



Insights into the kinetics of furfural production from different monomers and polymers derived from biomass in a subcritical water reaction medium intensified by CO₂ as pressurization agent

A.E. Illera , H. Candela , S. Beltrán, M.T. Sanz ^{*}

Department of Biotechnology and Food Science, Faculty of Science, University of Burgos. Plaza Misael Bañuelos S/n, 09001, Burgos, Spain

ARTICLE INFO

Keywords:

Furfural
Subcritical water/CO₂ reaction medium
Reaction pathways
Kinetic models

ABSTRACT

A systematic kinetic study was conducted on the production of furfural from different sugar monomers, including xylose, arabinose and glucose, and xylan, a biopolymer rich in pentoses, in a subcritical water reaction medium intensified by the presence of CO₂ as pressurization agent. The temperature range was from 150 to 200 °C, and different catalysts were employed, with CrCl₃ as a Lewis acid catalyst. Glucose yielded very low amounts of furfural. Regarding pentoses, different reaction pathways were analyzed. The proposed mechanism involved the presence of the corresponding ketoses, xylulose and ribulose, from xylose and arabinose, respectively, as intermediates in furfural production. Formic acid was identified as the main degradation product in this reaction medium. It was concluded that formic acid was released into the medium from both pentoses and furfural. Pentose aldoses isomerization to ketoses, followed by furfural formation was the primary reaction pathway in this system. When using an acidic resin such as Nafion NR50 as catalyst, the isomerization of xylose was the rate-controlling step. When starting from xylan, similar furfural yields were obtained, but productivity values evaluated over time were higher for xylose due to the two-step process involved in furfural production from xylan. The molecular weight distribution in the xylan system showed an initial increase for fractions in the range of 282–150 Da, while fractions of molecular weights higher than 1074 Da appeared only at the end of the treatment, likely due to the formation of different polymeric products.

1. Introduction

Furfural is a key chemical commercially produced from agricultural lignocellulosic residues with a high pentosan content under acidic conditions involving acid hydrolysis and dehydration reaction [1,2]. Furfural has been identified by the United States Department of Energy as one of the top building block chemicals that can be produced from lignocellulosic biomass, being corn cobs and sugarcane the major feedstocks currently used for furfural production [3]. Furfural can be transformed into various commodity chemicals with a wide range of industrial uses, especially in the production of pharmaceuticals, polymers, resins, solvents, fine chemicals, fuel additives and biofuels [4,5]. Due to its numerous applications, global furfural production has gained increasing attention with an estimated production between 200,000 and 360,000 tonnes in 2020. Currently, furfural is produced by using sulfuric acid (H₂SO₄) or hydrochloric acid as the most common catalysts, with operating temperatures typically ranging between 150 and

200 °C and achieving common yields of around 50 % [6]. High steam to furfural ratio are also employed to strip furfural to avoid its degradation. Therefore, these methodologies present drawbacks such as expensive purifications steps and safety and environmental concerns due to toxic waste effluents [7], what encourages the search for greener furfural production approaches.

In previous work, the intensified pressurized system subcritical water/CO₂ (subW/CO₂) treatment showed potential for furfural production from xylose, the main sugar derived from the hemicellulose fractions, using different homogeneous and heterogeneous Lewis acid catalysts [8].

SubW is defined as water at a temperature ranging from 100 °C to 374 °C and at a pressure high enough to keep it in its liquid state. It has proven to be a good solvent to be used not only in extraction processes, but also for chemical reactions due to its increasing self-ionization at high temperatures [9]. When CO₂ was added into the system as pressurization agent, higher furfural yields were obtained from xylose

^{*} Corresponding author.

E-mail address: tersanz@ubu.es (M.T. Sanz).

<https://doi.org/10.1016/j.biombioe.2024.107550>

Received 28 August 2024; Received in revised form 5 December 2024; Accepted 8 December 2024

Available online 24 December 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/>).

compared with the addition of an inert gas such as N₂. This is because CO₂ acts as a Brønsted acid when dissolved in water and there was a synergistic effect between CO₂ and the Lewis acid catalyst [8]. Among the different types of catalyst tested, CrCl₃ and Nafion NR50 resin were selected as the optimum catalysts for homogeneous and heterogeneous systems, respectively, due to their higher initial furfural production rate determined for CrCl₃ (51.9 ± 0.9 % moles of furfural/moles of xylose-h) and higher furfural selectivity (60.9 %) for the catalytic system for Nafion NR50 [8].

The development of kinetic models is a key factor within the framework of biorefinery concept for the production of chemical compounds. Understanding the mechanisms and kinetics of furfural formation is crucial for the successful development of this catalytic system. According to Relvas et al. [10] the reactive system subW/CO₂ is a promising green technology for integration into a biorefinery framework. Nevertheless, there is a lack of knowledge regarding reaction mechanisms and intricacies of these kinetic processes. Therefore, there is still much work to be done to understand the reactions in this highly reactive medium, which usually involves multiple reactions.

The main objective of this study is to evaluate different kinetic models for furfural production from various monomers derived from the polysaccharide fraction of lignocellulosic biomass. Xylose, being the most abundant sugar in hemicellulose and therefore the major component released by hydrolysis of this fraction, was taken as the primary starting material to develop different kinetic models in the subW/CO₂ pressurized system. Since glucose (a hexose) and arabinose (a pentose) are commonly found sugars in biomass, these two sugars were also investigated for furfural production. Additionally, xylan was also used as the biopolymer representative of hemicellulose fraction to produce furfural.

In this work, different reaction mechanisms will be proposed based on the kinetic experimental data, considering the formation of the corresponding ketose from its aldose form as the main intermediate compounds, namely xylulose and ribulose from xylose and arabinose, respectively. Furthermore the presence of the main degradation products in this reactive system, especially formic acid, will be also considered in the proposed kinetic models.

2. Experimental section

2.1. Chemicals

Glucose (99 %), xylose (99 %), furfural (99 %), xylulose (≥95 %), ribulose (≥90 %), glycoaldehyde (98 %) and chromium (III) chloride hexahydrate (98 %) were purchased from Sigma-Aldrich. Standards of 5-HMF (97 %) from Alfa Aesar, formic acid (98 %) from Fluka, acetic acid (99.8 %) from VWR, and levulinic acid (99 %) from Merck. *Nafion NR50* resin, was purchased from Thermo Scientific. Xylan from corn core was purchased from TCI. Other standards typically reported in similar systems have not been detected in appreciable quantities in this study, and therefore, they have not been included in the list of chemicals.

2.2. Equipment for subcritical water hydrolysis

Furfural production in subW/CO₂ reaction medium was conducted using a laboratory-assembled batch system equipped with a 0.5 L capacity reactor (p_{max} = 60 bar). The reactor was covered by a ceramic heating jacket (230 V, 4000 W, ø 95 mm, 160 mm height) to achieve the selected working temperature. After the reactor was closed, CO₂ was added until reaching the desired operating pressure. A Pt100 sensor placed inside the reactor and connected to a PID system allowed for temperature control and recording during the reaction process. The heating rate was 8 ± 1 °C/min. A magnetic stirring bar was placed at the bottom of the reactor to enhance homogeneity in the reaction medium. A needle valve (Autoclave Engineers) followed by a cooling system, was connected to withdraw samples to follow the reaction progress at

regular time intervals. After a specified reaction time, the vessel was cooled, and depressurized when the temperature was lower than 90 °C. After treatment, the solid residue generated was washed, dried, and subsequently weighed.

Different sugars synthetic solutions were prepared: (1) a xylose solution of 11 g L⁻¹, (2) an arabinose solution of 11 g L⁻¹ (3) a glucose solution of 12 g L⁻¹, and (4) a xylan solution of 9.8 g L⁻¹ in 200 mL of water. The synthesis of furfural was carried out at 180 °C using the optimal catalysts identified in previous work, where different homogeneous and heterogeneous catalysts were tested. CrCl₃·6H₂O (CrCl₃ from now on) and Nafion R50 were determined to be the best homogeneous and heterogeneous catalysts, respectively [8]. Among different trichloride catalysts tested by Illera et al. [8] (Al³⁺, Fe³⁺ and Cr³⁺), CrCl₃ was selected due to its initial faster furfural production. Different heterogeneous catalysts were also tested including zeolites (ferrierite ammonium, Zeolite Hβ), clays (montmorillonite K10) and acidic ion exchange resins (Nafion NR50). It was found that Nafion NR50 could be easily recovered after treatment and it provided the best selectivity values towards furfural. CrCl₃ concentration was 2 wt % in relation to sugars, while in case of Nafion NR50, supplied as solid spheres, 10 units were added (0.48 g).

The kinetics of xylose conversion to furfural in the presence of CrCl₃ as catalyst were investigated at three different temperatures: 150, 180 and 200 °C. Additionally, a kinetic was conducted using NaCl (4 %) as an enhancer of furfural production in conjunction with CrCl₃ as the catalyst.

Kinetics for furfural production from xylan, arabinose, and glucose were also determined at 180 °C by using CrCl₃ as the catalyst and at the concentrations previously indicated.

2.3. Analytical methods

2.3.1. Sugars and its degradation products

Monomeric sugars (glucose, xylose and arabinose) and their degradation products, including furfural, dioses, trioses, and organic acids, were determined by HPLC as described by Alonso-Riño et al. [11] and based on the National Renewable Energy Laboratory (NREL) protocols for “Determination of Sugars, byproducts, and degradation products in liquid fraction process samples” [12]. The HPLC apparatus was equipped with a Biorad Aminex-HPX-87H column, its corresponding pre-column, and two detectors: a variable wavelength detector (VWD) and a refractive index detector (RID). The mobile phase consisted of 0.005 M sulfuric acid, and both the column and the refractive index detector were maintained at 40 °C. Samples (10 µL) were injected after being filtered through a 0.2 µm syringe filter. Calibration was performed using pure standards. Peak identification was done by comparison of the retention times of sample peaks with those of standard pure compounds. Although the HPLC apparatus was equipped with two detectors (VWD and RID), the compounds determined in this work have been much better quantified by using the RID by comparison of retention times of sample peaks with those of pure standards.

Xylan characterization and the analysis of soluble xylan during catalytic hydrothermal treatment were performed following an acid hydrolysis step to release the monomeric sugars from the oligomer for quantification, in accordance with the NREL protocols for “Determination of structural carbohydrates and lignin in biomass” [13]. The oligomeric form present in the reaction medium was determined as:

$$Xylan_{oligomeric} = Monomer_{after\ hydrolysis} - Monomer_{before\ hydrolysis} \quad [1]$$

2.3.2. Xylan hydrolysis characterization by size exclusion chromatography

The molecular weight distribution of the xylan hydrolysis and subsequent furfural formation from the monomers released was characterized by size exclusion chromatography (SEC). The chromatographic equipment consisted of an Agilent 1260 Infinity II LC system (Agilent Technologies, CA, USA) with guard column (PL Aquagel-OH, 7.5 × 50 mm, 8 µm) and two columns linked in series (PL Aquagel-OH 30 and PL

Aquagel-OH 40, 300 mm × 7.5 mm, 8 μm) from Agilent Technologies. Characterization of xylan hydrolysis into smaller oligomers and the final monomer was performed at 35 °C. 10 μL of samples were eluted in isocratic mode with 0.01 M NH₄Ac, at a flow rate of 0.7 mL/min. A pullulan standard set (0.342–400 kDa) provided by PSS Polymer Standards Service GmbH (Mainz, Germany) was used for calibration and data were analyzed with Agilent OpenLab Data Analysis 2.5 software. Standards and samples were previously filtered through 0.22 μm syringe filters. The total area of the chromatogram was integrated and separated into fractions of five molecular weight (MW) ranges (>10000 Da, 10000–1074 Da, 1074–678 Da, 678–282 Da, <282 Da), expressed as the percentage of the total area.

