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Acidic ionic liquid catalyzed liquefactions of corn cobs and switchgrass in acetone: Analysis of bio-oils using LC-MS and GC-MS

Ananda S. Amarasekara*, Cristian D. Gutierrez Reyes

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

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ABSTRACT

The liquefaction of corn cobs and switchgrass was studied using 1-(3-propylsulfonic)-3-methylimidazolium chloride and 1-(4-butylsulfonic)-3-methylimidazolium chloride Brønsted acidic ionic liquids as catalysts in acetone at 120 °C for 5 h. The highest biomass conversions to liquefied bio-oil for corn cobs and switchgrass are 63.4 ± 0.9 and 56.4 ± 0.9 % (w/w) respectively. The liquefied products were fractionated to polar and non-polar fractions by solvent extractions and analyzed using liquid chromatography - mass spectrometry (LC−MS) and gas chromatography - mass spectrometry (GC-MS). The weights of polar fraction : non-polar fraction was 2 : 1 for all liquefied bio-oils. Sixteen products were identified from the polar fractions of liquefied bio-oils, whereas nineteen products were identified from methylene chloride soluble non-polar fractions. The compounds formed as a result of cross aldol condensations of biomass derived furans furfural and 5-hydrxymrthylfurfural with one or more acetone molecules were identified in bio-oils. Four lignin derived compounds were also found in non-polar factions of liquefied bio-oils. Corn cobs with higher hemicellulose content produced higher liquefaction product yields indicating that hemicellulose is more easily liquefied under the conditions used. The two catalysts, 1-(3-propylsulfonic)-3-methylimidazolium chloride and 1-(4-butylsulfonic)-3-methylimidazolium chloride produced practically comparable liquefaction yields, showing that structural effect of one methylene group in the catalyst is not significant.

1. Introduction

The hydrothermal liquefaction (HTL) using water as the biomass liquefaction medium is a widely studied approach for the production of fuels as well as chemical feedstocks from renewable lignocellulosic biomass resources [1], [2], [3]. A number of variants of this HTL process is known like the use of supercritical water [4], [1], microwave heating [5], [6], [7], and acid or metal catalyzed liquefaction [6], [8], [9], [10]. The use of organic solvent as the liquefaction medium is also known with somewhat fewer studies; this includes the use of ethanol [11], [12], methanol [13] iso-propanol [14], polyhydric alcohols [15], [16], [17], [18], phenol [19], [20], ethylene carbonate [21], 1-octanol [22] and acetone [13], [23]. In many examples of these liquefactions in organic solvents, the addition of a catalyst such as Brønsted or Lewis acid [17], [24], [25], potassium fluoride doped alumina [26], Raney Ni-NaOH [14], Na_2CO_3, Na_2CO_3-Fe [27], metal oxides such as La_2O_3, CeO_2, MnO, CaO [28] and CeZrOx [29] have shown significant improvements in quality as well as the quantity of liquefied bio-oils. The liquefaction of cellulose or biomass in a reactive organic solvent can lead to secondary reactions of biomass degradation products with the solvent as well. In addition, these secondary reactions may help to stabilize the components in bio-oils. For example, in a recent study we have found that acidic ionic liquid catalyzed liquefaction of cellulose in ethylene glycol leads to the formation of a relatively simple mixture of three products via these reactions with the solvent [18]. These compounds in the cellulose liquefaction bio-oil were identified as 2-hydroxyethyl levulinate, 2-hydroxyethyl levulinate ethylene ketal and 2,3,6,7-tetrahydro-cyclopenta [1,4]dioxin-5-one [18].

The ionic liquids are known for their extraordinary capacity to dissolve cellulose or lignocellulosic biomass, have been used as solvents and catalysts for depolymerization of biomass polysaccharides as well as dehydration of monosaccharides to furans [30,31], [32,33]. In 2009 our research group first introduced the use of sulfonic acid group functionalized Brønsted acidic ionic liquids (BAILs) for the depolymerization of cellulose and applications in biomass processing [30–33]. Later we have explored the use of immobilized acidic ionic liquids [34,35], as well as alkyl/aryl sulfonic acids [36,37] as catalysts for the depolymerization of cellulose and liquefaction of lignocellulosic biomass for biofuel applications. These sulfonic acid group functionalized imidazolium ionic liquids are known to be excellent catalysts for

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* Corresponding author.
E-mail address: asamarasekara@pvamu.edu (A.S. Amarasekara).

