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Research paper

Acidic ionic liquid catalyzed liquefaction of untreated switchgrass biomass in acetone and Pd-La(OTf)$_3$ catalyzed reduction of the products

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ABSTRACT

The cellulosic fraction of untreated switchgrass was partially liquefied by using acidic ionic liquid catalysts and heating in acetone at 120 °C for 3.5 h. The Brønsted acidic ionic liquids 1-(3-propylsulfonic)-3-methylimidazolium chloride and 1-(4-butylsulfonic)-3-methylimidazolium as catalysts produced 39.5% and 31.75% w/w liquefactions of switchgrass biomass and the lignin fraction remains unaffected by the mild conditions used. Sixteen C5-C15 range products were observed in the switchgrass liquefied product and 13 compounds were identified using GC-MS, including three products arising from dimerization of acetone under acidic conditions used. The liquefied product could be partially reduced by catalytic hydrogenation using Pd-La(OTf)$_3$ catalyst system in 50% aq. acetic acid at 200 °C, 1.38 MPa for 16 h. Thirteen, mainly alcohol and ketone products were identified in the catalytically reduced liquefied product.

1. Introduction

The liquefaction of lignocellulosic biomass by heating in a solvent at a high temperature and pressure is an alternative method to the conventional pyrolysis for the preparation of renewable fuels and fuel precursors from lignocellulosic biomass [1,2]. In comparison to the biomass pyrolysis typically carried out at 400–600 °C to produce bio-oil, liquefaction is considered as a more environmentally friendly process since a lesser amount of volatiles are formed and requires only a fraction of energy in comparison to the pyrolysis [3]. Most importantly liquefaction methods normally gives bio-oils with relatively fewer number of compounds, in comparison to the pyrolysis bio-oil, typically contains more than one hundred compounds [3,4]. The liquefaction bio-oil with relatively fewer number of compounds should be easier to upgrade to more stable products. The hydrothermal liquefaction is the widely studied technique and generally carried out around 280–370 °C, and at pressures in the range 10–25 MPa [1,2,5]. In addition to the use of water as the liquefaction medium a number of research groups have studied the use of organic solvents like ethanol, 1-octanol [6], polyhydric alcohols, phenol [7] and ethylene carbonate [8] as the solvent. The liquefaction of cellulose in phenol as well in phenol-water mixtures is known to give 5-hydroxymethylfurfural, glucose and oligosaccharides as major products [9]. The use of ethylene glycol as the solvent in cellulose liquefaction has resulted a water soluble as well as organic soluble products [10]. In these experiments the major water soluble compounds were reported as monosaccharides and ethylene glycol-glycosides, whereas, formic acid, levulinic acid and 2-hydroxyethyl levulinate were identified as hydrophobic products [10]. In many cases, the addition of an acid, base or metal salt as a catalyst is known to lower the liquefaction temperature and improve the quality as well as the quantity of liquefaction oil [11]. For example Long et al. has observed significant improvements in the bio-oil yields during the bagasse liquefaction in hot compressed water after the addition of SO_3H-, COOH-functionalized and HSO_4^- paired imidazolium ionic liquids as catalysts [12].

In our studies on development of catalysis methods for processing cellulosic biomass we have identified the -SO_3H group functionalized Brønsted acidic ionic liquids (BAILs) as cellulose depolymerization catalysts as well as solvents [13]. In these activities we have explored the use of BAILs as homogeneous catalysts in water [14], and also as heterogeneous catalysts in the immobilized forms [15]. In addition, we have found that BAIL catalyzed cellulose depolymerizations in reactive solvents such as ethylene glycol [16] and acetone [17] can lead to further transformations of cellulose depolymerization products as well as cross reactions of these products with the solvent. For example, BAIL catalyzed liquefaction of cellulose in ethylene glycol at 180 °C has produced a rather simple mixture of only three products as a result of further reactions of cellulose degradation products with ethylene glycol [16].

