



Evaluation of homogeneous and heterogeneous catalytic strategies for furfural production from sugar-derived biomass in a solvent-free green pressurized reaction media (subcritical water-CO₂)

Alba E. Illera^{a,*}, Helena Candela^a, Alejandro Bermejo-López^b, Pedro Barea^a, Patricia Alonso-Riaño^a, Óscar Benito-Román^a, Sagrario Beltrán^a, M. Teresa Sanz^a

^a Department of Biotechnology and Food Science, University of Burgos UBU, Plaza Misael Bañuelos s/n, 09001, Burgos, Spain

^b Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Barrio Sarriena, s/n, 48940, Leioa, Bizkaia, Spain

ARTICLE INFO

Keywords:

Catalysts
Furfural
Pressurized carbon dioxide
Subcritical water
Xylose

ABSTRACT

A green organic, solvent-free, subcritical water-CO₂ (subW-CO₂) system was proposed for the production of furfural from the main hemicellulose's sugar, xylose. Despite subW itself showed potential for furfural generation due to its catalytic properties under subcritical conditions; when CO₂ was added into the system as pressurization agent, higher yields were reached due to its effect as a Brønsted acid when dissolved in water. Furthermore, its combination with different Lewis acidic catalysts showed a synergistic effect, further improving furfural yield. In a batch configuration, five homogeneous and four heterogeneous catalysts were tested at 180 °C and 5.5 MPa and compared for the first time in a subW-CO₂ reaction medium. Different furfural production paths were determined for the two catalysts types, with higher xylose isomerization rates to xylulose when homogeneous trivalent metal catalysts were used. CrCl₃ and *Nafion NR50* resin were selected as best catalysts from each of the groups due to higher furfural production rates (51.9 ± 0.9 % yield/h) and higher furfural selectivity (60.9 %), respectively. Furthermore, *Nafion NR50* catalytic activity remained unchanged after 10 runs at 180 °C. The green subW-CO₂ system furfural yields were comparable to water-organic solvent biphasic ones, proving to be a promising green alternative.

1. Introduction

Furfural (C₅H₄O₂), also known as 2-furaldehyde, is an aromatic aldehyde obtained by the hydrolysis of pentoses or other polysaccharides rich in pentoses through their subsequent dehydration [1]. Due to the high number of its industrial applications, such as production of solvents, polymers or fuel additives, furfural production has gained great interest in the last years and current research [2]. It is considered a potential bio-based chemical, and its production has been predicted to grow. In 2020, its world production was estimated between 200,000 and 360,000 tonnes [3] by the International Energy Agency (IEA). Furfural is industrially produced worldwide by diverse processes where lignocellulosic biomass is used as the raw material [4,5]. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin. Composition varies with the type of biomass, but hemicellulose usually comprises the 23–32 % [6]. Hemicellulose is a heterogeneous polymer

formed by C₅ and C₆ sugars, such as xylose, arabinose, mannose or glucose, among others, that linked by glycosidic bonds, form polysaccharides such as xylans, arabinans and glucans, easily broken into their monomeric compounds [5]. The resulting pentoses and hexoses can be converted into valued chemicals, highlighting in this case furfural production from pentoses dehydration [7]. Currently, batch and continuous operating modes are used in the industry for furfural production, as well as a wide variety of lignocellulosic biomass, mainly wood of different origin, bagasse or corn cob. Despite the process differences, most of them use H₂SO₄ as the catalyst, organic solvents as reaction media, and operating temperatures ranging from 150 to 200 °C, although higher temperature can be used in specific cases. Due to the mentioned value of furfural, many are the research studies focused on its production by different means and raw materials, being sugars, polysaccharides or lignocellulosic biomass the main ones. Focusing on the synthesis of furfural from sugars, as the basis of the process, the most

* Corresponding author.

E-mail address: aeillera@ubu.es (A.E. Illera).

<https://doi.org/10.1016/j.biombioe.2024.107304>

Received 20 February 2024; Received in revised form 1 July 2024; Accepted 6 July 2024

Available online 10 July 2024

0961-9534/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>).

abundant methods found in literature are the ones where catalysts are used, mainly homogeneous ones such as mineral acids, organic acids, metal salts and ionic liquids, and in a lesser extent, heterogeneous ones, such as carbon acids, clays, ion-exchange resins or zeolites [8]. Overall, furfural yield of these biomass samples can be in the range from 40 up to 70 %, although it is frequently around 50 % [9,10]. However, these implemented methods also present some drawbacks, such as high amounts of solvents and chemicals consumption, with their corresponding disposal, contributing to the environment detriment, what makes necessary a greener approach for furfural production.

Another limiting factor for the obtention of higher furfural yields is its fast degradation in aqueous media into humins, insoluble polymers formed when furfural remains dissolved in the aqueous medium [9]. Therefore, a common technique to increase furfural yield is the use of biphasic systems formed by a water-organic solvent mixture, where the sugar is dissolved in the water solution, and furfural is transferred into the organic phase as it is produced, avoiding its degradation and therefore increasing its yield [10]. Although some of the solvents used are considered as green, their disposal once they are no longer needed will negatively affect the environment.

As a greener alternative, a biphasic system consisting in subcritical water (subW) as the aqueous medium, and CO₂ as the pressurizing agent was used for the first time for the production of furfural from xylose in a one-pot reaction, from now on named as subW-CO₂ system. The great advantage that this system offers over the previously mentioned ones is the fact that no mineral acids and no organic solvents are needed for furfural production, as the only required reaction media is water. Fig. 1 shows the two most commonly accepted pathways for the conversion of xylose to furfural, (1) through a direct dehydration in the presence of a Brønsted acid, or (2) indirectly, through first an isomerization of xylose to xylulose through a Lewis acid, and then its dehydration to furfural with a Brønsted acid [11]. However, based on experimental data and literature, it is also known that isomerization of monomers can take place in the absence of a Lewis acid, and dehydration to furfural can happen with no Brønsted acid addition, although the yields of these reactions are significantly lower due to higher activation energy requirements [12]. The second pathway presents some advantages since it produces less side reactions and requires milder conditions than the direct dehydration, providing higher furfural yields [13].

In the proposed subW-CO₂ system, xylose is dissolved in the subcritical water, which is water in its liquid state in the temperature range from 100 °C to 374 °C [14]. Under these conditions, the water

acquires new properties, such as an increase of its ionic product, which gives the water acidic and basic catalyst properties [14], due to the higher concentration of hydronium (H₃O⁺) and hydroxide (OH⁻) ions. In a recent study where glucose was dehydrated to hydroxymethylfurfural in a subW-scCO₂ treatment, it was determined that the subW itself could act as a Lewis and Brønsted acid at the same time. They observed that isomerization of the sugar monomer was favoured by hydroxide ions, acting as the Lewis acid, and the dehydration step of the isomer was produced by the hydronium ions, as a Brønsted acid [14]. This means that in a subW system at an appropriate temperature, xylose conversion to furfural could take place without further catalysts addition. In the proposed subW-CO₂ system, the Brønsted acid effect is reinforced through the election of CO₂ as the pressurizing agent, which partially dissolves in the water, and forms carbonic acid, acting as a Brønsted acid after its dissociation in water. Additionally, to further improve furfural production, catalysts that act as Lewis acids were added into the system.

Therefore, the aim of this work was to study for the first time the effect and interactions of different homogeneous and heterogeneous catalysts in a solvent-free subW-CO₂ system for furfural production in a one-step system from sugar-derived biomass, xylose.

2. Experimental section

2.1. Materials

Xylose (99 %), furfural (99 %), and the homogeneous catalysts used in this work, chromium (III) chloride hexahydrate (98 %), aluminum chloride hexahydrate (99 %), iron (III) chloride hexahydrate (97 %), aluminium potassium sulfate dodecahydrate (99 %) and aluminum sulfate tetradecahydrate (97 %), were purchased from Sigma-Aldrich. The heterogeneous catalysts, Montmorillonite K10, zeolite ferrierite, ammonium, Zeolite β, hydrogen (Hβ), and Nafion NR50 resin, were purchased from Thermo Scientific.

