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Microwave-assisted furfural synthesis from D-xylose in the presence of NaCl: Comparison between microwave heating and conventional heating

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Abstract: We investigate the existence of specific/non-thermal microwave effects for the case of xylose dehydration to furfural reaction in the presence of NaCl. Such effects are claimed in several literature reports for sugars dehydration reactions. To this end, we have adopted three approaches that involve comparison of microwave-assisted experiments a) with conventional heating experiments from the literature; b) with simulated conventional heating experiments using microwave-irradiated silicon carbide vials; and c) at different power levels, but the same temperature, using forced cooling. No significant differences in the reaction kinetics are obtained using any of these methods. However, microwave heating still proves advantageous, as it requires 30% less forward power compared to conventional heating (SiC vial) to achieve the same furfural yield at laboratory scale. This demonstrates the effective in-core volumetric heating of microwaves, in comparison to conventional surface heating.

Introduction

Furfural is a valuable platform chemical, derived from renewable lignocellulosic biomass and agricultural surpluses. It has several uses, such as extraction solvent for aromatic compounds or precursor for synthesizing specialty chemicals and liquid fuels [1]. Being among the few non-petroleum derived chemicals, it can play a vital role in the transition from fossil fuel resources to a more sustainable bio-based industry [2].

Furfural synthesis usually involves the acid hydrolysis of the pentosan fraction of biomass into pentoses (C-5 sugars), such as xylose or arabinose, and the subsequent dehydration of the pentoses to furfural [3]. The two reactions can take place in the same vessel under similar conditions, with the xylose dehydration to furfural being the rate limiting step [4]. Currently, furfural is produced in industry by an energy intensive process using superheated steam to heat the reaction and mineral acids such as HCl and H_2SO_4 as reaction catalysts [2,4]. Organic acids, such as acetic acid can also be used and would be more desirable from an environmental standpoint, but they usually lead to lower furfural yield. Furfural product yields are generally limited to 45%-55%, due to the occurrence of side reactions that give rise to degradation products. New and intensified processes for furfural production can potentially circumvent the yield limitations and lower the energy requirements, while minimizing the large waste streams associated with the process. In this way, the full potential of furfural as a biomass-derived intermediate versus oil derivatives could be exploited. Such intensified processes may be based on chemical activation through alternative energy forms, *i.e.* microwave heating. In many organic syntheses, microwave heating leads to reduced reaction times and higher reaction efficiency compared to conventional heating, in aqueous systems, which could allow the replacement of toxic organic solvents and catalysts with more benign aqueous systems [5,6].

Marcotullio and De Jong [7] have shown that the presence of Cl⁻ ions in aqueous acidic solutions could significantly enhance the dehydration reaction rate of D-xylose, under conventional heating, while also improving the selectivity and furfural yield. Another study investigated the effect of microwave heating on furfural yield using D-xylose in aqueous HCl solutions [8]. In their study, microwave heating showed no effect on the reaction kinetics of xylose dehydration. However, several studies of C-5 and C-6 sugars dehydration to furfural and 5-HMF, respectively, claim significant enhancement of the reaction rate under the presence of ions and microwave heating compared to conventional (e.g. oil-bath) heating [9–17]. Synergistic effects of ions and microwave heating, leading to higher furfural yield, have also been reported [16]. A discussion of several studies comparing microwave and conventional heating for the synthesis of furfural and 5-HMF from C-5 and C-6 sugars, respectively, is presented in Appendix A. The presence of ions in aqueous solutions is known to enhance electromagnetic energy dissipation and consequently increase the dielectric heating rate. The rapid temperature increase could explain some of the observed yield enhancements. However, ions participate in the dehydration chemistry as well; therefore, non-thermal microwave effects (*i.e.*, increase in the number of effective collisions or lowering of activation energy due to the direct interaction of the electromagnetic field with the polar species) have also been put forward to explain the kinetic rate enhancement of these reactions [9]. Nevertheless, it is known that the existence of such effects is largely speculative.

In this study, the application of microwave-assisted heating, combined with the use of NaCl salt, to xylose dehydration in dilute aqueous acidic solutions was investigated and the results were compared to conventionally heated experiments from the literature. In addition, the existence of non-thermal microwave effects was investigated in an experimental microwave setup that allows the simulation of conventional heating while maintaining all the other process parameters the same (bulk and

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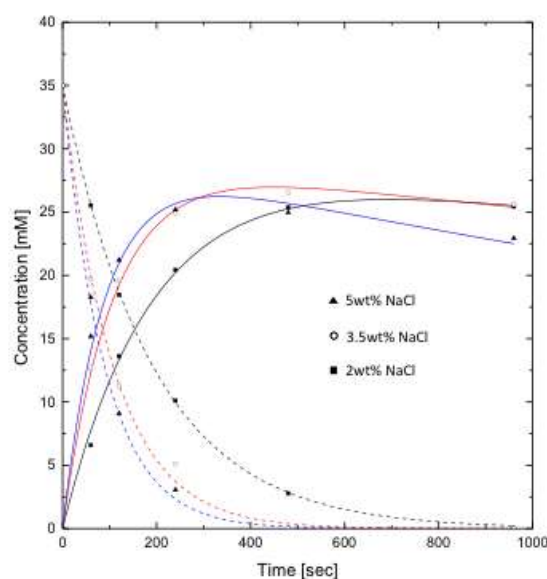
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       the document.

wall temperature, heating rate, reactor geometry and stirring rate). Finally, the rate constants of the pseudo-first order reactions of xylose conversion to furfural and xylose and furfural conversion to byproducts were determined under the two heating modes.