In continuation of our efforts on development of catalytic biomass

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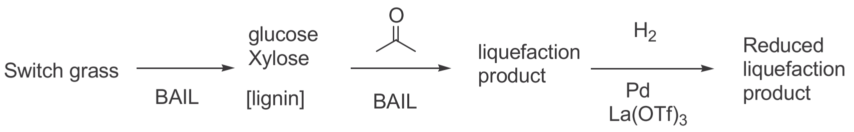

Fig. 1. Brønsted acidic ionic liquid (BAIL) catalyzed liquefaction of untreated switchgrass biomass in acetone and catalytic reduction using Pd-La(OTf)$_3$ catalyst.

processing methods we have studied the liquefaction of untreated switchgrass biomass in acetone at 120 °C. We have selected acetone as the reactive liquefaction medium as renewable acetone can be produced by acetone–butanol–ethanol (ABE) fermentation, making all the carbons in the final product originating from renewable resources [18,19]. The imidazolium type Brønsted acidic ionic liquids were chosen as catalysts as these homogeneous catalysts are superior to sulfuric acid for the difficult cellulose depolymerization step [14]. In addition we have studied the catalytic reduction of the switchgrass liquefied product using Pd/La(OTf)$_3$ as the catalyst to produce a partially reduced product as shown in Fig. 1. The reactive solvent acetone can undergo oligomerization under strongly acidic liquefaction conditions, therefore, in order to identify the products arising from self condensation of acetone itself, we have studied the oligomerization of acetone under similar conditions as well.

2. Experimental

2.1. Materials and instrumentation

Switchgrass sample was collected at USDA-Agricultural Research Station at Lincoln, NE. Switchgrass from matured plants; dry whole plant sample was finely milled and sieved through a mesh (Aldrich mini-sieve set, Z 675415, size 25, particle size 0.7 mm) to obtain a homogeneous powder. The switchgrass powder was then air dried in 70 °C oven for 15 h to achieve a constant weight and then stored in sealed glass bottles. Acetone (> 99%), hydrochloric acid (36.5%–38%), glacial acetic acid, 1-methylimidazole, 1,3-propanesultone, 1,4-butanesultone, palladium (5% w/w) on activated carbon, and lanthanum (III) trifluoromethanesulfonate hydrate were purchased from Aldrich Chemical Co. BAIL catalysts (**3a,b**) were prepared by mixing 1-methylimidazole (**1**) with 1,3-propanesultone (**2a**) or 1,4-butanesultone (**2b**), followed by acidification with HCl according to the literature procedure as shown in Fig. 2 [20,21]. The switchgrass biomass liquefactions were carried out in 25 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves from Lonsino Medical Products Co. Ltd., Jingsu, China. The reactions were carried out by placing the sealed reaction vessels in a temperature-controlled oven (WU-52402-91) with ± 1 °C accuracy. The thermogravimetric analysis was carried out using a PYRIS Diamond TG-DTA system from PerkinElmer Inc. Chemical compositions of switchgrass samples and solid residuals were analyzed by using curve fitting data processing on OriginLab 2018b Graphing & Analysis software from OriginLab Corporation, Northampton, MA, USA. Catalytic hydrogenation of the liquefied oil was conducted in a 50 mL stainless-steel pressure vessel (4720) controlled by a reactor controller (4838) from Parr Instrument Co. GC-MS analysis was performed on a Varian 3900/Saturn 2100 T GC/MS system. Carrier gas flow rate 1.0 mL/min, split ratio at 1:80, injector temperature was 280 °C, mass spectrums were identified by referring NIST 98 library. In order to ensure all liquefaction products pass through the column for identification, GC-MS was operated in a temperature program and after reaching the maximum temperature the column was further eluted at constant temperature for 15 min and until no more compounds are eluted from the column.

2.2. Oligomerization of acetone using Brønsted acidic ionic liquid catalyst

A mixture of acetone (9.00 g) and Brønsted acidic ionic liquid (BAIL-1,2, 150 mg) was prepared in a 25 mL stainless steel solvothermal reaction kettle with a Teflon inner sleeve. The reactor was tightly closed and heated in a pre-heated oven at 120 ± 1 °C for 3.5 h. After this period reactor was removed from the oven and reaction was quenched by cooling in an ice water bath. The reaction product was diluted with deionized water (20 mL), transferred in to centrifuge tube and centrifuged at 1700 g for 15 min. The supernatant was extracted with methylene chloride (3 × 5 mL) and the combined organic phase was concentrated under reduced pressure to give acetone oligomer product mixture for composition analysis using GC-MS.

2.3. Catalytic hydrogenation of the acetone oligomer products from 2.2

Acetone oligomer product from experiment *2.2* (200 mg) was dissolved in 5.0 mL of 50% v/v aqueous acetic acid and transferred to a 50 mL stainless steel Parr reactor. Next, 5 wt% Pd/C (100 mg) and La (OTf)$_3$ (160 mg) catalysts were added, sealed, the reactor was degassed, and pressurized with hydrogen to 0.69 MPa at room temperature. The reactor was then heated to 100 °C in 20 min, and held at 100 °C for 3 h at 0.86 MPa; and then heated to 200 °C and kept at 200 °C, at 1.38 MPa for 16 h. The reactor was then cooled to room temperature, products were diluted with 10 mL of deionized water, centrifuged at 1700 g for 15 min. The supernatant was neutralized with saturated $NaHCO_3$, extracted with methylene chloride (3 × 5 mL) and the combined organic phase was concentrated under reduced pressure to give catalytically reduced acetone oligomer product for composition analysis using GC-MS.

