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# Enhanced Conversion of Xylan into Furfural using Acidic Deep Eutectic Solvents with Dual Solvent and Catalyst Behavior

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An efficient process for the production of furfural from xylan by using acidic deep eutectic solvents (DESs), which act both as solvents and catalysts, is developed. DESs composed of cholinium chloride ([Ch]Cl) and malic acid or glycolic acid at different molar ratios, and the effects of water and γ-valerolactone (GVL) contents, solid/liquid (S/L) ratio, and microwave heating are investigated. The best furfural yields are obtained with the DES [Ch]Cl:malic acid (1:3 molar ratio)+5 wt% water, under microwave heating for 2.5 min at 150 °C, a S/L ratio of 0.050, and GVL at a weight ratio of 2:1. Under these condi- tions, a remarkable furfural yield (75%) is obtained. Direct dis- tillation of furfural from the DES/GVL solvent and distillation from 2-methyltetrahydrofuran (2-MeTHF) after a back-extrac- tion step enable 89% furfural recovery from 2-MeTHF. This strategy allows recycling of the DES/GVL for at least three times with only small losses in furfural yield (>69%). This is the fastest and highest-yielding process reported for furfural production using bio-based DESs as solvents and catalysts, paving the way for scale-up of the process.

## Introduction

The fast depletion of fossil resources and the environmental impact associated with their use has led to an increased focus on the utilization of renewable resources such as biomass to supply society with commodities.[1] It is estimated that at least 30% of all chemicals will be derived from renewable resources by 2050.[2] Furfural is amongst the most relevant value-added compounds derived from biomass. It has been identified by the US Department of Energy (DOE) as one of the top 12 value-added chemicals obtained from biomass, with a world market of 300 000 tons per year.[3] Furfural is a precursor of other relevant chemicals, such as furfuryl alcohol, 2-methyltet- rahydrofuran (2-MeTHF), furan, and tetrahydrofuran, which can be used as solvents, intermediates for fragrances, and pharma- ceuticals, among other applications.[4]

Furfural can be produced from xylose by acid dehydration, which in turn can be obtained from hemicelluloses, one of the three main fractions of lignocellulosic biomass.[4,5] Furfural can also be produced from xylans[6,7] and whole biomass.[8,9] The first industrial furfural production process dates back to 1921, with the Quaker Oats batch process using oat hulls.[10] Furfural production has been accomplished in acidic media using Brønsted acids as homogeneous catalysts, such as hydrochloric or sulfuric acid, and temperatures ranging between 160 and 200 °C.[8,11] In addition to low furfural yields below 50%,[4] these harsh conditions also required high energetic inputs and brought significant environmental and safety concerns. These downsides led to the closure of most batch-based plants for furfural production. A continuous process was later developed by Quaker Oats, increasing the furfural yields up to 55%; none- theless, the developed process had a high maintenance cost[11] and was shut down in 1997.[10] Since then, different industrial processes have been proposed. To our knowledge, the highest yield reported so far is 83%, demanding the use of pentosans and an extra isolation step. Currently, furfural is mainly pro- duced from agricultural wastes, such as corn cobs and sugar cane bagasse.[4] Aqueous media are often used in the presence of homogeneous catalysts, such as $H_2SO_4$ and HCl, or hetero- geneous catalysts, such as aluminum sulfate[7] or tin tetrachlo- ride.[6] However, these processes all require the use of high temperatures (170–240 °C) and strong acids.[10]

Continuous research efforts have been undertaken over the years to develop cost-efficient and sustainable processes for the production of furfural.[12,13] In this arena, not only the pro- duction of furfural needs to be optimized, but it is also neces- sary to avoid its degradation, which may occur by resinifica- tion, a reaction of furfural with its precursors or condensation reactions between furfural units.[11] Biphasic systems are com- monly employed in continuous processes to improve furfural yields by decreasing the occurrence of secondary reactions. In these systems, furfural is produced in aqueous media and con- tinuously extracted into the organic phase to which it has a higher affinity.[14] Conventional solvents, such as methyl isobu- tyl ketone,[15] tetrahydrofuran (THF),[16] and cyclopentyl methyl

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ether[17] have been used for this purpose. More recently, bio-based solvents such as γ-valerolactone (GVL)[7,9] and 2-MeTHF[6,18,19] have been applied as greener alternatives.