2.4. Parameters in furfural production

The reaction process was evaluated by determining the sugar monomer conversion, the furfural yield and the selectivity towards furfural formation. Sugar monomer conversion was evaluated as:

$$\text{Sugar conversion (\%)} = \frac{\text{moles of sugar}_0 - \text{moles of sugar}_{(t)}}{\text{moles of sugar}_0} \cdot 100 \quad [2]$$

Furfural yield was evaluated considering the initial C content in the solution feed and the C content in the furfural produced:

$$\text{Furfural yield (\%)} = \frac{\text{moles of C in furfural}_{(t)}}{\text{moles of C in the initial feed sugar}_0} \cdot 100 \quad [3]$$

A similar yield percentage was also evaluated for other organic compounds produced in the reaction process, such as organic acids.

Additionally, the selectivity of the process towards furfural production was evaluated considering the sugar consumption according to:

$$\text{Furfural selectivity (\%)} = \frac{\text{moles of furfural}_{(t)}}{\text{moles of sugar}_0 - \text{moles of sugar}_t} \cdot 100 \quad [4]$$

In equations [2–4], the subscripts (o) and (t) refer to initial time and any other time during the treatment.

2.5. Kinetic models

Based on the compound profiles determined in this work, several reaction mechanisms were screened, assuming first order kinetics for all of them (see Fig. 1). In literature, it is also common to propose different kinetic models gaining in complexity to account for different intermediates as well as other degradation products [2,14].

2.5.1. Model 1

The simplest model involves a first-order reaction rate for the degradation of xylose, leading to the formation of furfural or any other degradation product (DP_{xylose}). Variation of furfural concentration considers its formation from xylose and its degradation (DP_{Furfural}). This model does not consider any intermediate species and it has been considered in the majority of research papers [15]:

$$\frac{dC_{xylose}}{dt} = -k_{1,1}C_{xylose} - k_{2,1}C_{xylose} \quad [5]$$

$$\frac{dC_{furfural}}{dt} = k_{1,1}C_{xylose} - k_{3,1}C_{furfural} \quad [6]$$

where $k_{1,1}$ is the kinetic rate constant of furfural formation from xylose, and $k_{2,1}$ and $k_{3,1}$ are the kinetic rate constants of xylose and furfural degradation, respectively.

2.5.2. Model 2

Not many kinetic studies have focused on the determination of pentose intermediates and their further conversion to furfural [14]. Considering the compounds identified in the HPLC method described in section 2.3.1, it seems clear that isomerization of pentose from its aldose form to its ketose form takes place, which could also lead to furfural formation. This suggests model 2:

$$\frac{dC_{xylose}}{dt} = -(k_{1,2} + k_{2,2} + k_{4,2})C_{xylose} \quad [7]$$

$$\frac{dC_{xylulose}}{dt} = k_{4,2}C_{xylose} - (k_{5,2} + k_{6,2})C_{xylulose} \quad [8]$$

$$\frac{dC_{furfural}}{dt} = k_{1,2}C_{xylose} + k_{5,2}C_{xylulose} - k_{3,2}C_{furfural} \quad [9]$$

where $k_{1,2}$ and $k_{5,2}$ are the reaction rate constants for the formation of furfural from xylose and xylulose, respectively, and $k_{4,2}$ is the reaction rate constant for the formation of xylulose from xylose. $k_{2,2}$, $k_{3,2}$ and $k_{6,2}$ are the rate constants for the degradation of xylose, furfural and xylulose, respectively.

2.5.3. Model 3

According to the HPLC method, the major organic acid determined in these samples was formic acid. Therefore, the third model includes the formation of formic acid. The formation of formic acid was considered through two different pathways (1) formic acid only from furfural ($k_{7,3} = 0$) (2) formic acid from furfural and the initial pentose ($k_{7,3} \neq 0$).

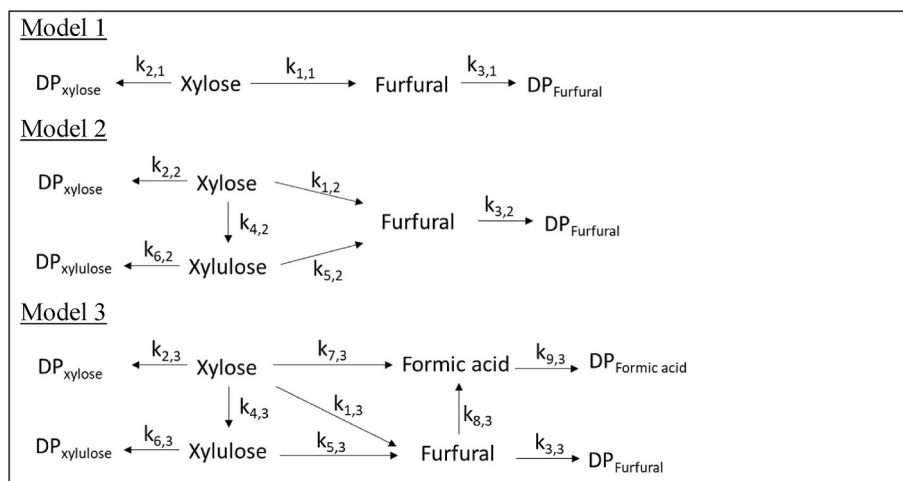


Fig. 1. Reaction pathways for the three models proposed in this work for furfural formation. DP: degradation products, $k_{i,j}$: kinetic rate constants.

$$\frac{dC_{xylose}}{dt} = -(k_{1,3} + k_{2,3} + k_{4,3} + k_{7,3})C_{xylose} \quad [10]$$

$$\frac{dC_{xylulose}}{dt} = k_{4,3}C_{xylose} - (k_{5,3} + k_{6,3})C_{xylulose} \quad [11]$$

$$\frac{dC_{furfural}}{dt} = k_{1,3}C_{xylose} + k_{5,3}C_{xylulose} - (k_{3,3} + k_{8,3})C_{furfural} \quad [12]$$

$$\frac{dC_{formic\ acid}}{dt} = k_{8,3}C_{furfural} + k_{7,3}C_{xylose} - k_{9,3}C_{formic\ acid} \quad [13]$$

Equations (5)–(13) also represent the rate equations for modelling the kinetics of arabinose to produce furfural, where the subscripts xylose and xylulose should be replaced by arabinose and the corresponding ketose, ribulose, respectively.

The rate constants for the different kinetic equations proposed were obtained by solving the set of differential equations simultaneously for each model. The differential equations were solved numerically using a fourth-order Runge-Kutta method, and the parameters were obtained by minimizing the following objective function (O.F.) using the simplex Nelder-Mead method:

$$O.F. = \sqrt{\frac{\sum_{\text{all compounds } i=1}^n abs(C_{i,exp} - C_{i,calc})}{n}} \quad [14]$$

The quality of the fitting was evaluated by the root mean square error (RMSE):

$$RMSE_{\text{each compound}} = \sqrt{\frac{1}{n} \sum_{i=1}^n (C_{i,exp} - C_{i,calc})^2} \quad [15]$$

where the subscript “i” refers to the experimental kinetic data points for each kinetic for the different individual compounds, the subscripts “exp” and “calc” refer to the experimental and calculated mole concentration (mM) of the different components, respectively, and n is the total experimental kinetic data considered in each expression.

3. Results and discussion

3.1. Furfural production from xylose

3.1.1. Catalysis by CrCl₃

Fig. 2a shows the furfural yield as a function of xylose conversion at 180 °C along with the yield of other by-products identified by HPLC. It can be clearly observed that furfural was identified as the main reaction product from xylose in the catalyzed subW/CO₂ system assisted by CrCl₃ as Lewis acid catalyst. However, the reaction mechanism is complex and some organic acids were also determined, mainly formic acid, but also small amounts of acetic acid. Retroaldol condensation products, mainly glycoaldehyde, were also determined but at very low concentrations. The product profile also indicated that isomerization reaction of xylose to xylulose seems to be an important intermediate in furfural formation in this reactive system, according to the amount of the ketose form determined during the course of the reaction process.

Fig. 2b also shows the different product yields obtained in a subW reaction medium in the absence of any Lewis acid catalyst, as reported in previous work [16]. Comparison of both systems (Figura 2a and 2b) showed the positive performance of the subW/CO₂ system assisted by CrCl₃ catalysis on furfural yield, with a maximum furfural yield of 49.4 % at 96 % of xylose conversion versus a maximum of 32.2–32.7 furfural yield at 60–80 % xylose conversion in the subW reaction medium. According to Sajid et al. [4] CrCl₃·6H₂O forms aqua-cations through complexation with water molecules, resulting in Cr(H₂O)₅OH²⁺, which are more reactive species and have a positive impact on sugar dehydration [4]. The positive charge facilitates proton loss from water in the hydration shell by weakening the O-H bond, with the metal ion acting as an

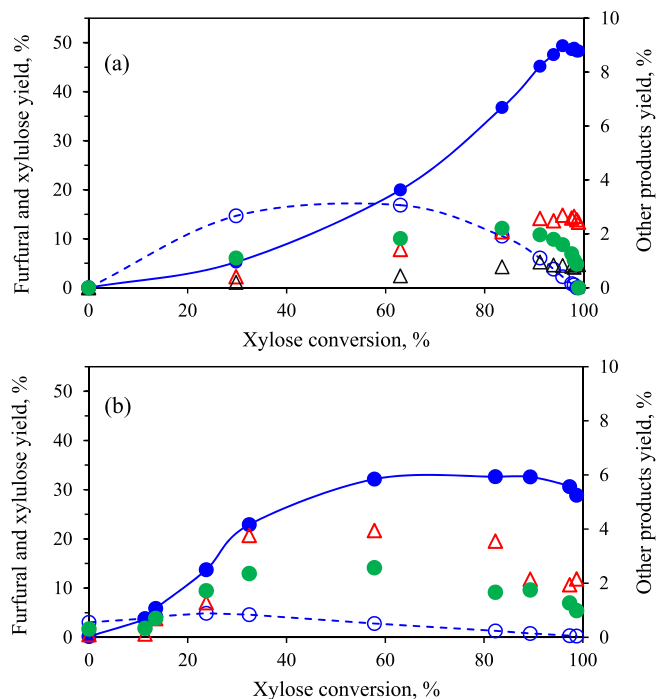
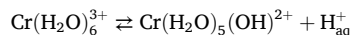


Fig. 2. Furfural and other degradation products yield as function of xylose conversion (a) subW/CO₂ assisted by CrCl₃ as catalyst (b) subW reaction medium [16] ● furfural, ○ xylulose, ● glycoaldehyde, △ formic acid, △ acetic acid. Lines plotted for furfural (continuous) and xylulose (discontinuous) are to guide the eye.

acid [4]:



Additionally, as indicated by Ershova et al. [15] the formation of intermediate complexes between the monomers and the metal ion may result in a weakening of intramolecular bonds, thereby enhancing the catalytic properties of cations. It is evident that the Lewis acid catalyst promotes the formation of the ketose form as an intermediate in furfural production, comparing to the yield of xylulose in a subW reaction medium.