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Table 1
The weight compositions of corn cobs and switchgrass [41].

Component	Corn cobs (weight %)	Switchgrass (weight %)
Cellulose	40.0	43.8
Hemicellulose	41.4	28.8
Lignin	5.8	9.2
Protein	2.5	3.9
Starch	2.1	1.0
Fat	0.7	0.9
Water soluble	1.1	2.2
Moisture	1.7	5.7
Ash	1.8	5.0

dehydration of monosaccharides as well. For example, sugars xylose, glucose and fructose can be converted to C5, C6 furans, furfural and 5-hydroxymethylfurfural (HMF) in high yields by treatment with 1-(3-propylsulfonic)-3-methylimidazolium chloride as a catalyst at 100 − 120 °C for short periods [38]. In addition, we have observed that these ionic liquid catalysts can promote the glucose to fructose isomerization without the use of expensive and toxic transition metal catalysts, during the conversion of glucose to HMF [39].

In our research attempts to produce a stable and non-acidic biocrude oil, that can be easily upgradable to a hydrocarbon mixture we have studied the degradation of cellulose in acetone medium using acidic ionic liquid catalysts [40]. In continuation of these studies we have experimented with real biomass forms as well, and in this publication we report a comprehensive study on analysis of complex product mixtures formed in liquefaction of untreated biomass in acetone. Two common biomass varieties, corn cobs and switchgrass with significantly different hemicellulose as well as lignin contents were chosen for the present study [41]. The typical compositions of corn cobs and switchgrass are shown in Table 1. In these experiments acetone was selected as the biomass liquefaction medium as this dipolar aprotic solvent is not expected to hydrogen bond with the imidazolium ionic liquid and reduce the effectiveness of the catalyst. Furthermore, the acetone used as the solvent and reactive component in liquefaction can be obtained from renewable resources based routes such as acetone-butanol-ethanol fermentation [42], making all the carbons in the final liquefaction product originating from renewable resources. In the liquefaction process the polysaccharides in biomass undergoes a depolymerization to C5 and C6 sugars, which are dehydrated to furfural, HMF and then acid catalyzed condensations with acetone gives the furanic biocrude product as shown in Fig. 1.

2. Experimental

2.1. Materials and instrumentation

Switchgrass and corn cobs used in this study are gift samples from National Renewable Energy Laboratory, Boulder, CO, USA. Switchgrass and corn cob samples were pulverized in a blender to obtain a homogeneous powder and sieved through a brass mesh (Aldrich mini-sieve set, Z 675415, size 25 particle size 0.7 mm). Then, the powders were dried in an oven at 60 °C for 10 h and stored in sealed plastic bottles until used for experiments. 1-methylimidazole, 1,3-propanesultone, 1,4-butanesultone, concentrated hydrochloric acid and acetone (> 99%) were purchased from Aldrich Chemical Co. BAIL catalysts were prepared by condensation of 1-methylimidazole with 1,3-propanesultone or 1,4-butanesultone and acidification of the resulting salts with conc. HCl according to the literature procedure as shown in Fig. 2 [43]. Biomass liquefaction 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 temperature accuracy ± 1 °C.