Concerning the production of furfural from hemicelluloses, improved furfural yields have been obtained using biphasic systems and microwave-assisted reactions.[7,16] Yang et al.[16] reported a furfural yield of 64.0% using microwave heating and a $H_2O$/THF biphasic system containing NaCl and $AlCl_3 \cdot 6H_2O$ at 140 °C.[16] Also by using microwave-induced reactions, Yang et al.[7] obtained an 87.8% yield of furfural with a GVL/$H_2O$ solvent system at 130 °C and $Al_2(SO_4)_3$ as catalyst.[7] However, in both studies, long reaction times of 45 min to 1 h were required[7,16] and the catalysts could be easily deactivated in aqueous solution or biphasic systems containing salts.[14] To overcome this drawback, the scientific community has been looking for other approaches, such as the use of supercritical solvents to dehydrate hemicellulose (68% furfural yield using xylose at 230 °C and 12 MPa),[20] or by the use of neoteric solvents, such as ionic liquids (ILs).[21,22] The ILs 1-butyl-3-methyl-imidazolium hydrogen sulfate and 1-ethyl-3-methylimidazolium hydrogen sulfate have been applied as acid catalysts, allowing 31% furfural yield from wheat straw at 161 °C and 104.5 min,[21] and 84% furfural yield from xylose at 100 °C and 6 h.[22] However, the furfural yields were still below those obtained by using biphasic systems and heterogeneous catalysis.

Deep eutectic solvents (DESs), another type of neoteric solvents, can also be applied and designed to have acidic characteristics, and thus are able to act as catalysts in furfural production. DESs, as first proposed by Abbott et al.,[23] are composed of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) species. They were initially reported as mixtures of two or more solid compounds that form a eutectic mixture deviating from ideality, thus presenting a significant decrease in the melting temperature. These solvents can be easily prepared by simply mixing, at an appropriate ratio, the compounds required to create the desired eutectic mixture at a given temperature.[24] Furthermore, DESs have a "designer solvent" character, though appropriate selection of HBAs and HBDs,[25,26] and may display low toxicity if properly designed.[27]

DESs have been used as solvents for polysaccharide modification and processing[28] and as catalytic media.[29,30] To our knowledge, the only work that has reported the production furfural in DES media used a DES composed of cholinium chloride ([Ch]Cl) and oxalic acid, but still required a Lewis acid as catalyst, that is, $AlCl_3 \cdot 6H_2O$.[31] The authors used a biphasic system using methyl isobutyl ketone within a continuous process, leading to a furfural yield of 55.5% from xylans at 100 °C.[31] Although some drawbacks are associated with the conditions used, namely the inherent toxicity of oxalic acid,[32] this study opens the door for effective use of DESs in furfural production. If a DES with acidic characteristics is used, the DES itself can act as both the solvent and the catalyst (not requiring the use of the $AlCl_3 \cdot 6H_2O$ catalyst as attempted by the authors).[31] This hypothesis is further supported by the unintentional production of small amounts of furfural when attempting biomass delignification with a DES composed of [Ch]Cl and lactic acid.[33,34] Based on this evidence, in this work, we de-signed a sustainable process for furfural production from xylans, in which DESs can act both as solvent and catalyst. DESs composed of [Ch]Cl and malic acid ([Ch]Cl:MA) or [Ch]Cl and glycolic acid ([Ch]Cl:GA) were investigated. These acids were chosen owing to their greener credentials[35,36] and lower viscosity (compared with citric acid, for example).[36] Different DESs with different proportions of the acids were tested and relevant operational conditions were optimized, namely solid/liquid (S/L, biomass/solvent) ratio, temperature, microwave heating, water content, and amount of acid in the DES. After identifying the most promising DES and operational conditions, GVL was added with the initial goal of decreasing the reaction activation energy, as reported by Delbecq et al.[12] Finally, the recovery of furfural was investigated, either by direct distillation or distillation after a back-extraction step, further allowing the recycling of the solvents.

## Results and Discussion

Xylan from beechwood was used as the substrate for the acidic hydrolysis and dehydration to furfural using two acidic DESs ([Ch]Cl:MA and [Ch]Cl:GA) with different proportions of the acid. First, reactions were performed with conventional heating and the best DESs were identified. The furfural yield was calculated in moles of furfural in relation to the number of moles of xylose present in the xylan sample used. Parameters such as solid/liquid (S/L, biomass/solvent) ratio, temperature and water content were optimized to improve the furfural production. Furthermore, to improve the process sustainability, microwave-assisted reactions were performed with the best DES. Then, the use of GVL was investigated with the initial goal of preventing furfural degradation and improving its yield. Finally, the recovery of furfural and recycling of the solvents was performed and the integrity of the DES after the recycling process was investigated.

