CHEMICAL HYDROLYSIS OF HEMICELLULOSE FROM SUGARCANE BAGASSE. A COMPARISON BETWEEN THE CLASSICAL SULFURIC ACID METHOD WITH THE ACIDIC IONIC LIQUID 1-ETHYL-3-METHYLIMIDAZOLIUM HYDROGEN SULFATE

Marcoaurélio Almenara Rodrigues
Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, I.P.
Estrada do Paço do Lumiar 22, 1649-038, Lisboa, Portugal
Permanent address: Departamento de Bioquímica, Instituto de Química
Universidade Federal do Rio de Janeiro
Av. Athos da Silveira Ramos, 149
Centro de Tecnologia, Cidade Universitária, 21941-909 Rio de Janeiro, Brazil, almenara@iq.ufrj.br
https://orcid.org/0000-0002-5217-0082

André M. da Costa Lopes
Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, I.P
Estrada do Paço do Lumiar 22, 1649-038, Lisboa, Portugal
Permanent address: CICECO, Aveiro Institute of Materials, Department of Chemistry
University of Aveiro, 3810-193 Aveiro, Portugal, andremcl@ual.pt.
https://orcid.org/000-0001-8855-6406

Rafal M. Lukasik
Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar 22, 1649-038, Lisboa, Portugal, fax: +351217163636; phone: +351210924600 ext. 4224, rafal.lukasik@lneg.pt.
https://orcid.org/0000-0002-7805-5744

Article history: Received 28 August 2022, Received in revised form 3 October 2022, Accepted 4 October 2022, Available online 4 October 2022

Highlight
Sugarcane bagasse was pretreated with acidic ionic liquid and dilute sulfuric acid, high furfural yield was found at high ionic liquid concentration, high pentose yield was found at 46.4 wt.% ionic liquid concentration, a liquid fraction richer in pentose was found for the ionic liquid treated biomass, and the biomass pretreatment can be tuned to produce pentose or furfural using Ionic liquid.

Abstract
Dilute sulfuric acid and acidic ionic liquids are pretreatment methods used to selectively hydrolyze hemicellulose from lignocellulosic biomasses. In this work, a comparison between these techniques is carried out by treating sugarcane bagasse both with 1-ethyl-3-methylimidazolium hydrogen sulfate at different ionic-liquid and water contents and with H_2SO_4 at the same conditions and equivalent ionic liquid molar contents. Results from the use of ionic liquid showed that it was possible to tune the biomass treatment either to achieve high hemicellulose hydrolysis yields of 72.5 mol% to very low furan and glucose co-production, or to obtain furfural at moderate yields of 18.7 mol% under conditions of low water concentration. In comparison to the use of ionic liquid, sulfuric acid pretreatment increased hemicellulose hydrolysis yields by 17%, but the 8.6 mol% furfural yield was also higher, and these yields were obtained at high water concentration conditions. Besides, no such tuning ability of the biomass treatment conditions can be made.

Keywords
sugarcane bagasse; acidic ionic liquid; biomass pretreatment; dilute sulfuric acid; pentose; furfural.

Introduction
Sugarcane bagasse, which is predominantly composed of cellulose, hemicellulose, and lignin [1], is the main by-product of the sugar/ethanol industry. This waste material is available in vast amounts and can be used for the production of high value-added products such as glucose, xylose furans, and other commodities [1–3]. The sugars glucose and xylose resulting from the enzymatic hydrolysis of cellulose and hemicellulose can be used in fermentation processes to produce fuel and chemicals [1,4–7]. Depending upon the biomass, pretreatment choice, and operational conditions, the cellulose-derived glucose can be transformed into 5-hydroxymethyl-

furfural (5-HMF) [2],and xylose can be transformed into furfural [3]. Because both furfural and 5-HMF are versatile chemical platform molecules in the biofuel and petrochemical industries [8], much effort has been devoted to converting biomass into these building-block molecules [2,9]. Lignocellulosic biomass can be pre-treated by several techniques to produce high value chemicals and fuels [3,10]. Pre-treatment with dilute sulfuric acid to selectively hydrolyze hemicellulose is the classic, most cost-effective reference method [3,10,11], reaching up to 85% of theoretical yield [5] and in some cases more than 95% [6]. However, this process has important drawbacks such as low selectivity and the formation of sugar dehydration products (e.g., furfural and 5-HMF), resulting in a highly impure and toxic pentose stream [12]. Besides, the sulfuric acid pre-treatment that has also been used to promote dehydration of xylose to furfural requires both the use of expensive construction materials to minimize corrosion, and the disposal of neutralization salts [6,10,13]. There is therefore great industrial interest in the development of more advanced processes for the production of a pentose syrup with very low furfural contamination and for the production of furfural in high yields without the use of sulfuric acid. Advances may come from a process option that avoids the detrimental industrial use of sulfuric acid and, more importantly, that enables the production of cleaner xylose or furfural currents more suitable to processing via biochemical or chemical pathways to higher value molecules.

Ionic liquids (ILs), particularly imidazolium based ILs, are an advantageous alternative to the use of sulfuric acid as they dissolve lignocellulosic biomass and can be used to convert biomass polysaccharides directly to furans [3,12,14]. ILs are made up of countless combinations of anions and cations and present highly tunable properties such as hydrophobicity, polarity, acidity, and miscibility with other solvents. Moreover, significant advances concerning the separation of biomass hydrolysis products from IL and the recovery of IL have been made, thereby decreasing the cost of using IL [15]. Acidic ILs have garnered special attention as they can act as both solvent and catalyst, selectively hydrolyze hemicellulose at high yield [16], and increase cellulose hydrolysability [17,18]. Novel superacid ILs have consequently been developed that improve hydrolysis of hemicellulose and its subsequent conversion to furfural [12]. In spite of the aforementioned wealth of information on the applications of IL for biomass processing, no thorough study has yet been done comparing hemicellulose hydrolyses from lignocellulosic biomass by acidic IL with the classic dilute sulfuric acid method. In the few studies found in the literature, the biomass used were either commercial hemicellulose [19] or cellulose [20]. Moreover, the sulfuric acid concentrations used in these studies were extremely low, less than 0.5 wt.%, which are inadequate to hydrolyze hemicellulose from lignocellulosic biomass since they result in low hydrolysis yields or require high temperatures (higher than 120°C) and/or treatment time longer than 1.5h to give hydrolysis yields higher than 50 mol% [21]. Accordingly, this work evaluated the treatment of sugarcane bagasse with the acidic IL 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO_4]) in reaction mixtures presenting different ionic liquid and water contents. Results were compared to those obtained by treating the biomass, at the same temperature and time conditions, with dilute H_2SO_4 at the same molar content and similar concentration of the IL at the studied mass fraction of 6.5 wt.%, which corresponded to a sulfuric acid mass fraction of 5.6 wt.%. As expected, treatment with dilute sulfuric acid resulted in a pronounced hydrolysis of hemicellulose into xylose, nevertheless the liquid stream was also highly and undesirably contaminated with furfural and glucose. However, the use of ([EMIM][HSO_4]), besides resulting in hemicellulose hydrolysis into pentoses at high yield (69.2 mol%), presented a minimum of furfural, 5-HMF, and glucose contamination. Moreover, it was observed that the use of ([EMIM][HSO_4]) could be tuned, under conditions of low water content, for furfural production with a yield of as much as 18.7 mol%. Tuning is a valuable feature of the IL process that is not obtainable for the dilute sulfuric acid method.

Materials and methods

Biomass and chemicals

Sugarcane bagasse was milled to particles up to 0.5 mm in a knife mill (IKA WERKE GmbH & Co, Staufen, Germany) and kept dry at room temperature. The ionic liquid [EMIM][HSO_4] for the biomass treatment was purchased from Ionic Liquid Technologies GmbH in Heilbronn, Germany. The reagent presented 99% purity grade and water content of 1693.8 µg/g as determined by a volumetric Karl-Fischer titration method. Sulfuric acid of analytical grade was purchased from Panreac Química (Barcelona, Spain). The HPLC analysis standards, glucose, xylose, arabinose, furfural, and 5-HMF were purchased from Sigma Aldrich (St. Louis, USA). Deionized ultrapure Milli-Q grade water was used for the HPLC analysis and for the biomass treatment assays.

Biomass characterization

Biomass humidity was estimated according to the NREL/TP-510-42621 method [22]. Biomass characterization was performed by total acidic hydrolysis following the NREL/TP-510-42618 procedure [23]. The residual non-

https://doi.org/10.32933/ActaInnovations.46.3 • ISSN 2300-5599 •

hydrolyzed biomass was determined gravimetrically after incubation in a glass crucible at 100°C for 16h. The ash content was also determined according to the NREL/TP-510-42622 [24] procedure by igniting the non-hydrolyzed biomass at 550°C for 16 h. The acid-insoluble lignin content was assumed to be the difference between the non-hydrolyzed biomass and the ash content. All biomass characterizations were performed in triplicate.

Table 1. Mass composition (wt.%) of the reaction mixtures (dry mass of ionic liquid, dry mass of biomass and water) for the sugarcane bagasse treatment. Also showing control mixtures without catalyst at three representative biomass mass fractions. *Source: Authors results.*

[EMIM][HSO_4]	**Sugarcane biomass**	**Water**
0.0	3.9	96.1
0.0	5.7	94.3
0.0	10.9	89.1
6.2	9.0	84.8
6.5	5.3	88.2
41.0	3.8	55.2
44.6	10.7	44.7
46.4	7.2	46.5
46.5	7.1	46.4
64.1	5.9	30.0
68.5	6.3	25.2
73.6	6.7	19.7
78.0	7.2	14.8
85.2	8.9	5.8

<u>Biomass Treatment</u>

- Ionic liquid treatment

The mass composition (mass fraction) of the reaction mixtures (water, biomass, and IL) for sugarcane bagasse treatment is presented in Table 1. Four hundred milligrams of sugarcane biomass were treated with increasing IL and varying biomass concentration. The amount of IL and ultrapure Milli-Q grade deionized water that had to be added, to achieve the desired concentrations, was calculated considering the IL and biomass water contents, see the following section for calculation formulae and their deduction. The reaction mixtures were incubated for 83 minutes at 125°C in sealed flasks immersed in an oil bath under constant agitation [14,25]. These conditions were chosen based on a previous study that determined the optimum conditions to obtain xylose from wheat straw biomass with the similar IL 1-butyl-3-methylimidazolium hydrogen sulfate [BMIM][HSO_4] [14]. After cooling, unless the reaction mixtures already presented IL concentrations lower than 28.8 wt.%, a known amount of deionized water was added as an anti-solvent in order to reach a final IL concentration in the liquid phase of 28.8 wt.%. This threshold IL concentration prevented the IL interference in the subsequent sugar analysis [14]. For all treatments, the total mass added was recorded and it was assumed that no mass was lost by vaporization. The reaction mixture was filtered with a 0.45 µm nylon filter. The filtrate density was estimated by weighing a known volume of the solution in a pre-weighed volumetric flask and kept under refrigeration until its sugar composition determination by HPLC. The solid residue was washed with deionized water for the removal of soluble materials, dried for 20h at 70°C, and kept at room temperature. The yield of solid residue was determined gravimetrically, and its chemical composition analyzed using the same procedure applied to the untreated biomass as already described.