3. Liquid chromatographic mass spectroscopy (LC-MS) analysis

LC-MS chromatography identification and quantification were performed on an Agilent 6130B Single Quadra pole LCMS System equipped with Electrospray ionization source (ESI) coupled to Agilent 1100 Series LC System equipped with a quaternary pump, auto sampler, column thermostat and degasification system (Agilent Technologies Inc.). The analytical column used was a Luna 5 μm C18(2) 100 Å, 150 X 4.6 mm, NP:00F-4252-E0 (Phenomenex Inc.). A linear gradient elution was used for the elution with two solvents A and B. Solvent A: 0.1% formic acid, HPLC grade water and Solvent B: acetonitrile; with flow rate of 0.400 mL/min. The linear gradient was as follows (time in minutes/flow rate/mobile phase composition ratio A : B): 0.0/0.400/95:5, 10.0/0.400/95:5, 15.0/0.400/75:25, 20.0/0.400/65:35, 10.0/0.400/65:35 and 40/0.400/95:5. The injection sample volume was 5.0 μL. The SCAN parameters were; positive mode, mass range 40–850 m/z, fragmentor 150, gain 3.0. The spray chamber parameters were: gas temperature 300 °C, drying gas flow 11.0 L/min, nebulizer gas 50 psig, Vcap (+) and (-) 3000 V.

3.1. Gas chromatography mass spectroscopy (GC-MS) analysis

The GC-MS chromatography identification and quantification was carried out on a gas chromatography instrument Varian Saturn 2100 T coupled to Varian 3900. The capillary column VF-5 ms (30 m X 0.25 mm I.D. coated with 0.25 μm film, NP:CP8944 Varian) was used. The GC conditions were as follows: the column temperature was programmed from 100 °C to 150 °C with a gradient of 10 °C/min; the injection port and the transfer line temperature were 200 °C; helium was used as carrier gas at a flow rate of 1.5 mL/min; split ratio 100. The mass analyzer operated at an electron impact energy of 70 eV. Mass spectra were recorded by scanning in the range 40–600 m/z. The peak area quantification was carried out using the software: Varian MS Workstation version 6.9.2.

3.2. General procedure: BAIL catalyzed liquefaction of biomass (corn cobs or switchgrass)

Dried, powdered biomass (switchgrass or corn cobs, 0.350 g) was thoroughly mixed with Brønsted acidic ionic liquid catalyst (BAIL1 or BAIL 2, 0.485 mmol) in a glass vial with a stainless-steel spatula, the closed vial was allowed to stand at room temperature for 96 h. After the incubation period, content in the vial was transferred into 25 mL

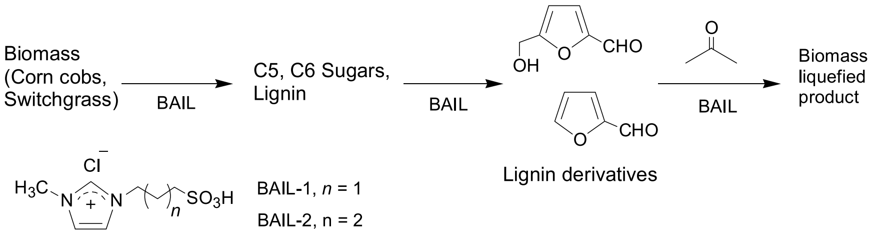


Fig. 1. Brønsted acidic ionic liquid (BAIL) catalyzed liquefactions of corn cobs and switchgrass biomass in acetone.

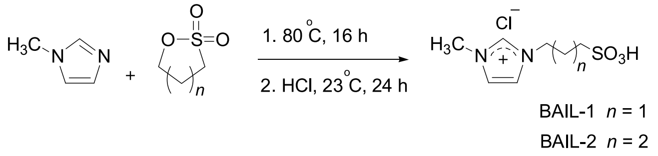


Fig. 2. Synthesis of 1-(3-propylsulfonic)-3-methylimidazolium chloride (BAIL-1) and 1-(4-butylsulfonic)-3-methylimidazolium chloride (BAIL-2) Brønsted acidic ionic liquids.

stainless steel solvothermal reaction kettles with Teflon inner sleeves, and 4.0 mL of acetone was added. The reaction kettle was firmly closed and heated in a thermostated oven maintained at 120 ± 1 °C for 5.0 h. At the end of this time period reactor was removed from the oven and quickly cooled in ice-cold water to end the reaction. Then product was separated to polar and non-polar products by successive extractions.

3.2.1. Extraction of polar fraction

The reactor content was transferred to a centrifuge tube, a 2.5 mL portion of a solvent mixture of water : methanol : acetonitrile 2:1:1 was added, mixed, centrifuged at 1700xg for 15 min. and the liquid fraction was collected. This process was repeated with two more 2.5 mL portions of the solvent mixture, the combined liquid phase was diluted to 14.0 mL, and was analyzed as the polar fraction using LC-MS. The interpretations of LC-MS analysis of polar fractions of corn cobs and switchgrass liquefaction products are shown in Table 2.

