

Production of Furan Compounds from Sugarcane Bagasse Using a Catalytic System Containing $ZnCl_2/HCl$ or $AlCl_3/HCl$ in a Biphasic System

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In this work, two catalytic systems combining Lewis and Brønsted acids ($ZnCl_2/HCl$ and $AlCl_3/HCl$) were applied in a tetrahydrofuran (THF)/ $NaCl_{aq}$ biphasic system to produce furan compounds from plant polysaccharides. The following cellulosic matrices were applied for this purpose: α -cellulose, microcrystalline cellulose and both native and steam-exploded sugarcane bagasse. The $AlCl_3/HCl$ catalytic system afforded the best yields for α -cellulose conversion to furan compounds (hydrolysis followed by dehydration). The highest yields of 5-(hydroxymethyl)-furfural (HMF) and furfural were 44.0 and 92.2% for $AlCl_3/HCl$ and 36.5 and 81.4% for $ZnCl_2/HCl$, respectively. Cellulosic materials with lower crystallinity indexes afforded the best performance in hydrolysis followed by dehydration, giving relatively high yields of HMF and furfural. The HMF yields were similar for both native and steam-exploded sugarcane bagasse and the presence of lignin had a negative effect on HMF production. The highest furfural yield from native sugarcane bagasse was 60.6% with $AlCl_3/HCl$ catalytic system.

Keywords: acid-catalyzed dehydration, furans, cellulose, sugarcane bagasse, crystallinity

Introduction

The integral use of renewable feedstocks for fuels and chemicals is key for the development of sustainable biorefineries. 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. In another definition, the American National Renewable Energy Laboratory (NREL) describes biorefinery as a facility that integrates equipment and processes for biomass conversion into fuels, energy and chemicals for industry.^{1,2}

Sugarcane bagasse is an important agro-industrial byproduct for biorefining because large amounts are readily available at low cost in sugarcane-processing industrial facilities such as autonomous distilleries and sugar mills.³ Sugarcane bagasse is majorly composed of glucans (mostly cellulose), hemicelluloses (mostly xylans) and lignin and these macromolecular components are involved in a strong chemical association that reduces its accessibility to chemical conversion.⁴ Different forms of pretreatment can break this

strong association and increase the chemical accessibility of cane bagasse polysaccharides. One of most interesting pretreatment technique is steam explosion, which combines chemical and physical processes to deconstruct the plant cell wall associative structure.^{5,6} For this, the biomass is treated with saturated steam at temperatures between 170-230 °C for 2 to 30 min in the absence or presence of an exogenous catalyst.⁷ The main feature of steam explosion is the total or partial acid hydrolysis of hemicelluloses to produce mono and oligosaccharides, which are intermediate chemicals for a variety of value-added products. In addition, changes in the lignin structure occur primarily due to the acid hydrolysis of aryl-ether linkages, while both xylan and glucan degree of polymerization is decreased with changes imparted to the substrate crystallinity index as well. In general, these effects improve the accessibility of plant polysaccharides to chemical conversion including enzymatic hydrolysis to fermentable sugars.^{6,8}

Sugarcane bagasse polysaccharides can be converted to 5-(hydroxymethyl)-furfural (HMF) and furfural and these furan compounds are included in the top 10 list of the most valuable biobased products from the carbohydrate biorefining platform.⁹ HMF and furfural derivatives have the potential to replace petroleum-based chemicals and

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building blocks, offering more sustainable routes to produce polymers, fuels and fine chemicals.¹⁰

HMF production from glucans can be described in three main steps: the acid hydrolysis of β -(1-4)glycosidic linkages to produce glucose, followed by α -hydroxy-carbonyl isomerization to produce fructose that can be readily converted to HMF through a series of dehydration reactions.¹¹ In this sense, a Lewis acid mediated isomerization followed by dehydration in the presence of a Brønsted acid was described as the best choice to achieve good HMF yields.^{12,13} As the monomeric substituents in hemicelluloses include both hexoses and pentoses, hemicelluloses may also give rise to HMF. By contrast, pentoses exclusively produce furfural and the mechanism comprises a Lewis acid mediated isomerization to xylulose which is further dehydrated to furfural.¹¹