2.2. Subcritical water (subW) treatments

Subcritical water (subW) treatments of xylose were performed in a 0.5 L reactor ($p_{\max} = 6$ MPa) in a batch configuration. This equipment has been described elsewhere [15]. Briefly, in a typical run, 200 mL of the prepared sugar monomer and the required amount of catalyst were charged into the reactor and homogenized with a magnetic stirrer. An initial sample was collected and pH was determined at the beginning of each kinetic experiment. The reactor was then sealed and working temperature was reached through a ceramic resistor jacket. At the same time, the system was pressurized up to 5.5 MPa using either N₂ as an inert gas, or CO₂. Average heating time was 8 ± 1 °C/min. Total treatment time was 4 h for each experiment, and initial time was considered as the time when the desired working temperature was reached. After that, samples were withdrawn periodically and kept refrigerated until their analysis to follow the furfural production kinetic. A final sample was collected by the end of the experiment and then the reactor was let to cool down until reaching a temperature below 90 °C, when it could be depressurized. pH was determined in all collected samples. In selected experiments, the depressurization gas phase was collected in two consecutive cold traps and further analysed in the same way as the subW collected samples. Filtration of the final liquid in the subW reactor allowed to collect formed solid materials.

The present study aims to elucidate furfural production from the biomass sugar-derived xylose conforming the polysaccharide fraction of lignocellulosic biomass. This information will serve for future treatments of biomass by subW. Therefore, considering this future approach, and based on the composition in hemicelluloses, specifically in xylose, of frequent studied biomass such as corn stover or brewer's spent grain, the initial concentration of xylose solutions was fixed as 11 g/L (73 mM). The effect of different operating conditions, such as pressurization

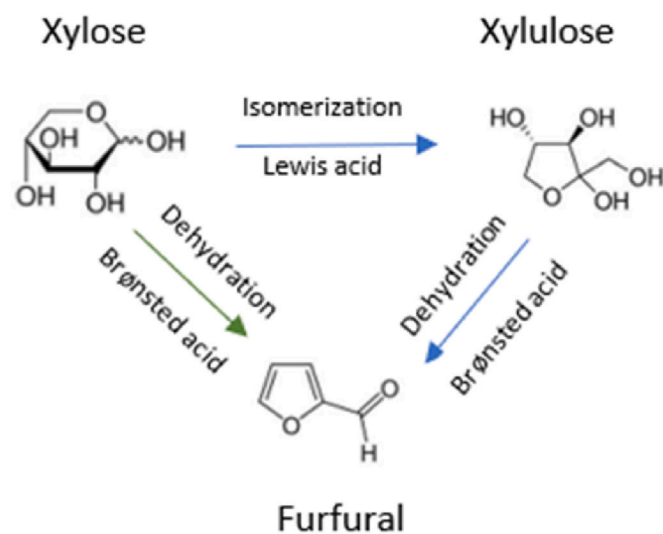


Fig. 1. Furfural production pathways, direct (green) and indirect (blue) [12]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

agent, and presence and type of catalyst were considered in this study.

2.2.1. Effect of pressurization agent and Lewis acid catalyst presence

The effect of the pressurization agent (N₂ or CO₂) on furfural production from xylose was carried out at 180 °C. This effect was studied in the absence of any added Lewis catalyst and by adding a 2 wt % of AlCl₃·6H₂O (0.91 mM). As a control system, the Lewis catalyzed system was carried out at atmospheric pressure and 75 °C.

2.2.2. Effect of homogenous and heterogeneous catalysts on furfural production

The effect of different homogeneous and heterogeneous catalysts was studied. All trials were performed at 180 °C and 5.5 MPa using CO₂ as pressurization agent and catalyst concentration of 2 wt % in relation to xylose (2.2 g xylose and 0.044 g catalyst in 200 mL). In the case of *Nafion NR50*, supplied as solid transparent spheres, 10 units were added (0.48 g).

Regarding homogeneous catalysts, three different metal trivalent salts acting as Lewis's acids, AlCl₃·6H₂O (0.91 mM), CrCl₃·6H₂O (0.83 mM) and FeCl₃·6H₂O (0.81 mM), and two aluminum catalysts containing sulfates, Al₂(SO₄)₃·14H₂O (0.64 mM) and KAl(SO₄)₂·12H₂O (0.73 mM), were selected to test their catalytic activity in the subW-CO₂ system and to study the effect of the cation and the anion on the catalytic process. From now on they will be named as AlCl₃, CrCl₃, FeCl₃, Al₂(SO₄)₃ and KAl(SO₄)₂.

Four heterogeneous catalysts were tested in the subW-CO₂ system. Two commercial zeolites: Zeolite ferrierite, ammonium (SiO₂:Al₂O₃), and Zeolite β, hydrogen (Hβ) (Al₂O₅Si), one clay: Montmorillonite K10, and one resin, *Nafion NR50*, a solid sulfonated polymer with a strong Brønsted acidity [16]. *Nafion NR50* reutilization was tested up to 10 times. For this, after each experiment with the resin spheres, those were collected and washed with distilled water, until clear water, in order to remove the remaining furfural or other degradation components that could have been formed.

To better characterize the mechanism of furfural production using different catalysts, the kinetics for xylose, xylulose and furfural variations were studied, as well as their effect in pH and in the formation of side products.

2.3. Furfural production evaluation

To evaluate the effectiveness of each of the conditions and catalysts tested, furfural yield was calculated using Equation (1).

$$\text{Furfural yield (\%)} = \frac{\text{moles of furfural}_{(t)}}{\text{moles of sugar monomer}_{(0)}} * 100 \quad (\text{Eq. 1})$$

The selectivity of the process was also evaluated according to Equation (2):

$$\text{Furfural selectivity (\%)} = \frac{\text{moles of furfural}_{(t)}}{\text{moles of sugar monomer}_{(0)} - \text{moles of sugar monomer}_{(t)}} * 100 \quad (\text{Eq. 2})$$

Additionally, sugar monomers conversion was also evaluated using Eq. (3).

$$\text{Sugar monomers conversion (\%)} = \left(1 - \left(\frac{\text{moles of unreacted monomer}_{(t)}}{\text{moles of monomer}_{(0)}} \right) \right) * 100 \quad (\text{Eq. 3})$$

where (t) indicates the time during the treatment when the sample was taken, and (0) the initial concentration.

Initial furfural production rate (% yield/h) and xylose conversion rate (% converted/h) were compared among catalysts. For this, a linear

regression of their initial reaction rate data was performed using furfural production (% yield) or xylose conversion (% converted) values corresponding to the linear reaction rate period, as the dependent variables, and time, (in average, the time from 0 to 0.5 h), as the independent one. The slope values obtained from each catalyst data representation were statistically compared among the homogeneous or heterogeneous groups using Statgraphics v.19.

2.4. Analytical methods

2.4.1. High-performance liquid chromatography (HPLC) analysis

All compounds present in the initial and hydrolyzed solutions were identified and quantified by high-performance liquid chromatography (HPLC) using an Aminex-HPX-87H column, a refractive index detector (RID), and a variable wavelength detector (VWD). The three items were maintained at 40 °C during analysis, and 0.005 M sulphuric acid was used as mobile phase. A calibration for each of the compounds was previously performed [17].

2.4.2. pH measurements

pH values were measured in all collected samples using a GLP 21 pH meter (Crison Instruments S.A.) right after their collection and prior to HPLC analysis.

