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Research article

Pd/C catalyzed room-temperature, atmospheric pressure hydrogenation of furanic bio-oils from acidic ionic liquid catalyzed liquefaction of biomass in acetone

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ABSTRACT

Furanic bio-oils were produced from liquefaction of corn cobs and switchgrass using 1-(3-propylsulfonic)-3-methylimidazolium chloride catalyst in acetone at 120 °C, 5 h. The biomass conversions to bio-oils for corn cobs and switchgrass were 43.8 ± 1.9 and 40.2 ± 1.4% (w/w) respectively. The bio-oils were then catalytically hydrogenated in water: methanol 3:1 (v/v) at room-temperature and atmospheric pressure using 5% Pd-C catalyst to give hydrogenated bio-oils and analyzed using GC–MS to identify the products. GC–MS analysis revealed that majority of the products in hydrogenated bio-oils is C4-C17 alcohols, ethers and furans. A total of 64 products were observed in GC–MS and 61 were identified with the use of mass spectroscopy. These products are arising from the partial reduction as well as deoxygenation of biomass derived furan aldehyde - acetone cross aldol products and acetone self condensation products. In addition, NMR analysis was used to quantify the effect of catalytic hydrogenation. ^{1}H NMR spectra peak integration for the alkene-furan region (6.0–8.0 ppm) showed reductions of 19.0 to 1.8% and 19.1 to 2.6% due to the catalytic hydrogenation of bio-oils from corn cobs and switchgrass, confirming the effect of Pd-C catalyzed, 1 Atm., room temperature hydrogenation.

1. Introduction

Biomass liquefaction in a non aqueous medium has attracted recent attention as a feasible approach to produce renewable fuels due to several reasons like lower operating temperatures, more stable product profiles and higher liquefaction yields. Some of the widely studied non-aqueous liquefaction mediums are methanol [1], ethanol [2,3], iso-propanol [4,5], 1-octanol [6], polyhydric alcohols [7–10], phenol [11,12], ethylene carbonate and acetone [1,13]. As in the case of using water, the addition of catalysts such as Brønsted or Lewis acids [9,14,15], metal oxides like La_2O_3, CeO_2, MnO, CaO [16], CeZrOx [17], potassium fluoride doped alumina [18], Raney Ni-NaOH [4], Na_2CO_3, Fe-zeolite [19], Na_2CO_3-Fe [20] have shown enhancements in quality and the quantity of bio-oils in non-aqueous medium liquefactions. Then there are cases of secondary reactions between biomass degradation products and the non-aqueous liquefaction medium and these reactions, especially with reactive organic solvents can be beneficial in stabilization of reactive products formed during the liquefaction. These reactions can reduce the complexity of the product mixture by preventing the degradation of unstable compounds, can suppress unwanted processes such as re-polymerization, humin and char formation as well. For instance, recently we have shown that a relatively simple mixture of only three products are formed in good yields in the ionic liquid catalyzed liquefaction of cellulose in the reactive solvent ethylene glycol at 120 °C [10]. In this case all three components in cellulose liquefaction bio-oil: 2-hydroxyethyl levulinate, 2-hydroxyethyl levulinate ethylene ketal and 2,3,6,7-tetrahydro-cyclopenta[1,4]dioxin-5-one were formed via condensation reactions with ethylene glycol under acid catalysis conditions used [10].

Since the 2002 report on the use of room temperature ionic liquids (ILs) for the dissolution of cellulose, considerable efforts have been devoted to improve the solubility of cellulose in ILs and to use ILs as solvents for processing cellulosic biomass [21,22]. The first application of ILs for hydrolysis of cellulose was reported in 2007, where Zhao et al. showed that cellulose could be hydrolyzed by adding a catalytic amount of sulfuric acid to the cellulose-IL solution [23,24]. Then in 2009, as a follow up work, our research group first introduced the use of sulfonic acid group functionalized Brønsted acidic ionic liquids (BAILs) for the hydrolysis of cellulose and applications in biomass processing [25–28]. The imidazolium type BAILs in particularly are known to be excellent catalysts for dehydration of monosaccharides as well; for example, monosaccharides can be converted to furan aldehydes: furfural and 5-

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hydroxymethylfurfural (HMF) in high yields by treatment with 1-(3-propylsulfonic)-3-methylimidazolium chloride as a catalyst at 100–120 °C for short periods [29]. In addition, we have shown that these BAILs can catalyze the glucose to fructose isomerization during the conversion of glucose to HMF as well, without the use of expensive and toxic transition metal catalysts [30].

In the last decade a few research groups have focused their attention on the potential of cross-aldol reaction between biomass derived C5,6 furan aldehydes with acetone as a technique of building carbon numbers to fuel range molecules and stabilizing the reactive aldehyde functions in these furans [31–34]. However this approach necessitate a second catalytic hydrogenation step for the reduction of furan, alkene and enone functions in the products as well as deoxygenation of the cross-aldol products in order to produce a fuel type hydrocarbon mixture. A handful of studies are reported in this area; in one of the early examples, Sutton et al. have demonstrated the complete reductive deoxygenation of the representative cross-aldol product, HMF-acetone aldol adduct: 4-[5-(hydroxymethyl)-2-furanyl]-3-buten-2-one, to *n*-nonane in a two step process. In this landmark study, aldol adduct was first converted to nonane 2,5,8 trione by hydrolyzing in aqueous acetic acid at 100 °C. Then in a second step, trione was completely deoxygenated to *n*-nonane using Pd-La(OTf)$_3$ catalyst under a hydrogen atmosphere in glacial acetic acid, at 200 °C, for 16 h [35]. Even though the reductive deoxygenation of biomass furan aldehyde - acetone aldol adducts were possible with this conditions, this process required a high temperature, pressure reaction conditions and the removal of a large excess of acetic acid from the product in the isolation of the product. Then in a more recent development Gupta and Singh showed that related furfural - acetone adduct 4-[2-furanyl]-3-buten-2-one, can be hydrogenated to 4-[2-tetrahydrofuranyl]-2-butanol in over 99% conversion by using simple, cost-effective, $Ni_{0.9}Pd_{0.1}$ alloy nanoparticles at room temperature using 1 Atm. H_2 in a balloon [36]. Further, they have demonstrated the applicability of this operationally simple hydrogenation for a series of furans and furan/acetone aldol adducts having C5 − C15 carbon chains [36]. Later the same research group have shown the applications of silica and rice husk ash supported $Ni_{0.9}Pd_{0.1}$ catalysts in the hydrogenation of furan aldehyde - acetone adducts as well [37]. In this instance room temperature, atmospheric pressure hydrogenation of 4-[2-furanyl]-3-buten-2-one using rice husk ash supported $Ni_{0.9}Pd_{0.1}$ produced a mixture of 4-[2-tetrahydrofuranyl]-2-butanol and 4-[2-tetrahydrofuranyl]-2-butanone in 55% yield [37].

