Valorization of sugarcane bagasse C5-fraction by furfural production mediated by renewable glycine-based ionic liquid

Gustavo R. Gomes [1], Eupídio Scopel [1], Márcia C. Breitkreitz, Camila A. Rezende [*], Julio C. Pastre [*]

Institute of Chemistry, University of Campinas, Unicamp, 13083-970 Campinas, SP, Brazil

ABSTRACT

In this work, a green method to produce furfural from sugarcane bagasse (SCB) acid hydrolysates is proposed *via* a route mediated by a renewable glycine-based ionic liquid, [GlyIm][HSO$_4$], and using a green biphasic system composed of water (reaction solvent) and 2-methyltetrahydrofuran (2-MeTHF - extraction solvent) to avoid side reactions and optimize furfural yields. The process was carried out in two steps: (i) SCB acid hydrolysis and (ii) furfural production from the acid hydrolysates. The best conditions for C5 sugar extraction from sugarcane bagasse (150 °C, 30 min, 4% v/v H$_2$SO$_4$) were determined based on a 2^3 full factorial design. The best conditions extracted up to 85% of hemicellulose, mainly as xylose, resulting in a solid prone to further valorization as a co-product. Optimized conditions for furfural production using xylose as the sugar source (180 °C for 10 min using 10 eq. of ionic liquid) were also determined using a 2^3 full factorial design and resulted in 87 ± 2% of furfural yield. According to the Design of Experiments (DoE), higher furfural yields were achieved at 180 °C, regardless of the reaction time (10 or 60 min). By applying the optimized conditions for furfural production in the sugarcane hydrolysates, a 90% furfural yield was achieved, and no lignin interference was observed in furfural production.

1. Introduction

The use of lignocellulosic substrates to replace non-renewable resources may be achieved by suitable fractionation and conversion methodologies of their components, mainly cellulose, hemicelluloses, and lignin, in a biorefinery concept. Biorefineries are innovative and efficient approaches for biomass valorization to coproduce power, heat, and biofuels alongside food and feed ingredients, pharmaceuticals, chemicals, materials, minerals, and short-cyclic CO$_2$ (Manzanares, 2020). Ideally, these processes must be as green and sustainable as possible, guided by the Green Chemistry Principles, including using non-toxic and renewable solvents and reactants (Erythropel et al., 2018).

Bearing this in mind, the production of value-added chemicals, such as furan derivatives from biomass, corroborates with the biorefinery concept. Furfural is an important building block produced from the C5-sugar chemical platform that is useful as a precursor to obtain materials, green solvents, and bulk and fine chemicals, among others (Xu et al., 2020). Furfural is produced by pentose dehydration, which has already

been evaluated in several reaction media, for instance, in water, organic solvents, and non-conventional systems, *e.g.*, ionic liquids (Chen et al., 2018). However, the use of a single-phase system to produce furanic derivatives usually presents lower yield and selectivity due to competing side reactions, such as rehydration to levulinic acid and condensation forming humins, which occurs mainly in aqueous media using conventional catalysts like mineral acids (*e.g.,* HCl), (Lee and Wu, 2021).

An alternative to optimize furfural yields is by using a biphasic system composed of the reaction solvent, usually water, and an organic extraction solvent to prevent side reactions *via in situ* extraction of furfural while it is produced (Esteban et al., 2020). THF is one of the most efficient extraction solvents reported for furanic derivatives (Román-Leshkov and Dumesic, 2009). However, according to several solvent selection guides, THF is a toxic and non-green solvent (Alder et al., 2016). In addition, the use of THF for furfural extraction demands the addition of a massive load of NaCl to induce the salting-out effect due to the high THF miscibility in pure water. Likewise, 2-MeTHF is a promising substitute for THF as an extraction solvent since both solvents have similar properties, with the advantage of being a bio-based solvent

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immiscible to water (Liu et al., 2020). An additional benefit is that 2-MeTHF has a high partial coefficient for furfural extraction, which means that furfural concentration in 2-MeTHF is around 8 times higher than in water (Lin et al., 2021). 2-MeTHF has some applications as a solvent in organic synthesis; however, it is still poorly explored as an extraction solvent for furfural production (Bijoy et al., 2022).

The use of ionic liquids (ILs) is an interesting approach for sugar dehydration to produce furfural. ILs have compelling properties compared to conventional organic solvents, such as low vapor pressure, tunable polarity, and hydrophilicity according to the cation and anion composition (Lopes, da and Bogel-Łukasik, 2015). The most usual system described in the literature is imidazolium-based ILs as solvent and metal chlorides as external catalysts (Nie et al., 2019; Zhao et al., 2019a, 2019b). However, IL can also play a bifunctional role, acting both as solvent and catalyst, thus eliminating the use of metallic catalysts.

Despite the significant advances brought by the use of ILs in biomass conversion, the typical synthetic procedures to obtain these solvents are not considered green due to the use of toxic and petroleum-based reactants (Singh and Savoy, 2020). To keep the furfural production process as greener as possible, a promising route to produce ILs is through the Debus-Radziszewski imidazole synthesis using amino acids, a renewable source of amino groups as starting material (Kirchhecker and Esposito, 2016). However, despite the significant advantages of using this clean synthesis method, there is still a lack in the use of synthesized ILs to produce sugar derivatives, such as furfural.

To be converted into value-added products, lignocellulosic biomasses are typically prior fractionated into their components using pretreatments. C5 sugars used for furfural production, especially xylose and arabinose, can be obtained, for instance, *via* acid-catalyzed hydrolysis of lignocellulosic biomass, which is a well-established and widespread pretreatment for hemicelluloses extraction (Mikulski and Kłosowski, 2018). Acid-catalyzed hydrolysis is usually carried out using mineral acids (*e.g.,* HCl, H_3PO_4, and often H_2SO_4) (Sivagurunathan et al., 2017), which represent a cheap approach to biomass pretreatments. However, the high cost of neutralization and issues with reactor corrosion due to high acid concentrations are pointed out as the main drawbacks of this method (Dulie et al., 2021; Qi et al., 2018).

Besides extracting hemicellulose, acid-catalyzed hydrolysis does not hinder the further use of the biomass compounds (cellulose and lignin) that remain in the solid fraction. However, the C5 liquid fraction still imposes a considerable challenge for the traditional biotechnological pathway because the acid treatment produces compounds such as furanics, phenolics, and acetic acid that are inhibitory for enzymes and yeasts (Shao et al., 2017). Therefore, the direct use of acid hydrolysates to produce furfural assisted by IL is a promising straightforward pathway for C5 fraction valorization.

Among the available lignocellulosic biomasses, sugarcane bagasse (SCB), the feedstock used in this work, is a key bio-based platform due to its large-scale production as an agro-industrial waste in countries such as Brazil, where its annual production is estimated in more than 592 million tons in 2021/22 (Companhia Nacional de Abastecimento - (CONAB), 2021). Furthermore, acid-catalyzed hydrolysis has been applied to sugarcane bagasse, mainly as a pretreatment to obtain a cellulose-rich solid to facilitate further enzymatic hydrolysis for 2G-ethanol production (Rezende et al., 2011; Shirkavand et al., 2016). Thus, coupling green and efficient methodologies for furfural production from the C5 sugars, commonly neglected in this process, can add value to biomass processing by fulfilling the requirements for a biorefinery approach.