3. Results

3.1. Effect of pressurizing agent and catalyst presence

Fig. 2 shows the effect of the pressurization agent and the synergic effect of a Lewis catalyst, specifically AlCl₃, on furfural yield from xylose. Regarding the pressurization gas, it can be observed that in the subW system, furfural was produced even in the absence of any catalyst. When N₂ was used, a 30 % maximum yield was obtained for furfural, confirming the role of subW as a Lewis and Brønsted acid itself, and its action as a catalyst [14]. But when CO₂ was used, the furfural yield showed an increase up to 41 %, produced by the partial dissolution of

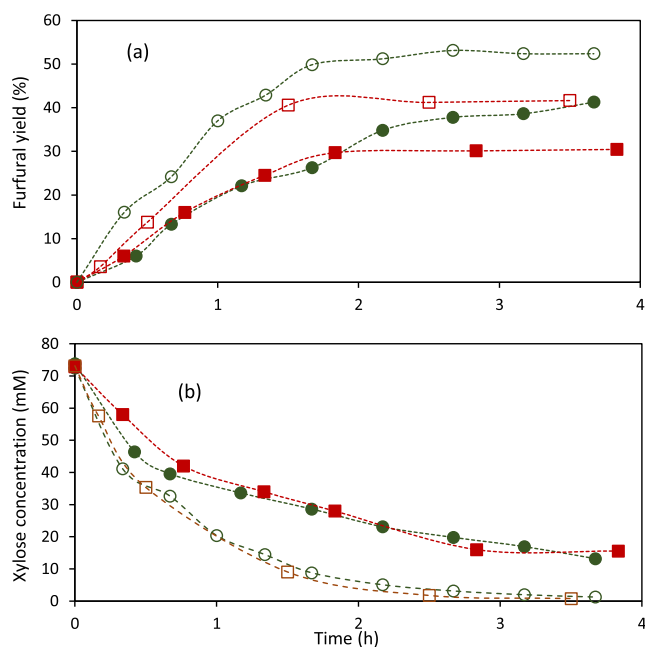


Fig. 2. (a) Furfural yield (%) and (b) xylose concentration (mM) in the liquid phase during subW experiences at 180 °C and 5.5 MPa using xylose (73 mM) and AlCl₃ (0.91 mM): CO₂-no catalyst (●), CO₂-2 % AlCl₃ (○), N₂-no catalyst (■) and N₂-2 % AlCl₃ (□). Lines are a guide to the eye.

the gas in water, producing carbonic acid, which acts as a Brønsted acid, and therefore improving furfural production compared to N_2 . When a Lewis acid ($AlCl_3$) was added, furfural production further increased for both pressurization agents. In the case of the N_2 experiment, furfural yield approximately increased from 30 to 41 %, and in the CO_2 one, from 41 to 53 %.

Xylose consumption was initially slower in the absence of catalyst (Fig. 2b). However, despite of the similar xylose consumption rate from 1 h of treatment, higher furfural yield was obtained in the CO_2 -no catalyst experiment than when nitrogen was used. The same behaviour was observed in the comparison where catalyst was included, confirming a higher selectivity of the subW- CO_2 system towards furfural production compared to the subW- N_2 system.

When the CO_2 -no catalyst treatment was compared with the N_2 -2 % $AlCl_3$ one, it was observed a faster furfural production for the second one, but the non-catalyzed- CO_2 system reached the same furfural yield by the end of the treatment (approximately 41 %) (Fig. 2a). This indicates that the catalytic activity of adding CO_2 as a pressurization agent can be comparable to the addition of a Lewis acid in a subW system, although with a slower rate since probably the direct path (Fig. 1), with a higher activation energy, is being promoted due to the increased Brønsted acidity compared to the Lewis one. The system CO_2 -2 % $AlCl_3$ showed the highest furfural production rate and yield, showing a maximum of 53.1 % after 2.7 h (Fig. 2a). Therefore, it can be concluded that there is a synergistic effect when using $AlCl_3$ as a Lewis acid and dissolved CO_2 as a Brønsted acid, combination that yielded the best results in subW reaction medium for furfural production. Furfural yield production in the subW system can be established in the following order: N_2 -no catalyst < CO_2 -no catalyst \leq N_2 -2 % $AlCl_3$ < CO_2 -2 % $AlCl_3$. The gas phase in the subW system was collected and analysed after depressurization in the N_2 -2 % $AlCl_3$ and CO_2 -2 % $AlCl_3$ experiments, to better understand the furfural partition behaviour in the two different pressurizing agents. 0.098 mg of dissolved furfural were found in the N_2 gas phase, while 1.136 mg in solution were collected in the CO_2 gas phase, more than 10 times more. These values indicate that the distribution coefficient of furfural between the liquid and gas phases, seems to be favourable to carbon dioxide when compared to nitrogen, as well as the confirmation of a higher production of furfural when using this gas.

A Lewis-catalyzed ($AlCl_3$) trial was performed in an aqueous reaction medium at atmospheric pressure and 75 °C to evaluate the performance of the catalyst in the absence of subcritical conditions. After 4 h, no significant conversion of xylose or furfural production was observed. Therefore, it can be said that not only the presence of a Lewis acid is necessary for furfural production, but also specific treatment conditions, such as the ones provided by subW. As previously explained, under subcritical conditions, water suffers properties changes, being the increase in its self-ionization product (K_w) with temperature, a key one. At room temperature, water pKa is 13.99, 12.70 at 75 °C and 11.44 at 180 °C at their corresponding saturated pressure at each temperature [18]. This makes pH of the reaction medium to decrease and a corresponding increase of the ionic strength, making subW to act as a catalyst.

Based on the findings of this section, the subW- CO_2 system was selected for further studies for catalytic furfural production.

3.2. Effect of different catalysts over furfural yield

3.2.1. Homogeneous catalysts

In Fig. 3, the furfural yield and furfural selectivity during the subW experiments using five different homogeneous catalysts have been plotted. According to section 3.1, in the absence of catalyst, the maximum furfural yield observed was 41.6 % after a total 4-h experiment, while when using any of the selected homogeneous catalysts, the maximum furfural yield was close to 50 % in all cases.

3.2.1.1. Effect of the cation on furfural production.

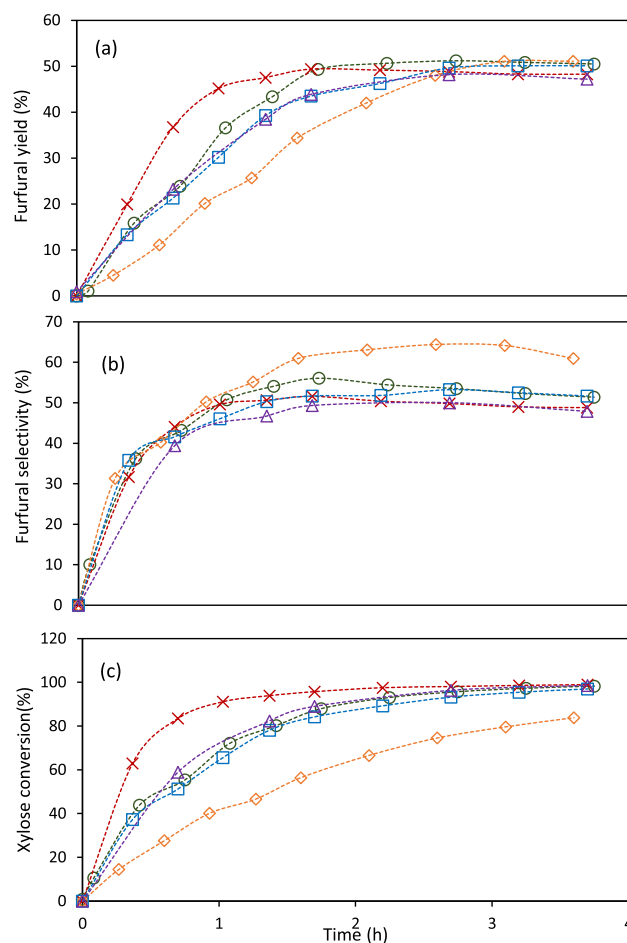


Fig. 3. Furfural yield (a) and selectivity (b) and xylose conversion (c) during subW experiments in a subW- CO_2 system at 180 °C and 5.5 MPa using xylose (73 mM) with the homogeneous catalysts: $CrCl_3$ (0.83 mM) (x), $AlCl_3$ (0.91 mM) (o), $FeCl_3$ (0.81 mM) (e), $KAl(SO_4)_2$ (0.73 mM) (□) and $Al_2(SO_4)_3$ (0.64 mM) (△). Lines are represented as a guide to the eye.

