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# Furfural Synthesis from D-Xylose in the Presence of Sodium Chloride: Microwave versus Conventional Heating

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We investigate the existence of specific/nonthermal microwave effects for the dehydration reaction of xylose to furfural in the presence of NaCl. Such effects are reported for sugars dehydration reactions in several literature reports. To this end, we adopted three approaches that compare microwave-assisted experiments with a) conventional heating experiments from the literature; b) simulated conventional heating experiments using microwave-irradiated silicon carbide (SiC) vials; and at c) different power levels but the same temperature by using forced cooling. No significant differences in the reaction kinetics are observed 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 a laboratory scale.

## Introduction

Furfural is a valuable platform chemical derived from renewable lignocellulosic biomass and agricultural surpluses. It has several uses, such as an extraction solvent for aromatic compounds or as a precursor for synthesizing specialty chemicals and liquid fuels.[1] As one of a 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 as 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% owing to the occurrence of side reactions that give rise to degradation products. New processes for furfural production can potentially circumvent the yield limitations, lower the energy requirements and minimize the large waste streams associated with the conventional process. In this way, the full potential of furfural as a biomass-derived intermediate could be exploited as a replacement for oil derivatives. Such intensified processes may be based on chemical activation through alternative energy forms (e.g., microwave heating). In many organic syntheses, microwave heating leads to reduced reaction times and higher reaction efficiency in aqueous systems compared to conventional heating. As a result, toxic organic solvents and catalysts may be replaced 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 and improve the selectivity and furfural yield. Another study investigated the effect of microwave heating on furfural yield using D-xylose in aqueous HCl solutions.[8] Microwave heating showed no effect on the reaction kinetics of xylose dehydration. However, several studies of the dehydration of C-5 and C-6 sugars to furfural and 5-hydroxymethylfurfural (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 the Appendix. 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, nonthermal microwave effects (i.e., increase in the number of ef-

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fective collisions or lowering of activation energy owing 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 for the dehydration of xylose in dilute aqueous acidic solutions was investigated and the results were compared to conventionally heated experiments reported in the literature. In addition, the existence of nonthermal 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 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.

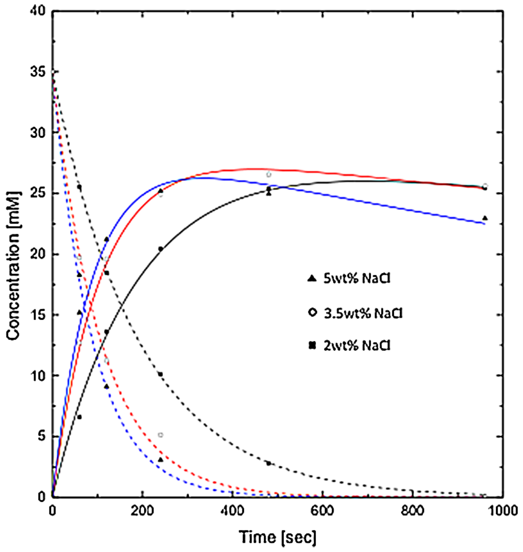

**Figure 1.** Evolution of xylose and furfural concentration over the course of the reaction at different NaCl concentrations (2, 3.5, and 5 wt %). The dashed and solid lines are the kinetic model estimations of the xylose and furfural concentrations, respectively (black: 2 wt %, red: 3.5 wt %, blue: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

## 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 dehydration reaction of xylose to furfural. Three different NaCl concentrations (2, 3.5 and 5 wt %, or 342, 599 and 856 mm, respectively), close to those 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 between the two modes of heating can be made. The results of these experiments in terms of the time evolution of the xylose and furfural concentrations are presented in Figure 1.

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 2, 3.5 and 5 wt %, 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. Conversely, prolonged residence times, particularly at higher NaCl concentrations, seem to slightly decrease the 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, Table 1) reveal that increasing salt concentration, at a 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 the NaCl concentration is increased from 2 to 3.5 wt %. However, when 5 wt % NaCl was used, $k_3$ almost doubled, similar to the comparison study, conducted under conventional heating. This suggests that the addition of NaCl might eventually enhance furfural degradation reactions, but only after a certain threshold NaCl concentration is exceeded. However, the rates of the furfural degradation reactions do not seem to have a straightforward relation with the $Cl^-$ concentration, according to the proposed kinetics.

