



Microwave technology as a green and fast alternative for furfural production and biomass pre-treatment using corn stover: Energetic and economic evaluation

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ABSTRACT

Pressurized microwave treatments were used for the production of furfural using three different pentose-containing materials with different structural complexity levels; pure xylose, xylan from corn core and corn stover. Only water was used as the one-pot reaction medium, as an alternative to the frequently used organic solvents. The presence of CrCl₃ as a Lewis acid catalyst was essential for furfural production. In general, higher temperature and longer treatments led to higher furfural yield, although treatment times over 40 minutes did not show any improvement. Using the severity factor (logR₀) and the power consumption it was possible to determine that for equal furfural production treatments, it was more energy requiring to maintain a lower temperature during more time, than to perform shorter treatments at higher temperature. Best MW treatment conditions for xylose were 200 °C for 25 minutes, with a furfural yield of 43 %, which corresponded to a logR₀ of 2.56. When treating xylan and corn stover, lower furfural yields were achieved under these conditions due to higher energy requirements to break the structural components, being 39 and 23 %, respectively. When treating corn stover under these conditions, best energy consumption values per amount of generated furfural were found, being 0.8 kWh/g furfural, what is equivalent to the emission of 195 g CO₂/g furfural, a much lower value than other MW tested conditions. MW treatments were proposed as a pre-treatment to enrich biomass in cellulose while producing furfural with an environmentally friendly technology.

1. Introduction

Corn is one of the major globally used cereal crops for human nutrition, but also includes other uses as animal feed or derived products. According to the United States Department of Agriculture (USDA), total corn production in 2023 was 1.22 billion tons (USDA, 2024). During corn harvesting and processing, several by-products are generated, being the main ones corn stover and corn cob (Ruan et al., 2019). According to harvest data, around 50 % of the external corn plant is stover, what means that production of corn stover is practically equal to the amount of corn grain, and therefore, more than 1 billion tons of this residue are generated per year (Li et al., 2014). As a lignocellulosic biomass, corn stover presents a high carbohydrate content, and it is mainly formed of cellulose, hemicellulose and lignin. With this

composition, corn stover is a key source for biofuel and other value-added chemicals such as lactic acid, furfural or levulinic acid. Lignocellulosic material often needs a pre-treatment for the separation or solubilization of the biomass fractions, to liberate the sugars of interest that can be later transformed into the aimed compounds. In a general way, it can be said that during pre-treatment, the macromolecular structure is modified, hemicellulose is broken down, and makes the cellulose fraction available (Agbor et al., 2011).

Among the above-mentioned value-added products that can be obtained from corn stover, the focus of this study will be in furfural production. Furfural is a versatile chemical with interest for pharmaceutical, chemical, plastics or fuel industries among others (Eseyin and Steele, 2015). Although in some studies furfural has been produced from hexoses, its main production comes from the dehydration

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of pentoses (Choudhary et al., 2012). In lignocellulosic biomass, pentoses such as D-xylose and L-arabinose are present in the hemicellulose fraction in the form of β -1,4-linked polysaccharides. For the production of furfural from those linked pentoses, a previous step for their hydrolysis is needed so that monosaccharides and oligosaccharides are available for their consequent reaction into value-added chemicals (Kang et al., 2021). To avoid a two-step furfural production process, a common technique is to combine in one treatment, the conditions where hemicelluloses are broken down, and pentoses convert to furfural. This is commonly reached by applying temperatures around 150–240 °C for the first step, combined with acid catalysts, which promote the second one. Industrially, furfural is produced in this way by using average temperatures of 200 °C and sulfuric or phosphoric acid as catalyst (Yong et al., 2022). Plenty of studies aim to improve the furfural yield by testing different catalysts (Yang et al., 2017), using organic biphasic systems to avoid furfural degradation (Xiouras et al., 2016), or employing various heating reaction media, such as microwave or ultrasound (Chen et al., 2017).

In a previous study of the research group, different catalysts were tested in an intensified subcritical water (subW) and CO₂ system for furfural production from xylose, and optimal conditions were found when Lewis acid catalyst CrCl₃·6 H₂O was used in a 73 mM xylose water solution at 180 °C and 55 bar for 1.7 hours, obtaining almost 50 % furfural yield (Illera et al., 2024). In the present study, the aim was to obtain similar results but using a one-pot microwave treatment, due to its simpler operation, its energy-efficiency characteristics, and for the shorter heating times needed (Chen et al., 2017). Commonly, a two-step process where biomass is first hydrolyzed, and the hydrolysate is then microwave-treated is performed. In this study, both reactions were combined in a single MW treatment. The selected substrates were sugar monomers, mainly xylose, as the primary hemicellulose sugar-derivative, but also its more complex form, xylan. Finally, a highly abundant lignocellulosic biomass, as it is corn stover, was also used in order to study how furfural yield and production routes are modified depending on the availability of pentoses for its production. Previous studies have achieved furfural production through microwave heating, although most of them focus on xylose conversion (Guenic et al., 2015; Padilla-Rascón et al., 2020; Weingarten et al., 2010), and to a lesser extent, xylan and lignocellulosic materials (Hricovíniová, 2013; Le Guenic et al., 2016; Zha et al., 2022), achieving very different furfural yield values depending on the treated substrate, reaction medium, catalyst and operating conditions. What almost all previous microwave focused studies have in common is the use of organic solvents in combination with water. Their use presents the problematic contaminant residues disposal and corrosion of the systems.

Therefore, in the present study, a one-pot microwave treatment using only water as solvent and CrCl₃·6 H₂O as catalyst was tested for furfural production from three complexity levels of pentoses to avoid the use of organic solvents and try to use milder subW conditions than the previously used, while improving furfural yield.

2. Experimental section

2.1. Materials

Xylose (99 %), arabinose (99 %), glucose (99 %), furfural (99 %) and chromium (III) chloride hexahydrate (98 %) (from now on CrCl₃) were purchased from Sigma-Aldrich. Acetic acid (98 %) was purchased from VWR Chemicals, and formic acid (98 %) from Panreac AppliChem. Xylan from corn core was purchased from TCI. Corn stover was kindly provided by a local farmer from Saldaña (Palencia, Spain).

2.2. Microwave heating for furfural production

Furfural production through microwave technology (MW) was performed using the main derived sugar monomers from biomass (xylose,

arabinose and glucose), the oligomer xylan, and the corn stover leaves and stems (from now on corn stover). Corn stover was first ground to a particle size of < 2 mm using a Retsch SM100 mill. Treatments were performed using a flexiWAVE microwave (Milestone Srl, Italy) with 100 mL high-pressure (SK-15S) reactors and internal temperature and pressure control probe. These reactors can bear a maximum temperature of 300 °C and 100 bar of pressure. Sugar monomers were first treated at a fixed concentration of 11 g/L (73 mM xylose), xylan was treated at 12.5 g/L (83 mM xylose) to simulate xylose content in corn stover, and corn stover treatment concentration was 5 % w/v (89 mM xylose). Water volume in sugar monomers and xylan treatments was 50 mL, while it was 40 mL in the corn stover ones to maintain a similar total volume in the reaction vessel. CrCl₃ (2 % w/w respect to xylose content) was used as catalyst to improve furfural production. MW treatments were divided in three stages, (1) heating, (2) isothermal treatment, and (3) cooling. Heating time was fixed as 5 minutes for all treatments, and therefore, the reported treatment times in the manuscript refer to the isothermal treatment periods. Cooling down time varied from 15 to 30 minutes for 150 and 200 °C treatments, respectively, until sample temperature was lower than 90 °C. After the MW treatment, the reactor content was filtered, and the liquid was analyzed. In corn stover treatments, the residual solid after the treatment was washed with deionized water and dried for its structural composition determination. The effect of different treatment parameters such as catalyst presence, treatment time (5–90 minutes) and temperature (150–200 °C) were evaluated on furfural yield. The effect of heating power (200–1500 W) was studied on the treatment temperature profiles. The given value of power for each treatment corresponds to the maximum power that the MW equipment would apply to reach the fixed temperature. The MW regulates the applied power (W) according to the solution temperature inside the vessel, continuously registered through the corresponding probe. The equipment provided the applied power per treatment time, allowing to calculate average applied power. Operating pressure was registered along treatments through a specific vessel lid with a pressure sensor. Working pressure varied among treatment times from 4.5 to 5.0 bar at 150 °C, 9.5–11.1 bar at 180 °C, and 15.5–17.3 bar at 200 °C (Saturation pressures at 150 °C = 4.8 bar, 180 °C = 10.0 bar and 200 °C = 15.6 bar. Each of the represented kinetic points in the manuscript correspond to an individual treatment, and all treatments were performed in duplicate.

