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### PRODUCTION OF 5-(HYDROXYMETHYL)-FURFURAL FROM WATER-SOLUBLE CARBOHYDRATES AND SUGARCANE MOLASSES

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### **Graphical Abstract**



### Highlights

- 1. ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl were used in a biphasic system to produce HMF from water-soluble carbohydrates
- 2. No matrix interference was observed in the dehydration of sugarcane molasses
- Acid dehydration in aqueous medium produced levulinic and formic acids selectively
- 4. Both catalytic systems produced humins with a furanic backbone

#### Abstract

In this work, two catalytic systems were applied for the production of 5-(hydroxymethyl)-furfural (HMF) from different water-soluble carbohydrates. These systems combined Lewis (ZnCl<sub>2</sub> and AlCl<sub>3</sub>) and Brønsted (HCl) acids in a biphasic system composed of an extraction solvent (ES) and a reaction solvent (RS). Tetrahydrofuran (THF) was used to control yield losses that are due to undesirable side reactions by promoting the continuous extraction of HMF from the aqueous phase, which was nearly saturated with sodium chloride (NaClaq). HMF production was enhanced when high temperatures (180 °C) and high ES/RS ratios (10) were employed in short reaction times (60 min). The combination of Lewis and Brønsted acids and the use of the THF/NaClaq biphasic system proved to be the right choice for HMF production. AICl<sub>3</sub>/HCl was best for glucose dehydration while ZnCl<sub>2</sub>/HCl gave higher HMF yields from sucrose and sugarcane molasses (65.6 and 49.6%, respectively). Compared to synthetic mixture containing the same amount of sugars, no matrix interference was observed during dehydration of sugarcane molasses. ZnCl<sub>2</sub>/HCl humins were primarily composed of furan derivatives, whereas AICI<sub>3</sub>/HCI humins had higher molecular mass and benzofurans content, which were a result of the higher acidity of this reaction system.

**Keywords:** sucrose • sugarcane molasses • acid-catalyzed dehydration • hydroxymethylfurfural • biphasic systems

#### 1. Introduction

The conversion of renewable feedstocks into fuel, chemicals and materials plays an important role in the development of sustainable chemical processes and this has been generally referred to as the biorefinery concept. According to the National Renewable Energy Laboratory (NREL), biorefinery is a facility that integrates equipment and processes for biomass conversion into fuels, energy and chemicals for a variety of industrial applications. Likewise, the International Energy Agency (IEA) defines biorefinery as the sustainable processing of biomass into a spectrum of products to be marketed as food, chemicals and supplies [1].

Sugarcane is a suitable example of biomass for biorefinery applications [2]. The sugarcane processing for sugar (sucrose) and ethanol generates a

large number of by-products such as cane bagasse from the juice extraction step, filter cake from juice filtration and molasses after crystallization of sucrose from the concentrated juice. Cane molasses are low cost feedstocks that contain high concentrations of soluble sugars (mostly sucrose) with small amounts of fructose and glucose along with other minor components such as phenolic compounds, organic acids and salts [3]. With these properties and composition, cane molasses can be considered a valuable feedstock for biorefinery applications through their chemical or biochemical conversion to platform chemicals and high value-added compounds.

5-(Hydroxymethyl)-furfural (HMF) is considered one of the top 10 most valuable chemicals that can be produced from plant biomass and this is due to its wide range of applications in polymers, food and fuel chemistry[3,4]. Also, HMF is a versatile chemical intermediate that can be converted to a variety of interesting molecules such as 2,5-hydroxymethylfuran (DHMF), 5- (hydroxymethyl)-furanoic acid (HMFA) [5], 2,5-furandicarboxylic acid [6], levulinic acid [7], 2,5-dimethylfuran [8] and 2,5-diformylfuran [9], among others.

The most widely accepted mechanism for the production of furans from hexoses such as glucose first encompasses its catalytic  $\alpha$ -hydroxy-carbonyl isomerization to produce fructose, which can be readily converted to HMF through a series of dehydration reactions [10,11]. The endeavour for achieving good yields under acceptable reaction conditions has shown that a Lewis acid mediated isomerization followed by dehydration in the presence of a strong Brønsted acid works best for the production of these furan compounds [12,13] while the use of basic catalysts typically leads to several undesirable side reactions [14]. However, earlier studies have also evaluated the use of both mineral and organic acids acting alone, metallic salts and heterogeneous catalysts with high Brønsted acid strength [11].

Carbohydrate dehydration has been studied in several reaction media such as aqueous, organic, biphasic and non-conventional systems such as ionic liquids and sub- or supercritical fluids [15]. Wang *et al.* (2013) [16] employed a 67% ZnCl<sub>2</sub> aqueous solution for glucosamine dehydration at 120 °C for 90 min to obtain an HMF yield of 21.9%. However, a singular advance in these reaction systems was based on the use of a two-phase environment involving a reaction solvent (aqueous phase) and an extraction solvent (organic

phase) because the *in situ* extraction of HMF avoids undesirable side reactions such as rehydration to levulinic and formic acids and condensation to dark insoluble solid residues generally referred to as humins [17]. However, despite the good selectivity of biphasic systems for carbohydrate dehydration, due to the good reactivity of aldehyde group of this furan compound the formation of humins has also been reported in organic solvents [18].

Appropriate extraction solvents for carbohydrate dehydration must have a high partition coefficient for furan compounds, meaning that, once formed, these reactive species will be readily transferred to the organic phase. For water-miscible organic solvents, an electrolyte such as sodium chloride (NaCl) must be added to induce the formation of a biphasic system [19,20].