### Xylan conversion into furfural with conventional heating

The production of furfural from xylan in acidic DES was initially evaluated with [Ch]Cl:MA and [Ch]Cl:GA. The solid–liquid phase diagrams of [Ch]Cl:MA and [Ch]Cl:GA, in which both starting materials are solid at room temperature, have been reported by Crespo et al.,[37] demonstrating that this system deviates from ideality behaving like a DES. In this first screening, distinct conditions were evaluated, namely the xylan/DES weight fraction ratio (0.050 and 0.175 w/w), temperature (90 and 130 °C), acid content in the DES (molar ratio of 1:2 and 1:3 of [Ch]Cl in respect to MA or GA) and water content (because of its ability to promote xylan hydrolysis).[12] The DESs were prepared without previous drying but their water content was determined (2.5 wt%). To decrease their viscosity, DESs with 5 wt% water were also prepared. A [Ch]Cl:Lactic acid DES with a molar ratio of 1:10 with 15 wt% water was also prepared for comparison, as furfural production has been reported with this DES when addressing biomass delignification.[33,34]

The furfural production yields obtained in this first screening are depicted in Figure 1. [Ch]Cl:MA was more efficient as a cat-
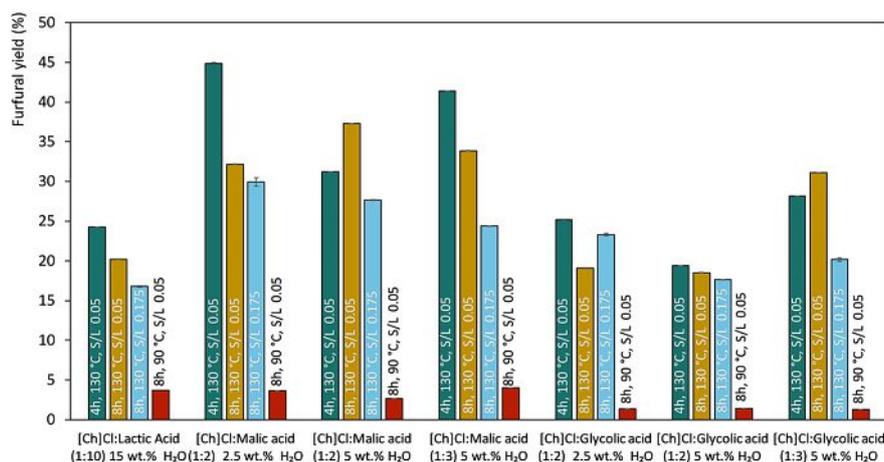
**Figure 1.** Furfural yields obtained with conventional heating at different: reaction time, S/L ratio and temperature (■: 4 h, 130 °C, S/L ratio = 0.050, ■: 8 h, 130 °C, S/L ratio = 0.050, ■: 8 h, 130 °C, S/L ratio = 0.175, ■: 8 h, 90 °C, S/L ratio = 0.050).

alyst and solvent than [Ch]Cl:GA, leading to furfural yields of up to 44.87 %. Taking into consideration that GA and MA have similar first p$K_a$'s (p$K_{a1}$ = 3.61 vs. p$K_{a1}$ = 3.51),[38] the higher conversions with [Ch]Cl:MA can be linked to the higher acidity of the media afforded by the dicarboxylic MA (p$K_{a2}$ = 5.03). Interestingly, and despite the high content of lactic acid, the furfural yields obtained with the [Ch]Cl:Lactic acid (1:10, p$K_a$ = 3.86)[38] were considerably lower (< 25 %). Additionally, high temperatures seemed to boost furfural yield, as observed by comparing the results obtained at 90 and 130 °C. A lower S/L ratio was also relevant, resulting in higher furfural yields, as observed by comparing the results at 130 °C and 8 h, owing to a better access of the solvent to xylan.

Although good results were obtained, [Ch]Cl:MA (1:2) was still a viscous solvent, thus requiring higher energetic inputs, which could negatively contribute to mass transfer phenomena. Knowing that water content is important for xylan hydrolysis into xylose,[12] 5 wt % added water was tested in the [Ch]Cl:MA (1:2) system (Figure 1). An increased amount of water resulted in a slight decrease in the furfural yield, which was due to the decrease of the system's acidity. Therefore, to increase the furfural yield while decreasing the DES viscosity, a molar ratio of [Ch]Cl to MA or to GA of 1:3 with 5 wt % of water was investigated (cf. Figure 1). The increase of the solvent's acidity resulted in an increase in the furfural yield up to 41.42 % with the DES [Ch]Cl:MA. Overall, under the best conditions, that is, a molar ratio of 1:3 of [Ch]Cl to MA, with 5 wt % water at 130 °C and 4 h of reaction time, a furfural yield of 44.87 % was achieved. This value was comparable with the yields obtained in studies using mineral acids, such as HCl, at higher temperature (≈180 °C).[15, 39] The high furfural yield obtained was most probably related with the findings of Vigier and co-workers,[40] who demonstrated that in presence of [Ch]Cl the production of furfural is fostered by the formation of a choline xyloside intermediate.