2.3. Furfural production evaluation

To evaluate the effectiveness of each of the reaction conditions, furfural yield was calculated using Eq. 1, and furfural selectivity using Eq. 2.

$$\text{Furfural yield (\%)} = \frac{\text{moles of C in furfural}_{(t)}}{\text{moles of C in pentoses monomers}_{(0)}} \cdot 100 \quad (1)$$

$$\text{Furfural selectivity (\%)} = \frac{\text{moles of furfural}_{(f)}}{\text{moles of pentose}_{(0)} - \text{moles of pentose}_{(f)}} \cdot 100 \quad (2)$$

Where subscript (t) corresponds to the concentration in the treated sample, (0) to the initial one, and (f) to the final one. In the case where xylan and corn stover were treated, the moles of pentoses correspond to the sum of xylose and arabinose moles present in the untreated materials.

Another parameter of interest is the severity factor, which allows to evaluate the combined effect of temperature and treatment time on hydrothermal processes. Severity factor is expressed as logR₀, being R₀ calculated through Eq. 3.

$$R_0 = t \cdot \exp\left(\frac{T - 100}{14.75}\right) \quad (3)$$

where t is the isothermal treatment time and T the temperature of the isothermal treatment period. 14.75 is the activation energy for the cleavage of glycosidic bonds in carbohydrates assuming a first order conversion, and 100 °C is the reference temperature for a significant depolymerization of the hemicellulose (Alonso-Riaño et al., 2023).

To quantify the energy consumption for furfural production, the kWh per gram of produced furfural were calculated using Eq. 4.

$$\frac{\text{kWh}}{\text{g furfural}} = \frac{\text{Average power (kW)} \cdot \text{treatment time (h)}}{\text{g furfural}} \quad (4)$$

where t is the total treatment time, including the heating and the isothermal periods. Average power in kW was calculated from the provided power from the equipment.

2.4. Analytical methods

2.4.1. High-performance liquid chromatography (HPLC) analysis

Sugar monomers and furfural were quantified by HPLC using 0.005 M sulphuric acid as mobile phase and an Aminex-HPX-87H column (40 °C) coupled to a refractive index detector (RID) (40 °C) and a variable wavelength detector (VWD). Previous calibrations were performed with pure standards.

2.4.2. pH measurements

pH values were measured in treated and untreated samples using a GLP 21 pH meter (Crison Instruments S.A.).

2.4.3. Structural composition determination

The structural compounds present in the untreated and microwave-treated corn stover and in the generated hydrolysates were determined according to the National Renewable Energy Laboratory (NREL) protocols (A. Sluiter et al., 2008b; A. Sluiter, et al., 2008a). Briefly, biomass was subjected to a double hydrolysis, first with sulfuric acid and then in autoclave at 121 °C. From the resulting liquid, structural carbohydrates were determined by HPLC and soluble lignin by absorbance at 240 nm. Acid insoluble lignin and ash content were determined from the hydrolyzed solid. Oligomer determination in the MW hydrolysates was performed by autoclave hydrolysis with sulfuric acid and HPLC quantification. Quantification of oligomers in the MW hydrolysate were determined using Equation 5.

$$\text{Sugar oligomer}_{(MW)} (\text{g/L}) = \frac{\text{Sugar monomer}_{(total)} - \text{Sugar monomer}_{(MW)} (\text{g/L})}{\text{Eq. 5}}$$

where (MW) corresponds to the sugar oligomer or monomer content in the MW hydrolysate and (total) corresponds to the sugar monomer content after H₂SO₄ and autoclave hydrolysis.

3. Results

3.1. Structural composition of xylan and corn stover

Table 1 shows the structural composition of raw xylan and corn

Table 1
Structural composition of xylan and corn stover in a dry basis.

| Composition (%) | | Xylan | Corn stover |
|-----------------|-------------|------------|-------------|
| Hemicellulose | Extractives | n.d. | 8.7 ± 0.6 |
| | Xylans | 84.5 ± 0.1 | 25 ± 3 |
| | Arabinans | 2.3 ± 0.1 | 4.1 ± 0.5 |
| | Acetyl | 3.2 ± 0.1 | 4.2 ± 0.2 |
| Cellulose | Glucans | 13.2 ± 0.1 | 41.4 ± 4 |
| Lignin | Soluble | n.d. | 1.7 ± 0.5 |
| | Insoluble | n.d. | 18 ± 3 |
| | Ash | n.d. | 2.7 ± 0.4 |
| | Protein | n.d. | 3.2 ± 0.2 |

n.d.: not determined

stover in a dry basis. As previously mentioned, xylans (xylose residues linked by β-1-4 glycosidic bonds) are the main fraction of xylan from corn core, accounting for 84.5 ± 0.1 %. The other pentose, arabinose, is present in a much lower extent (2.3 ± 0.1 %). Acetic acid is an important structural component in substrates containing hemicellulose, and was also included in xylan and corn stover structural composition.

Regarding corn stover, hemicellulose formed by C₅ sugars comprises approximately 29 %, while cellulose content is closer to 39 %. Lignin also represents a significant part of the biomass, mainly the insoluble one (18 ± 3 %). These differences in the composition of the raw materials will be later evaluated towards furfural production, but in a general way, the following order regarding pentoses content can be established as: Xylose (100 %) > xylan (86.8 %) > corn stover (29.5 %).

3.2. Effect of heating power and catalyst presence on furfural production from xylose

The effect of MW heating power on 73 mM xylose solutions was studied at 200, 400, 600, 800 and 1500 W during 25 minutes at 180 °C. Furfural yield was evaluated under these conditions in the presence and absence of Lewis acid catalyst CrCl₃ (2 % w/w xylose), and plotted in Fig. 1. Regarding the effect of the catalyst, it can be clearly observed how its addition to the pentose solution significantly increased furfural yield, which presented values around 8 % when no catalyst was present, and increased to around 30 % for the samples with CrCl₃. This difference can be also observed in the pH values of the samples, which inversely correlated with furfural yield (Fig. 1). The highest furfural yield of 30 % corresponded to pH value of 2.30, and the lowest pH value reached in non-catalyst experiments was 3.22. This observation was also made by Yang et al. (2017), who after testing different catalysts for furfural production from xylan, obtained the highest furfural yields in the solutions with the lowest pH. They explained this effect due to the Lewis acidity added by the catalyst (Yang et al., 2017), necessary to obtain higher furfural yields.

Regarding MW power, it could seem that higher power values correspond to higher furfural production (up to 800 W), but it was then determined that this effect was due to the differences in the heating period depending on the applied power. In the 200 and 400 W experiments, treatment temperature of 180 °C was not reached in the established 5 minutes, and therefore, total isothermal treatment time was reduced, being 16.3 and 18.1 min, respectively, instead of 25 min. From 600 W and above, the desired temperature was reached in 5 minutes, and treatment time reached the complete 25 minutes. The temperature profile of the different treatments has been plotted in Fig. 2. Temperature profiles for the 800 and 1500 W treatments was equal to the 600 W one, since, as explained, the set power is the maximum that the MW could apply, and not the actual applied one.

According to the results obtained in this section, the addition of the catalyst was fixed for the following experiments, and regarding the

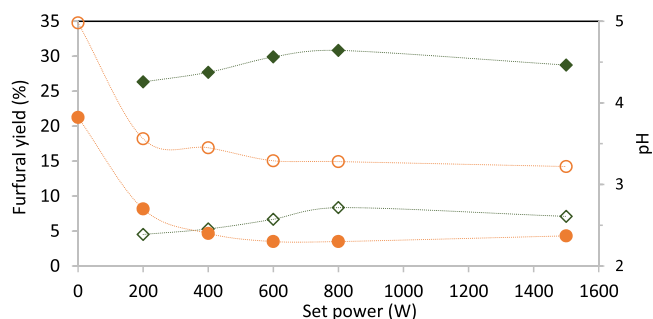


Fig. 1. Furfural yield (◆,◇) and pH values (●,○) of xylose treated using different heating power (W) in the absence (empty) and presence (solid) of CrCl₃ as catalyst. Fixed parameters: 73 mM xylose, 2 % (w/w xylose) CrCl₃, 180 °C and 25 minutes. Lines are a guide to the eye.