Yang *et al.* (2012) [21] demonstrated that AlCl<sub>3</sub> is a promising catalyst for HMF production from glucose in a THF/NaCl<sub>aq</sub> biphasic system under microwave irradiation. HMF yields of 65% were achieved. Pagán-Torres *et al.* (2012) [22] reached a 62% HMF yield from 5 wt.% glucose in a biphasic system containing H<sub>2</sub>O/2-butylphenol and AlCl<sub>3</sub>/HCl at 170 °C and pH 2.5 using a glucose/Lewis acid ratio of 67. Ma *et al.* (2015) [23] obtained HMF yields of 5.5% and 30.3% by glucose and sucrose dehydration, respectively, using a H<sub>2</sub>O/MIBK biphasic system at high temperatures. At these same conditions, fructose dehydration resulted in HMF yields of 73.6%, which was readily attributed to the higher reactivity of ketohexoses compared to aldohexoses. Solid acids containing both Lewis and Brønsted acid sites have also been applied as heterogeneous catalysts for carbohydrate dehydration. Jain *et al.* (2015) [24] employed mesoporous zirconium phosphate for sucrose dehydration in a biphasic system of water and diglyme. In this case, a 53% HMF yield was achieved at the best reaction conditions.

In this work, HMF was successfully produced from glucose, sucrose and sugarcane molasses in a THF/NaCl<sub>aq</sub> biphasic system using two catalytic systems in which both Lewis and Brønsted acids were combined (ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl). To the best of our knowledge, this is the first time that sugarcane molasses is used as feedstock for HMF production in a biphasic system, therefore revealing probable matrix effects that could partially compromise the efficiency of carbohydrate dehydration. Besides, humins that were formed under these reaction conditions were isolated and characterized

by analytical pyrolysis coupled to mass spectrometry (py-GC/MS) and by alkaline hydrolysis followed by mass spectrometry.

### 2. Experimental

#### 2.1. Materials

Glucose of analytical grade and HCl<sub>aq</sub> 37% were purchased from Vetec (Duque de Caxias, RJ). AlCl<sub>3</sub> (99%) was obtained from Sigma-Aldrich Brazil (Jurubatuba, SP), while ZnCl<sub>2</sub> (96%), acetic acid (99.7%) and NaCl (99.7%) came from Neon (Suzano, SP). THF, acetonitrile and H<sub>2</sub>SO<sub>4</sub> of HPLC grade were purchased from Tedia (Rio de Janeiro, RJ) and sucrose of analytical grade was acquired from F. Maia Indústria e Comércio (Belo Horizonte, MG). Sugarcane molasses were kindly provided by Novozymes Latin America (Araucária, PR) from batches that were collected in a large-scale sugar mill. This mill is located in the Western region of the São Paulo State (Brazil).

#### 2.2. Dehydration in a biphasic system

Dehydration experiments were performed in a Büchi Glas Uster<sup>®</sup> stainless steel reactor (Uster, Switzerland), model miniclave drive, that was equipped with mechanical stirring and both temperature and pressure controls. The actual operating pressure corresponded to the vapor pressure of the reaction mixture. All experiments were carried out with 0.75 mmol of carbohydrate (0.135 g glucose; 0,257 g sucrose), whereas for sugarcane molasses, the sample mass was 0.150 g (dry basis).

Different temperatures and ratios between extraction and reaction solvents (ES/RS) were applied in this study. The temperature levels were 140, 160 and 180°C. The biphasic system was composed of 3 mL deionized water and THF at three different ES/RS ratios: 5 (15 mL), 7.5 (22.5 mL) and 10 (30 mL). The amount of NaCl required to form a biphasic system was 1.05 g and mechanical stirring was set at 1500 rpm [21]. The kinetics of glucose dehydration was profiled in both catalytic systems (ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl) by withdrawing reaction aliquots at every 5 min. The applied temperature and

ES/RS ratio were those that performed best in the experimental assessments described above.

HMF yields were calculated in relation to the corresponding theoretical yield, which was based on the stoichiometric amount of HMF that could have been produced from the total carbohydrate content of the starting material. Equations 1 and 2 show the calculation for glucose and sucrose, respectively, where  $HMF_{exp}$  is the amount of HMF that was determined experimentally, m<sub>Glc</sub> and m<sub>Suc</sub> are the initial mass of glucose (Glc) and sucrose (Suc), and 0.70 and 0.74 are the stoichiometric factors for glucose and sucrose conversion to HMF, respectively.

$$HMF_{Glc}(\%) = \frac{HMF_{exp}(g)}{m_{Glc}(g) \times 0.70} \times 100$$
 (1)

$$HMF_{Suc}(\%) = \frac{HMF_{exp}(g)}{m_{Suc}(g) \times 0.74} \times 100$$
 (2)

HMF yields from sugarcane molasses were also calculated in relation to the theoretical yield. However, the contribution of each carbohydrate type that was found in the matrix (glucose, Glc; fructose, Fru; sucrose, Suc) had to be taken into account, along with their corresponding conversion factors as described in Equation 3.

$$Y_{HMF} (\%) = \frac{HMF_{experimental} (g)}{m_{molasses} (g) \times \{ [Suc (\%) \times 0.74] + [Glc (\%) \times 0.70] + [Fru (\%) \times 0.70] \}} \times 100$$
(3)