Results and Discussion

Indirect comparison of microwave and conventional heating using varying amounts of NaCl

Microwave heating in combination with NaCl was investigated for the xylose dehydration to furfural reaction. Three different NaCl concentration levels (2wt%, 3.5wt% and 5wt%, or 342, 599 and 856 mM, respectively), close to the ones found in seawater, were studied in dilute aqueous HCl solutions (50 mM HCl concentration, initial xylose concentration: 35 mM) at 200 °C. The conditions of these experiments are similar to a previous study, which used a conventionally heated autoclave reactor [7]. This way, an indirect comparison of the two modes of heating can be made. The results of these experiments in terms of the time evolution of xylose and furfural concentration are presented in Figure 1.

Figure 1. Evolution of xylose and furfural concentration over the course of the reaction at different NaCl concentrations (2wt%, 3.5wt% and 5wt%). The dashed and solid lines are the kinetic model estimations of xylose and furfural concentrations, respectively (black – 2wt%, red – 3.5wt% and blue – 5wt% NaCl concentrations), based on the experimental results of the present study (triangle, circle and square marks). Conditions: 35 mM xylose initial concentration, 50 mM HCl concentration, 200 °C reaction temperature and 600 rpm magnetic stirring.

Based on the experimental results, it appears that NaCl has a significant catalytic effect on the reaction under microwave heating leading to complete xylose conversion within 1000 s in all cases. The maximum experimental furfural yields were 73%,

76% and 72%, for NaCl concentrations of 2wt%, 3.5wt% and 5wt%, respectively. Even though increasing the NaCl concentration, within the evaluated range, does not seem to significantly affect the furfural yield and selectivity, the reaction rate is increased considerably. On the other hand, prolonged residence times, particularly at higher NaCl concentrations, seem to slightly decrease furfural concentration. This can possibly be explained by the higher concentration of furfural or xylose-to-furfural intermediates that may undergo (enhanced) side reactions, under these conditions.

The first order rate constants k_1, k_2 and k_3 were derived based on the experimental data and are presented in Table 1. The estimated rate constants (entries 1-3 of Table 1) reveal that increasing salt concentration, under constant acidity, leads to an almost proportional increase in both k_1 and k_2, implying that both xylose reactions (towards furfural and byproducts) are enhanced. The rate constant k_3 seems to remain roughly unchanged when NaCl concentration is increased from 2wt% to 3.5wt%. However, when 5wt% NaCl was used, k_3 was almost doubled, similarly to the comparison study. This suggests that the addition of NaCl may eventually enhance furfural degradation reactions as well, but only after a certain threshold value in NaCl concentration is exceeded. However, the rate of furfural degradation reactions does not seem to have a straightforward relation with the Cl^- concentration, according to the proposed kinetics.

Table 1. Derived rate constants (entries 1-3), by least square regression with their standard errors. Entries 4-6 are retrieved from literature [7] for comparison. The concentrations and reaction temperature are the same as in the comparison study [7]: 35 mM xylose concentration, 50 mM HCl concentration, 200 °C reaction temperature.

Entry	NaCl [wt%]	k_x[a] /10^{-4} [s^{-1}]	k_1 /10^{-4} [s^{-1}]	k_2 /10^{-4} [s^{-1}]	k_3 /10^{-4} [s^{-1}]	Selectivity[b] [%]	Max yield[c] [%]
1	2.0	52.3 ±4.1	43.2 ±1.8	9.1 ±2.3	1.53 ±0.9	82.6 ±7.3	74.2 ±8.2
2	3.5	93.3 ±8.4	76.9 ±4.1	16.4 ±4.3	1.50 ±0.9	82.4 ±8.6	77.2 ±8.6
3	5.0	112.8 ±10.8	93.0 ±5.4	19.8 ±5.4	2.85 ±0.9	82.4 ±9.2	74.9 ±8.7
4	2.0	64.5	52.8	11.7	2.2	81.9	72.8
5	3.5	74.4	63.1	11.3	2.2	84.8	76.1
6	5.0	119.1	107.4	11.6	3.4	90.2	81.3

