# Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating

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In this paper we report a kinetic model for the dehydration of xylose to furfural in a biphasic batch reactor with microwave heating. There are four key steps in our kinetic model: (1) xylose dehydration to form furfural; (2) furfural reaction to form degradation products; (3) furfural reaction with xylose to form degradation products, and (4) mass transfer of furfural from the aqueous phase into the organic phase (methyl isobutyl ketone - MIBK). This kinetic model was used to fit experimental data collected in this study. The apparent activation energy for xylose dehydration is higher than the apparent activation energy for the degradation reactions. The biphasic system does not alter the fundamental kinetics in the aqueous phase. The organic layer, which serves as "storage" for the extracted furfural, is crucial to maximize product yield. Microwave heating does not change the kinetics compared to heating by conventional means. We use our model to describe the optimal reaction conditions for furfural production. These conditions occur in a biphasic regime at higher temperatures (*i.e.* 170 °C) and short reaction times. We estimate that at these conditions furfural yields in a biphasic system can reach 85%. At these same conditions in a monophase system furfural yields are only 30%.

## 1. Introduction

Furfural is a renewable biochemical produced from lignocellulosic biomass that has many different uses. It is considered an excellent solvent for many organic materials, such as resins and polymers. It is also a precursor to other desired compounds such as furfuryl alcohol (*via* hydrogenation), furan (*via* decarbonylation) and tetrahydrofuran (*via* hydrogenation of furan).[1] Likewise, it can serve as the starting material for the production of 5-hydroxymethylfurfural (by way of hydroxymethylation with formaldehyde).[2] A comprehensive assessment of the various applications for furfural was published by Bir Sain *et al.*[3] Furfural can also be used as a feedstock to make both gasoline, diesel or jet fuel. Huber *et al.* showed that furfural can serve as a precursor for production of liquid alkanes.[4] It has also been shown that methyl-tetrahydrofuran (MTHF, produced from hydrogenation of furfural) can directly serve as a gasoline blendstock.[5] The US-DOE has approved MTHF as a component of P Series type fuels.[6] It is highly likely that furfural demand will continue to grow as the price of petroleum based feedstocks continues to rise.

Furfural is produced by the dehydration of xylose. Xylose is primarily obtained from the depolymerization of hemicellulose found in lignocellulosic biomass. Furfural was first produced industrially in the beginning of the twentieth century by the Quaker Oats Company.[1] Today commercially, furfural is produced in an energy intensive process using batch or continuous reactors with a mineral acid (*i.e.* sulfuric acid) serving as the reaction catalyst.[1] Current production of furfural uses high pressure steam to heat the reaction. The steam also serves as an extractant to continuously remove the furfural from the reaction media. Downstream, the furfural-water vapor mixture is condensed and fed through a stripping column to form a furfural-rich vapor mixture which is then condensed. Due to the limited solubility of furfural in water (8.3% at 20 °C),[1] phase splitting occurs and the furfural-rich lower phase is separated in a decanter. Further dehydration and distillation take place to purify the commercial product. The water-rich upper layer is recycled from the decanter back to the stripper column as reflux.[1]

A number of kinetic studies on the production of furfural from xylose dehydration have appeared in the literature. The undesired products produced as a by-product with furfural are humins, which are a solid carbonaceous species.[7–10] Product furfural yields in industrial batch processes are between 45% and 50% due to formation of degradation products like humins.[11] It has been proposed that the humins are produced by a reaction between furfural and xylose.[12]

Several studies have suggested ways to inhibit the formation of humins and subsequently increase the furfural yield. One approach is to selectively extract the furfural from the aqueous solution into an organic phase. This technique has been reported to be the most promising in terms of yield and flexibility.[13] Trimble and Dunlop[14] originated this concept using ethyl acetate as the extracting media. Subsequent research included studies on various organic solvents such as methyl isobutyl ketone (MIBK).[15–17] Alternatives to organic solvents have been studied as well, such as supercritical carbon dioxide.[18] Recent work by Dumesic and co-workers[19,20] has shown viable promise in using a biphasic system. Dumesic and co-workers have demonstrated this concept with a variety of feedstocks, high feedstock

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concentration, and recycling of organic phase. Similarly, they have shown that applying a low-boiling solvent system, such as MIBK, is energetically more advantageous.

