Eugenol (4-allylguaiacol) has been noted to be produced during acid pretreatment (Varanasi *et al.* 2013). In this work, the lignin degradation products were observed to be dependent upon the IL used. Guaiacol, syringol, and vanillin were observed when [HPY]Cl was used (Fig. 2). Various products that included guaiacol, 4-allylguaiacol (eugenol), 4-ethylguaiacol, syringol, and vanillin were observed when [HNMP]Cl and [MIM(CH_2)$_3$$SO_3$H]Cl were used during IL pretreatment. It seemed that more degradation products were observed when the IL had a stronger acidity.

As shown in Fig. 3, the amount of lignin degradation products increased as the pretreatment time increased from 3 h to 10 h. Specifically, high quantities of syringol and vanillin were obtained from the pretreatment with [HPY]Cl, [HNMP]Cl, and [MIM(CH_2)$_3$$SO_3$H]Cl for 10 h.

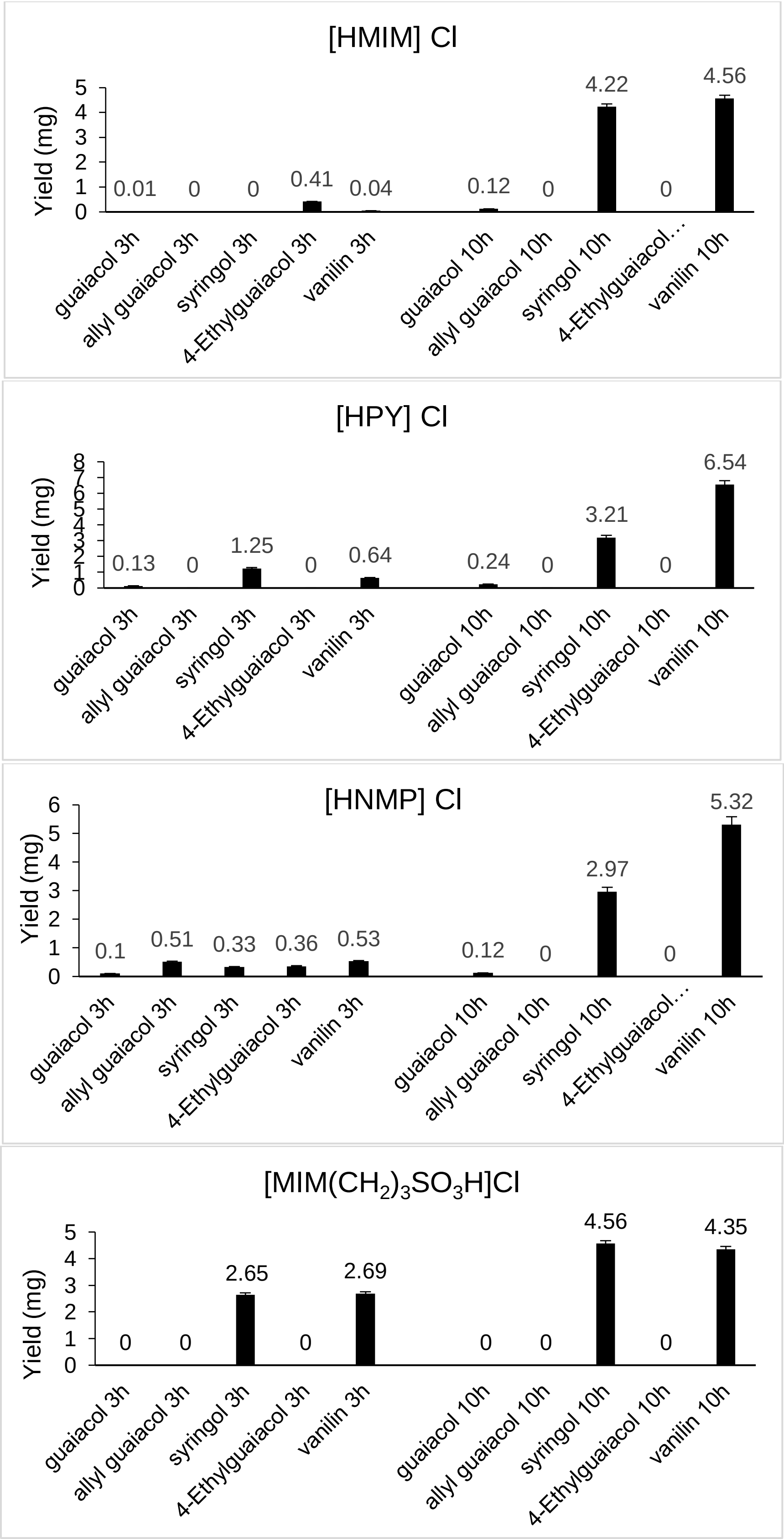

Fig. 2. Lignin degradation products

Enzymatic Hydrolysis

The yields from enzymatic hydrolysis of the isolated cellulose from the IL pretreatment processes (as calculated from Eq. 3) are summarized in Table 5. As expected, high yields of glucose and cellobiose, as well as high enzymatic conversion, were obtained with [HNMP]Cl and [HPY]Cl pretreatments. Enzymatic yields of 86.1% glucose and 14.7% cellobiose were obtained, along with 91.4% cellulose conversion, when [HNMP]Cl was used. When [HPY]Cl was used, enzymatic yields of 87.0% glucose and 13.4% cellobiose were observed. The effective removal of lignin and hemicelluloses by hydrolysis are attributed to the high digestibility of the cellulose residual by the cellulase treatment.

Enzymatic yields of glucose (77 to 79%) and cellobiose (10 to 14%) were noted when [MIM$(CH_2)_3SO_3H$]Cl, [MIM$(CH_2)_3OH$]Cl and [MIM$(CH_2)_2COOH$]Cl were used in the IL pretreatment; these yields corresponded to 80 to 83% cellulose conversion. Protic IL pretreatment of the corn stocks resulted in the complete enzymatic hydrolysis of the isolated cellulose residual.

