

Microwave-Assisted Green Production of Furfural from D-xylose of Sugarcane Bagasse

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D-xylose is a component of sugarcane bagasse that can be used as a renewable resource for the production of a variety of chemicals. By means of catalytic reactions in an aqueous medium, it was determined that D-xylose can efficiently be converted into furfural by the application of microwave as a green synthetic methodology. The highest yields of furfural were obtained at a HCl concentration of 4 mg/mL. When the reaction was performed at 200 °C, an optimum yield of 64% of furfural was observed after 10 min of reaction time, with 95% of the D-xylose being converted.

Keywords: Renewable chemistry; Green chemistry; Green processes

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INTRODUCTION

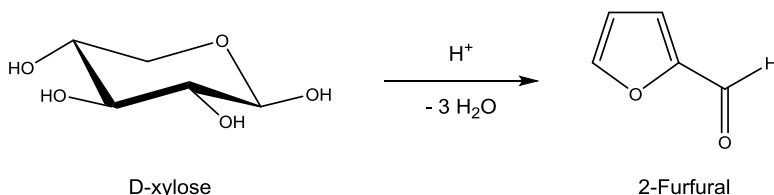
Transitioning from the current dependence on non-renewable raw materials to biomass as an oil substitute has become a strategic challenge in the twenty-first century. Chemicals have the highest potential to add value on a vegetable biomass chain because of the importance of the conventional chemical industry and fine chemical chemistry for different sectors of the economy, highlighting compounds that may be used as building blocks, intermediates of synthesis, and specialties (Vaz Jr. 2014).

2-Furaldehyde, also known as furfural, is a platform or building block molecule and can replace petrochemicals in several applications. Examples of useful molecules derived from furfural are furfuryl alcohol and furoic acid (Gallezot 2012). Furfural is one of the few chemicals produced commercially from lignocellulosic biomass. It is obtained by the acid dehydration (*e.g.*, sulfuric acid) of pentoses (such as xylan) (Luterbacher *et al.* 2014). Because furfural represents a truly sustainable platform-chemical for many green applications, their commercialisation has been stymied by the lack of a stable supply (Dalin Yebo 2015). The use of sugarcane bagasse as a feedstock for furfural production is not established by the industry or biorefineries, but has been described in the literature for the conversion of D-xylose into furfural (vom Stein *et al.* 2011; Hricovíniová 2013).

The use of microwave heating to conduct chemical transformations has increased in recent years (Clark and Deswarte 2008). Microwave energy is attractive in the area of chemistry because it elicits highly efficient energy transfer and selectivity, which reduces reaction time significantly (Loupy 2006; Pistará *et al.* 2014). Furthermore, if feasible, it can be applied in conversion processes for lignocellulosic biorefineries to obtain better yields in a short time.

The objective of this work was to investigate a green and sustainable route for furfural production from D-xylose (Scheme 1) to demonstrate the potential production of

furfural from sugarcane bagasse based on microwave technology and corresponding green chemistry and biorefinery concepts.



Scheme 1. Conversion of D-xylose into 2-furfural

EXPERIMENTAL

Materials

All analytical standards and chemicals were purchased from Sigma-Aldrich (Sao Paulo, Brazil) with a high purity degree. Unless noted otherwise, all the standards and chemicals were commercially available and used without further purification.

Analytical Method

For the analysis of the reaction mixtures in the screening experiments, an analytical HPLC system with RI-detection (Infinity 1260, Agilent, Santa Clara, USA) was installed with a Phenomenex Rezex-RFQ column (100 x 7.8 mm, 8 μ m particle size) using a diluted solution of (0.01 M) H_2SO_4 in water as the eluent (Scarлата and Hyman 2010). An excellent separation of the components D-xylose, 2-furfural, xylitol, and levulinic acid was observed in a reasonably short analysis time.

