

Brønsted acidic ionic liquid catalyzed one-pot conversion of cellulose to furanic biocrude and identification of the products using LC-MS

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ABSTRACT

The degradation of cellulose was studied using 1-(3-propylsulfonic)-3-methylimidazolium chloride and 1-(4-butylsulfonic)-3-methylimidazolium chloride acidic ionic liquids as catalysts in acetone at 120 °C for 3.5 h. The products were analyzed using LC-MS with a C18 column and 0.1% formic acid in water - methanol as the eluent solvent. Eleven cellulose degradation products were identified in the furanic biocrude formed using mass spectroscopy. The identified compounds include: 5-hydroxymethylfurfural (HMF), seven products formed from aldol condensation of HMF with one to three acetone molecules, one furfural-acetone aldol product and two HMF ether products. The percent conversions of cellulose to the furanic biocrude product for the two catalysts 1-(3-propylsulfonic)-3-methylimidazolium chloride and 1-(4-butylsulfonic)-3-methylimidazolium chloride were 25.7 and 19.3% respectively.

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1. Introduction

The pyrolysis bio-oil production is one of the widely studied approaches for conversion of lignocellulosic biomass to a renewable fuel product. Bio-oils are known for more than a century and are complex mixtures of several hundreds of organic compounds, mainly acids, alcohols, aldehydes, esters, ketones, phenols and lignin-derived oligomers [1]. In comparison with heavy petroleum crude oil, the bio-oils are notorious for undesired properties like: high water, oxygen contents, corrosiveness and low heating value. These properties limits the range of direct applications of bio-oil [2], and as a result a vast amount of research have been carried out in past two decades in attempts to upgrade bio-oils to a higher quality fuel product [3]. However, with all the research efforts none of these upgrading techniques have been commercialized to date due to serious setbacks in development of a unified catalysis process required in the upgrading of a very complex mixture. The most insurmountable problem is the chemical complexity of pyrolysis bio-oil with large variations in functional groups at high oxidation levels such as carboxylic acids and phenolic compounds. Therefore an alternative more energy efficient approach to produce a chemically simpler biocrude with lower oxygen content would be a

highly desirable proposition.

The biomass liquefaction or degradation in a solvent medium is another major path in current efforts to produces a biocrude and can be carried out in water or in solvents like phenol [4], ethanol [5], 1-octanol [6], polyols [7], acetone [8], ethylene carbonate [9] with or without catalysts such as $AlCl_3$ [10]. This approach has often resulted a less complex mixture of degradation products and can also give products like levulinate esters and ketals due to their reactions with alcohols, when a reactive solvent is used as the liquefaction medium [5,7].

Ionic liquids are known for their ability to dissolve cellulose and these organic salts have been used as solvents for depolymerization of cellulose and dehydration of monosaccharides to furans [11–13]. Since 2009 we have been exploring the sulfonic acid group functionalized acidic ionic liquids [14–17], immobilized acidic ionic liquid catalysts [18,19], as well as alkyl/aryl sulfonic acids [20,21] as catalysts for the depolymerization of cellulose and liquefaction of lignocellulosic biomass for biofuel applications. Under this project we first reported that Brønsted acidic ionic liquids (BAILs) like 1-(3-propylsulfonic)-3-methylimidazolium chloride can be used as acid catalysts for the depolymerization of cellulose dissolved in the ionic liquid itself [14] as well as in aqueous solutions [20]. These functionalized imidazolium ionic liquids are known to be excellent catalysts for dehydration of carbohydrates as well. The monosaccharides: glucose, fructose, xylose can be converted to C5, 6 biomass furans furfural and 5-hydroxymethylfurfural (HMF) in

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excellent yields by heating with 1-(3-propylsulfonic)-3-methylimidazolium chloride as a catalyst at 100–120 °C for short periods [22]. Furthermore, we have observed that BAILs can promote the glucose to fructose isomerization without the use of transition metal ions, during the conversion of glucose to HMF [23].