- Biomass, ionic liquid and water contents calculations

The amounts of biomass, IL and water added to achieve the reaction mixtures compositions presented in Table 1 were calculated as follows:

The biomass mass fraction, [*Biomass*], in the reaction mixture is described by equation (1).

$$[Biomass] = \frac{dmB}{mIL + mB + mw} \tag{1}$$

Where *dmB* is the dry mass of biomass added, *mIL* is the mass of IL to be added, *mw* is the mass of water to be added, and *mB* is the mass of biomass added, in this case, set in 400 mg.
The IL mass fraction in the reaction mixture, [*IL*], is described by equation (2).

(2) $$[IL] = \frac{dmIL}{mIL + mB + mw}$$

Where *dmIL* is the dry mass of the IL added. Equations (1) and (2) can be rearranged in the following:

(3a) $$\frac{dmB}{[Biomass]} = mIL + mB + mw$$

and

(3b) $$\frac{dmIL}{[IL]} = mIL + mB + mw$$

Equaling equations 3a and 3b and rearranging the following equation is deduced:

(4) $$dmIL = \frac{[IL] \times dmB}{[Biomass]}$$

The IL and biomass dry masses are their masses subtracted from their respective mass of water.

(5a) $$dmIL = mIL - wIL$$

and

(5b) $$dmB = mB - wB$$

Where *wIL* and *wB* are their respective mass of water. However, *wIL* and *wB* are respectively the product of IL and biomass masses with their respective water content or humidity (*hIL* and *hB*).

(6a) $$wIL = mIL \times hIL$$

and

(6b) $$wB = mB \times hB$$

Therefore,

(7a) $$dmIL = mIL \times (1 - hIL)$$

and

(7b) $$dmB = mB \times (1 - hB)$$

Substituting equations (7a) and (7b) into equation (4) the following expression is deduced:

(8) $$mIL = \frac{[IL] \times mB}{[Biomass]} \times \frac{1 - hB}{1 - hIL}$$

https://doi.org/10.32933/ActaInnovations.46.3 • ISSN 2300-5599 •

The mass of water to be added can be then, derived from equation (1)

(9)
$$mw = \frac{dmB}{[Biomass]} - mB - mIL$$

Once the intended [IL] and [Biomass] are established, the IL and biomass humidities determined, and the biomass load set, the masses to be added of IL and water are calculated by equations (8) and (9).

- Dilute sulfuric acid treatment

In order to compare the biomass treatment with the acidic IL [EMIM][HSO_4] with the classic dilute sulfuric acid treatment, a different set of sugarcane bagasse biomass was treated with dilute sulfuric acid at the same molar content and concentration that was used for the ionic liquid treatment at mass fraction of 6.5 wt.% — that is, the concentrations either IL or sulfuric acid were set in 6.7 wt.%, which corresponded respectively to an IL and sulfuric acid mass fractions of 6.5 and 5.6 wt.%, see section below. The reaction mixture was incubated at 125°C for 83 minutes and deionized water was added to achieve a final liquid mass content of 10 g. The reaction mixture was then processed as already described for the treatment using IL.

- Sulfuric acid, water, and biomass content calculations.

For the design of the aforementioned comparative conditions, it was sought the same IL and sulfuric acid molar content, as well as the same concentration in the liquid phase of both chemicals, following the same rationale of previous works [19,20]. This approach secured comparative reaction conditions as the use of the same mass fraction for [EMIM][HSO_4] and H_2SO_4 would result in different concentrations of the reagents in the liquid phase as IL and sulfuric acid have different molar masses of 197.97 and 98.08 g/mol, respectively. The desired working conditions were designed as follows: (i) it was set the initial IL and biomass concentrations and considering the biomass load it was calculated the corresponding amount of IL; (ii) it was calculated the mass of the sulfuric acid solution corresponding to the same IL molar content; (iii) it was calculated the mass of the final solution for the same IL concentration; (iv) it was calculated the amount of deionized water to be added to achieve the mass of the final solution, considering the amount of water brought along with the biomass; (v) finally, the sulfuric acid and biomass concentrations were recalculated . The calculation and formulae deduction are described in the following:
The IL concentration in the liquid phase (*cIL*) is given by:

(10)
$$cIL = \frac{dmIL}{mIL + wB + mw}$$

The biomass concentration in the liquid phase (*cB*) is given by:

(11)
$$cB = \frac{dmB}{mIL + wB + mw}$$

The required IL dry mass (*dmIL*) to a given *cIL*, *cB*, and biomass dry mass load (d*mB*) can be deduced by analogy of the deduction of equation (4) as described previously:

(12)
$$dmIL = \frac{[cIL] \times dmB}{cB}$$

The IL and sulfuric acid molar contents (*nIL and nsa*) are given by the ratio of their masses (*dmIL* and *msa*) to their respective molar masses (*MMIL* and *MMsa*):

(13a)
$$nIL = \frac{dmIL}{MMIL}$$

and

(13b)
$$nsa = \frac{msa}{MMsa}$$

If *nIL* is equal to *nsa*, then (13a) = (13b) and *msa* can be derived after rearrangement;

(14)
$$msa = \frac{dmIL}{MMIL} \times MMsa$$

The sulfuric acid mass (*msa*) is the product of the mass of the sulfuric acid solution (*msasol*) to the concentration of sulfuric acid in the solution (*csas*):

(15)
$$msa = msasol \times csas$$

Substituting equations (12) and (15) into (14), *msasol*, the mass of sulfuric acid that gives the same IL molar content can be derived:

(16)
$$msasol = \frac{dmB}{cB} \times \frac{cIL}{MMIL} \times \frac{MMsa}{csas}$$

However, it is also desired that the IL and sulfuric acid concentrations in the reaction mixture (*cIL* and *csar*) are the same. The *csar* is given by the expression:

(17)
$$csar = \frac{msa}{msasol + wB + mw}$$

Substituting equation (15) into (17) and making *csar* = *cIL*, the mass of water needed to satisfy this condition can be calculated by:

(18)
$$mw = msasol \times \left(\frac{csas}{cIL} - 1\right) - wB$$

However, the biomass concentration no longer holds, and it must be recalculated by the expression:

(19)
$$cfB = \frac{dmB}{msasol + wB + mw}$$

Where *cfB* is the final biomass concentration in the reaction mixture. To calculate their respective mass fractions, the term *wB* must be replaced by *mB*, the mass of biomass, in equations (10), (11), (17) and (19).

Once the initial conditions are set, the amount of sulfuric acid solution and water needed to satisfy the conditions of equal molar content and concentrations can be calculated by these formulae however, it is not possible to keep the same biomass concentration. This approach differs from those previous works, where similar biomass load and concentrations of IL and sulfuric acid or similar biomass load and presumed [H^+] concentrations were kept [19,20].

Sugar, furans and acetic acid analysis

The composition of the liquid stream of the IL or sulfuric acid treated biomass was determined by HPLC. Glucose, xylose, arabinose, acetic acid, furfural, and 5-HMF were identified against standards and quantified by the construction of standard analytical curves in the range of 0.5 to 20.0 g/L for glucose, xylose, and arabinose, 0.5 to 3.0 g/L for acetic acid, and 0.1 to 4.0 g/L for furfural and 5-HMF. HPLC analyses were performed using an Agilent Technologies Liquid Chromatographer 1100 Series System (Santa Clara, CA, USA) equipped with a diode

https://doi.org/10.32933/ActaInnovations.46.3 • ISSN 2300-5599 •

array for furans and refractive index detectors for organic acids and monosaccharides. It was used with an Aminex HPX-87H column (Bio-Rad, USA) in combination with a cation H^+-guard column (Bio-Rad, USA). Elution was performed with H_2SO_4 5 mmol·L^{-1} at 50°C with a flow rate of 0.6 mL·min^{-1} for liquors obtained by the biomass treatment with IL and dilute acid and a flow rate of 0.4 mL·min^{-1} for the analysis of total acidic hydrolysates.

Calculation of the relative composition of the liquid phase

The relative composition regarding the glucose, pentose, furans and acetic acid mass contents was calculated using formulas (20) and (21). Firstly, the normalized mass content of each component (*Ci*) was calculated by dividing the component mass content (*mi*) by the amount of dry biomass used (*dmB*). Its relative amount (*Ri*) was calculated by dividing it by the sum of the normalized content of each component, automatically by the MS Excel software.

$$Ci\ (wt.\%) = 100 \times \frac{mi}{dmBi} \tag{20}$$

$$Ri\ (\%) = 100 \times \frac{Ci}{\sum Ci} \tag{21}$$

Polysaccharide hydrolysis yield, furans and acetyl yields calculation

Polysaccharide hydrolysis yields were calculated using formulas (22) and (23) for glucan and arabinoxylan, respectively, where YG is the glucan hydrolysis yield (Glucose yield), Gb is the glucan content in the dry biomass, YAX is the arabinoxylan hydrolysis yield (Pentose yield), AXb is the arabinoxylan content in the dry biomass, and 90 and 88 are factors representing the conversion of sugar content into its respective polysaccharide equivalent.

$$YG(mol\%) = \frac{m_{glucose}}{dmB} \times \frac{90}{Gb} \tag{22}$$

$$YAX(mol\%) = \frac{(m_{arabinose} + m_{xylose})}{dmB} \times \frac{88}{AXb} \tag{23}$$

Furans and acetyl production yields were calculated similarly according to formulas (24), (25) and (26), where YHMF, YF, YAc are the respective yields of 5-HMF, furfural, and acetyl production. The numbers 128.7, 137.3 and 71.7 are conversion factors relating furans and acetic acid to their corresponding polysaccharide equivalent. *Acb* is the biomass acetyl content.

$$YHMF(mol\%) = \frac{m_{HMF}}{dmB} \times \frac{128.7}{Gb} \tag{24}$$

$$YF(mol\%) = \frac{m_{furfural}}{dmB} \times \frac{137.3}{AXb} \tag{25}$$

$$YAc\ (mol\%) = \frac{mHAc}{dmB} \times \frac{71.7}{Acb} \tag{26}$$

Results

Biomass Composition

Sugarcane bagasse composition, with a humidity of 5.8±0.6 wt.%, was as follows: 36.9±0.5 wt.% glucan, 22.1±0.3 wt.% xylan, 2.6±0.2 wt.% arabinosyl group (corresponding to 24.7 wt.% arabinoxylan), 3.9±0.5 wt.% acetyl groups, 21.8±0.2 wt.% lignin, 4.5±1.1 wt.% ash, and 8.2 wt.% of others (all data on a dry weight basis).