### Xylan conversion into furfural with microwave heating

The furfural yields obtained with conventional heating are already promising compared with previous studies, in which lower yields were obtained by using higher temperatures and in presence of strong acids as catalysts.[14] Nonetheless, the furfural yield obtained under the investigated conditions was still below 50 % and a 4 h reaction time was required. To improve the furfural yield while reducing the reaction time, microwave-assisted reactions were investigated with the DES [Ch]Cl:MA (1:3) with 5 wt % water. The reactions were initially performed at 130, 140, and 150 °C for 2.5, 5.0, and 7.5 min (Figure 2). The results clearly showed that the best furfural yields were obtained at 150 °C for 2.5 min; the furfural yield decreased at longer reaction times, most likely owing to furfural degradation.

To optimize the reaction time, other reaction times closer to 2.5 min were tested (see the Supporting Information, Fig-
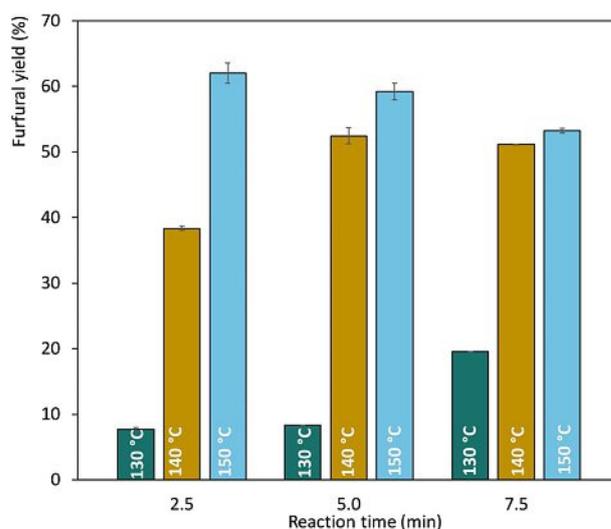


**Figure 2.** Furfural yields obtained with microwave-assisted reactions using [Ch]Cl:MA (1:3) + 5 wt % H$_2$O at different reaction times and temperatures (■: 130 °C, ■: 140 °C, ■: 150 °C).

ure S1). 2.5 min was the optimal reaction time for furfural production under the selected conditions. In all the studied assays, the power pulse was below 400 W, demonstrating the capability of the DES to absorb microwave radiation and to decrease the energy required for the reaction to occur. The reported power pulse was also considerably lower than those described previously with a single beam microwave reactor.[15] Overall, the best results under microwave-assisted reaction conditions were achieved with a 2.5 min reaction time at 150 °C, leading to a furfural yield of 62.02%.

The effect of water content under microwave heating was then investigated with [Ch]Cl:MA (1:3) containing 2.5, 5 and 10 wt% water under the best identified reaction conditions (150 °C and S/L ratio = 0.050) and at two different reaction times (1.5 and 2.5 min). As verified before with conventional heating, the results revealed that water plays a significant role in this process (Figure 3). Under microwave heating, there was a positive effect of the addition of water to the DES up to 5 wt%, improving the furfural yield. However, a higher water content, that is, 10 wt%, was not beneficial and resulted in a decrease of the furfural yield. These results were in agreement with the observations under conventional heating: the addition of water decreased the solvent viscosity but at the same time decreased the solvent acidity. Therefore, an intermediate amount of water leads to improved furfural yields.
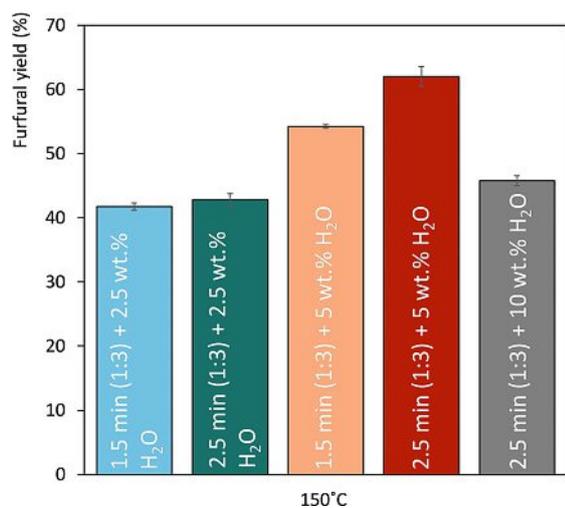