2.4. Liquefaction of switchgrass in acetone using Brønsted acidic ionic liquid catalysts

The dried switchgrass powder (900 mg) and Brønsted acidic ionic liquid (BAIL-1, 2; 150 mg) was mixed in a glass vial and allowed to stand at room temperature for 48 h. The BAIL treated switchgrass was then transferred to a 25 mL stainless steel solvothermal reaction kettle with a Teflon inner sleeve and mixed with acetone (9.00 mL). The reactor was tightly closed and heated in a pre-heated oven at 120 ± 1 °C for 3.5 h the product analysis procedures were similar to the procedures in section 2.2.

2.5. Catalytic hydrogenation of the switchgrass liquefaction products

The switch grass liquefaction product (200 mg) was dissolved in 50% v/v aqueous acetic acid and transferred to a 50 mL stainless steel

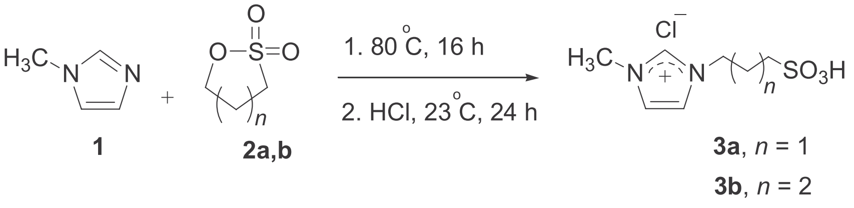

Fig. 2. Synthesis of Brønsted acidic ionic liquid catalysts 1-(3-propylsulfonic)-3-methylimidazolium chloride (**3a**, BAIL-1) and 1-(4-butylsulfonic)-3-methylimidazolium chloride (**3b**, BAIL-2).

Parr reactor. Next, 5 wt% Pd/C (100 mg) and La(OTf)$_3$ (160 mg) catalysts were added, sealed, the reactor was degassed, and pressurized with hydrogen to 0.69 MPa at room temperature. The reactor was then heated to 100 °C in 20 min, held at 100 °C for 3 h at 0.86 MPa; heated to 200 °C and kept at 200 °C, at 1.38 MPa for 16 h. The reactor was then cooled to room temperature, the product analysis procedures were similar to the procedures in section 2.3.

2.6. Composition analysis of switchgrass and liquefaction residues using thermogravimetry

Thermogravimetric analysis (TGA) was carried out in air using TA instruments TGA 2050 system. The mass of the biomass sample for a TG scan was approximately 10 mg and platinum crucibles were used in all experiments. The TG curves were recorded in the 100–800 °C temperature range using a scanning rate of 10 °C/min. The oven was kept at 600 °C for at least 3 h to burn leftovers from the previous run. First the switchgrass sample used was analyzed to find the natural composition of the biomass. The residue obtained after separation of the liquefied product by centrifugation was dried in an oven at 90 °C for 24 h before the thermogravimetric analysis. The derivative thermogravimetric (DTG) curves were analyzed using OriginLab 2018b software as described in literature [22].

2.7. Statistical analysis

All experiments were conducted in duplicates. Results shown are the mean values, with standard errors $< 5\%$. Statistical significance was detected by analysis of variance (ANOVA) and Tukey's honest significant difference (HSD) test at a 95% confidence level using R.

3. Results and discussion

3.1. Oligomerization of acetone using Brønsted acidic ionic liquid catalyst and catalytic reduction of the product

The imidazolium ionic liquids, 1-(3-propylsulfonic)-3-methylimidazolium chloride (**3a,** BAIL-1) and 1-(4-butylsulfonic)-3-methylimidazolium (**3b,** BAIL-2) were chosen as catalysts for the experiments since our earlier studies have shown that these ionic liquids are excellent catalysts for cellulose depolymerization as well as for further transformations of carbohydrates [13,16,23]. In addition, previous studies have shown that the ionic liquids 1-(3-propylsulfonic)-3-methylimidazolium chloride and 1-(4-butylsulfonic)-3-methylimidazolium chloride are generally stable up to about 245 °C [24].