In this work, we proposed a clean strategy for furfural production using a glycine-based IL in a water/2-MeTHF biphasic system assisted by microwave (MW) irradiation. This experimental setup uses green solvents and a renewable-sourced IL, in addition to the high furfural yields obtained. In the first part, we optimized the furfural production using xylose as a model platform and then evaluated the yields in real sugarcane bagasse hydrolysates obtained from acid-catalyzed hydrolysis (Fig. 1). Furthermore, the best conditions for hemicellulose extraction and furfural production were also investigated using Design of Experiments (DoE), which enabled a complete screening of the reaction conditions taking into account interactions between variables. Finally, sugarcane bagasse hydrolysates were also compared with synthetic media to analyze the effect of byproducts extracted together with C5 sugars in the furfural production (*e.g.,* acid-soluble lignin and acetic acid).

2. Material and methods

2.1. Materials and biomass

All reagents used in the experiments were analytical grade. Glycine was purchased from Synth (Diadema, São Paulo, Brazil); sulfuric acid from LS Chemicals (Mumbai, India); Glyoxal 40% in aqueous solution and 2-acetylfuran from Sigma-Aldrich (St. Louis, Missouri, EUA); formaldehyde 37% in aqueous solution and furfural from Neon (Suzano, São Paulo, Brazil). Sugarcane bagasse was kindly donated by Raízen (Piracicaba, Brazil) and dried in a convection oven (Tecnal, TE-394/3) at 60 °C for 6 h before storage.

2.2. Synthesis of glycine-based IL [GlyIm][HSO₄]

20 mmol of glycine (1.50 g), 10 mmol of 37% w/v formaldehyde in aqueous solution (745 μL), and 40% w/v glyoxal in aqueous solution
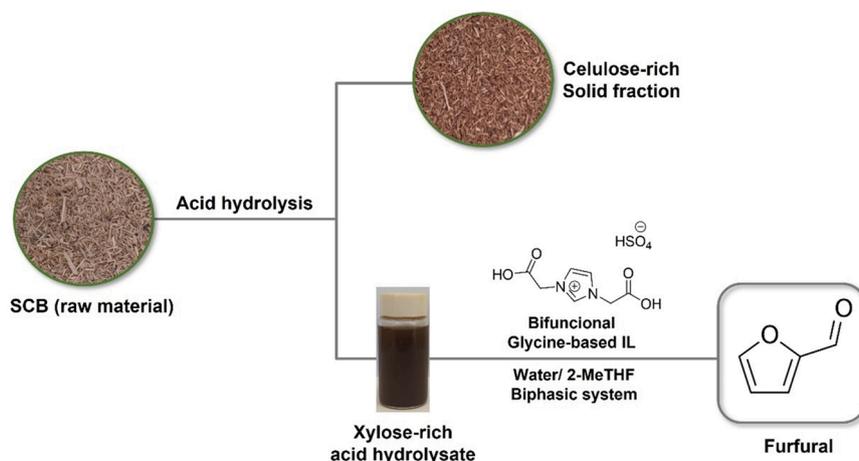
Fig. 1. Schematic representation of furfural production from SCB acid hydrolysates.

(1.14 mL) were added in a round-bottom flask in 40 mL of distilled water. The reaction was stirred for 24 h at room temperature to form the zwitterion intermediate (Kirchhecker et al., 2014). After 24 h, 10 mmol of H_2SO_4 98% (533 µL) were added and heated at 95 °C for 30 min (Albert-Soriano et al., 2018). After this period, water was evaporated, and the product was dried under vacuum to achieve the [GlyIm][HSO_4] (yield: 90%; 2.54 g). The NMR spectra (Fig. S1) is presented in the Support Information.

[GlyIm][HSO_4]: Dark yellow liquid; Tg = - 55 °C; ^{1}H NMR (250 MHz, D$_2$O) δ_H 8.93 (s, 1 H, ArH), 7.57 (d, J = 1.4 Hz, 2 H, ArH), 5.15 (s, 4 H, CH$_2$); ^{13}C NMR (62.5 MHz, D$_2$O) δ_C 169.7; 138.2; 123.4; 50.1; HRMS (ESI+): m/z calculated for $C_7H_9N_2O_4^+$ [cation] 185.05568; found: 185.05555.

2.3. Furfural production

All experiments were conducted in a Biotage® Initiator + Microwave Synthesizer using 5 mL pressurized vials. In a typical experiment, 0.1 mmol of xylose was loaded in a biphasic system composed of 1 mL of distilled water (reaction solvent) and 4 mL of 2-MeTHF (extraction solvent). Temperature (140–180 °C), time (10–60 min), and the quantity of ionic liquid (1–10 Equiv.) were evaluated according to a 2^3 full factorial design. For furfural production from acid hydrolysates, xylose and distilled water were substituted for 1 mL of the acid hydrolysate.

Furfural was analyzed by gas chromatography-mass spectrometry (GC-MS) using an Agilent 7890 GC system. The chromatographic column was an Agilent HP-5MS (60 m length, 0.25 mm diameter, 0.25 µm film). A temperature ramp was used as follows: temperature kept at 40 °C for 1 min, then increased to 90 °C at 10 °C.min^{-1}, then to 280 °C at 30 °C.min^{-1}, and hold for 2 min. The injector and MS source temperatures were 280 and 230 °C, respectively. MS ionization impact was set at 70 eV, and the mass spectrometer was operated with a mass scan range of 30–400 m/z. Furfural quantification was carried out through internal calibration, using 2-acetylfuran as the internal standard (IS). The response factor between furfural and 2-acetylfuran and the furfural concentration from the experiments were determined according to Eq. (1). The yields for furfural production from xylose were calculated according to Eq. (2), where m$_{furfural}$ is the dried mass of furfural obtained in the experiment, m$_{xylose}$ is the dried initial xylose mass and 0.64 is the ratio between the molar masses of furfural and xylose. For furfural production from acid hydrolysates, the total yield was calculated according to the total concentration of pentoses in the matrix (xylose + arabinose).

$$Response \quad factor = \frac{Area_{furfural}}{Area_{IS}} X \frac{[IS]}{[furfural]} \tag{1}$$

$$Furfural \quad (\%) = \frac{m_{furfural}}{m_{xylose} \ X \ 0.64} \ X \ 100 \tag{2}$$

2.4. Sugarcane bagasse (SCB) acid-catalyzed hydrolysis

All experiments were conducted in a stainless-steel reactor using 5 g of raw SCB (dry mass) in 50 mL of water. Time (30–60 min), temperature (100–150 °C), and sulfuric acid concentration (1–4% v/v) were evaluated according to a 2^3 full factorial design with a central point triplicate. After acid hydrolysis, the reactors were cooled in an ice bath for 30 min. Then, the solid fraction was washed with 50 mL of water and filtered in a 149 µm mesh sieve. The SCB acid hydrolysates were used for furfural production without additional treatment.