#### 2.3 Chromatographic analysis

Carbohydrate and organic acid analyses were carried out by high performance liquid chromatography (HPLC) using a Shimadzu workstation that was equipped with two detection systems: diode array UV spectrophotometry (UV-DAD) and differential refractometry (RID). The chromatographic column was an Agilent Hi-Plex-H that was operated at 65 °C using H<sub>2</sub>SO<sub>4</sub> 5 mmol L<sup>-1</sup> as mobile phase in a flow rate of 0.6 mL min<sup>-1</sup>. HMF was analyzed in Metrohm 882 Compact IC Plus HPLC, which was equipped with a dual wavelength ultraviolet detector. The chromatographic column was a Kinetex 5µ EVO C18 100 A (Phenomenex, 150 x 4.6 mm) that was eluted with a mobile phase containing

88% water, 11% acetonitrile and 1% acetic acid in a flow rate of 0.8 mL min<sup>-1</sup>. In both chromatographic systems, quantification was carried out by external calibration using the following concentration ranges: 0.5 to 5.0 g L<sup>-1</sup> for glucose and fructose, 2.0 to 20 mg L<sup>-1</sup> for HMF, 0.03 a 1.50 g L<sup>-1</sup> for levulinic acid and 0.01 to 0.50 g L<sup>-1</sup> for formic acid.

#### 2.4. Humins characterization

Analytical pyrolysis was carried out with solid samples (humins) that were derived from glucose dehydration in THF/NaClaq using both catalytic systems, ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl. The py-GC/MS analyses were carried out in a Thermo (Waltham, MA USA) workstation using a DB-5MS column (30 m x 0.2 mm; 0.25 µm). The pyrolysis temperature was set at 400 °C. The temperature in the injection system was 230 °C and the sample split ratio was 1:100. The total analysis time reached 60 min using the following temperature program: isocratic at 50 °C for 2 min, heating at 4 °C min<sup>-1</sup> until 280 °C and isocratic at 280°C until the end of the run. The ionization energy was set in 70 eV, the mass analyzer was an ion trap type and the total ion current (TIC) was used to build the GC-MS chromatograms, which were analyzed with the AMDIS software (NIST) using a mass range of 50 to 650 m/z. All detected structures were identified according to the NIST (National Institute of Standards) MS library. For quantitative analysis by area normalization, all unidentified peaks corresponding to less than 0.8% of the total chromatogram area were regarded as background noise and removed from the py-GC/MS reports. Elution bands that were derived from column bleeding were also ignored.

Alkaline hydrolysis of humins that were derived from glucose dehydration was carried out in 0.5 mol L<sup>-1</sup> NaOH at 100°C for 2 h [25]. After hydrolysis, the oligomeric fraction was passed through a SPE C18 cartridge that was further eluted with methanol. The cartridge eluate was analyzed by direct infusion in a Varian 320 MS Spectrometer (Palo Alto, USA). The ionization energy was set in 70 eV and the scan range was established between 70 and 1280 m/z.

#### 3. Results and discussion

Initially, the efficiency of glucose dehydration was evaluated in the THF/NaClag biphasic system by employing the ZnCl<sub>2</sub>/HCl catalyst under several temperatures and ES/RS ratios. According to Román-Leshkov and Dumesic (2009) [20], THF fulfills the solvent requirements for proper furans extraction in aqueous biphasic systems. However, THF is partially miscible in water so it is necessary to add a simple electrolyte such NaCl to induce the formation of a biphasic system. Table 1 depicts the influence of temperature and ES/RS ratio on glucose dehydration with ZnCl<sub>2</sub>/HCl. The main products were fructose, HMF, and a black residue that is attributed to the formation of humins [18]. Satisfactory HMF yields were obtained at higher temperatures with full carbohydrate conversion being achieved at 180 °C (entries 5 and 6). Also, HMF production was improved at higher ES/RS ratios (entries 1 and 2, 3 and 4, and 5 and 6) even at the highest temperature levels of 180 °C (entry 6). Fructose was observed in the reaction media only at the lowest reaction temperature (entries 1 to 4), suggesting that an efficient aldose-ketose isomerization is the first step for the subsequent conversion of a six- to a five-membered ring [26]. Also, higher temperatures accelerated the rate of unwanted side reactions such as condensation involving carbohydrates, furan compounds and organic acids to produce humins (entries 5 and 6) [27]. However, the effective extraction of furan compounds at high ES/RS ratios reduced the extent of such side reactions because furans became less exposed to the more reactive aqueous phase.

#### Table 1

A comparative study involving both Lewis and Brønsted acid types acting separately or in combination was carried out to investigate their influence in the catalytic dehydration of glucose (**Fig. 1**). The combined catalytic systems resulted in good HMF yields, which corresponded to  $48.8 \pm 0.9\%$  for ZnCl<sub>2</sub>/HCl and to  $48.6 \pm 0.9\%$  for AlCl<sub>3</sub>/HCl.

Fig. 1

Glucose dehydration with AlCl<sub>3</sub> alone gave also acceptable HMF yields. AlCl<sub>3</sub> dissociates in presence of water to produce an hexaaquo complex (4) that is further hydrolyzed to release the corresponding Brønsted acid in the reaction medium (5 and 6) and these events enhanced the production of HMF when AlCl<sub>3</sub> was applied as the reaction catalyst [28].

$$AICI_3 + 6 H_2O = AI(H_2O)_6^{3+} 3 CI^-$$
 (4)

$$AI(H_2O)_6^{3+} \longrightarrow AI(H_2O)_5(OH)^{2+} + H_3O^+$$
 (5)

$$AI(H_2O)_5(OH)^{2+} \longrightarrow AI(H_2O)_4(OH)_2^+ + H_3O^+$$
 (6)

Screening of different reaction times for glucose dehydration revealed that both  $ZnCl_2/HCl$  and  $AlCl_3/HCl$  catalytic systems reached their maximum HMF yields after 60 and 55 min, which corresponded to 48.8 ± 0.9% and 54.3 ± 1.0% of the theoretical yield, respectively (**Fig. 2**). At longer reaction times, the HMF yields decreased in both catalytic systems due to the formation of humins and this is readily attributed to the excessive exposure of HMF and other carbohydrate derivatives to the catalyst acid strength. Such yield losses were more pronounced with AlCl<sub>3</sub>/HCl because this catalytic system is more acidic than ZnCl<sub>2</sub>/HCl.