The analyses of an initial set of reaction mixtures were carried out without the use of an internal standard to avoid potential complications with co-elution of the standard with possible unexpected side products. In several experiments, a black tar was formed, which was a clear indication that side reactions had occurred, leading to incomplete mass-balances. This result clearly demonstrates the need for an internal standard method to accurately determine the conversion of D-xylose and the yield of the products (in solution, prior to work-up).

A series of calibration mixtures comprising D-xylose, furfural, xylitol, levulinic acid, and 2-methoxyethanol (internal standard) were made and analyzed with the described HPLC method. From these results, the detector response factors of the components *versus* 2-methoxyethanol were calculated. As a methodology for sample preparation, after the given reaction time, the mixtures were cooled and the internal standard was added and mixed. Samples of 200 μL were taken, diluted with 1 mL of 0.01 M H_2SO_4 , filtered, and analyzed by HPLC.

Microwave Reactions

Experiments were performed in a microwave apparatus (Initiator+, Biotage®, Uppsala, SW). The reactions were carried out in magnetically stirred closed glass microwave reactor vials that could withstand high pressures. The reaction mixture was irradiated for the specified period (see tables) in the microwave oven in the range of 150 to 200 $^{\circ}\text{C}$ (power of microwave used: 400 watts). The yields of furfural and conversions

of D-xylose in the reaction mixtures were calculated from the obtained detector response factors. The mass balances were calculated in the following manner:

$$\frac{(\text{mmol product after reaction} + \text{mmol D-xylose after reaction})}{(\text{mmol D-xylose before reaction})} \times 100 \quad (1)$$

To determine the experimental conditions for the reproducible conversion of D-xylose into furfural, D-xylose was dissolved in a previously prepared 1 mg/mL of HCl solution in water (Table 1, Entry 1: 50 mg of D-xylose in 1 mL; Entries 2 and 3: 100 mg of D-xylose in 2 mL). The reaction mixtures were stirred for the given time at 150 °C using microwave radiation as the heat source. When reactions were complete, the reaction products were then analyzed.

To investigate the influence of the reaction temperature (175 °C) and the presence of NaCl as the additive and ethanol as the co-solvent (Table 2), 50 mg of D-xylose (Entries 1 through 3) or furfural (Entry 4) was dissolved in a solution of 1 mg/mL of HCl in water (1 or 2 mL). The reaction mixtures were heated for 4 h in the microwave reactor. The reaction products were then analyzed.

The influences of reaction time, temperature, and NaCl concentration were investigated by dissolving 50 mg of D-xylose in 2 mL of a solution of 1 mg/mL HCl in water (Table 3). An amount of NaCl was added to Entries 8 through 11. The reaction mixtures were heated in the microwave reactor; then, the reaction products were analyzed.

To investigate whether there was an optimum in the yield of furfural in the reactions at 200 °C, a new series of reactions with shorter reaction times (5, 10, 20, and 30 min) was carried out (Table 4). For the reaction, 50 mg of D-xylose was dissolved in 2 mL of a solution of 1 mg/mL HCl in water. The reaction mixtures were heated in the microwave reactor; then, the reaction products were analyzed.

To understand the influence of the HCl concentration, 50 mg of D-xylose was dissolved in 2 mL of a solution of HCl in water (Table 5). The reaction mixtures were heated in the microwave reactor at 175 °C for 1 h; then, the reaction products were analyzed.

To understand the influence of the starting concentration of the precursor molecule, D-xylose was dissolved in 2 mL of a solution of 1 mg/mL HCl in water (Table 6). The reaction mixtures were heated in the microwave reactor at 175 °C for 1 h. The reaction mixture was then cooled, and the internal standard was added and mixed. Samples of 200, 100, 66, 50, 40, and 33 µL were taken, diluted with 1 mL of 0.01 M H₂SO₄, filtered, and analyzed by HPLC.

The influence of a co-solvent addition was studied by dissolving 50 mg of D-xylose in 1 mL of a solution of 2 mg/mL HCl in water and 1 mL of co-solvent (Table 7). The reaction mixtures were heated in the microwave reactor at 175 °C for 1 h; then, the reaction products were analyzed.