It has also been suggested that microwave heating may also increase the yield of dehydration products from carbohydrates.[21–23] Microwave-assisted organic synthesis was introduced over 20 years ago by Gedye *et al.*[24] This alternative heating method offers a means of rapid and efficient heating which minimizes temperature gradients within the reaction sample due to selective heating of the reaction media. In turn, microwave irradiation can result in accelerated reaction rates, higher yields and lower amounts of by-products for certain reactions.[25,26] Hence, this non-conventional energy source has since evolved into a very popular and useful technology in the world of organic chemistry. Recent studies have investigated the production of biomass-derived chemicals *via* microwave heating. Qi *et al.* studied the dehydration of fructose to produce 5-hydroxymethylfurfural (HMF) in a microwave-assisted reaction system in acetone-water media with ion-exchange resin as catalyst.[21] Under their reaction conditions, fructose conversion and HMF yields by microwave heating (91.7% and 70.3%, respectively) greatly surpassed those by sand bath heating (22.1% and 13.9%, respectively). The same authors also developed a process to efficiently convert fructose to HMF by combining the use of ion-exchange resins as catalysts with ionic liquid.[27,28] The application of ionic liquids in carbohydrates (lignocellulosic biomass) chemistry is relatively new and further studies combining these two fields are presented by Zakrzewska *et al.*[29] Additionally, Qi *et al.* also reported promising results when they studied the production of HMF from glucose and fructose catalyzed by $TiO_2$ and $ZrO_2$ under microwave irradiation.[22] When taking energy efficiency into consideration, Gronnow *et al.* have reported up to an 85-fold reduction in energy consumption on switching from a conventional oil bath to microwave-assisted set up for a heterogeneous Suzuki reaction.[30]

The objective of this study is to develop a mechanistically based kinetic model for the dehydration of xylose to furfural in a biphasic reactor system heated with microwave energy. MIBK was chosen as the extracting solvent. From this kinetic model we will study the effects of both microwave heating and how the biphasic solvent may influence the reaction chemistry. We will also use our kinetic model to show the conditions which will maximize furfural yields.

## 2. Experimental

### 2.1 Reaction kinetics measurements

Mono and biphase batch reactions were performed by way of microwave heating. Reactions were carried out in the Discover™ System (CEM Corporation) with an 80 mL batch reactor. Monophase reactions consisted of an aqueous solution of 10 wt% xylose (Acros Organics), unless otherwise stated. Biphasic systems consisted of 1 : 1 wt/wt aqueous solution and MIBK (Fisher Scientific). In all experiments, the acid concentration was constant at 0.1 M HCl (relative to aqueous phase). All solutions were mixed at a maximum constant rate using a magnetic stir bar. Temperatures in the reactor were measured by way of a fiber optic sensor. The reaction vessel was pressurized due to the vapor pressure of the solution at the defined reaction temperature. A dip tube was inserted into the reaction media for sampling purposes. Samples were immediately quenched with dry ice and filtered with a 0.2 μm syringe filter prior to analysis. Conventional reactions took place in a 100 mL Parr reactor with a sampling port. Sample handling was as described above.

### 2.2 Analysis

Each phase of the reaction mixture was analyzed separately by way of a Shimadzu© LC-20AT. Xylose was detected with a RI detector (RID-10A) and products were detected with a UV-Vis detector (SPD-20AV) at wavelengths of 210 and 254 nm. The column used was a Biorad© Aminex HPX-87H sugar column. The mobile phase was 0.005 M $H_2SO_4$ flowing at a rate of 0.6 mL $min^{-1}$. The column oven was set to 30 °C. Total organic carbon (TOC) measurements were performed with a Shimadzu© TOC-VCPH Analyzer. Any experimental errors associated with the measurements reported below pertain solely to the calibraton technique used to quantify the concentrations of the reactants and products.

### 2.3 Modeling

Experimental data were collected and used to compare with the proposed kinetic model to estimate rate parameters of the reaction paths in a xylose dehydration system.

The kinetic model for the overall reaction path was a set of coupled nonlinear ordinary differential equations (ODEs) and rate constants were correlated by the Arrhenius equation to include temperature dependency. A complete set of concentration data of reactants and products at different temperatures was used to numerically adjust the rate parameters of the overall governing reaction equations. Matlab and Athena Visual Studio v14.0 were used for the numerical integration of ODEs and parameter estimations.

In the model, it was assumed that the furfural decomposition occurred only in the aqueous phase and was not significantly dependent on the concentration of xylose and other derived products. Separate experiments with 0.16 M furfural (1.5 wt%) as feedstock were executed in order to determine the rate parameters for furfural decomposition. A value of 0.74 M xylose (10 wt%) was used as the initial conditions of rate equations in the numerical integration and the sum of absolute errors between estimated and observed values at experimental sampling points was minimized to find the optimal prediction for the rate of xylose decomposition and furfural formation.

All kinetic data at temperatures between 130 and 170 °C (5–15 points for each temperature) obtained from monophase experiments were included in the kinetic parameter estimation. Rate parameters determined from monophase data were used further to estimate the furfural distributions between organic and aqueous layers in the biphasic system.