In the initial phase we have studied the self-condensation of acetone under BAIL catalyzed liquefaction conditions, in order to identify the products arising from acetone itself, during the biomass liquefaction process. The compositions of acetone oligomerization products using BAIL-1 and BAIL-2 catalysts are shown in Table 1. The 4-methyl-3-pentene-2-one formed due to the acid catalyzed aldol dimerization is the major product in this process with both BAIL catalysts. In addition, small amounts of trimerization products are also observed in the mixture. In an attempt to collect data on the possible reductive deoxygenation products arising from acetone oligomers in the reduced liquefaction product, we have catalytically reduced the acetone oligomerization product. The compositions of acetone oligomerization products after catalytic reduction is shown in Table 2. The major product in this mixture is 2-propyl-ethanoate, arising from the esterification of the reduction product 2-proponal with acetic acid used as a solvent in the catalytic reduction. The other products are from the reduction of acetone dimerization products, and only partial reductions are observed under the experimental conditions employed.

Table 1
The compositions of acetone oligomerization products formed using BAIL-1 and 2 catalysts. 120 °C, 3.5 h.

Peak No.	Compounds	BAIL-1	BAIL-2
1	4-Methyl-4-pentene-2-one	2.42	2.55
2	3-Hexene-2-one	8.37	5.11
3	4-Methyl-3-pentene-2-one	71.16	68.55
4	4-Hydroxy-4-methyl, 2-pentanone	5.13	3.27
5	6-Hydroxy-2-hexanone	11.52	17.91
6	1,2,4-Trimethylbenzene	0.70	1.26
7	2,6-Dimethyl-2,5-heptadiene-4-one	0.71	0.74
8	Unknown	–	0.60

Table 2
The compositions of catalytically reduced acetone oligomerization products (produced using BAIL-1, 2 catalysts). H$_2$, 1.38 MPa a 200 °C, 16 h, Pd-La(OTf)$_3$.

Peak No.	Compounds	BAIL-1	BAIL-2
1	2-Propyl-ethanoate	79.86	73.62
2	4-Methyl-2-pentanone	17.41	24.33
3	4-Methyl-2-pentanol	2.41	2.05

3.2. The liquefaction of untreated switchgrass in acetone using Brønsted acidic ionic liquid catalysts and reduction of the products

The liquefaction of untreated switchgrass biomass in acetone was studied using the acidic ionic liquids 1-(3-propylsulfonic)-3-methylimidazolium chloride (**3a,** BAIL-1) and 1-(4-butylsulfonic)-3-methylimidazolium (**3b,** BAIL-2) at 120 °C. The compositions of liquefaction products formed in using catalysts BAIL-1 and 2 are shown in Table 3, and the GC-MS chromatogram of the representative liquefaction product using catalyst **3a** is shown in Fig. 3. Thirteen compounds were identified in the product mixture and the three products: 4-methyl-4-pentene-2-one, 4-methyl-2-pentene-2-one and 4-hydroxy-4-methyl, 2-pentanone are arising from the self-condensation of acetone and these products were observed in the acetone oligomerization experiment also and shown in Table 1 as well. The other ten compounds are formed directly from cellulosic fraction of switchgrass or by cross condensation of biomass derived compounds with acetone. The cellulose and hemicellulose in switchgrass first undergoes a Brønsted acidic ionic liquid catalyzed depolymerization to glucose and xylose. Secondly these monomeric sugars are dehydrated to 5-hydroxymethylfurfural and furfural in the presence of the BAIL catalyst. Thirdly the BAIL catalyzed aldol condensations of biomass derived furans with acetone gives the biomass furan - acetone condensation compounds in switchgrass

Table 3
The percentage compositions of liquefaction products produced from switchgrass in acetone using BAIL-1 and 2 catalysts at 120 °C, 3.5 h.