Table 2. Composition of the liquid phase resulting from sugarcane bagasse treatment with [EMIM][HSO_4] or dilute H_2SO_4 at 125°C for 83 minutes at the indicated catalyst and biomass mass fractions and of control experiments without catalyst at three representative biomass mass fractions. Results are presented as gram of the component per 100 g of treated dry biomass and show at least, one significative algorism. *Source: Authors results.*

Catalyst	**Catalyst mass fraction (wt.%)**	**Biomass mass fraction (wt.%)**	**Component content (wt.% dry biomass)**					
			Glucose	Xylose	Arabinose	Furfural	5-HMF	Acetic Acid
[EMIM][HSO_4]	0.0	10.9	0.2	0.07	0.2	0.00	0.00	0.14
	0.0	5.7	0.2	0.07	0.2	0.00	0.00	0.11
	0.0	3.9	0.2	0.06	0.2	0.00	0.00	0.10
	6.2	9.0	0.3	6.6	1.6	0.02	0.01	2.3
	6.5	5.3	0.3	6.8	1.6	0.03	0.02	2.4
	41.0	3.8	1.2	17.5	2.0	0.5	0.02	4.2
	44.6	10.7	1.0	15.5	1.9	0.4	0.02	4.1
	46.4	7.2	0.9	16.3	2.0	0.3	0.02	4.2
	64.1	5.9	1.3	15.8	2.0	0.8	0.03	4.0
	68.5	6.3	1.3	15.1	2.0	1.0	0.04	4.1
	73.6	6.7	1.2	14.1	1.9	0.7	0.03	4.1
	78.0	7.2	1.1	12.9	1.6	1.1	0.04	3.9
	85.2	8.9	1.0	7.5	1.4	3.4	0.08	2.1
H_2SO_4	5.6	16.1	3.3	20.4	2.4	1.5	0.03	4.3

Liquid phase composition and hydrolysis yield

Composition of the liquid phase resulting from sugarcane bagasse treatment with [EMIM][HSO_4] or dilute H_2SO_4 at 125°C for 83 minutes at different catalyst and biomass mass fractions and that of control experiments without catalyst at three representative biomass mass fractions are shown in Table 2, and their relative composition in Figure 1. Table 3 shows the polysaccharide hydrolysis yields, and the furans and acetic acid production yields. Treatments without catalysts resulted in a low overall sugar content in the liquid phase with predominance of arabinose and glucose regardless the biomass mass fraction (Figure 1 and Table 2). Moreover, as their hydrolysis yields were very low (Table 3), it suggests that no auto-hydrolysis occurred at any biomass concentration, and probably that, these solubilized sugars are extractives components or hemicellulose labile structures. Quantitative acidic hydrolysis of these liquid fractions showed no further increment in the sugars content, suggesting the absence of extracted oligosaccharides.

Glucose and 5-HMF

Regarding glucose and 5-HMF, it was observed in the IL reaction mixtures a low glucose content and negligible degradation into 5-HMF whose maximal yield was of 0.3 mol% at IL mass fraction of 85.2 wt.%. The glucose mass content corresponded to 0.3 wt.%, (yield of 0.8 mol%) at IL mass fractions of 6.2 and 6.5 wt.%, increased to 1.3 wt.% (yield of 3.2 mol%) at IL mass fraction 68 wt.% and declined as the IL mass fraction increased. Glucose contributed to the range of 3.0 to 6.4% of the total solute mass, increasing its contribution as the IL mass fraction increased, reaching its highest value of 6.4% for the IL mass fraction of 85.2 wt.%. When treated with dilute sulfuric acid, glucose mass content was of 3.3 wt.% (yield of 8.0 mol%) and contributed to 10.3% of solute´s total mass. The liquid phase resulting from dilute acid treatment presented 2.5-fold more glucose than those resulting from IL treatment. Negligible amounts of 5-HMF were formed for the biomass treatment with either [EMIM][HSO_4] or dilute sulfuric acid. The results indicate that the liquid phase obtained from dilute acid treatment is at least 1.6-fold richer in and contains at least 2.5-fold more glucose than those obtained from IL treatment.

Acetic Acid

The acetic acid mass contents and production yields in the liquid phase increased substantially in the presence of 6.2 wt.% of IL, from 0.10 wt.% (1.8 mol%) to 2.3 wt.% (41.8 mol%), rose to 77.2 mol% at 41.0 wt.% of IL, peaked at 46.4 wt.% of IL (78.5 mol%) and started to decrease slightly as the IL mass fraction increased. The mass contribution in the liquid phase was relatively constant (20%), and the acetic acid content increased contribution

https://doi.org/10.32933/ActaInnovations.46.3 • ISSN 2300-5599 •

in the liquid phase was relatively constant (20%), and the acetic acid content increased proportionally to the increase of all other components. At 85.2 wt.% IL its mass content, production yield and mass contribution decreased sharply, suggesting mass loss due to degradation or vaporization. When treated with 5.6 wt.% sulfuric acid, the acetic acid yield was as high as those obtained for treatment with IL at 46.4 wt.% but with a mass contribution of 13.5% against 17.9%, probably due to the increased pentose and glucose yields (Tables 2 and 3 and Figure 1).

Table 3. Glucan and hemicellulose hydrolysis yields after sugarcane biomass treatment with [EMIM][HSO_4] for 83 min at 120°C at several IL and biomass mass fractions. Biomass treatment with dilute H_2SO_4 at the same conditions are shown for comparison. Sugar, acetyl and furans yields were calculated as described in Materials and methods. *Source: Authors results.*

Catalyst	**Catalyst mass fraction (wt.%)**	**Biomass mass fraction (wt.%)**	**Component hydrolysis yield (mol%)**						
			Glucose	5-HMF	Xylose	Arabinose	Pentoses	Furfural	Acetyl group
[EMIM][HSO_4]	0.0	10.9	0.4	0.0	0.3	8.2	1.1	0.0	2.7
	0.0	5.7	0.5	0.0	0.3	7.2	1.0	0.0	2.0
	0.0	3.9	0.4	0.0	0.2	6.9	1.0	0.0	1.8
	6.2	9.0	0.8	0.1	26.1	53.9	29.1	0.1	41.8
	6.5	5.3	0.8	0.1	27.2	52.7	29.9	0.2	45.0
	41.0	3.8	2.8	0.1	69.8	68.4	69.6	2.9	77.2
	44.6	10.7	2.3	0.1	61.9	64.0	62.1	2.1	75.1
	46.4	7.2	2.3	0.1	64.9	68.0	65.3	1.4	78.5
	64.1	5.9	3.1	0.1	62.8	67.8	63.3	4.2	74.8
	68.5	6.3	3.2	0.1	60.3	67.2	61.0	5.6	76.4
	73.6	6.7	2.8	0.1	56.3	63.1	57.1	3.9	75.4
	78.0	7.2	2.6	0.1	51.2	54.5	51.6	6.1	72.2
	85.2	8.9	2.4	0.3	29.9	48.0	31.8	18.7	38.4
H_2SO_4	5.6	16.1	8.0	0.1	81.3	79.4	81.1	8.6	79.8

<u>Pentoses and furfural</u>

In the presence of 6.2 and 6.5 wt.% of IL (biomass concentrations of 9.0 wt.% and 5.3 wt.%), the pentose mass content showed a considerable increase when compared to treatment in the absence of catalyst, from 0.3 to 8.4 wt.%. Its yield reached 29.1 mol%, with negligible 0.1-0.2 mol% furfural yield. Maximal arabinoxylan conversion of 72.5 mol% (the sum of pentose and furfural yields) was observed upon increasing the IL concentration to 41.0 wt.% (biomass concentration of 3.8 wt.%), corresponding to a 2.4-fold increase relative to the previous treatment condition. The treatment also resulted in a pentose yield of 69.6 mol% and low furfural production of 2.9 mol% with corresponding mass contents of 19.5 and 0.5 wt.%. Treatments at IL concentration in the range of 41.0 to 46.4 wt.% resulted in similar pentose and arabinoxylan conversion yields, around 65.7 and 67.8 mol%, respectively. Furfural production at these IL concentrations showed a decrease of 33.3% with a final yield of 1.4 mol%.