[a]: $k_x = k_1 + k_2$, [b]: Selectivity calculated as k_1/k_x, [c]: Maximum theoretical

yield calculated as: $\frac{k_1}{k_1+k_2}\left[\left(\frac{k_1+k_2}{k_3}\right)^{\frac{k_3}{k_3-k_1-k_2}}\right]$, 95% confidence interval in

parameter estimation

In Table 1, the estimated rate constants of this work (entries 1-3) are compared to the ones derived by Marcotullio and De Jong [7] (entries 4-6) under conventional heating. The derived values of k_1, k_2, k_3 are similar in the two studies. The small differences may be attributed to differences between the conventional and microwave setups, causing small residence time variations in the experiments, as well as the different temperature measurement systems. However, the estimated values are close enough to suggest that microwave heating does not show any
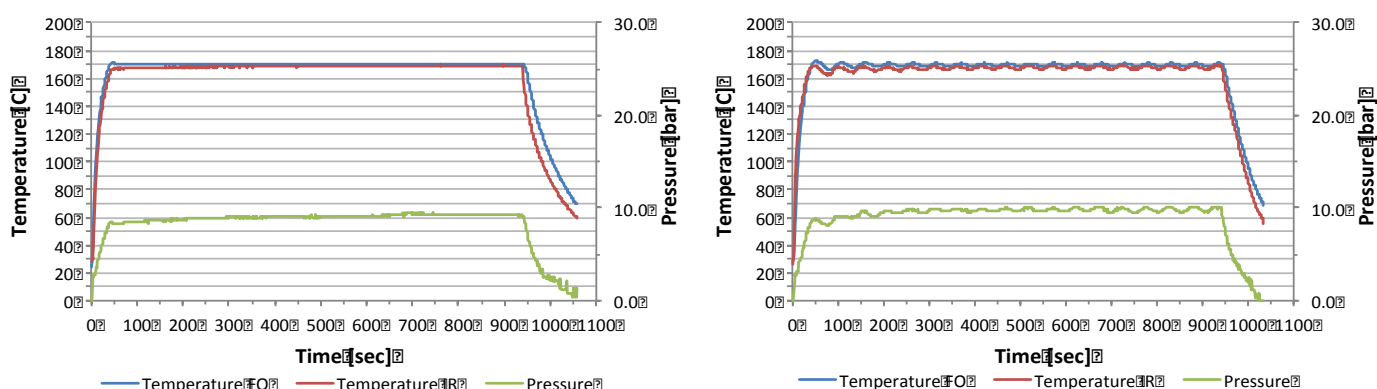
significant effect on the xylose dehydration reaction to furfural under dilute acidic conditions versus conventional heating. This finding contradicts previous studies on C-5 and C-6 sugars dehydration that claim significant furfural or 5-HMF yield enhancement in aqueous systems employing acid catalysis and/or salts in combination with microwave heating [10,11,13,16].

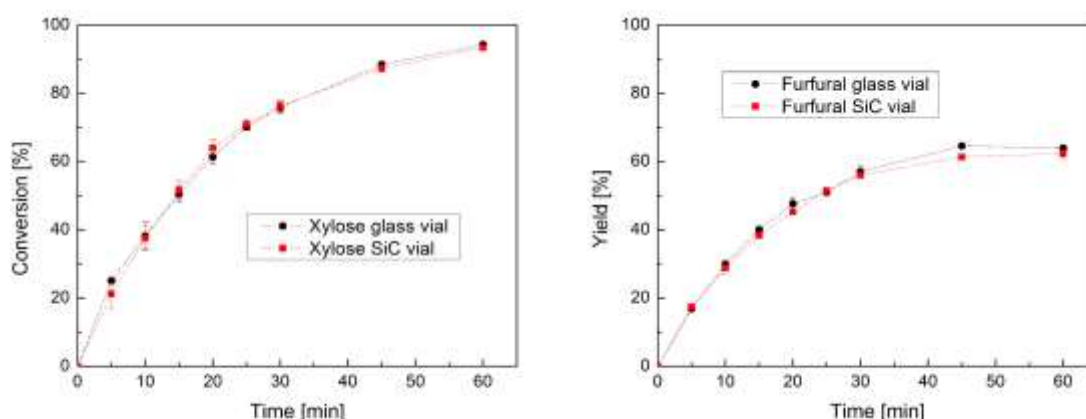## Direct comparison of microwave and conventional heating