In an attempt to produce a structurally less complex, non-acidic and a stable biocrude that can be relatively easily upgradable to a hydrocarbon mixture, we have studied the degradation of cellulose in acetone medium using acidic ionic liquid catalysts. Acetone was selected as the solvent medium as this dipolar solvent is not expected to hydrogen bond with the ionic liquid catalyst and reduce the effectiveness of the catalyst. In addition acetone can be obtained from renewable resources, using well known technologies such as acetone-butanol-ethanol fermentation [24]; making all carbons in the final product originating from renewable resources. The Brønsted acid catalysts are known to promote intermolecular aldol condensation between ketones and aldehydes as well [25]. Therefore, imidazolium acidic ionic liquids were chosen as catalysts for the triple role of Depolymerization, Dehydration and Aldol condensation (DDA) in the conversion of biomass to furanic biocrude as shown in Fig. 1.

In this approach an acid catalyzed furan aldehyde-acetone aldol condensation will be used as the key step in building the carbon number of the product. In fact, Dumesic and co-workers have investigated the base catalyzed aldol condensation of furan aldehydes and ketones as a synthetic approach to build C6–C15 range molecules that could be converted to deoxygenated liquid fuels [26–29]. They studied the aldol condensation between various furan aldehydes (furfuraldehyde, methyl furfural, and 5-hydroxymethylfurfural) and ketones (acetone, acetol, dihydroxyacetone, 2-hexanone, and 3-hexanone) in a THF-aq. NaOH biphasic system, where the basic NaOH act as the catalyst. The same research group earlier reported the use of a bi-phase system, in cooperation with Pd based bifunctional catalyst for the single-reactor, aqueous phase aldol condensation-hydrogenation of carbohydrate-derived compounds, furfural and 5-hydroxymethylfurfural, leading to large water-soluble intermediates that can be converted to liquid alkanes [30]. In addition a few researchers have explored the heterogeneous catalysis for aldol condensation between biomass furans and ketones as heterogeneous catalysts are easier to separate from the products. Lopez Granadoz and co-worker have investigated Mg–Zr mixed oxides for aq. aldol condensation of furfural with acetone [31,32]. In a recent investigation, Salvador Ordoñez and co workers compared the catalytic activities of Mg–Zr, Mg–Al and Ca–Zr [33] with different basic site distributions, as well as they examined the hydrotalcite-derived mixed oxides (Mg_3AlO_x) [34] for the liquid-phase condensation of furfural with acetone. Bi-functional Pd catalysts supported on Mg–Zr, Mg–Al and Ca–Zr mixed oxides for aldolization–hydrogenation of furfural–acetone mixtures is another interesting approach for single reactor operations for producing furanic fuel precursors [33]. However, our approach

presented in this communication using the BAIL catalyst allows us to carry out the three step DDA process with a single catalyst as a one-pot reaction, using abundant cellulose or lignocellulosic biomass as the starting material.

As we are expecting to upgrade the furanic-aldol product from this one-pot multistep process to a hydrocarbon mixture, it is vital to understand the chemical composition of the biocrude in order to choose the proper catalytic system for the next reductive deoxygenation step. Furthermore our initial attempts to identify the constituents by using GC, GC-MS and NMR in the furanic-aldol product from DDA process yielded only limited success [8]. Therefore we have applied the high performance liquid chromatography-mass spectrometry (LC-MS) to analyze the product directly after the reaction, allowing us to collect information on the complete product profile on the DDA process. In this publication we report the degradation of cellulose in acetone with low catalyst loading under mild conditions using two different BAIL catalysts, identification of the products and quantitative analysis using LC-MS.

2. Materials and methods

2.1. Materials and instrumentation

Sigmacell cellulose - type 101 (DP ~ 450, from cotton linters), 1-methylimidazole, 1,3-propanesultone, 1,4-butanedisulfone, concentrated hydrochloric acid and acetone (>99%) were purchased from Aldrich Chemical Co. BAIL catalysts were prepared by condensation of 1-methylimidazole with 1,3-propanedisulfone or 1,4-butanedisulfone and acidification of the resulting salts with conc. HCl according to the literature procedure [35]. Cellulose liquefaction experiments were carried out in 25 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, purchased from Lonsino Medical Products Co. Ltd. Jiangsu, China. These reaction kettles were heated in a preheated Precision Scientific model-28 laboratory oven with temperature accuracy ± 1 °C.