The use of IL at concentrations in the range of 64.1 to 68.5 wt.% resulted in a steady decrease in pentose yield, reaching values found for treatments at IL concentration of 44.6 wt.%. This was accompanied by an increase in the furfural production, which resulted in similar arabinoxylan conversion. A further increase in IL concentration, from 68.5 to 78.0 wt.%, resulted in a sharp decrease in the pentose yield whereas the furfural yield increased reaching a final value of 6.1 mol% at IL concentration of 78.1 wt.%. Despite that, the sum of both components decreased continuously. The increment of IL from 78.0 to 85.2 wt.%, which corresponded to a water concentration of only 5.8 wt.%, had a dramatic effect on pentose and furfural production yields. Pentose yield decreased 38.4% to a final value of 31.8 mol%, and furfural yield increased sharply, reaching a final value of 18.7 mol%, however, the sum of both components yields decreased further 12.5% at the same rate. This increase of furfural yield occurred despite the increase of 41.3% in the biomass concentration; at IL 41-46 wt.% the increase in biomass concentration was followed by a decrease in the furfural production yields (Tables 2 and

3). The pentose relative mass contribution followed somewhat the same trend of pentose yield. Maximal valueswere observed at IL mass fraction of 41-46.4 wt.%, then it decreased steadily as the IL mass fraction increased and decreased sharply when the IL increase from 78.0 to 85.2 wt.%. However, the sum of pentose and furfural relative mass contributions showed a different pattern of their corresponding sum of yields, it remained relatively constant since the decrease in pentose mass contribution was accompanied by an increase of furfural relative mass contribution. These results suggest that at IL concentrations higher than 78.0 wt.% a considerable fraction of hydrolyzed pentose undergoes further conversion to furfural. Treatment of sugarcane bagasse with dilute sulfuric acid resulted in 89.7 mol% arabinoxylan conversion, 81.1 mol% pentose, 8.0 mol% glucose, and 8.6 mol% furfural production yields, as well as negligible 5-HMF production. The pentose relative mass contribution to the liquid phase was 71.2% whereas furfural was 4.8%. The arabinoxylan conversion and pentose yields when compared with those obtained after biomass treatment with a similar concentration of [EMIM][HSO_4], were 3.0 and 2.7-fold higher, respectively, and extremely higher for furfural production yield. Comparing with the results obtained by treating biomass with IL at concentrations ranging from 44.6 to 46.5 wt.%, where arabinoxylan hydrolysis yield was 65.3 mol%, the pentose content in the dilute acid hydrolysate was 24.3 to 30.6% higher. However, the amount of furfural produced was also 4 to six-fold higher resulting in a liquid stream 3.0 -4.4-fold richer in furfural and around 7.0% poorer in pentoses. Therefore, the pentose/furfural yield ratio was 4.0-fold higher, and the pentose/glucose ratio was 2.7-fold higher in the syrup obtained after IL biomass treatment, showing a greater specificity of IL hydrolysis towards hemicellulose. Thus, although the pentose content was 24.3 to 30.6% higher using the dilute acid treatment, the syrup obtained by treating biomass with [EMIM][HSO_4] at these concentrations contains a considerable amount of free pentose and much less contamination with glucose and the sugar degradation products. As the IL concentration increases and the pentose yields and relative mass contribution decreases whereas of those of furfural increases, the pentose/furfural ratios decrease accordingly. The pentose content is 28-42% higher and the furfural content present at dilute acid hydrolysate is twice of that present in the hydrolysate of IL 64-73.6 wt.%. Nevertheless, the pentose mass contribution was similar in both treatments, but the furfural contribution was 1.5 times higher in the dilute acid treatment, and consequently the pentose/furfural ratio was still 1.6 higher in the IL syrup. A comparison of biomass treated with dilute H_2SO_4 and with IL at concentrations near 78.0 wt.% shows that, although the yield of free pentose at this IL concentration had decreased to 51.6 mol% (a yield 1.6 times lower than that obtained by dilute acid treatment), it still displayed a selectivity towards hemicellulose. The pentose/glucose yield ratio was twice that obtained by dilute acid treatment. However, given that the conversion of pentose into furfural increased at these IL concentrations, the pentose/furfural yield ratios were comparable. These results clearly indicate that the syrup obtained by treating biomass at these IL concentrations is enriched not only with pentose but also with large amounts of furfural, albeit 29% less furfural than was obtained with dilute acid treatment, its relative mass contribution is similar in both treatments. At the highest IL concentration, the pentose yield was 20.6% lower and furfural production yield was twice that obtained with dilute acid treatment, and the ratio of pentose/furfural was 5 times lower. However, the yield ratio of pentose/glucose was still 1.3 times higher than that obtained with dilute acid treatment. These results suggest that at these [EMIM][HSO_4] concentrations a syrup enriched with pentoses, and furfural can be obtained with low glucose and 5-HMF contamination, which allows for improvements to the furfural production process.

Characterization of residual biomass

- Solids yield

The solid yields, compositions, and polysaccharide contents from the IL and dilute sulfuric acid treatments are shown in Table . IL treatments in the range of 6.2 and 6.5 wt.% resulted in a similar yield of 81.4 wt.% indicating a 18.6% biomass dissolution despite their low yields (Tables 2 and 3). These yields were 24.6% higher in comparison to that for the sulfuric acid treatment at similar concentration which corresponded to 46.3% less biomass dissolution. The solids yield decreased steadily in response to the IL concentration increase up to 64.1 wt.% and fluctuated around values near 70.8 wt.% which were approximately 8.4% higher in comparison to that for dilute sulfuric acid treatment, showing that biomass treatment with 5.6 wt.% dilute sulfuric acid extracted more biomass than the highest IL at its highest concentration. Comparing the solids yields in Table 4 with the sum of the quantified components in the liquid streams in Table 2, after correction to their glycosyl or acetyl equivalent, it is found that the sum of the quantified components is smaller than the expected value suggested by the solid yields. At 6.2-6.5 wt.% IL concentration the quantified values were 50% less than expected. At 41.0-46.4 wt.% IL and dilute H_2SO_4 they were in average 19% less. At 64.1-78.0 wt.% IL they were 34% less, and at 85.2 wt.% IL they were 45% less. The reasons for these discrepancies can be partial hydrolysis with soluble oligosaccharide production (as might be the case for biomass treated at 6.2-6.5 wt.% IL), product degradation into either non quantified or volatile compounds (such as formic and levulinic acids, and CO_2) [26] that were lost by vaporization, especially for those treatments with dilute sulfuric acid or with high IL concentrations.

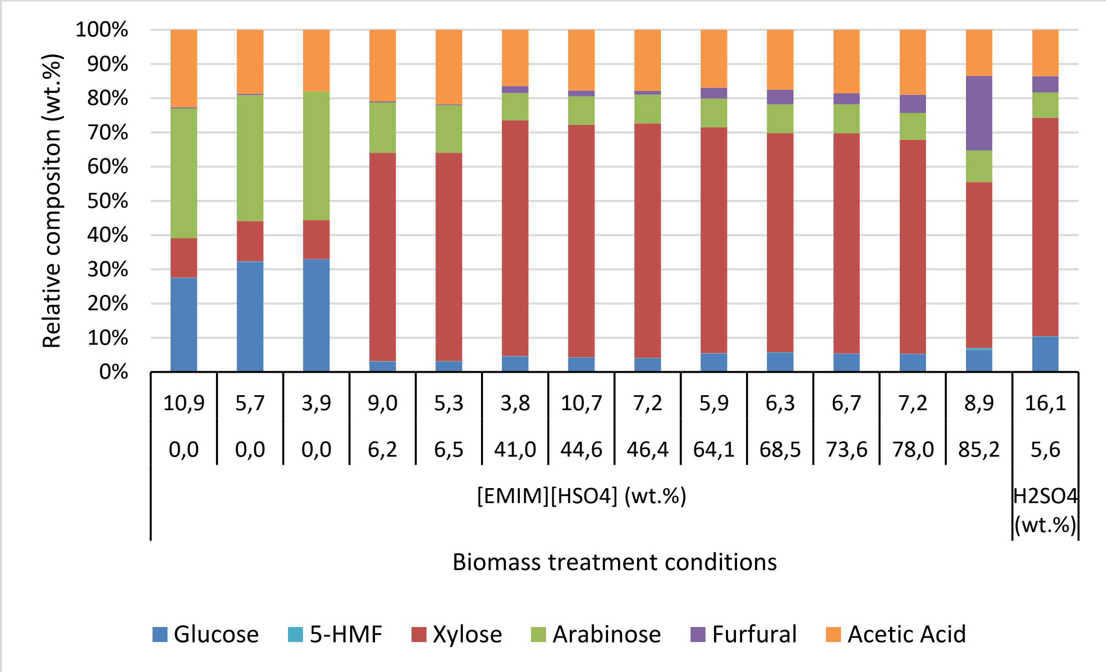

Figure 1. Relative composition of the liquid phase after sugarcane biomass treatment with [EMIM][HSO_4] or H_2SO_4 at the indicated conditions. The total component contents were set as 100% and each component relative content was calculated. In the horizontal axis, the upper values represent biomass mass fractions (wt.%) and the lower values, the catalyst mass fraction (wt.%). *Source: Authors results*.

- Glucan content

The polysaccharide content composition in the solids obtained after biomass treatment somewhat reflected the polysaccharide hydrolysis yield of the liquid phase. In all treatments there was an enrichment in glucan, lignin and ashes and impoverishment in xylan, arabinan and acetyl (Table 4). The glucan content, compared to the original biomass, enriched 18.7% by treating the biomass with 6.2-6.5 wt.% IL, reaching its maximal value of 38% enrichment at IL concentrations of 41.0 and 64.1 wt.% with respective biomass mass fractions of 3.8 and 5.9 wt.%. Treatments with IL in the range of 46.4-68.5 wt.% showed an average enrichment of 33.6% with corresponding 49.3 wt.% glucan. Treatments at IL concentrations higher than 68.5 wt.% resulted in a slow and steadily decrease in the glucan content with a final content of 47.8 wt.%, at IL concentration of 85.2 wt.%, corresponding to an enrichment of 29.0%. Solid residues obtained after biomass treatment with dilute sulfuric acid were 42.7% enriched in glucan with a content of 52.6 wt.%. These solids were from 3.4 to 20.4% richer in glucan than the solids obtained from IL, despite its higher glucan hydrolysis yield (Table 3).

- Lignin and ashes content

Although the contents of ashes and lignin increased in the solids obtained from biomass treatment with IL, there were no clear trends as the IL concentration increased. The lignin content in the solids averaged in 26.1 wt.% corresponding to an enrichment of 19.7%, nevertheless, they were 19.4% poorer in lignin when compared to the diluted acid treatment, in which the lignin content was 32.4 wt.%, an enrichment of 48.6%. This higher content may be the result of sugar decomposition, molecular condensation, and precipitation as nonhydrolyzable material. The ashes content in the solids obtained from biomass treatment with IL averaged in 7.8 wt.% an enrichment of 75.3% which was very similar to those obtained with 5.6 wt.% sulfuric acid treatment.