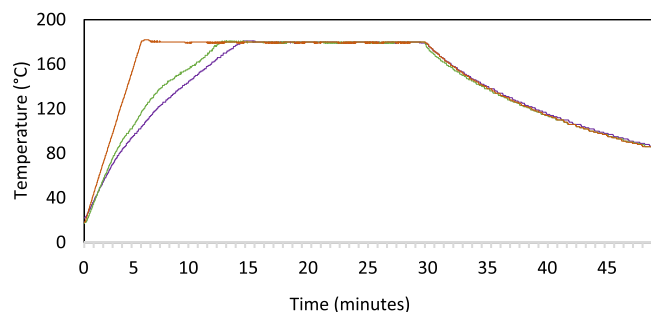


Fig. 2. Temperature profile at 180 °C and 25 min treatment at 200 (---), 400 (---), 600 (---) W.

power heating, based on furfural yield results, it was determined that higher power did not produce higher yield, as long as treatment temperature was reached in the established time. Comparing the samples with catalyst, at 600 and 800 W, a slight increase in yield was observed at the highest power value, but it was lower than 1 %, and therefore, it was considered that the increase in energy consumption due to higher power needs was not worth the yield difference. Higher power than 800 W did not improve furfural production. Therefore, 600 W was established as the treatment power for 180 °C treatments.

3.3. Furfural production from different sugar monomers

Prior to continue testing the effect of other parameters on xylose, a series of experiments were performed on the other sugars present in corn stover (Table 1); arabinose, glucose, and also a mixture of the pentoses, xylose and arabinose. Sugar solutions were treated at 180 °C from 5 to 40 minutes, and furfural yield was evaluated (Fig. 3).

A clear difference can be observed between the pentoses (xylose and arabinose) and the hexose (glucose) regarding furfural production. Treatment of glucose up to 40 minutes at 180 °C did not produce higher furfural yields than 1 %. Under the applied treatment conditions of high temperature and acid environment, glucose conversion route is mainly towards HMF (5-Hydroxymethylfurfural) (Fan et al., 2022). Therefore, the production of furfural under these treatment conditions will be focused on furfural generation from the pentoses present in the biomass. Fig. 3 shows how arabinose and xylose have very similar furfural production trends, showing similar values under the different treatment times. As it was determined in the structural characterization of corn stover (Table 1), arabinose is the other present pentose together with xylose, so their similar behaviour towards furfural production is key to understand how both sugars will perform when corn stover is treated. To better understand if a different effect would be observed when both

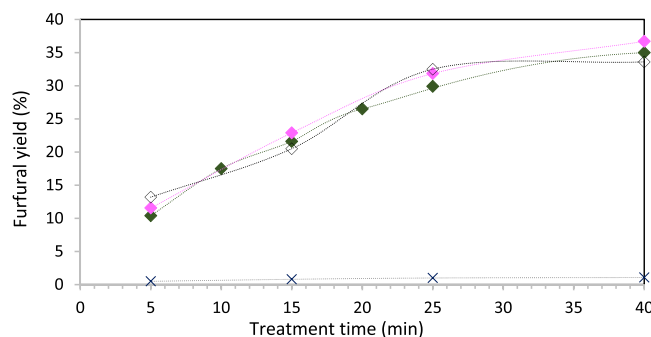


Fig. 3. Furfural yield after treatment of xylose (◆), arabinose (◆), xylose + arabinose (◊) and glucose (X) at different times. Fixed parameters: 11 g/L monomer in individual sugar treatments, and 14.4 g/L xylose and 2.4 g/L arabinose in the pentoses mixture, 2 % (w/w pentose) CrCl_3 , 180 °C and 600 W. Lines are included as a guide to the eye.

monomers are treated together, a mixture of xylose and arabinose was prepared in the same proportion as present in a corn stover solution, as if hemicellulose fraction was totally hydrolysed. Fig. 3 shows that a very similar trend for furfural production was obtained as when both sugars were separately treated, reaching a maximum furfural yield of 32.5 % after 25 minutes of treatment (29.9 and 31.8 % for xylose and arabinose, respectively). Some authors have reported worse efficiency of arabinose to produce furfural compared to xylose. For example, Castro et al. (2023) treated separately xylose and arabinose in a MW treatment for 10 minutes at 160 °C in a biphasic system containing an organic solvent and catalyst. They obtained a furfural yield of 77.0 % from xylose, but only a 40.5 % from arabinose (Castro et al., 2023). In a different study, they attributed this difference to a higher activation energy and structural stability of arabinose, requiring more severe conditions than xylose to dehydrate to furfural (Le Guenic et al., 2016). However, this difference was not observed in the present study, and it was considered that both separated and combined, main pentoses reached same furfural yield values, so it can be concluded that the applied treatment conditions are sufficient to equally convert both pentoses. Therefore, following testing was only performed with xylose solutions, as the main pentose present in the selected biomass.

3.4. Effect of temperature and treatment time over furfural production from xylose and its relation to energy consumption

Xylose solutions were treated at 150, 180 and 200 °C during different times from 5 to 90 min, depending on treatment temperature. As heating power showed not to be a parameter significantly affecting furfural yield, 150 and 180 °C treatments were treated at 600 W, and 200 °C at 1000 W, to assure treatment temperature was reached in 5 min.

Fig. 4a shows the furfural yield after the different treatments. At the lowest temperature, 150 °C, it can be seen how by increasing treatment time, furfural yield also increased, and reached a value of 19 % after an isothermal MW treatment of 90 minutes. Only at this temperature a yield increase was observed when increasing treatment time over 40 min. However, the required time is too long for the obtained furfural yield, which could be reached at 180 °C or 200 °C in 10 or less than 5 min, respectively (Fig. 4a).

Fig. 4a shows how the furfural production trend was the same at 180 and 200 °C, but furfural yield was around a 10–15 % higher at all treatment times at 200 °C. Best furfural yield was found after 40 min of treatment, being 35 % at 180 °C, and 45 % at 200 °C. Increasing treatment time up to 90 minutes did not improve xylose conversion to furfural at 180 or 200 °C. Weingarten et al. (2010) also studied the effect of MW treatment temperature on furfural yield in xylose dissolved in water and HCl as catalyst. As observed in the present study, the increase in temperature produced an increase in furfural yield. They observed a maximum yield of 30 % after 30 minutes at 170 °C (Weingarten et al., 2010), which corresponds to the yield observed in the present study after the same time at 180 °C. At lower temperatures, Wang et al. (2012) obtained a 15.2 % yield when treating xylose in water/THF (1:3) and $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ at 140 °C for 45 minutes (Wang et al., 2012). In our similar tested conditions, furfural yield was 9 %. When comparing the use of CrCl_3 as catalyst, Le Guenic et al. (2015) used it in a biphasic mixture of cyclopentyl methyl ether (CPME) and water (3:1) at 170 °C during 20 min. They obtained a 42 % furfural yield, which is higher than the 26.5 % obtained in the present work at 180 °C and the same time. This difference can be explained by the use of the organic solvent combined with water, which has shown to generally produce higher furfural yields independently of the heating method (Padilla-Rascón et al., 2020; Xiouras et al., 2016). However, it is also important to mention that in most of these studies, xylose concentration usually ranges from 1 to 5 mM, and total reaction volume does not exceed 5 mL in MW treatments, making comparisons difficult since scaling up could not provide the same yield values.

Furfural yield was plotted as a function of the severity factor ($\log R_0$)