the cation was analysed considered the catalysis by $AlCl_3$, $CrCl_3$ and $FeCl_3$. All catalysts showed furfural selectivity values around 50 % except $FeCl_3$, which nearly reached 65 %, showing to be the catalyst with the highest selectivity towards furfural, although the one with the lowest furfural production rate. The catalyst activity was also evaluated through the initial furfural production and xylose conversion rates (Table S1). Among the three trichloride catalysts, Cr^{3+} had the highest slope value for the initial rate for furfural production, with a 51.9 ± 0.9 % yield/h, followed by Al^{3+} with a 32.6 ± 1.5 value and finally Fe^{3+} with 20.8 ± 0.6 % yield/h. They were all significantly different among them both for furfural yield and xylose conversion rates. Regarding initial xylose conversion rate, a similar trend was determined, showing Fe^{3+} the lowest slope for xylose conversion rate among all the tested catalysts.

Cr^{3+} and Al^{3+} reached their maximum furfural yield in around 1.5 h of isothermal treatment, while Fe^{3+} needed 3 h to produce the same furfural yield values. Although the three catalysts could be expected to have similar effect as Lewis acid catalysts, the slower conversion of Fe^{3+} when compared to Cr^{3+} and Al^{3+} complexes has been previously proved in a similar scenario, where glucose conversion mechanism to fructose was studied at 140 °C and 80 bar [19]. While the three metals are hard Lewis acids, Al^{3+} and Cr^{3+} showed pKa values of 5.5 and 4.1, and the pKa value for Fe^{3+} was 2.2. This much higher Lewis acidity was attributed as the reason for lower conversion rates, as it was found that it prevented the formation of ligands of interest that lead to the formation

of furfural. On the other hand, Al^{3+} and Cr^{3+} fitted into the optimal catalyst criteria, favoring the furfural production path [19].

Lyu et al. (2021) also performed an extensive study regarding furfural production/inhibition when using metal chloride catalysts [5]. Their conclusion was that the best properties for furfural production in a catalyst were mainly three: (1) to have a strong Lewis acid strength. Regarding the three tested catalysts their Lewis acid strength is Al^{3+} (0.58) > Fe^{3+} (0.53) > Cr^{3+} (0.50). (2) To have weak oxidizing properties, which measured through the standards reduction electrode potentials is Fe^{3+} (+0.77 V) > Cr^{3+} (-0.42 V) > Al^{3+} (-1.68 V), and finally, (3) to form hydroxides of the metal ions with high solubility when dissolved, which in this case are $\text{Cr}(\text{OH})_3$ (6.7×10^{-31}) > $\text{Al}(\text{OH})_3$ (1.9×10^{-33}) > $\text{Fe}(\text{OH})_3$ (6.3×10^{-38}). As explained before, the higher Lewis acid strength of Fe^{3+} did not promote furfural production, so it would not be a determining parameter. The lower solubility products obtained with FeCl_3 could be also a reason for lower furfural production. However, Lyu et al. (2021) found that while precipitation of $\text{Fe}(\text{OH})_3$ took place at 90 °C, it did not at 170 °C. Therefore, it is probable that Fe^{3+} presents worse properties for furfural production than Cr^{3+} or Al^{3+} due to its higher oxidizing action. The authors found that 90 % of Fe^{3+} ions had been reduced to Fe^{2+} after xylose treatment with FeCl_3 at 170 °C, drastically reducing the action of Fe^{3+} and the formation of the corresponding hydroxide $\text{Fe}(\text{OH})_3$ [5]. This effect is clearly observed in the low and much slower furfural yield rate of this catalyst (Table S1 and Fig. 3a), due to the small availability of Fe^{3+} . The main side products quantified during xylose treatment with the 3 metal chloride catalysts were included in Fig. S1. Formic and acetic acid were the main detected compounds. In the case of formic acid, CrCl_3 showed a similar trend as for furfural production, much higher and faster than the other two compared catalysts, reaching 9.5 mM as the highest concentration. In the case of acetic acid, the three metal catalysts showed a similar trend, with average values of 1.5 mM. With these results, it can be concluded that although lower furfural concentration was obtained using FeCl_3 , it was not due to a higher production of side products, but due to the lower availability of the metal ion due to its oxidation. This lower concentration of side products is in accordance with FeCl_3 having the highest selectivity towards furfural.

Other studies showed similar results for CrCl_3 and AlCl_3 . Binder et al. (2010), synthesized furfural in a biphasic aqueous:organic solvent from xylose using CrCl_3 as catalyst, and dimethylacetamide (DMA) as solvent plus LiBr as additive. After 4 h at 100 °C, a furfural yield of 47 % was reached [20]. In the literature, synergic effects by combining Brønsted and Lewis acid catalysis were also considered. Choudhary et al. (2012) used HCl as a Brønsted acid, and CrCl_3 as Lewis acid in an aqueous media. When only using HCl at 145 °C, a maximum furfural yield of 29 % was obtained after 2 h, while when CrCl_3 was added, the yield increased to 39 % at the same temperature and 1 h of treatment [11]. The same behavior was observed by Lopes et al. (2017), when furfural yield from xylose was increased from approximately 40 % to 68 and 65 % when formic acid (55 wt%) was added to CrCl_3 or AlCl_3 , respectively [21]. Those results are in agreement with the present work, where furfural yield was 41.6 % in the subW-CO₂ system and no Lewis catalyst (high Brønsted acidity), and it increased up to around 50 % with any of the Lewis acid catalysts addition, proving the effectiveness of their synergistic effect. Therefore, it can be concluded that the use of pressurized CO₂ as a Brønsted acid through its dissolution in water can be equivalent to other conventional ones, such as HCl or formic acid. However, the use of those acids presents many disadvantages such as being corrosive for the used materials, specific disposal requirements and air and water pollutants, what makes the subW-CO₂ system a convenient and ecofriendly alternative.

3.2.1.2. Effect of the anion on the furfural production. The kinetic catalyzed by $\text{Al}_2(\text{SO}_4)_3$ was also plotted in Fig. 3, showing similar or lower results as to AlCl_3 (maximum furfural yield of 48.2 %). Under the tested

conditions, the SO_4^{2-} group did not improve furfural production from xylose, although this anion has shown to improve furfural yield when compared with others in previous studies [22]. Yang et al. (2017) highlighted the importance of the SO_4^{2-} ions to catalyze xylose isomerization to xylulose [23], but as previously stated, the reaction medium and the used substrate are key parameters in order to compare the performance of catalysts. In this study, the two catalysts containing sulfates, $\text{KAl}(\text{SO}_4)_2$ and $\text{Al}_2(\text{SO}_4)_3$ showed similar maximum furfural yield values between them, with maximum values close to 50 %. $\text{KAl}(\text{SO}_4)_2$, commonly known as “alum”, is frequently used in organic synthesis due to its low cost and non-toxicity, and has shown its effectiveness on furfural production from feedstocks in biphasic reaction media. No previous studies, where non-organic biphasic media were used, were found for comparison, but furfural yield obtained in this work was similar to the results obtained in the studies using organic biphasic media. Gupta et al. (2017) obtained a furfural yield of 47 % when treating xylose in a water + MIBK system and $\text{KAl}(\text{SO}_4)_2$ at 180 °C for 6 h [24,25], and in the present study, using the same catalyst and a shorter treatment, a furfural yield of 50.1 % was obtained in the subW-CO₂ system (Fig. 3a), showing once again that the new proposed system can be equivalent to the biphasic organic ones.