#### Fig. 2

To demonstrate the advantages of using a biphasic system, HMF yields in THF/NaCl<sub>aq</sub> were compared to those derived from reactions that were carried out in the absence of an organic solvent (**Table 2**). As already expected, the best performances were achieved in THF/NaCl<sub>aq</sub> with both ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl because HMF was continuously extracted from the acidic aqueous phase, thereby minimizing its further conversion to humins (by aldol condensation) and both levulinic and formic acids (by rehydration). By contrast, when the reaction was carried out in aqueous system, the latter two organic acids were formed predominantly and selectively. Also, ZnCl<sub>2</sub>/HCl was slightly better than AlCl<sub>3</sub>/HCl for the production of both levulinic and formic acids. This observation is interesting because levulinic acid is an important value-added

chemical intermediate and its formation could be easily directed by a simple change in the reaction solvent.

#### Table 2

**Table 3** shows the effect of catalyst loading on the conversion of glucose to HMF in THF/NaCl<sub>aq</sub> using both AlCl<sub>3</sub>/HCl and ZnCl<sub>2</sub>/HCl catalytic systems. Three different catalyst loadings were evaluated using the same molar ratio between both Lewis and Brønsted acid types. Both catalytic systems were relatively equivalent for glucose dehydration, with the highest HMF yields being obtained by adding 0.2 mmol (27 mol%) of the acid catalysts. These HMF yields corresponded to 62.7  $\pm$  0.7% for ZnCl<sub>2</sub>/HCl (entry 2) and 66.9  $\pm$  1.5% for AlCl<sub>3</sub>/HCl (entry 5).

#### Table 3

The pH of the catalytic solutions was measured to evaluate its correlation with HMF yields. In all experiments described in Table 3, the AICI<sub>3</sub>/HCI system always exhibited the lowest pH values (entries 4-6) and this was attributed to the intrinsic properties of this harder Lewis acid, since the Brønsted/Lewis acid ratio was always the same [28]. The best HMF yields were reached using 0.2 mmol (27 mol%) of catalyst at intermediate pH values of 1.36 for ZnCl<sub>2</sub>/HCl and 1.12 for AlCl<sub>3</sub>/HCl (entries 2 and 5). A further increase in the catalyst loading to 0.3 mmol (40 mol%) had negligible impact on HMF formation using both catalytic systems (entries 3 and 6). By contrast, the HMF yield decreased at lower pH values because this promoted the aldol addition/condensation of HMF, which is the primary reaction for humins formation [29]. In order to investigate the effect of catalytic systems applied on glucose dehydration, experiments were also carried out in absence of any added catalyst. The HMF yield that was obtained from glucose by thermal conversion was 9.7 ± 1.6%, which is much lower compared to the performance of both catalytic systems.

Compared to glucose, ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl had considerably different catalytic performances in sucrose dehydration (**Table 3**). The highest

HMF yields were produced with 0.2 mmol (27 mol%) of ZnCl<sub>2</sub>/HCl (65.6 ± 0.4%, entry 2), showing values 17% higher than those obtained with AlCl<sub>3</sub>/HCl (entry 5). This was a remarkable change in catalytic activity because AlCl<sub>3</sub>/HCl was the best catalyst for glucose dehydration. Sucrose is a non-reducing disaccharide whose glycosidic linkage is relatively weak and its faster acid hydrolysis facilitates the direct formation of the fructofuranosyl cation, which is readily converted to HMF by tautomerization followed by dehydration (**Scheme** 1) [30]. However, probably due to its rapid built up in the AlCl<sub>3</sub>/HCl more acidic reaction medium, the longer exposure of this HMF moiety to acid-catalyzed aldol condensation caused a significant drop in its final yield [31,32].

#### Scheme 1

Since sucrose is hydrolyzed to equivalent amounts of glucose and fructose, one additional experiment was carried out to assess the effect of hydrolysis on sucrose dehydration. For this, an equimolar mixture of glucose and fructose (0.135 g each, which is equivalent to 0.257 g of sucrose) was dehydrated to HMF under the same reaction conditions using both AlCl<sub>3</sub>/HCl and ZnCl<sub>2</sub>/HCl in a THF/NaCl<sub>aq</sub> biphasic system (**Fig. 3**). The HMF yields from glucose plus fructose were lower than those from sucrose alone, reaching 53.3  $\pm$  0.4% for ZnCl<sub>2</sub>/HCl and 46.0  $\pm$  0.9% for AlCl<sub>3</sub>/HCl compared to entries 2 (65.6  $\pm$  0.4%) and 4 (54.4  $\pm$  1.4%) of **Table 3**, respectively. The glycosidic bond of sucrose can be easily hydrolyzed by either Brønsted or Lewis acid catalysts to form directly the fructofuranosyl cation. By contrast, free fructose has to be converted to this HMF precursor and this is not so easily achieved under these reaction conditions [11,30].