## 3. Results

### 3.1 Comparison of microwave and conventional heating

Initial tests were performed to compare the efficiency of the reaction with microwave and conventional heating at three different temperatures as shown in Fig. 1. This figure reveals that microwave heating slightly enhanced xylose decomposition, as well as furfural yield. Nonetheless, the results obtained with both heating sources were comparable to each other.

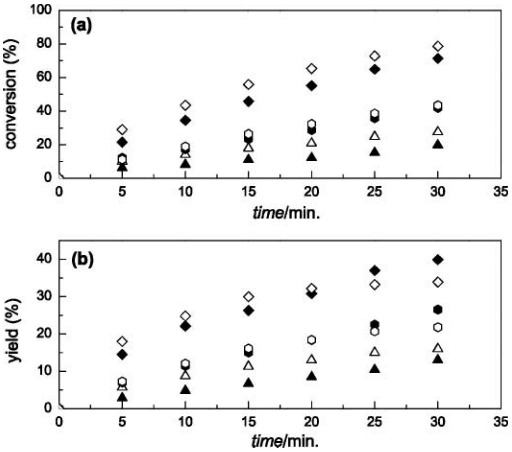

**Fig. 1** Comparison between microwave (open symbols) and conventional (closed symbols) heating in a monophase system for 10 wt% xylose and 0.1 M HCl. *T*/°C = 150 (▲), 160 (●), 170 (◆). (**a**) xylose conversion; (**b**) furfural yield.

### 3.2 Effect of xylose concentration

The effect of xylose concentration on the dehydration of xylose was studied at a temperature of 160 °C as shown in Fig. 2. The furfural yield was found to be independent of the xylose concentration. However, the xylose degradation rate increased with increasing xylose concentration. The furfural selectivity also showed dependency on the xylose concentration as shown in Fig. 3. The furfural selectivity decreased with increased xylose (and furfural) concentration. This coincides with the concept stated earlier that by-products (humins) could be formed from a reaction between xylose and furfural.[12] The remaining portion of this study was performed with a xylose concentration of 10 wt%.

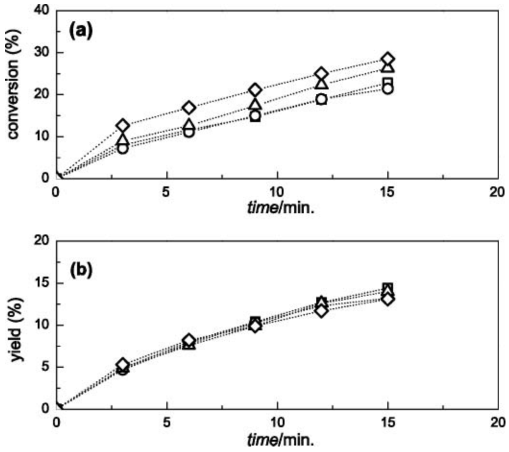

**Fig. 2** Effect of initial xylose concentration on (**a**) xylose conversion and (**b**) furfural yield in a monophase system at 160 °C and 0.1 M HCl. $[X]_o$ (wt%) = 1 (□), 5 (○), 10 (△), 15 (◇).

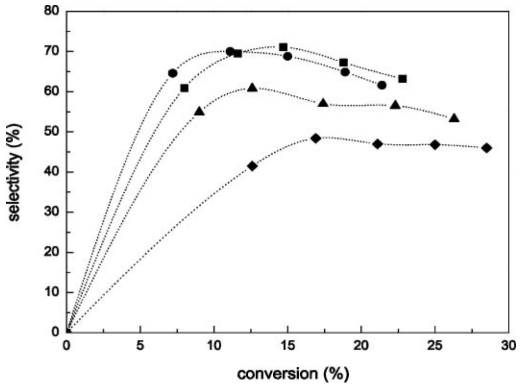

**Fig. 3** Effect of initial xylose concentration on furfural selectivity in a monophase system at 160 °C and 0.1 M HCl. $[X]_o$ (wt%) = 1 (■), 5 (●), 10 (▲), 15 (◆).