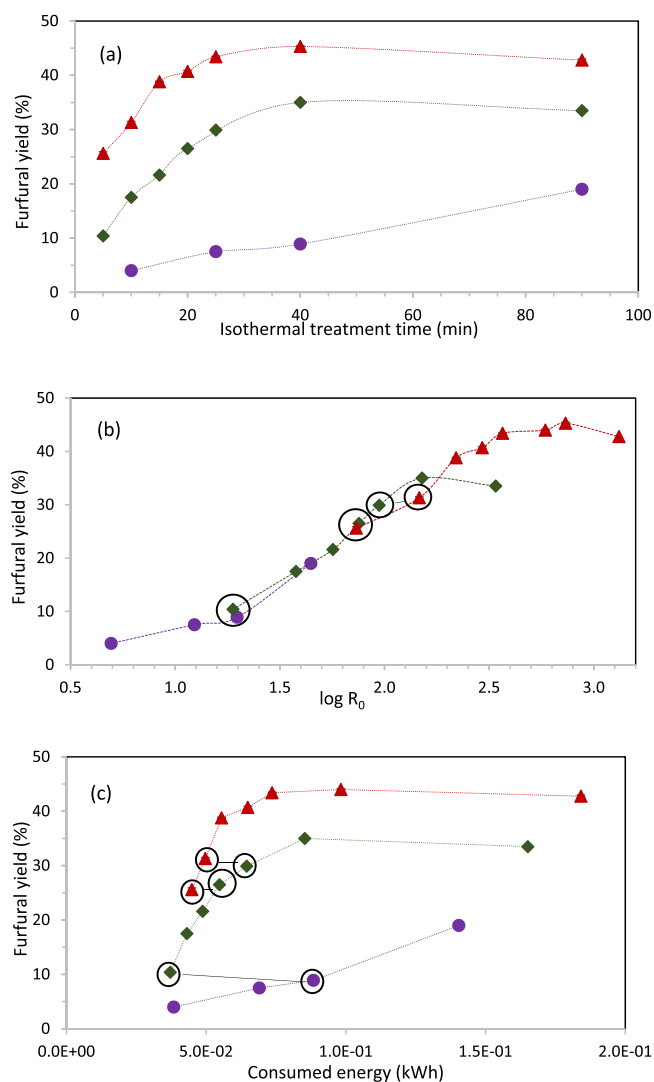


Fig. 4. Furfural yield after treatment of xylose at (●) 150 °C, (◆) 180 °C, and (▲) 200 °C related to (a) treatment time (min), (b) $\log R_0$, and (c) MW energy consumption (kWh). Connected bubbles correspond to compared pair of treatments. Fixed parameters: 73 mM xylose, 2% (w/w xylose) CrCl_3 , 600 W (150 and 180 °C) and 1000 W (200 °C). Lines are a guide to the eye.

in the isothermal period in Fig. 4b. This value makes possible to unify the effect of temperature and treatment time in one parameter and compare it regarding furfural yield. The lowest severity factor corresponded to the 10 minutes treatment at 150 °C, being $\log R_0 = 0.69$, and the highest one was the 90 minutes treatment at 200 °C, with a $\log R_0$ value of 3.12 (Fig. 4b). However, higher severity factors do not always correspond to higher yield values, as it can be seen. In the case of 180 and 200 °C treatments, the highest yields were obtained at $\log R_0$ values of 2.18 and 2.87, respectively. By comparing $\log R_0$ values, it is also possible to establish similarities among treatments performed at different temperatures. For example, same or similar severity factors were found for treatments at 150 °C (40 min) and 180 °C (5 min), 180 °C (20 min) and 200 °C (5 min), or 180 °C (25 min) and 200 °C (10 min). All compared pair of treatments showed very similar furfural yield results as well (Fig. 4b).

To better analyze which of the similar treatments would be more profitable, Fig. 4c shows furfural yield of the MW treatments and its energy consumption in kWh. When comparing some pair of treatments with similar furfural yields, it can be seen how the energetic use was always higher in the treatments that were performed at lower temperature, but for a longer period of time. More energy was required to

maintain the temperature during time, than to achieve it. For example, treating xylose for 40 minutes at 150 °C consumed 0.088 kWh, while its paired treatment at 180 °C for 5 minutes used less than half of the energy, being 0.037 kWh. The same effect occurred at the highest temperatures. Focusing in our lab scale results, and according to the furfural yield-energy consumption, best results would correspond to the MW treatment at 200 °C for 25 minutes.

3.5. Comparison of furfural production and selectivity from xylose, xylan and corn stover

The three complexity levels of the main pentose present in the lignocellulosic biomass were compared for furfural production; (1) xylose monomers, (2) xylan from corn core and (3) corn stover. The effect of temperature at 180 and 200 °C was studied for the three substrates at different MW treatment times from 5 to 90 minutes. Furfural yield values of the mentioned experiments was plotted in Fig. 5. When comparing among substrates, it is important to take into account that while in xylose treatments only xylose is considered as furfural precursor, in the case of xylan and corn stover, the second most abundant pentose, arabinose, also plays a role towards furfural production, and was included in all calculations (Eq. 1 and Eq. 2).

Temperature effect can be clearly observed when comparing Fig. 5a (180 °C) and Fig. 5b (200 °C). At 180 °C, furfural production follows a slower but continuously increasing trend when compared to 200 °C. On the contrary, at 200 °C, furfural concentration rapidly increases in short treatment times, and then remains unchanged from 40 min treatments (Fig. 5b), but higher furfural yield was found in the three substrates at this temperature.

At 180 °C (Fig. 5a), xylose and xylan showed a very similar behaviour, with almost equal furfural yield values. This shows that probably at this temperature, the bonds between xylose residues present in xylan easily break and then follow same furfural production routes as when xylose is treated in its monomer way. A similar observation was done by Xia et al. (2023), when after MW treatments at different temperatures they obtained even higher furfural yields treating bamboo hemicellulose (87.6% xylose) than when treating xylose itself. They attributed this effect to a gradual release of pentose monomers due to a continuous hydrolyzation in the more complex structure, reducing side reactions and increasing furfural yield (Xia et al., 2023). In our case this effect was not so significant since the reaction medium is a single water phase, and their best results were obtained due to the continuous transfer of furfural to the organic phase. This effect was not observed at 200 °C, where best furfural yields were obtained for xylose monomers conversion.

A very different result was observed for corn stover. After 40 minutes of treatment at 180 °C, the furfural yield reached from the treated corn was just 4.5%, what means an 87% lower yield than the obtained after treating xylose and xylan for the same time (35%). This result makes sense since one more step has to take place prior to xylose conversion. In the case of corn stover, the hemicellulose fraction needs to be hydrolyzed and then undergo the breakage of glycosidic bonds to xylose and consecutive dehydration to furfural. When xylose and xylan were treated, no furfural yield improvement was observed from 40 minutes of treatment, while in the corn stover case, an increase in yield from 7% to 15% was observed when increasing treatment time from 60 to 90 minutes, what suggests that probably by increasing the treatment time, the yield could be further improved. When corn stover was treated at 200 °C (Fig. 5b), much higher furfural yield values were observed, reaching a maximum of 28% after 40 minutes. In similar studies, treatment of lignocellulosic biomass has always produced lower furfural yield than treating sugar monomers or xylan. For example, Yang et al. (2012) treated xylose and xylan at 140 °C and corn stover at 160 °C for 45 minutes, obtaining furfural yield values of 75, 64 and 55%, respectively. Corn stover showed a 20% lower furfural yield compared to xylose, even though the treatment was 20 °C higher (Yang et al., 2012). Similar results were found in the present study if we compare xylose and

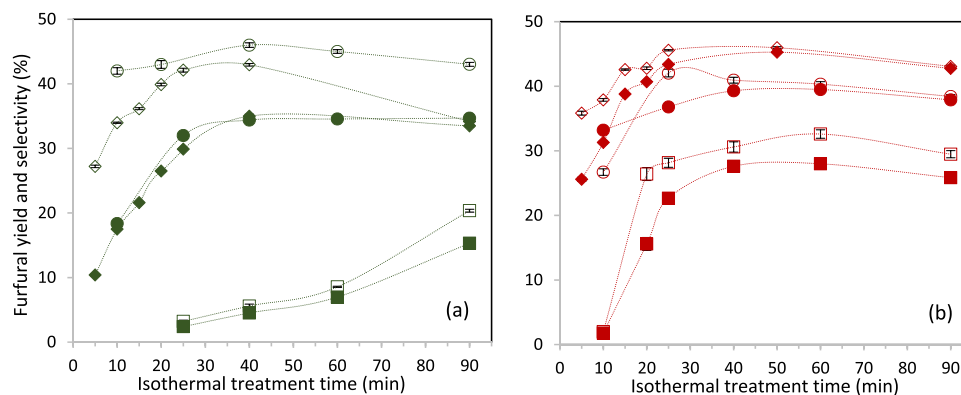


Fig. 5. Furfural yield after treatment of xylose (◆,◇), xylan (●,○) and corn stover (■,□) and furfural selectivity after treatment of xylose (◇,◇), xylan (○,○) and corn stover (□,□) at (a) 180 °C and (b) 200 °C, respectively. Lines are included as a guide to the eye.

xylan treated at 180 °C and corn stover at 200 °C, obtaining around 34 % furfural yield for xylose and xylan, and 27.6 % for corn stover. However, the lower values compared to literature are due to the use of one aqueous phase reaction system instead of organic solvents. This effect was also appreciated by Castro et al. (2023). In that study, they treated xylose at 160 °C during 10 minutes in a NaCl saturated aqueous solution, and in a solution with butyl acetate (3:1 organic phase: water). A clear effect of the organic phase was observed, showing a furfural yield of 36.1 % and 77 % when it was added, being almost the double yield. When they treated corn cob in the biphasic system for 60 minutes they obtained 56 % furfural yield, showing also lower yield than in the treatment of pure xylose (Castro et al., 2023).