In our research attempts to produce stable biocrude oils, that can be easily upgraded to renewable hydrocarbon fuels, via non-pyrolysis routes, we have studied the degradation of cellulose as well as untreated biomass forms such as corn stover and switchgrass in acetone medium using acidic ionic liquid catalysts [38,39]. In continuation of these efforts, now we have focused our attention on the catalytic reduction step as an approach to produce a fuel grade product from biomass in a two step process. In the current study, biomass liquefaction product was first prepared by heating powdered biomass (corn cobs and switchgrass) in acetone at 120 °C in a closed reactor as shown in scheme in Fig. 1. During this 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 bio-oil product [38,39]. Then furanic bio-oil was subjected to a catalytic hydrogenation under one atmosphere of hydrogen at room temperature using Pd/C as the catalyst as shown in the last step in Fig. 1.

2. Experimental

2.1. Materials and instrumentation

Switchgrass and corn cobs used in this study are a gift sample from National Renewable Energy Laboratory, Boulder, CO, USA. Switchgrass and corn cobs 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 switchgrass and corn cobs 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, conc. hydrochloric acid, acetone ($>$ 99%), ethyl acetate and Pd 5 wt% on activated carbon (Sigma-Aldrich, product number 205680) were purchased from Aldrich Chemical Co. The Brønsted acidic ionic liquid 1-(3-propylsulfonic)-3-methylimidazolium chloride was prepared by condensation of 1-methylimidazole with 1,3-propanesultone and acidification of the resulting salt with conc. HCl according to the literature procedure as shown in Fig. 2 [40]. Biomass liquefaction experiments were carried out in 100 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. ^{1}H NMR Spectra were recorded in $CDCl_3$ on a Varian Mercury plus spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$).

2.2. Gas chromatography mass spectroscopy (GC–MS) analysis

The chromatography identification was carried out on a GC–MS instrument Varian Saturn 2100 T coupled at Varian 3900 oven. The capillary column used was a VF-5 ms (30 m × 0.25 mm i.d. coated with 0.25 mm film, NP:CP8944 Varian). Helium was used as carrier gas with a flow rate of 1 mL/min. The column temperature was initially programmed at 50 °C for 10 min and increased to 100 °C at 10 °C/min and held for 10 min, then to 150 °C at 10 °C/min and held for 30 min, and finally to 250 °C at 20 °C/min and held for 10 min, the total run time was 75 min. The injector temperature was 200 °C; the ionization energy was 70 eV with a mass range of 40 to 600 m/z. The mass spectra acquisition for all ion (m/z) signals presents in the samples and the quantification of their peak area was carried out using the software Varian MS Workstation version 6.9.2., the mass spectrums were identified by referring NIST 98 library. The GC–MS analysis samples were filtered through Syr Filter, 13 mm, 0.20 μm, GF/PTFE (MicroLiter Analytical Supplies, Inc.) before injection.

2.3. General procedure for the BAIL catalyzed liquefaction of biomass (corn cobs or switchgrass) in acetone

Dried, powdered biomass (switchgrass or corn cobs, 1.050 g) was thoroughly mixed with 1-(3-propylsulfonic)-3-methylimidazolium chloride (0.340 g, 1.455 mol) 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 100 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, then, 12.0 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, reactor content was transferred to a centrifuge tube, 2.5 mL of solvent mixture water: methanol 1:1 (v/v) was added, the suspension was mixed and centrifuged at 1700 $\times g$ for 15 min, and the liquid fraction was collected. The solvent extraction process was repeated twice with equal portions of solvent mixture and the combined liquid phase extract was diluted to 20.0 mL with the solvent used in the extraction process to give a consistent solvent volume. The diluted extract was directly used in the catalytic hydrogenation reactions in the next step. 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:

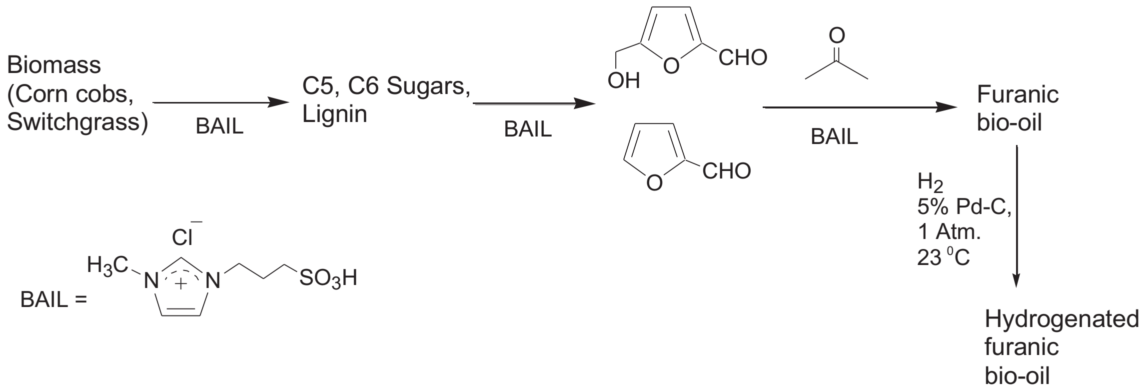

Fig. 1. Brønsted acidic ionic liquid (BAIL) catalyzed liquefactions of corn cobs and switchgrass biomass in acetone to furanic bio-oil and 5% Pd-C catalyzed reduction to hydrogenated furanic bio-oil at room temperature and atmospheric pressure.