The volume collected after filtration was measured (Table S1) and the quantification of the acid hydrolysates was carried out by high-performance liquid chromatography (HPLC) according to the NREL protocol (NREL/TP-510–42618) (Sluiter et al., 2012). The hemicellulose extraction yield was calculated according to Eq. (3) where V$_{(recovered)}$ is the volume recovered and shown in Table S1; m$_{biomass}$ is the initial dry

mass in grams; 23.6 is the hemicellulose content in raw SCB; [Xyl], [Ara], [Hac], [Fur] are the xylose, arabinose, acetic acid, and furfural concentrations (g/L), respectively. The hydrolysis factors are 0.88 for xylose and arabinose, 0.72 for acetic acid, and 1.37 for furfural.

$$\begin{aligned} Hemicellulose \quad Extraction \quad (\%) = & \frac{V_{(recovered)}(mL)}{m_{biomass}(g) \times 23.6} \times ([Xyl] \\ & \times 0.88 + [Ara] \times 0.88 + [HAc] \\ & \times 0.72 + [Fur] \times 1.37) \end{aligned} \tag{3}$$

Acid-soluble lignin was quantified according to the NREL protocol (Sluiter et al., 2012) by UV-spectroscopy. Sample pH was adjusted to 10 with NaOH 6.5 mol/L and the measure was carried out at 280 nm.

2.5. Statistical analysis

All statistical calculations, including ANOVA, response surfaces, effects, and model coefficients, were carried out using the software Design Expert (Stat-Ease, USA, version 10).

3. Results and discussion

3.1. Selecting the best conditions for glycine IL-assisted conversion of xylose to furfural

We selected glycine as an amino acid feedstock for synthesizing renewable imidazolium-IL using a green methodology, as described in Fig. 2. As reported in the literature, glycine-based ILs are easily prepared through the Debus-Radziszewski reaction. Glycine-based ILs have already been used to synthesize commercial ILs (Kirchhecker et al., 2014) and conventional organic synthesis (Albert-Soriano et al., 2018), but not to produce furfural, especially from raw feedstocks, like SCB acid hydrolysates. [GlyIm][HSO_4] was obtained in 90% overall yield (for two steps) and characterized by nuclear magnetic ressonance (NMR), high resolution mass spectroscopy (HRMS), and differential scanning calorimetry (DSC) analyses. This IL exhibited a Tg value of − 55 °C, thus being a room-temperature ionic liquid.

The major polysaccharide chains in SCB hemicelluloses are arabinoglucuronoxylans and xyloglucans (Fig. 3) (Neves et al., 2016). Arabinoglucuronoxylans are formed by a main chain of β-(1−4) xylan with ramifications of arabinose or glucuronic acid residues linked to the main chain by α-(1−3) or α-(1−2) bonds, respectively. Xyloglucans, in turn, have a β-(1−4) glucan main chain and ramifications of xylose residues linked by α-(1−6) bonds. In all these structures, the hydroxyl groups may be acetylated in C2 and C3 (Gírio et al., 2010).

According to hemicellulose structure (Fig. 3), xylose residues are the most significant pentoses in SCB that can be converted to furfural. Thus, a 2^3 full factorial design for furfural production from xylose was carried out using the renewable IL [GlyIm][HSO_4] to select the best conditions to be later applied to the raw feedstocks. The levels of each evaluated factor were chosen according to previous works (Gomes et al., 2021, 2018, 2017; Gomes and Pastre, 2020). Temperature (T, 140–180 °C), time (t, 10–60 min), and amount of IL (1–10 eq.) were the factors evaluated in this design, as presented in Table 1.

According to the Pareto Chart (Fig. S2), the amount of [GlyIm][HSO_4] (C) is the most important effect on furfural production. It should be noted that the Pareto chart brings the t-value of the effect (*i.e.*, effect divided by its standard error) and not the standard effect in the y-axis. For the numerical interpretation, we will consider the standard effect values, since they bring a straightforward interpretation of the importance of each variable. The increase in the ionic liquid concentration from 1 eq. to 10 eq. led to a rise of 40.5% in the furfural yield (positive effect; t-value of the effect in Pareto chart = 15.95). The second most important effect was the temperature (A), which was also positive: an increase of the temperature from 140° to 180°C resulted in a rise in furfural near 32.5% (t-value of the effect in Pareto chart = 12.90). Time
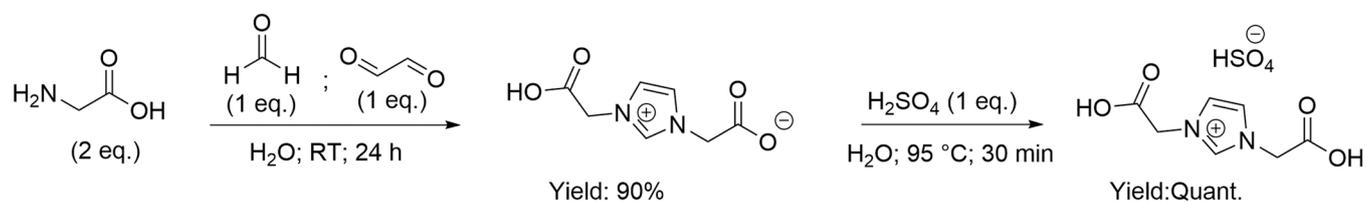
Fig. 2. Synthesis of renewable imidazolium IL [GlyIm][HSO$_4$].
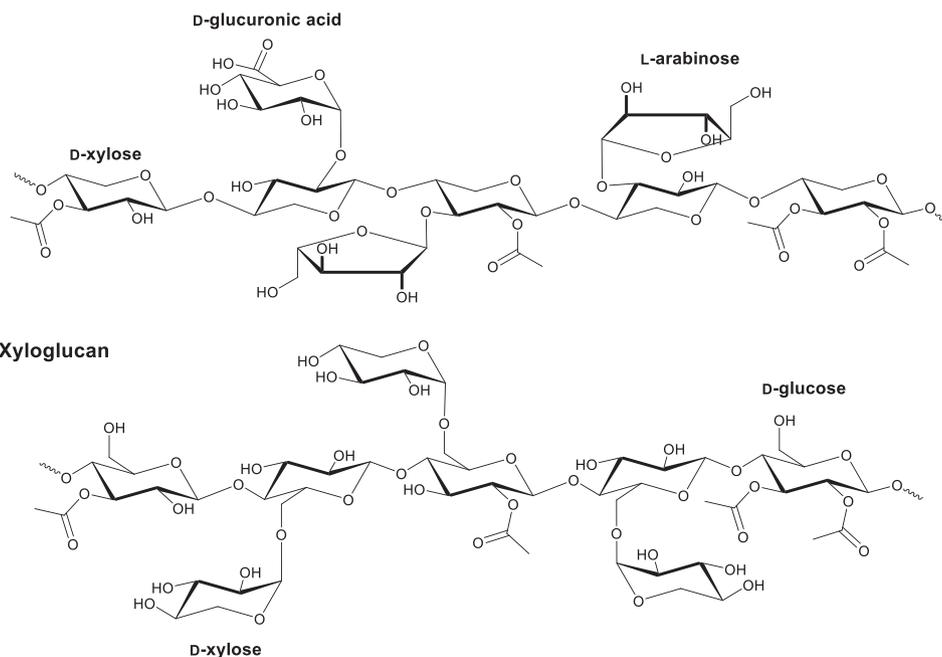
Fig. 3. Main hemicellulose chains from SCB: arabinoglucuronoxylans and xyloglucans.