Additionally, it is interesting to evaluate the furfural selectivity of the different treatments, which directly relates the production of furfural from the available pentoses in the reaction medium. Furfural selectivity values follow similar trends as furfural production (Fig. 5). As a general observation, the higher the temperature, the higher the furfural selectivity, since also an increase in furfural production and pentoses conversion was observed. Among substrates, corn stover showed the lowest selectivity, reaching values of 20.4 and 29.5 % after 90 min at 180 and 200 °C, respectively. Xylose and xylan showed similar highest selectivity values at both temperatures, being those 34 and 46 % for xylose at 180 and 200 °C, respectively, and 46 and 42 % at 180 and 200 °C, respectively, for xylan. At both temperatures, especially at 200 °C (Fig. 5b), it can be seen how furfural selectivity decreased at the longest treatment times, when the concentration of pentoses and their intermediates decreased or remained constant (Fig. 6b), and there was no increase in

furfural generation. This effect was observed for the 3 substrates at 200 °C, and for xylose and xylan at 180 °C at the longest treatments.

3.6. Furfural yield comparison with different MW treatment approaches in literature

As it has been mentioned, the use of xylose, xylan and corn stover for furfural production has been a study field of great interest in the last decades, and the different approaches used related to reaction media, treatment conditions, catalyst, or heating mode vary in a great extent the obtained results. Due to this high diversity in the field, it is difficult to establish similarities and differences among studies. However, in order to highlight the innovative aspect of the one-pot water MW treatments performed in the current study, a selection and comparison of studies where MW technology is used for furfural production from different substrates has been made (Table 2). The current study has been included at the bottom line of the table for comparison.

As it can be seen, the seven selected studies used xylose or a biomass hydrolysate as substrate for furfural production. Gupta et al. (2017) showed the most similar results to the current study ones. Their maximum furfural yield when treating xylose was also 45 %, and they also used a one-pot water MW treatment, although using Nb₂O₅ as catalyst. The main advantage compared to this work is the lower temperature used, 120 °C, but the required time to achieve the mentioned yield was of 3 hours, which is 4.5 times longer than the present work. Their catalyst requirements were also much higher (133.3 % wt./wt. xylose) (Gupta et al., 2017). Higher temperatures would be needed for

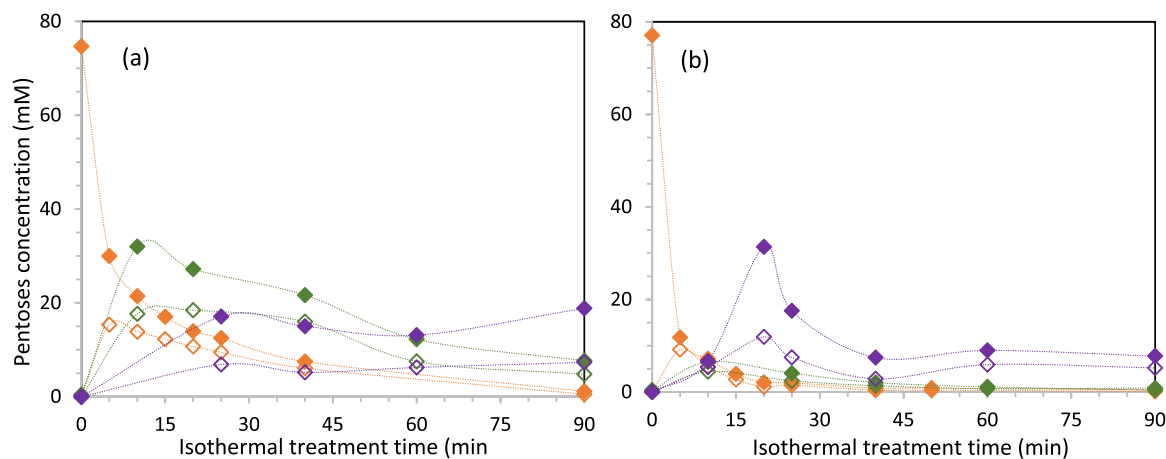


Fig. 6. Concentration (mM) of pentoses (◆,◇,◇) and intermediates (◇,◇,◇) after treatments of xylose (---), xylan (---) and corn stover (---) at (a) 180 °C and (b) 200 °C.

Gupta et al. (2017) application if corn stover or any other lignocellulosic biomass is used as the substrate, since 120 °C is not enough for hemicellulose breakage. Kim et al. (2012) obtained up to 67 % furfural yield when using maleic acid 0.25 M in water, but in this case, a two-pot approach was used, with a hydrolysis of the corn stover prior to the hydrolysate MW treatment (Kim et al., 2012). A similar study was performed by Sánchez et al. (2013) treating corn cobs with a HCl dilution, and then MW treating the hydrolysis liquor, obtaining 37 % furfural yield (Sánchez et al., 2013). Weingarten et al. (2012) showed the improvement in furfural yield that the addition of an organic solvent produces in a one-pot reaction. They obtained a 30 % furfural yield from xylose when only water and 0.1 M HCl was used, and it increased to 50 % when MIBK was used with water in a 1:1 ratio (Weingarten et al., 2010). However, their results did not show a great difference with the ones obtained in literature or this work when using only water.

Two studies where a one-pot MW treatment was directly applied to biomass were also included. In first place, Li et al. (2018) treated corn cobs with GVL as the reaction medium, using carbon-based solid acids as catalysts, obtaining 43 % furfural yield (Li et al., 2018), higher than the current 28 % obtained in this work from corn stover (Table 2). However, they required a catalyst concentration of 256 % w/w xylose, and 4 hours at 190 °C, what can be a too long treatment time when using MW. A shorter one-pot treatment was required by Castro et al. (2023) to achieve a 56 % furfural yield when treating corn cob, being 60 minutes at 160 °C. However, they needed the addition of butyl acetate and NaCl to the reaction medium, and CX4SO₃H as catalyst to obtain this result (Castro et al., 2023), making a direct comparison difficult due to the medium differences.

Yang et al. (2012) performed a similar study to the current one, treating the three complexity levels substrates, xylose, xylan and corn stover, and using the Lewis acid AlCl₃·6 H₂O as catalyst. Their furfural yield results showed higher values than the obtained in this work, being 75, 64 and 55 %, respectively for each substrate, and 45, 37 and 28 % where the ones achieved in this work. The higher complexity of the treated substrate, the higher the difference between the two studies. This is because Yang et al. (2012) used water: THF 1:3 as the reaction medium, once again showing a clear difference in the results due to the addition of an organic phase (Yang et al., 2012). An interesting fact to highlight is that in all the compared studies, treated volumes in the MW did not exceed 5 mL, being 10 times lower than the treated volume in the case of xylose and xylan, an 8 times lower than corn stover in the current study treatments. Indeed, treatment volume affects to the results, and it would be interesting to observe studies with higher volume treatments.

As a general conclusion, although many interesting approaches had been previously tested, no studies where one-pot MW treatment was performed using corn stover in the absence of an organic solvent, as it was performed in the current study. This fact highlights the need of a shorter, and greener approach towards furfural production, as well as the need of treating higher volumes to get closer to a more real approach of scaled-up MW systems.

Different letters in a study indicate two or more different reaction media or substrates.

Different numbers in a study indicate two different set of conditions, each of them corresponding to a stage in a two-pot treatment

3.7. Comparison of production routes and degradation products from xylose, xylan and corn stover MW treatment

When comparing furfural yield from the three treated pentose-substrates, it is clear that the complexity of the matrix structure is a key parameter. To better understand the furfural production routes, Fig. 6 shows the concentration (mM) of the compounds determined in the furfural production system, as well as furfural selectivity of the treatments at 180 and 200 °C for xylose, xylan and corn stover. In furfural production, total pentose concentration corresponded to xylose

and arabinose, and the reaction intermediates were their isomers, xylulose and ribulose, respectively.