To summarize, as it can be seen in Table S1, no significant difference was found among the initial furfural rate of the three catalysts containing Al^{3+} as cation, as well as similar maximum furfural yield values (Fig. 3a), what means that in these catalytic systems, the main element promoting furfural production is the trivalent metal itself and the anion group effect was not as relevant.

3.2.1.3. Furfural production paths among homogeneous catalysts. To better understand the role of the trivalent cation metals and the different anion groups in furfural production paths, the formation of the intermediate xylulose (indirect furfural production path) was further investigated. The variation in the concentration (mM) of the main three components involved in the furfural formation path during subW-CO₂ experiments was plotted in Fig. 4 for all homogeneous catalyst trials.

Regarding the metal trivalent catalysts, as previously observed, great differences were found in the rate of xylose conversion and furfural production, with Cr^{3+} showing the highest rates and Fe^{3+} the lowest, what aligns with the previously lower xylose conversion rates found for this ion. It is also interesting to observe the differences in the formation of the intermediate xylulose. In Fig. 4b–c it is possible to observe that the formation of xylulose was directly related to the furfural production, since, the higher the xylulose concentration obtained, the faster the furfural rate production. In the case of the Cr^{3+} catalyst, the maximum in xylulose concentration observed was 12.3 mM, being 10.8 mM for Al^{3+} and 5.8 mM for Fe^{3+} .

This maximum was found in early treatment times (less than 1 h), and then its value gradually decreased, although furfural concentration kept increasing in a greater extent than xylulose consumption. This behavior indicates that furfural production was led by the indirect formation path (Fig. 1), with furfural production coming from xylose isomerization to xylulose and its consequent dehydration to furfural. While there is xylose available, xylulose is being formed and then transformed into furfural. After longer time, when there is no xylose or it is present in a low concentration, the xylulose concentration decreases and disappears as well, and furfural concentration remains unchanged. On the other hand, when xylose has not been completely consumed, as in the case of FeCl_3 and no-catalyst experiments, xylulose is still present after long treatment times, and furfural concentration does not stabilize, keeps slightly continuously increasing (Fig. 4b). Regarding the sulfate-containing catalysts, very similar xylose, xylulose and furfural kinetics can be observed as to AlCl_3 , with intermediate rates between Cr^{3+} and Fe^{3+} catalysts. This confirms the leading effect of Al^{3+} over the sulfate group.

The subW-CO₂-no catalyst xylulose formation was higher than

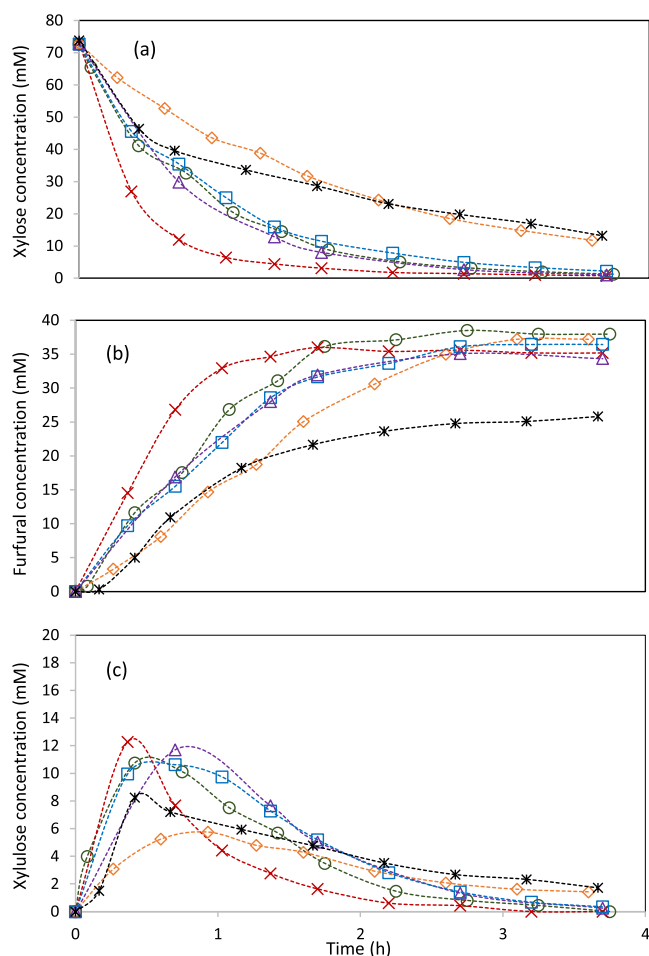


Fig. 4. (a) Xylose, (b) furfural and (c) xylulose concentration (mM) during subW-CO₂ experiences using xylose (73 mM) at 180 °C and 5.5 MPa with no catalyst (*) and the homogeneous catalysts: CrCl₃ (0.83 mM) (x), AlCl₃ (0.91 mM) (o), FeCl₃ (0.81 mM) (◊), KAl(SO₄)₂ (0.73 mM) (□) and Al₂(SO₄)₃ (0.64 mM) (△). Lines are a guide to the eye.

expected, with a maximum concentration of 8.2 mM, close to the values obtained by the Al³⁺ catalysts. However, furfural production was much lower than when any of the catalysts were used (Fig. 4b), confirming the previously mentioned synergistic effect of the catalyst and the subW-CO₂ system.

Based on all results in this section, CrCl₃ was selected as the best homogeneous catalyst under the experimental conditions used in this work, due to its significantly higher furfural production rates in the subW-CO₂ system that led to higher furfural productivities in the first hour. An additional advantage of the metal trivalent salts is their low price and abundance, and that they are environmentally friendly [23,26,27].

3.2.2. Heterogeneous catalysts

In Fig. 5, the furfural yield and selectivity and xylose conversion for the four heterogeneous catalysts tested at 180 °C in the system subW-CO₂ can be observed. In general, the reached yields were similar among all the heterogeneous catalysts with values around 40–45 %, but those values were lower than the previously reported ones by the homogeneous catalysts, with yields closer to 50 % (see Fig. 3a). Also, slower furfural initial production and xylose initial conversion rates were determined for heterogeneous catalysis (Table S2) probably due to internal mass transfer limitation to reach the active sites in the heterogeneous catalysts.

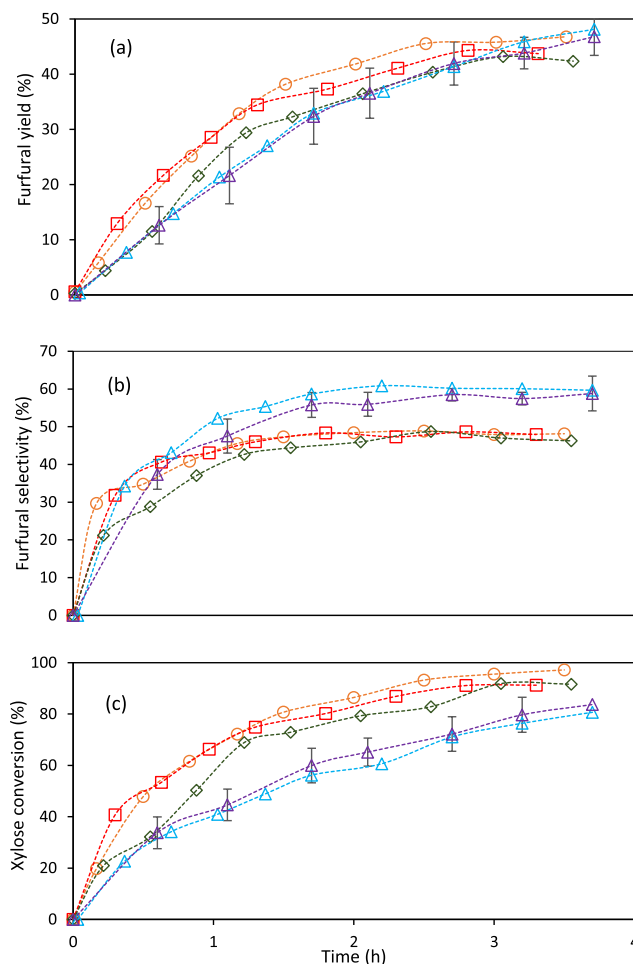


Fig. 5. (a) Furfural yield (b) and selectivity and (c) xylose conversion (%) during subW experiments in a subW-CO₂ system at 180 °C and 5.5 MPa using xylose (73 mM) with heterogeneous catalysts: Ferrierite ammonium (o), Montmorillonite K10 (□), Zeolite Hβ (◊), Naftion NR50 (△) and average 10 runs Naftion NR50 (△). Lines are represented as a guide to the eye.