Higher product selectivity and yields can be achieved by applying biphasic systems to the dehydration of carbohydrate to furfural and HMF.^{5,14-16} These systems avoid the main side-reactions in dehydration, such as rehydration to produce levulinic and formic acids and condensation of furan derivatives to produce a dark insoluble solid residue called humins.^{17,18} The best choice for the production of furan compounds is the use of a biphasic system that is formed by an aqueous phase (reaction solvent) and an organic phase (extraction solvent).¹⁹ This system must have a high partition coefficient for furan compounds and, in case of water miscible solvents such as THF, it is necessary to add an electrolyte to induce phase separation.²⁰

In our previous work, a THF/ NaCl_{aq} biphasic system was applied in the catalytic dehydration of water-soluble carbohydrates using a combination of Lewis and Brønsted acids.²¹ AlCl_3/HCl was best for glucose dehydration while ZnCl_2/HCl gave higher HMF yields from sucrose and sugarcane molasses. Compared to synthetic mixtures containing the same amount of sugars, no matrix interference was observed during dehydration of sugarcane molasses. Given its potential advantages, the THF/ NaCl_{aq} biphasic system was used in this work to produce HMF and furfural from different cellulosic materials, employing ZnCl_2/HCl and AlCl_3/HCl to provide a catalytic active mixture of Lewis and Brønsted acids. Microcrystalline cellulose (Avicel PH-101), α -cellulose, Wiley-milled sugarcane bagasse and a steam-exploded material derived from it were employed in these dehydration studies.

Experimental

Materials

Sugarcane bagasse was provided by the São Manuel mill. Steam-exploded bagasse was obtained in our research

group using reaction conditions that were pre-optimized for optimal sugar yields and glucan accessibility to enzymatic hydrolysis.^{7,22} HCl_{aq} 37% was purchased from Vetec, α -cellulose (Catalog #C8002, batch BCBF5683V) and AlCl_3 (99%) from Sigma-Aldrich, ZnCl_2 (96%) and acetic acid (99.7%) from Inpex, NaCl (99.7%) from Neon, and Avicel PH-101 from Blanver. THF, acetonitrile and H_2SO_4 , all in HPLC grade, were obtained from Tedia.

Hydrolysis and dehydration in a biphasic system

Experiments were performed in a Büchi Glas Uster miniclave drive stainless steel reactor that was equipped with mechanical stirring and both temperature and pressure controls. The operating pressure corresponded to the vapor pressure of the solvents used in the reaction environment and all experiments were carried out with 0.150 g of the cellulosic materials. Reactions were carried out with Avicel PH-101, α -cellulose, sugarcane bagasse and steam-exploded sugarcane bagasse (195 °C, 7.5 min) at 180 °C with an extraction/reaction solvent ratio of 10:1 (3 mL of deionized water and 30 mL of THF). The total amount of NaCl required to form a biphasic system was 1.05 g and mechanical stirring was set at 1500 rpm.²¹ The sugarcane bagasse samples were Wiley-milled to pass a 40-mesh screen. Kinetics of α -cellulose dehydration was profiled in both catalytic systems (ZnCl_2/HCl and AlCl_3/HCl) and this was done by withdrawing reaction aliquots at every 15 min for ZnCl_2/HCl and 5 min for AlCl_3/HCl . After the reaction, aliquots from both reaction (aqueous) and extraction (THF) phases were analysed by high performance liquid chromatography (HPLC) as described below.

HMF and furfural yields were expressed in relation to their theoretical yields (molar basis), which are based on the stoichiometric amounts of furan compounds that could have been produced from the total carbohydrate content of the reaction medium. Equations 1 and 2 show the calculation for glucans and xylans, respectively, where 0.90 and 0.88 represent the incorporation of one water molecule for each glycosidic linkage broken by acid hydrolysis while 0.70 and 0.64 are the conversion factors for glucose and xylose conversions to HMF and furfural, respectively. Mass (m) yields ($\text{g } 100 \text{ g}^{-1}$ dry matter) were also reported to reveal the amount of furan compounds that was obtained from a given amount of dry biomass.

$$\text{HMF}(\%) = \frac{\text{HMF}_{\text{experimental}}(\text{g})}{\{[\text{m}_{\text{initial}}(\text{g}) \times \text{glucan}(\%)] / 0.9\} \times 0.70} \times 100 \quad (1)$$

$$\text{F}(\%) = \frac{\text{F}_{\text{experimental}}(\text{g})}{\{[\text{m}_{\text{initial}}(\text{g}) \times \text{xylan}(\%)] / 0.88\} \times 0.64} \times 100 \quad (2)$$