3.2.2. Extraction of non-polar fraction

The residue from the polar fraction extraction was mixed with 2.5 mL of methylene chloride and centrifuged at 1700xg for 15 min. and the liquid fraction was collected. This process was repeated with two more 2.5 mL portions of methylene chloride, combined liquid phase was diluted to 14.0 mL and was analyzed as the polar fraction using GC-MS. The interpretations of GC-MS analysis of non-polar fractions of corn cobs and switchgrass liquefaction products are shown in Table 3.

The solid residue left after extraction was dried in an oven at 60 °C for 24 h. and weighed. The biomass percent conversion to bio-oil was calculated using the formula:

$$\text{Percent conversion to bio-oil} = \frac{(\text{weight of biomass} - \text{weight of residue after liquefaction})}{\text{weight of biomass}} \text{ x } 100\ \%$$

The evaporation of solvents from 2.00 mL samples of polar fraction and non-polar fraction extracts under reduced pressure was used to calculate the weight ratio of polar fraction : non-polar fraction as 2 : 1 for all liquefied bio-oils. All experiments were carried out in duplicate.

3.3. General procedure for the study on effect of catalyst loading on the BAIL catalyzed liquefaction of corn cobs

Dried, powdered corn cobs (0.350 g) was thoroughly mixed with BAIL-1 or BAIL-2 catalyst (0.121, 0.243, 0.485 and 0.97 mmol) in a glass vial with a stainless-steel spatula, the closed vial was allowed to stand at room temperature for 96 h. After the incubation period, content in the vial was transferred into 25 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, and 4.0 mL of acetone was added. The reaction kettle was firmly closed and heated in a thermostated oven maintained at 120 ± 1 °C for 5.0 h. At the end of this time period reactor was removed from the oven and quickly cooled in ice-cold water to end the reaction. Then product was separated to polar and non-polar products by successive extractions as described in procedure 3.2.1. The solid residue left after extraction was dried in an oven at 60 °C for 24 h. and weighed. The biomass percent conversion to bio-oil was calculated as described in procedure 3.2.2. All experiments were carried out in duplicate and the results of effect of catalyst loading is shown in Table 4.

4. Results and discussion

The Brønsted acidic ionic liquids with built in sulfonic acid groups 1-(3-propylsulfonic)-3-methylimidazolium chloride (BAIL-1) and 1-(4-butylsulfonic)-3-methylimidazolium chloride (BAIL-2) were chosen as catalysts for biomass (corn cobs and switchgrass) liquefaction experiments because our earlier studies have shown that these imidazolium ionic liquids are better catalysts than pyridinium and triethanol ammonium cation based BAILs for the challenging cellulose depolymerization step [30]. The catalysts BAIL-1 and 2 were prepared by condensations of C3 and C4 sultones with 1-methyl imidazole and then acidification with HCl as shown in Fig. 2, according to the literature procedure [43]. The Brønsted acidity (H_o) of the catalysts BAIL-1 and 2 in water were determined as 2.446 and 1.896 respectively using the standard 4-nitroaniline method [44]. Earlier we have studied the thermal stabilities of these ionic liquids BAIL-1 and 2 and these catalysts are generally stable up to about 245 °C [45]. Our previous work on

Table 2
Interpretations of LC-MS analysis of polar fractions of corn cobs and switch grass liquefaction products. 0.350 g of Biomass (corn cobs or switchgrass), 0.485 mmol catalyst (BAIL-1 or BAIL-2) and 4.0 mL of acetone at 120 °C for 5.0 h were used in all experiments. G = glucose, X = xylose, F = furfural, HMF = 5-hydroxymethylfurfural, A = acetone, U = unknown, R_t - Retention time.