The results presented in the previous section do not seem to indicate that a strong microwave effect is present for the xylose dehydration to furfural reaction. However, the comparison was based on experiments performed in different setups. It should be remarked that accurate comparison between microwave and conventional heating often proves challenging, not only due to inherent difficulties in determining the actual temperature in microwave heated transformations, but also due to difficulties in reproducing heating rates attained with microwaves in a conventional heating setup [18]. To address these potential limitations, we carried out two series of experiments, using a different microwave reactor setup (Anton Paar Monowave 300) that allows for variation of the heating mode while maintaining all other process parameters similar. This is achieved by using a SiC vial to mimic conventional heating and a same geometry glass vial to study microwave heating. The SiC vial "shields" the reactant mixture from the microwave field, while still enabling high heating rates due to electromagnetic dissipation in the SiC vial wall itself (further discussion on the SiC vials is provided in Supporting Information). In this case, instead of volumetric heat generation due to microwave dissipation in the reactant mixture, mixture heating occurs conventionally, *i.e.* due to heat transfer from the wall to the mixture [18]. The conditions for these experiments were 50 mM initial xylose concentration, 50 mM HCl concentration, 500 mM NaCl concentration and 600 rpm stirring speed. For these experiments a temperature of 170 °C was selected to study the reaction at longer residence times (5-60 minutes). This way, the preheating and cooling times for both vials are negligible compared to the residence time at the reaction temperature.

As expected, the temperature and pressure profiles recorded throughout the experiments using the glass and SiC vials are very similar, as shown in Figure 2, enabling a reliable comparison of microwave and conventional heating, keeping the rest of the process parameters similar. However, in the SiC vial, temperature fluctuates in a cyclic manner. The vial wall is heated directly in case of the SiC vial, which leads to faster dynamics.

Figure 2. Left: Temperature and pressure profile of a typical glass vial experiment. Right: Temperature and pressure profile of a typical SiC vial experiment. Conditions: 50 mM initial xylose concentration, 50 mM HCl concentration, 500 mM NaCl concentration, 600 rpm stirring speed. Power control system was the same in both vials and was set to reach the target temperature of 170 °C as fast as possible, preventing overshoots.

Figure 3. Analytical results (mean values with standard error bars) of the microwave (glass vial) and conventional (SiC vial) heating experiments at 170 °C (xylose: 50 mM, HCl: 50 mM, NaCl: 500 mM, stirring at 600rpm) at different residence times. Left: Xylose conversion vs. residence time for glass and SiC vials. Right: Furfural yield vs. residence time for glass and SiC vials. The almost identical results indicate that the kinetics of xylose dehydration are unaffected by the heating mode.

Specifically, the temperature rises and drops faster on microwave power increase and decrease, respectively. This causes the temperature controller to continually over- and undershoot its reference, leading to the oscillatory temperature trend. Retuning the controller may prevent this from happening, although the device does not allow for this. Depending on the activation energies of the reactions involved, even short times at higher temperatures might have an influence on the observed reaction kinetics. To make sure that this is not the case for the SiC vial, we calculated the mean kinetic temperature (MKT), based on the residence time at the high and low temperatures. For the calculation, we used the typical range of pseudo-activation energies (70-140 kJ mol^{-1}), which is reported for xylose dehydration to furfural reaction in dilute aqueous acidic solutions [2]. The mean kinetic temperatures calculated (169.83 °C -169.85 °C) are in close agreement to the average reaction temperature of 170 °C, thus the small cyclic temperature behavior in the SiC vial can be safely neglected.

Figure 3 presents the xylose conversion and furfural yield measured for the glass vial (microwave heating) and SiC vial (conventional heating) experiments and Table 2 shows the estimated rate constants for the same experiments. By comparing the values, it appears that microwave heating has no influence on the xylose dehydration to furfural reaction kinetics. This finding contradicts previous publications comparing microwave and conventional heating for the case of xylose dehydration under acidic conditions with or without the presence of salts [16,17]. For example, Yang et al. [17] reported 16% increase in furfural selectivity when applying microwave heating, compared to conventional heating, at the same process conditions (140 °C, 45 min, AlCl3 and NaCl in water-THF system). However, the exact temperature profile of the microwave heated transformation could not be accurately reproduced using an oil-bath; in addition, 18 more minutes were required to bring the temperature to 140 °C using conventional heating. Therefore, any observed selectivity improvement can be due to the increased heating rate in the microwave heated reaction, as the authors correctly suggest [17]. In another study [10], the authors report that application of microwaves to fructose dehydration in an aqueous-HCl system results in 16% increase in the 5-HMF yield in comparison to conventional heating. However, the authors also report significant dissimilarities between the heating rates in the microwave and conventional heating setup. Such discrepancies in the heating rate may be even more pronounced when large concentration of salts or ionic liquids are used (see further discussion in Appendix A). Ionic liquids couple very efficiently with microwaves, leading to heating rates easily exceeding 10 °C/s, which are difficult to reproduce conventionally. In cases where the heating rates between various experimental setups cannot be kept similar, the use of a non-isothermal kinetic analysis might be more suitable, *e.g.* by estimating an equivalent isothermal temperature [19]. Here, it is shown that at similar heating rates between the two heating modes, the results are almost identical, indicating that xylose conversion and furfural yield are only dependent on the temperature profile attained either by conventional or microwave heating.

Table 2. Derived rate constants for conventional and microwave heating. Conditions: 50 mM initial xylose concentration, 50 mM HCl concentration, 500 mM NaCl concentration, 600 rpm stirring speed and 170 °C reaction temperature. The derived values are very similar for the conventional and microwave heating.