Lignocellulose chemical composition analysis

Moisture content determinations were carried out in triplicate using a Shimadzu MOC63u moisture analyzer. The total extractives content was determined after two consecutive extractions in a Soxhlet apparatus, the first using water and the second using ethanol according to the NREL/TP-510-42619 method.²³ Total lignin and carbohydrate contents were determined according to the NREL/TP-510-42618 method,²⁴ in which acid-insoluble lignin is determined gravimetrically and acid-soluble lignin is quantified by UV spectrophotometry at 240 nm. Carbohydrates were quantified by HPLC as described below.

Chromatographic analysis

Carbohydrate and organic acid analyses were carried out in a Shimadzu LC-20AD HPLC workstation equipped with a SIL-10AF autosampler and two detection systems: differential refractometry (Shimadzu RID-10A) and diode array detector for UV spectrophotometry (Shimadzu SPD-M10AVP). The chromatographic column was an Hi-Plex-H (Agilent, 300 × 7.7 mm; 8 mm) that was operated at 65 °C using H₂SO₄ 5 mmol L⁻¹ as mobile phase in a flow rate of 0.6 mL min⁻¹. HMF and furfural were analyzed in a Metrohm 882 Compact IC Plus liquid chromatograph that was equipped with a Metrohm 863 autosampler and a Metrohm 887 Professional UV detector. The chromatographic column was a Kinetex 5 μm EVO C18 100 Å (Phenomenex, 150 × 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⁻¹. In both chromatographic systems, quantification was performed by external calibration using standards in the following concentration range: 0.08 to 0.8 g L⁻¹ for cellobiose; 0.2 to 2.0 g L⁻¹ for glucose; 0.1 to 1.0 g L⁻¹ for xylose; 0.08 to 0.8 g L⁻¹ for arabinose; 0.12 to 1.2 g L⁻¹ for formic acid; 0.1 to 1.0 g L⁻¹ for acetic acid and 0.2 to 2.0 mg L⁻¹ for HMF and furfural.

X-ray diffractometry (XRD)

XRD analysis was carried out in a Shimadzu XRD-7000 diffractometer. The device contained a radiation generator tube operating with the copper Kα line (λ of 0.1542 nm) at 40 kV and 30 mA. Analyses were carried out in a 2θ range of 5 to 50° at 2° min⁻¹. From the XRD profiles, crystallinity indexes (CrI) of cellulosic materials were calculated by equation 3, in which I₀₀₂ is the intensity of 002 diffraction plan at 22.5° of 2θ and I_{am} is the intensity of amorphous region at 18.5° of 2θ.²⁵

$$\text{CrI} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100 \quad (3)$$

Results and Discussion

Production of HMF was initially performed with a commercially available α-cellulose that contained 81.4% glucans and 18.1% hemicelluloses (mostly xylans) in its chemical composition. For making the biphasic system, THF was chosen as the extraction solvent due to its high partition coefficient (up to 7) for furan compounds.²⁰ However, since THF is partially miscible in water, NaCl was added (35 wt.%) as a simple electrolyte to induce the formation of a biphasic system.²⁰ In the first attempts, a comparative study between both catalytic systems (ZnCl₂/HCl and AlCl₃/HCl) was carried out together with a reaction control for the thermal conversion of α-cellulose to furan compounds (Figure 1). The catalytic systems contained 0.3 mmol of each acid (ZnCl₂ or AlCl₃ and HCl) and the reaction was carried out at 180 °C for a total reaction time of 1 h. The presence of monosaccharides and organic acids in the reaction solvent (aqueous phase) was never observed and this was consistent with our previous work with sucrose and cane molasses, in which carbohydrates were totally consumed at temperatures of 180 °C.²¹ By contrast, HMF and furfural were measured in the extraction solvent (THF) and their corresponding molar yields from glucans (equation 1) and xylans (equation 2) were determined in the extraction solvent (THF), respectively.