Table 1
2^3 full factorial design for furfural production from xylose mediated by [GlyIm][HSO$_4$].

Entry	T (°C)	t (min)	IL (eq.)	Furfural (%)
1	140	10	1	1
2	180	10	1	47
3	140	60	1	18
4	180	60	1	68
5	140	10	10	63
6	**180**	**10**	**10**	**85**
7	140	60	10	68
8	**180**	**60**	**10**	**80**
9A	160	35	5.5	74
9B	160	35	5.5	77
9C	160	35	5.5	70
9D	160	35	5.5	78

Conditions: xylose: 0.1 mmol; H$_2$O: 1 mL; 2-MeTHF: 4 mL. The two highest yield values are shown in bold.

(B) presented a small positive effect - slightly significant if the t-value limit is considered and not significant if the Bonferroni limit is considered. The interactions between temperature and ionic liquid (AC) and time and ionic liquid (BC) were also significant, highlighting the importance of using a multivariate approach to study this system. Interaction is significant when the influence of one factor on the response depends on the level of the second factor. On the other hand, the interaction between temperature and time (AB) and the third order interaction (ABC) were not significant. According to Table 1, the two highest furfural yields were achieved at the upper limits of temperature and IL equivalent (180 °C and 10 eq., respectively), and reaction times played a minor role (see entries 6 and 8), which corroborates with the

effect analysis.

To visualize the variable effects, contour plots (Fig. 4) showed that higher furfural yields were achieved at higher temperatures and higher IL loadings, regardless of the reaction time (in agreement with entries 6 and 8 of Table 1). Thus, according to the contour graphs fixed at 10 min (Fig. 4A) and 60 min (Fig. 4B), the region of high furfural yields approaches the upper limits of temperature and ionic liquid (180 °C and 10 eq.) in both cases.

The ANOVA table from the experimental design for furfural production from xylose indicated that the curvature on the response surface was significant (Table S2). This curvature calculation was performed by removing the central point from the design to carry out an independent curvature test. When the central points are included and presented as a traditional ANOVA table, there is a significant lack of fit, and the regression is not significant, due to the high contribution of the lack of fit term to the residual sum of squares. The fact that the curvature term is important means that adding the axial points to fit in a quadratic model would be necessary. However, at the best conditions (180 °C, 10 min, 10 eq. IL), the furfural yield from xylose was high (85%); therefore, we decided not to expand the experimental matrix to avoid side reactions associated with higher reaction temperatures, as evidenced by our preliminary tests.

Regarding the IL amount, since it has a duo role as catalyst and co-solvent, we also limited it to 10 eq. to keep the process as greener as possible. However, recycling could also be a strategy to improve the greenness of the process. Therefore, even though the linear model cannot be used for prediction, the analysis of the main effects that contribute to furfural production is valid, and the best conditions were applied for the SCB hydrolysates.

The variable effects follow the chemical pathways involved in the conversion processes. The glycine-based IL follows the classical isomerization/dehydration mechanism in terms of the chemical path. The most remarkable difference between [GlyIm][HSO$_4$] compared to other acidic imidazolium ILs is the presence of three Brønsted acid sites: two carboxylic acid groups in the cation and the hydrogen sulfate anion. These Brønsted acids can interact with xylose and have enough strength to promote dehydration to furfural. Therefore, an enhancement in the IL content can enhance the furfural production.

A proposed mechanism for furfural production following this pathway is depicted in Fig. 5. In summary, xylose dehydration starts with the isomerization step, which is the conversion of a 6-membered ring (xylose) to a 5-membered ring (xylulose), followed by sequential water elimination to form furfural (Rasmussen et al., 2014). As described above, the acid strength of the IL is a key factor in furfural production. Some protic-ILs, such as [EMIN][HSO$_4$], have been reported as efficient catalysts for hemicelluloses hydrolysis to produce pentoses (Da Costa Lopes et al., 2018), which requires low acid strength

compared to the dehydration reaction presented herein.

Furfural production from pentoses is favored in temperatures above 140 °C in acidic media, which justifies the positive effect of increasing temperature on the furfural yield (Zhao et al., 2021). However, there is a balance between the furfural production and their conversion into non-desirable byproducts, such as humins. Likewise, the reaction time needs to be balanced to avoid side-product formation. It is well-known that microwave irradiation is an efficient method for sugar dehydration, besides following Principle 6 of Green Chemistry for energy efficiency (Erythropel et al., 2018). Microwave irradiation can directly interact with all polar linkages and dipoles in the solution providing a homogeneous, rapid, and efficient heating compared to conventional methods, resulting in good yields of furan derivatives in short reaction times (Sweygers et al., 2018). Therefore, lower reaction times are enough to promote furfural production in the higher temperatures evaluated in this study.

The glycine-derived IL presented a similar performance to petroleum-based imidazolium IL for furfural production from xylose, with the advantage of being a renewable IL. However, the comparison with similar systems is not straightforward because the processes are conducted in different ionic liquids, extraction solvents, and reactors, which change the heat and mass transfer, for example, impacting the kinetics of the reaction. Therefore, Table 2 compares the use of different protic ionic liquids for furfural production from xylose without metallic catalysts, showing representative examples of furfural production by IL-mediated reactions. As shown in Table 2, furfural production from xylose can reach moderate to high yields (50–90%) when using protic ILs. It can also be noticed that using an extraction solvent tends to optimize the furfural yields, reinforcing the advantage of the biphasic system for furan derivatives production.