The estimated rate constants of this work (Entries 1–3) are compared to the ones derived by Marcotullio and De Jong[7]

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

| Entry | NaCl [wt %] | $k_x$[a] $\times 10^{-4}$ [$s^{-1}$] | $k_1 \times 10^{-4}$ [$s^{-1}$] | $k_2 \times 10^{-4}$ [$s^{-1}$] | $k_3 \times 10^{-4}$ [$s^{-1}$] | Select.[b] [%] | 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.

under conventional heating (Entries 4–6). 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 variations in the residence time 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 dehydration reaction of xylose to furfural under dilute acidic conditions compared with conventional heating. This finding contradicts previous studies on the dehydration of C-5 and C-6 sugars, which claimed significant enhancement of the yield of furfural or 5-HMF in aqueous systems by using 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 dehydration reaction of xylose to furfural. 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 because of 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 performed two series of experiments using a different microwave reactor setup (Anton Paar Monowave 300) that allows for variation of the heating mode while keeping all the other process parameters similar. This is achieved by using a silicon carbide (SiC) vial to mimic conventional heating and a glass vial with the same geometry to study microwave heating. The SiC vial "shields" the reaction mixture from the microwave field but still enables high heating rates to be achieved because of the electromagnetic dissipation in the SiC vial wall itself (further discussion about the SiC vials is provided in the Supporting Information). In this case, instead of volumetric heat generation owing to microwave dissipation in the reactant mixture, the heating of the reaction mixture occurs conventionally, that is, 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. A temperature of 170 °C was selected to study the reaction at longer residence times (5–60 min). Therefore, 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. This enables a reliable comparison of microwave and conventional heating by keeping the rest of the process parameters similar. However, in the SiC vial, the temperature fluctuated in a cyclic manner. The vial wall of the SIC vial is heated directly, which leads to faster dynamics. Specifically, the temperature rises and drops faster as the microwave power increases and decreases, respectively. This causes the temperature controller to continuously over- and undershoot its reference, leading to an oscillatory temperature trend. Re-tuning 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 the dehydration reaction of xylose to furfural in dilute aqueous acidic solutions.[2] The calculated MKTs (169.83–169.85 °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 reaction kinetics of the dehydration of xylose to furfural. This finding contradicts previous publications that have compared microwave and conventional heating for xylose dehydration under acidic conditions with or without the presence of salts.[16,17] For example, Yang et al.[17] reported a 16 % increase in furfural selectivity when applying microwave heating

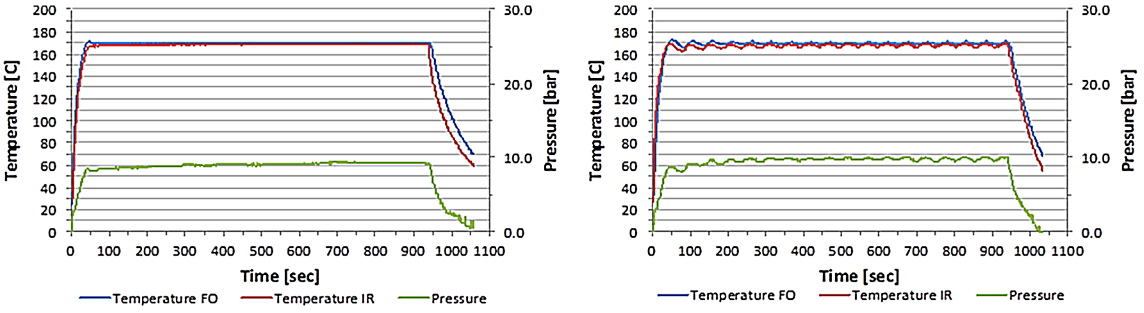

**Figure 2.** Left: Temperature and pressure profile of a typical glass vial experiment. Right: Temperature and pressure profile of a typical SiC vial experiment. Conditions: 50 mM xylose, 50 mM HCl, 500 mM NaCl, stirring speed of 600 rpm. The power control system was the same for both vials and was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

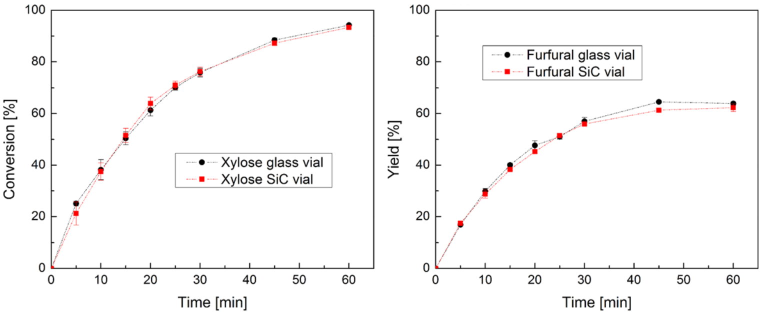

**Figure 3.** Analytical results (mean values with standard error bars) of the microwave (glass vial) and conventional (SiC vial) heating experiments at 170 °C (xylose: 50 mм, HCl: 50 mм, NaCl: 500 mм, stirring at 600 rpm) at different residence times. Left: Xylose conversion versus residence time for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