#### Fig. 3

Sugarcane molasses are interesting materials for chemical conversion because of their high carbohydrate content and low cost. This matrix contains 62.4 wt.% sucrose, 8.5 wt.% glucose and 4.5 wt.% fructose, in addition to other minor components such as phenolic compounds, organic acids and inorganic

salt [33]. Hence, it would be extremely relevant to know if the conditions used in this study were also adequate to produce HMF from this widely available industrial residue. For this purpose, cane molasses were dehydrated using both AlCl<sub>3</sub>/HCl and ZnCl<sub>2</sub>/HCl in THF/NaCl<sub>aq</sub> and the results were compared with those obtained from a synthetic mixture containing the same concentration of sucrose, glucose and fructose (**Fig. 3**).

Compared to sucrose alone, lower HMF yields were obtained from sugarcane molasses ( $49.6 \pm 0.4\%$  for  $ZnCl_2/HCl$  and  $43.2 \pm 1.0\%$  for  $AlCl_3/HCl$ ) because part of the available sugars were found as glucose and fructose and these are less stable under the reaction conditions. However, identical HMF yields were derived from a synthetic mixture that contained the same carbohydrate composition as cane molasses. Therefore, other minor components of this complex matrix such as proteins, organic acids and inorganic salts had no influence on HMF yields as well as on the activity of both catalytic systems employed in this study.

It is well known that the acid-catalyzed carbohydrate dehydration may lead to the accumulation of undesired reaction by-products that are derived from HMF by two different pathways, one leading to humins and another to levulinic and formic acids. Humins formation depends on the process conditions as well as on the nature of the acid catalysts used for conversion. Hence, the characterization of these reaction by-products is an interesting way to elucidate the pathway of such catalytic conversion processes [34].

Humins derived from glucose in THF/NaCl<sub>aq</sub> using both ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl catalytic systems were analyzed by py-GC/MS at 400 °C (**Fig. 4**) and the qualitative analysis of the pyrolysate was carried out by comparison with the NIST MS library [34]. After subtraction of the background elution bands, the remaining peaks accounted for 90% of the total chromatogram area. Both ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl humins had similar py-GC/MS profiles, with 19 components identified on the basis of their mass spectra (**Table 4**). Furan derivatives responded for nearly 90% of the list of identified organic compounds, led by 2-methylfuran (2), 2,5-dimethylfuran (3), 2-acetylfuran (9), one unidentified alkylfuran derivative (5), furan (1), 5-methylfurfural (12) and 5-methyl-2-furanone (7), in this order (Table 4). The furan-based structure of the isolated humins was revealed by the predominance of these and other furan

derivatives in the py-GC/MS profiles, as well as by the low contribution of benzene derivatives and HMF rehydration by-products such as levulinic acid and 2,5-dioxo-6-hydroxy hexanal (DHH) [27].

### Fig. 4

Phenolic componds such as m-cresol (14) and 2,4-di-(tert-butyl)-phenol (19), benzofurans such as 2-methylbenzofuran (16), 7-methylbenzofuran (15) and 4,7-dimethylbenzofuran (18), and ketones such as 2-cyclohexen-1-one (8), 3-methyl-2-cyclohexen-1-one (11) and allylacetone (10) were also observed by analytical pyrolysis in lower amounts, particularly in the py-GC/MS profile of AlCl<sub>3</sub>/HCl humins. Benzofurans are derived from the Diels-Alder reaction and dehydration of the active furanyl intermediates and olefin fragments [35,36]. Unsaturated ketones come from the pyrolysis of carbohydrates [37] and phenols have been observed already as a result of humins pyrolysis [38]. The presence of 5-methyl-2-furanone in both py-CG/MS profiles was probably arisen from levulinic acid moieties that were physically entrapped in humin clusters [39].

Wang et al. (2016) [34] investigated the analytical pyrolysis of humins that were derived from glucose dehydration in dilute sulfuric acid at high temperatures (600°C). A wide product distribution was observed including a range of benzofurans, phenols and reactive furan derivatives. Similar compounds were observed in the py-GC-MS analysis of both ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl humins but phenol and benzofuran derivatives were present in a much lower extent, meaning that the pathways of humins formation were the same but the use of lower temperatures and acid strengths in a biphasic system produced humins with a more characteristic furanic backbone.

#### Table 4

Humins were also characterized by mass spectrometry after alkaline hydrolysis. Van Zandvoort et al. (2015) [25] developed this approach to investigate the structure and chemical composition of highly recalcitrant humins that were produced by acid-catalysed dehydration of glucose. Alkaline

hydrolysis is important because humins that are hardly soluble in organic solvents can be solubilized completely after alkaline oligomerization [40].

The mass spectra of humins that were synthesized from glucose using ZnCl<sub>2</sub>/HCl in THF/NaCl<sub>aq</sub> showed a maximum m/z of 613 and 3 fragmentation signals of m/z of 475, 301 and 129. The first mass loss was equivalent to an m/z of 138 and the two subsequent mass losses corresponded to an m/z of 173. On the other hand, the mass spectra of humins derived from the AlCl<sub>3</sub>/HCl system showed a maximum m/z of 1240, which is twice bigger than that of ZnCl<sub>2</sub>/HCl. In addition, there were several fragments whose mass losses were around an m/z of 158. Based on these data, it is clear that a more acidic catalytic system such as AlCl<sub>3</sub>/HCl contributed more to condensation reactions than ZnCl<sub>2</sub>/HCl, leading to the formation of humins of higher molecular mass. Also, a much larger number of stable fragments were observed in the mass spectrum of AlCl<sub>3</sub>/HCl humins.