3.2. Selecting the best conditions for xylose extraction from sugarcane bagasse

After selecting the best conditions for furfural production from xylose, we evaluated the use of sugarcane bagasse (SCB) acid hydrolysates as raw feedstock for the dehydration reaction. Acid treatments are one of the most efficient alternatives for hemicellulose extraction, which occurs concomitantly to its hydrolysis into monosaccharides on a large scale because of the high susceptibility of the glycosidic bonds between pentose residues (Baruah et al., 2018). Likewise, various chemical pathways involved in the pentose conversion into other valuable molecules occur in acidic media, including the furfural production by acid dehydration. Acid media thus provide a suitable environment for both xylose extraction and its conversion to furfural. Finally, acid media is a practical first step for biomass processing because it commonly does not hinder the further use of the remaining solid after hemicellulose
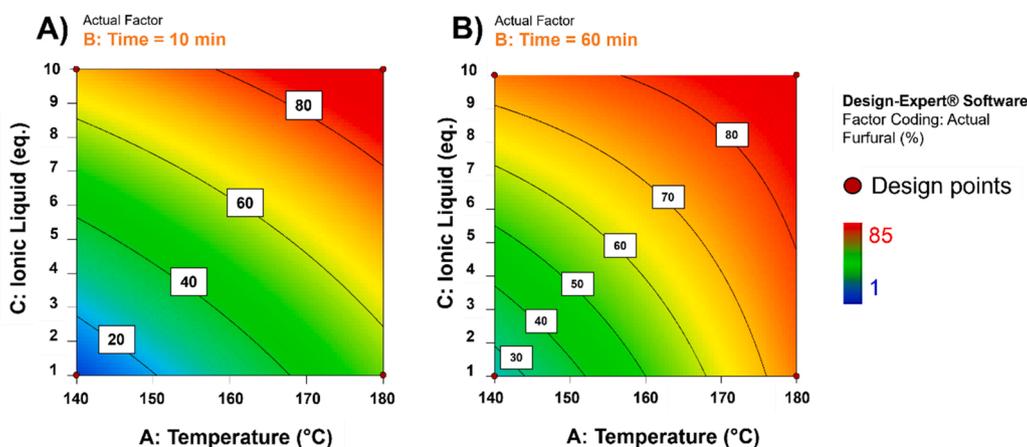
Fig. 4. Contour plots for furfural production considering the time fixed at (A) 10 min and (B) 60 min.
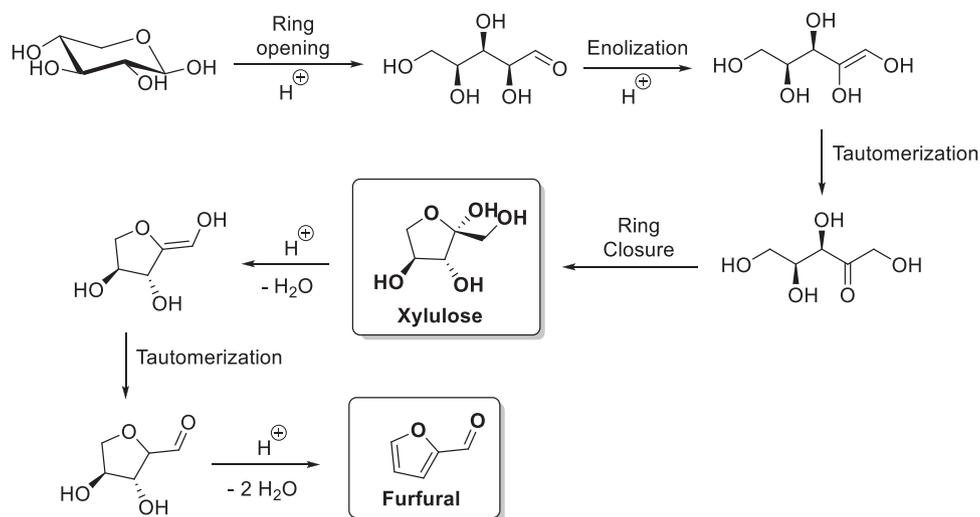
Fig. 5. Reaction sequence proposed for furfural production from xylose.

Table 2

Comparative yields for furfural production from xylose mediated by protic ionic liquids (IL), using different experimental conditions of time (t), temperature (T), extraction (ES), and reaction (RS) solvents.

RS	ES	IL	T (°C)	t (min)	Yield (%)	Ref.
Water	Toluene	[BMIM][HSO$_4$]	140	240	74[a]	(Peleteiro et al., 2015a)
Water	Dioxane	[BMIM][HSO$_4$]	140	240	82[a]	(Peleteiro et al., 2015b)
Water	–	[HO$_3$SBCMIM] [HSO$_4$]	160	180	68[b]	(Hua et al., 2021)
Water	–	C$_1$MF	205	8	50[c]	(Huang et al., 2021)
Water	–	[BMIM][HSO$_4$]*	140	240	90[d]	(Nowicki and Stanek, 2021)
Water	2-MeTHF	[GlyIm][HSO$_4$]	180	10	85	This work

[BMIM][HSO$_4$]: 1–butyl-3-methylimidazolium hydrogen sulfate; [HO$_3$SBCMIM] [HSO$_4$]: 1-(4-sulfonic acid) butyl-3-cetyl-2-methyl imidazolium hydrogen sulfate; C$_1$MF: 3,3′-methylenebis(1- methyl-1 H-imidazol-3-ium) hexafluorophosphate; * use of H$_2$SO$_4$ as co-catalyst; [a] conventional heating - oil bath; [b] conventional heating - autoclave; [c] microwave irradiation – CEM ® Discover Microcave Synthesizer; [d] conventional heating - pressurized reactor.

extraction if appropriate experimental conditions are adopted (Camargos et al., 2019; Scopel and Rezende, 2021).

The 2[3] full factorial design allowed optimizing the xylose extraction from SCB, aiming at its further conversion into furfural in a two-step approach. The experimental matrix is presented in Table 3, showing the levels of the factors investigated in SCB acid hydrolysis (temperature, time, and sulfuric acid concentration) and the full characterization of the hydrolysates for each condition (in terms of xylose, arabinose, glucose, acetic acid, and furfural concentrations). The ranges of each factor were selected based on typical procedures for acid pretreatments for an efficient hemicellulose extraction without polysaccharide

degradation and allowing the further processing of the remaining solid (Baruah et al., 2018; Rezende et al., 2011).

According to Table 3, sample AH-2 provided the higher xylose concentration (13.1 g/L), using temperature at the upper level (150 °C) and time and sulfuric acid concentration at lower levels (30 min and 1% v/v of acid). This experimental condition also provided low sugar dehydration caused by acid-hydrolysis (0.41 g/L of furfural). It allowed 74% of the total hemicellulose content in SCB to be extracted (63% of the total as xylose or arabinose). The condition that provided the best extraction yield was achieved in AH-6 (84% of the total hemicellulose and 58% as xylose and arabinose), also at a higher temperature (150 °C)

Table 3

Sample identification with the corresponding experimental conditions used in the full 2[3] factorial design for SCB acid hydrolysis, and the chemical composition of the acid hydrolysate (AH) in terms of xylose (Xyl), arabinose (Ara); glucose (Glu), acetic acid (HAc) and furfural.

| Sample | Acid hydrolysis experimental conditions and yields | | | | AH composition | | | | |
	T (°C)	t (min)	H$_2$SO$_4$ (v/v%)	Hemicellulose Extraction (%)	Xyl (g/L)	Ara (g/L)	Glu (g/L)	HAc (g/L)	Furfural (g/L)
AH-1	100	30	1	8	0.53	1.09	nd	0.75	nd
AH-2	**150**	**30**	**1**	**74**	**13.1**	**0.86**	**0.97**	**2.11**	**0.41**
AH-3	100	60	1	14	1.59	0.85	0.029	1.09	nd
AH-4	**150**	**60**	**1**	**82**	**12.4**	**0.97**	**1.76**	**2.41**	**1.74**
AH-5	100	30	4	18	2.45	0.77	nd	1.54	nd
AH-6	**150**	**30**	**4**	**84**	**9.59**	**0.84**	**2.29**	**2.30**	**1.78**
AH-7	**100**	**60**	**4**	**55**	**8.51**	**0.81**	**0.12**	**1.92**	**nd**
AH-8	150	60	4	54	1.10	0.040	2.86	2.42	4.59
AH-9A	125	45	2.5	60	12.5	0.84	0.62	2.15	nd
AH-9B	125	45	2.5	57	10.0	0.71	0.47	1.78	nd
AH-9C	125	45	2.5	75	12.0	0.60	0.96	1.85	nd

nd: not detected.

and shorter time (30 min), but at a higher sulfuric acid concentration (4%). These extraction yields are similar to those typically reported for SCB treated with diluted acid solutions (Chen et al., 2012; Zhao et al., 2012). The experiment using all factors at a higher level was not feasible because it resulted in sugar degradation and hindered the use of the remaining solid. Nevertheless, we considered this a significant result highlighting the advantage of using DoE tools to optimize the process.