**Table 2.** Derived rate constants for conventional and microwave heating. Conditions: 50 mм xylose, 50 mм HCl, 500 mм NaCl, stirring speed of 600 rpm and a raction temperature of 170 °C. The derived values are very similar for the conventional and microwave heating.

| Vial | $k_x \times 10^{-4}$ [$s^{-1}$] | $k_1 \times 10^{-4}$ [$s^{-1}$] | $k_2 \times 10^{-4}$ [$s^{-1}$] | $k_3 \times 10^{-4}$ [$s^{-1}$] | Select.[a] [%] | Yield[b] [%] |
|---|---|---|---|---|---|---|
| Glass | 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 | 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.

instead of conventional heating under the same process conditions (140 °C, 45 min, $AlCl_3$ and NaCl in a water/tetrahydrofuran (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 could be a result of the increased heating rate in the microwave heated reaction, as the authors correctly suggest.[17] In another study,[10] the authors report that the application of microwaves to fructose dehydration in an aqueous HCl system results in a 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 if large concentrations of salts or ionic liquids are used (see further discussion in the Appendix). Ionic liquids couple very efficiently with microwaves, leading to heating rates that easily exceed 10 °C $s^{-1}$, which are difficult to reproduce using conventional heating methods. If the heating rates between various experimental setups cannot be kept similar, the use of a non-isothermal kinetic analysis might be more suitable, for example, by estimating an equivalent isothermal temperature.[19] In this study, we show 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.

## Increasing microwave power under constant temperature

To probe further into the existence of potential specific/nonthermal microwave effects on the dehydration reaction of xylose to furfural, the microwave power was varied, this time using only the glass vial (microwave heating). If the temperature profile remains unchanged as the applied microwave power is varied, any measured yield/selectivity differences can be attributed to specific/nonthermal 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 the simultaneous application of microwaves to the reaction vessel and forced external cooling using compressed air for the entire duration of the experiment. This type of experiment allows for the examination of the effect of microwave power alone at constant temperature, and consequently, for implicit verification of nonthermal microwave effects. According to the instrument readings of the forward-emitted microwave power, the high power (forced cooling) mode required approximately 5 times more power to maintain the temperature at 170 °C compared to the low power mode (no cooling). 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 were 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 30 min. However, the authors do not mention whether the same heating rate was maintained during these experiments. Because

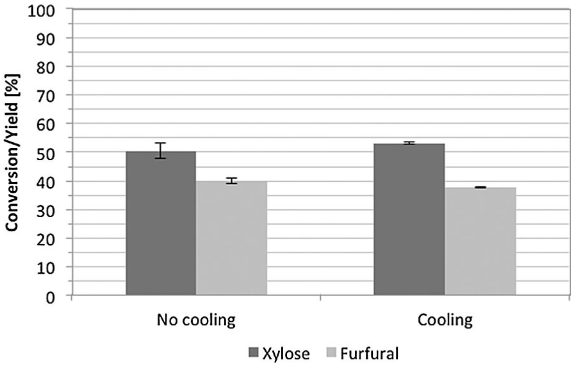

**Figure 4.** Xylose conversion and furfural yield without cooling (10 W) and with cooling (50 W). The results show that the applied microwave power has a negligible effect on the xylose dehydration and furfural yield. Conditions: 50 mм xylose, 50 mм HCl, 500 mм NaCl, stirring speed of 600 rpm, reaction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

ionic liquids were used in their work, the heating rate would probably be more readily affected by changes in the applied microwave power. If the reaction temperature in their high power experiment was attained faster, this would explain the higher yield/conversion. Another study of HCl-catalyzed fructose dehydration to 5-HMF under microwave irradiation showed that the 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.

### Comparison of energy consumption

We have shown that the two heating modes result in the same xylose conversion and furfural yield if the rest of the process conditions are kept the same. However, a critical evaluation of the process also requires an assessment of the energy consumption of the two heating modes. However, such precise assessment is difficult as 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, also accounting 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 Refs. [24, 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, as presented in Figure 5. At the initial stages of the experiment, high power is supplied to quickly reach the reaction temperature of 170 °C. In turn, the power is reduced to hold the temperature constant, balancing the thermal losses to the surroundings and the reaction heat. The same power control system was used to regulate the temperature using both vials and it is based on a proportional-integral-derivative (PID) controller built-in to the device. This system is designed to reach the reaction temperature as fast as possible, but also to prevent overshooting the temperature, and it leads to the same heating rate in both vials under 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, whereas 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 properties of the materials. The microwave-transparent borosilicate glass vial, which is used in the case of volumetric microwave heating, has a significantly lower density than the highly conductive SiC vial (2.23 g mL$^{-1}$ versus 3.1 g mL$^{-1}$, 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 during conductive heating owing to the higher mass of the SiC vial. The thermophysical properties of SiC and borosilicate glass are presented in Table S1.