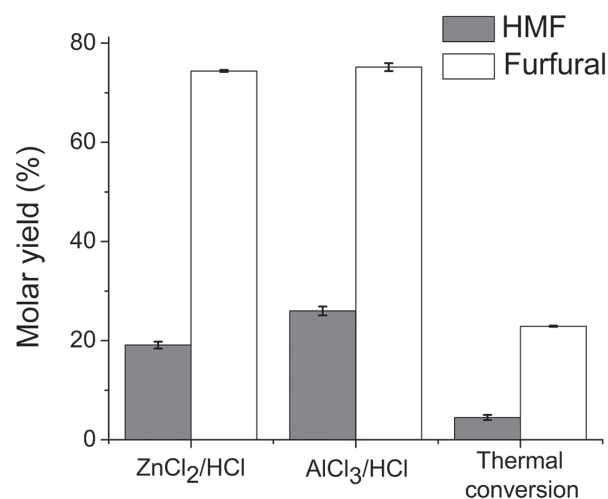


Figure 1. Comparison of the catalytic and thermal conversions of α-cellulose into HMF and furfural after 1 h at 180 °C.

Furfural yields were similar in both catalytic systems (up to 70%) and this was attributed to the easier hydrolysis of hemicelluloses compared to glucans such as cellulose, releasing xylose and arabinose that could be easily

dehydrated under these reaction conditions.²⁶ Also, the rate of xylose dehydration is faster than that of glucose in complex saccharide solutions using homogeneous catalysts, leading to the rapid formation of furfural and the achievement of high reaction yields.^{27,28} It is well known that the Lewis acids catalyze xylose isomerization to xylulose through a 1,2-hydrate shift (or enediol mechanism), which is a key step in the furfural formation from xylose.^{27,29} Likewise, the production of HMF from glucose follows a similar mechanism in the presence of Lewis acids.

The α -cellulose provided lower HMF yields compared to the corresponding furfural yields from its hemicellulose component ($19.1 \pm 0.7\%$ for ZnCl_2/HCl and $26.0 \pm 0.9\%$ for AlCl_3/HCl). The AlCl_3/HCl system afforded a slightly better performance for HMF production since this catalytic system is composed of two strong acids that facilitate both acid hydrolysis and dehydration. In order to obtain an efficient chemical conversion from cellulose, the acid catalyst must be strong enough to disrupt the intricate network of intermolecular interactions and promote hydrolysis.³⁰ In addition, the thermal conversion of α -cellulose provided lower yields of furan compounds ($4.5 \pm 0.5\%$ of HMF and $22.9 \pm 0.1\%$ of furfural) compared to both catalytic systems. Hence, the advantages of using ZnCl_2/HCl and AlCl_3/HCl for carbohydrate dehydration was characterized within the experimental conditions used in this work.

The effect of reaction time on HMF molar yields from α -cellulose was evaluated at 180°C (Figure 2). The best HMF yields were reached in 55 and 90 min for ZnCl_2/HCl and AlCl_3/HCl , respectively. The HMF yields started to decrease at longer reaction times for both catalytic systems probably due to side reactions such as condensation to form water insoluble humins.^{21,31} These undesirable side reactions took more time to occur in the ZnCl_2/HCl system

due to its lower acidic character, which slowed cellulose hydrolysis and decreased the availability of glucose for isomerization and dehydration to produce HMF.

The effect of the catalyst loading was also assessed to select the optimal reaction conditions for both catalytic systems (Table 1). Four different catalyst loadings were evaluated for each combination of AlCl_3/HCl and ZnCl_2/HCl using the same molar number of Lewis and Brønsted acids in the reaction medium.

The highest HMF yields were $36.5 \pm 0.7\%$ for ZnCl_2/HCl (entry 3) applying 0.3 mmol of catalyst and $44.0 \pm 0.1\%$ for AlCl_3/HCl applying 0.2 mmol of catalyst (entry 6). Hence, each catalytic system resulted in a

Table 1. Influence of catalyst loading in α -cellulose hydrolysis and dehydration using the $\text{THF}/\text{NaCl}_{\text{aq}}$ biphasic system at 180°C

entry	Catalyst loading / mmol	ZnCl_2/HCl		
		HMF / mol%	Furfural / mol%	pH
1	0.1	23.0 ± 0.8	58.3 ± 0.6	1.43 ± 0.04
2	0.2	26.2 ± 0.4	63.4 ± 1.7	1.36 ± 0.05
3	0.3	36.5 ± 0.7	81.4 ± 0.1	1.18 ± 0.04
4	0.5	36.5 ± 1.5	70.1 ± 0.1	0.95 ± 0.04
entry	Catalyst loading / mmol	AlCl_3/HCl		
		HMF / mol%	Furfural / mol%	pH
5	0.1	29.8 ± 1.0	61.3 ± 0.3	1.40 ± 0.06
6	0.2	44.0 ± 0.1	67.2 ± 1.7	1.12 ± 0.04
7	0.3	42.0 ± 1.0	92.2 ± 1.3	0.98 ± 0.04
8	0.5	25.4 ± 0.8	71.1 ± 1.1	0.83 ± 0.07