- Acetyl Content

The acetyl content diminished in the solids obtained from all biomass treatments, especially those treated with 5.6wt.% sulfuric acid where its content decreased 91.8%. Solids obtained from biomass treated with IL at 6.2 – 6.5 wt.% showed a decrease of 44.1% whereas those from biomass treated with IL at 41.0-85.2 showed an average decrease of 71.7%. The acetyl content in the solids at these IL concentrations was relatively constant and averaged in 1.1 wt.%, suggesting that at IL concentrations above 41.0 wt.% the hemicellulose hydrolysis achieved its maximum efficiency. Compared with the sulfuric acid treatment, the solids were in average, 6.8-fold

https://doi.org/10.32933/ActaInnovations.46.3 • ISSN 2300-5599 •

richer, for IL concentrations at 6.2-6.5 wt.%, and 3.4-fold richer for IL concentrations at 41.0-85.2 wt.% indicating a higher efficiency of dilute sulfuric acid to hydrolyze hemicellulose.

- Arabinoxylan content

Solids obtained from sulfuric acid treated biomass diminished 86.8% their arabinoxylan content when compared with the original biomass, whereas solids obtained from IL treated biomass decreased on average 17.9% at IL concentrations in the range of 6.2-6.5 wt.% and 42.5% for IL concentrations in the range of 41.0 to 73.6 wt.%, from then on, its content decreased continuously to a final decrease of 48.8% at IL concentration of 85.2 wt.%. These results show that the arabinoxylan hydrolysis efficiencies were relatively constant at IL concentrations between 41.0 to 73.6 wt.% and increased as the IL concentration increased further but decreased if the IL concentration was low. Compared to the sulfuric acid treatment, the arabinoxylan contents in the solids obtained from IL treatments were 4 to 5.5-fold higher indicating a far greater hydrolytic capacity of dilute sulfuric acid over IL.

Table 4. Solid yield and composition after sugarcane biomass treatment with [EMIM][HSO_4] for 83 min at 120°C at the indicated IL and biomass mass fractions. Biomass treatment with dilute H_2SO_4 at the same conditions are shown for comparison. *Source: Authors results*

Catalyst	Catalyst mass fraction (wt.%)	Biomass mass fraction (wt.%)	Component content in solids (wt.%)								Solid Yield (wt.%)
			Glucan	Xylan	Arabinan	Arabinoxylan	Acetyl	Lignin	Ashes	Others	
[EMIM][HSO_4]	0.0	10.9	38.9	21.7	2.0	23.7	4.0	23.2	4.5	5.8	101.1
	0.0	5.7	40.0	22.4	2.4	24.8	4.1	21.9	2.6	6.6	101.0
	0.0	3.9	39.8	21.9	2.2	24.1	4.1	20.1	3.9	8.0	101.2
	6.2	9.0	43.9	16.2	1.7	18.0	2.2	26.5	9.1	0.3	82.1
	6.5	5.3	43.7	15.8	1.9	17.7	2.1	25.4	8.9	2.2	80.7
	41.0	3.8	50.9	13.7	1.3	14.9	1.2	25.8	5.6	1.5	74.3
	44.6	10.7	47.3	12.5	1.2	13.7	1.2	23.8	11.1	3.0	75.4
	46.4	7.2	49.1	12.9	1.0	13.9	1.2	24.7	8.3	2.9	73.2
	64.1	5.9	50.9	12.9	1.2	14.1	1.0	25.8	4.6	3.6	69.4
	68.5	6.3	49.4	12.5	2.1	14.6	1.2	28.4	5.7	0.7	68.4
	73.6	6.7	48.5	13.1	1.0	14.1	1.0	28.3	4.6	3.6	70.9
	78.0	7.2	47.6	12.2	1.0	13.3	1.1	28.2	7.7	2.2	72.8
	85.2	8.9	47.8	11.7	1.0	12.7	1.1	24.4	12.4	1.7	72.5
H_2SO_4	5.6	16.1	52.6	2.5	0.7	3.2	0.3	32.4	7.9	3.5	65.3

Polysaccharide recovery

The recovery of the constituents was analyzed after calculating their yields in the solid residue and plotted against their yields and of their degradation products (furfural or 5-HMF) in the liquid phase.

Glucan recovery

The residual glucan yield fluctuated around 98 mol% up to an IL concentration of 46.5 wt.%, and then it decreased slightly up to an IL concentration of 68.5 wt.%, whereupon it fluctuated around 94 mol%, which also coincided with a decrease in its content in the solids (Table 4). When added to its and of 5-HMF yields in the liquid phase, the glucan recovery in the biomass treated with no catalyst was higher than 100 mol%, near 107.5 mol%. That might be the result of an overestimation of the glucan content in the solids. Glucan recovery for biomass treated with either 5.6 wt.% sulfuric acid or IL in the range of 6.2 – 64.1 wt.% was near 100 mol%, showing that at IL concentrations where the hydrolysis yields were the greatest (Table 3), there was no glucan loss. At higher IL concentrations the recovery oscillated near 96.1 mol% that might be the result of degradation into non quantified products. Nevertheless, results show a high glucan recovery in all biomass treatments and a greater contribution of hydrolyzed glucan at IL concentration in the range of 41.0 – 86.2 mol%. They also show a much greater hydrolyzed glucan in diluted sulfuric acid treated biomass, despite an obtained solid richer in glucan (Figure 2 and Table 4).

Arabinoxylan recovery

At IL concentration of 6.2 wt.%, 60 mol% of the biomass arabinoxylan remained in the solid. As the IL concentration rose from 46.4 up to 73.6 wt.%, the remaining arabinoxylan fluctuated around 40 mol% and decreased slightly as the IL concentration increased to 78.0 and 85.2 wt.%. Treatments in the range of 41.0 to 68.5 wt.% resulted with total arabinoxylan recovery with results constant near 107.0 mol%. As the IL rose, the recovery dropped with concomitant increase of furfural production yield. At the highest IL concentration, the recovery was 87.7 mol%, representing a 12.3 mol% loss. These indicate that the decrease in the observed pentose yield at the highest IL concentrations (Table 3) was not due to a decrease in the IL hydrolysis efficiency but due to further degradation of pentoses into furfural and into volatile and non-quantified compounds. If the hydrolysis efficiency had decreased under high IL concentrations, the arabinoxylan remained in the solids should have increased, rather than remaining constant in 40 mol%. A recovery of just 88.4 mol% for treatments at 6.2 – 6.5 wt.% IL concentration, and well above the 100 mol% for treatments at 41.0 wt.% IL concentration were observed for reasons not understood (Figure 3). Arabinoxylan recovery for biomass treated with dilute H_2SO_4 was 98.3 mol% showing almost a complete recovery of all biomass arabinoxylan. Its content in the residual solid was only 8.6 mol%, most of it was in the liquid phase either as hydrolyzed pentose or as furfural (Figure 3) explaining why the solid was so enriched in glucan (Table 4) despite the higher glucan hydrolysis yield (Table 3).

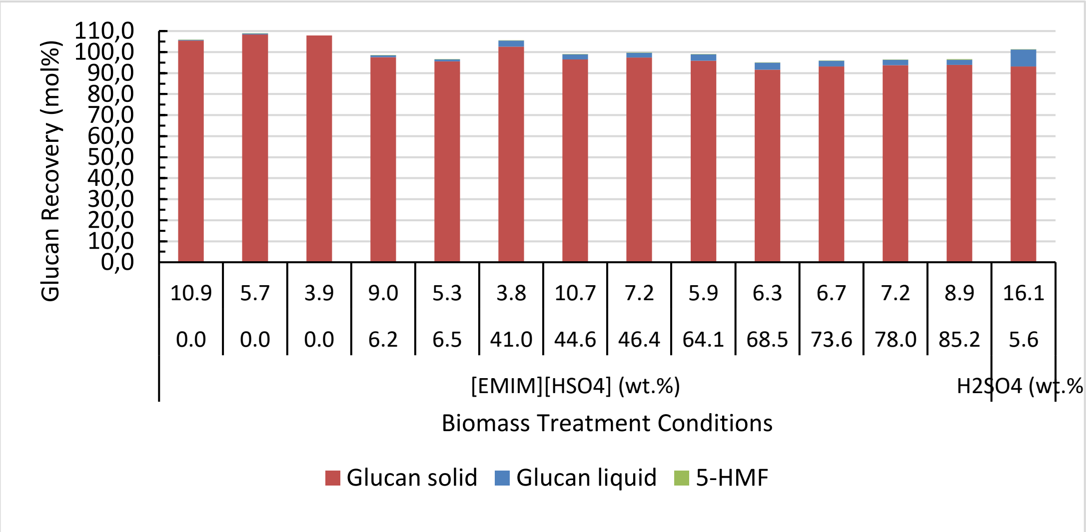

Figure 2. Glucan recovery after biomass treatment at different ionic liquid (upper line) and biomass (lower line) concentrations. Biomass treated with diluted sulfuric acid are shown for comparison. Biomass treatment conditions were as described in materials and methods. *Source: Authors results*

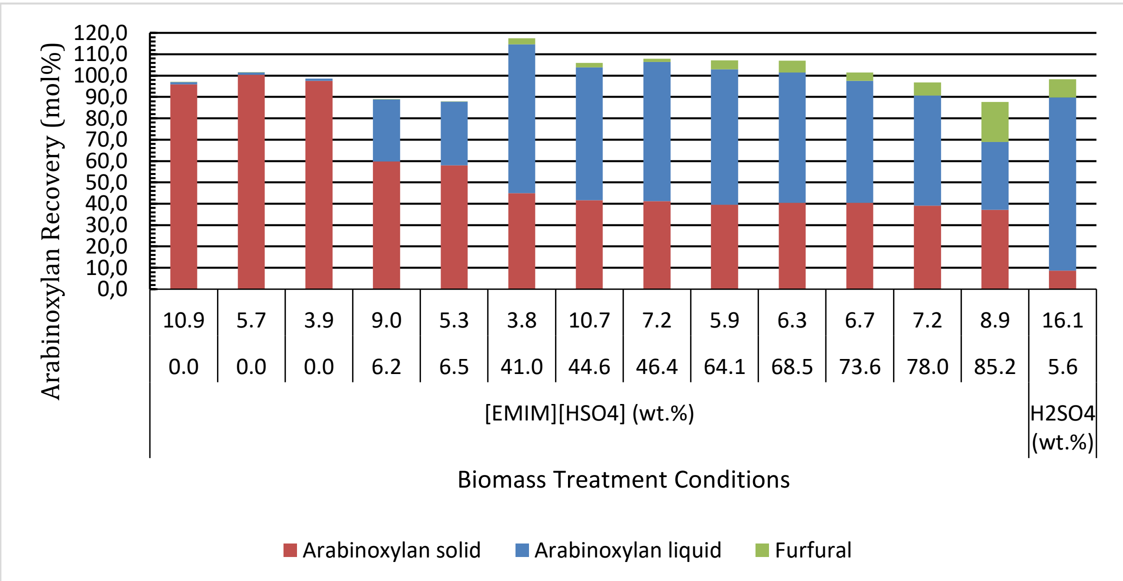

Figure 3. Arabinoxylan recovery after biomass treatment at different ionic liquid (upper line) and biomass (lower line) concentrations. Biomass treated with diluted sulfuric acid are shown for comparison. Biomass treatment conditions were as described in materials and methods. *Source: Authors results.*