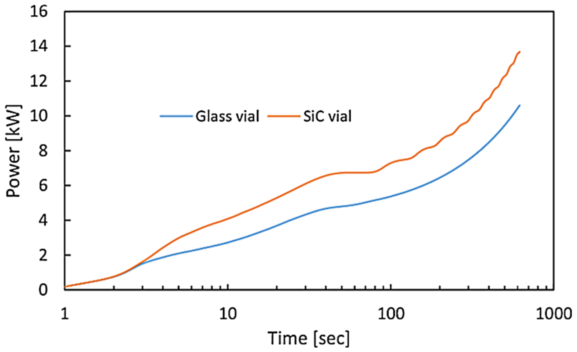

**Figure 5.** Cumulative forward microwave power supplied in glass and SiC reactor vials. The use of the SiC vial (simulated conventional heating) results in significantly higher power input compared to the glass vial (microwave heating) for the xylose dehydration reaction.

## Conclusions

In this work, the dehydration of xylose to furfural using microwave heating in the presence of NaCl at concentrations close to that of seawater concentrations was studied and compared with conventional heating. The highest furfural yield of 76% was obtained using 3.5 wt% NaCl at 200 °C, which led to complete xylose conversion in 440 s. The existence of nonthermal microwave effects was investigated in three ways: a) comparison of microwave heating experiments with literature results from 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 reaction mixture temperature. The results indicate that microwave heating does not have a prominent effect on the dehydration reaction kinetics under the examined conditions. However, microwave heating eliminates the need for 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. Furthermore, at a laboratory scale, the forward-emitted microwave power was 30% higher in the case of the denser SiC vials owing 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 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

### Discussion of studies on microwave-assisted dehydration of C-5 and C-6 sugars

A number of studies have been published comparing conventional and microwave heating for the synthesis of furfural and 5-HMF by dehydration of C-5 and C-6 sugars, respectively. Water is employed as a solvent in most of these studies, although ionic liquids have also been tested in some cases. Biphasic systems have also been used; in these systems, an organic water-immiscible phase [e.g., tetrahydrofuran (THF) or methylisobutylketone (MIBK)] is employed to extract the produced furfural or 5-HMF immediately, 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 that includes two first order reactions for the disappearance of the sugars (the reaction of the sugars to furfural or 5-HMF and the reaction of the sugars to undesired byproducts). In the case of combined hydrolysis of xylan or biomass and subsequent dehydration of the obtained pentoses, the latter is considered to be the rate-limiting step. The resulting yield of 5-HMF and furfural under microwave and conventional heating for these studies, as well as the temperatures and catalysts used, are summarized in Table 3 and Table 4. Because not all studies include the calculation of the 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 in which 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. For the sake of brevity, 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.

Comparison between the data in Table 3 and Table 4 is not straightforward owing to the diverse systems and conditions used by the various research groups. However, it is clear that contradicting results exist regarding the role of microwave heating in these studies. For instance, one study (Table 4, Entry 1) reported no significant difference in furfural yield using microwave heating and conventional heating with HCl as a catalyst.[8] Conversely, two other studies claimed a 16% increase in the yield of 5-HMF and a 14% increase in the yield of furfural from fructose and xylan, respectively, using HCl and microwave heating (Table 3, Entry 3 and Table 4, Entry 3).[10,16] Even more striking differences between microwave and conventional heating yields are reported if chloride salts or ionic liquids are added, with a study[13] reporting a striking 42% increase in the yield of 5-HMF from dehydration of fructose using $AlCl_3$ in water (Table 3, Entry 7).

To rationalize such yield improvements, several authors have proposed the existence of nonthermal microwave effects, such as lowering of the activation energy or an increase of the pre-exponential factor in the Arrhenius law owing to possible orientation effects of polar species in response to the electromagnetic field.[9,12,33] The existence of such effects has not been proven yet and is highly debated in the literature.