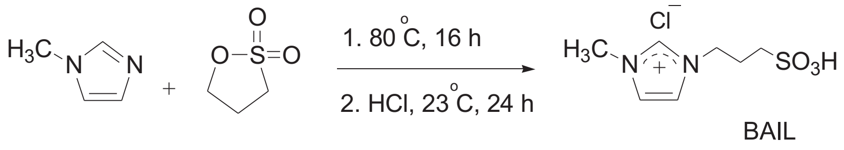

Fig. 2. Synthesis of 1-(3-propylsulfonic)-3-methylimidazolium chloride Brønsted acidic ionic liquid (BAIL) [40].

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

All experiments were carried out in duplicate.

2.4. General procedure for the room temperature, atmospheric pressure hydrogenation of the furanic bio-oil

Catalytic hydrogenation of the furanic bio-oil was carried out in a 50 mL round bottom flask. A 10.0 mL portion of the furanic bio-oil in water: methanol 1:1 (v/v) solvent mixture from experiment 2.2. was added to the hydrogenation reaction flask, diluted with 10.0 mL of deionized water and 20 mg of 5% Pd/C was added. The flask was purged three times with hydrogen and the reaction mixture was stirred under a hydrogen atmosphere at room temperature for 48 h with the use of a H_2 filled balloon. After this period the reaction mixture was transferred to a centrifuge tube, centrifuged at 1700 ×g for 20 min to recover the catalyst and the liquid phase was extracted with ethyl acetate (5 × 10.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4 filtered and analyzed using GC–MS. A representative total ion chromatogram (TIC) of catalytically hydrogenated furanic bio-oil from BAIL catalyzed liquefaction of switchgrass in acetone at 120 °C is shown in Fig. 3. The recovered Pd/C catalyst was washed with ethanol (1 × 2.0 mL) and distilled water (2 × 2.0 mL) and used in the repeat hydrogenation experiment under similar reaction conditions.

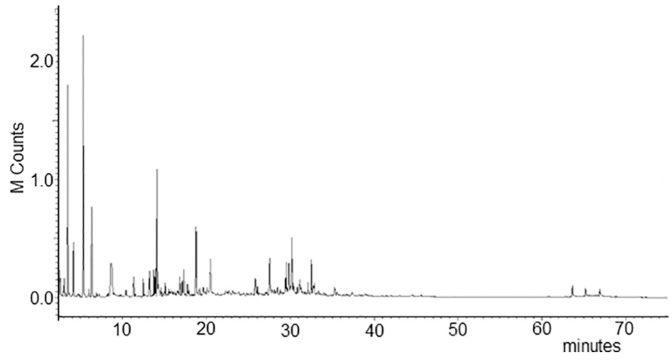

Fig. 3. A representative total ion chromatogram (TIC) of catalytically hydrogenated furanic bio-oil from BAIL catalyzed liquefaction of switchgrass in acetone at 120 °C.

2.5. NMR Spectroscopy of furanic bio-oil and catalytically hydrogenated furanic bio-oil

2.5.1. Furanic bio-oil

A 2.0 mL portion of the water: methanol 1:1 (v/v) extract of furanic bio-oil from experiment 2.2 was diluted with 5.0 mL of water and repeatedly extracted with methylene chloride (3 × 2 mL). The combined methylene chloride layer was evaporated on a stream of nitrogen gas (40 mL/min) at room temperature for 15 min and the bio-oil was then dissolved in 0.6 mL of $CDCl_3$ for NMR analysis.

2.5.2. Catalytically hydrogenated furanic bio-oil

A 2.0 mL portion of the ethyl acetate extract of catalytically hydrogenated furanic bio-oil from experiment 2.3 was evaporated on a stream of nitrogen gas (40 mL/min) at room temperature for 15 min and the oil was then dissolved in 0.6 mL of $CDCl_3$ for NMR analysis. The representative ^{1}H NMR spectra of furanic bio-oil and catalytically hydrogenated furanic bio-oil produced from switchgrass are shown in Fig. 4. The integration area percentages representing different functional group compositions of furanic bio-oil and catalytically hydrogenated furanic bio-oil from corn cobs and switchgrass are shown in Table 3.