The influence of the H₂SO₄ on the conversion was studied because it is the most common acid used in the industry to produce furfural. First, 50 mg of D-xylose was dissolved in 2 mL of a solution of H₂SO₄ in water (Table 8). The reaction mixtures were heated in the microwave reactor at 175 °C for 1 h; then, the reaction products were analyzed.

The influence of the addition of chlorides and bromides was studied. Fifty milligrams of D-xylose and 1 mmol (in Cl^-/Br^- ions; 0.5 mmol of CuCl_2 , CaCl_2 , NiCl_2 , MgCl_2 , ZnBr_2 , MgBr_2 , and CuBr_2 ; or 0.33 mmol of FeCl_3) of additive were dissolved in 2 mL of a solution of 1 mg/mL HCl in water (Table 9). The reaction mixtures were heated in the microwave reactor at 175 °C for 1 h; then, the reaction products were analyzed.

Finally, the stability of furfural under microwave conditions was studied: 50 mg of furfural was dissolved in 2 mL of a solution of 1 mg/mL HCl in water (Table 10). The reaction mixtures were heated in the microwave reactor. After 1 to 4 h of reaction time, the reaction mixture was cooled; then, the reaction products were analyzed.

RESULTS AND DISCUSSION

When analyzing an initial set of reaction mixtures from the microwave irradiation of D-xylose in HCl solution at 150 °C, no unexpected side products were detected in the range of 4.5 to 10 min in the HPLC chromatograms. A series of compounds was tested; from this series, 2-methoxyethanol, eluting at 4.9 min, was selected as a suitable internal standard. From analysis of a mixture of the starting materials, possible reaction products, and the internal standard, it was demonstrated that a good separation was obtained for all components (Fig. 1); furthermore, satisfactory calibration curves were obtained (Fig. 2). The peak at 1.8 min, which was frequently observed in the chromatograms, is related to unresolved components, such as inorganic salts.

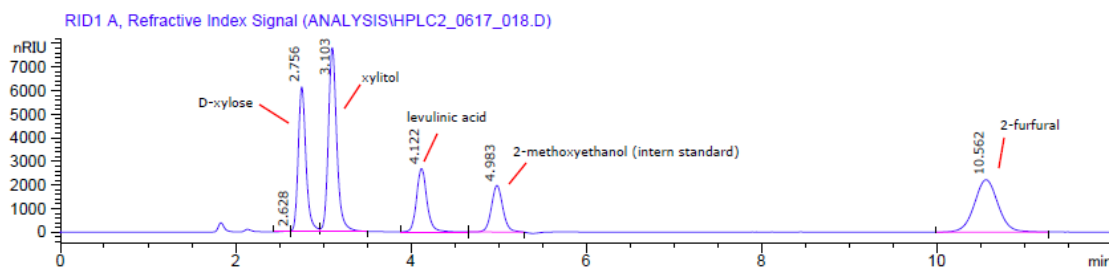


Fig. 2. HPLC-chromatogram of D-xylose, possible products (xylitol, levulinic acid, and 2-furfural), and 2-methoxyethanol (internal standard)