**Figure 3.** Effect of water in furfural yields using [Ch]Cl:MA (1:3), at 150 °C and S/L ratio = 0.050 (■: 1.5 min + 2.5 wt% H$_2$O, ■: 2.5 min + 2.5 wt% H$_2$O, ■: 1.5 min + 5 wt% H$_2$O, ■: 2.5 min + 5 wt% H$_2$O, ■: 2.5 min + 10 wt% H$_2$O).

### Addition of γ-valerolactone to increase the furfural yield

The use of bio-based solvents such as GVL has been reported by Dumesic and co-workers[41] to be beneficial for furfural production from xylose using Brønsted acids. In particular, xylose dehydration occurs faster in GVL than in water, which in turn minimizes the formation of degradation products, thus boosting furfural yield.[41] Moreover, it has been reported that GVL decreases the activation energy required for the dehydration of xylose into furfural.[12] Yang et al.[7] reported the possibility of
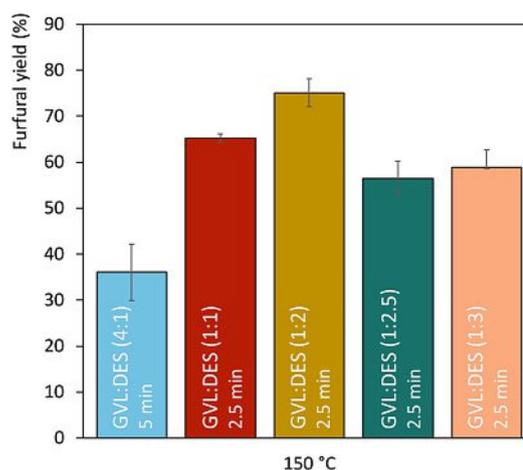


**Figure 4.** Effect of the ratio of GVL in furfural yields using the DES [Ch]Cl:MA (1:3) + 5 wt% H$_2$O at 150 °C, S/L ratio = 0.050 (■: GVL/DES (4:1) 5 min, ■: GVL/DES (1:1) 2.5 min, ■: GVL/DES (1:2) 2.5 min, ■: GVL/DES (1:2.5) 2.5 min, ■: GVL/DES (1:3) 2.5 min).

having a biphasic system between water and GVL, which would be ideal for the continuous separation of furfural during microwave-assisted reactions.

Based on these reports, the production of furfural was studied under the previously optimized conditions with different GVL/DES proportions (Figure 4). No biphasic system was formed with a GVL/DES system with a weight ratio of 4:1 and furfural yields below 40% were obtained. Interestingly, higher yields were obtained with decreased GVL content (GVL/DES of 1:1, 1:2, 1:2.5 and 1:3 w/w). Furfural yields of up to 75.09% were achieved with the 1:2 w/w GVL/DES. These results demonstrate the advantages of using GVL under appropriate conditions, leading to approximately 15% increase in furfural yield. This increase in yield owing to the presence of GVL further confirmed the aforementioned advantages of using GVL as cosolvent.[12, 41] The addition of MeTHF during microwave irradiation was also investigated (results not shown). However, the furfural yields obtained were considerably lower than those obtained with GVL.

To our knowledge, this is the highest furfural yield (75%) obtained in a short reaction time (2.5 min) and using xylan as a raw material. Furthermore, we have shown for the first time that acidic DESs can be simultaneously used as solvents and catalysts for the production of furfural directly from xylose. These results open a path to investigating a more integrated strategy for the use of DESs in biorefinery processes comprising furfural recovery and DES recycling (see below).