3. Results and discussion

In the present study, sulfonic acid group functionalized single catalyst was chosen for the one-pot three step biomass liquefaction process since our previous studies have shown that this type of imidazolium ionic liquids are better catalysts than triethanol ammonium and pyridinium cation based BAILs for the challenging cellulose depolymerization step [25]. The 1-(3-propylsulfonic)-3-methylimidazolium chloride was prepared by condensation of 1,3-propane sultone with 1-methyl imidazole and then acidification with HCl as shown in Fig. 2, according to the literature procedure [40]. In addition, we have determined the Brønsted acidity (H_o) of the BAIL catalyst in water as 2.446 using the standard 4-nitroaniline method [41]. In our earlier studies on a series of BAILs we have studied the thermal stabilities of these -SO_3H functionalized ionic liquids and 1-(3-propylsulfonic)-3-

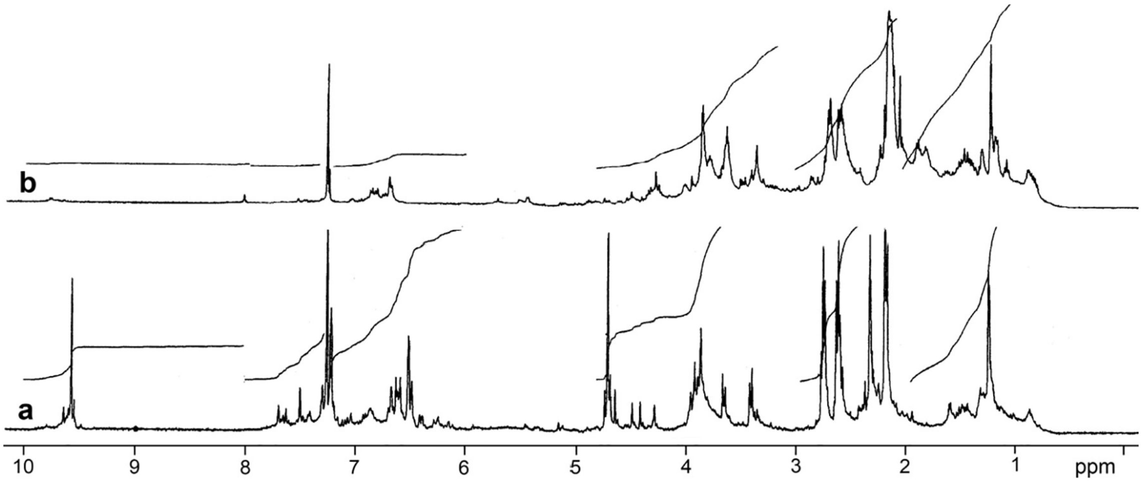

Fig. 4. The representative ^{1}H NMR spectra of furanic bio-oil (a) and catalytically hydrogenated furanic bio-oil (b) produced from switchgrass recorded in $CDCl_3$ at 400 MHz.

methylimidazolium chloride catalyst is stable up to about 245 °C [42]. We have chosen the reaction conditions for the corn cobs and switchgrass liquefaction process based on our previous experience on liquefaction of cellulose in acetone using the same BAIL catalyst [38]. In our past experiments on cellulose liquefaction in acetone using the same BAIL catalyst have shown a significant increase in liquefaction yields by standing the sample at room temperature after the mixing the catalyst with cellulose, giving adequate time for the absorption of BAIL catalyst on to surface [38]. Additionally, the visual assessment also showed that it takes a long time of about 96 h for the complete adsorption of viscous 1-(3-propylsulfonic)-3-methylimidazolium chloride on to corn cobs and switchgrass particles. The complete adsorption of BAIL on to biomass particles was evident from the disappearance of liquid from the surface and swelling of the particles. 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 reduces the effectiveness of the catalyst. Furthermore, the acetone used as the solvent as well as a reactive component for stabilizing aldehyde groups via aldol condensation. Most importantly, acetone can be obtained from renewable resources based routes such as acetone-butanol-ethanol fermentation [43], making all the carbons in the final bio-oil originating from renewable resources.

The percent conversions of biomass to furanic bio-oil during the liquefactions of corn cobs and switch grass using 1-(3-propylsulfonic)-3-methylimidazolium chloride as catalyst were calculated using the procedure 2.3. Corn cobs and switchgrass produced 43.8 ± 1.9% and 40.2 ± 1.4% (w/w) conversions to bio-oil respectively. The weight compositions of corn cobs and switchgrass are shown in Table 1 [44]. Even though the corn cobs with higher hemicellulose content produced a slightly higher average percent conversion to bio-oil the difference is only marginally significant. For comparison we have tested the liquefaction of biomass in acetone at 120 °C for 5 h, without adding the BAIL catalyst. These control experiments resulted only 6–7% dissolution of biomass in hot acetone.

Table 1
The weight compositions of corn cobs and switchgrass [44].

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

In the next step the furanic bio-oils produced in the liquefaction process was directly subjected to catalytic hydrogenation in water containing 25% methanol. In recent studies on catalytic reduction of biomass derived furan - acetone aldol adducts Gupta and Singh have shown excellent results by using $Ni_{0.9}Pd_{0.1}$ alloy nanoparticles as catalysts at room temperature and 1 Atm. H_2 for the conversions of furanic enone to reduced alcohol and tetrahydrofuran ether products [36,37]. Inspired by these recent developments in the field we have tested the commercially available 5% Pd-C as a catalyst for the reduction of our furanic bio-oil as these furanic bio-oils are composed mainly of a mixture of biomass derived furan - acetone aldol adducts as we have shown earlier [38].

The GC–MS analysis of reduced furanic bio-oils gave 64 significant peaks eluted in retention times between 2.49 and 66.89 min, and 61 of these compounds were identified as C4-C17 range alcohols, ethers and furans as shown in Table 2. The 5% Pd-C catalyst used in the hydrogenation process could be easily recovered by centrifugation of the reaction mixture after hydrogenation. The catalyst was then reused in the repeat run, and the Pd/C catalyst could be reused without appreciable loss in the catalytic activity and the average peak area percent for each compound from corn cobs and switchgrass derived hydrogenated furanic bio-oils and uncertainty in the determinations are shown in the last two columns of Table 2. We have been able to identify most of these compounds, except the peak numbers 25, 57 and 58 eluting at 17.10, 41.20 and 41.18 min and these are marked as unknowns in Table 2. The peak number 7 eluting at 5.32 min in the chromatograms is due to hexane-2,5-diol (Table 2). This most prominent peak in GC–MS corresponds to area integrations of 17.44 ± 1.02 and 12.16 ± 0.11% of sum of the peak areas of all in GC–MS total ion current (TIC) peaks in chromatograms of hydrogenated bio-oils from corn cobs and switchgrass. Some of the other prominent peaks in the GC–MS TIC chromatograms of hydrogenated bio-oils from corn cobs and switchgrass are hexane-1,2-diol, 2-hydroxymethyl tetrahydrofuran and 5-hydroxymethylfurfural, eluting at 6.33, 8.70 and 14.09 min respectively.