Conditions: 90 min for ZnCl_2/HCl and 55 min for AlCl_3/HCl ; 0.1 mmol: 0.014 g ZnCl_2 or 0.024 g AlCl_3 with 10 μL HCl_{aq} 37%; 0.2 mmol: 0.029 g ZnCl_2 or 0.049 g AlCl_3 with 15 μL HCl_{aq} 37%; 0.3 mmol: 0.043 g ZnCl_2 or 0.072 g AlCl_3 with 25 μL HCl_{aq} 37%; 0.5 mmol: 0.072 g ZnCl_2 or 0.122 g AlCl_3 with 42 μL HCl_{aq} 37%.

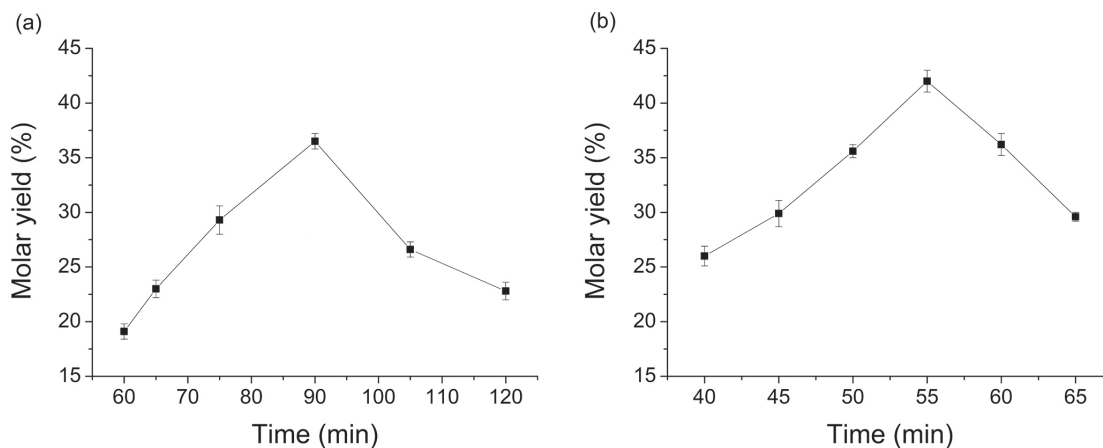


Figure 2. α -Cellulose hydrolysis and dehydration in $\text{THF}/\text{NaCl}_{\text{aq}}$ at 180°C using 0.3 mmol of each of the acids present in the following catalytic systems: (a) ZnCl_2/HCl and (b) AlCl_3/HCl .

different dehydration profile. The ZnCl_2/HCl has a linear behavior in the range of 0.1 to 0.3 mmol of catalyst and, after that, HMF yields were stabilized at 36.5%. On the other hand, when the AlCl_3/HCl system was used, the HMF yields peaked at 0.2 mmol of catalyst and decreased after that due to the apparent predominance of side reactions including oligomerization to humins, as evident from the reaction mixtures turning yellow to brown after a prolonged reaction time due to retro aldol reactions that are involved in sugar degradation (entries 7 and 8). Furfural production from the hemicellulose fraction of α -cellulose had similar dehydration profiles in both catalytic systems, with the highest yields being achieved with 0.3 mmol of catalyst resulting in $81.4 \pm 0.1\%$ for ZnCl_2/HCl and $92.2 \pm 1.3\%$ for AlCl_3/HCl (entries 3 and 7). The high furfural yields observed in Table 1 are related to the higher susceptibility of hemicelluloses to acid hydrolysis and dehydration compared to glucans.