### Proof of concept: Furfural recovery and DES recycling

To foster the sustainability of the developed process, the recovery of furfural from the DES/GVL solvent and solvent recycling were investigated. To recover furfural from the reaction media, and because no biphasic system was formed with GVL under the optimal conditions for furfural production, two strategies were followed: (i) direct distillation of furfural from the DES/GVL solvent and (ii) liquid–liquid extraction (1:1 w/w) using

a bio-based solvent, namely 2-MeTHF, which is immiscible with the DES, followed by distillation. The distillation step seems to be an adequate strategy owing to the difference in the boiling temperatures of 2-MeTHF, furfural, GVL, and the DES components (MA, GA, and [Ch]Cl degrade above 302 °C): 80 °C, 169 °C, 208 °C, 306 °C and 265 °C, respectively.[42]

The steps required for the two recovery and recycling strategies are summarized in Figure 5. In the first strategy, furfural was directly distilled from the DES-GVL mixture. In the second strategy, in which 2-MeTHF was applied as a back-extraction solvent, distillation was used to remove this solvent (lower boiling point than furfural). The furfural recovery yields obtained through both strategies are given in Figure 6. Remarkably, 89.5% of furfural was recovered by distillation from the 2-MeTHF solvent, whereas 75.7% of furfural was obtained from the DES/GVL solvent. Better results were achieved for the recovery of furfural from 2-MeTHF, although an additional step was required compared with the other strategy. Furthermore, this strategy allowed faster extraction and stabilization of furfural by removing it from the acidic media, and therefore was chosen as the ideal methodology to be used in further assays. The purity of the recovered furfural was confirmed by $^1$H and $^{13}$C NMR spectroscopy, as well as HPLC spectroscopy at 268 nm (Figures S2 and S3). Although distillation is often reported as a possible way to recover furfural,[42] actual methods for furfural recovery are scarce. Nonetheless, the reported furfural recovery from the 2-MeTHF fraction was similar to optimized continuous processes.[43]

After the successful recovery of furfural, the recyclability of the DES and DES/GVL solvent was evaluated in additional reactions to produce furfural from xylan (Figure 7). The DES stability/integrity was confirmed through $^1$H and $^{13}$C NMR spectroscopy throughout the different recycles, which was maintained with and without GVL. Although furfural has a high affinity to
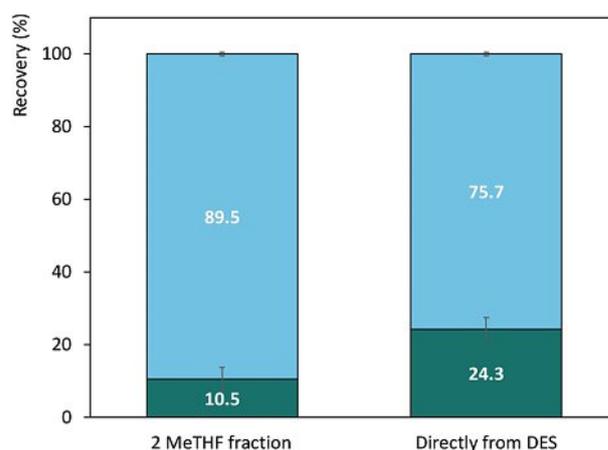


**Figure 6.** Furfural recovery by reduced pressure distillation from the 2-MeTHF and GVL/DES solvents. (■: recovered furfural and ■: furfural remaining in 2-MeTHF or GVL/DES fractions).

the 2-MeTHF organic phase, 94.6% being extracted, a small fraction of furfural remains in the recycled solvent. Accordingly, a slight decrease in the furfural yield is observed as the number of recycling steps increases. Nonetheless, in at least three recycles of the DES-based solvent, the furfural yields obtained in the 2-MeTHF fraction were maintained above 69.0%, which were higher than those obtained in most industrial processes developed to date.[4]