We have proposed reaction paths for all the identified products in hydrogenated bio-oils. A representative sample of the proposed paths for the formation of the compounds with peak numbers 9, 19, 20, 24, 26, 32, 34, 38, and 45 from Table 2 are shown in Fig. 5. The complete collection of proposed reaction paths for all the identified compounds and all the mass spectra including unknowns are shown in the supplementary material of this article. The compounds shown in Fig. 5 are derivatives of HMF, which is formed as a result of BAIL catalyzed

Table 2

Interpretation of GC–MS analysis for catalytically hydrogenated furanic bio-oil products. 5.0 mol% C-Pd catalyst, stirred at room temperature equipped with H_2 balloon for 48 h. solvent: water:methanol 3:1 (v/v).

Peak no:	R_t (min)	Compound interpretation		Peak area (%)	
		Assigned formula	Name	Corn cobs	Switchgrass
1	2.49	$C_4H_{10}O_2$	butane-1,3-diol	1.16 ± 0.02	0.66 ± 0.07
2	2.56	C_5H_8O	5-methyl-2,3-dihydrofuran	0.66 ± 0.11	1.15 ± 0.01
3	3.04	$C_5H_{12}O_2$	pentane-1,4-diol	0.83 ± 0.05	0.55 ± 0.09
4	3.24	$C_5H_{12}O_2$	pentane-1,2-diol	0.29 ± 0.07	0.20 ± 0.00
5	3.47	$C_6H_{14}O$	4-methylpentan-2-ol	10.73 ± 1.14	6.02 ± 0.10
6	4.15	$C_6H_{14}O_2$	2-methylpentane-2,4-diol	2.97 ± 0.13	1.70 ± 0.16
7	5.32	$C_6H_{14}O_2$	hexane-2,5-diol	17.44 ± 1.02	12.16 ± 0.11
8	6.02	$C_6H_{12}O$	4-methylpent-3-en-2-ol	0.57 ± 0.02	0.91 ± 0.10
9	6.33	$C_6H_{14}O_2$	hexane-1,2-diol	6.36 ± 0.44	8.13 ± 0.11
10	6.95	$C_5H_6O_2$	(furan-2-yl) methanol	0.42 ± 0.08	0.28 ± 0.00
11	8.32	$C_9H_{12}O_2$	(3E,7E)-9-hydroxynona-1,3,7-trien-5-one	0.32 ± 0.06	0.26 ± 0.05
12	8.70	$C_5H_{10}O_2$	(oxolan-2-yl) methanol	7.63 ± 0.28	10.66 ± 0.35
13	10.41	$C_9H_{12}O_2$	{5-[(1E)-but-3-en-1-yl]furan-2-yl]} methanol	0.47 ± 0.29	0.89 ± 0.03
14	11.35	$C_6H_{10}O_2$	hexane-2,5-dione	0.93 ± 0.30	1.75 ± 0.05
15	12.47	$C_8H_{16}O$	2-butyloxolane	0.78 ± 0.22	1.13 ± 0.03
16	13.17	$C_8H_{14}O_2$	4-(oxolan-2-yl)butan-2-one	0.59 ± 0.08	0.39 ± 0.04
17	13.22	$C_8H_{18}O_2$	octane-1,4-diol	0.99 ± 0.14	0.91 ± 0.08
18	13.78	$C_8H_{14}O_2$	4-oxooctanal	1.18 ± 0.02	1.11 ± 0.29
19	13.94	$C_9H_{20}O_3$	nonane-2,5,8-triol	1.14 ± 0.05	1.18 ± 0.04
20	14.09	$C_6H_6O_3$	5-(hydroxymethyl)furan-2-carbaldehyde	4.25 ± 1.07	5.90 ± 0.24
21	14.30	$C_6H_{10}O_3$	5-(hydroxymethyl)oxolane-2-carbardehyde	0.57 ± 0.03	0.84 ± 0.32
22	14.63	$C_8H_{14}O_3$	(5E)-1,7-dihydroxyoct-5-en-4-one	0.28 ± 0.04	0.41 ± 0.06
23	15.11	$C_{11}H_{20}O_2$	(3E)-4-methyl-6-(oxolan-2-yl)hex-3-en-2-ol	0.44 ± 0.08	0.67 ± 0.11
24	16.86	$C_9H_{14}O_3$	4-[5-(hydroxymethyl)furan-2-yl]butan-2-ol	1.03 ± 0.00	1.16 ± 0.32
25	17.10	Unknown	Unknown	0.73 ± 0.05	1.00 ± 0.15
26	17.32	$C_9H_{18}O_3$	4-[5-(hydroxymethyl)oxolan-2-yl]butan-2-ol	1.52 ± 0.02	1.25 ± 0.63
27	17.74	$C_9H_{16}O_2$	(5-butyl-2,3-dihydrofuran-2-yl)methanol	0.73 ± 0.21	0.53 ± 0.32
28	18.75	$C_8H_{16}O_2$	4-(oxolan-2-yl)butan-2-ol	4.59 ± 0.06	0.17 ± 0.05
29	19.20	$C_9H_{20}O_2$	nonane-1,5-diol	0.47 ± 0.11	0.37 ± 0.01
30	19.68	$C_9H_{18}O_2$	(5-butyloxolan-2-yl)methanol	0.64 ± 0.09	0.91 ± 0.03
31	20.08	$C_9H_{12}O_4$	4-hydroxy-4-[5-(hydroxymethyl)furan-2-yl]butan-2-one	0.61 ± 0.15	0.49 ± 0.16