Regarding pentoses concentration, different profiles can be observed for the three C₅ starting materials. Xylose is fully available in the xylose solution (73 mM) from the beginning of the furfural production process, and a decrease in its concentration can be observed with increasing time, reaching its lowest value of 1.2 and 0.5 mM after the 90 min treatment at 180 and 200 °C, respectively. It can be seen how xylose consumption was faster at the highest temperature (Fig. 6b), directly related to the faster furfural production (Fig. 5b). Regarding xylan and corn stover, pentose concentration along time, varies differently. As mentioned before, pentoses are mainly linked forming the hemicellulose structure, so they first need to be released in the form of monomers, to then follow their dehydration towards furfural. At both temperatures (Fig. 6a,b), it can be seen a maximum on pentose concentration after 10 min for xylan, and 20–25 min for corn stover, and then a decrease and maintenance of the concentration. The maximum was more pronounced at 200 °C, and corresponds to the breakage of hemicellulose into its pentose monomers. More time and temperature are required to break hemicellulose structure in corn stover than in xylan, due to its higher complexity and configuration with cellulose and lignin fractions. As long as pentoses are being released, furfural starts to be produced, corresponding the highest furfural concentration to the treatment time following the one where the highest pentose concentration was observed. For example, when treating corn at 200 °C, there was a pentose concentration of 6.7 mM after the 10 min treatment, and 31.4 mM after the 20 min one, being the highest one among all treatment times at these conditions. Regarding furfural concentration, a noticeable increase was observed after 20 min, and a much higher value was obtained in the 40 min treatment, reaching, 29.2 mM (27.6 % yield). At longer treatments, pentose and furfural concentration remained more or less unchanged, showing not further hemicellulose breakage or furfural production. Similar relation of pentose liberation and furfural production were observed for xylan.

Intermediates concentration varied among substrates as well. In the xylose treatments, independently of temperature, a maximum was observed in the 5 min treatment, corresponding to the great decrease in pentose concentration. Xylulose concentration at this time was 32 mM at 180 °C and 9 mM at 200 °C. After this point, a gradual decrease following the same trend as pentoses was observed, corresponding to a furfural production increase. Yang et al. (2012) studied the evolution of xylose, xylulose and furfural during MW treatments. They observed that in milder treatments, xylulose reached maximum values, while its concentration was significantly decreased when highest furfural yield values were obtained at higher temperatures, confirming xylulose as an intermediate in the production of furfural (Yang et al., 2012). The same effect was observed in the present study, with an inverse correlation between intermediates and furfural concentration. Lower intermediates concentration was obtained from xylose when comparing among substrates, due to the lower initial pentose concentration (Fig. 6).

The consumption of pentoses and intermediates and no further “net” furfural formation can be directly related to the occurrence of side reactions, decreasing furfural selectivity. Sánchez et al. (2013) reported higher concentration of degradation products when increasing MW treatment temperature from 160 to 200 °C (Sánchez et al., 2013). Weingarten et al. (2010), measured the degradation rate of furfural in a monophasic aqueous system from 130 to 170 °C, and determined that to detect a significant degradation of furfural, at least 8 hours were required, being this reaction much lower than the xylose dehydration one (Weingarten et al., 2010). Therefore, the furfural selectivity probably decreases in the longest treatments due to the promotion of side reactions, rather than furfural degradation.

The main side products found in the hydrolysates of the three substrates were formic and acetic acids. Their concentration profiles at 180 and 200 °C have been plotted in Fig. 7. As it was mentioned before, acetic acid is a structural component in hemicelluloses, and it shows a significant percentage in the composition of xylan and corn stover, 3.2 ±

Table 2
Furfural yield comparison between furfural production studies using MW technology in literature.

| Study | Reaction medium | Substrate/ biomass | Catalyst | T (°C) | Time (min) | MW reaction volume (mL) | Maximun furfural yield (%) | One or two-pot |
|--------------------------|---------------------------------|--|--|---|----------------------------|----------------------------|----------------------------|----------------|
| Weingarten et al. (2010) | (a) Water (b) Water:MIBK 1:1 | Xylose (10 % wt.) | 0.1 M HCl | 160 °C | 30 | n.s. | (a) 30 (b) 50 | One-pot |
| Gupta et al. (2017) | Water | Xylose (1 mmol) | Nb ₂ O ₅ (133.3 % wt. /wt. xylose) | 120 °C | 180 | 5 | 45 | One-pot |
| Kim et al. (2012) | Water | Xylose from corn stover | Maleic acid 0.25 M | (1) 160 °C (2) 200 °C | (1) 19 °C(2) 28 °C | n.s. | 67 | Two-pot |
| Sánchez et al. (2013) | Water | Corn cobs autohydrolysis liquor (1:8) | HCl | (1) 180 °C(2) 200 | (1) 30(2) 5 | 3 | 37 | Two-pot |
| Li et al. (2018) | Gamma valerolactone (GVL) | Corn stover (2.2 % wt.) | Carbon-based solid acids (256 % wt./wt. xylose) | 190 °C | 240 | 4.5 | 43 | One-pot |
| Castro et al. (2023) | Water:butyl acetate 1:3 +NaCl | Corn cob (1.25 % wt.) | CX4SO ₃ H (12.5 % wt) | 160 °C | 60 | 4 | 56 | One-pot |
| Yang et al. (2012) | Water:THF 1:3 + NaCl | (a) Xylose (b) Xylan (c) Corn stover | AlCl ₃ •6 H ₂ O | (a) 140 ° C (b) 140 ° C (c) 160 ° C | (a) 30 (b) 60 (c) 60 | 4 | (a) 75 (b) 64 (c) 55 | One-pot |
| Current study | Water | (a) Xylose (b) Xylan (c) Corn stover | CrCl ₃ •6 H ₂ O (2 % wt./wt. xylose) | 200 °C | (a) 40 (b) 40 (c) 40 | (d) 40 (e) 40 (f) 50 | (a) 45 (b) 37 (c) 28 | One-pot |

n.s.: non-specified.

0.1, and 4.2 ± 0.2 , respectively (Table 1). In the treated preparations, if all acetic acid contained in the substrate was released into the hydrolysate, acetic acid concentration would correspond to 7 mM for xylan, and 38 mM for corn stover. These values should be taken into account when analyzing the acetic acid data shown in Fig. 7.

It can be seen how all detected reaction byproducts increased with higher temperature and treatment time. As hemicellulose is hydrolyzed, its structural components are released into the hydrolysate, as it is the case of acetic acid. Its concentration is directly related to the severity of the treatments. By increasing time and temperature, there is a higher breakage of hemicellulose in xylan and corn stover, and therefore an increase of acetic acid in the hydrolysates. However, taking into account the structural content of acetic acid in xylan and corn stover, the total release of this component could be only considered in the treatments where acetic acid concentration is higher than the initial content, showing also a side reaction to acetic acid formation. All corn stover treatments at 180 °C showed lower acetic acid concentration than 38 mM, showing that the applied treatment times were not enough to completely release it from the hemicellulose structure. On the other hand, at 200 °C, 40 min and longer treatments showed a generation of acetic acid as side product, with an average production of 3–4 mM over the structural 38 mM. Acetic acid release from xylan was faster, since its hemicellulose structure is not linked to other fractions as cellulose or lignin as in corn stover, facilitating its hydrolysis. After 10 min treatments, its concentration in the hydrolysate was higher than the initial one (7 mM). Average acetic acid production was also 3–4 mM, with slightly higher values at 200 °C. When treating xylose, all produced acetic acid comes from the pentose side reaction, and not from the substrate itself. As in xylan, slightly higher values were found at 200 °C, especially at shorter treatments. Highest acetic acid produced concentration in xylose treatments were around 3 mM, in the range of the other substrates, taking into account its lower initial pentose concentration.

Formic acid showed to be another abundant side reaction product. Sánchez et al. (2013) also found those acids after the microwave treatment of a corn cob hydrolysate. They explained that formic acid was generated from glucose and xylose oxidation (Sánchez et al., 2013). In xylose and xylan hydrolysates, formic acid concentration increased with longer treatment times up to 20–25 min. Formic generation from xylose was the lowest, reaching 15 mM at 200 °C, and 12 mM at 180 °C (Fig. 7). Xylan hydrolysates showed higher formic concentration, as aside from pentoses, its structure contains around 13 % glucose polymers (Table 1), which also contributes to the production of formic acid. Corn stover showed a different trend. Formic acid continuously increased along longer treatment times, and showed higher concentrations at 200 °C. As cellulose is a significant component of this substrate (39 %), apart from hemicellulose, the concentration of possible formic acid precursors is higher than in xylose or xylan treatments. However, as these monomers

need severe conditions to be released, formic acid from corn stover, does not reach higher concentration than xylose or xylan treatments until a certain time or temperature is applied, as it happened with acetic acid formation. 5-(Hydroxymethyl)furfural (HMF) is the main dehydration product from glucose, but its concentration was not plotted since almost no formation was observed at the tested conditions.