2.2. Liquid chromatography mass spectrometry (LC-MS)

Chromatography identification and quantification were performed on Agilent 6130B Single Quadrupole LC/MS System equipped with Electrospray ionization source (ESI) coupled at 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 $\times$ 4.6 mm, NP:00F-4252-E0 (Phenomenex Inc.). The solvents for the mobile phase and sample preparations were formic acid, water and methanol HPLC grade (J.T. Baker), the final samples were filtered through Syringe Filter, 13 mm, 20 μm , GF/PTFE (MicroLiter Analytical Supplies, 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

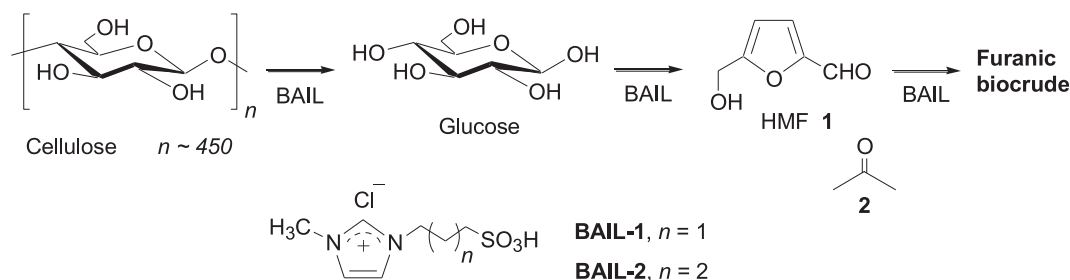


Fig. 1. Brønsted acidic ionic liquid (BAIL) catalyzed one-pot conversion of cellulose to furanic biocrude via Depolymerization, Dehydration and Aldol condensation (DDA) process.

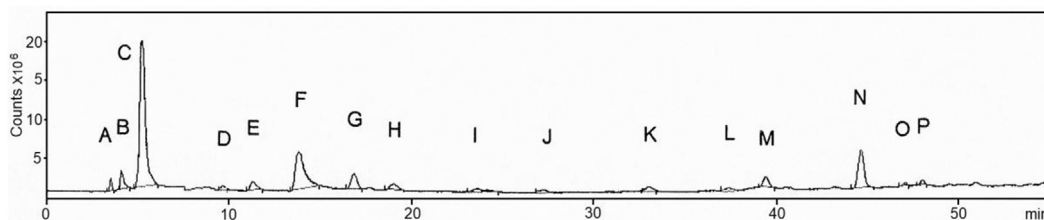


Fig. 2. The representative LC-MS Total Ion Chromatogram for the analysis of furanic biocrude from Experiment 1, using BAIL-1.

Solvent B: methanol, with flow rate of 0.300 mL/min. The linear gradient was as follows (time in minutes/flow rate/mobile phase composition ratio): 0.0/0.300/85:15, 17.0/0.300/85:15 and 50/0.500/65:45, after 55 min all the analytes were eluted from the column and the chromatographic conditions returned to the initial composition of mobile phase. The injection samples volume were 2.5 μ L and 2.0 μ L respectively for the identification and quantification of the compounds formed in each experiment.

2.2.1. MS conditions

Identification SCAN parameters: ESI positive mode, mass range 50–1000 m/z, fragmentor 150, gain 3.0. The spray chamber parameters: gas temperature 300 °C, drying gas flow 10.0 L/min, nebulizer gas 50 psig, Vcap (+) and (–) 3000 V. Agilent Chem Station Rev. B.04.03–54 software was used in the qualitative determination of the compounds presents in the furanic biocrude oil samples.

2.2.2. Quantification of the compounds

The quantitative analysis was carried out based on the assumption that total ion current responses for the components in the furanic biocrude oil mixtures are similar to the response to 5-hydroxymethylfurfural as the identified compounds are derivatives from 5-hydroxymethylfurfural and acetone. The concentration of each component identified in the qualitative analysis experiments were calculated by the comparison of its response against the response of a standard 5-hydroxymethylfurfural following the standard addition method.