Considering the different heterogeneous catalysts groups used, some conclusions can be raised.

3.2.2.1. Zeolites as catalyst. Ferrierite ammonium showed the fastest xylose conversion and furfural production (Fig. 5) among all tested heterogeneous catalysts. Regarding zeolites, significantly higher initial furfural production rate and furfural yield values than Zeolite Hβ (Table S2) were obtained with ferrierite ammonium (maximum furfural yield of 46.8 and 43.8 % for ferrierite ammonium and Zeolite Hβ, respectively). Zeolites are microporous aluminosilicates that differ among them in their surface area and Si/Al ratio. The Si/Al mole ratio was 20:1 for ferrierite ammonium and 360:1 for zeolite Hβ. The higher the Si/Al ratio value, the lower the acidity of the zeolite due to the lower Al content. Therefore, the higher initial furfural production rate was due to the higher acidity of ferrierite ammonium when compared to zeolite Hβ [28].

According to our knowledge this is the first time that zeolite has been used in a subW-CO₂ reaction medium. Wang et al. (2022), obtained a 77.5 % furfural yield from xylose at 180 °C when using water/n-butanol as reaction media and modified zeolites as catalyst [29].

3.2.2.2. Clays as catalyst. Using Montmorillonite K10, the highest furfural yield value was 44.3 % (after 2.8 h). Furfural production and

xylose conversion rates were similar to the Zeolite ferrierite ammonium ones, although statistical differences were found (Table S2). The use of clays for furfural production is not very common in literature. Nanao et al. (2017), used Montmorillonite K10 to produce furfural from xylose in a biphasic mixture of water and toluene 1:4 for 5h at 140 °C, reaching a furfural yield of 27 % when using xylose [30]. Higher furfural yield was obtained in the present study, although comparison is difficult since higher temperature was employed in this work (180 °C) and reaction was carried out in subW-CO₂ reaction medium.

3.2.2.3. Nafion NR50 as catalyst. Finally, regarding *Nafion NR50*, it showed the lowest initial furfural production and xylose conversion (Table S2) among all heterogeneous and homogeneous catalysts. However, it also showed a high furfural yield (48.1 %) and the highest selectivity (60.1 %) (Fig. 5b) among all the heterogenous catalysts and most of the homogeneous ones. Furfural initial formation rate is lower in *Nafion* resins since the hydrophilic cluster-channels of the catalytic sulfonic acid groups are dispersed in the hydrophobic matrix of the resin. For furfural production, xylose must first migrate through these clusters, and its dehydration is catalyzed once it reaches the mentioned acid groups [31].

The benefit of using heterogeneous catalysts is the easiness to separate them from the liquid phase and the option to reuse them. It is important to mention that although these catalysts are considered as heterogeneous, all of them except *Nafion NR50* got completely dissolved in the subW-CO₂ reaction medium at the end of the kinetic experiments. Therefore, only the *Nafion NR50* resin could be tested for its reutilization. *Nafion NR50* resin was reutilized during 10 runs at 180 °C in the subW-CO₂ reaction medium. In Fig. 5, the average furfural yield and xylose conversion along the 10 runs reusing the resin were plotted. As it can be appreciated, no significant loses of *Nafion NR50* catalytic activity for furfural production occurred by reusing the resin spheres, with average furfural yield values similar to those of the first run.

Le Guenic et al. (2016) also tested the reusability of *Nafion NR50* through consecutive reactions of 40 min at 170 °C in a biphasic water-CPME 1:3 system and overnight regeneration of the resin with HCl. After the third cycle, they observed a decrease in furfural yield from 80 to 65 %, attributed to the deposition of humins in the pellets, deactivating the resin [32]. In the present study, *Nafion NR50* spheres were washed with water after each kinetic run, but no deactivation of the pellets occurred during 10 cycles, what indicates a probable lower production of humins (solid degradation by-products) in the subW-CO₂ system than in organic solvents, as it will be later discussed.

3.2.2.4. Furfural production paths among heterogeneous catalysts. As previously described for the homogeneous catalysts, xylose, xylulose and furfural concentration profile during the subW-CO₂ treatments were plotted in Fig. S2. Data for the non-catalyst trial has been also added for comparison.

Xylulose formation in the non-catalyzed experiment was higher than in any of the trials with the heterogeneous catalyst with a concentration of 8.2 mM. The zeolites, followed it with values close to 7 mM, the clay reached 5.5 mM, and finally the *Nafion* resin just reached a maximum of 4 mM, half of the non-catalyzed one. The zeolites, clay and resin led to a lesser extent the isomerization of xylose into xylulose compared to the trivalent metals.

It is also interesting to highlight the only slightly higher furfural production reached by the heterogeneous catalysts studied in this work, compared to the non-catalyzed trial, especially in the initial stages of the treatments (Fig. S2a). This leads to the conclusion that, in general, the addition of the heterogeneous catalysts studied in this work did not contribute in a great extent to improve furfural production from xylose in the subW-CO₂ system, or at least, not as much as the homogeneous ones. Among the tested heterogeneous catalyst, *Nafion NR50* resin was selected as the preferred one, due to its high furfural yield and selectivity

(Fig. 5), and due to the possibility of its reutilization during at least 10 runs in the tested conditions with no detrimental of its catalytic properties.

3.2.2.5. Effect of catalyst type on water pH. To further understand the differences in furfural production from different kinds of catalysts, pH was determined right after its mixing with each catalyst, and its variations during the subW treatments, by pH determination in the collected samples, has been plotted in Fig. 6.

As it can be observed, there was a clear difference between the homogeneous and heterogeneous catalysts. Homogeneous catalysts instantly decreased the pH value from its initial pH of 5.8 to 5.0 in the case of Fe³⁺, values around 4.5 for the Al³⁺ containing catalysts, and as low as 3.8 for the Cr³⁺. The difference between those values is related to the previously explained difference among their solubility products, with Cr³⁺ leading the highest pH decrease and furfural formation rates. During the heating period, pH continuously decreased, but always maintaining the observed difference among cations. It then remained constant during the isothermal period.

On the other hand, when heterogeneous catalysts were added, an opposite effect was observed, increasing pH to values between 7.0 and 7.6. During the heating period, these values decreased and then kept progressively decreasing during the isothermal period up to 1h, reaching a pH value of 3.5 (see Fig. 6). From this time and up to the completion of the treatment, pH values did not vary (data not shown), and showed the smallest difference between homogeneous and heterogeneous catalysts.