Fig. 8 shows the composition of the residual solid generated after treatment of corn stover at different treatment times. Regarding the carbohydrate-containing fractions, cellulose (glucans) and hemicellulose (xylans and arabinans), it can be seen how at both temperatures, up to 25 min treatments, they follow opposite trends. Hemicellulose was rapidly hydrolyzed, from a 29 % of the initial corn stover to 10 % in the residual solid after 25 min, corresponding to the increase of pentoses an isomers concentration in the liquid phase previously observed at this time (Fig. 6). Meanwhile, the percentage of cellulose fraction increased in the same time from 39 % in the initial corn stover to 73 % in the residual solid. From the 25 min treatment, cellulose fraction slightly decreased, corresponding to the hydrolysis of cellulose at longer times, which is also the same time as when more side products were produced, as well as when the highest liberation of acetic acid was observed (Fig. 7).

Both the cellulose and hemicellulose hydrolysis took place faster and to a greater extent at 200 °C, confirming how temperature affects the breakage of those fractions from the biomass, previously reflected in intermediates and furfural production (Figs. 5 and 6). Fig. 8c shows the concentration of xylose and arabinose (pentoses) and glucose present in the MW hydrolyzed liquid, in their oligomer form. This means, fractions of carbohydrates that have been released from the hemicellulose and cellulose structures, but have not been totally hydrolyzed to their monomer form, not being available for furfural production yet. Pentoses oligomers concentration along treatment time follows a very similar trend as the observed for pentoses monomers (Fig. 6), showing much faster release at 200 °C. At this temperature and 90 min treatment, all released pentoses have been hydrolyzed to their monomer form (Fig. 8c). Glucose oligomers showed less variation, with a slightly higher concentration after the 10 min treatment, but then a constant concentration, showing not further reaction, which corresponds to the stable concentration of glucose-derivate side components at these times (Fig. 7). Ashes content remained constant in the solid fraction along treatment time (Fig. 8b), and lignin fraction showed highest values in the final solid after treatments at 200 °C, due to higher hydrolysis of the carbohydrate fraction, mainly hemicellulose.

3.8. Energetic and pollutant study of MW treatments

Applied power (W) was registered automatically per minute of treatment. Average applied power was calculated according to each

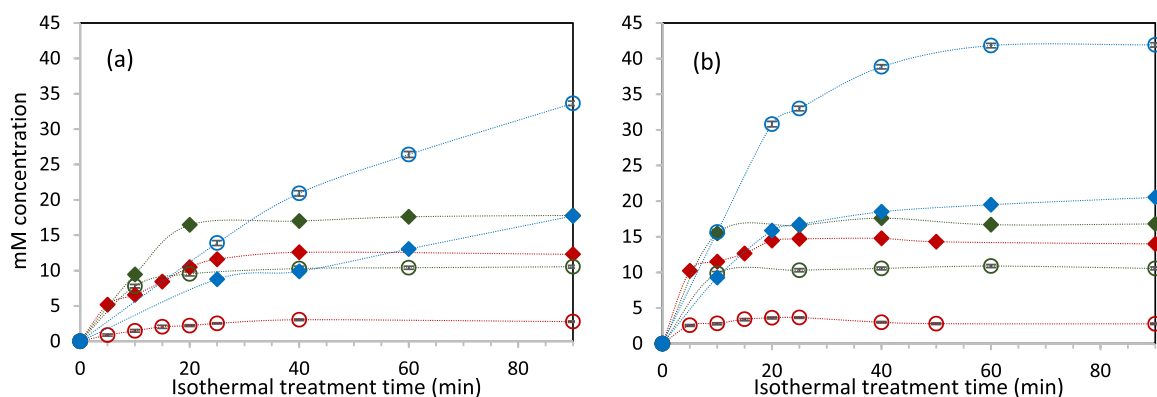


Fig. 7. Concentration (mM) of formic acid (◆, ◆, ◆) and acetic acid (○, ○, ○) after treatments of xylose (---), xylan (---) and corn stover (---) at 180 °C (a) and 200 °C (b).

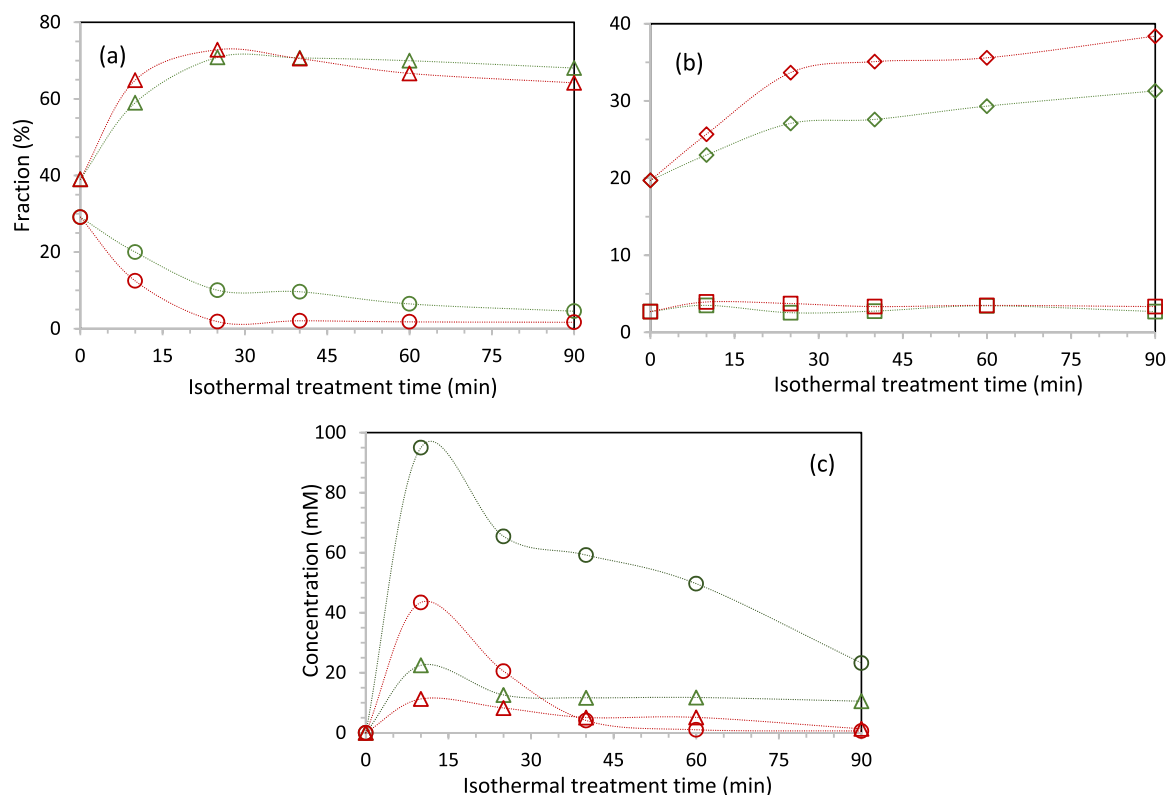


Fig. 8. Solid fraction (%) of (a) cellulose (C₆-biopolymers, glucans) (Δ , Δ), hemicellulose (C₅-biopolymers, xylans and arabinans) (\circ , \circ), (b) lignin (\diamond , \diamond) and ashes (\square , \square) after treatments of and corn stover at 180 °C (---) and 200 °C (---). Values at initial time (0 min) correspond to the initial corn stover composition (Table 1). (c) mM concentration of glucose oligomers (Δ , Δ) and pentoses oligomers (xylose and arabinose) (\circ , \circ) in the corn stover MW hydrolysates. Lines are a guide to the eye.

treatment time and temperature for the three different substrates (Fig. 9a, b). Both at 180 and 200 °C, the average applied power was higher when the complexity of the substrate matrix also increased. Heat transfer was diffcult by the corn stover solids suspension in the liquid.

As expected, the average applied power was higher at 200 °C. However, the longer the treatment, the smaller this difference is between the two temperatures. Average power decreased with increasing treatment time, since, as it was observed before (Fig. 4), more energy was required to achieve a certain temperature than to maintain it, and in short treatments, heating period constitutes a more significant part of the treatment than in the longest ones.

Fig. 9(c, d) shows the calculated energy (kWh) per g of furfural produced from xylose, xylan and corn stover at 180 and 200 °C. Energy consumption was the same for furfural production from xylose and xylan at both temperatures, which correlates with the similar furfural yield obtained for those substrates. However, when treating corn stover, the required energy per gram of produced furfural was much higher, especially at 180 °C (Fig. 9c). These results fit with the previously observed ones, where the lowest furfural was obtained from corn stover at 180 °C (Fig. 5). At 200 °C, the value of kWh/ g furfural for corn stover was similar to the xylose and xylan one, except for the shortest treatment time, where the lowest furfural yield had been obtained. According to the Spanish Consumers Organization (OCU), average kWh price in 2023 was 0.148 € (OCU, 2024). As MW treatments are proposed as a green alternative, the equivalent produced CO₂ was calculated per gram of produced furfural. According to the European Union Energy Agency (EA), in 2022, 1 kWh was equivalent to the production of 251 g of CO₂ (European Environment Agency, 2023). The price and amount of equivalent carbon dioxide are tabulated in Table 3 for corn stover treatments.