Heating mode	$k_x/10^{-4}$ [s^{-1}]	$k_1/10^{-4}$ [s^{-1}]	$k_2/10^{-4}$ [s^{-1}]	$k_3/10^{-4}$ [s^{-1}]	Selectivity[a] [%]	Max yield[b] [%]
Glass vial	8.01 ± 0.53	6.37 ± 0.23	1.64 ± 0.30	0.60 ± 0.23	79.5 ± 5.9	64.5± 7.5
SiC vial	8.05 ± 0.38	6.22 ± 0.17	1.83 ± 0.21	0.61 ± 0.19	77.2 ± 4.2	62.5 ± 5.6

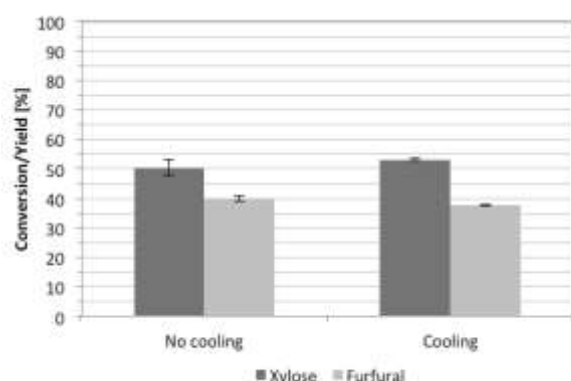[a]: Selectivity calculated as k_1/k_x, [b]: Maximum theoretical yield calculated

as: $\frac{k_1}{k_1+k_2}\left[\left(\frac{k_1+k_2}{k_3}\right)^{\frac{k_3}{k_3-k_1-k_2}}\right]$, 95% confidence interval in parameter estimation

Increasing microwave power under constant temperature

To probe further into the existence of potential specific/non-thermal microwave effects on the xylose dehydration to furfural reaction, the microwave power was varied, this time using only the glass vial (microwave heating). If the temperature profile remains unchanged, while varying the applied microwave power, any yield/selectivity differences measured may be attributed to specific/non-thermal microwave effects. To increase the microwave power at constant reaction temperature, the so-called Enhanced Microwave Synthesis (EMS) technique was used [20]. It is based on simultaneous application of microwaves to the reaction vessel and external forced cooling via compressed air for the entire duration of the experiment. This type of experiment allows for examination of the effect of microwave power alone at constant temperature and consequently for implicit verification of possible non-thermal microwave effects. According to the instrument readings, regarding the forward emitted microwave power, the high power (forced cooling) mode required ~ 5 times more power to maintain the temperature at 170 °C compared to the low power mode (no cooling). It is mentioned that the preheating times are the same in both experiments. Even though the applied power was significantly higher when forced cooling was applied (10 W versus 50 W), xylose conversion and furfural yield are not affected, as shown in Figure 4. Slightly different results have been reported by Serrano Ruiz et al. [21], where the authors observed a small increase in xylose conversion and furfural yield (10% and 7% respectively) by increasing the applied microwave power from 100 W to 300 W at 150 °C in a 30 minute experiment. However, the authors do not mention whether the same heating rate was maintained at these experiments. Since in their work ionic liquids were used, heating rate would probably be more readily affected by changes in the applied microwave power. If the reaction temperature was attained faster in their high power experiment, the higher yield/conversion can be explained. Another study on HCl-catalyzed fructose dehydration to 5-HMF under microwave irradiation showed that 5-HMF yield and fructose conversion were independent of the applied microwave power (100-300 W) [10]. In the present study, it is shown that furfural yield and xylose conversion are independent

of the applied microwave power, provided that enough microwave power is supplied to sustain the reaction temperature.
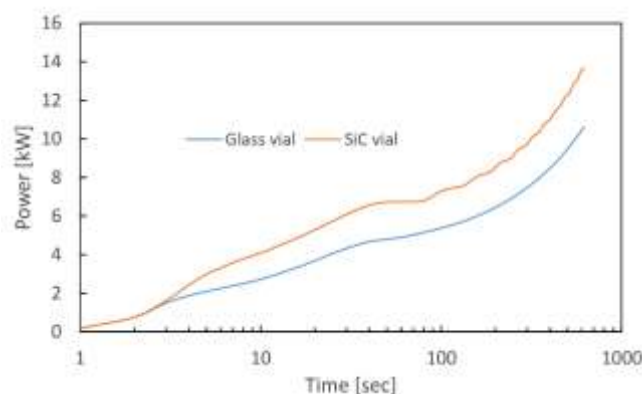

Figure 4. Xylose conversion and furfural yield without cooling (10 W) and with cooling (50 W). The results show that the applied microwave power has a negligible effect on the xylose dehydration and furfural yield. Conditions: 50 mM initial xylose concentration, 50 mM HCl concentration, 500 mM NaCl concentration, 600 rpm stirring speed 170 °C reaction temperature and 15 minutes reaction time.