The different pH values for homogeneous and heterogeneous catalysts in the earlier stages of the treatment could also support the difference observed in the initial furfural production for both types of catalyst. The homogeneous catalysts easily dissolve in water, rapidly decreasing its pH and favoring the start of furfural production. On the other hand, heterogeneous catalysts show less solubility in water, requiring the increase in water temperature to dissolve (as they were all dissolved at the end of the kinetic, except *Nafion NR50*) and initiate xylose conversion to furfural. Relating this information with the previously preferred defined paths for furfural formation, it can be said that lower pH of the medium promotes the isomerization of xylose to xylulose in a greater extent than when pH is closer to neutral values, and that the lower pH values registered during the homogeneous catalyzed reactions could be related to higher formation of furfural degradation products such as acids, due to the also faster production of furfural. A comparison of the degradation product profiles was plotted in Fig. S3 for CrCl₃ and *Nafion NR50* as best selected catalysts from each group and the ones which showed the lowest and highest initial pH values,

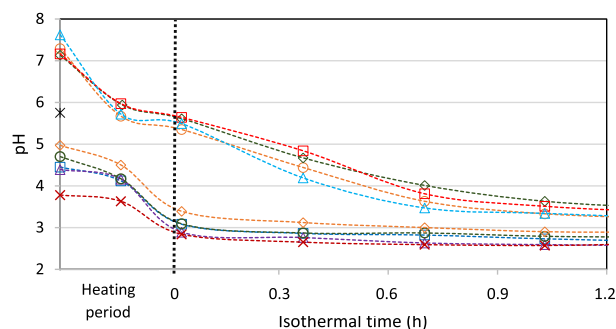


Fig. 6. pH values during subW-CO₂ experiences using xylose at 180 °C and 5.5 MPa with no catalyst (*), homogeneous catalysts: CrCl₃ (0.83 mM) (x), AlCl₃ (0.91 mM) (o), FeCl₃ (0.81 mM) (e), KAl(SO₄)₂ (0.73 mM) (□) and Al₂(SO₄)₃ (0.64 mM) (△) and the heterogeneous catalysts: Ferrierite ammonium (○), Montmorillonite K10 (□), Zeolite Hβ (◇), *Nafion NR50* (△). Lines are represented as a guide to the eye. The black dash line represents the start of the isothermal treatment at 180 °C.

respectively.

In general, all degradation products were formed in higher concentrations in the case of CrCl_3 . As reported in the literature formic acid is the main furfural degradation product in subcritical water solutions [33], showing a maximum concentration of 9.5 mM with CrCl_3 and 7.5 mM with Nafion. Formic acid formation from furfural follows an acid-catalyzed mechanism, and some of the studied paths show that its formation can be reversible to furfural, what makes that somehow, the formic acid formation itself mitigates furfural degradation [33]. This could explain why no losses of furfural happen during long time treatments. Acetic acid was found in much lower concentrations for both catalysts (<2 mM). It is also interesting to mention the lower solid material recovered after subW treatments with the resin, being 10 mg, while after CrCl_3 treatment, solid weight was 81 mg, confirming the higher side reactions taking place. These solid by-products are called “secondary char” and are usually a result of furfural and other dissolved organics degradation or self-polymerization reactions [34]. The lower formation of degradation products under Nafion action proves again the higher selectivity of the resin towards furfural formation (Fig. 5b), with the further advantage of lower solids formation, which can affect later isolation and purification of furfural.

4. Conclusions

The effect of different operating parameters on furfural production from xylose was evaluated in a subW- CO_2 reaction medium for the first time. Dissolution of carbon dioxide in water showed to provide a strong Brønsted acidity, producing similar furfural yields as when N_2 was combined with a Lewis acid catalyst. Among all tested homogeneous catalysts, CrCl_3 was selected as the best due to its faster furfural production rate at 180 °C. Among all tested heterogeneous catalysts, Nafion NR50 provided the best furfural yield and selectivity values. Furthermore, it was possible to reuse it up to 10 times with no furfural yield losses at 180 °C and 5.5 MPa, making it a great option as a catalyst for furfural production. In the deeper study of furfural production paths, it could be determined that the homogeneous catalysts promoted the isomerization of xylose into xylulose in a greater extent, when compared with the heterogeneous ones. This mechanism could be related to the fast pH decrease caused by these catalysts when dissolved in water. Overall, the new proposed subW-pressurized CO_2 system was proved as an efficient green technology for furfural production from xylose, showing a synergistic effect when used with Lewis acid catalysts. Furfural yields obtained with this system were comparable in many cases to the biphasic ones using organic solvents in literature. The use of the new subW- CO_2 system eliminates the use of strong acids or organic solvents required for the obtention of high furfural yields, making of it a promising choice as an eco-friendly technology.

Funding

This work was supported by the Agencia Estatal de Investigación (AEI), Ministerio de Ciencia e Innovación (MICINN) and Next Generation UE (Plan de Recuperación, Transformación y Resiliencia) [grant numbers TED2021-129311B-I00 and PDC2022-133443-I00] and the Junta de Castilla y León (JCyL) and the European Regional Development Fund (ERDF) [grant number BU050P20]. Benito-Román post-doctoral contract was funded by AEI through project PID2020-116716RJ-I00. P. Barea predoctoral contract was funded by JCyL and the European Social Fund (ESF) by ORDEN EDU/1868/2022, de 19 de diciembre.

CRediT authorship contribution statement

Alba E. Illera: Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Methodology, Investigation. **Helena Candela:** Writing – review & editing, Investigation. **Alejandro Bermejo-López:** Writing – review & editing, Investigation. **Pedro Barea:**

Writing – review & editing, Methodology, Investigation. **Patricia Alonso-Riño:** Writing – review & editing, Methodology. **Óscar Benito-Román:** Writing – review & editing, Methodology. **Sagrario Beltrán:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization. **M. Teresa Sanz:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biombioe.2024.107304>.