The dehydration of xylose to furfural in the subW/CO₂ system assisted by CrCl₃ as Lewis acid catalyst was conducted at 150, 180 and 200 °C. Before discussing model fitting, a comparison of furfural production at the three selected temperatures is provided. The furfural yield and xylose conversion were significantly influenced by the operating temperature (see Fig. 3). At the highest temperature investigated in this work, the furfural yield from xylose reached a maximum and then decreased with increasing reaction time, probably due to decomposition and depolymerization resulting in char formation [17]. This maximum shifts to shorter reaction times with increasing temperature, but degradation occurs at a common severity factor of 4.5–4.7 (see Fig. 3b), evaluated according to Alonso-Riaño et al., 2023 [11]:

$$\log R_o = \log \left(t \cdot \exp \left(\frac{T - T_{ref}}{14.75} \right) \right) \quad [16]$$

where t is the treatment time (min), T is the operating temperature (°C) and T_{ref} is equal to 100 °C. This fact is supported by the increasing amount of solids collected after reaction process: 1.4 %, 3.7 %, and 4.5 % of the initial xylose charged into the reactor at 150 °C, 180 °C and 200 °C, respectively. According to Ershova et al. [14] the solids produced are formed either by resinification and polymerization reactions of furfural or by condensation reactions between furfural and xylose. In

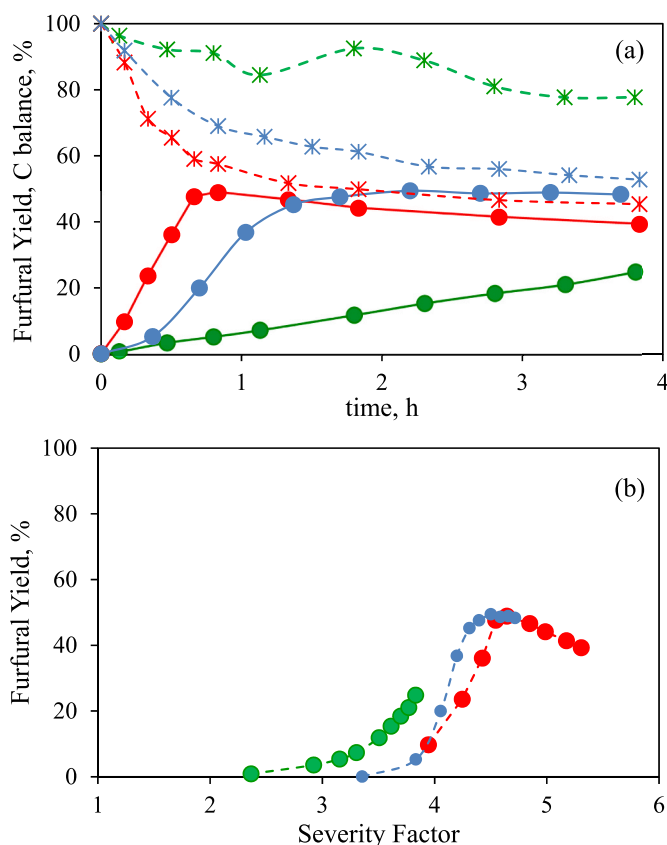


Fig. 3. (a) Furfural yield (circles) from xylose and C mass mass balance (stars) in the subW/CO₂ + CrCl₃ system at 150 °C (●, *), 180 °C (●, *), and 200 °C (●, *). (b) Furfural yield as a function of the severity factor, 150 °C (●), 180 °C (●), and 200 °C (●). Lines are to guide the eye.

any case, these values were lower than the solids collected in the study of xylose degradation in subW reaction medium with values of 0.5 %, 6.5 % and 12.9 % at 150, 180 and 200 °C, respectively [16], proving that char formation reactions are more prone to produce in subW reaction medium supporting also the higher furfural yields obtained in subW/CO₂ assisted by CrCl₃.

Fig. 3a also shows the mass balance of C species evaluated as the ratio of the C amount contained in the quantified reaction products to the initial C content of the xylose introduced into the reactor:

$$C \text{ mass balance } (\%) = \frac{\sum_i \text{moles of C in the compounds identified}_t}{\text{moles of C in the initial feed sugar}_0} \cdot 100 \quad [17]$$

By increasing temperature, deviations in the C mass balance increased, probably due to the formation of degradation products that could not be identified and quantified by the HPLC method. Analysis of total organic carbon (TOC) was performed on the final reaction mixture sample of each temperature, obtaining the following results: 4081 mgC/L, 2573 mg C/L, and 2326 mg C/L at 150, 180 and 200 °C, respectively. These results were compared with the total organic C obtained by considering the chemical compounds identified and quantified by HPLC, yielding values of 3408 mgC/L, 2307 mg/L and 1962 mg C/L, at 150, 180 and 200 °C, respectively. Therefore, more than 84 % of the organic C in the liquid phase was properly identified (84 %, 90 % and 84 % at 150, 180 and 200 °C, respectively). In this regard, beside liquid and solid products, gaseous products were presumable formed during the experiments, specially at high temperatures; however, the analysis of these products was not within the scope of this study. In any case, of the

identified chemical species in this reactive system (see Fig. 2a) more than 95 % correspond to xylose, xylulose, furfural and formic acid. In addition, when comparing the C-yield, formic acid was approximately two to three times higher than acetic acid, with molar concentrations four times higher for formic acid. Based on these results, model discussion will be mainly focused on these four reaction products.

3.1.1.1. Model 1. Table 1 presents the kinetic parameters determined for the simplest two-step mechanism proposed, involving first-order furfural formation and degradation. This model was able to fit the kinetic data quite well (see Fig. S1). However, the model does not consider intermediates such as xylulose from xylose in the pathway to furfural formation or any specific degradation products from xylose and/or furfural. The good fit supports the assumption that furfural formation from xylose in this reactive system can be predicted by a first order kinetic model. This is due to relatively low concentration of chemical species and the non simultaneous high concentrations of furfural and xylose, which minimizes the possible side reactions between xylose and furfural, as indicated by Ershova et al. [14].

The ratio of the reaction rate constants $k_{1,1}/k_{3,1}$ showed that the furfural formation was much faster than its degradation, with values for this ratio much higher than the unity, although this ratio decreased with temperature due to faster furfural degradation with temperature. This trend agrees with the furfural productivity as a function of severity factor (Fig. 3b), since severity conditions for the kinetic at 150 °C for 3.8 h did not reach this maximum value. According to the ratio $k_{2,1}/k_{3,1}$, xylose degradation was faster than furfural degradation at all the temperatures tested.

3.1.1.2. Model 2. The second proposed mechanism for furfural formation from xylose involves either the isomerization to xylulose as an intermediate or a “direct” pathway from xylose that could involve the formation of different intermediate compounds. The formation of xylulose has been previously demonstrated in a previous study of xylose degradation in subW reaction medium [16]. However, as previously described (see Fig. 2b), the formation in a subW medium reaches a maximum of only 1.7 %, whereas in the subW/CO₂ system assisted by a Lewis acid catalyst such as CrCl₃, the xylulose yield increased to a maximum of 17 %. at 180 °C This indicates that the presence of a Lewis catalyst favors the isomerization of aldose to ketose enhancing furfural formation, as pointed out by Illera et al. [8].

The highest xylulose concentration was observed in the initial stages of the reaction kinetics, showing a maximum that shifted to shorter reaction times with increasing temperature. The highest amount of xylulose formed was experimentally found at 200 °C with a molar concentration of 14.5 mM (2.2 g L⁻¹) after 0.17 h of treatment time (see Fig. 2S). Ershova et al. also identified xylulose as important intermediate in the formation of furfural from xylose catalyzed by sulfuric acid (0.1 mol L⁻¹) in a microwave reactor [14].

The kinetic parameters for model 2 are presented in Table 2 and results are plotted in Fig. 2S. This model accurately fits furfural formation via xylulose ($k_{4,2} + k_{5,2}$, see Fig. 1) or any other intermediates from xylose ($k_{1,2}$), according to the RMSD for xylose, xylulose and furfural. The potential isomerization of xylulose back to xylose was also tested by adding an additional kinetic parameter to model 2. However, this did not improve the final fitting, and to avoid unnecessary complexity, it

Table 1
Kinetic rate constants (h⁻¹) for model 1 (see Fig. 1) in the subW/CO₂ system + CrCl₃.

T, °C	k _{1,1}	k _{2,1}	k _{3,1}	k _{1,1} /k _{3,1}	k _{2,1} /k _{3,1}
150	0.0962	0.1949	0.0002	481	975
180	1.0093	0.9802	0.0148	68	66
200	1.9612	2.0665	0.0607	32	34
RMSD	Xylose = 2.83		Furfural = 3.340		

Table 2Kinetic rate constants (h^{-1}) for model 2 (see Fig. 1) in the subW/ CO_2 system + CrCl_3 .

T, °C	$k_{1,2}$	$k_{2,2}$	$k_{3,2}$	$k_{4,2}$	$k_{5,2}$	$k_{6,2}$	$k_{5,2}/k_{1,2}$	$k_{5,2}/k_{4,2}$	$k_{4,2}/(k_{1,2}+k_{2,2})$
150	0.0444	0.0120	0.00002	0.2348	0.3180	0.6274	7.2	1.4	4.2
180	0.0580	0.5916	0.0472	1.4298	2.9128	0.9453	50.2	2.0	2.2
200	0.2709	1.4989	0.0994	2.7316	3.7655	1.2230	13.9	1.4	1.5
RMSD	Xylose = 2.93		Xylulose = 1.48		Furfural = 1.19				

was not considered in the final model. This agrees with Ershova et al. in the study of xylose conversion in a microwave reaction assisted by sulfuric acid who concluded that isomerization of xylulose back to xylose was not identified [14].