32	20.46	$C_9H_{12}O_3$	4-[5-(hydroxymethyl)furan-2-yl]butan-2-one	3.35 ± 0.61	4.35 ± 0.21
33	22.32	$C_{12}H_{16}O_3$	(3E,5E)-6-[5-(hydroxymethyl)furan-2-yl]-4-methylhexa-3,5-dien-2-ol	0.51 ± 0.02	0.72 ± 0.01
34	23.18	$C_9H_{16}O_4$	(6E)-1,5,8-trihydroxynon-6-en-2-one	0.54 ± 0.18	0.69 ± 0.04
35	24.82	$C_9H_{12}O_3$	(4E)-1-hydroxynona-4,8-diene-3,6-dione	0.29 ± 0.05	0.27 ± 0.08
36	25.83	$C_{11}H_{18}O_2$	(3E)-4-methyldec-3-ene-2,7-dione	1.47 ± 0.25	1.56 ± 0.04
37	26.08	$C_{11}H_{20}O_2$	(7E)-9-hydroxy-7-methyldec-7-en-4-one	0.72 ± 0.14	0.91 ± 0.03
38	27.51	$C_9H_{16}O_3$	(2E)-1,8-dihydroxynon-2-en-5-one	2.40 ± 0.33	1.81 ± 0.14
39	27.78	$C_{11}H_{18}O_2$	(3E,5E)-4-methyl-6-(oxolan-2-yl)hexa-3,5-dien-2-ol	0.48 ± 0.00	0.75 ± 0.02
40	27.83	$C_{11}H_{24}O_3$	7-methyldecane-1,4,9-triol	0.44 ± 0.06	0.34 ± 0.04
41	28.13	$C_{12}H_{18}O_3$	1-[5-(hydroxymethyl)furan-2-yl]-5-methylhex-1,4-en-3-ol	0.65 ± 0.11	0.69 ± 0.02
42	28.49	$C_{11}H_{16}O_3$	(2E,5E,7E)-1,9-dihydroxy-7-methyldeca-2,5,7-trien-4-one	0.58 ± 0.06	0.65 ± 0.02
43	28.81	$C_{11}H_{18}O_3$	(2E,5E,7E)-7-methyldeca-2,5,7-trien-1,4,9-triol	0.46 ± 0.11	0.43 ± 0.03
44	29.41	$C_8H_{14}O_3$	7-hydroxy-4-oxooctanal	1.02 ± 0.10	1.29 ± 0.15
45	29.53	$C_9H_{10}O_3$	(3E)-4-[5-(hydroxymethyl)furan-2-yl]but-3-en-2-one	1.64 ± 0.21	1.74 ± 0.10
46	29.81	$C_{14}H_{18}O_2$	(1E,4E)-1-(furan-2-yl)-5,7-dimethylocta-1,4,6-trien-3-ol	1.66 ± 0.29	1.49 ± 0.27
47	30.19	$C_{13}H_{26}O_3$	1-(oxolan-2-yl)nonane-3,6-diol	2.61 ± 0.10	3.04 ± 0.01
48	30.37	$C_{11}H_{18}O_2$	(3E,5E)-7-hydroxy-4-methyldeca-3,5-dien-2-one	1.03 ± 0.02	1.32 ± 0.02
49	31.11	$C_{11}H_{24}O_2$	2-methyldecane-4,7-diol	1.04 ± 0.16	0.87 ± 0.04
50	32.08	$C_9H_{16}O_4$	(3E)-1,2,8-trihydroxynon-3-en-5-one	0.79 ± 0.11	0.90 ± 0.04
51	32.52	$C_{11}H_{20}O_3$	(2E)-9-methyldeca-2,8-diene-1,4,7-triol	2.44 ± 0.40	3.00 ± 0.04
52	32.86	$C_{11}H_{14}O_2$	(3E,5E)-6-(furan-2-yl)-4-methylhexa-3,5-dien-2-ol	0.88 ± 0.11	1.18 ± 0.09
53	33.40	$C_{12}H_{22}O_3$	(8E)-1,2,10-trihydroxy-8-methylundec-8-en-5-one	0.43 ± 0.02	3.90 ± 0.26
54	35.29	$C_{12}H_{22}O_2$	(E)-1-[5-(hydroxymethyl)oxolan-2-yl], 3-methyl-hex-1-ene	0.80 ± 0.19	0.85 ± 0.07
55	37.41	$C_{16}H_{26}O_4$	(3E,6E)-3-methyl-1,7-bis(oxolan-2-yl)hepta-3,6-diene-1,5-diol	0.48 ± 0.23	0.49 ± 0.04
56	40.94	$C_{12}H_{20}O_4$	(3E)-1,2,8-trihydroxy-10-methylundeca-3,9-dien-5-one	0.09 ± 0.06	0.11 ± 0.01
57	41.20	Unknown	Unknown	0.06 ± 0.00	0.08 ± 0.05
58	41.48	Unknown	Unknown	0.57 ± 0.15	0.09 ± 0.04
59	43.06	$C_{12}H_{16}O_5$	(3E,6E)-1,10-dihydroxy-10-methylundeca-3,6-diene-2,5,8-trione	0.14 ± 0.04	0.21 ± 0.02
60	44.52	$C_{17}H_{20}O_4$	(1E,4E,6E)-1-[5-(hydroxymethyl)furan-2-yl]-5-methyl-7-(oxolan-2-yl)hepta-1,4,6-trien-3-one	0.13 ± 0.04	0.75 ± 0.24
61	55.61	$C_{14}H_{16}O_5$	(1E,8E)-7-hydroxy-9-[5-(hydroxymethyl)furan-2-yl]-4-oxonona-5,8-dienal	0.17 ± 0.14	0.09 ± 0.04
62	63.55	$C_{14}H_{22}O_5$	4,7-dihydroxy-9-[5-(hydroxymethyl)furan-2-yl] nonanal	0.56 ± 0.27	0.82 ± 0.20
63	65.19	$C_{16}H_{26}O_4$	(3E,6E)-3-methyl-1,7-bis(oxolan-2-yl)hepta-3,6-diene-1,5-diol	0.39 ± 0.25	0.34 ± 0.11
64	66.89	$C_{17}H_{18}O_5$	(1E,4E)-7-(furan-2-yl)-7-hydroxy-1-[5-(hydroxymethyl)furan-2-yl]-5-methylhepta-1,4-dien-3-one	0.31 ± 0.16	0.05 ± 0.02