Additionally, pH measurements of the catalytic solutions were carried out to evaluate their correlation with yields of furan compounds. The highest HMF yields were achieved in pH around 1.1 (entry 3 and 6). HMF productions using 0.2 and 0.3 mmol of AlCl_3/HCl were similar ($44.0 \pm 0.1\%$ and $42.0 \pm 1.0\%$, respectively) and this was related to the similar pH values that were reached in both of these catalyst loadings (entry 6 and 7). In pH values lower than 1.0, HMF production drastically decreased in the AlCl_3/HCl system (entry 8). For furfural production, the highest yields were achieved in a pH range of 1.2 to 1.0 for both catalysts but under pH values below 1.0 (entries 4, 7 and 8), the furfural yields started to decrease particularly for AlCl_3/HCl , in which a furfural loss of 20.1% was observed when the pH was changed from 0.98 to 0.83.

In order to investigate the effect of crystallinity on reaction yields, experiments with microcrystalline cellulose (Avicel PH-101) were carried out and compared with α -cellulose as shown in Table 2. HMF yields from Avicel PH-101 were $8.3 \pm 0.4\%$ and $25.0 \pm 0.4\%$ using ZnCl_2/HCl and AlCl_3/HCl , respectively, which were considerably lower than those derived from α -cellulose. Hence, cellulose crystallinity acted as a supramolecular barrier for hydrolysis and dehydration.^{32,33} On the basis of the XRD profiles, the CrI of Avicel PH-101 was 84.4%, which is similar to the value reported by Ju *et al.*³⁴ Avicel PH-101 has a degree of polymerization of 300 anhydroglucose units and this makes the interactions between cellulose chains stronger, resulting in highly organized cellulose crystallites.³⁵ The CrI for α -cellulose was 61.2%, a value much lower than that of Avicel PH-101. α -Cellulose derives from kraft pulping followed by chlorine bleaching and this process affects cellulose crystallinity, making it more

susceptible to chemical conversion. Therefore, the lower crystallinity indexes led to higher HMF yields.

Table 2. Crystallinity indexes of different cellulosic matrices and their corresponding HMF molar yields using ZnCl_2/HCl and AlCl_3/HCl in THF/ NaCl_{aq} at 180 °C

Cellulosic matrix	CrI / %	HMF yield / mol%	
		ZnCl_2/HCl	AlCl_3/HCl
Avicel PH-101	84.4	8.3 ± 0.4	25.0 ± 0.4
α -Cellulose	61.1	36.5 ± 0.7	44.0 ± 0.1

Conditions: 90 min for ZnCl_2/HCl and 55 min for AlCl_3/HCl . CrI: crystallinity indexes.

Yang *et al.*³⁶ studied cotton cellulose dehydration using superacid solid catalysts composed by $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$, in which the mixed oxides contained tin, aluminum and zirconium.³⁶ The authors achieved HMF yields in range of 3 to 11% at 190 °C, which was lower than the HMF yields obtained in this work in both catalytic systems. Nandiwale *et al.*³⁷ studied microcrystalline cellulose dehydration using bimodal-HZ-5 as catalyst at 190 °C for 4 h and achieved 46% HMF yields. However, the catalyst amount used in this work was extremely high, reaching 200% in relation to the amount of carbohydrate used for conversion. Therefore, it seems that the catalytic systems combining Lewis and Brønsted acids in a biphasic system could be the best choice for milder HMF production from cellulose matrices of relatively high crystallinity indexes.

For sugarcane bagasse dehydration, two different materials were applied, Wiley-milled native bagasse and steam-exploded samples that were prepared without the addition of an exogenous catalyst (auto-hydrolysis). The chemical composition of these cellulosic materials is given in Table 3.

The AlCl_3/HCl catalytic system gave higher yields in both types of cane bagasse samples (Figure 3) but these

Table 3. Chemical composition of native and steam-exploded sugarcane bagasse in dry basis

Component	Native / wt.%	Steam-exploded / wt.%
Anhydroglucose	40.15 ± 0.69	59.73 ± 0.42
Anhydroxylose	21.99 ± 0.41	3.59 ± 0.07
Anhydroarabinose	1.66 ± 0.03	nd ^a
Acetyl group	3.27 ± 0.08	nd
Total lignin	23.01 ± 0.70	33.48 ± 0.23
acid-soluble lignin	0.06 ± 0.01	0.04 ± 0.01
acid-insoluble lignin	22.94 ± 0.69	33.44 ± 0.23
Extractives	5.21 ± 0.09	nd

^aComponent present in undetectable levels (nd: not detected).

yields were lower compared to α -cellulose. As presented in Table 3, both lignocellulosic materials have a high amount of lignin in their chemical composition and this may have acted as a macromolecular barrier for hydrolysis and dehydration. In general, the catalyst can chemically interact with lignin making it unavailable to the catalytic conversion of cane bagasse polysaccharides.