Peak No:	R_t (min.)	Assigned formula	Interpretation	M/z of $[M+H]^+$ pseudo-molecular ion	Peak area (%)			
					Corn cobs		Switchgrass	
					BAIL-1	BAIL-2	BAIL-1	BAIL-2
P1	2.7	$C_5H_{10}O_5$	X	151.0	0.1	0.1	0.1	0.1
P2	3.7	–	U	383.0	0.9	0.9	–	–
P3	4.4	$C_6H_{12}O_6$	G	181.0	1.0	0.4	2.5	1.4
P4	13.7	–	U	467.0	0.9	1.7	–	–
P5	14.2	$C_{15}H_{16}O_3$	HMF + 3A -3H_2O - 2H	245.0	1.1	1.8	–	–
P6	15.0	$C_6H_6O_3$	HMF	127.0	14.8	16.8	5.7	7.2
P7	16.9	$C_{14}H_{10}O_4$	HMF + F + A - 2H_2O - 2H	243.0	0.6	1.1	–	–
P8	25.6	$C_9H_{10}O_3$	HMF + A - H_2O	167.0	3.9	3.7	1.9	2.0
P9	25.8	$C_{24}H_{32}O_6$	2HMF + 4A - 4H_2O + 4H	417.0	0.5	0.4	–	–
P10	28.7	$C_{17}H_{24}O_5$	F + 4A - H_2O -2H	309.0	2.8	3.4	12.1	13.5
P11	30.0	$C_{11}H_{14}O_3$	F + 2A - H_2O	195.0	1.0	0.6	3.1	0.4
P12	31.9	$C_{16}H_{14}O_4$	2F + 2A - 2H_2O - 2H	271.0	14.8	13.9	15.1	14.4
P13	32.0	$C_9H_8O_2$	HMF + A - 2H_2O	149.0	2.3	2.2	1.8	0.4
P14	32.9	$C_{17}H_{16}O_4$	HMF + F + 2A - 3H_2O	285.0	10.9	10.6	11.0	12.2
P15	34.6	$C_{17}H_{16}O_5$	HMF + F + 2A - 2H_2O - 2H	301.0	43.5	41.6	46.6	48.3
P16	39.0	$C_{18}H_{20}O_6$	2HMF + 2A - 2H_2O	333.0	0.9	0.9	–	–

Table 3
Interpretation of GC-MS analysis of non-polar fractions of corn cobs and switch grass liquefaction products. 0.350 g of Biomass (corn cobs or switchgrass), 0.485 mmol catalyst (BAIL-1 or BAIL-2) and 4.0 mL of acetone at 120 °C for 5.0 h were used in all experiments. F = furfural, HMF = 5-hydroxymethylfurfural, A = acetone, L = lignin derivative, R_t - Retention time.

Peak No:	Rt (min.)	Assigned formula	Interpretation	M/z of $M^{+\circ}$ molecular ion	Peak area (%)			
					Corn cobs		Switchgrass	
					BAIL-1	BAIL-2	BAIL-1	BAIL-2
NP1	1.5	C_5H_6O	F - H_2O + 4H	82.0	0.3	0.5	0.7	0.4
NP2	1.6	$C_6H_{10}O$	2A - H_2O	98.0	39.4	33.7	45.8	41.6
NP3	1.7	$C_5H_6O_2$	F + 2H	92.0	–	1.0	–	–
NP4	1.8	$C_5H_{10}O_3$	F	96.0	31.1	26.5	28.8	36.1
NP5	1.9	$C_6H_6O_3$	HMF	126.0	0.7	0.4	–	–
NP6	2.4	$C_6H_{12}O_2$	2A	116.0	0.1	0.2	0.4	0.1
NP7	2.6	$C_6H_6O_2$	HMF - O	110.0	0.3	0.2	0.6	0.6
NP8	4.3	C_8H_8O	F + A - $2H_2O$ + 2H	120.0	0.1	–	0.2	0.2
NP9	4.9	$C_9H_{10}O$	L	134.0	0.3	0.3	0.5	0.3
NP10	5.0	$C_8H_{10}O$	F + A - $2H_2O$ + 4H	122.0	0.5	0.7	0.6	0.5
NP11	6.3	$C_6H_6O_4$	HMF + O	142.0	5.8	8.5	2.7	3.2
NP12	6.5	$C_8H_{10}O_2$	L	138.0	6.7	9.0	10.5	8.3
NP13	7.1	$C_6H_4O_3$	HMF - 2H	124.0	4.2	6.2	2.4	2.8
NP14	7.2	$C_9H_{10}O_2$	L	150.0	2.0	2.3	2.1	1.8
NP15	9.3	$C_{26}H_{26}O_4$	2HMF - $2H_2O$ + O	250.0	–	–	0.5	0.2
NP16	9.6	$C_{13}H_{10}O_3$	2F + A - $2H_2O$	214.0	1.8	1.2	1.5	1.6
NP17	11.0	$C_{13}H_{14}O_5$	2F + A	250.0	0.2	0.4	0.6	0.3
NP18	12.8	$C_{10}H_{12}O_3$	L	180.0	0.3	0.8	0.8	0.3
NP19	14.6	$C_{17}H_{18}O_4$	HMF + F + 2A - $3H_2O$ + 2H	286.0	6.2	8.0	1.2	1.7