2.3. General procedure for Brønsted acidic ionic liquid catalyzed degradation of cellulose in acetone

A mixture of Sigmacell cellulose-type 101 (DP ~ 450) (0.450 g, 2.78 mmol of glucose units of cellulose), catalyst (BAIL-1 or BAIL-2,

0.623 mmol) was prepared in a glass vial and the contents of the vial was mixed with a stainless steel spatula, and the closed vial was allowed to stand at room temperature for 45 h. After the incubation period, content in the vial was carefully transferred into a 25 mL stainless steel solvothermal reaction kettle with Teflon inner sleeve and 4.5 mL of acetone was added. The reaction kettle was firmly closed and heated in a thermostated oven maintained at 120 ± 1 °C for 3.5 h. At the end of this time period, reactor was removed from the oven and quickly cooled in ice-cold water to quench the reactions. The liquefied product was diluted with 8.0 mL of deionized water transferred to a centrifuge tube and centrifuged at 1700 g for 10 min, to remove the suspended solids; residue was dried at room temperature for 48 h and weighed to determine the solid residue. The liquid fraction was diluted to 12.0 mL with deionized water and transferred into a glass vial and subjected to the qualitative and quantitative analysis using LC-MS.

3. Results and discussion

Imidazolium type sulfonic acid group functionalized BAIL-1 and 2 (Fig. 1) were chosen as catalysts for cellulose liquefaction in acetone by DDA process because our earlier studies have shown that these ILs are better catalysts than pyridinium and triethanol ammonium cation based BAILS for the challenging cellulose depolymerization step [14]. The BAIL-1 and 2 catalysts were prepared according to the literature procedure [35]. The Brønsted acidity (H_0) of BAIL-1 and 2 in water were determined as 2.446 and 1.896 using 4-nitroaniline dye, following the standard literature method [36]. We have studied the thermal stabilities of both ionic liquids using TG/DTA methods in our earlier studies. These studies showed that BAILS used are stable up to about 245 °C [37].

In an attempt to identify the polar as well as non polar products formed in the experiment we have analyzed the liquefied product without separation of the products and as a result some unreacted

Table 1

The identifications and yields of compounds found in furanic biocrude prepared by using BAIL catalysts BAIL-1 and BAIL-2. Sigmacell cellulose-type 101 (DP ~ 450) (0.450 g, 2.78 mmol of glucose units of cellulose), catalyst (BAIL-1 or 2, 0.623 mmol), 4.50 mL acetone, 120 °C, 3.5 h, in both experiments. A = acetone, HMF = 5-hydroxymethylfurfural, F = furfural.

Peak (t_R , min.)	Interpretation	Assigned formula	[M+H] (m/z)	Experiment 1: BAIL-1 Yield (mg/450 mg cellulose)	Experiment 2: BAIL-2 Yield (mg/450 mg cellulose)
D (9.66)	A (2)	C_3H_6O	59.1	0.8	0.5
E (11.27)	3A-2H ₂ O (3)	$C_9H_{14}O$	139.0	0.6	0.5
F (13.77)	HMF (1)	$C_6H_6O_3$	127.0	56.5	42.3
G (16.83)	HMF+2A (4)	$C_{12}H_{18}O_5$	243.0	10.9	7.6
H (18.97)	F + A-H ₂ O+[2H] (5)	$C_8H_{10}O_2$	139.0	6.4	4.5
I (23.53)	HMF+2A-2H ₂ O (6)	$C_{12}H_{14}O_3$	207.0	1.2	1.0
J (27.27)	HMF+3A-2H ₂ O (7)	$C_{15}H_{20}O_4$	265.0	0.6	0.5
K (33.09)	HMF+3A-3H ₂ O+[2H] (8)	$C_{15}H_{20}O_3$	248.9	0.3	0.2
L (37.40)	HMF+2A-H ₂ O (9)	$C_{12}H_{16}O_4$	225.0	0.4	0.3
M (39.41)	HMF + A-H ₂ O (10)	$C_9H_{10}O_3$	167.0	8.9	6.8
N (44.62)	HMF + A-2H ₂ O+[H tr.] (11)	$C_9H_8O_2$	149.0	15.9	12.3
O (47.01)	2HMF-H ₂ O (12)	$C_{12}H_{10}O_5$	235.0	0.6	0.4
P (47.99)	2HMF-H ₂ O+[O] (13)	$C_{12}H_{10}O_6$	251.0	0.3	0.4

Table 2

The percent conversion of cellulose to furanic biocrude and weights of unreacted residue formed in using catalysts BAIL-1 and BAIL-2. Sigmacell cellulose-type 101 (DP ~ 450) (450 mg, 2.78 mmol of glucose units of cellulose), catalyst (BAIL-1 or 2, 0.623 mmol), 4.50 mL acetone, 120 °C, 3.5 h, in both experiments. *% Conversion = (Σ mole of cellulose derived compound)/(mole of glucose equivalent in cellulose) $\times$ 100%.