The results suggests that furfural formation from both pathways ($k_{1,2}$ and $k_{4,2} + k_{5,2}$) coexists. However, the ratio of the reaction rate constants $k_{5,2}/k_{1,2}$ (furfural formation from xylulose versus furfural formation from xylose) indicates that furfural formation is much faster from xylulose than from xylose. Choudhary et al. [18] reported that dehydration of xylulose to furfural over Brønsted acids was faster than the dehydration of xylose to furfural, which is beneficial for the furfural production. When considering the ratio $k_{4,2}/(k_{1,2}+k_{2,2})$, it is evident that the isomerization of xylose to xylulose is faster than the combined rate of its consumption for furfural production via other intermediates and its degradation to other unknown products. The ratio of furfural formation from xylulose to the isomerization of xylose to xylulose ($k_{5,2}/k_{4,2}$) suggest that the isomerization is only slightly lower than furfural formation ranging from 1.4–2.0. In contrast, Ershova et al. reported higher values for this ratio, ranging from 70 to 288 for sulfuric acid-catalyzed xylose dehydration at temperatures from 180 °C to 220 °C, concluding that the formation of xylulose from xylose can be considered as the rate-limiting step in furfural production via Brønsted acid catalysis by sulfuric acid [14]. The differences in the ratio $k_{5,2}/k_{4,2}$ can be explained by the fact that sugar isomerization is catalyzed by Lewis acids, such as CrCl_3 , but not by sulfuric acid. This demonstrates the efficiency of the intensified systems subW/ CO_2 assisted by CrCl_3 , where the metal chloride acts as a Lewis acid catalyst, and water and CO_2 as Brønsted acids, enhancing xylulose conversion to furfural.

3.1.1.3. Model 3. As previously described, the discussion will focus mainly on the main four reaction products: xylose, furfural, xylulose, and formic acid. Regarding formic acid formation, Ershova et al. [14] observed in their study of furfural degradation in a microwave-assisted system that furfural autooxidation could lead to its decomposition into formic acid and polymeric products. When considering formic acid formation only from furfural, the model did not yield good results for formic acid fitting, and these data were not included in this work. Therefore, model 3 includes formation of formic acid from both xylose and furfural. According to Lange et al. protonation at C3-OH of xylose would result in decomposition to formic acid and a C4 fragment, which degrades very rapidly and it is not observed experimentally according to these authors [19].

The good fit of model 3 to the kinetic data can be observed in Fig. 4a–c. The kinetic parameters are listed in Table 3. Similar to model 2, the ratio of the kinetic rate constants $k_{5,3}/k_{1,3}$ shows that furfural formation at the three studied temperatures was much faster from xylulose as intermediate than through a “direct” pathway from xylose. Furthermore, the ratio $k_{5,3}/k_{4,3}$ varies in the range 1.4–2.0 indicating only slightly faster furfural formation from xylulose than the corresponding isomerization reaction from xylose. In any case, xylulose isomerization cannot be considered the rate-limiting step in furfural production, as the presence of a Lewis acid catalyst contributes to faster xylulose formation compared to a Brønsted acid such as sulfuric acid [14]. The ratio $k_{7,3}/k_{8,3}$ compares the reaction rate of formic acid formation from xylose and furfural. This ratio was higher than the unity, indicating that formic acid production is faster from xylose than from furfural, except at 150 °C, where the values was 0.65. A comparison of

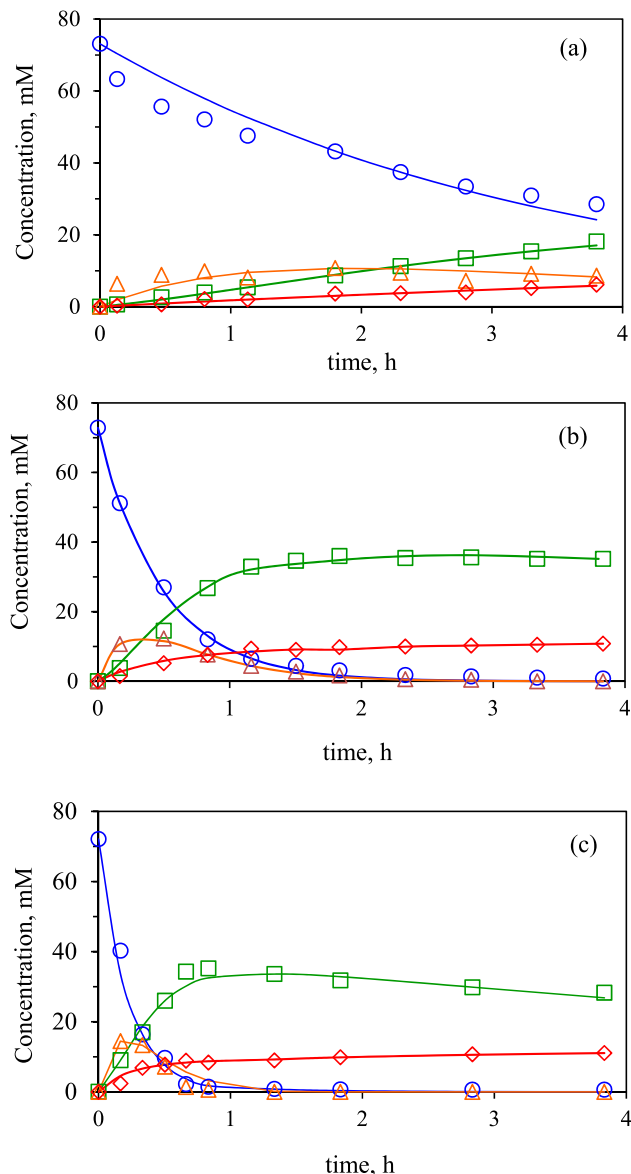


Fig. 4. Xylose (○), furfural (◻), xylulose (△) and formic acid (◇) kinetic profile in the reactive system subW/ CO_2 + CrCl_3 at different temperatures: (a) 150 °C (b) 180 °C (c) 200 °C. The continuous lines represent the results obtained with model 3 (parameters are reported in Table 3).

the degradation kinetic rate constants for the four chemicals considered in the furfural formation process showed that xylulose degradation was the fastest among the compounds. At 180 °C and 200 °C, the trend in the degradation kinetic constants followed the order: xylulose degradation ($k_{6,3}$) > xylose degradation ($k_{2,3}$) > formic acid degradation ($k_{9,3}$) > furfural degradation ($k_{3,3}$). At 150 °C, the degradation kinetic constant for xylose, furfural and formic acid were very low and of the same order.

Table 3Kinetic rate constants (h^{-1}) for model 3 (see Fig. 1) in the subW/ CO_2 system + CrCl_3 .

T, °C	$k_{1,3}$	$k_{2,3}$	$k_{3,3}$	$k_{4,3}$	$k_{5,3}$	$k_{6,3}$	$k_{7,3}$	$k_{8,3}$	$k_{9,3}$	$k_{5,3}/k_{1,3}$	$k_{5,3}/k_{4,3}$	$k_{7,3}/k_{8,3}$
150	0.0483	0.00009	0.0002	0.2163	0.3118	0.5355	0.0265	0.0406	0.0005	6.5	1.4	0.7
180	0.0605	0.3294	0.0096	1.4298	2.8933	0.9645	0.2598	0.0360	0.0732	47.8	2.0	7.2
200	0.2757	0.9668	0.0411	2.7308	3.7537	1.2097	0.5352	0.0595	0.1102	13.6	1.4	9.0
E_a , $\text{kJ}\cdot\text{mol}^{-1}$	53.2	322.1	182.6	86.1	86.5	27.6	102.3	10.8	187.6			
$\ln k_0$	11.9	82.8	43.5	23.0	23.6	7.3	25.5	-0.24	46.1			
RMSD	Xylose = 2.93		Xylulose = 1.53			Formic acid = 0.56		Furfural = 1.14				

The relationship between the reaction rate constants, k_i , and temperature was established by an Arrhenius type expression:

$$k_i = k_0 \exp\left(-\frac{E_{act}}{RT}\right) \quad [18]$$

where k_0 is the preexponential factor (h^{-1}), E_a the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$) and T the absolute temperature (K). The higher the activation energy, the higher temperature dependence of the process. Based on the activation energy values, the steps involving xylose, furfural and formic acid degradation appear to be the most temperature-dependent process. Danon et al. [20] studied the furfural formation from xylose ($0.05 \text{ mol L}^{-1} = 7.5 \text{ g L}^{-1}$) in the presence of HCl (0.05 M) and NaCl as catalysts, proposing a simple mechanism similar to model 1 of this work, in the temperature range from 160 to 200 °C. These authors reported activation energies of 126 kJ/mol and 102 kJ/mol for the degradation of xylose and furfural, respectively. Compared to the values reported in Table 3, higher E_a were obtained in the present work. According to Table 3, lower E_a values for furfural formation from xylose and xylulose (53 kJ/mol and 86.5 kJ/mol, respectively) were obtained compared to those reported by Ershova et al. (166.2 and 133.9 kJ/mol, respectively) in a H_2SO_4 -catalyzed system ($0.1 \text{ mol}\cdot\text{L}^{-1}$ of catalyst) proposing a reaction mechanism similar to model 2 [14]. Surprisingly, E_a values of the same order for xylose isomerization to xylulose were obtained, 86.1 kJ/mol, when compared to the values reported by Ershova et al., 67.4 kJ/mol, although a different catalytic system was employed. Conversely, higher E_a values for the degradation rates of furfural and xylose, and a lower E_a value for xylulose degradation were obtained compared to their reported values (72 kJ/mol, 162.9 kJ/mol and 134.5 kJ/mol, respectively) [14]. These differences can be attributed to the different reaction media, catalyst systems, or the choice of the reaction pathway.

According to the authors' knowledge, the reaction rate constants and E_a values for the formation of formic acid from xylose and furfural, as well as formic acid degradation have not been previously reported in literature, and thus no comparison can be established.

3.1.2. Modelling the effect of salt in the catalysis by CrCl_3 in the system subW/ CO_2

The furfural production from xylose was also studied by adding 4 % of NaCl when performing the treatment under the same conditions in the subW/ CO_2 + CrCl_3 reaction medium at 180 °C. The kinetic profiles of the main identified reaction products are plotted in Fig. 5a. Comparing the kinetic profiles of the reactive system with and without NaCl addition, it can be observed that adding NaCl to the medium results in faster furfural formation and higher furfural concentration. For instance, 41.5 mM of furfural was achieved at 1.2 h with NaCl addition, compared to 35.9 mM of furfural at 1.8 h without NaCl addition. Accordingly, xylose consumption was faster, and the maximum xylulose concentration was reached sooner with the addition of NaCl to the medium. In this regard,

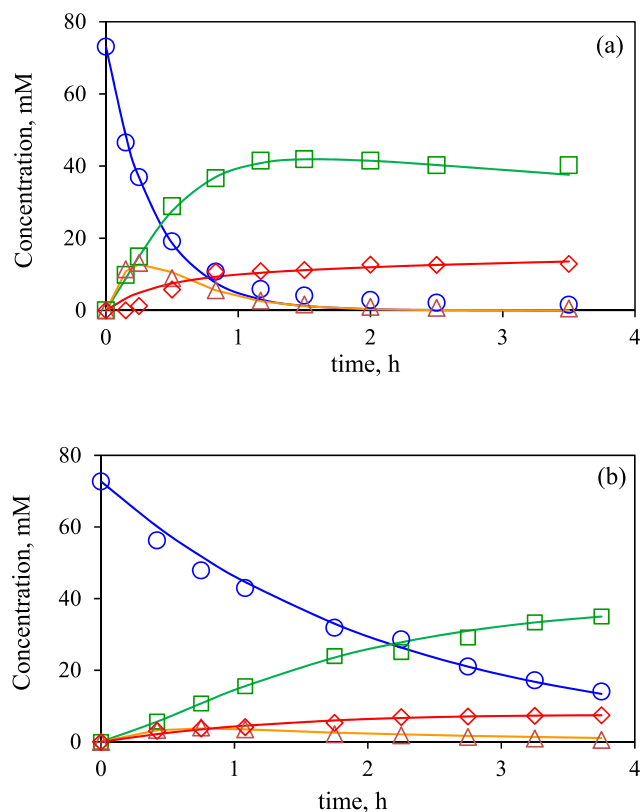


Fig. 5. Xylose (○), furfural (□), xylulose (△) and formic acid (◇) kinetic profile at 180 °C in the reactive system: (a) subW/ CO_2 + CrCl_3 + NaCl (b) subW/ CO_2 + Nafion NR50. The continuous lines represent the results obtained with model 3 (parameters are reported in Table 4).