Results on xylose concentration (Table 3) can be explained based on the significance of the factors. As aforementioned, xylose is the primary monosaccharide of sugarcane bagasse hemicelluloses, and its concentration was thus used as the response because it indicates the efficiency of the hemicellulose extraction. According to the Pareto Chart (Fig. S3), the most significant effect was temperature (A). The standard effect indicated that when the temperature increases from 100° to 150 °C there is an average increase of near 5.8 g/L of xylose (t-value of effect in the Pareto chart = 6.0). The interaction between temperature and sulfuric acid concentration (AC), temperature and time (AB), and the ternary interaction ABC were also significant, leading to a complex behavior of the data that cannot be described by a linear model. The interaction terms involving temperature indicates that the influence of this factor is dependent on the level of the other factors.

As previously shown in the factorial design for furfural production, the curvature term on the ANOVA table appears in the SCB acid hydrolysis design (Table S3) and it was also significant (p-value = 0.0023). When the curvature test is carried out, the lack-of-fit test from ANOVA includes only the factorial points and therefore it does not test for curvature on the center of the design space - this should be rather observed in the Curvature test outcome. The procedure of separating the curvature term allows the building of a better model for the factorial points when one is interested on the extreme results, as it was in this study.

The simultaneous variation of the time and temperature allowed the visualization of the xylose concentration as the response in a 3D response surface (Fig. 6A-B). For example, when the sulfuric acid concentration is fixed at 1%, the response surface shows that the region of high xylose concentrations is found at temperatures above 140 °C, regardless of the time (Fig. 6A). On the other hand, when the sulfuric acid concentration is fixed at 4% (Fig. 6B), two opposite regions for maximum xylose are presented at the response surface: the first at lower temperatures and longer reaction time (100 °C and 60 min); and the second at higher temperatures and shorter reaction time (150 °C and 30 min).

The idea of a balance between reaction time and temperature is corroborated by the combined severity factor (CSF) for hemicellulose extraction, which is a factor that considers the effect of time, temperature, and acid concentration (Equation S1) (Gonzales et al., 2016; Qin et al., 2012). As noticed in Fig. S4, xylose concentration increased as the CSF increased, except for the most severe experimental condition (AH-8), where polysaccharide degradation is probably taking place. On

the other hand, conditions AH-1, AH-3, and AH-5 are mild (lower levels for all the factors or at least 2 of them) and result in low xylose concentration.

Based on these observations in the response surface plots, we selected three SCB acid hydrolysates for furfural production: (i) AH-2 (obtained at 150 °C, 30 min, 1% H$_2$SO$_4$); (ii) AH-6 (at 150 °C, 30 min, 4% H$_2$SO$_4$) and (iii) AH-7 (at 100 °C, 60 min; 4% H$_2$SO$_4$). Using these hydrolysates, furfural was produced using the conditions previously determined in the first part of this study (10 IL eq., 180 °C, 10 min). Despite its high hemicellulose extraction, AH-4 was not selected due to its similarity to AH-2, which was obtained under the same conditions but at a reduced time. On the other hand, sample AH-7 was chosen by following the DoE analysis because this sample showed a similar xylose concentration to sample AH-6 despite its lower CFS.

3.3. Applying the glycine-IL in real matrices of sugarcane bagasse acid-hydrolysates

Acid hydrolysates resulting from the first step were directly forwarded to IL treatment without additional processing. Sample AH-6 provided the highest furfural yield (90 ± 4%) among the evaluated hydrolysates (Fig. 7). Acid hydrolysis can also cleave the aryl-ether bonds of the lignin present in raw SCB and then solubilize lignin fragments into the hydrolysates. Therefore, a control experiment was carried out using a synthetic media, *i.e.*, an aqueous solution containing only xylose and arabinose in the same acid hydrolysates concentrations, to evaluate the influence of phenolics on pentoses dehydration. As shown in Fig. 7, the synthetic AH-6 also provided excellent furfural yield (91 ± 2%), indicating that the pentoses dehydration to furfural mediated by [GlyIm][HSO$_4$] is a robust method that is not affected by the presence of acid-soluble lignin. Indeed, AH-6 has a higher quantity of soluble lignin
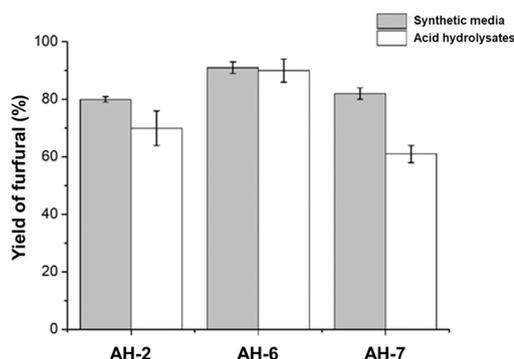
Fig. 7. Furfural production from synthetic media and SCB acid hydrolysates mediated by [GlyIm][HSO$_4$].
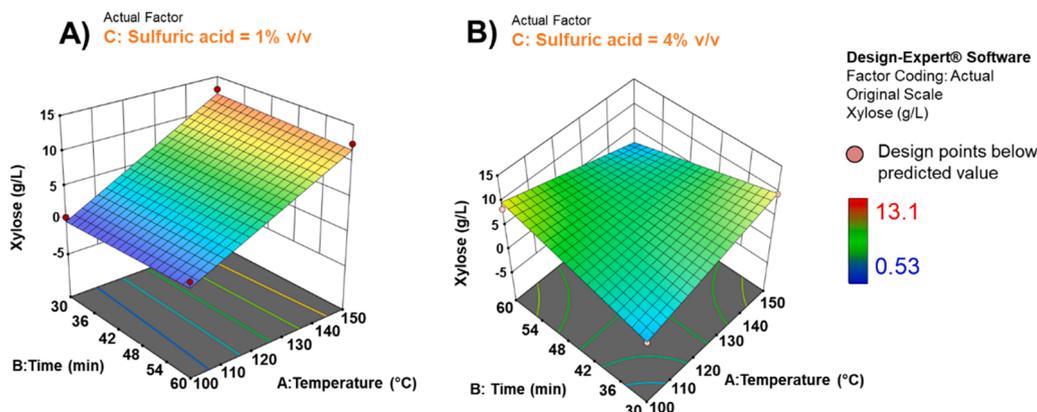
Fig. 6. Response surfaces for SCB acid hydrolysis when sulfuric acid is fixed at (A) 1% v/v or (B) 4% v/v.

(7.7 g/L) than AH-2 (2.2 g/L) and AH-7 (1.0 g/L), which corroborates the observation that the quantity of lignin does not influence the sugar conversion to furfural.

To confirm that the glycine-based IL accounted for the high yields of furfural, a control experiment was carried out using the AH-6 hydrolysate in the absence of [GlyIm][HSO$_4$] but keeping the same temperature and time (180 °C and 10 min) under microwave irradiation (Fig. S5). Under these conditions, furfural yield was considerably low (19 ± 6%), proving the outstanding dehydration efficiency that the renewable IL [GlyIm][HSO$_4$] provided on hydrolysate conversion to furfural.