### 4. Conclusion

The combination of Lewis and Brønsted acids was a good way to improve the production of HMF from simple sugars such as glucose and sucrose. Also, the use of a biphasic system containing THF reduced the extent of undesirable side reactions. HMF production was enhanced when high temperatures (180 °C) and extraction/reaction solvent ratios (ES/RS) were used. The best HMF yields from glucose were 62.7 ± 0.7% for ZnCl<sub>2</sub>/HCl and 66.9 ± 1.5% for AICI<sub>3</sub>/HCI. For saccharinic matrices, ZnCI<sub>2</sub>/HCI performed better than AICI<sub>3</sub>/HCI. The best HMF yields from sucrose were 65.6 ± 0.4% for ZnCl<sub>2</sub>/HCl and 54.4 ± 1.4% for AlCl<sub>3</sub>/HCl. Good HMF yields were also obtained from sugarcane molasses and no matrix interference was observed in dehydration reactions, indicating that this feedstock has a great potential for HMF production. The analytical pyrolysis of both ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl humins revealed that they are formed mostly by furan derivatives, especially by 2-methylfuran. Also, the alkali oligomerization of AICI<sub>3</sub>/HCI humins produced m/z fragments twice as big as those derived from ZnCl<sub>2</sub>/HCl humins, showing that the catalyst with higher acid strength contributed to condensation reactions even in the presence of a suitable biphasic system.

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#### 6. References

[1] S. K. Maity, Renewable Sustainable Energy Rev. 43 (2015) 1427-1445.

[2] J. Liu, J. Basnayake, P.A. Jackson, X. Chen, J. Zhao, P. Zhao, L. Yang, Y. Bai, H. Xia, F. Zan, W. Qin, K. Yang, L. Yao, L. Zhao, J Zhu, P. Lakshmanan, X. Zhao, Y. Fan, Field Crop Res. 196 (2016) 418-425.

[3] D. (D. J.) Liu, E. Y-X. Chen, ACS Catal. 4 (2014) 1302-1310.

[4] P. Mäki-Arvela, E. Salminen, T. Riittonen, P. Virtanen, N. Kumar, J-P. Mikkola, Int. J. Chem. Eng. 2012 (2012) 1-10.

[5] S. Subbiah, S. P. Simeonov, J. M. S. S. Esperença, L. P. N. Rebelo, C. A.M. Afonso, Green Chem. 15 (2013) 2849-2853.

[6] S. Siankevich, G. Savoglidis, Z. Fei, G. Laurenczy, D. T.L. Alexander, N. Yan, P.J. Dyson, J. Catal. 2014, 315, 67-74.

[7] N. A. S. Ramli, N. A. S. Amin, Appl. Catal., B 163 (2015) 487-498.

[8] L. Hu, L. Lin, S. Liu, Ind. Eng. Chem. Res. 53 (2014) 9969-9978.

[9] G. A. Halliday, R. J. Young, V. V. Grushin, Org. Lett. 11 (2003) 2003-2005.

[10] H. Rasmussen, H. R. Sørensen, A. S. Mayer, Carbohydr. Res. 385 (2014) 45-57.

[11] R-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, Chem. Rev. 113 (2013) 1499–1597.

[12] J. B. Binder, R. T. Raines, J. Am. Chem. Soc. 131 (2009) 1979-1985.

[13] V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler, D. G. Vlachos, J. Am. Chem. Soc. 135 (2013) 3997-4006.

[14] B. Y. Yang, R. Montgomery, Carbohydr. Res. 280 (1996) 27-45.

[15] S. P. Teong, G. Yi, Y. Zhang, Green Chem. 16 (2014) 2015-2026.

[16] Y. Wang, C. M. Pedersen, T. Deng, Y. Qiao, X. Hou, Bioresour. Technol.143 (2013) 384-390.

[17] B. Saha, M. M. Abu-Omar, Green Chem. 16 (2014) 24-38.

[18] X. Zhang, B. B. Hewetson, N. S. Mosier, Energy Fuels 29 (2015) 2387-2393.

[19] F. N. D. C. Gomes, L. R. Pereira, N. F. P. Ribeiro, M. M. V. M. Souza, Braz.J. Chem. Eng. 32 (2015) 119-126.

[20] Y. Román-Leshkov, J. A. Dumesic, Top. Catal. 52 (2009) 52, 297-303.

[21] Y. Yang, C. Hu, M. M. Abu-Omar, Green Chem. 14 (2012) 509-513.

[22] Y. J. Pagán-Torres, T. Wang, J. M. R. Gallo, B. H. Shanks, J. A. Dumesic, ACS Catal. 2 (2012) 930-934.

[23] H. Ma, F. Wang, Y. Yu, L. Wang, X. Li, Ind. Eng. Chem. Res. 54 (2015) 2657-2666.

[24] A. Jain, A. M. Shore, S. C. Jonnalagadda, K. V. Ramanujachary, A. Mugweru, Appl. Catal., A 489 (2015) 72-76.

[25] I. van Zandvoort, E. R. H. van Eck, P. de Peinder, H. J. Heeres, P. C. A. Bruijnincx, B. M. Weckhuysen, ACS Sustainable Chem. Eng. 3 (2015) 533–543.

[26] Y. Yang, C. Hu, M. M. Abu-Omar, J. Mol. Catal. A: Chem. 376 (2013) 98-102.

[27] I. van Zandvoort, Y. Wang, C. B. Rasrendra, E. R. H. van Eck, P. C. A. Bruijnincx, H. J. Heeres, B. M. Weckhuysen, ChemSusChem 6 (2013) 1745-1758.

[28] F. Fringuelli, F. Pizzo, L. Vaccaro, J. Org. Chem. 66 (2001) 4719-4722.