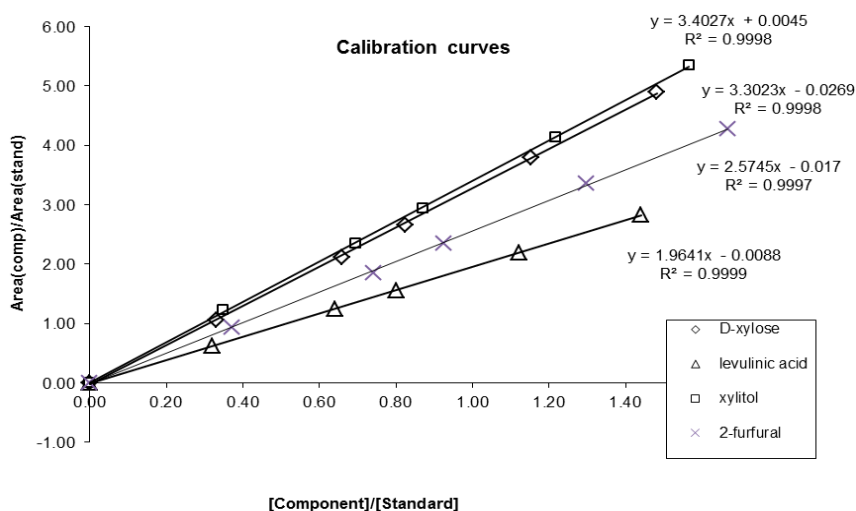


Fig. 2. Calibration curves of D-xylose, levulinic acid, xylitol, and 2-furfural vs 2-methoxyethanol

As the relative detector response factors of all the components was known, the composition of the reaction mixtures could accurately be determined after the addition of a known amount of internal standard. It was decided not to add the standard before the reaction, but just after the reaction, prior to the analysis. In this manner, complications related to the reactivity of 2-methoxyethanol under the chosen reaction conditions or evaporation of the standard during the reactions, which would lead to inaccurate results, were avoided.

In the microwave reactor at 150 °C, good conversion of D-xylose into furfural was observed (65%). Up to 35% *in situ* yield of furfural was achieved after 12 h (Entry 3, Table 1). The volume of the reaction mixture after the reaction was equal to the volume before the reaction, indicating that no solvent and no other volatiles were lost during the experiment.

Table 1. D-Xylose Conversion with HCl Solution in Water in the Microwave Reactor

Entry	Reagent	Solvent	T (°C)	Time (h)	D-xylose Conversion	Furfural Yield	CMB*
1	1 mg/mL HCl	water	150	1	7	0	93
2	1 mg/mL HCl	water	150	4	39	27	88
3	1 mg/mL HCl	water	150	12	65	35	69

*Calculated mass balance

Because the experimental conditions for the reproducible conversion of D-xylose into furfural were found in a microwave reactor system, a further series of experiments was performed to study this reaction.

The results of sequential reactions with respect to the influence of the reaction temperature, the presence of NaCl as an additive (Subramaniam and Spado 2013), and ethanol as a co-solvent were investigated, and results are given in Table 2. At 175 °C, a much higher conversion of D-xylose into furfural was observed (94% after 4 h, Entry 1, Table 2), in comparison to the same reaction at 150 °C (39% of conversion after 4 h, Entry 2).

Compared to that experiment, the addition of NaCl (Entry 2, Table 2) appeared to have a small positive influence on the yield of furfural (30% *vs.* 27% after 4 h). When 1 mL of ethanol (EtOH) was added as a co-solvent (Entry 3, Table 2), the yield of furfural dropped dramatically to only 6%. In this experiment the stability of furfural under the microwave conditions was also tested (Entry 4, Table 2). After reacting for 4 h at 150 °C, 87% of the furfural remained, which amounts to a much lower loss than what was previously observed (Table 1). The loss of the product is, however, still significant and a clear sign of instability under the applied reaction conditions.

Because an almost complete conversion of D-xylose was obtained after 4 h of reaction time at 175 °C (Entry 1, Table 2), the reaction was followed over time at temperatures of 175 and 200 °C. Without taking samples, the reactions were performed four times under the exact same conditions, except for the reaction time. The influence of the addition of various amounts of NaCl at 175 °C was also investigated in this series of experiments (Subramaniam and Spado 2013).

Table 2. Influence of Reaction Temperature and Additive on the D-Xylose Conversion

Entry	Starting Material	HCl Amount**	Additive	T (°C)	D-xylose Conversion	Furfural Yield	CMB*
1	D-xylose	2	no	175	94	48	53
2	D-xylose	2	99 mg NaCl	150	51	30	79
3	D-xylose	1	1mL EtOH	150	56	6	50
4	furfural	2	no	150	n/a	87	87

*Calculated mass balance; ** mL of a 1 mg/mL of HCl solution in water

As shown in Table 3, at a reaction temperature of 200 °C, the formation of furfural is much faster compared to lower reaction temperatures. After 1 h at 200 °C, already 53% of the furfural was obtained (Entry 1, Table 3) *versus* 33% at 175 °C (Entry 4, Table 3).