Marcotullio & De Jong [21] concluded that the addition of metal halides to aqueous acidic solutions has beneficial effect in terms of xylose conversion into furfural.

The three proposed models were also tested for this reactive system, and good fitting was obtained for all three. However, the fitting quality is only presented for model 3, as it is the most comprehensive. The kinetic rate constants are presented in Table 4, along with the quality of fitting. When comparing the reaction rate constants between the systems with and without the addition of NaCl, the most important difference was the high value determined for furfural formation from xylose through the “direct pathway”, $k_{1,3}$, which is ten times higher in the system with NaCl. This high value of $k_{1,3}$ could explain the low degradation rate constant of xylose in the system with NaCl addition ($k_{2,3} = 0.0002$) and support the lower value of the ratio $k_{5,3}/k_{1,3}$ in the system

Table 4

Kinetic rate constants (h^{-1}) for model 3 at 180 °C for different reaction systems for furfural production: (1) From xylose: subW/CO₂ + CrCl₃ + NaCl (2) From xylose: subW/CO₂ + Nafion NR50 (3) From arabinose: subW/CO₂ + CrCl₃.

Sugar	Catalyst	$k_{1,3}$	$k_{2,3}$	$k_{3,3}$	$k_{4,3}$	$k_{5,3}$	$k_{6,3}$	$k_{7,3}$	$k_{8,3}$	$k_{9,3}$	$k_{5,3}/k_{1,3}$	$k_{5,3}/k_{4,3}$	$k_{7,3}/k_{8,3}$
Xylose	CrCl ₃ +NaCl	0.6887	0.0002	0.0002	1.6781	2.7041	1.5946	0.3653	0.0719	0.1408	3.93	1.61	5.08
	RMSD	Xylose = 2.17		Xylulose = 0.72		Formic acid = 1.83		Furfural = 1.07					
Xylose	Nafion NR50	0.0563	0.0214	0.0043	0.2912	3.4392	0.5988	0.0824	0.0456	0.3530	61.1	11.81	1.81
	RMSD	Xylose = 2.14		Xylulose = 0.32		Formic acid = 0.41		Furfural = 1.11					
Arabinose	CrCl ₃	0.0186	0.1260	0.0077	1.2456	2.2240	0.9530	0.2603	0.0591	0.1623	119.6	1.79	4.40
	RMSD	Xylose = 1.15		Xylulose = 0.66		Formic acid = 0.61		Furfural = 0.63					

with NaCl compared to the system without NaCl, 3.93 and 47.8, respectively. In the presence of NaCl xylose reacts faster to form furfural due to the faster “direct pathway”, but no significant effect was observed on the isomerization to xylulose and further dehydration to furfural, since the values of the $k_{5,3}$ and $k_{4,3}$ were of the same order in both systems, with and without NaCl. No significant difference was also observed in the formation of formic acid, with faster production from xylose than from furfural, indicated by the ratio $k_{7,3}/k_{8,3}$ of 5.08.

Similar conclusions were reached by Marcocuttillo & De Jong [21] in their study on the effect of increasing chloride salt concentration on furfural production. These authors observed that xylose reacts significantly faster to form furfural, while no significant effect was observed on the side reactions. This led to a higher furfural yield, around 10 % higher, along with higher furfural selectivity in the presence of NaCl. This outcome is clearly illustrated in Fig. 6a and b, where furfural yield and selectivity for the systems with and without NaCl are plotted for comparison. For instance, selectivity in the NaCl system was 53.5 %

after 0.5 h, whereas in the system without NaCl this value was 31.7 %.

In any case, it must be pointed out that although higher NaCl concentrations could lead to increased furfural yields, there are three main disadvantages to its use; 1) Salt depositions in the pressure reactor and sampler, increasing cleaning time and difficulty, 2) Analytical problems related with salt depositions in the HPLC column, being necessary to improve analysis methods, and 3) Further step is required to remove NaCl from the final solution. Harry et al. [1] also pointed out that a high salinity can corrode components of the reactor or form scale due to a high percentage of salts particles.

3.1.3. Modelling the catalysis by the heterogeneous catalyst Nafion NR50

In previous work, extensive testing was carried out on different heterogeneous catalysts for furfural production in a subW/CO₂ reactive system. Among them, the perfluorosulfonic acid Nafion NR50 was selected as the optimum heterogeneous catalyst due to its higher selectivity towards furfural and the possibility of reuse, as its catalytic activity remained unchanged after 10 runs. Nafion NR50 showed a good chemical and thermal stability ($T_{\text{max}} = 220$ °C according to the manufacturer) under the treatment conditions for furfural production from xylose tested in this work, specially compared to the other heterogeneous catalyst tested by Illera et al. [8], being worth modelling furfural production from xylose in the Nafion NR50 system.

The kinetic profile for the four selected components is plotted in Fig. 5b. It can be clearly observed that xylose conversion and furfural formation rates were lower compared to those observed when using the homogeneous Lewis acid, CrCl₃. When dealing with heterogeneous catalyst, mass transfer limitations could be of importance. Internal mass transfer limitations must be considered due to prior diffusion step of xylose through the matrix of the resin to reach the hydrophilic cluster-channels of the acid groups [8]. Nafion NR50 may shrink or swell when exposed to harsh conditions, such as those tested in subcritical water treatments. In the literature, it has been noted that water showed a moderate capability for swelling the resin, which is advantageous to provide a greater acid site accessibility [22].

Swelling of Nafion NR50 in water would lead to a significantly reduction in internal mass transfer limitation in this heterogeneous catalytic system. Therefore, the three proposed models were tested for this reactive system to compare the results with homogeneous catalysts. The kinetic parameters and the fitting quality are only presented for the model 3 (see Table 4). An analysis of the reaction rate constant values can help elucidate and compare the mechanism in the presence of CrCl₃ and Nafion NR50. The ratio $k_{5,3}/k_{1,3}$ was of the same order as for the CrCl₃ system with values of 61.1 and 47.8, respectively, indicating that furfural is produced faster through xylulose than from the “direct pathway” from xylose for both catalysts. However, the ratio $k_{5,3}/k_{4,3}$ was an order of magnitude higher for Nafion NR50 compared to CrCl₃ (with values of 11.81 and 2.0, respectively), suggesting that sugar isomerization reactions are catalyzed by Lewis acids, but not by the acid sites of Nafion NR50, being xylose isomerization the rate limiting step. This conclusion was also reached in the literature in furfural production from xylose via Brønsted acid catalysis by sulfuric acid [14]. Regarding formic acid formation, as a degradation product, its formation from both xylose and furfural is significant, as indicated by the ratio $k_{7,3}/k_{8,3}$ which has a value of 1.81 (compared to 7.2 for CrCl₃).

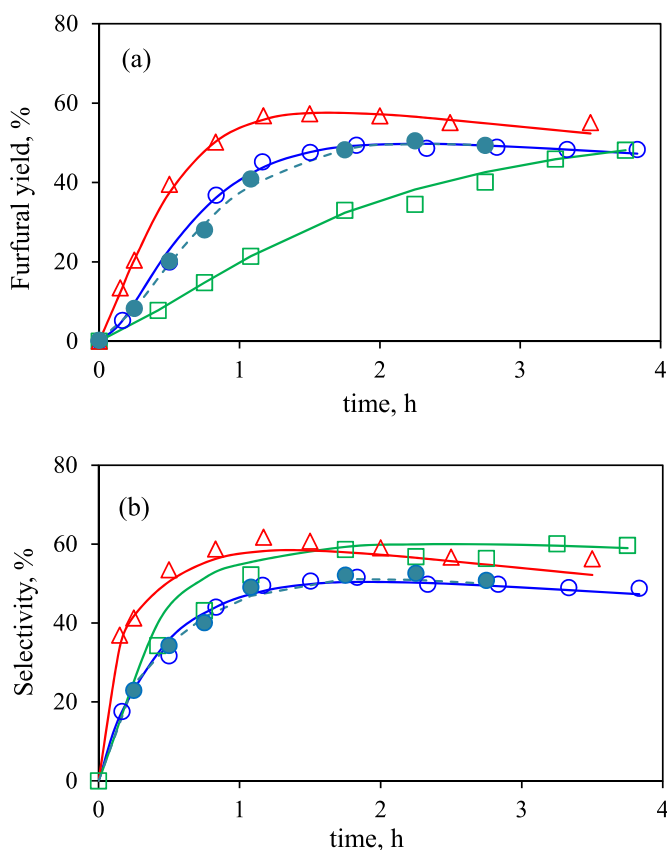


Fig. 6. (a) Furfural yield and (b) Furfural selectivity at 180 °C in different reactive systems (●): xylose as starting sugar: subW/CO₂ + CrCl₃ (Δ); xylose as starting sugar: subW/CO₂ + CrCl₃ + NaCl (□); xylose as starting sugar: subW/CO₂ + Nafion NR50 (●); arabinose as starting sugar subW/CO₂ + CrCl₃. The continuous and discontinuous lines represent model 3 (parameters listed in Tables 3 and 4).

Fig. 6 also includes the furfural production yield and selectivity for the Nafion NR50 catalytic system. Furfural production was slower by using Nafion NR50; however, selectivity towards furfural remained 10 % higher during the treatment, which also aligns with the lower formic acid production (see Fig. 5b).

3.2. Furfural production from other sugars catalyzed by CrCl_3

3.2.1. Furfural production from arabinose

D-xylose is the main component of most of the hemicellulose fraction in most lignocellulosic biomass. It has been used as a model compound for the conversion to furfural to explore various reaction models. However, arabinose can also constitute a significant fraction of hemicelluloses, making it worthwhile to investigate its behavior in the subW/ $\text{CO}_2 + \text{CrCl}_3$ system. The kinetic of furfural formation from arabinose has also been studied at 180 °C. Fig. 7 shows the kinetic profile of the main identified compounds in the reactive system when arabinose was used as pentose. A similar profile to that described for xylose was obtained. The ketose form of arabinose, ribulose, was identified as an intermediate in the furfural production pathway, showing a maximum in the initial stages of the reaction. This indicates a similar reaction pathway to the one observed for xylose.