[29] S. Wang, H. Lin, J. Chen, Y. Zhao, B. Ru, K. Qiu, J. Zhou, RSC Adv. 5 (2015) 84014-84021.

[30] C. P. Locas, V. A. Yaylayan, J. Agric. Food Chem. 56 (2008) 6717–6723.

[31] A. S. Amarasekara, L. D. Williams, C. C. Ebede, Carbohydr. Res. 343 (2008) 3021-3024.

[32] H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, Science 316 (2007) 1597-1600.

[33] M. Sharma, S. N. Patel, K. Lata, U. Singh, M. Krishania, R. S. Sangwan, S.P. Singh, Bioresour. Technol. 219 (2016) 311-318.

[34] S. Wang, H. Lin, Y. Zhao, J. Chen, J. Zhou, J. Anal. Appl. Pyrolysis 118 (2016) 259-266.

[35] Y. T. Cheng, G. W. Huber, ACS Catal. 1 (2011) 611-628.

[36] S. Vaitheeswaran, S. K. Green, P. Dauenhauer, S. M. Auerbach, ACS Catal. 3 (2013) 2012-2019.

[37] S. Wang, X. Guo, K. Wang, Z. Luo, J. Anal. Appl. Pyrolysis 91 (2011) 183-189.

[38] T. M. C. Hoang, E. R. H. van Eck, W. P. Bula, J. G. E. Gardeniers, L. Leffertsa, K. Seshan, Green Chem. 17 (2015) 959-972.

[39] N. Baccile, G. Laurent, F. Babonneau, F. Fayon, M-M. Titirici, M. Antonietti,J. Phys. Chem. C 113 (2009) 9644–9654.

[40] G. Tsilomelekis, M. J. Orella, Z. Lin, Z. Cheng, W. Zheng, V. Nikolakis, D.G. Vlachos, Green Chem. 18 (2016) 1983-1993.

### **Figure Captions**

**Fig. 1.** Comparative study involving the use of Lewis and Brønsted acids in glucose dehydration. Reactions were carried out in THF/NaCl<sub>aq</sub> at 180 °C for 60 min using 0.75 mmol glucose with aqueous HCl pH 1.9 (0.3 mmol or 25  $\mu$ L HCl<sub>aq</sub> 37%) and 0.98 (3.6 mmol or 300  $\mu$ L HCl<sub>aq</sub> 37%) as well as with 0.3 mmol ZnCl<sub>2</sub> (0.043 g) or AlCl<sub>3</sub> (0.073 g) with and without 0.3 mmol HCl.

**Fig. 2.** Glucose dehydration profiles for (A)  $ZnCl_2/HCI$  (B) AlCl<sub>3</sub>/HCI in THF/NaCl<sub>aq</sub>. Reactions were carried out at 180 °C employing 0.75 mmol glucose plus 0.3 mmol ZnCl<sub>2</sub> (0.043 g) or AlCl<sub>3</sub> (0.073 g) containing 0.3 mmol HCl (or 25 µL HCl<sub>aq</sub> 37%).

**Fig. 3.** HMF production from sugarcane molasses and their main carbohydrate components using ZnCl<sub>2</sub>/HCl (0.029 g ZnCl<sub>2</sub> plus 15  $\mu$ L HCl<sub>aq</sub> 37%) and AlCl<sub>3</sub>/HCl (0.024 g AlCl<sub>3</sub> and 10  $\mu$ L HCl<sub>aq</sub> 37%) in THF/NaCl<sub>aq</sub>. Reactions were carried out at 180 °C for 60 (ZnCl<sub>2</sub>/HCl) and 55 min (AlCl<sub>3</sub>/HCl) using (A) sucrose (0.257 g); (B) glucose and fructose (0.135 g each); (C) cane molasses (0.150 g) and (D) synthetic media containing sucrose (0.094 g), glucose (0.013 g) and fructose (0.006 g).

**Fig. 4.** Py-GC-MS analysis of humins that were derived from glucose using (A)  $ZnCl_2/HCl$  and (B)  $AlCl_3/HCl$  in a THF/NaCl<sub>aq</sub> biphasic system. Reactions were carried out at 180 °C for 60 min using 0.75 mmol glucose plus 0.3 mmol  $ZnCl_2$  (0.043 g) or  $AlCl_3$  (0.073 g) containing 0.3 mmol HCl (or 25 µL HCl<sub>aq</sub> 37%).

**Scheme 1.** Formation of the fructofuranosyl cation from sucrose followed by its conversion to HMF.



Fig. 1.







Fig. 3.



Fig. 4.



Scheme 1.

Entry <sup>a</sup>	T (°C)	ES/RS⁵	Conversion	Yield (mol %)		Solid
			(mol %)	Fructose	HMF	residue (wt %)
1	140	5	73.3	11.9	2.4	12.5
2	140	10	70.4	9.0	8.5	10.7
3	160	7.5	85.2	1.5	18.9	20.1
4	160	7.5	79.3	5.9	21.0	16.1
5	180	5	100	nd <sup>c</sup>	33.1	36.4
6	180	10	100	nd	48.8	33.7

 Table 1. Influence of temperature and solvent ratio in glucose dehydration using

 ZnCl<sub>2</sub>/HCl as the reaction catalyst in a THF/NaCl<sub>aq</sub> biphasic system.

<sup>[a]</sup>Reactions were carried for 60 min in the THF/NaCl<sub>aq</sub> biphasic system using 0.75 mmol glucose (0.135 g) plus 0.3 mmol ZnCl<sub>2</sub> (0.043 g) containing 0.3 mmol HCl (or 25  $\mu$ L HCl<sub>aq</sub> 37%);<sup>[b]</sup>ES/RS= extraction solvent/reaction solvent; <sup>[c]</sup> nd = not detected.