Peak No.	Compounds	BAIL-1	BAIL-2
1	4-Methyl-4-pentene-2-one	0.74	0.54
2	4-Methyl-2-pentene-2-one	13.71	16.42
3	Furfural	30.69	21.96
4	4-Hydroxy-4-methyl, 2-pentanone	1.23	3.58
5	Unknown	0.40	0.89
6	5-Methylfurfural	2.20	–
7	Furfuryl alcohol	0.42	–
8	4-(2-Furanyl)-3-butene-2-one	3.39	4.82
9	5-Hydroxymethylfurfural	4.13	7.49
10	D-Xylofuranose -diacetonide	11.03	11.63
11	Diacetone-D-xylose	18.34	15.78
12	D-Xylofuranose-acetonide	0.42	–
13	Unknown	1.83	5.31
14	Unknown	3.45	1.54
15	Hexitol-triacetonide	1.33	1.95
16	Hexitol-dicetonide	6.70	8.09

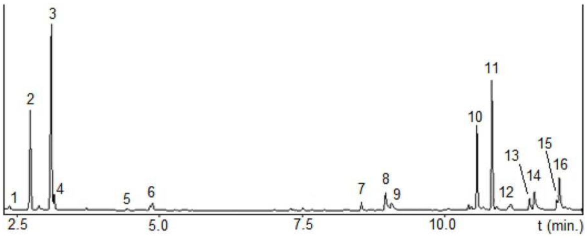

Fig. 3. GC-MS chromatogram of switchgrass liquefaction product using BAIL-1 catalyst.

liquefaction products.

The major product in the liquefaction is furfural formed as a result of dehydration of xylose from hemicellulose depolymerization. The C8, C9 compounds 4-(2-furanyl)-3-butene-2-one and 4-(5-hydroxymethyl-2-furanyl)-3-butene-2-one are formed as a result of BAIL catalyzed cross aldol condensations between acetone and biomass derived furfural and 5-hydroxymethylfurfural. In addition, a number of acetonides of C5 and C6 sugars formed from hemicellulose and cellulose depolymerization products are also seen in the mixture. Interestingly we have not observed any lignin derived products in detectable amounts in the product mixture indicating that lignin remains unaffected under the reaction conditions used.

The switch grass liquefaction product was then reduced with hydrogen in the presence of Pd-La$(OTf)_3$ catalyst system. This catalyst combination was chosen for the process as Sutton et al. has used the same catalyst for hydrodeoxygenation of bio-derived furan compounds [25]. The compositions of liquefaction product after hydrogenation using Pd-La$(OTf)_3$ catalyst are shown in Table 4. The GC-MS chromatogram of the representative hydrogenated product sample produced using BAIL-2 catalyst is shown in Fig. 4. Thirteen products were identified in the reduced liquefaction products. The acetone derived 4-methyl-2-pentanone is the prominent product formed with both catalysts. Tetrahydrofuran-2-methanol, 5-methyldihydrofuran-2(3H)-one and 2-(1-butyl)-tetrahydrofuran were also identified as major products with both catalysts. These furan products are derived from monosaccharide dehydration products formed as intermediates.

3.3. Analysis of chemical compositions of untreated switchgrass and residues after liquefaction with acetone

We have analyzed the residue left after liquefaction of switchgrass biomass by thermogravimetric analysis to determine the composition of the residue. The TGA results of untreated switchgrass and biomass residue after liquefaction process are shown in Figs. 5 and 6 respectively. The pink curves in both figures represents the weight derivatives (dw/dT) of samples in the thermogravimetric analysis. The rest of the lines are fitted curves to identify the composition of the switchgrass samples. The fitting peaks 1–4 in Fig. 5 and peaks 1–3 in Fig. 6 were generated using OriginLab 2018b curve fitting software. For the untreated switchgrass in Fig. 5, both cellulose and hemicellulose peaks are resolved in the thermogram due to the relatively high hemicellulose concentration. As Biney et al. has shown in their thermogravimetric analysis of switchgrass, hemicellulose fraction decomposes in the

Table 4
The percentage compositions of catalytically hydrogenated switchgrass liquefaction products. H_2, 1.38 MPa a 200 °C, 16 h, Pd-La$(OTf)_3$.

Peak No.	Compounds	BAIL-1	BAIL-2
1	2-Propyl-ethanoate	6.06	11.62
2	2,3-Dimethyl-1-butanol	16.13	11.98
3	2-Pentanone	3.42	3.26
4	1-Propyl-ethanoate	2.28	1.97
5	4-Methyl-2-pentanone	26.07	16.39
6	2-Hexene	6.87	7.88
7	4-Hydroxy-4-methyl-2-pentanone	3.20	3.54
8	Tetrahydrofuran-2-methanol	9.10	8.59
9	Cyclohexanone	2.33	3.59
10	5-Methyl-tetrahydrofuran-2-methanol	2.41	4.27
11	Hexane-2,5-dione	3.51	5.83
12	5-Methyldihydrofuran-2(3H)-one	7.41	12.03
13	2-(1-Butyl)-tetrahydrofuran	11.21	9.06

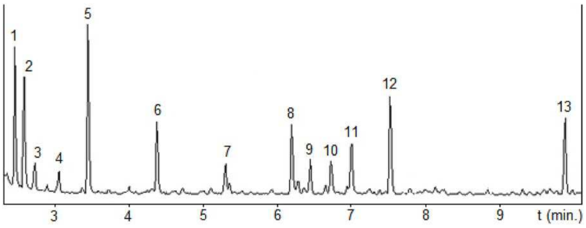

Fig. 4. GC-MS chromatogram of catalytically hydrogenated switch grass liquefaction product (produced using BAIL 2 catalyst). H_2, 1.38 MPa a 200 °C, 16 h, Pd-La$(OTf)_3$.