Table 4
The effect of catalyst loading on the BAIL catalyzed liquefaction of corn cobs 0.350 g of corn cobs and 4.0 mL of acetone at 120 °C for 5.0 h were used in all experiments. The average of duplicate experiments. BAIL-1: 1-(3-propylsulfonic)-3-methylimidazolium chloride and BAIL-2: 1-(4-butylsulfonic)-3-methylimidazolium chloride.

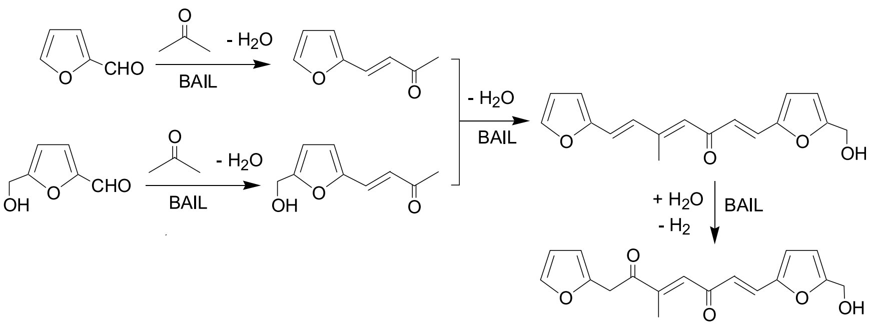
Catalyst	Catalyst loading mmol/0.350 g corn cobs	Catalyst weight (mg)	The percent conversions of biomass to bio oil (w/w)
BAIL-1	0.121	29	18.2 ± 0.7
	0.243	58	52.7 ± 1.4
	0.485	117	63.4 ± 0.9
	0.97	233	64.0 ± 1.7
BAIL-2	0.121	31	21.7 ± 1.0
	0.243	62	50.1 ± 1.5
	0.485	124	62.6 ± 1.3
	0.97	247	61.1 ± 1.8

cellulose liquefaction in acetone using the same Brønsted acidic ionic liquids as catalysts have shown improvements in liquefaction yields by standing the sample at room temperature giving adequate time for the absorption of ionic liquid on to surface [40]. In addition, the visual examination also showed that it takes a long time of about 96 h for the complete adsorption of highly viscous ionic liquid on to biomass particles. We have selected the reaction conditions based on our previous experience on liquefaction of cellulose in acetone using the same Brønsted acidic ionic liquids as catalysts [40].

The Brønsted acidic ionic liquid (BAIL) catalyzed liquefactions of corn cobs or switchgrass biomass in acetone is outlined in Fig. 1. In the first step BAIL catalyzed depolymerization of biomass gives C5 sugars from hemicellulose and C6 sugars from cellulose, in addition some of the lignin may have also depolymerized at this stage. Secondly C5, C6 sugars undergo a BAIL catalyzed dehydration to give furfural and 5-hydroxymethylfurfural as shown. In the third and last step, furfural and 5-hydroxymethylfurfural can undergo BAIL catalyzed single or multiple aldol condensations to give a complex mixture of furan aldehyde - acetone cross aldol products as well as their rearranged products.