Comparison of energy consumption

It is shown that the two modes of heating result in the same xylose conversion and furfural yield, when the rest of the process conditions are kept the same. However, a critical evaluation of the process requires an assessment of the energy consumption for two heating modes as well. Such precise assessment is difficult though, since it has been shown that the total heat generation in microwave cavities employing resonant microwave fields is very sensitive to even slight variations in the geometric aspects of the load and the process conditions and can also deviate significantly from the power readings provided by these instruments [22]. In addition, the microwave power generated in such cavities is not exclusively dissipated in the load, but also in other locations of the microwave circuit (e.g. the magnetron) leading to significant energy losses. Detailed energy balances in small scale microwave reactors, accounting also for energy losses, have shown that the power absorbed by the load can be as low as 44% [23]. An accurate estimation of the total heat generation in the load requires tailor-made microwave applicators, such as the ones used in [24] and [25] in which the electromagnetic field is well defined and the reflected power can be accurately estimated (and minimized), for instance by including power transfer sensors in different parts of the system. Commercial microwave heating devices for laboratory applications do not provide such capability.

The cumulative forward emitted microwave power supplied to a typical glass vial (microwave heating) and SiC vial (simulated conventional heating) during the preheating and the reaction time was recorded and it is presented in Figure 5. At the initial stages of the experiment, high power is supplied to allow for fast reach of the reaction temperature of 170 °C. In turn, the power is reduced in order to hold the temperature constant, balancing the

heat losses to the surroundings and the reaction heat. The same power control system (PID controller, built-in to the device) was used to regulate the temperature using both vials. This system is designed to reach the reaction temperature as fast as possible, but preventing overshoots, and it leads to the same heating rate in both vials at the conditions examined here. However, in the case of the SiC vial, the power required to reach the set reaction temperature (preheating period) was 43% higher compared to the glass vial, while the total power supplied during the entire course of the reaction was 30% higher. The reflected microwave power is unknown and can be different in the two modes of heating. However, the difference in the supplied power can be explained by the differences in the materials properties. The microwave-transparent borosilicate glass vial, which is used in the case of volumetric microwave heating, has significantly lower density than the highly conductive SiC vial (2.23 g/mL versus 3.1 g/mL, respectively) that is used to simulate conductive heating at similar heating rates as in microwave heating. Consequently, more energy is required to reach and maintain the same reaction temperature in the conductive heating cases, owing to the higher mass of the SiC vial. The thermophysical properties of SiC and borosilicate glass are presented in Table S1 of the Supporting Information.

Figure 5. Cumulative forward microwave power supplied in the cases of glass and SiC reactor vials. Use of the SiC vial (simulated conventional heating) results in significantly higher power input, compared to the glass vial (microwave heating) for the xylose dehydration reaction.

Conclusions

In this work, xylose dehydration to furfural using microwave heating in the presence of NaCl, at near seawater concentrations, was studied and compared with conventional heating. The highest furfural yield of 76% was obtained when 3.5wt% NaCl was used, at 200 °C, leading to complete xylose conversion in 440 sec. The existence of non-thermal microwave effects was investigated in three different ways, namely: a) comparison of microwave heating experiments with literature results on conventional heating experiments; b) direct

comparison of microwave and conventional heating in the same monomode cavity using strongly microwave absorbing SiC vials to simulate conventional heating; and c) comparison between experiments at different microwave power levels at the same mixture temperature. It appears that microwave heating shows no prominent effect on the dehydration reaction kinetics at the examined conditions. However, microwave heating eliminates the need of long preheating times and can thus reduce the uncertainty of kinetic measurements in cases of slow conductive heating during the initial stage of the experiments. Further, the forward emitted microwave power was at laboratory scale 30% higher in the case of the denser SiC vials due to heating of a larger thermal mass compared to the glass vials. However, the overall energy consumption might not always be lower in the case of microwave heating processes. The overall energy efficiency depends mainly on two factors: a) the magnetron efficiency and b) the reflected (undissipated) power. Magnetron efficiency can be maximized by operating at alternative operating frequencies (up to 85% electric-to-microwave power efficiency at 915 MHz). The reflected power can be minimized through appropriate design and operation of the overall microwave applicator including the reactor itself. Furthermore, if a different solvent that couples more effectively with microwaves (*e.g.* ionic liquids or higher salt concentration aqueous solutions) is selected, the heating rate of the solution can be significantly higher and difficult to attain by conventional heating, possibly resulting in enhanced product selectivity. Scale-up of the microwave process is also possible using either novel, non-cavity based, reactor designs, such as the Internal Transmission Line technology (INTLI, up to 500 L of batch processing) [23], or continuous flow microwave reactors at high temperature and pressure conditions [26], as those commonly applied in laboratory batch microwave equipment (up to 300 °C and 60 bar).