## Conclusions

A new process for furfural production from xylan using DES, acting both as solvent and catalyst, was designed and validated. DESs composed of [Ch]Cl and MA and GA at different molar ratios, and different operating conditions such as time
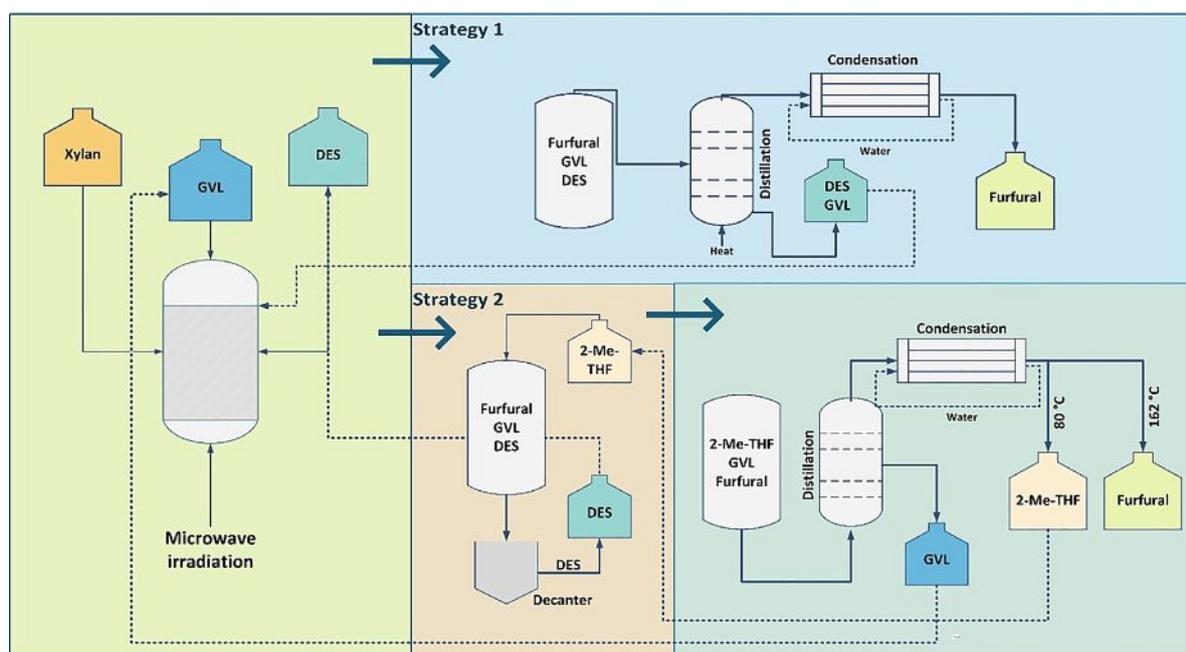


**Figure 5.** Scheme depicting the two strategies that can be adopted for the recovery of furfural and solvent recycling.
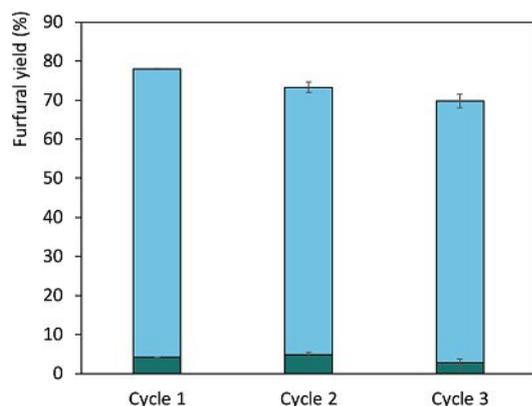
**Figure 7.** Furfural yields using GVL/DES (1:2 *w/w*) solvent with the DES [Ch]Cl:MA (1:3) $+5$ wt% $H_2O$ at 150 °C, S/L ratio $= 0.05$, 2.5 min (■: furfural yield in the 2-MeTHF fraction and ■: furfural remaining in the DES-based solvent).

of reaction, solid/liquid (biomass/solvent) ratio, presence of water and GVL, and conventional or microwave heating, were investigated. The best furfural yields ($>75\%$) were obtained with the DES [Ch]Cl:MA (1:3, molar ratio) $+5$ wt% water in a weight ratio of 2:1 with GVL under microwave heating (2.5 min of reaction time and a solid/liquid ratio of 0.050). The use of water and GVL contributed to improved yields by decreasing the solvent viscosity and by potentiating the xylan hydrolysis into xylose and by decreasing the degradation of furfural. Finally, furfural was recovered by distillation from the DES/GVL solvent or from 2-MeTHF after a back-extraction step. The second approach led to higher recovery yields of furfural (up to 89.5%), further allowing the DES/GVL solvent recycling for at least 3 times, in which the furfural production yield was maintained above 69% in the 2-MeTHF fraction.

The process developed in this work has the potential to be scaled up, offering several advantages compared with the current industrial processes, namely a shorter time of reaction, the use of less harsh conditions, and the use of bio-based and recyclable solvents/catalysts. To our knowledge, compared with previously reported studies, this is the fastest and highest-yielding process for the production of furfural.

## Experimental Section

### Chemicals

Cholinium chloride ([Ch]Cl; $\geq 99\%$ purity), furfural ($\geq 99\%$ purity), γ-valerolactone (GVL) (98% purity) and lactic acid (LA, 85% (*w/v*)) were supplied by Sigma (USA). DL-Malic acid (MA, 99.5% purity) was obtained from Panreac (Spain) and glycolic acid (GA, purity 99%) was obtained from Acros Organics (USA). 2-Methytetrahydrofuran (2-MeTHF, 99% purity) was obtained from Alfa Aeasar (Germany). Commercial beechwood xylan (9.39 wt% humidity) was purchased from Apolo Scientific (UK).