Table 3. Influence of Reaction Times, Higher Temperatures, and NaCl Concentration on the D-Xylose Conversion

Entry	T (°C)	Time (h)	Additive	D-xylose Conversion	Furfural Yield	CMB*
1	200	1	None	99	53	55
2	200	2	None	99	41	42
3	200	3	None	99	34	34
4	175	1	None	50	33	83
5	175	2	None	76	46	70
6	175	3	None	86	50	63
7	175	5	None	96	48	52
8	175	1	51.1 mg NaCl	64	44	80
9	175	1	100.2 mg NaCl	73	50	77
10	175	1	150.6 mg NaCl	77	51	74
11	175	1	206 mg NaCl	82	57	75

*Calculated mass balance

After prolonged reaction times at 200 °C, the yield of furfural rapidly declined to 41% and 34% after 2 and 3 h, respectively (Entries 2 and 3, Table 3). At 175 °C, an optimum furfural yield of 50% was reached after 3 h of reaction (Entry 6, Table 3). At longer reaction times at this temperature, the amount of product more or less remained

constant (48% to 50%), while the conversion of D-xylose increased up to 96% (Entry 7, Table 3). This led to a lower calculated mass balance after prolonged reaction time. The addition of NaCl appeared to have a positive influence on the reaction rate (Entries 8 through 11, Table 3). According to the HPLC analysis, after 1 h of reaction at 175 °C, already 44% to 57% of the furfural was formed in these mixtures.

The results for an optimum furfural yield in the reactions at 200 °C are given in Table 4. In this series, it was found that the yield in furfural increased in time up to 56% after 30 min. Similar to what was observed earlier (Table 3), the calculated mass balance decreased with time. The optimum in yield of furfural at 200 °C is between 20 min (Entry 3, Table 4) and 1 h of reaction time (Entry 1, Table 3).

Table 4. D-Xylose Conversion at 200 °C Among 5 and 30 min of Reaction Times

Entry	T (°C)	Time (min)	D-xylose Conversion	Furfural Yield	CMB*
1	200	5	45	25	80
2	200	10	58	38	80
3	200	20	79	52	73
4	200	30	90	56	66

*Calculated mass balance

Table 5 shows the results of a series of experiments in which the influence of the concentration of aqueous HCl was studied at 175 °C for 1 h. An optimum in furfural yield (56%) was observed at a concentration of 4 to 6 mg/mL of HCl in water (Entries 3 and 4, Table 5).

Table 5. Influence of the HCl (aq) Concentration on the D-Xylose Conversion

Entry	Concentration HCl in water (mg/mL)	Conversion D-xylose	Furfural Yield	CMB*
1	1	47	33	86
2	2	72	46	75
3	4	89	56	67
4	6	96	56	60
5	8	99	51	52
6	10	99	50	51

*Calculated mass balance

The influence of the D-xylose concentration on the conversion was also investigated. As shown in Table 6, the reaction rate was approximately the same for all starting material concentrations tested. The yield of furfural observed at the higher concentrations was slightly less than that of the more diluted mixtures (26% vs. 32%),

which could be related to a faster decomposition reaction of 2-furfural, which is likely to be dependent on the concentration of this component (higher concentration leads to a faster decomposition).

Table 6. Influence of the Concentration of Starting Material on the D-Xylose Conversion

Entry	Concentration of D-xylose (mg/mL)	D-xylose Conversion	Furfural Yield	CMB*
1	25**	48	32	84
2	50	48	29	81
3	75	51	31	80
4	100	49	29	79
5	125	49	28	79
6	150	49	26	77

*Calculated mass balance; **Standard concentration

The influence of the addition of a co-solvent (to dissolve the formed product 2-furfural) was also investigated (

Table 7). For this series of reactions, the solvents 1,4-dioxane, acetic acid (HOAc), ethylene glycol, and *n*-butanol were selected (Hu *et al.* 2014), and the reactions were performed at 175 °C for 1 h.