Appendix A: Discussion of studies on microwave-assisted C-5 and C-6 sugars dehydration

A number of studies have been published comparing conventional and microwave heating for the synthesis of furfural and 5-HMF from C-5 and C-6 sugars dehydration, respectively. In most of these studies, water is employed as a solvent, although in some cases, ionic liquids have also been tested. Biphasic systems have also been used; in these systems, an organic water-immiscible phase (e.g. THF, MIBK) is employed to extract the produced furfural or 5-HMF immediately, hence preventing its further decomposition to undesirable products and improving the yield. The catalysts employed in most studies are chloride salts in combination with mineral acids and/or ionic liquids. Most kinetic studies assume a reaction mechanism, which includes two first order reactions for the sugars disappearance (sugars reaction to furfural or 5-HMF, sugars reaction to loss products). For the cases of the combined hydrolysis of xylan or biomass and dehydration of the occurring pentoses, the latter is considered to be the rate-limiting step. The resulting 5-HMF and furfural yield under microwave and

conventional heating for these studies, as well as the temperatures and catalysts used, are synopsized in Table A1 and Table A2. Since not all studies include the calculation of kinetic parameters, these are not included here either. Instead, the process times to achieve the respective furfural yield are presented. The studies mentioned herein are only limited to cases where homogeneous catalysis is employed, although there is a number of studies that compare microwave and conventional heating in the presence of heterogeneous catalysts as well [27–31]. The effect of microwave heating in such heterogeneous systems is beyond the scope of this work. Other studies that compare microwave and conventional heating for the synthesis of other furan compounds, such as 5-chloromethyl furfural (5-CMF) [32] are also not included, for the sake of brevity.

Comparison between the data in Table A1 and Table A2 is not straightforward, due to the diverse systems and conditions used by the various research groups. However, it can be clearly seen that contradicting results exist concerning the role of microwave heating in these studies. For instance, one study (Table A2, Entry 1) reports no significant difference in furfural yield using microwave heating and conventional heating with HCl as catalyst [8]. Conversely, two other studies claim a 16% 5-HMF yield increase and 14% furfural yield increase from fructose and xylan, respectively, using HCl and microwave heating (Table A1, Entry 3 and Table A2, Entry 3) [10,16]. Even more striking differences between microwave and conventional heating yields are reported when chloride salts or ionic liquids are added, with a study [13] reporting a striking 42% 5-HMF yield increase from fructose dehydration using $AlCl_3$ in water (Table A1, Entry 7).

In order to rationalize such yield improvements, several authors claim the existence of non-thermal microwave effects, such as a lowering of the activation energy or an increase of the pre-exponential factor in the Arrhenius law due to possible orientation effects of polar species in response to the electromagnetic field [9,12,33]. The existence of such effects is not yet proven and is highly debated in the literature.

Table A1. Studies comparing microwave and conventional heating for the dehydration of hexoses to 5-HMF in terms of 5-HMF yield and sugars conversion.

Entry	Feed (mM)	Solvent	Catalyst amount (mM)	Temperature (°C)	Time (min)	5-HMF Yield (%)		Substrate Conversion (%)		Ref.
						Micr.	Conv.	Micr.	Conv.	
1	Glucose (500)	[BMIM]Cl	$CrCl_3 6H_2O$ (50)	120	5	67.0	45.0	-	-	[9]
2	Glucose (500)	[BMIM]Cl	$CrCl_3 6H_2O$ (50)	140	0.5	71.0	48.0	-	-	[9]
3	Fructose (1766)	Water	HCl (100)	160	5[a], 10[b]	28.0	12.0	48.0	29.0	[10]
4	Glucose (278)	Water/MIKB 1:1 (v/v)	$Zr(O)Cl_2$ (10mol%)	120	5[a], 30[b]	42.0	24.0	-	-	[11]
5	Fructose (500)	[BMIM]Cl	No catalyst	155	1[a], 5[b]	98.0	82.0	99.0	84.0	[12]
6	Glucose (730)	[BMIM]Cl	$CrCl_3 6H_2O$ (50)	80	2.5[a], 180[b]	85.0	57.0	93.0	84.0	[14]
7	Fructose (278)	Water	$AlCl_3$ (50mol%)	120	20[a], 60[b]	55.7	14.1	-	-	[13]

[a]: residence time with microwave heating, [b]: residence time with conventional heating

Table A2. Studies comparing microwave and conventional heating for the dehydration of pentoses, pentosans and biomass to furfural, in terms of furfural yield and sugars conversion.