Acetyl recovery

The acetyl group remaining in the solid residues showed the same trend observed for arabinoxylan, oscillating around 22.6 mol% in the IL concentration range of 41.0-46.4 wt.% and then around 19.1 mol% at IL concentrations of 64.1-85.2 wt.%, further suggesting that the at high IL concentration there was no decrease in its hydrolysis efficiency (Figure 4). The acetyl recovery was almost complete at IL concentrations where the pentoses hydrolysis yield were the highest (Table 3). It showed a slight decrease to values near 93.6 mol% at 64.1-78.0 wt.% IL and decreased considerably to 58.3 mol% at the highest IL concentration, showing a high acetyl loss at this treatment condition. Biomass treated with dilute sulfuric acid resulted in solids with only 5.4 mol% acetyl group, four times lower than those obtained with IL, which indicates the higher hydrolytic efficiency of dilute sulfuric acid towards hemicellulose. Most of the acetyl group was in the liquid phase, yet the acetyl recovery was 85.2 mol% suggesting a 14.8 mol% of acetyl loss.

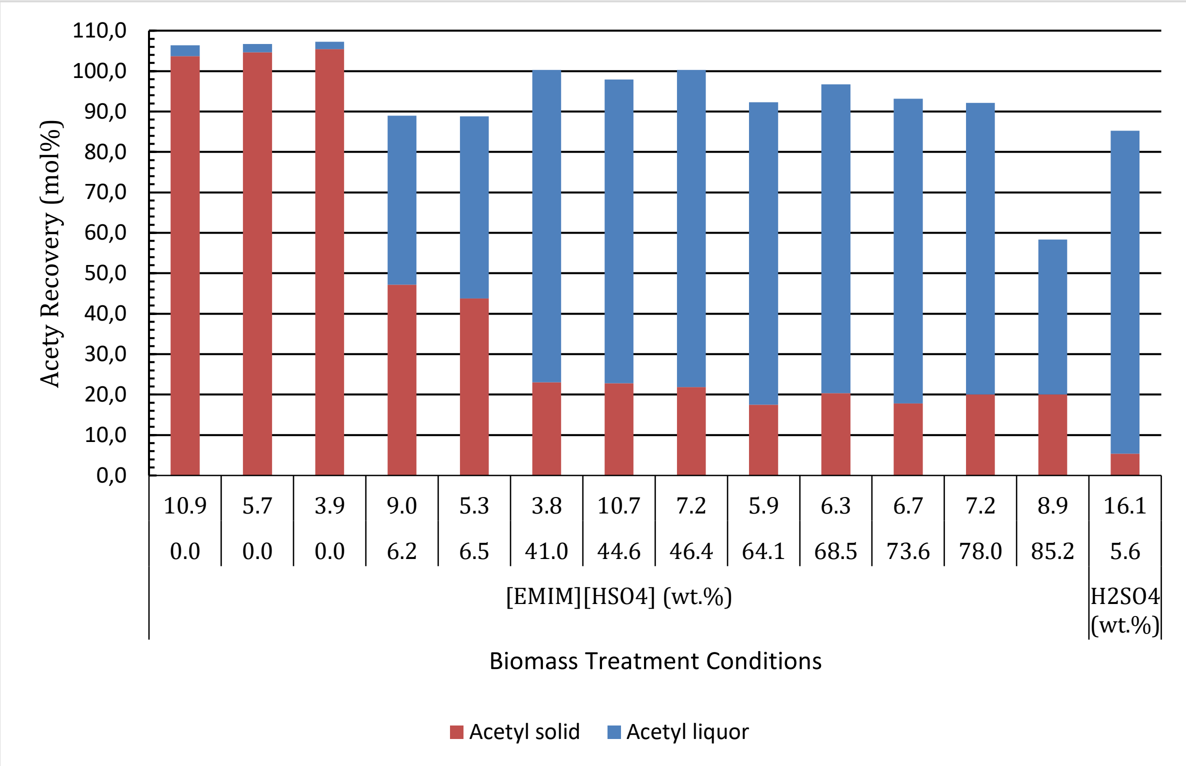

Figure 4. Acetyl recovery after biomass treatment at different ionic liquid (upper line) and biomass (lower line) concentrations. Biomass treated with diluted sulfuric acid are shown for comparison. Biomass treatment conditions were as described in materials and methods. *Source: Authors results*.

Discussion

This study compared the uses of [EMIM][HSO_4] and diluted sulfuric for the treatment of sugarcane biomass. Sugarcane biomass was treated at several IL and biomass fractions, or with diluted sulfuric acid with the same mass concentration and molar content used for the lowest IL concentration. Such condition was met by iterative calculations as demonstrated in section sulfuric acid, water, and biomass content calculations. Sugarcane biomass treated with IL up to 44.6 wt.% produced a syrup highly enriched in pentose with minimal contamination of glucose and furans. As the IL concentration increased, the furfural production yield increased concomitantly to the pentose yield decrease, resulting in a syrup with a high mass proportion of furfural, specially at the highest IL concentration. Furthermore, the pentose recovery decreased with the increase of the IL concentration, but at these higher IL concentrations, the arabinoxylan and acetyl contents in the solid were essentially the same of those found at 44.6 wt.% IL (Table 4), where the maximum pentose yield was obtained in the syrup, indicating that the observed decreased of the pentose yield at these high IL concentrations, consequently low water content, was not due to a lower IL hydrolysis efficiency, but due to further degradation of pentose and furfural into non quantified or volatile products. At very low water content, acidic ionic liquids tend to form degradation products along with biomass, particularly if treatment conditions are very severe [27,28]. Similar results were also found by da Costa Lopes et al. [16] when treating wheat straw with [EMIM][HSO_4] at different IL concentrations and temperatures. High pentose yields were obtained at moderate treatment severity with similar IL concentration and water content. At higher treatment severity, furfural yields rose to values near 30 butyl-3-methylimidazolium hydrogen sulfate [BMIM][HSO_4], where lignocellulosic biomass treatment at moderate IL concentrations results in hemicellulose hydrolysis near 40% with negligible furfural co-production [29]. Furfural production with yields in the range of 13-33% was favored when biomass was treated at low water content [14,17], especially when treated with superacidic ionic liquids [12]. Despite this, when biomass is treated with acidic ionic liquids, a syrup enriched with free pentoses and a cellulose-enriched solid are obtained. This solid is prone to enzymatic hydrolysis [16,30,31], and its hydrolysis yield is superior to that which results from treating biomass with dilute acid [32]. As compared with IL treatment, dilute acid treatment resulted in a solid residue not only enriched with but possessing a higher glucan content and far less arabinoxylan content (Table 4), making it an obvious substrate to produce glucose syrups via enzymatic hydrolysis, since dilute acid pre-treated biomass is more prone to enzymatic hydrolysis than the nontreated ones [33]. The hemicellulose hydrolysis yield (Table 3) and the pentose content in the resulting syrup were also higher (Table 2), and since the costs in using dilute sulfuric acid are much less than using ionic liquid, one may ask why ionic liquids should be used to treat lignocellulosic biomass after all. The reasons are many, despite the hemicellulose hydrolysis yield (Table 3) and the amount of free pentoses in the resulting syrup were smaller, they were significant at 41.0 to 64.1 wt.% IL concentration (Table 2). They were also richer in free pentoses and far less contaminated with glucose and furans, therefore treatments with IL result in a liquid stream with concentrated and purer free pentoses. It could also be argued that the higher amount of glucose and furans in the syrups obtained by treating sugarcane biomass with dilute sulfuric acid was due to the concentration used, 6.7 wt.% with a corresponding mass fraction of 5.6 wt.%. The acidic strength of H_2SO_4 is much stronger than that of HSO_4^-, which pKa at room temperature is 1.9, consequently the H^+ molar content, in the sulfuric acid treatment would be equimolar to H_2SO_4 whereas in the IL treatment it would be less than HSO_4^- molar content. In fact, treatment of *Sorghum* biomass with 0.2 mol/L (approximately 2 wt.%) sulfuric acid at 121°C for 120 min [26], resulted in free pentose and furfural production yields close to those found by treating sugarcane biomass with IL in the range of 41-46.4 wt.%, however despite the temperature used was near of that used in this study, it took to 37 minutes longer to reach similar free pentose yield found in this study. High free pentose yields when treating lignocellulosic biomass with sulfuric acid with concentrations of 2 wt.% or less are achieved only at long treatment times or high temperatures but in this case, the furfural and glucose yields are similar to those found at this study [32]. When biomass of Bamboo was treated with 0.2 mol/L sulfuric acid for 2h the glucose production yield was not much different of that found when treated with 0.6 mol/L sulfuric acid, a concentration close to the one used in this work, besides the glucose production yield was also very near to that found at this work [32] (Table 3). Therefore, biomass treatment with dilute sulfuric acid in concentrations below or near 2wt.% must be performed at high temperatures and long times to achieve high hydrolysis yield. Acidic IL despite having lower acidic strength, its organic cation moiety interaction with biomass increases considerably its hydrolysis efficiency [18,19,34] explaining the efficiencies found at IL concentration in the range of 41.0-64.1 wt.%. The second reason in using IL against dilute acid is the concentration itself. While biomass can be treated with pure IL or with mixture of IL with very low water content, where some biomass degradation may occur, the same cannot be performed with mineral acids where considerable biomass degradation and loss of yield occur as the concentration increases. In other words, to achieve high hydrolysis yield with low degradation, biomass must be treated with dilute acid resulting in a liquid stream with a very large water content as opposed to IL where high hydrolysis yield can be accomplished with IL at 41-64 wt.% or even higher, resulting in a liquid stream with low water content, in the range 40-60 wt.% or less, which greatly facilitates the recovery of sugars and of the IL itself. The recovery of sugars and IL usually is done by the addition of anti-solvents, and as less water is present in the liquid stream, less anti-solvent and energy shall be required for the separation, thus making the whole process much more environmentally and economically sustainable, provided the IL is recycled. The third reason is the versatility that the acidic IL may offer regarding the desired product simply by tuning the biomass treatment conditions. At the highest IL concentration, a relatively high hemicellulose hydrolysis yield is achieved, and the obtained syrup is highly enriched with furfural. Moreover, furfural can be extracted with a green solvent and the hydrolyzed pentoses can be separated and recovered with considerable purity and the IL recycled [15] processes favored by the low water content. Treatments with dilute H_2SO_4, on the other hand, do not possess such versatility. Despite selectively hydrolyzing hemicellulose at a higher yield, the resulting syrup contains high amounts of glucose, furfural, and high-water content rendering the recovery process more difficult.