HMF yields from both types of cane bagasse had similar performances for both catalytic systems (around 9.0% for ZnCl_2/HCl and 26.5% for AlCl_3/HCl) when the chemical composition of each material was considered in the calculation of reaction yields (Figure 3). It was originally hypothesized that hemicellulose hydrolysis and cell wall deconstruction by steam explosion would facilitate the catalytic conversion of glucans and improve the HMF yields. However, this favorable effect was not observed.

For furfural production, native bagasse gave lower yields compared to α -cellulose and this was attributed once again to the presence of lignin. However, relatively good furfural yields of $60.6 \pm 1.2\%$ were achieved from native bagasse using AlCl_3/HCl . By contrast, furfural yields from steam-exploded bagasse were stoichiometric for both catalytic systems, therefore revealing the beneficial effect of pretreatment on hemicellulose conversion, which includes deacetylation, partial hydrolysis and swelling from their tight association with cellulose and lignin in the original material.⁴⁻⁷

In terms of mass yields, α -cellulose was the cellulosic matrix that produced more furan compounds, which corresponded to 33.1% for ZnCl_2/HCl and 38.3% for AlCl_3/HCl (Figure 4). These higher mass yields were related to the low crystallinity and absence of lignin in this

cellulosic material. Surprisingly, native bagasse gave higher mass yields of furan compounds (12.1% for ZnCl_2/HCl and 19.8% for AlCl_3/HCl) compared to steam-exploded bagasse (6.7% for ZnCl_2/HCl and 14.8% for AlCl_3/HCl), whose hemicellulose content was low as well as its contribution to the overall mass yield of furan compounds. However, glucan conversion after pretreatment was lower and this was readily associated with the shielding effect of lignin on hydrolysis, resulting in lower amounts of glucose for its subsequent dehydration to HMF.

Yang *et al.*³⁸ studied the hydrolysis and dehydration of different lignocellulosic materials using AlCl_3 as catalyst in a THF/ NaCl_{aq} biphasic system. At 180 °C for 30 min under microwave irradiation, the authors achieved HMF yields in the range of 20 to 35% and furfural yields between 51 to 66%. These yields were similar to those obtained with AlCl_3/HCl in this work. Iryami *et al.*³⁹ studied sugarcane bagasse hydrolysis and dehydration using a hydrothermal pretreatment at high temperatures. HMF yields of 3.09% were achieved at 270 °C for 10 min, which was much lower than the results obtained in this work for both catalytic systems using a milder reaction temperature of 180 °C.

Conclusions

The production of HMF and furfural from plant polysaccharides was demonstrated using ZnCl_2/HCl and AlCl_3/HCl in a THF/ NaCl_{aq} biphasic system. AlCl_3/HCl had the best catalytic performance for all cellulosic matrices used in this study. The crystallinity acted as supramolecular barrier for polysaccharide hydrolysis and dehydration while the presence of lignin was detrimental to the chemical