Table 7. Influence of Addition of a Co-Solvent on D-Xylose Conversion

Entry	Co-solvent	D-xylose Conversion	Furfural Yield	CMB*
1	1,4-Dioxane	93	59	66
2	HOAc	83	58	75
3	Ethylene glycol	79	24**	45
4	<i>n</i> -Butanol	73	28***	56

*Calculated mass balance

**Inaccurate results due to incomplete separation of the co-solvent and the internal standard

***Inaccurate results due to incomplete separation of the co-solvent and the product

The reactions with 1,4-dioxane or acetic acid as the co-solvent gave 59% and 58% yields of furfural, respectively (Entries 1 and 2). These results are comparable to those obtained after 30 min at 200 °C (Entry 4, Table 4) and with the addition of 200 mg of NaCl (Entry 11, Table 3). The reactions with acetic acid (Entry 2) or 200 mg of NaCl (Entry 11, Table 3) had a better mass balance (CBM = 75%) than that of the reactions with 1,4-dioxane as the co-solvent (Entry 1) or in neat water for 30 min at 200 °C (Entry

4, Table 4) (CBM = 66%). The co-solvents ethyleneglycol (Entry 3) and *n*-butanol (Entry 4) had a poor effect on the yield of furfural, at 24% and 28%, respectively.

It is important to note that ethylene glycol eluted at 4.35 min and was not completely base-line separated from the 2-methoxyethanol (internal standard) in the HPLC analysis. The co-solvent *n*-butanol eluted at 9.3 min and was not completely base-line separated from the furfural; therefore, inaccurate results were obtained. Nevertheless, from the UV-detector measurement (furfural is the only UV-active component), it cannot be concluded that using either ethylene glycol or *n*-butanol as a co-solvent had a negative effect on the yield of furfural.

The acid H₂SO₄ (Table 8) was also investigated to see if it would perform equally well in the conversion of D-xylose into furfural. The reactions were performed at 175 °C for 1 h under equal conditions as previously studied for HCl (Table 5). The results obtained in the reactions with H₂SO₄ were quite comparable to the results observed previously with HCl. An optimum furfural yield (55%) was observed at a H₂SO₄ concentration of 4 mg/mL (Entry 3). The highest conversion of D-xylose was 88% under these conditions (Entry 1), also similar to the results obtained with HCl (Entry 1, Table 5).

Table 8. Influence of H₂SO₄ (aq) Concentration on D-Xylose Conversion

Entry	Concentration of H ₂ SO ₄ in Water (mg/mL)	D-xylose Conversion	Furfural Yield	CMB*
1	1	47	35	88
2	2	70	46	76
3	4	88	55	66
4	6	97	52	55
5	8	98	51	53
6	10	98	49	50

*Calculated mass balance

Just as NaCl was found to have a positive influence on the reaction rate (Subramaniam and Spado 2013), the influences of other chloride and bromide salts were investigated (Table 9). The results showed that there are no large differences in the yield of furfural with the various additives.

Favorable results were obtained with NaCl, KCl, NaBr, LiBr, KBr, NH₄Cl, CaCl₂, MgCl₂, MgBr₂, and the tested tetraalkylammonium salts. Noticeably lower mass balances were observed in the reactions with LiCl (CBM = 51%), NH₄Cl (CBM = 56%), and NiCl₂ (CBM = 50%), although with these salts the yields of furfural were high (50% to 56%). In the case of CuCl₂, FeCl₃, ZnBr₂, and CuBr₂, much lower yields were observed (21% to 34%). The reactions proceeded best in the presence of a strong Brønsted acid, such as hydrochloric acid or sulfuric acid. The addition of some inorganic salt was also helpful in the reaction. No conclusion could be drawn about the reason for this, as many inorganic salts had the same positive effect (Binder *et al.* 2010; Zhang and Yu 2013). Perhaps a high ionic strength would be important, as water is formed as one of

the reaction products. For instance, FeCl₃ in presence of NaCl promotes good furfural yield (74%) for a biphasic system water-cyclopentyl methyl ether microwave-assisted (Le Guenic *et al.* 2015).