### DES preparation

[Ch]Cl was used as the HBA and malic acid (MA), glycolic acid (GA) and lactic acid (LA) as HBDs. The HBA and HBDs were prepared by

weight at the desired molar ratio in sealed glass vials. The water content of all compounds was determined through a Metrohm 831 Karl Fisher coulometer. Mixtures in closed vials were then heated to 70 °C and stirred for at least 1 h until a transparent liquid was formed. Mixtures were cooled to room temperature and kept in sealed glass vials until use. In assays in which water was used (5 and 10 wt%), it was added after the DES preparation.

### Xylan hydrolysis and production of furfural

The furfural production reactions were performed in a Radleys Tech carousel in 30 mL glass vials, with a fixed stirring of 400 rpm. Two xylan/DES weight ratios were tested, namely 0.050 and 0.175. The reactions were performed at 90 or 130 °C, and after the established reaction time (2, 4 or 8 h) the samples were left to cool down then diluted appropriately with deionized water and filtered through a nylon Whatman filter of 0.45 μm pore into appropriate HPLC glass vials. Triplicates were performed in all assays. The test conditions are summarized in Table S1.

The microwave-assisted reactions were performed in a Monowave 300 microwave synthesis reactor from Anton Paar (Austria). Heating was applied as fast as possible, with a heating time always less than 1 min. The best solid/liquid ratio was selected from the previous results (0.050) and both xylan and DES mixtures were weighed and prepared in sealed vials (10 mL). Then, vials were placed in the microwave reactor at a fixed stirring of 600 rpm and removed at the end of the established reaction times (1.5, 2, 2.5, 3.5, 5.0 and 7.5 min). The tested conditions are summarized in Table S2. All reactions were performed in triplicate and presented as average yield.

To increase the furfural production yield, the addition of GVL was tested under microwave irradiation. GVL was added to the DESs that were previously identified as most promising at several weight ratios in relation to the DES (4:1, 1:1, 1:2 and 1:3), and the mixtures were weighed after xylans addition. These mixtures were then placed in the microwave and left to react for the previously determined optimal time.

After the reaction was stopped, 2-MeTHF was added in a 1:1 ratio with the GVL/DES system. Afterwards, the 2-MeTHF was removed and another cycle was performed with fresh solvent. Afterwards, the remaining DES fraction was separated and diluted with deionized water and the recovered 2-MeTHF was diluted with methanol. Samples were filtered using a nylon Whatman filter of 0.45 μm pore into HPLC glass vials.

### Furfural recovery and DES recycling

Furfural was separated from the 2-MeTHF organic phase by distillation. because 2-MeTHF has a lower boiling point ($\approx 80$ °C) than furfural ($\approx 162$ °C), it was distilled first followed by furfural, which has a lower boiling point than GVL (208 °C).[42] The distilled furfural was recovered, weighed and the furfural yield calculated. The recovered furfural was then redissolved in water, diluted and filtered through a nylon Whatman filter of 0.45 μm pore into HPLC glass vials. The recovered DES-based solvent was used in at least three more cycles of xylan conversion to investigate the effect solvent recycling on the furfural production yield. Furthermore, the solvents stability was monitored through $^1H$ and $^{13}C$ NMR spectroscopy. The obtained furfural was compared with a reference sample of furfural. The $^1H$ NMR and $^{13}C$ NMR spectra were recorded using a Bruker Avance 300 at 300.13 MHz and 75.47 MHz, respectively, using deu-

terated water as solvent and trimethylsilyl propanoic acid (TMSP) as internal reference.

## Furfural quantification

The quantification of furfural in each sample was performed by HPLC-DAD (Shimadzu, model PROMINENCE). HPLC analyses were performed with an analytical $C_{18}$ reverse-phase column (250× 4.60 mm), Kinetex 5 μm $C_{18}$ 100 Å, from Phenomenex. The mobile phase consisted of 20% methanol and 80% ultrapure water. The separation was performed in isocratic mode at a flow rate of 0.8 mL min$^{-1}$ and an injection volume of 10 μL. Furfural detection was performed at 268 nm with a diode array detector (DAD). Each sample was analyzed at least in duplicate. The column oven and the autosampler were operated at a controlled temperature of 35 °C. Calibration curves were established with pure furfural dissolved in water. Furfural yield is expressed in moles of furfural in relation to the number of moles of xylose present in the xylan sample used.

## Acknowledgements

## Conflict of interest

The authors declare no conflict of interest.

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