Experiment	BAIL catalyst	% Conversion of cellulose to furanic biocrude*	Residue mg/450 mg cellulose
1	BAIL-1	25.7	181.7
2	BAIL-2	19.3	234.1

glucose, its oligomers and BAIL catalyst were also found in the first three peaks of the Total Ion Chromatogram (TIC). These compounds were eluted early (within the first 6 min) in the C-18 reversed phase column eluting with 0.1% formic acid-water/methanol as shown in peaks A-C in the representative LC-MS TIC in Fig. 2. These peaks were not included in the quantitative analysis as these compounds are structurally dissimilar to the relatively non polar HMF and related aldol condensation products.

The significant compounds eluted after the polar sugars and BAIL catalyst are shown as peaks D-P in the TIC (Fig. 2). These 13

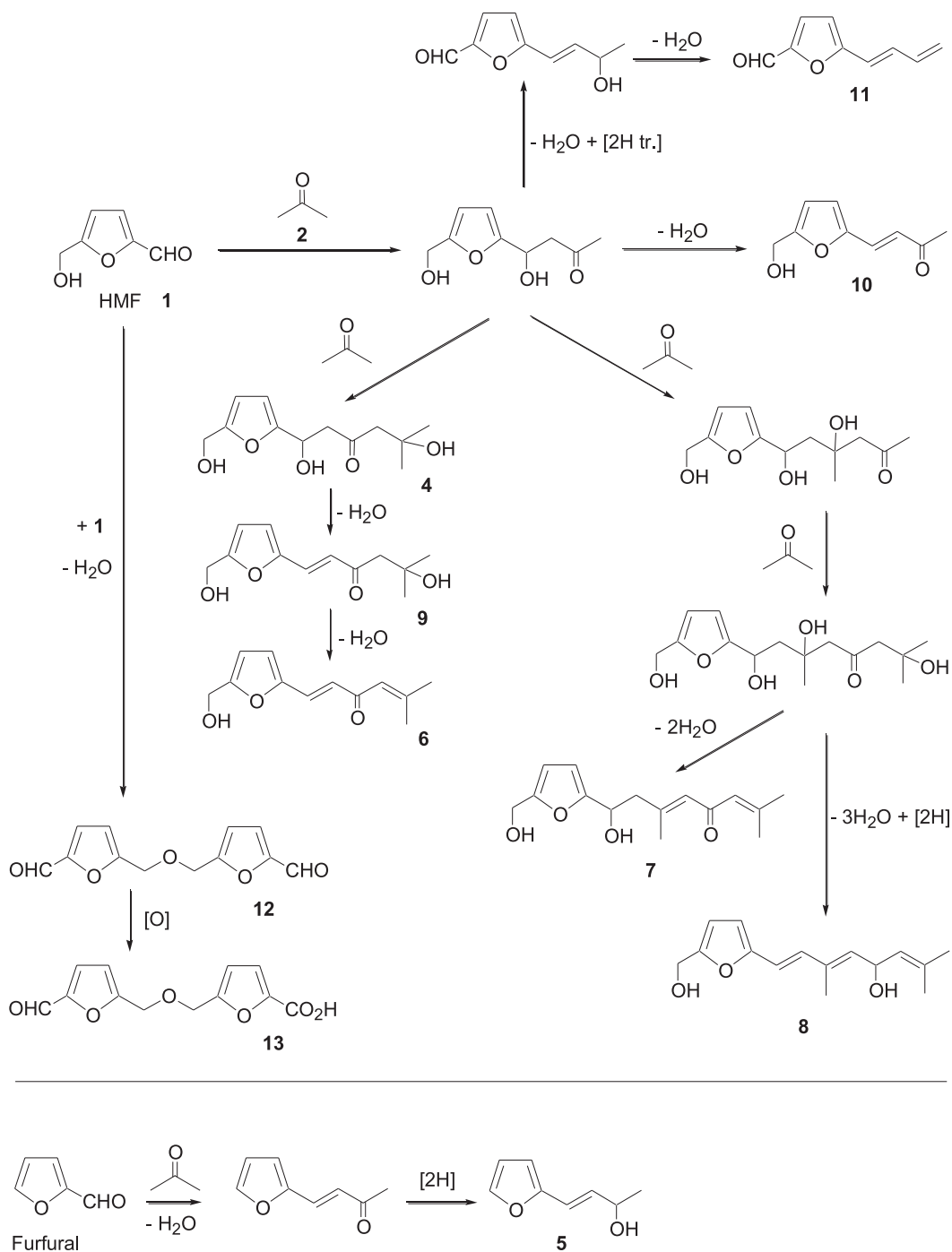


Fig. 3. Proposed reaction paths for the formation of 5-hydroxymethylfurfural (HMF) and furfural condensation products 4–13.

peaks with retention time (t_R) in the 9–50 min range were identified by mass spectroscopy and the interpretation of these components in the furanic biocrude is shown in Table 1. The quantitative analysis was carried out based on the assumption that TIC responses for the components in the furanic biocrude are similar to the response of HMF as the identified compounds are derivatives from 5-hydroxymethylfurfural and acetone. The concentration of each component identified was calculated by comparison of its responses against the response of a HMF standard, following the standard addition method and the calculated weights of the components are shown in Table 1. The percent conversion of cellulose to furanic biocrude and weights of unreacted residue formed in using catalysts BAIL-1 and BAIL-2 are shown in Table 2. The percent conversion of cellulose to furanic biocrude was calculated using the formula:

$$\% \text{ Conversion} = \left(\frac{\sum \text{mole of cellulose derived compound}}{\text{(mole of glucose equivalent in cellulose)}} \right) \times 100\%$$

The peaks D and F were identified as acetone and HMF. The peak E was identified as 2,6-dimethyl, 2,5-heptadien-4-one (**3**), formed as a result of acid catalyzed aldol-trimerization of acetone [38]. The other ten compounds in biocrude are produced *via* acid catalyzed condensation reactions of HMF and furfural formed in the dehydration steps as shown in Fig. 3. These compounds are formed *via* three different reaction paths. The majority of products are formed through BAIL catalyzed aldol condensations of HMF with one to