The furfural yield and selectivity was also included in Fig. 6, along with the results from the different reactive systems using xylose at the same temperature. A very similar behaviour was observed for both pentoses in the subW/ $\text{CO}_2 + \text{CrCl}_3$ system. In contrast, Danon et al. [20] observed much faster xylose conversion and furfural production compared to arabinose in the temperature range from 160 °C to 200 °C, using a 0.5 mol L^{-1} pentose solution catalyzed by HCl and sodium chloride. This difference in furfural yield between the two pentoses has been attributed in the literature to the difference in the activation energies for the dehydration reaction of the two pentoses, with lower values for xylose compared to arabinose [23–26]. However, in this study, it can be concluded that in the Lewis acid (CrCl_3) catalyzed subW/ CO_2 system, both pentoses exhibit similar kinetic behaviour for furfural production, indicating a similar stability in this reactive medium.

The three models (1–3) were tested for furfural production from arabinose. Nevertheless, the kinetic parameters and the fitting quality were only presented for model 3 (see Table 4), as it was the most complete one. A comparison between the kinetic reaction constants between xylose and arabinose at 180 °C can be established. The ratio $k_{5,3}/k_{1,3}$ for both pentoses shows that furfural formation from the ketoses, xylulose and ribulose, respectively, was faster than via other intermediates, as represented in model 3 as a “direct pathway”. However, a higher value for this ratio was obtained for arabinose, 119.6, compared

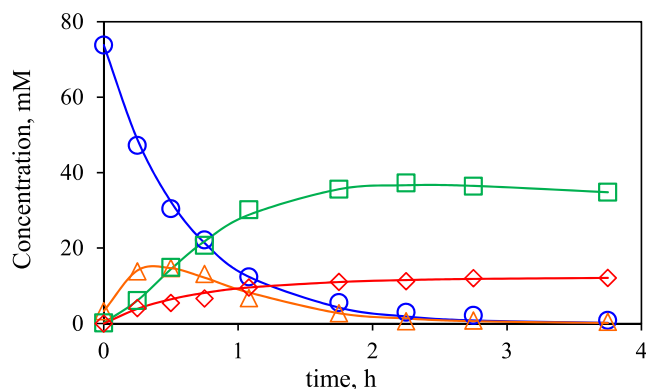


Fig. 7. Arabinose (○), furfural (□), ribulose (△) and formic acid (◇) kinetic profile at 180 °C in the reactive system subW/ $\text{CO}_2 + \text{CrCl}_3$. The continuous lines represent the results obtained with model 3 (parameters are reported in Table 4).

to xylose, 47.8, which agrees with the slightly higher value of the ribulose (maximum value of 14.7 mM) during the course of reaction compared to the value of xylulose (maximum value of 11.5 mM). For both pentoses, the ratio $k_{5,3}/k_{4,3}$ was of the same order, showing the isomerization is not the rate-controlling step, opposite to a Brønsted acid catalyst systems [14]. Formic acid was produced faster from both pentoses than from furfural. Finally, furfural degradation was similar in both systems ($k_{3,3} = 0.077, 0.0096$ for arabinose and xylose, respectively).

3.2.2. Furfural production from glucose

Glucose is one of the primary sugars derived from biomass. Consequently, the potential production of furfural from glucose using CrCl_3 as Lewis acid catalyst in the subW/ CO_2 system was explored at 180 °C. Fig. 8a shows the kinetic profile of some of the products identified in the glucose system. The major identified product was the dehydration product of glucose, 5-hydroxymehtylfurfural (HMF), while furfural was present at very low concentrations, lower than 1.05 mM. This low concentration implies a yield of less than 1.3 % on a C basis (Eq. (3)). The primary reaction products identified using glucose as the substrate were HMF, fructose, and levulinic and formic acids (see Fig. 8b). Glucose degradation routes in a subW reaction medium have been described in the literature [16]. Glucose isomerizes to fructose, and both isomers can

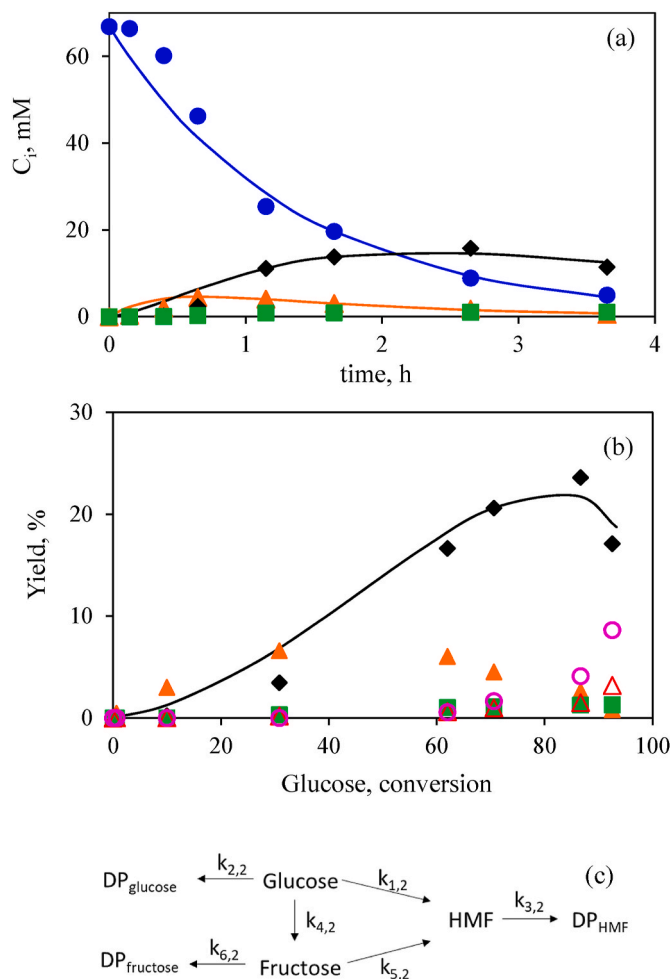


Fig. 8. (a) Kinetic profile of glucose (●), fructose (▲), HMF (◆), and furfural (■) (b) Compounds yield as function of glucose conversion: HMF (▲), fructose (◆), furfural (■), formic acid (△), levulinic acid (○) (c) Glucose degradation (model 2) in the reactive system: glucose - subW/ $\text{CO}_2 + \text{CrCl}_3$ at 180 °C. The continuous lines represent the results obtained with model 2 adapted to glucose (parameters reported in Table 5).

Table 5Kinetic rate constants (h^{-1}) at 180 °C for the catalyzed subW/CO₂ + CrCl₃ system. Model 2 applied to glucose (see Fig. 8c and Eqs [7–9]).

$k_{1,2}$	$k_{2,2}$	$k_{3,2}$	$k_{4,2}$	$k_{5,2}$	$k_{6,2}$	$k_{5,2}/k_{1,2}$	$k_{5,2}/k_{4,2}$	$k_{4,2}/(k_{1,2}+k_{2,2})$
0.0507	0.4040	0.3705	0.2869	2.4788	0.0033	48.9	8.6	0.63
RMSD		Glucose = 4.85		Fructose = 1.02		HMF = 1.97		

dehydrate to HMF. Additionally, water can rehydrate HMF to form levulinic and formic acids. The addition of a Lewis acid reduces the retro-aldol pathway since very few retro aldol products were detected.

Based on the product profiles, none of the previously established models apply to the formation of furfural from glucose due to its low production. Additionally, the aim of this work was not to model glucose degradation in the reactive medium subW/CO₂ + CrCl₃. However, to compare the HMF formation pathway via glucose isomerization to fructose with the furfural formation pathway via xylose isomerization to xylulose, a similar kinetic model to model 2 was tested. A set of differential equations, analogous to those proposed for model 2 (Eqs (7)–(9)) can be arranged by simply substituting xylose, xylulose, and furfural for glucose, fructose, and HMF, respectively, as well as their corresponding degradation products, according to the mechanism proposed in Fig. 8c.

Table 5 presents the corresponding kinetic parameters for glucose dehydration in the presence of CrCl₃ in a subW/CO₂ reaction medium. According to the ratio $k_{5,2}/k_{1,2}$, it can be concluded that HMF formation is faster from fructose than from glucose. This is similar to the formation of furfural, from xylulose and xylose, with similar values for both systems: 48.9 and 50.2, respectively. However, the ratio $k_{5,2}/k_{4,2}$ (HMF formation from fructose/isomerization of glucose to fructose) was higher for glucose, 8.6, compared to the xylose system, 2.0. This indicates that glucose isomerization is slower than xylose isomerization when compared to the formation of the corresponding dehydration products from ketoses. The degradation kinetic rate constants followed the order: glucose ($k_{2,2}$) > HMF ($k_{3,2}$) > fructose ($k_{6,2}$).

3.3. Modelling of furfural production from xylan catalyzed by CrCl₃

The furfural production study was extended to use xylan as the starting material. Xylan, a polysaccharide rich in pentoses, constitutes a major fraction of the hemicelluloses in the biomass. Characterization of the commercial xylan used in this work was performed according to the NREL protocols. It revealed that the pentose content comes mainly from xylose (86.9 wt %), while arabinose accounted only for 2.1 wt% and glucose 10.0 wt %. The initial acetic acid group content was 1.0 wt %. Due to its physical and chemical structure, the hydrolysis of the cellulose fraction in most lignocellulosic biomass will be limited under subcritical water conditions tested in this work. Under these conditions, the production of platform chemicals from the hemicellulose fraction of the biomass will primarily be derived from xylose and small amounts of arabinose and glucose. Therefore, xylan is a good candidate for studying the potential interactions between monomers released from the polysaccharide fraction hydrolyzed under the conditions tested in this work. An aqueous solution of xylan was prepared to obtain a pentose concentration similar to that used in experiments with pure xylose.

Fig. 9a and b show the kinetic profile of the chemical compounds determined in this reactive system. The content of xylan, arabinan, and glucan as oligomers in the course of the reaction was determined by performing a sulfuric acid hydrolysis step to release monomeric sugars from oligomers. The free monomer content before hydrolysis was subtracted to determine the actual oligomer content. The monomers

released -xylose, arabinose, and glucose-showed a maximum in their concentrations. This maximum indicates that, initially, the production rate of these monomers was faster than their degradation. After reaching this maximum, the monomers underwent various degradation pathways, leading to a continuous decrease in their concentrations. The ketose intermediates from arabinose and glucose were not detected in significant amounts due to the lower concentration of these monomers in the reaction medium.