Compounds	Biphasic system <sup>[a,c]</sup>		Aqueous	Aqueous system <sup>[b,c]</sup>		
(mol%)	ZnCl <sub>2</sub> /HCl	AICI <sub>3</sub> /HCI	ZnCl <sub>2</sub> /HCl	AICI <sub>3</sub> /HCI		
HMF	48.8 ± 0.9	54.3 ± 1.0	$0.26 \pm 0.02$	0.06 ± 0.01		
Levulinic acid	nd <sup>[d]</sup>	nd	46.8 ± 0.7	41.1 ± 0.1		
Formic acid	nd	nd	$40.4 \pm 0.2$	$36.0 \pm 0.8$		

**Table 2.** Comparative study of glucose dehydration using both ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl catalyst in biphasic and aqueous systems.

<sup>[a]</sup> Binary system composed of THF and NaCl<sub>aq</sub> (30 mL THF plus 1.05 g NaCl in 3 mL H<sub>2</sub>O) plus 0.75 mmol glucose and the indicated amount of catalyst;

<sup>[b]</sup> Aqueous system containing water (30 mL) plus 0.75 mmol glucose and the indicated amount of catalyst;

<sup>[c]</sup> Reactions were carried at 180 °C using 0.3 mmol ZnCl<sub>2</sub> (0.043 g) or AlCl<sub>3</sub> (0.073 g) containing 0.3 mmol HCl (or 25  $\mu$ L HCl<sub>aq</sub> 37%); the reaction time was 60 min for ZnCl<sub>2</sub>/HCl and 55 min for AlCl<sub>3</sub>/HCl;

<sup>[d]</sup> nd, not detected

Entry <sup>a</sup>	Catalyst loading <sup>b</sup>	Catalyst loading <sup>b</sup> HMF/glucose HMF/sucros		ъH	
	(mmol)	(mol %)	(mol (%)	рп	
		ZnCl <sub>2</sub> /HCl			
1	0.1 (13 mol%)	$59.6 \pm 0.2$	$60.6 \pm 0.6$	$1.43 \pm 0.04$	
2	0.2 (27 mol%)	$62.7 \pm 0.7$	$65.6 \pm 0.4$	$1.36 \pm 0.05$	
3	0.3 (40 mol%)	$48.8 \pm 0.9$	$60.0 \pm 0.7$	$1.18 \pm 0.04$	
		AICI <sub>3</sub> /HCI			
4	0.1 (13 mol%)	$64.6 \pm 0.4$	54.4±1.4	$1.40 \pm 0.06$	
5	0.2 (27 mol%)	66.9 ± 1.5	$48.6 \pm 0.3$	$1.12 \pm 0.04$	
6	0.3 (40 mol%)	54.3 ± 1.0	$49.6 \pm 0.4$	$0.98 \pm 0.04$	

 Table 3. Influence of different catalyst loadings in both glucose and sucrose

 dehydration using ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl in a THF/NaCl<sub>aq</sub> biphasic system.

<sup>[a]</sup> Reactions were carried for 60 min in the THF/NaCl<sub>aq</sub> biphasic system using 0.75 mmol glucose (0.135 g) or sucrose (0.257 g) plus the indicated amount of catalyst; the reaction time was 60 min for ZnCl<sub>2</sub>/HCl and 55 min for AlCl<sub>3</sub>/HCl;

<sup>[b]</sup> 0.1 mmol: 0.014 ZnCl<sub>2</sub> or 0.024 g AlCl<sub>3</sub> with 10  $\mu$ L HCl<sub>aq</sub> 37%; 0.2 mmol: 0.029 ZnCl<sub>2</sub> or 0.049 g AlCl<sub>3</sub> with 15  $\mu$ L HCl<sub>aq</sub> 37%; 0.3 mmol: 0.043 ZnCl<sub>2</sub> or 0.072 g AlCl<sub>3</sub> with 25  $\mu$ L HCl<sub>aq</sub> 37%.

#	Compound	m/z	Area (%)		
		111/2	ZnCl <sub>2</sub> /HCl	AICI <sub>3</sub> /HCI	
1	furan	68	8.6	8.0	
2	2-methylfuran	53; 82	24.7	21.0	
3	2,5-dimethylfuran	96	12.1	10.3	
4	5-methyl-2-ethylfuran	95; 110	2.1	2.5	
5	unidentified alkyllfuran	95	9.5	12.4	
6	2-allylfuran	79; 108	0.82	1.7	
7	5-methyl-2-furanone	55; 98	9.10	7.6	
8	2-cyclohexen-1-one	68; 96	3.5	3.8	
9	2-acetylfuran	95; 110	11.9	11.6	
10	allylacetone	55; 98	3.2	3.6	
11	3-methyl-2-cycloexen-1-one	110	0.83	1.1	
12	5-methylfurfural	110	7.4	6.4	
13	5-methyl-2-acetylfuran	109; 124	1.8	3.3	
14	m-cresol	108	0.93	1.4	
15	7-methylbenzofuran	132	nd	1.1	
16	2-methylbenzofuran	132	1.5	1.2	
17	3-(cycloexen-1-yl)-furan	148	nd	0.85	
18	4,7-dimethylbenzofuran	146	0.94	2.1	
19	2,4-di-tert-butylphenol	191	1.1	nd	

### Table 4. Py-GC/MS analyses of ZnCl<sub>2</sub>/HCl and AlCl<sub>3</sub>/HCl humins

<sup>[a]</sup> nd, not detected