three molecules of acetone. The first aldol product from the reaction between HMF and acetone can undergo dehydrations to give two C9 compounds **10** and **11**. The path involving an intramolecular oxidation-reduction with 2H transfers from $-\text{CH}_2\text{OH}$ to $\text{C}=\text{O}$ function may lead to the formation of diene **11**. The first HMF-acetone aldol product can undergo further aldol condensations with one or two acetone molecules. The second aldol condensation can lead to C12 compounds **4**, **6** and **9** as shown in Fig. 3. The path involving three aldol condensations with three acetone molecules may lead to C15 compounds **7** and **8**. The loss of two water molecules from C15 adduct leads to **7**, whereas the loss of three water molecules followed by an inter molecular H transfer reduction can lead to **8**. This reduction can be explained as a result of an intermolecular oxidation-reduction process involving another component in the mixture. For instance the aldehyde function in **12** can undergo an oxidation to give **13** as shown in Fig. 3, in the transfer redox system. The products **12** and **13** are formed due to dehydrative ether formation of HMF under strongly acidic conditions and this is a well known reaction of HMF under acidic conditions [39]. The path for the formation of a furfural derived aldol product is shown in the last scheme of Fig. 3. Even though the dehydration of glucose gives HMF as the major product (Fig. 1), furfural formation as a minor product appears to be common in BAIL catalyzed dehydrations [40]. The aldol condensation of furfural with acetone followed by an intramolecular transfer reduction may lead to the only C8 compound **5**.

4. Conclusion

We have shown that acidic ionic liquid catalyzed degradation of cellulose in acetone at 120 °C, 3.5 h gives a structurally well defined furanic biocrude in fair yields. Eleven products were identified and the majority are formed from aldol condensation of HMF with 1–3 acetone molecules. In contrast to the energy intensive classical pyrolysis bio-oil preparation, giving a complex and unstable mixture, this energy efficient process produce a well defined C5–C15 range partially oxygenated mainly furanic mixture. The new

simpler furanic biocrude should be easily upgradable to a hydrocarbon fuel product using the well established reductive catalytic deoxygenation techniques.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.renene.2018.12.108>.

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