The maximum furfural yield from xylan (48.23 %) was similar to the maximum furfural yield from xylose (49.4 %, see Fig. 9c). However, the maximum yield in case of xylose was achieved significantly faster. This is evident when examining the furfural productivity, evaluated as the ratio of the amount of furfural produced to the initial amount of xylose in the substrate over time (mol furfural/mol xylose·h). The productivity is markedly higher when starting from xylose (see Fig. 9c). The lower productivity of furfural from xylan can be attributed to the two-step mechanism involved in its production. Initially, xylan is converted to xylose through hydrolysis, followed by the dehydration of xylose to furfural. This two-step process is outlined in the proposed mechanism for the commercial reaction of xylan reaction in the subW/CO₂ + CrCl₃ system, as illustrated in Fig. 10a. This mechanism also takes into account the conversion of arabinan to arabinose and glucan to glucose, as well as the formation of acetic acid from xylan. Although some acetic acid is produced from pentose degradation, its yield was very low, as previously described, and thus it was not included in previous models. The corresponding equations are provided in Equations (19)–(28).

$$\frac{dC_{xylan}}{dt} = -(k_{10,3} + k_{11,3})C_{xylan} \quad [18a]$$

$$\frac{dC_{xylose}}{dt} = k_{10,3}C_{xylan} - (k_{1,3} + k_{2,3} + k_{4,3} + k_{7,3})C_{xylose} \quad [19]$$

$$\frac{dC_{xylulose}}{dt} = k_{4,3}C_{xylose} - (k_{5,3} + k_{6,3})C_{xylulose} \quad [20]$$

$$\frac{dC_{arabinan}}{dt} = -k_{13,3}C_{arabinan} \quad [21]$$

$$\frac{dC_{arabinose}}{dt} = k_{13,3}C_{arabinan} - (k_{14,3} + k_{15,3})C_{arabinose} \quad [22]$$

$$\frac{dC_{furfural}}{dt} = k_{1,3}C_{xylose} + k_{5,3}C_{xylulose} + k_{14,3}C_{arabinose} - (k_{3,3} + k_{8,3})C_{furfural} \quad [23]$$

$$\frac{dC_{formic\ acid}}{dt} = k_{8,3}C_{furfural} + k_{7,3}C_{xylose} - k_{9,3}C_{formic\ acid} \quad [24]$$

$$\frac{dC_{acetic\ acid}}{dt} = k_{11,3}C_{xylan} - k_{12,3}C_{acetic\ acid} \quad [25]$$

$$\frac{dC_{glucan}}{dt} = -k_{16,3}C_{glucan} \quad [26]$$

Table 6
Kinetic rate constants, h^{-1} , for furfural production from commercial xylan at 180 °C.

$k_{1,3}$	$k_{2,3}$	$k_{3,3}$	$k_{4,3}$	$k_{5,3}$	$k_{6,3}$	$k_{7,3}$	$k_{8,3}$	$k_{9,3}$	$k_{10,3}$	$k_{11,3}$	$k_{12,3}$	$k_{13,3}$	$k_{14,3}$	$k_{15,3}$	$k_{16,3}$	$k_{17,3}$
0.2298	0.0016	0.0372	0.3683	2.0079	0.3311	0.1143	0.0688	1.0868	2.0873	0.2215	0.0002	2.0578	0.4438	0.0537	1.0178	0.3626
Ratio of rate constants																
RMSD																
Arabinan = 0.07				Arabinose = 0.08				Glucan = 0.43				Xylose = 3.52				Xylulose = 00.32
Furfural = 0.80				Formic = 0.19				Glucose = 0.36				Acetic = 0.84				Xylan = 1.95
$k_{5,3}/k_{1,3} = 8.7$ $k_{7,3}/k_{8,3} = 1.7$																

$$\frac{dC_{glucose}}{dt} = k_{16,3}C_{glucan} - k_{17,3}C_{glucan} \quad [27]$$

The kinetic rate constants of equations (19)-(28) are listed in Table 5. For some of the parameters a comparison has been established between the systems of pure monomers. The ratio $k_{5,3}/k_{1,3}$ was lower for the xylan system compared to the pure monomer xylose system with values of 8.7 for xylan and 47.8 for xylose. Nonetheless, furfural production from xylulose was faster than for xylose in both systems. Additionally, the ratio $k_{5,3}/k_{4,3}$ is higher for xylan than for xylose, indicating a relative slowdown in the conversion of xylose to xylulose compared to its transformation into furfural. Furthermore, the reaction rate for the production of formic acid from xylose and furfural becomes more similar in the xylan reactive medium ($k_{7,3}/k_{8,3} = 1.7$) than in the pure xylose system, with a value of 7.2. The degradation reaction rate constant for furfural was higher in the xylan system ($k_{3,3} = 0.0372$), compared to xylose system ($k_{3,3} = 0.0096$). In this context, Danon et al. [23] observed a faster degradation rate in more complex saccharide solutions, attributing this behaviour to the presence of pentose and hexose degradation products that enhance furfural degradation. In any case, high furfural yields were still achieved in this system. Finally, the reaction rate constants for the conversion of biopolymers -xylan, arabinan, and glucan-into their respective monomers -xylose, arabinose, and glucose-were similar for xylan ($k_{10,3} = 2.0873$ and arabinan ($k_{13,3} = 2.0573$), and slightly lower for glucan ($k_{16,3} = 1.0178$).

Molecular weight distribution. Fig. 10b presents the molecular weight distribution (MWD) of the samples collected throughout the treatment process. Initially, the percentage of fractions in the range 150–282 Da (corresponding to 1–2 units of xylose, expressed as pullulan equivalents) showed an increasing trend due to the hydrolysis of the biopolymer. The percentage reached a maximum at approximately 1.2 h of reaction time, after which it experienced a slight decline. Conversely, the larger fractions in the range 282–678 Da (3–5 xylose units expressed as pullulan equivalents) and 678–1074 Da (5–8 xylose units expressed as pullulan equivalents) initially decreased, but showed a slight increase at approximately 1.7 h. Notably, there were no fractions detected in the range of 10000–1074 Da at the start of the treatment. However, by the end of the treatment, this fraction exceeded 10 %. This can be attributed to the nature of furfural as an intermediate product itself, which is sensitive to acidic compounds. Acid-catalyzed cleavage of the furan structure and auto-oxidation can lead to the decomposition of furfural into formic acid and various polymeric products. This polymeric products likely accounts for the increase in high molecular weight polymeric fractions observed by the end of the treatment.

4. Conclusions

The presence of a Lewis acid catalyst ($CrCl_3$) in the furfural production system from pentoses in a subW/ CO_2 reaction medium led to higher furfural yield and lower char formation compared with the yield obtained in a subW reaction medium.

The furfural production kinetic route proposed in this work included intermediates as well as the presence of the main degradation product. Based on the kinetic parameters it can be concluded that the pentose isomerization from its aldose form to their corresponding ketoses, xylulose and ribulose, from xylose and arabinose respectively and their further furfural formation is the primary reaction pathway in the subW/ $CO_2 + CrCl_3$ system. Lewis acid catalyst enhanced sugar isomerization reaction, but in the presence of acidic resins, such as Nafion NR50, xylose isomerization was rate-limiting. The “direct pathway” to furfural production was promoted by the addition of NaCl. Based on the kinetic profile of the main identified compounds and the kinetic parameters, it was also concluded that formic acid was released into the medium from both pentose and furfural.

When starting from xylan to obtain furfural, similar yields were obtained, but productivity of furfural evaluated over time was much

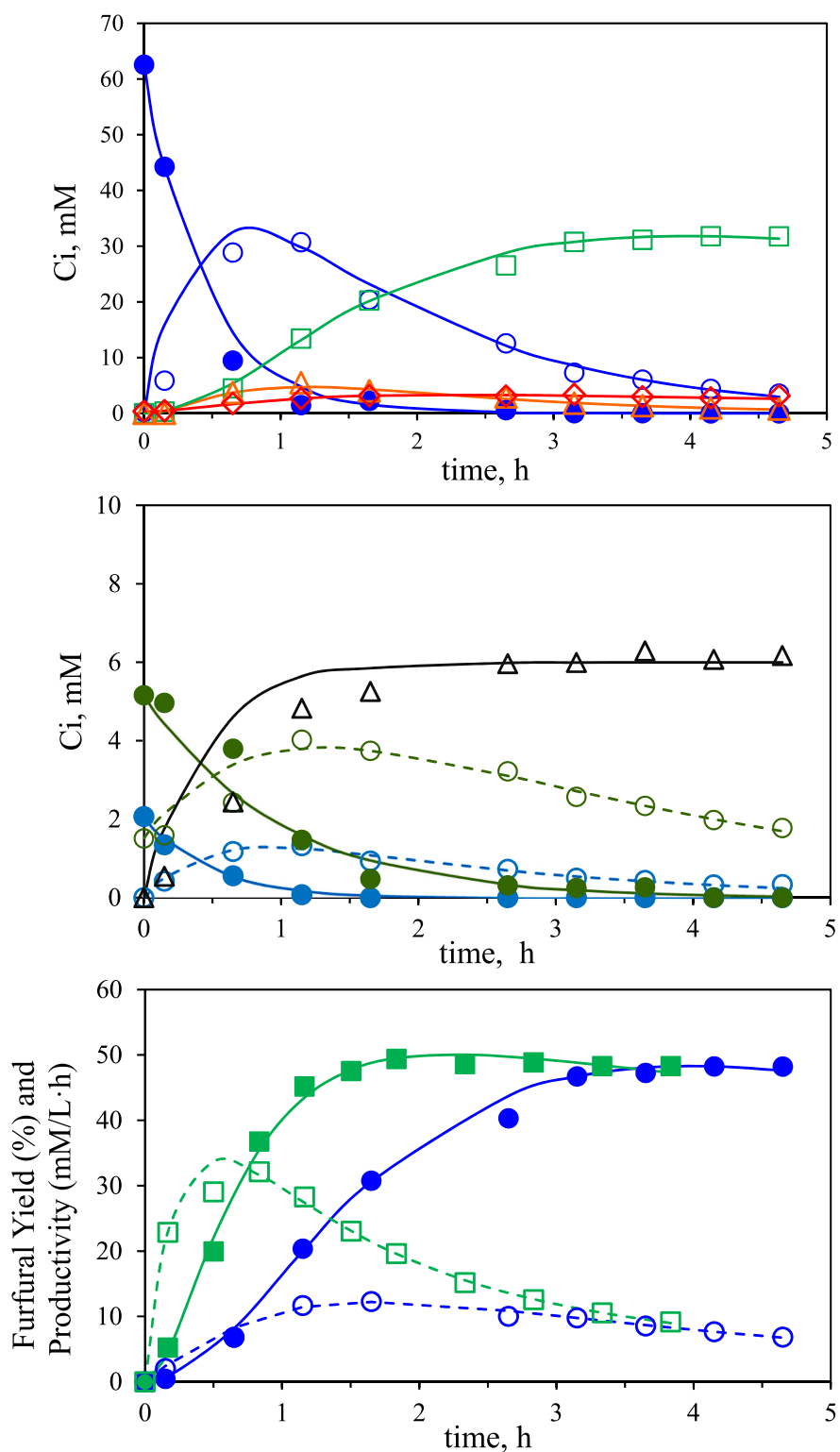


Fig. 9. (a) Xylan ●, xylose ○, furfural □, xylulose △, and formic acid ◇ kinetic profile (b) Arabinan ●, arabinose ○, glucan ●, glucose ○, and acetic acid △. (c) Furfural yield from xylan ●, from xylose ■, Productivity of furfural from xylan ○ and from xylose □ as a function of time. Reactive system subW/CO₂ + CrCl₃ at 180 °C. The continuous and discontinuous lines represent the results obtained with model 3 (parameters are reported in Table 6 for xylan and Table 3 for xylose).