Table 5. Enzymatic Hydrolysis of Cellulose Residual

	Reducing sugar		Glucose		Cellobiose		Conversion of cellulose	
Ionic liquid (IL)	Ave. (%)	SD	Ave. (%)	SD	Ave. (%)	SD	Ave. (%)	SD
[MIM$(CH_2)_3OH$]Cl	89.16	1.0	78.21	0.4	10.63	0.5	80.46	0.9
[MIM$(CH_2)_2COOH$]Cl	90.70	1.3	78.90	0.6	11.75	0.3	82.14	0.8
[MIM$(CH_2)_3SO_3H$]Cl	89.69	2.0	77.82	0.6	14.31	0.6	83.59	1.2
[HPY]Cl	93.43	1.7	87.02	1.6	13.38	0.6	90.99	2.1
[HNMP]Cl	94.89	2.7	86.12	0.6	14.66	0.3	91.40	0.9

CONCLUSIONS

1. Lignocellulosic biomass is a sustainable and valuable feedstock for the large-scale production of biofuels and bioproducts. A series of functional acidic ionic liquids (ILs) with various heterocyclic organic cations were synthesized in this study. [Hnmp]Cl, [Hpy]Cl and [HSO_3Prmim]Cl achieved the high yields of lignin and sugars.
2. High yields of IL-isolated lignin (18.3% to 19.6%) and (8.3% to 14.6%) were achieved using ILs in the absence and presence of water, respectively. The yield of cellulose ranged from 40.0 to 77.0% from IL treatments, whereas the yield of hemicelluloses ranged from 1.1% to 17.3%.
3. Enzymatic hydrolysis of the isolated cellulose residual produced 89.2% to 94.9% reducing sugar with 77.8% to 86.1% glucose, which corresponded to 80.5% to 91.4% enzymatic cellulose conversion.
4. Syringol and vanillin were found as the main lignin degradation products during IL treatment. Functional ILs could be valuable solvents to facilitate the effective conversion of biomass into biofuels.

ACKNOWLEDGMENTS

This work was financially supported by the Harbin Science and Technology Innovative Talents Project (2017RAQXJ148), and the University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (UNPYSCT-2017021).

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Article submitted: December 12, 2018; Peer review completed: February 10, 2019; Revised version received: March 20, 2019; Accepted: April 9, 2019; Published: April 25, 2019.
DOI: 10.15376/biores.14.2.4721-4732