References

- [1] A. Komesu, J. Oliveira, D.K.T. Moreira, A.H. Khalid, J.M. Neto, L.H. Da Silva Martins, Biorefinery approach for production of some high-value chemicals, *Advanced Biofuel Technologies: Present Status, Challenges and Future Prospects* (2021) 409–429, <https://doi.org/10.1016/B978-0-323-88427-3.00002-7>.
- [2] W. Adhami, A. Richel, C. Len, A review of recent advances in the production of furfural in batch system, *Mol. Catal.* 545 (2023), <https://doi.org/10.1016/j.mcat.2023.113178>.
- [3] E. de Jong, H. Stichnothe, G. Bell, H. Jørgensen, *Bio-Based Chemicals*, IEA Bioenergy, 2020.
- [4] K.J. Yong, T.Y. Wu, C.B.T.L. Lee, Z.J. Lee, Q. Liu, J.M. Jahim, Q. Zhou, L. Zhang, Furfural production from biomass residues: current technologies, challenges and future prospects, *Biomass Bioenergy* 161 (2022) 106458, <https://doi.org/10.1016/j.biombioe.2022.106458>.
- [5] X. Lyu, G.G. Botte, Investigation of factors that inhibit furfural production using metal chloride catalysts, *Chem. Eng. J.* 403 (2021), <https://doi.org/10.1016/j.cej.2020.126271>.
- [6] L. Axelsson, M. Franzén, M. Ostwald, G. Berndes, G. Lakshmi, N.H. Ravindranath, Perspective: Jatropha cultivation in southern India: assessing farmers' experiences, *Biofuels, Bioproducts and Biorefining* 6 (2012) 246–256, <https://doi.org/10.1002/bbb>.
- [7] C.B.T.L. Lee, T.Y. Wu, A review on solvent systems for furfural production from lignocellulosic biomass, *Renew. Sustain. Energy Rev.* 137 (2021) 110172, <https://doi.org/10.1016/j.rser.2020.110172>.
- [8] F. Delbecq, Y. Wang, A. Muralidhara, K.E. El Ouardi, G. Marlair, C. Len, Hydrolysis of hemicellulose and derivatives—a review of recent advances in the production of furfural, *Front. Chem.* 6 (2018), <https://doi.org/10.3389/fchem.2018.00146>.
- [9] R. Li, Q. Lin, Y. Liu, X. Wang, C. Liu, F. Peng, J. Ren, Insights into solvent effect on selective production of furfural and 5-hydroxymethylfurfural from fructose, *J. Catal.* 424 (2023) 162–172, <https://doi.org/10.1016/j.jcat.2023.05.022>.
- [10] G. Gómez Millán, S. Hellsten, A.W.T. King, J.P. Pokki, J. Llorca, H. Sixta, A comparative study of water-immiscible organic solvents in the production of furfural from xylose and birch hydrolysate, *J. Ind. Eng. Chem.* 72 (2019) 354–363, <https://doi.org/10.1016/j.jiec.2018.12.037>.
- [11] V. Choudhary, S.I. Sandler, D.G. Vlachos, Conversion of xylose to furfural using lewis and brønsted acid catalysts in aqueous media, *ACS Catal.* 2 (2012) 2022–2028, <https://doi.org/10.1021/cs300265d>.
- [12] V. Choudhary, S.H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N.S. Marinkovic, A. I. Frenkel, S.I. Sandler, D.G. Vlachos, Insights into the interplay of lewis and Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media, *J. Am. Chem. Soc.* 135 (2013) 3997–4006, <https://doi.org/10.1021/ja3122763>.
- [13] T. Tongtummachat, A. Jaree, N. Akkarawatkhoo, Continuous hydrothermal furfural production from xylose in a microreactor with dual-acid catalysts, *RSC Adv.* 12 (2022) 23366–23378, <https://doi.org/10.1039/d2ra03609f>.
- [14] R. Inoue, J.K.C.N. Agutaya, A.T. Quittain, M. Sasaki, M.J. Cocero, T. Kida, Supercritical CO_2 -subcritical H_2O system: a green reactive separation medium for selective conversion of glucose to 5-hydroxymethylfurfural, *J. Supercrit. Fluids* 168 (2021), <https://doi.org/10.1016/j.supflu.2020.105079>.
- [15] P. Barea, R. Melgosa, A.E. Illera, P. Alonso-Riño, E.D. De Cerio, Ó. Benito-Román, S. Beltrán, M.T. Sanz, Production of small peptides and low molecular weight amino acids by subcritical water from fish meal: effect of pressurization agent, *Food Chem.* 418 (2023), <https://doi.org/10.1016/j.foodchem.2023.135925>.
- [16] S. Le Guenic, D. Gergela, C. Ceballos, F. Delbecq, C. Len, Furfural production from D-xylose and xylan by using stable nafion NR50 and NaCl in a microwave-assisted biphasic reaction, *Molecules* 21 (2016), <https://doi.org/10.3390/molecules21081102>.
- [17] P. Alonso-Riño, A.E. Illera, M.S.T. Amândio, A.M.R.B. Xavier, S. Beltrán, M. Teresa Sanz, Valorization of brewer's spent grain by furfural recovery/removal

- from subcritical water hydrolysates by pervaporation, *Sep. Purif. Technol.* 309 (2023), <https://doi.org/10.1016/j.seppur.2022.123008>.
- [18] A. V Bandura, The ionization constant of water over wide ranges of temperature and density, *American Institute of Physics* 35 (2006), <https://doi.org/10.1063/1.1928231>.
- [19] C. Loerbroks, J. Van Rijn, M.P. Ruby, Q. Tong, F. Schüth, W. Thiel, Reactivity of metal catalysts in glucose-fructose conversion, *Chem. Eur J.* 20 (2014) 12298–12309, <https://doi.org/10.1002/chem.201402437>.
- [20] J.B. Binder, J.J. Blank, A.V. Cefali, R.T. Raines, Synthesis of furfural from xylose and xylan, *ChemSusChem* 3 (2010) 1268–1272, <https://doi.org/10.1002/cssc.201000181>.
- [21] M. Lopes, K. Dussan, J.J. Leahy, Enhancing the conversion of D-xylose into furfural at low temperatures using chloride salts as co-catalysts: catalytic combination of AlCl₃ and formic acid, *Chem. Eng. J.* 323 (2017) 278–286, <https://doi.org/10.1016/j.cej.2017.04.114>.
- [22] Q. Zhou, A. Ding, L. Zhang, J. Wang, J. Gu, T.Y. Wu, X. Gu, L. Zhang, Furfural production from the lignocellulosic agro-forestry waste by solvolysis method – a technical review, *Fuel Process. Technol.* 255 (2024), <https://doi.org/10.1016/j.fuproc.2024.108063>.
- [23] T. Yang, Y. Zhou, S. Zhu, H. Pan, Y. Huang, Insight into aluminum sulfate-catalyzed xylan conversion into furfural in a *g*-valerolactone/water biphasic solvent under microwave conditions, *ChemSusChem* 10 (2017) 4066–4079, <https://doi.org/10.1002/cssc.201701290>.
- [24] N. Dubasi, R. Varala, H.B. Bollikolla, V. Kotra, Review article: applications of alum (KAl(SO₄)₂·12H₂O) in organic synthesis and as catalysis : a quinquennial update (2017-2022), *Journal of Chemical Reviews* 5 (2023) 263–280.
- [25] D. Gupta, E. Ahmad, K.K. Pant, B. Saha, RSC Advances a green catalyst for production of furfural, *RSC Adv.* 7 (2017) 41973–41979, <https://doi.org/10.1039/C7RA07147G>.
- [26] A. Wang, A.T. Bell, Continuous pervaporation-assisted furfural production catalyzed by CrCl₃, *Green Chem.* 20 (2018) 2903–2912, <https://doi.org/10.1039/c8gc00842f>.
- [27] Y. Yang, C. Hu, M.M. Abu-omar, Synthesis of furfural from xylose, xylan, and biomass using AlCl₃·6H₂O in biphasic media via xylose isomerization to xylulose, *ChemSusChem* 5 (2012) 405–410, <https://doi.org/10.1002/cssc.201100688>.
- [28] J. Li, M. Gao, W. Yan, J. Yu, Regulation of the Si/Al ratios and Al distributions of zeolites and their impact on properties, *Chem. Sci.* 14 (2023) 1935–1959, <https://doi.org/10.1039/d2sc06010h>.
- [29] Y. Wang, Y. Dai, T. Wang, M. Li, Y. Zhu, L. Zhang, Efficient conversion of xylose to furfural over modified zeolite in the recyclable water/n-butanol system, *Fuel Process. Technol.* 237 (2022), <https://doi.org/10.1016/j.fuproc.2022.107472>.
- [30] H. Nanao, H. Amanuma, K. Yoshida, O. Sato, A. Yamaguchi, M. Shirai, Furfural production from xylose and bamboo powder over natural clays, *Clay Sci.* 21 (2017) 35–39, https://doi.org/10.11362/jcssjclayscience.21.2_35.
- [31] E. Lam, E. Majid, A.C.W. Leung, J.H. Chong, K.A. Mahmoud, J.H.T. Luong, Synthesis of furfural from xylose by heterogeneous and reusable nafion catalysts, *ChemSusChem* 4 (2011) 535–541, <https://doi.org/10.1002/cssc.201100023>.
- [32] S. Le Guenic, F. Delbecq, C. Ceballos, C. Len, Microwave-assisted dehydration of D-xylose into furfural by diluted inexpensive inorganic salts solution in a biphasic system, *J. Mol. Catal. Chem.* 410 (2015) 1–7, <https://doi.org/10.1016/j.molcata.2015.08.019>.
- [33] L. Almhofer, R.H. Bischof, M. Madera, C. Paulik, Kinetic and mechanistic aspects of furfural degradation in biorefineries, *Can. J. Chem. Eng.* 101 (2023) 2033–2049, <https://doi.org/10.1002/cjce.24593>.
- [34] P. Alonso-Riaño, A.E. Illera, O. Benito-Román, R. Melgosa, A. Bermejo-López, S. Beltrán, M.T. Sanz, Degradation kinetics of sugars (glucose and xylose), amino acids (proline and aspartic acid) and their binary mixtures in subcritical water: effect of Maillard reaction, *Food Chem.* 442 (2024) 138421, <https://doi.org/10.1016/j.foodchem.2024.138421>.