Impact

Furans, especially furfural and xylose are compounds of increasing interest, furans are important chemical platform [35] from which several compounds can be synthesized. Xylose is the precursor of furfural and also can be used to produce several other chemicals such as xylitol [36–38] . This increased interest has prompted several investigations in how to obtain these compounds in high yields and in an environmentally sustainable manner from lignocellulosic biomass [36,39–41]. To this end, biomass pretreatments methods applying dilute mineral acid [36,37,39,42,43], solvolysis and green solvents, among them, molten salts [39], deep eutectic solvents [39,44–46] and ionic liquids [39,47–50] were investigated. Each of these approaches have clear advantages and disadvantages concerning the environmental impact, reusability, and economical feasibility. Nevertheless, the conventional processes still used for furfural production lignocellulosic biomasses are uneconomical since it is produced from a diluted xylose solution, obtained from acid-catalyzed hydrolysis of biomass rich in hemicellulose. Xylose on the other hand, can be recovered after evaporation of the excess of water and the addition of an antisolvent, resulting in an energy-intensive process [36,51]. This work contributes to the state of art of knowledge as it compares two hemicellulose hydrolysis methods: the classical dilute sulfuric acid, and the acidic ionic liquid [EMIM][HSO_4] using a different approach. It indicates that the biomass treatment with acidic IL has many advantages over the dilute sulfuric acid treatment, among them, the use of less water and less solvent to recover the products, xylose and furfural. This work shall contribute to the decision-making and paves the way to the development of new technologies to produce pentoses and furfural of high qualities in a sustainable manner. It is also an UpToDate investigation for the industrial technology still uses diluted acid to produce xylose and furfural, resulting in a diluted solution which is one of the difficulties to their recovery.

Conclusions

The stepwise evaluation of the reaction conditions for the use of the ionic liquid [EMIM][HSO_4] for sugarcane bagasse treatment enabled the identification of reaction conditions for the selective hydrolysis of hemicellulose into xylose with high yields, and at the same time, lessening the dehydration of xylose into furfural, and the release of glucose from the cellulose. In contrast, the use of dilute sulfuric acid results in xylose syrup highly contaminated with furfural and glucose. Unlike the use of sulfuric acid, the use of 1-ethyl-3-methylimidazolium hydrogen sulfate can be tuned either towards the predominant formation of xylose with very low degradation to furfural or towards an increase in furfural production. In both cases, a solid cellulose-lignin residue is obtained that can be further used for the production of glucose syrups via enzymatic hydrolysis. In a biorefinery context, these findings can enable the customized production of either a xylose-rich or a furfural-rich stream.

Author Contributions

Marcoaurélio Almenara Rodrigues contributed to the conception and execution of experiments, the analysis of data, and the writing of this manuscript. Andre M. da Costa Lopes contributed to the conception and execution of experiments, the analysis of data, and to the review and critique of this manuscript. Rafal M. Lukasik contributed to the conception of the scientific problem, the analysis and interpretation of the data, and the critical revision of this manuscript regarding both its coherence and scientific contribution. All authors have given approval to the final version of this manuscript.

Funding Sources

This work, done at the Biomass and Bioenergy Research Infrastructure (BBRI) – LISBOA – 01-0145-FEDER-022059, was supported by the Operation Program for Competitiveness and Internalization (PORTUGAL2020), by the Lisbon Portugal Regional Operation Program (Lisboa 2020), and by the North Portugal Regional Operation Program (Norte 2020) under the Portugal 2020 Partnership Agreement through the European Regional Development Fund (ERDF). Additionally, this research was supported by the Fundação para a Ciência e a Tecnologia (FCT, Portugal) through grants SFRH/BD/90282/2012 (AMdCL) and IF/00471/2015 (RML). This work was also supported by CAPES (Brazil) through the CAPES 371/14, AUXPE Nr 0005/2015, project 23038.002463/2014–98.

Conflict of Interest

There are no conflicts to declare

Acknowledgment

Dr. Marcoaurélio Almenara Rodrigues acknowledges the financial support received through a post-doctoral scholarship from CAPES (Brazil), BEX n° 10189/14-9. The authors also wish to thank Mrs. Maria do Céu Penedo for help in the execution of the HPLC analysis.

References

[1] A. Pandey, C.R. Soccol, P. Nigam, V.T. Soccol, Biotechnological potential of agro-industrial residues. I: sugarcane bagasse, Bioresour. Technol. 74 (2000) 69–80. https://doi.org/10.1016/S0960-8524(99)00142-X.

[2] M.E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik, Ionic liquid-mediated formation of 5-

hydroxymethylfurfural-A promising biomass-derived building block, Chem. Rev. 111 (2011) 397–417.https://doi.org/10.1021/cr100171a.

[3] Y. Luo, Z. Li, X. Li, X. Liu, J. Fan, J.H. Clark, C. Hu, The production of furfural directly from hemicellulose in lignocellulosic biomass: A review, Catal. Today. 319 (2019) 14–24. https://doi.org/10.1016/j.cattod.2018.06.042.

[4] L. de F. Vilela, V.P.G. de Araujo, R. de S. Paredes, E.P. da S. Bon, F.A.G. Torres, B.C. Neves, E.C.A. Eleutherio, Enhanced xylose fermentation and ethanol production by engineered Saccharomyces cerevisiae strain, AMB Express. 5 (2015) 16. https://doi.org/10.1186/s13568-015-0102-y.

[5] P.J. Du Toit, S.P. Olivier, P.L. Van Biljon, Sugar cane bagasse as a possible source of fermentable carbohydrates. I. Characterization of bagasse with regard to monosaccharide, hemicellulose, and amino acid composition, Biotechnol. Bioeng. 26 (1984) 1071–1078.

[6] F.M. Gírio, C. Fonseca, F. Carvalheiro, L.C. Duarte, S. Marques, R. Bogel-Łukasik, Hemicelluloses for fuel ethanol: A review, Bioresour. Technol. 101 (2010) 4775–4800. https://doi.org/10.1016/j.biortech.2010.01.088.

[7] V. Kumar, P. Binod, R. Sindhu, E. Gnansounou, V. Ahluwalia, Bioconversion of pentose sugars to value added chemicals and fuels: Recent trends, challenges and possibilities, Bioresour. Technol. 269 (2018) 443–451. https://doi.org/10.1016/j.biortech.2018.08.042.

[8] B. Kamm, P.R. Gruber, M. Kamm, Biorefineries–Industrial Processes and Products, Ullmann's Encycl. Ind. Chem. (2016) 1–38. https://doi.org/doi:10.1002/14356007.l04_l01.pub2.

[9] T. Ståhlberg, W. Fu, J.M. Woodley, A. Riisager, Synthesis of 5-(hydroxymethyl)furfural in ionic liquids: Paving the way to renewable chemicals, ChemSusChem. 4 (2011) 451–458. https://doi.org/10.1002/cssc.201000374.

[10] M.H.L. Silveira, A.R.C. Morais, A.M. Da Costa Lopes, D.N. Olekszyszen, R. Bogel-Łukasik, J. Andreaus, L. Pereira Ramos, Current Pretreatment Technologies for the Development of Cellulosic Ethanol and Biorefineries, ChemSusChem. 8 (2015) 3366–3390. https://doi.org/10.1002/cssc.201500282.

[11] V.T. de O. Santos, G. Siqueira, A.M.F. Milagres, A. Ferraz, Role of hemicellulose removal during dilute acid pretreatment on the cellulose accessibility and enzymatic hydrolysis of compositionally diverse sugarcane hybrids, Ind. Crops Prod. 111 (2018) 722–730. https://doi.org/10.1016/j.indcrop.2017.11.053.

[12] W. Hui, Y. Zhou, Y. Dong, Z.J. Cao, F.Q. He, M.Z. Cai, D.J. Tao, Efficient hydrolysis of hemicellulose to furfural by novel superacid SO4H-functionalized ionic liquids, Green Energy Environ. 4 (2019) 49–55. https://doi.org/10.1016/j.gee.2018.06.002.

[13] N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, Bioresour. Technol. 96 (2005) 673–686. https://doi.org/10.1016/j.biortech.2004.06.025.

[14] A. V. Carvalho, A.M. Da Costa Lopes, R. Bogel-Łukasik, Relevance of the acidic 1-butyl-3-methylimidazolium hydrogen sulphate ionic liquid in the selective catalysis of the biomass hemicellulose fraction, RSC Adv. 5 (2015) 47153–47164. https://doi.org/10.1039/c5ra07159c.

[15] A.M. da Costa Lopes, R.M. Łukasik, Separation and Recovery of a Hemicellulose-Derived Sugar Produced from the Hydrolysis of Biomass by an Acidic Ionic Liquid, ChemSusChem. 11 (2018) 1099–1107. https://doi.org/10.1002/cssc.201702231.

[16] A.M. da Costa Lopes, R.M.G.G. Lins, R.A. Rebelo, R.M. Lukasik, Biorefinery approach for lignocellulosic biomass valorisation with an acidic ionic liquid, Green Chem. 20 (2018) 4043–4057. https://doi.org/10.1039/c8gc01763h.

[17] J.R. Bernardo, F.M. Gírio, R.M. Łukasik, The effect of the chemical character of ionic liquids on biomass pre-treatment and posterior enzymatic hydrolysis, Molecules. 24 (2019) 808. https://doi.org/10.3390/molecules24040808.