The biomass liquefied product formed in these experiments requires a reductive deoxygenation step to convert into a saturated hydrocarbon mixture suitable for fuel and bioenergy applications. In order to design this second step it is essential to identify the nature of functional groups and components present in the bio-oil formed from the liquefaction process. Therefore, in an attempt to identify as many compounds as possible in the complex biomass liquefied products, we have separated the polar and non-polar fractions by solvent extraction and the polar fractions were analyzed by LC-MS and the methylene chloride soluble non-polar fractions were analyzed using GC-MS. The interpretations of components in polar and non-polar fractions of bio-oil produced from corn cobs as well as switchgrass with the use of BAIL-1, 2 catalysts are shown in Tables 2 and 3. The LC-MS analysis of the polar fraction showed the presence of 16 peaks with retention times in the range of 2.7–39.0 min. (Table 2). We have been able to identify most of these compounds, and the unknowns are marked as U. The peak number P6 eluting at 15.0 min. in the chromatogram is due to HMF (Table 2). The peak area integration for HMF was 5.7–7.2 % of sum of the peak areas of all LC-MS peaks in switchgrass samples, whereas in corn cobs the corresponding HMF peak area was 14.8–16.8 % of sum of the peaks as shown in Table 2. The cellulose, hemicellulose and lignin contents of switchgrass and corn cobs are not similar. Hemicellulose and lignin contents are in particularly very different; the lignin contents of corn cobs and switchgrass are 5.8 and 9.2 % respectively. The cellulose fibrils in biomass are encapsulated in lignin. In comparison with corn cobs, the higher lignin content in switchgrass can make it difficult to release the cellulose in switchgrass for hydrolysis to glucose. The C6 furan HMF is formed via dehydration of the glucose formed through cellulose hydrolysis. Therefore the comparatively high lignin content in switchgrass may be the reason for differences in HMF peak area percentages in liquefaction products.

A number of compounds in the polar fractions are formed as a result of single or multiple cross-aldol condensations between acetone (A) and furan aldehydes: furfural (F), and 5-hydroxymethyl furfural (HMF) or both. The product eluting at a retention time 34.6 min. as P15, corresponds to 43.5 and 41.6 % of total peak areas of the chromatograms of bio-oils from corn cobs when BAIL-1 and BAIL-2 were used as catalysts. In the case of switchgrass, P15 peak corresponds to 46.6 and 48.3 % of the total peak areas of bio-oils from switchgrass, when BAIL-1 and BAIL-2 were used as catalysts respectively. The mass spectrum of this peak corresponds to the formula $C_{17}H_{16}O_5$. The formation of this C17



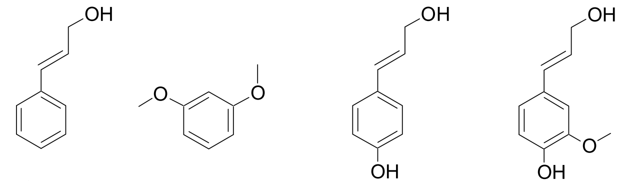
P15
R_t = 34.6 min.

Fig. 3. The possible reaction pathway for the formation of the major product $C_{17}H_{16}O_5$ in polar fraction in liquefaction products from corn cobs and switch grass, as the representative example. Table 2, component P15, Retention time 34.6 min.

product can be explained as shown in Fig. 3. The BAIL catalyzed aldol condensation reactions of furfural and HMF with acetone can result C8 and C9 aldol products. Next a cross aldol reaction between these two products can lead to the C17 adduct; which then undergoes an acid catalyzed hydration and an oxidation to give this highly conjugated product. This type of BAIL catalyzed oxidations and reductions are known in alcohols and carbonyl compounds [46,33]. Similar reactions between biomass derived furans, furfural and HMF with one or more acetone molecules can lead to the formation of other components in the liquefaction bio-oils as shown in Tables 2 and 3. Interestingly, the product resulting from aldol condensations of two molecules of furfural with two molecules of acetone ($C_{16}H_{14}O_4$) is also found as a component in polar fractions of liquefied bio-oils from both biomass samples. This compound elutes at R_t = 31.9 min. as peak P12 in the chromatograms.