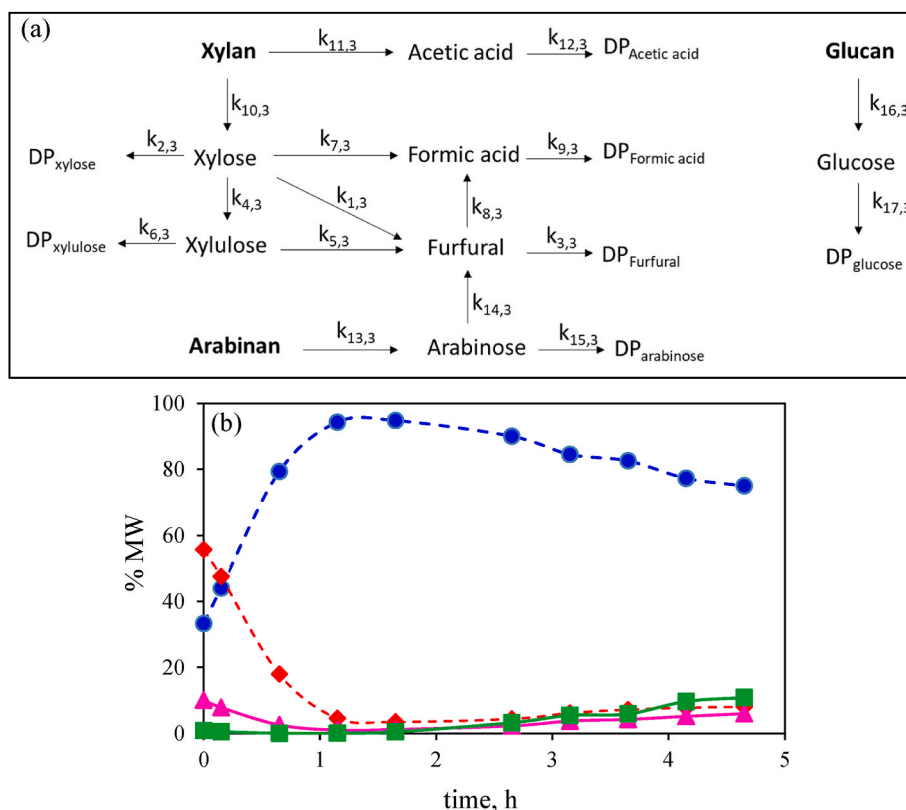


Fig. 10. (a) Xylan degradation route in the reactive system subW/CO₂ + CrCl₃ at 180 °C (b) Molecular weight distribution profile of commercial xylan kinetics (● < 282 Da, ◆ 282–678 Da, ▲ 678–1075 Da, ■ > 1074 Da). The lines are to guide the eye.

higher for xylose than from xylan. Molecular weight distribution of xylan system showed an initial increase for fractions in the range of 282–150 Da due to the first hydrolysis step of the biopolymer while the fraction corresponding to MW higher than 1074 Da appeared only at long treatment times, likely due to the formation of different polymeric products.

CRedit authorship contribution statement

A.E. Illera: Writing – review & editing, Writing – original draft, Methodology, Data curation. **H. Candela:** Writing – review & editing, Methodology, Data curation. **S. Beltrán:** Writing – review & editing, Validation, Funding acquisition. **M.T. Sanz:** Writing – original draft, Funding acquisition, Formal analysis, Conceptualization.

Funding

This work was supported by the Agencia Estatal de Investigación [grant numbers PID2022-136385OB-I00, TED2021-129311B-I00, PDC2022-133443-I00] and the Junta de Castilla y León (JCyL) and the European Regional Development Fund (ERDF) [grant number BU027P23]. A. E. Illera postdoctoral contract was funded by BU027P23. H Candela-Gil pre-doctoral contract was funded by JCyL and the European Social Fund [ORDEN EDU/1009/2024].

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biombioe.2024.107550>.

Data availability

Data will be made available on request.

References

- [1] I. Harry, H. Ibrahim, R. Thring, R. Idem, Catalytic subcritical water liquefaction of flax straw for high yield of furfural, *Biomass Bioenergy* 71 (2014) 381–393, <https://doi.org/10.1016/j.biombioe.2014.09.017>.
- [2] H. Liu, H. Hu, M.M. Baktash, M.S. Jahan, L. Ahsan, Y. Ni, Kinetics of furfural production from pre-hydrolysis liquor (PHL) of a kraft-based hardwood dissolving pulp production process, *Biomass Bioenergy* 66 (2014) 320–327, <https://doi.org/10.1016/j.biombioe.2014.02.003>.
- [3] A. Mazar, N. Jemaa, W. Wafa Al Dajani, M. Marinova, M. Perrier, Comparative study: furfural production from two types of pre-hydrolysates produced using aspen and maple chips, *Biomass Bioenergy* 111 (2018) 103–113, <https://doi.org/10.1016/j.biombioe.2018.02.013>.
- [4] M. Sajid, M. Rizwan Dilshad, M. Saif Ur Rehman, D. Liu, X. Zhao, Catalytic conversion of xylose to furfural by p-toluenesulfonic acid (Ptsa) and chlorides: process optimization and kinetic modeling, *Molecules* 26 (2021), <https://doi.org/10.3390/molecules26082208>.
- [5] C. Sener, A.H. Motagamwala, D.M. Alonso, J.A. Dumesic, Enhanced furfural yields from xylose dehydration in the γ -valerolactone/water solvent system at elevated temperatures, *ChemSusChem* 11 (2018) 2321–2331, <https://doi.org/10.1002/cssc.201800730>.
- [6] 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>.
- [7] I. Agirrezabal-Telleria, J. Requies, M.B. Güemez, P.L. Arias, Furfural production from xylose + glucose feedings and simultaneous N 2-stripping, *Green Chem.* 14 (2012) 3132–3140, <https://doi.org/10.1039/c2gc36092f>.
- [8] A.E. Illera, H. Candela, A. Bermejo-López, P. Barea, P. Alonso-Riño, Ó. Benito-Román, S. Beltrán, M.T. Sanz, 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), *Biomass Bioenergy* 187 (2024), <https://doi.org/10.1016/j.biombioe.2024.107304>.
- [9] A. Bermejo-López, A.E. Illera, R. Melgosa, S. Beltrán, M.T. Sanz, Comparative selective conversion of biomass-derived mono- and polysaccharides into lactic acid with lanthanide Lewis acid catalysts, *Food Bioproc Tech* (2024), <https://doi.org/10.1007/s11947-024-03416-x>.
- [10] F.M. Relvas, A.R.C. Morais, R. Bogel-Lukasik, Kinetic modeling of hemicellulose-derived biomass hydrolysis under high pressure CO₂-H₂O mixture technology, *J. Supercrit. Fluids* 99 (2015) 95–102, <https://doi.org/10.1016/j.supflu.2015.01.022>.
- [11] P. Alonso-Riño, M.T. Sanz, O. Benito-Román, S. Beltrán, E. Trigueros, Subcritical water as hydrolytic medium to recover and fractionate the protein fraction and

- phenolic compounds from craft brewer's spent grain, *Food Chem.* 351 (2021), <https://doi.org/10.1016/j.foodchem.2021.129264>.
- [12] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, Determination of sugars, byproducts, and degradation products in liquid fraction process samples. <http://www.nrel.gov/docs/gen/fy08/42623.pdf>, 2008.
- [13] A. Sluiter, B. Hames, R.O. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. of Energy, Determination of structural carbohydrates and lignin in biomass. *Biomass Analysis Technology Team Laboratory Analytical Procedure*, 2012.
- [14] O. Ershova, J. Kanervo, S. Hellsten, H. Sixta, The role of xylulose as an intermediate in xylose conversion to furfural: insights via experiments and kinetic modelling, *RSC Adv.* 5 (2015) 66727–66737, <https://doi.org/10.1039/c5ra10855a>.
- [15] O. Ershova, K. Nieminen, H. Sixta, The role of various chlorides on xylose conversion to furfural: experiments and kinetic modeling, *ChemCatChem* 9 (2017) 3031–3040, <https://doi.org/10.1002/cctc.201700269>.
- [16] 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), <https://doi.org/10.1016/j.foodchem.2024.138421>.
- [17] M. Möller, U. Schröder, Hydrothermal production of furfural from xylose and xylan as model compounds for hemicelluloses, *RSC Adv.* 3 (2013) 22253–22260, <https://doi.org/10.1039/c3ra43108h>.
- [18] V. Choudhary, S. Caratzoulas, D.G. Vlachos, Insights into the isomerization of xylose to xylulose and lyxose by a Lewis acid catalyst, *Carbohydr. Res.* 368 (2013) 89–95, <https://doi.org/10.1016/j.carres.2012.12.019>.
- [19] J.P. Lange, E. Van Der Heide, J. Van Buijtenen, R. Price, Furfural-A promising platform for lignocellulosic biofuels, *ChemSusChem* 5 (2012) 150–166, <https://doi.org/10.1002/cssc.201100648>.
- [20] B. Danon, W. Hongsiri, L. van der Aa, W. de Jong, Kinetic study on homogeneously catalyzed xylose dehydration to furfural in the presence of arabinose and glucose, *Biomass Bioenergy* 66 (2014) 364–370, <https://doi.org/10.1016/j.biombioe.2014.04.007>.
- [21] G. Marcotullio, W. De Jong, Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions, *Green Chem.* 12 (2010) 1739–1746, <https://doi.org/10.1039/b927424c>.
- [22] D.E. López, J.G. Goodwin, D.A. Bruce, Transesterification of triacetin with methanol on Nafion® acid resins, *J. Catal.* 245 (2007) 381–391, <https://doi.org/10.1016/j.jcat.2006.10.027>.
- [23] B. Danon, G. Marcotullio, W. De Jong, Mechanistic and kinetic aspects of pentose dehydration towards furfural in aqueous media employing homogeneous catalysis, *Green Chem.* 16 (2014) 39–54, <https://doi.org/10.1039/c3gc41351a>.
- [24] G.A.D. Castro, R.C. Batista, R. de C.S. de Sousa, A. de C.O. Carneiro, S. A. Fernandes, Green synthesis of furfural from xylose and corn cob biomass, *React. Chem. Eng.* 8 (2023) 1969–1980, <https://doi.org/10.1039/d3re00017f>.
- [25] S. Le 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>.
- [26] 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>.