[18] A. Sant'Ana da Silva, S.H. Lee, T. Endo, E.P. Bon, Major improvement in the rate and yield of enzymatic saccharification of sugarcane bagasse via pretreatment with the ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]), Bioresour. Technol. 102 (2011) 10505–10509. https://doi.org/10.1016/j.biortech.2011.08.085.

[19] B.M. Matsagar, P.L. Dhepe, Brönsted acidic ionic liquid-catalyzed conversion of hemicellulose into sugars, Catal. Sci. Technol. 5 (2015) 531–539. https://doi.org/10.1039/c4cy01047g.

[20] A.S. Amarasekara, B. Wiredu, Degradation of Cellulose in Dilute Aqueous Solutions of Acidic Ionic Liquid 1-(1-Propylsulfonic)-3-methylimidazolium Chloride, and p-Toluenesulfonic Acid at Moderate Temperatures and Pressures, Ind. Eng. Chem. Res. 50 (2011) 12276–12280. https://doi.org/Doi 10.1021/Ie200938h.

[21] A. Rusanen, K. Lappalainen, J. Kärkkäinen, T. Tuuttila, M. Mikola, U. Lassi, Selective hemicellulose hydrolysis of Scots pine sawdust, Biomass Convers. Biorefinery. 9 (2019) 283–291.

https://doi.org/10.1007/s13399-018-0357-z.
[22] A. Sluiter, B. Hames, D. Hyman, C. Payne, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, J. Wolfe, Determination of total solids in biomass and total dissolved solids in liquid process samples, National Renewable Energy Laboratory, Golden, Colorado, USA, 2008.
[23] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Determination of structural carbohydrates and lignin in biomass - Laboratory Analytical Procedure (LAP), National Renewable Energy Laboratory, Golden, Colorado, USA, 2011.
[24] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, Determination of Ash in Biomass, National Renewable Energy Laboratory - NREL, Golden, Colorado, USA, 2005.
[25] S.P. Magalhães da Silva, A.M. da Costa Lopes, L.B. Roseiro, R. Bogel-Łukasik, Novel pre-treatment and fractionation method for lignocellulosic biomass using ionic liquids, RSC Adv. 3 (2013) 16040–16050. https://doi.org/10.1039/c3ra43091j.
[26] N.N. Deshavath, M. Mohan, V.D. Veeranki, V. V Goud, S.R. Pinnamaneni, T. Benarjee, Dilute acid pretreatment of sorghum biomass to maximize the hemicellulose hydrolysis with minimized levels of fermentative inhibitors for bioethanol production, 3 Biotech. 7 (2017) 139. https://doi.org/10.1007/s13205-017-0752-3.
[27] A. Brandt, M.J. Ray, T.Q. To, D.J. Leak, R.J. Murphy, T. Welton, Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid–water mixtures, Green Chem. 13 (2011) 2489–2499. https://doi.org/10.1039/c1gc15374a.
[28] F. Tao, H. Song, L. Chou, Catalytic conversion of cellulose to chemicals in ionic liquid, Carbohydr. Res. 346 (2011) 58–63. https://doi.org/10.1016/j.carres.2010.10.022.
[29] Z. Chen, J. Long, Organosolv liquefaction of sugarcane bagasse catalyzed by acidic ionic liquids, Bioresour. Technol. 214 (2016) 16–23. https://doi.org/10.1016/j.biortech.2016.04.089.
[30] Z. Wang, J. Gräsvik, L.J. Jönsson, S. Winestrand, Comparison of [HSO4]−, [Cl]− and [MeCO2]− as anions in pretreatment of aspen and spruce with imidazolium-based ionic liquids, BMC Biotechnol. 17 (2017) 82. https://doi.org/10.1186/s12896-017-0403-0.
[31] P. Halder, S. Kundu, S. Patel, A. Setiawan, R. Atkin, R. Parthasarthy, J. Paz-Ferreiro, A. Surapaneni, K. Shah, Progress on the pre-treatment of lignocellulosic biomass employing ionic liquids, Renew. Sustain. Energy Rev. 105 (2019) 268–292. https://doi.org/10.1016/j.rser.2019.01.052.
[32] M. Mohan, N.N. Deshavath, T. Banerjee, V. V Goud, V.V. Dasu, Ionic Liquid and Sulfuric Acid-Based Pretreatment of Bamboo: Biomass Delignification and Enzymatic Hydrolysis for the Production of Reducing Sugars, Ind. Eng. Chem. Res. 57 (2018) 10105–10117. https://doi.org/10.1021/acs.iecr.8b00914.
[33] A.S. Patri, L. McAlister, C.M. Cai, R. Kumar, C.E. Wyman, CELF significantly reduces milling requirements and improves soaking effectiveness for maximum sugar recovery of Alamo switchgrass over dilute sulfuric acid pretreatment, Biotechnol. Biofuels. 12 (2019) 177. https://doi.org/10.1186/s13068-019-1515-7.
[34] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, Determination of ash in biomass. NREL Laboratory Analytical Procedure (LAP), 2008. http://www.nrel.gov/docs/gen/fy08/42622.pdf.
[35] R. Bielski, G. Grynkiewicz, Furan platform chemicals beyond fuels and plastics, Green Chem. 23 (2021) 7458–7487. https://doi.org/10.1039/d1gc02402g.
[36] S.J. Chen, X. Chen, M.J. Zhu, Xylose recovery and bioethanol production from sugarcane bagasse pretreated by mild two-stage ultrasonic assisted dilute acid, Bioresour. Technol. 345 (2022) 126463. https://doi.org/10.1016/j.biortech.2021.126463.
[37] H. Xu, X. Li, W. Hu, L. Lu, J. Chen, Y. Zhu, H. Zhou, C. Si, Recent advances on solid acid catalyic systems for production of 5-Hydroxymethylfurfural from biomass derivatives, Fuel Process. Technol. 234 (2022) 107338. https://doi.org/10.1016/j.fuproc.2022.107338.
[38] Y. Dai, S. Yang, T. Wang, R. Tang, Y. Wang, L. Zhang, High conversion of xylose to furfural over corncob residue-based solid acid catalyst in water-methyl isobutyl ketone, Ind. Crops Prod. 180 (2022) 114781. https://doi.org/10.1016/j.indcrop.2022.114781.
[39] J.Y. Zhu, X. Pan, Efficient sugar production from plant biomass: Current status, challenges, and future directions, Renew. Sustain. Energy Rev. 164 (2022) 112583. https://doi.org/10.1016/j.rser.2022.112583.
[40] E.K. New, S.K. Tnah, K.S. Voon, K.J. Yong, A. Procentese, K.P. Yee Shak, W. Subramonian, C.K. Cheng, T.Y. Wu, The application of green solvent in a biorefinery using lignocellulosic biomass as a feedstock, J. Environ. Manage. 307 (2022) 114385. https://doi.org/10.1016/j.jenvman.2021.114385.
[41] S. Dutta, Valorization of biomass-derived furfurals: reactivity patterns, synthetic strategies, and applications, Biomass Convers. Biorefinery. (2021). https://doi.org/10.1007/s13399-021-01924-w.
[42] K. Świątek, S. Gaag, A. Klier, A. Kruse, J. Sauer, D. Steinbach, Acid hydrolysis of lignocellulosic biomass:

Sugars and furfurals formation, Catalysts. 10 (2020) 437. https://doi.org/10.3390/catal10040437.
[43] Y. Lu, Q. He, Q. Peng, W. Chen, Q. Cheng, G. Song, G. Fan, Directional synthesis of furfural compounds from holocellulose catalyzed by sulfamic acid, Cellulose. 28 (2021) 8343–8354. https://doi.org/10.1007/s10570-021-04070-8.
[44] Z. Zhang, J. Xu, J. Xie, S. Zhu, B. Wang, J. Li, K. Chen, Physicochemical transformation and enzymatic hydrolysis promotion of reed straw after pretreatment with a new deep eutectic solvent, Carbohydr. Polym. 290 (2022) 119472. https://doi.org/10.1016/j.carbpol.2022.119472.
[45] E.L.N. Escobar, M.J. Suota, L.P. Ramos, M.L. Corazza, Combination of green solvents for efficient sugarcane bagasse fractionation, Biomass and Bioenergy. 161 (2022) 106482. https://doi.org/10.1016/j.biombioe.2022.106482.
[46] K.N. Guo, C. Zhang, L.H. Xu, S.C. Sun, J.L. Wen, T.Q. Yuan, Efficient fractionation of bamboo residue by autohydrolysis and deep eutectic solvents pretreatment, Bioresour. Technol. 354 (2022) 127225. https://doi.org/10.1016/j.biortech.2022.127225.
[47] L. Huang, H. Peng, Z. Xiao, H. Wu, G. Fu, Y. Wan, H. Bi, Production of furfural and 5-hydroxymethyl furfural from Camellia oleifera fruit shell in [Bmim]HSO4/H2O/1,4-dioxane biphasic medium, Ind. Crops Prod. 184 (2022) 115006. https://doi.org/10.1016/j.indcrop.2022.115006.
[48] L. Mesa, V.S. Valerio, M.B. Soares Forte, J.C. Santos, E. González, S.S. da Silva, Optimization of BmimCl pretreatment of sugarcane bagasse through combining multiple responses to increase sugar production. An approach of the kinetic model, Biomass Convers. Biorefinery. 12 (2022) 2027–2043. https://doi.org/10.1007/s13399-020-00792-0.
[49] P. Liu, S. Shi, L. Gao, G. Xiao, Efficient conversion of xylan and rice husk to furfural over immobilized imidazolium acidic ionic liquids, React. Kinet. Mech. Catal. 135 (2022) 795–810. https://doi.org/10.1007/s11144-022-02172-3.
[50] K.S. Khoo, X. Tan, C.W. Ooi, K.W. Chew, W.H. Leong, Y.H. Chai, S.H. Ho, P.L. Show, How does ionic liquid play a role in sustainability of biomass processing?, J. Clean. Prod. 284 (2021) 124772. https://doi.org/10.1016/j.jclepro.2020.124772.
[51] H. Mao, S.H. Li, A.S. Zhang, L.H. Xu, H.X. Lu, J. Lv, Z.P. Zhao, Furfural separation from aqueous solution by pervaporation membrane mixed with metal organic framework MIL-53(Al) synthesized via high efficiency solvent-controlled microwave, Sep. Purif. Technol. 272 (2021) 118813. https://doi.org/10.1016/j.seppur.2021.118813.