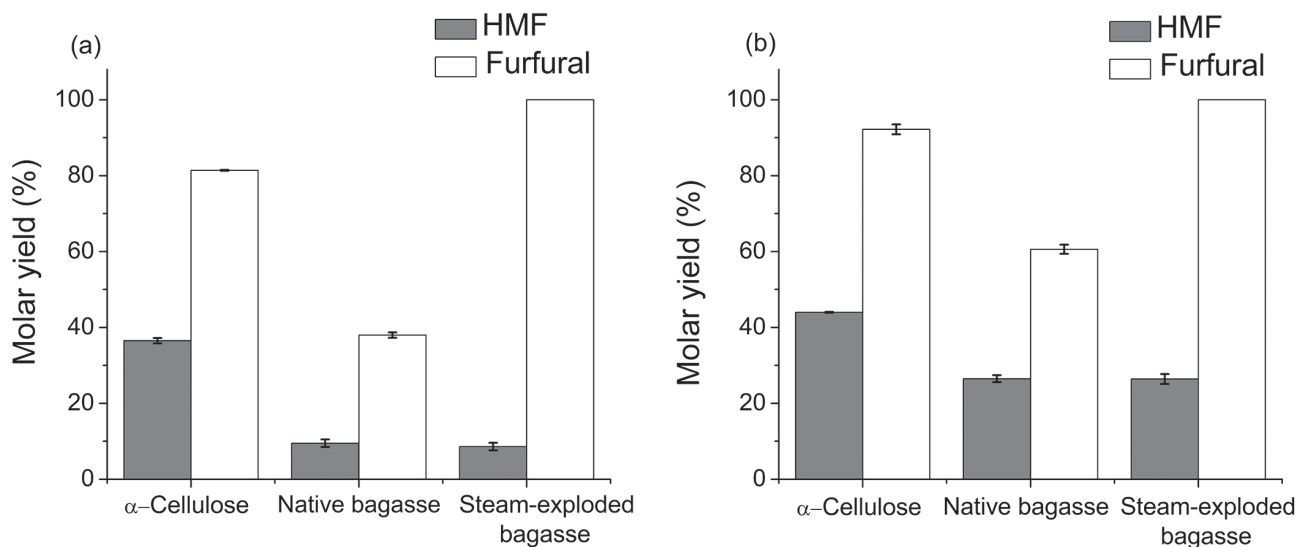


Figure 3. Molar yields of furan compounds from different cellulosic matrices using (a) ZnCl_2/HCl and (b) AlCl_3/HCl in THF/ NaCl_{aq} at 180 °C for 90 and 55 min, respectively.

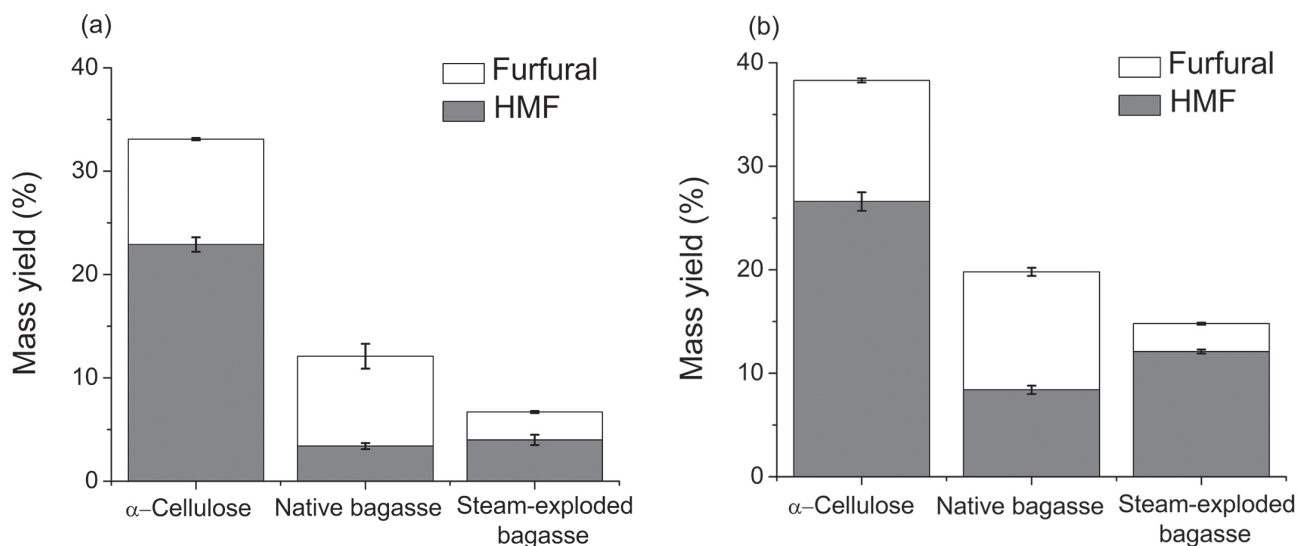


Figure 4. Mass yields of furan compounds from different cellulosic materials using (a) ZnCl₂/HCl and (b) AlCl₃/HCl in THF/NaCl₃₀ at 180 °C for 90 and 55 min, respectively.

conversion of sugarcane bagasse glucans. The chemical effects of steam explosion did not improve HMF yields from sugarcane bagasse glucans but its hemicellulose component was made more susceptible to hydrolysis and dehydration. Hydrolysis followed by dehydration with the *in situ* extraction of reaction products provided an interesting route for the production of biobased value-added chemicals that have a great potential to replace petroleum-based derivatives and building blocks.

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