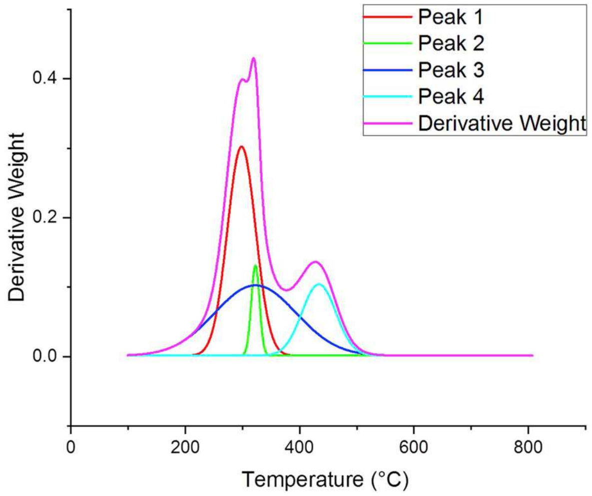

Fig. 5. TGA derivative weight curve (dw/dT) of switchgrass and fitted peaks 1-4.

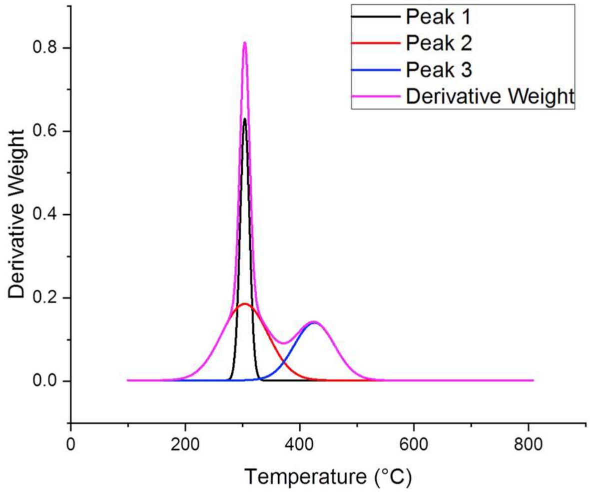

Fig. 6. TGA derivative weight curve (dw/dT) of the residue from liquefaction of switchgrass using Brønsted acidic ionic liquid catalyst BAIL-1 and fitted peaks 1-3.

Table 5

Chemical compositions of switchgrass and residues after liquefactions using BAIL-1 and 2 catalysts at 120 °C, 3.5 h.

	Switchgrass	Residue (BAIL-1)	Residue (BAIL-2)
Percent (g/100g dry biomass)			
Ash	4.22	4.10	6.57
Cellulose	42.01	40.97[a]	45.21[a]
Hemicellulose	38.39		
Lignin	15.38	15.43	16.46
Remaining Solids	100.00	60.50	68.25

[a] Cellulose + Hemicellulose.

200–280 °C temperature range and the area under the fitting peak 1 in Fig. 5 corresponds to the hemicellulose fraction in the sample [22]. The cellulose fraction decomposes in the 250–300 °C range and this process corresponds to fitting peaks 2 and 3 in Fig. 5. The lignin fraction decomposes in the 315–654 °C temperature range and the fitting peak 4 in Fig. 5 represents the lignin content in the sample [22].

The representative thermogravimetric analysis curve for biomass reside left after the Brønsted acidic ionic liquid BAIL-1 catalyzed liquefaction is shown in Fig. 6. The cellulose and hemicellulose decompositions are not completely resolved in the curve; this is similar to the cases of corn stover and sawdust type biomass thermograms reported in the literature [26,27]. Therefore, the fitted peaks 1 and 2 together in the 144–368 °C temperature range in Fig. 6 represents the decomposition of cellulose and hemicellulose. As in the cases of untreated switchgrass the lignin decomposition occurs in the 315–654 °C temperature range and the peak 3 in Fig. 6 represents the lignin content in the switchgrass residue after the liquefaction [26].