The experiments performed herein reached furfural yields higher than the typical values reported in the literature (typically, 50% of furfural is produced from SCB using sulfuric acid as the catalyst) (Dulie et al., 2021; Ntimbani et al., 2021). The best result reported in the literature using sugarcane bagasse as substrate and sulfuric acid to produce furfural achieved 110 mg of furfural / g of raw SCB applying H$_2$SO$_4$ 1% v/v at 170 °C for a long reaction time (90 min) under continuous removal of the furfural (vapor) produced, which is a high energy consumption process. However, despite the higher furfural quantity, the authors reported a higher degradation of the cellulose that remains in the solid substrate due to the harsh conditions of acid hydrolysis, which hinders the further use of the remaining solid. Indeed, the authors pointed out the conditions that produced 76 mg of furfural / g of SCB to be more feasible because they also enabled the cellulose fraction use to produce bioethanol (Ntimbani et al., 2021).

Herein, 90 mg of furfural/g of dried SCB was produced under the best experimental conditions due to the synergistic action of the glycine IL and the biphasic system that extracted furfural as soon as it was formed. In addition, DoE tools combined with microwave-assisted synthesis allowed faster reactions (only 10 min), thus contributing to the process efficiency. It is important to highlight that the most common approaches to xylose conversion to furfural are still focused on evaluating pure xylose conversion, not applied in real matrices. Therefore, the result presented herein from a biomass hydrolysate contributes significantly to advance toward a more sustainable process for biomass processing.

Comparing the best results for furfural production from SCB acid hydrolysates achieved here (91% furfural yield) with other ionic liquid-based processes, it is possible to notice the excellent catalytic performance of the renewable [GlyIm][HSO$_4$]. For example, Parajó and co-workers reported on the furfural production from the hemicellulose fraction of hydrothermally-treated *Eucalyptus nitens* using [BMIM][HSO$_4$] and 1-(3-sulfopropyl)− 3- methylimidazolium hydrogen sulfate, [C$_3$SO$_3$HMIM][HSO$_4$], as catalytic systems. The authors achieved 77% and 86% of furfural yield at 180 °C for 30 min using [BMIM][HSO$_4$] and [C$_3$SO$_3$HMIM][HSO$_4$], respectively (Penín et al., 2022). Another recent example of furfural production mediated by ionic liquids was reported by Peng and coworkers, that evaluated the furan derivatives production from pretreated *Camellia oleifera* fruit shell. The authors obtained a 68% furfural yield at 180 °C for 20 min under microwave irradiation, using [BMIM][HSO$_4$] as a catalyst in an H$_2$O/1,4-dioxane biphasic system (Huang et al., 2022).

As described earlier, our methodology for furfural production from SCB is divided in two steps: (i) a classical acid pretreatment for hemicellulose extraction and (ii) the furfural production from the SCB acid hydrolysates mediated by [GlyIm][HSO$_4$]. We also perform the one-pot furfural production from raw SCB to evaluate the need for hemicellulose extraction before its dehydration. To do so, SCB was directly treated with the IL at the best conditions used for furfural production without sulfuric acid (Fig. S6). As a result, furfural was obtained in 31 ± 4% yield, indicating the superior efficiency of the 2-step process. Similar results were also achieved for other IL catalytic systems for furfural production from raw biomass. For example, Welton and coworkers reported a direct furfural production from *Miscanthus* using [BMIM][HSO$_4$] as the solvent/catalyst system at 120 °C for 22 h, achieving a 33% furfural yield (Brandt et al., 2011). In turn, Chang and coworkers
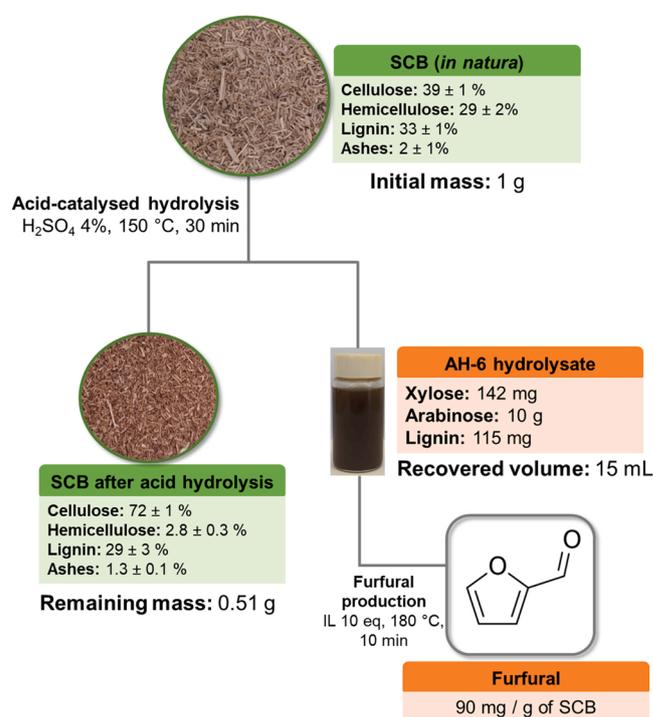
Fig. 8. Chemical composition of SCB before and after acid hydrolysis and summary of furfural yield (condition AH-6).

described a furfural production from corncob using [EMIM][Cl] as the solvent and a boron-based catalytic system, resulting in 12% of furfural yield at 140 °C for 120 min (Ofrasio et al., 2020). These last two examples highlight that the use of a two-step process, a biphasic system, and more acidic ionic liquids are critical factors in achieving high furfural yields. The considerable amount of furfural obtained in the one-pot experiment confirmed herein that acidic [GlyIm][HSO$_4$] had a catalytic effect on hemicellulose hydrolysis in the absence of the sulfuric acid pretreatment.

Besides increasing furfural yields, another positive aspect in favor of the two-step process is that the one-pot approach hinders the use of the remaining solid fraction in further applications for integrated processes in a biorefinery. This strategy was reported under similar conditions (Cavali et al., 2020; Trevisan and Rezende, 2020). Fig. 8 summarizes the furfural production yields and the chemical composition of the remaining solid after acid treatment (which resulted under AH-6 conditions). The remaining solid after acid-catalyzed hydrolysis is composed of 72 ± 1% of cellulose and 29 ± 3% of lignin and can be
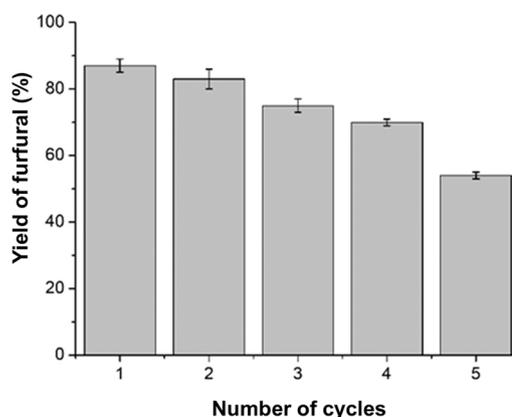
Fig. 9. Recycling tests of [GlyIm][HSO$_4$], showing furfural yields around 50–60% after 5 cycles.
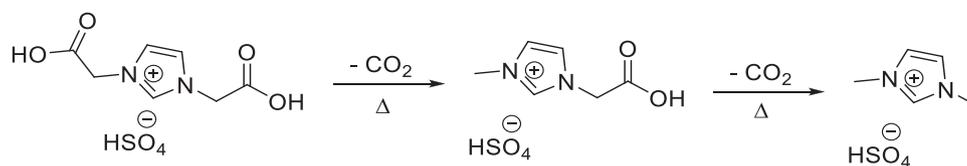
Fig. 10. Proposed decarboxylation reactions of [GlyIm][HSO_4].