The analysis of non polar fractions using GC-MS showed a maximum of 19 peaks in chromatograms and the interpretation of these peaks are shown in Table 3. The peak number NP2 eluted at a retention time of 1.6 min. in the GC-MS analysis was identified as the acetone aldol dimer 4-methyl 3-pentene-2-one. This peak due to $C_6H_{10}O$ enone corresponds to 33.7–39.4 % and 41.6–45.8 % of the total peak areas of the chromatograms of non polar fractions of bio-oil formed using corn cobs and switchgrass respectively. The product eluted after 1.8 min. (NP4, Table 3) in the non-polar fractions of bio-oils from both biomass forms was identified as furfural. Four lignin derived components are also seen in the non-polar fractions of bio-oils, as peak numbers NP9, NP12, NP14 and NP18, eluting at 4.9, 6.5, 7.2 and 12.8 min. respectively. These products were identified as NP9: cinnamyl alcohol, NP12: *m*-dimethoxybenzene, NP14: *p*-coumaryl alcohol and NP18: coniferyl alcohol as shown in Fig. 4. The results from the two BAIL catalysts are similar as shown in Tables 2 and 3, the small differences seen in some compounds are not statistically significant.

The effect of catalyst loading on the BAIL catalyzed liquefaction of corn cobs is shown in Table 4. With both catalysts, the increase in catalyst loading from 0.121 to 0.485 mmol showed a rapid increase in the percentage conversion of corn cobs to bio-oil. Further increase in catalyst loading beyond 0.485 mmol/0.350 g corn cobs failed to produce significant improvements in conversion to bio-oil and this may be due to polymerization of the products due to high acidity at 0.97 mmol/0.350 g catalyst loading conditions. The liquefactions of switch grass using 0.350 g of switchgrass, 0.485 mmol catalyst under similar conditions produced lower yields of 56.4 ± 0.9 and 53.6 ± 0.8 % bio-oils with BAIL-1 and BAIL-2 respectively. For comparison we have tested the liquefaction of biomass in acetone at 120 °C for 5 h, without adding the ionic liquid catalyst. These experiment resulted only 6–7 % dissolution of biomass in hot acetone.



NP9
R_t = 4.9 min.

NP12
R_t = 6.5 min.

NP14
R_t = 7.2 min.

NP18
R_t = 12.8 min.

Fig. 4. The proposed structures for lignin derived components NP9, 12, 14 and 18 in the non-polar fraction (Table 3).

5. Conclusion

We have shown that Brønsted acidic ionic liquids can be used as catalysts for efficient liquefactions of untreated biomass forms corn cobs and switchgrass under mild conditions in acetone at 120 °C, for 5 h. The highest biomass conversions to liquefied bio-oil were achieved with 1-(3-propylsulfonic)-3-methylimidazolium chloride catalyst for corn cobs and switchgrass; these conversions were 63.4 ± 0.9 and 56.4 ± 0.9 % (w/w) respectively. The liquefaction in reactive solvent acetone gives a structurally well defined liquefied bio-oils with secondary products from aldol condensation reactions of biomass derived furans furfural and 5-hydroxymethylfurfural with acetone. The bio-oils could be separated to polar and non-polar fractions by solvent extraction; weights of polar fraction : non-polar fraction was 2 : 1 for all liquefied bio-oils. Corn cobs with higher hemicellulose content produced higher liquefaction product yields; this is probably due to relatively facile degradation of hemicellulose under acid catalysis conditions used. This Brønsted acidic ionic liquid catalyzed liquefaction in acetone provides a simple and energy efficient route to produce bio-oils composed of well defined stable components with furan, alkene, ketone and alcohol functional groups, which allows a facile upgrading to a hydrocarbon fuel product via a second step of catalytic hydrogenation/deoxygenation process. We are currently working on the catalyst selection for the reductive deoxygenation of liquefied bio-oil products to hydrocarbon fuels as well as recycling of the Brønsted acidic ionic liquid catalyst.

CRediT authorship contribution statement

Ananda S. Amarasekara: Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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