As it can be seen, the price per produced furfural varies in a great extent among treatment conditions. The most profitable treatments correspond to the 200 °C ones except for the shortest and longest tested times. Equivalent produced carbon dioxide was also much lower at this temperature, showing the lowest value after the 25 min treatment, nearly ten times lower to the same experiment at 180 °C. Again, the 25 min treatment at 200 °C showed to be the best MW treatment conditions for furfural production from corn stover using only water as the reaction medium, with a furfural yield of 23 %, an energy consumption of 0.8 kWh, a price of 0.11 €, and a production of 195 g CO₂e per gram of produced furfural. However, these values correspond to a 40 mL treatment, and it has to be taken into account that scaling up will significantly increase those values.

3.9. Use of MW treatments as a pre-treatment for cellulose enriched biomass

Through the continuous comparison that has been made along the manuscript, it has been possible to conclude that, although the use of a single water phase in MW treatments is a much greener approach than the use of biphasic systems containing organic solvents, the furfural yields obtained are far from reaching optimized values in literature, where furfural yield values over 50 % have been produced at lower temperature and shorter treatments when using organic solvents. Therefore, with the aim of continuing to study a sustainable approach for the valorization of residues, as corn stover in this case, the authors would like to propose a different approach for MW treatments. As MW treatments have shown to be low energy and time consuming, easy to use and just need water with a small amount of a Lewis acid catalyst to produce furfural, the authors propose these treatments as a pre-

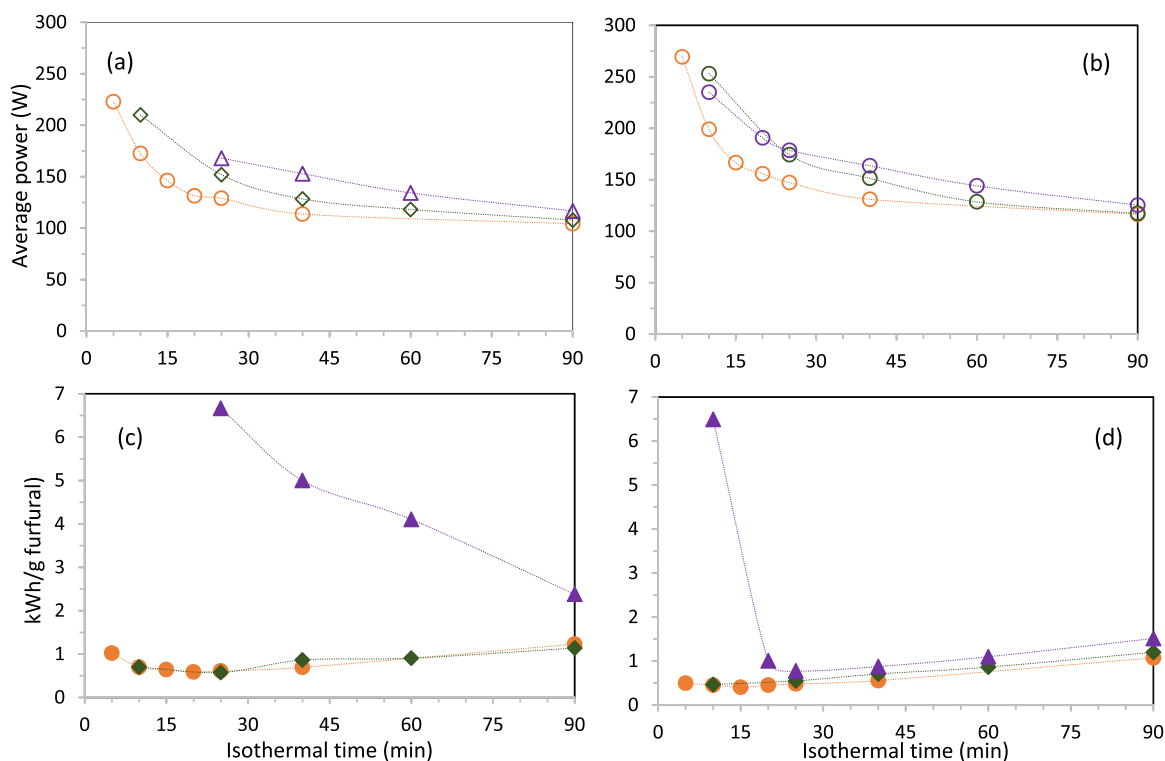


Fig. 9. (a, b) Average applied power (W) and (c, d) Energy consumption per g of produced furfural (kWh/ g furfural) when treating xylose (○, ●), xylan (◇, ◆) and corn stover (△, ▲) at (a, c) 180 °C (max. applied power of 600 W) and (b, d) 200 °C (max. applied power of 1000 W). Lines are a guide to the eye.

treatment to enrich the biomass in cellulose content. In this way, while furfural is produced in a less expensive and greener way than conventional treatments using organic solvents or strong acids, a cellulose-enriched solid is generated. Almost all hemicellulose has been removed from the solid, which still presents a high cellulose content (Fig. 8), which can be used for a subsequent valorization process towards other value-added compounds, such as lactic acid, HMF, or levulinic acid. In the tested conditions, the best corn stover MW treatment for this approach would be 200 °C treatment for 25 minutes, since although there is a slight decrease in furfural yield when compared to 40-minute treatment, 90 % of cellulose is still in the solid, and its energetic cost is significantly lower when compared to the longer one (Fig. 9c), and the cost per g of furfural showed to be lower (Table 3).

4. Conclusions

One-pot microwave treatments using water as a single reaction phase showed to be able to produce significant amounts of furfural when treating xylose solutions at different temperatures and time. Heating

Table 3

Price (€) and equivalent produced CO₂ (g CO₂e) per gram of produced furfural after different treatment of corn stover.

| T (°C) | Isothermal time (min) | kWh/g furfural | €/ g furfural | g CO ₂ e/g furfural |
|--------|-----------------------|----------------|---------------|--------------------------------|
| 180 | 25 | 6.7 | 0.99 | 1673 |
| | 40 | 5.0 | 0.74 | 1255 |
| | 60 | 4.1 | 0.61 | 1030 |
| | 90 | 2.4 | 0.35 | 598 |
| 200 | 10 | 6.5 | 0.96 | 1629 |
| | 20 | 1.0 | 0.15 | 252 |
| | 25 | 0.8 | 0.11 | 195 |
| | 40 | 0.9 | 0.13 | 220 |
| | 60 | 1.1 | 0.16 | 276 |
| | 90 | 1.5 | 0.22 | 380 |

power showed to be a key parameter to reach the desired isothermal temperature during the heating time, although it did not have any direct effect on furfural production. The addition of CrCl₃•6 H₂O as a catalyst was essential to boost furfural production, favored by the action of the Lewis acid and the pH decrease in the reaction media. Higher MW temperatures led to higher furfural yields, although longer treatments did not always have the same effect. The severity factor of all treatments showed similarities among treatments performed at different conditions, and it was possible to directly compare different treatment conditions by their energy cost. It could be concluded that increasing time at a specific temperature was more costly than increasing treatment temperature. When treating more complex structures containing xylose, such as xylan and corn stover, lower furfural yields were obtained than when the monomer was treated alone, due to higher energy requirements for the separation of hemicellulose from the biomass matrix, or its breakage into monomers. Formic acid and acetic acid were the main formed side products. 200 °C showed to be the best treatment temperature for the more complex structures, achieving a nearly total hydrolysis of the hemicellulose fraction, allowing to achieve higher furfural yield. Best treatment time for furfural production from corn stover was 25 minutes, which showed best efficiency by means of consumed energy and price per amount of produced furfural. Due to the lower furfural yield obtained when compared to treatments where organic solvents are used, one-pot MW treatments in water were proposed as a pretreatment where furfural is produced, and corn stover biomass is enriched in cellulose, being possible to further valorize it by the production of value-added products derived from cellulose.

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CRedit authorship contribution statement

M. Teresa Sanz: Writing – review & editing, Supervision, Methodology, Funding acquisition, Data curation, Conceptualization. **Alba E Illera:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sagrario Beltrán:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Alejandro Bermejo-López:** Writing – review & editing, Methodology. **Pedro Barea:** Writing – review & editing, Methodology. **Helena Candela:** Writing – review & editing, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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