The integration areas under the fitting curves were used as described by Moreno et al. in the calculation of compositions of initial switchgrass sample and biomass residues remains after liquefaction using BAIL 1 and 2 catalysts [27]. The compositions of samples calculated based on fitted peak areas are summarized in Table 5. The residue weights were 60.50 and 68.25% of the weight of switchgrass used in the cases of liquefactions using BAIL-1 and BAIL-2 catalysts respectively. Therefore, approximately 49% and 44% of the cellulose/hemicellulose portion of the biomass have been converted during the liquefactions using BAIL-1 and BAIL-2 catalysts. As observed in the GC-MS analysis of the liquefied products the higher proportion of C5 products such as furfural are formed than C6 products like 5-hydroxymethylfurfural, indicating that higher proportion of hemicellulose fraction liquefied with both BAIL catalysts. Thus, the major weight loss of switchgrass after the liquefaction may be due to the hemicellulose decomposition in the biomass. Additionally, the residue analysis shows that no significant changes in the lignin content occurs due to liquefaction with BAIL catalysts. Furthermore, no lignin-based products were observed in the GC-MS analysis, supporting the observation that lignin fraction remains unaffected by the BAIL catalyzed liquefaction of switchgrass biomass in acetone.

4. Conclusion

We have shown that Brønsted acidic ionic liquids can be used as catalysts for the partial liquefaction of untreated switchgrass in acetone to produce hydrophobic liquefied oils. The use of 1-(3-propylsulfonic)-3-methylimidazolium chloride and 1-(4-butylsulfonic)-3-methylimidazolium as catalysts produced 39.5% and 31.75% total liquefactions of switchgrass at 120 °C, after 3.5 h. Unlike the classical pyrolysis method, acidic ionic liquid catalyzed liquefaction in acetone under mild conditions gives a stable hydrophobic product with relatively fewer number of components. Sixteen C5-C9 range products were found in the liquefied product and 13 compounds were identified using GC-MS, including three products arising from dimerization of acetone. The switchgrass liquefied product could be partially reduced by catalytic hydrogenation using Pd-La(OTf)$_3$ catalyst system in 50% aq. acetone at 200 °C, 1.38 MPa for 16 h. Thirteen mainly alcohol and ketone products were identified in the catalytically reduced liquefied product, including biomass derived tetrahydrofuran-2-methanol, 5-methyldihydrofuran-2(3H)-one and 2-(1-butyl)-tetrahydrofuran as some of the major products.