Entry	Feed (mM)	Solvent	Catalyst amount (mM)	Temperature (°C)	Time (min)	Furfural Yield (%)		Substrate Conversion (%)		Ref.
						Micr.	Conv.	Micr.	Conv.	
1	Xylose (740)	Water	HCl (100)	170	30	~ 40	~ 35	~ 80	~ 75	[8]
2	Xylose (33)	Water	HCl (100)	180	30	59.8	-	-	-	[34]
3	Xylose (667)	Water	HCl (100)	180	30	39	-	-	-	[34]
4	Pine wood (100 mg)	[BMIM]Cl	$CrCl_3·6H_2O$ (10mg)	200	3[a],6[b]	31	18	-	-	[15]
5	Xylan (2000 mg)	Water	HCl (100)	~ 150	5[a],30[b]	42	28	-	-	[16]
6	Xylan (2000 mg)	Water	HCl (100) & $Na_2MoO_4·6H_2O$ (206)	~ 150	5[a],30[b]	53	36	-	-	[16]
7	Xylose (667)	Water-THF (1:2 w/w)	SO_3H- ionic liquids	180	60	85	-	>95	-	[21]
8	Xylose (67)	Water	Maleic acid (250)	200	28	67	-	100	-	[35]
9	Xylose (250)	Water-THF (1:3 v/v)	$AlCl_3·6H_2O$ (100) & NaCl (6000)	140	45	15.2	12.8	81	98	[17]
10	Xylose (~125)	[BMIM]Cl	$AlCl_3$ (~62.5)	160	1.5	82.2	-	>95	-	[33]
11	Xylose (57)	Water	None	200	60	49	-	89	-	[36]
12	Xylose (312.5)	Water-CPME (1:3 v/v)	$FeCl_3$ (31) & NaCl (312.5)	170	20	74	-	100	-	[37]

[a]: residence time with microwave heating, [b]: residence time with conventional heating, ~ means that the values were not clearly mentioned in the studies and are interpolated based on figures or other data.

Experimental Section

In all experiments, 4 mL of solution containing D-xylose, 50 mM HCl (constant) and NaCl was transferred into a 10 mL borosilicate (glass) or SiC vial and subsequently to the microwave applicator cavity (CEM Discover™ or Anton Paar Monowave 300) for the required reaction time. All reactions took place under pressure, due to the solution vapour pressure at the reaction temperature (170 °C or 200 °C). Stirring was applied at 600 rpm using a magnetic stirring bar. Once the experiment was complete, microwaves were stopped and compressed air cooling was applied. For the experiments at a higher power, air-cooling was applied from the beginning and for the entire duration of the experiment. After the temperature of the mixture dropped below 70 °C, air-cooling was terminated and the vial, containing the reaction mixture, was immediately quenched in ice to allow further cooling. Once the temperature dropped below room temperature, samples were taken for HPLC analysis. All experiments were performed at least twice and the results did not deviate more than 10%.

Experiments varying the NaCl concentration

This set of experiments was carried out in the CEM Discover™ microwave reactor at 200 °C. Reaction temperature was measured using the built-in infrared (IR) sensor of the instrument. Prior to the experiments, the IR sensor was calibrated to the reaction temperature and vessel using an internal FISO optical fiber temperature sensor.

Experiments comparing microwave and conventional heating

These experiments were carried out in the Anton Paar Monowave 300 microwave reactor at 170 °C, since this instrument allows for a direct comparison of conventional and microwave heating, using the strongly absorbing SiC vials that are available with this device. Temperature was measured and controlled using the internal optical fiber (Ruby) sensor of the instrument, but the built-in IR sensor measurements were also recorded to allow for comparison.

Analysis

The reaction products were analyzed using an HPLC apparatus with a Rezex RHM-Monosaccharide column. The xylose concentration in the samples was measured using an RI detector at 35 °C while furfural was determined using both the RI and UV detector at 254 nm. The eluent was 0.005 N sulfuric acid solution in ultrapure (MilliQ) water at a flow rate of 0.6 mL/min, and the column temperature was at 80 °C. The injection volume was 10 μL and the total analysis time was 40 minutes for each sample. Under these conditions, xylose and furfural had approximate retention times of 11.5 and 35.5 minutes, respectively. The concentrations of the samples were quantified by integrating the detector response peak area, on the basis of calibration curves, developed by analyzing known external standards.

Modelling

The degradation rate of xylose was modelled using the following first-order rate expression [7]:

$$X(t) = X_0 e^{-(k_1+k_2)t} \quad (1)$$

Furfural formation and degradation to byproducts is expressed by the following first-order rate equation [7]:

$$F(t) = X_0 \left(\frac{k_1}{k_3 - k_1 - k_2}\right)\left(e^{-(k_1+k_2)t} - e^{-k_3 t}\right) \quad (2)$$

Where X is the xylose concentration (mM), X_0 is the initial xylose concentration (mM), F is the furfural concentration (mM), t is the time (s) and k_1, k_2, k_3 are the reaction rate constants (s^{-1}). k_1 is the reaction rate constant towards furfural production and k_2 is the reaction rate constant accounting for side reactions of xylose. k_3 is the furfural decomposition rate constant to byproducts. The values of the rate constants were estimated based on the experimental results by least square regression (95% confidence interval in parameter estimation).

Acknowledgements

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