Table 9. Influence of the Addition of Chlorides and Bromides on D-Xylose Conversion

Entry	Additive	D-Xylose Conversion	Furfural Yield	CMB*
1	NaCl	65	44	79
2	LiCl	91	42	51
3	KCl	62	42	79
4	NaBr	62	46	83
5	LiBr	56	41	84
6	KBr	58	42	84
7	CuCl**	-	-	-
8	CuCl ₂	98	22	24
9	NH ₄ Cl	95	51	56
10	CaCl ₂	71	47	76
11	FeCl ₃	99	34	35
12	(Me) ₄ NCl	54	39	84
13	(Et) ₄ NCl	61	43	82
14	(Bu) ₄ NCl	55	41	86
15	(Bu) ₄ NBr	52	41	89
16	ZnBr ₂	100	21	21
17	NiCl ₂	100	50	50
18	MgCl ₂	75	45	70
19	MgBr ₂	65	49	84
20	CuBr ₂	99	23	24
21	(Me) ₄ NBr	53	42	90

*Calculated mass balance

**Reaction was not heated because CuCl does not dissolve at room temperature

In the next series of reactions, the stability of furfural under microwave conditions was tested. The series was performed with a solution of 1 mg/mL of HCl in water (Table 10), as most of the reactions were performed under these conditions. The results showed that the loss of the product was significant and a clear sign of the instability of the product under the applied reaction conditions. As expected, the instability of furfural is larger at higher temperatures. An amount of 21% of the original amount of furfural had decomposed after 1 h at 200 °C.

Table 10. Furfural Conversion with 1 mg/mL of HCl in Water at 150, 175, and 200 °C

Entry	Reagent	Time (h)	T (°C)	Furfural Conversion	Furfural Yield	CMB*
1	1 mg/mL HCl	1	175	9	91	91
2	1 mg/mL HCl	1	200	21	79	79
3	1 mg/mL HCl	4	150	13	87	87

*Calculated mass balance

CONCLUSIONS

In this work, the catalytic conversion of D-xylose was investigated under a range of conditions. It was found that in aqueous mixtures, in the presence of Brønsted acid catalysts, moderate conversions of D-xylose into furfural were achieved. By means of suitable HPLC analyses, using 2-methoxyethanol as an internal standard, the conversion and yields in the reaction mixtures were calculated, without the need for isolation of the reaction products.

The advantages of using a microwave technique are as follows:

1. The reaction mixture is rapidly heated to reaction temperature and subsequently quickly cooled down to room temperature, which is beneficial for the yield of product, since it was found that the starting material and products are not very stable at elevated temperatures.
2. The reaction is performed in a closed vessel that prevented the loss of solvent (and product) that was seen in the other types of equipment used.
3. The highest yields of furfural were obtained at a HCl concentration of 4 mg/mL.
4. When the reaction was performed at 200 °C, an optimum yield of 64% of furfural was observed after 10 min of reaction time, while 95% of the D-xylose was converted.

The disadvantages of this procedure are as follows:

1. The reactions could not be run in parallel, but only in a sequential fashion, which limited the number of results.
2. The microwave reactions cannot easily be scaled-up.

3. As the reactions were performed in water, it was observed from the HPLC analyses that the reactions looked rather clean, with furfural usually being found as the main reaction product. However, under these conditions, incomplete mass balances were generally calculated and the formation of black tars in the reaction mixtures indicated that some side reactions had occurred.

In summary, the optimal conditions found in this study to efficiently convert D-xylose into furfural where the use of HCl as a catalyst, water as a solvent, and NaCl as an additive was employed. This work should help to develop a new greener process based on renewable feedstocks.

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