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References

[1] A. Gollakota, N. Kishore, S. Gu, A review on hydrothermal liquefaction of biomass, Renew. Sustain. Energy Rev. 81 (2017) 1378–1392.
[2] A. Kruse, A. Funke, M.-M. Titirici, Hydrothermal conversion of biomass to fuels and energetic materials, Curr. Opin. Chem. Biol. 17 (3) (2013) 515–521.
[3] H.A. Baloch, S. Nizamuddin, M.T.H. Siddiqui, S. Riaz, A.S. Jatoi, D.K. Dumbre, N.M. Mubarak, M.P. Srinivasan, G.J. Griffin, Recent advances in production and upgrading of bio-oil from biomass: a critical overview, J. Environ. Chem. Eng. 6 (2018) 5101–5118.
[4] T. Kan, V. Strezov, T.J. Evans, Lignocellulosic biomass pyrolysis: a review of product properties and effects of pyrolysis parameters, Renew. Sustain. Energy Rev. 57 (2016) 1126–1140.
[5] F. Behrendt, Y. Neubauer, M. Oevermann, B. Wilmes, N. Zobel, Direct liquefaction of biomass, Chem. Eng. Technol. 31 (5) (2008) 667–677.
[6] Z. Lu, H. Zheng, L. Fan, Y. Liao, B. Ding, B. Huang, Liquefaction of sawdust in 1-octanol using acidic ionic liquids as catalyst, Bioresour. Technol. 142 (2013) 579–584.
[7] H. Chen, Y. Zhang, S. Xie, Selective liquefaction of wheat straw in phenol and its fractionation, Appl. Biochem. Biotechnol. 167 (2) (2012) 250–258.
[8] T. Yamada, H. Ono, Rapid liquefaction of lignocellulosic waste by using ethylene carbonate, Bioresour. Technol. 70 (1) (1999) 61–67.
[9] T. Yamada, H. Ono, S. Ohara, A. Yamaguchi, Characterization of the products resulting from direct liquefaction of cellulose I. Identification of intermediates and the relevant mechanism in direct phenol liquefaction of cellulose in the presence of water, Mokuzai Gakkaishi 42 (11) (1996) 1098–1104.
[10] T. Yamada, H. Ono, Characterization of the products resulting from ethylene glycol liquefaction of cellulose, J. Wood Sci. 47 (6) (2001) 458–464.
[11] J. Lu, X. Li, R. Yang, J. Zhao, Y. Liu, Y. Qu, Liquefaction of fermentation residue of reed- and corn stover-pretreated with liquid hot water in the presence of ethanol with aluminum chloride as the catalyst, Chem. Eng. J. 247 (2014) 142–151.
[12] J. Long, B. Guo, J. Teng, Y. Yu, L. Wang, X. Li, SO3H-functionalized ionic liquid: efficient catalyst for bagasse liquefaction, Bioresour. Technol. 102 (21) (2011) 10114–10123.
[13] A.S. Amarasekara, O.S. Owereh, Hydrolysis and decomposition of cellulose in Brønsted acidic ionic liquids under mild conditions, Ind. Eng. Chem. Res. 48 (22) (2009) 10152–10155.
[14] A.S. Amarasekara, B. Wiredu, 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, Ind. Eng. Chem. Res. 50 (21) (2011) 12276–12280.
[15] A.S. Amarasekara, O.S. Owereh, Synthesis of a sulfonic acid functionalized acidic ionic liquid modified silica catalyst and applications in the hydrolysis of cellulose, Catal. Commun. 11 (13) (2010) 1072–1075.
[16] A.S. Amarasekara, B. Wiredu, Acidic ionic liquid catalyzed liquefaction of cellulose in ethylene glycol; identification of a new cellulose derived cyclopentenone derivative, Ind. Eng. Chem. Res. 54 (2015) 824–831.
[17] A.S. Amarasekara, B. Wiredu, Single reactor conversion of corn stover biomass to C5-C20 furanic biocrude oil using sulfonic acid functionalized Bronsted acidic ionic liquid catalysts, Biomass Convers. Biorefin. 4 (2014) 149–155.
[18] S. Sreekumar, Z.C. Baer, A. Pazhamalai, G. Gunbas, A. Grippo, H.W. Blanch, D.S. Clark, F.D. Toste, Production of an acetone-butanol-ethanol mixture from Clostridium acetobutylicum and its conversion to high-value biofuels, Nat. Protoc. 10 (3) (2015) 528–537.
[19] M. Kheyrandish, M.A. Asadollahi, A. Jeihanipour, M. Doostmohammadi, H. Rismani-Yazdi, K. Karimi, Direct production of acetone–butanol–ethanol from waste starch by free and immobilized Clostridium acetobutylicum, Fuel 142 (2015) 129–133.
[20] J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu, Z. Sun, Novel Brønsted acidic ionic liquid as efficient and reusable catalyst system for esterification, Catal. Commun. 5 (9) (2004) 473–477.
[21] Q. Yang, Z. Wei, H. Xing, Q. Ren, Brönsted acidic ionic liquids as novel catalysts for the hydrolyzation of soybean isoflavone glycosides, Catal. Commun. 9 (6) (2008) 1307–1311.

[22] P.O. Biney, M. Gyamerah, J. Shen, B. Menezes, Kinetics of the pyrolysis of arundo, sawdust, corn stover and switch grass biomass by thermogravimetric analysis using a multi-stage model, Bioresour. Technol. 179 (2015) 113–122.

[23] A.S. Amarasekara, Acidic ionic liquids, Chem. Rev. 116 (10) (2016) 6133–6183.

[24] A.S. Amarasekara, O.S. Owereh, Thermal properties of sulfonic acid group functionalized Broensted acidic ionic liquids, J. Therm. Anal. Calorim. 103 (2011) 1027–1030.

[25] A.D. Sutton, F.D. Waldie, R. Wu, M. Schlaf, A. Louis III, J.C. Gordon, The hydrodeoxygenation of bioderived furans into alkanes, Nat. Chem. 5 (5) (2013) 428–432.

[26] C. Di Blasi, Modeling chemical and physical processes of wood and biomass pyrolysis, Prog. Energy Combust. Sci. 34 (1) (2008) 47–90.

[27] C. Lucas-Torres, A. Lorente, B. Cabañas, A. Moreno, Microwave heating for the catalytic conversion of melon rind waste into biofuel precursors, J. Clean. Prod. 138 (2016) 59–69.