directly forwarded, for instance, to produce fermentable sugars by enzymatic hydrolysis and the use of the residual lignin for energy generation (Ntimbani et al., 2021). Another alternative is the sequential extraction of lignin by conventional methods (*e.g.,* alkaline or organosolv treatments), resulting in a cellulose-rich solid. The extracted lignin can be used to produce aromatic molecules, such as vanillin (Fache et al., 2016), lignin nanoparticles (Bertolo et al., 2019), or lignin-based materials (Kai et al., 2016). Concomitantly, cellulose can be converted into nanoparticles (Pinto et al., 2019), or chemicals (Gomes et al., 2018; Guan et al., 2018; He et al., 2017), besides the usual conversion into glucose by enzymatic hydrolysis (Rezende et al., 2011; Scopel and Rezende, 2021).

3.4. Evaluation of the IL recycling

One of the major challenges in IL-based biomass processing is the IL recovery, its separation from the product, and its reuse without losing its performance as a reaction medium and catalyst (Peleteiro et al., 2016). In this context, the recovery of ILs from the reaction mixture using several separation methods such as chromatography, ultra- and nano-filtration, liquid-liquid and supercritical extractions, for example, have been described (Zhou et al., 2018). Recently, Łukasik and coworkers described an efficient method based on column chromatography for separating the reaction products from the IL and its reuse (Da Costa Lopes et al., 2018). Although the proof of concept of the chromatographic separation of pentoses and IL was successfully demonstrated, from an economical and sustainable point of view, chromatography is not ideal considering the high amount of organic solvents typically used. Therefore, the search for greener alternatives should be beneficial. In our approach, the recovery of the IL and its reuse was sought through the phase separation after the reaction taking advantage of the biphasic reaction system. Therefore, the aqueous phase, containing the [GlyIm][HSO_4] ionic liquid, was reused in other reaction cycles using xylose as a sugar source (Fig. 9). It can be noticed that the IL remains efficient in converting xylose to furfural to a certain extent. For example, the furfural yield is the same after two cycles using the same initial IL and gradually drops with the cycles, achieving $54 \pm 1\%$ (56 mg furfural/ g raw SCB) at the fifth one. A similar profile of loss of activity has been reported for an immobilized imidazolium IL, ImmHSO4-IL; the furfural yield from a xylan substrate decreased from 72% to 45% at four cycles, leaving, in this case, a loss of activity of almost 30% (Liu et al., 2022). Likewise, the extraction solvent used in this synthetic route (2-MeTHF) can be recovered by distillation and reused.

After the experiment for furfural production, the formation of a fine dark powder from furanic condensation (known as humins) can be noticed, which forms a complex mixture with IL (Fig. S7) that cannot be separated using traditional purification methods. The presence of humins in the aqueous phase can consume the furfural produced mainly by condensation reactions, which could account for the decrease of furfural yields, as the formation of humins increase in each cycle.

Another possible explanation for the performance loss of the [GlyIm][HSO_4] could be related to decarboxylation reactions (Fig. 10) (Gomes and Pastre, 2020). The loss of carboxyl groups on the IL structure would reduce its acidic strength, consequently decreasing furfural yields. DSC analysis of the [GlyIm][HSO_4] (Fig. S8) showed two endothermic events at 140 °C and 161 °C, which could be related to CO_2 loss and would therefore hinder the use of the IL at these temperatures (Kirchhecker and

Esposito, 2016). On the other hand, thermogravimetric analysis (TGA) (Fig. S9) showed a 10–15% weight loss at 100 °C, probably related to the adsorbed water in the IL, and a 55–60% weight loss at temperatures above 250 °C. A closer inspection of the derivative TGA curve on Fig. S9 also reveals a discrete weight loss in the 120–200 °C range (~5%) that could account for the gradual yield loss after multiple reaction cycles. In comparison to the protic-IL [EMIN][HSO_4], previously discussed, which could only perform the hydrolysis reaction of hemicelluloses affording pentoses, the decarboxylation reaction of the [GlyIm][HSO_4] would lead to an IL with low acid strength (*i.e.*, without the Brønsted acid sites), which in turn could also account for the moderate furfural yield achieved in the last cycle.

As initially proposed, our integrated approach for furfural production presented herein follows at least seven of the twelve principles of Green Chemistry, namely: (1) Prevent waste by using SCB, a residue from the agroindustry, and the acid hydrolysate, which is poorly explored in biomass processing; (3) Less hazardous synthesis by choosing the Debus-Radziszewski methodology for IL synthesis, which uses low toxicity reactants to form the imidazole ring; (4) Design benign chemicals by producing furan derivatives as building blocks for industrial applications, which present less toxicity compared to petrochemical analogs; (5) Benign solvents and auxiliaries, with only green solvents used, including water, ionic liquids and 2-MeTHF; (6) Design for energy efficiency by using microwave irradiation for furfural production; (7) Use of renewable feedstocks, by using agro-industrial residues as feedstock for furfural production, and synthesizing ILs derived from amino acids; and last but not least (9) Catalysis, from the IL bifunctional role that act as solvent and catalyst providing the sugar dehydration.

In addition to the green and sustainable aspects of this process, the yields achieved here are higher than most of those reported in the literature, indicating that it is possible to associate a renewable character with furfural production while keeping higher production yields. Finally, this process can be incorporated into sugarcane bagasse processing currently using acid treatments (Gurgel et al., 2012; Rocha et al., 2015), contributing to more sustainable and efficient biorefineries.

4. Conclusions

Furfural was produced here from sugarcane bagasse acid hydrolysates mediated by a renewable amino acid-based ionic liquid [GlyIm][HSO_4] and using only green solvents. The ionic liquid acts as both a co-solvent and a catalyst, and excellent furfural yields (up to 90%) were provided, resulting in 90 mg of furfural / g of raw SCB at short reaction times (10 min) at 180 °C and using 10 eq. of the IL. Furthermore, the furfural yields from SCB acid hydrolysates were similar to the synthetic media, proving that some SCB components, such as acid-soluble lignin, did not inhibit the pentoses conversion mediated by [GlyIm][HSO_4]. Therefore, this new renewable approach for furfural production by the valorization of the C5 fraction obtained after acid treatment of SCB could be coupled in biorefineries contributing to the integral use of lignocellulose.

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CRediT authorship contribution statement

Gustavo R. Gomes: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Eupídio Scopel:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Márcia C. Breitkreitz:** Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Supervision, Visualization. **Camila A. Rezende:** Conceptualization, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Julio C. Pastre:** Conceptualization, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

Declaration of Competing Interest

Data Availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2022.115940.

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