**Table 3.** Studies comparing microwave (micr.) and conventional (conv.) heating for the dehydration of hexoses to 5-HMF in terms of 5-HMF yield and sugar conversion.

| Entry | Feed (amt. [mM]) | Solvent | Catalyst (amt. [mM]) | $T$ [°C] | $t$ [min] | Yield [%] micr. | conv. | Convers. [%] micr. | conv. | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | glucose (500) | [BMIM]Cl | $CrCl_3 \cdot 6H_2O$ (50) | 120 | 5 | 67.0 | 45.0 | – | – | [9] |
| 2 | glucose (500) | [BMIM]Cl | $CrCl_3 \cdot 6H_2O$ (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*) | $Zr(O)Cl_2$ (10 mol%) | 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 | $CrCl_3 \cdot 6H_2O$ (50) | 80 | 2.5,[a] 180[b] | 85.0 | 57.0 | 93.0 | 84.0 | [14] |
| 7 | fructose (278) | Water | $AlCl_3$ (50 mol%) | 120 | 20,[a] 60[b] | 55.7 | 14.1 | – | – | [13] |

[a] Residence time with microwave heating. [b] Residence time with conventional heating.

**Table 4.** Studies comparing microwave (micr.) and conventional (conv.) heating for the dehydration of pentoses, pentosans, and biomass to furfural, in terms of furfural yield and sugar conversion.

| Entry | Feed (amt. [mM]) | Solvent | Catalyst (amt. [mM]) | $T$ [°C] | $t$ [min] | Yield [%] | | Convers. [%] | | 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 | $CrCl_3 \cdot 6H_2O$ (10 mg) | 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)+$Na_2MoO_4 \cdot 6H_2O$ (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*) | $AlCl_3 \cdot 6H_2O$ (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. The ~ indicates 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 a solution containing D-xylose, 50 mM HCl (constant) and an appropriate amount of 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 were performed under pressure owing to the solution vapor pressure at the reaction temperature (170 °C or 200 °C). Stirring was applied at 600 rpm using a magnetic stirring bar. At the completion of the experiment, 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 for 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 by more than 10 %.

### Variation of the NaCl concentration

This set of experiments was performed in the CEM Discover™ microwave reactor at 200 °C. The NaCl concentrations were varied at 2, 3.5, and 5 wt %, or 342, 599, and 856 mM, respectively The 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 optical fiber temperature sensor (FISO Technologies, Inc.).

### Comparison of microwave and conventional heating

These experiments were performed in the Anton Paar Monowave 300 microwave reactor at 170 °C, as this instrument allows for a direct comparison of conventional and microwave heating using the strongly absorbing SiC vials that are available with this device. The temperature was measured and controlled using the internal optical fiber (Ruby) sensor of the instrument and the built-in IR sensor measurements were also recorded to allow for comparison. For these experiments, the concentration of NaCl was kept at 500 mM.

### Analysis

The reaction products were analyzed using an HPLC apparatus equipped with a Rezex RHM-Monosaccharide column. The xylose concentration in the samples was measured using a Varian Pro Star 350 refractive index (RI) detector at 35 °C whereas 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$^{-1}$ and the column temperature was at 80 °C. The injection volume was 10 µL and the total analysis time was 40 min for each sample. Under these conditions, xylose and furfural had approximate retention times of 11.5 and 35.5 min, 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.

### Modeling

The degradation rate of xylose was modeled using the following first-order rate expression [Eq. (1)]:[7]

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

Furfural formation and degradation to byproducts is expressed by the following first-order rate expression [Eq. (2)]:[7]

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

where $X$ is the xylose concentration [mM], $X_0$ is the initial xylose concentration [mM], $F$ is the furfural concentration, $t$ is the time (s) and $k_1$, $k_2$ and $k_3$ 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 decomposition rate constant of furfural 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).

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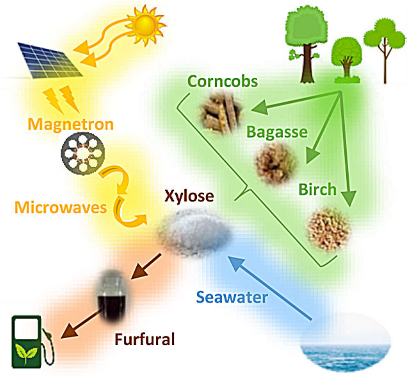
**Microwave adventure!** The dehydration of xylose to furfural in the presence of NaCl is investigated under microwave and conventional heating. The highest furfural yield of 76% is obtained using 3.5 wt% NaCl at 200 °C. Microwave heating does not show a prominent effect on the reaction kinetics, but lowers the energy consumption compared to simulated conventional heating (using SiC vials) at similar heating rates.



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### Furfural Synthesis from D-Xylose in the Presence of Sodium Chloride: Microwave versus Conventional Heating