dehydration of C6 sugars arising from hydrolysis of cellulose in biomass. The 5-hydroxymethylfurfural itself was also found as peak number 20, eluting at 14.09 min. The formation of hexane-1,2-diol appearing as peak 9 at Rt = 6.33 min can be explained as a result of a loss of a water molecule and addition of 10H with the opening of the furan ring in HMF. The BAIL catalyzed aldol condensation of HMF with acetone results the (3E)-4-[5-(hydroxymethyl)furan-2-yl]but-3-en-2-one, eluting at 29.53 min as peak number 45. The successive reduction of enone function in acetone - HMF aldol adduct 45 can lead to 4-[5-(hydroxymethyl)furan-2-yl]butan-2-ol, as peak number 24, eluting at

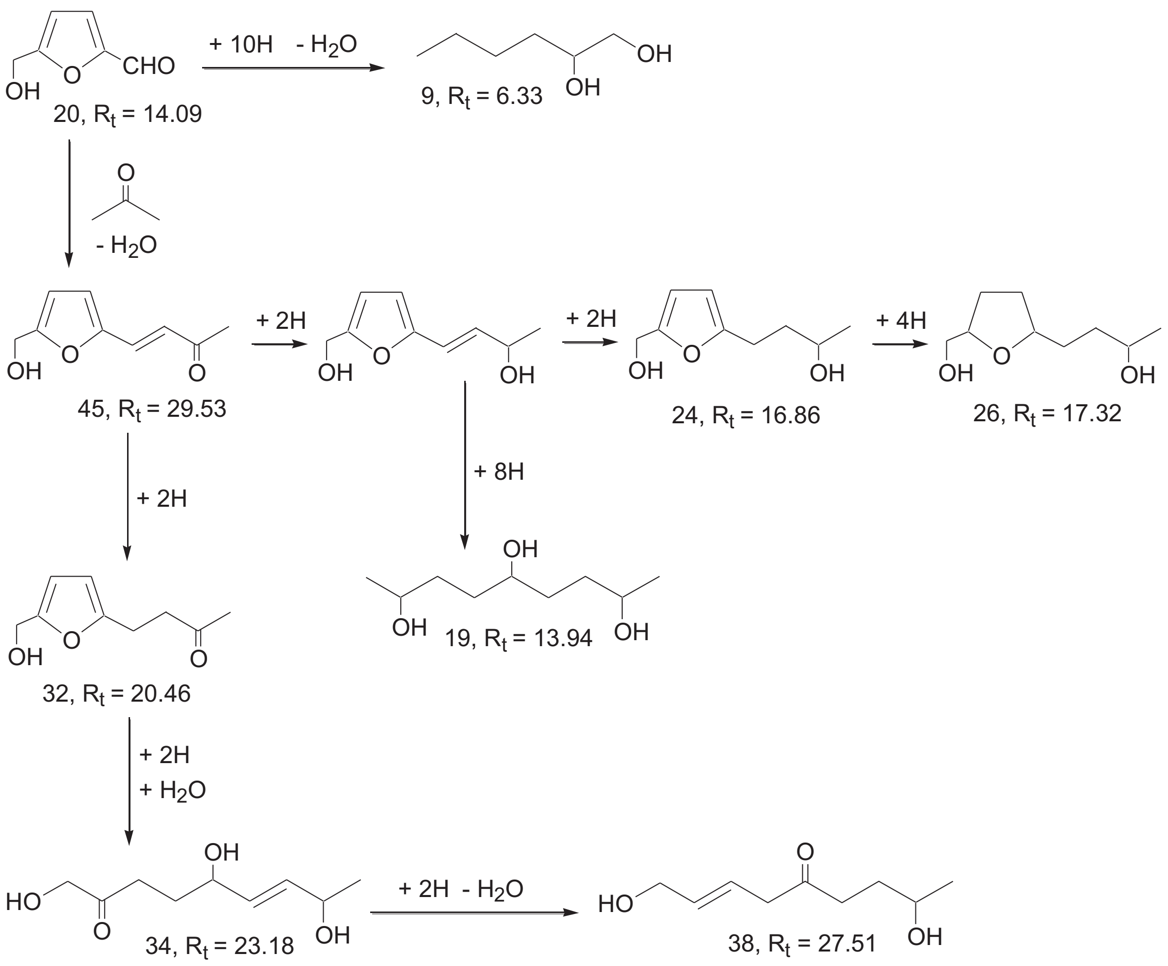

Fig. 5. The representative scheme for the formation of compounds 9, 19, 20, 24, 26, 32, 34, 38, and 45 in the catalytic reduction of furanic bio-oils produced from corn cobs and switchgrass. Retention times Rt are in minutes.

16.86 min. The complete hydrogenation of the furan ring in 24 can produce the tetrahydrofuran derivative 26. The selective reduction of the alkene function in (3E)-4-[5-(hydroxymethyl)furan-2-yl]but-3-en-2-one (peak number 45) can give 4-[5-(hydroxymethyl)furan-2-yl]butan-2-one eluting as peak number 32, at 20.46 min. The complete hydrogenation of all unsaturation in (3E)-4-[5-(hydroxymethyl)furan-2-yl] but-3-en-2-one (peak number 45) with the addition of 10H together with furan ring opening results nonane-2,5,8-triol as peak number 19, Rt = 13.94 min. The furan ring opening of 4-[5-(hydroxymethyl)furan-2-yl]butan-2-one (peak number 32), with the addition of 2H and a molecule of water gives a C9 linear product as peak number 34, eluting at 23.18 min. Further reduction and dehydration of this C9 linear product can lead to (2E)-1,8-dihydroxynon-2-en-5-one eluting as peak number 38 at 27.51 min. Among the identified compounds, the majority is alcohols; 51 out of 61 identified compounds contain one or more alcohol functional groups, whereas only 17 compounds contained carbonyl groups and only 10 compounds are found with furan rings.

Table 3
The integration area percentage compositions of different functional groups in furanic bio-oil and catalytically hydrogenated furanic bio-oil from corn cobs and switchgrass.

Functional group (s), Integration region in ^{1}H NMR (ppm)	Corn cobs		Switchgrass	
	Furanic bio-oil (%)	Catalytically hydrogenated furanic bio-oil (%)	Furanic bio-oil (%)	Catalytically hydrogenated furanic bio-oil (%)
Alkane 0.8–2.0	22.1	39.8	20.7	36.7
CH-, CH$_2$- CH$_3$- α to C=O and C=C 2.0–3.0	34.3	36.6	36.9	37.6
Ether (-CH-O, -CH$_2$-O) 3.2–4.8	20.5	21.4	20.0	22.8
Alkene, furan 6.0–8.0	19.0	1.8	19.1	2.6
Aldehyde 8.0–10.0	4.1	0.4	3.3	0.3

In addition to the GC–MS analysis for the identification of products, we have quantified the effect of Pd-C catalyzed hydrogenation on furanic bio-oils by comparing the composition of various functional groups in furanic bio-oils to catalytically hydrogenated furanic bio-oils by NMR spectroscopy. In this experiment five selected regions in the proton NMR spectra were manually integrated and the areas were compared to quantify the effect of catalytic hydrogenation. The integration area percentage compositions of different functional group types in furanic bio-oils and catalytically hydrogenated furanic bio-oils from corn cobs and switchgrass are shown in Table 3. The most significant changes were seen in the integrations of 6.0–8.0 ppm alkene-furan region; which showed reductions of 19.0 to 1.8% and 19.1 to 2.6% due to the catalytic hydrogenation of bio-oils from corn cobs and switchgrass. Moreover, an increase in alkane percentage was seen at the expense of the reduced alkene-furan percentage. In this instance the integration in the 0.8–2.0 ppm alkane region showed an increase of 22.1 to 39.8% and 20.7 to 36.7% due to the catalytic hydrogenation of bio-oils from corn cobs and switchgrass, further confirming the effect of hydrogenation. As both GC–MS and ^{1}H NMR analysis discloses, the hydrogenation of furanic bio-oils using 5% Pd-C catalyst in 25% methanol in water at room-temperature under 1 Atm. of hydrogen for 48 h is effective in partially reducing the un-saturation of the furan aldehyde-acetone aldol products as well as acetone self condensation products.

4. Conclusion

We have shown that untreated corn cobs and switchgrass can be partially liquefied in acetone using 1-(3-propylsulfonic)-3-methylimidazolium chloride Brønsted acidic ionic liquid catalyst and heating in a high-pressure reactor at 120 °C for 5 h. The liquefied bio-oil was composed of cross-aldol condensation products between biomass derived furans and acetone as well as acetone self-condensation products. This furanic bio-oil could be catalytically hydrogenated in aqueous methanol under mild conditions of room-temperature and atmospheric pressure using 5% Pd-C catalyst to give hydrogenated furanic bio-oils. A total of 64 significant peaks were observed in the GC–MS analysis of the hydrogenated furanic bio-oils and 61 of these C4-C17 range products were identified with the use mass spectroscopy. The majority of identified compounds were found to contain one or more alcohol functional groups, whereas 17 compounds contained carbonyl groups and only 10 compounds were found with furan rings. The peak area integrations at selected regions of the ^{1}H NMR spectra of furanic bio-oils and catalytically hydrogenated furanic bio-oils could be used to quantify the effect of catalytic hydrogenation process. For instance, ^{1}H NMR spectra integration for the alkene-furan region (6.0–8.0 ppm) showed reductions of 19.0 to 1.8% and 19.1 to 2.6% due to the catalytic hydrogenation of bio-oils from corn cobs and switchgrass, confirming the effect of Pd-C catalyzed, 1 Atm., room temperature hydrogenation. In conclusion, GC–MS and NMR analysis of bio-oils points out that catalytic hydrogenation of furanic bio-oils using 5% Pd-C catalyst in 25% aqueous methanol at room-temperature and 1 Atm. of hydrogen for 48 h is effective in reducing the un-saturation in the furan aldehyde-acetone aldol products as well as acetone self-condensation products. The alkene, carbonyl and furan functions in furanic bio-oils undergo hydrogenation during this process. However the catalysis system is ineffective in complete deoxygenation and reduction of alcohol functions to hydrocarbons. Therefore, the acidic ionic liquid catalyzed liquefaction of biomass in acetone followed by Pd-C catalyzed hydrogenation in 25% methanol under mild conditions is suitable for producing a partially oxygenated renewable fuel product with mainly alcohol compounds.

Author statement

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Cristian D. Gutierrez Reyes: Laboratory experiments, data collection, analysis.

Declaration of competing interest

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication.

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Appendix A. Supplementary data

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