### 3.3 Xylose dehydration and furfural degradation in a monophase system

Dehydration of xylose was performed in a single (aqueous) phase at temperatures between 130–170 °C. In order to measure the decomposition rate of furfural in the aqueous phase, experiments were also performed with furfural as the feedstock (1.5 wt%) in acidic media (0.1 M HCl). Reaction times of up to 8 hrs were required to detect any considerable decomposition of furfural. This finding also coincides with previous investigations[9,31] which found furfural degradation to be relatively slow compared to xylose dehydration. It is notable to mention that quantifiable amounts of formic acid were also detected as a by-product of this reaction. Williams and Dunlop suggested that this was a result of hydrolytic fission of the furfural aldehyde group.[7,31]

### 3.4 Xylose dehydration in a biphasic system

Biphasic experiments were performed by employing two immiscible liquid phases in the reactor. A 1 : 1 wt/wt ratio of MIBK to aqueous xylose solution was used. The MIBK served as the upper phase and the aqueous xylose solution constituted the bottom phase. The xylose was only soluble in the aqueous phase. Biphasic studies with MIBK were conducted at temperatures between 140–160 °C. The rate of xylose decomposition was found to be higher in the monophase system compared to the biphasic as shown in Fig. 4(a). Additionally, as expected, the overall furfural yield in the biphasic system surpassed the values obtained in the monophase system (Fig. 4(b)).

The furfural distribution ratio $[F]_{org}/[F]_{aq}$ was also calculated and plotted as a function of reaction time as shown in Fig. 5. This ratio did not significantly vary with temperature. All temperatures approached a $[F]_{org}/[F]_{aq}$ value of 7.1 as the time of reaction increased. Consequently, separate extraction experiments showed the furfural distribution to be constant and equal to 7.1. These tests were performed with furfural in a biphasic system at different temperatures. Furfural aqueous solutions (with no acid) were mixed with MIBK for a fixed time. The two phases were then left to phase separate and samples were taken at the mixing temperature.

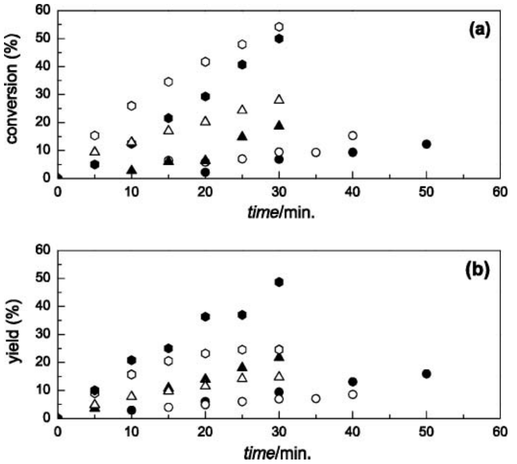

**Fig. 4** Effect of monophase (open symbols) and biphase (closed symbols) reaction systems on (**a**) xylose conversion and (**b**) furfural yield for 10 wt% xylose and 0.1 M HCl. Biphase system consisted of 1 : 1 wt/wt aqueous solution and MIBK. *T*/°C = 140 (●), 150 (▲), 160 (⬢).

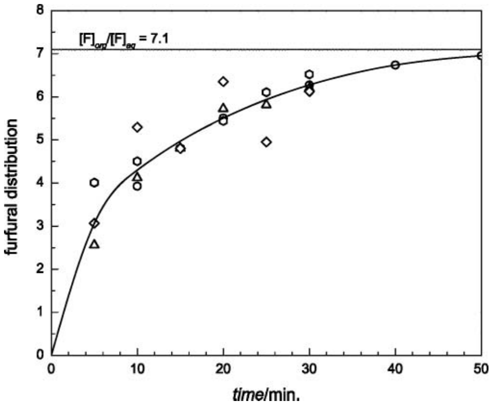

**Fig. 5** Effect of temperature on furfural distribution between organic and aqueous phase for 10 wt% xylose and 0.1 M HCl. Biphase system consisted of 1 : 1 wt/wt aqueous solution and MIBK. $[F]_{org}$ and $[F]_{aq}$ denote furfural concentrations in the organic and aqueous phase respectively. *T*/°C= 140 (○), 150 (△), 160 (⬡), 170 (◇).

### 3.5 Kinetic model for xylose dehydration in a monophase system

The adopted reaction scheme for monophase dehydration of xylose is shown below in Scheme 1. All three of these reactions are irreversible. Xylose can undergo two parallel reactions eqn (1) and eqn (2). The first reaction is the dehydration of xylose to produce furfural. The second reaction involves the reaction of xylose and furfural to produce humins and other decomposition products. The third reaction is the degradation of furfural to produce humins. Reaction 1 is reported to be pseudo first order with respect to xylose.[9,10,31,32] This coincides with the kinetic data we reported in Fig. 2(b). Furfural decomposition as depicted by eqn (3) is found to be first order with respect to furfural. This is also similar to previous studies.[7,8,10,32] Reaction 2 is first order with respect to xylose and first order with respect to furfural.

$$\mathrm{X} \xrightarrow[k_1]{} \mathrm{F} + 3\mathrm{H_2O} \tag{1}$$

$$\mathrm{X} + \mathrm{F} \xrightarrow[k_2]{} \mathrm{D_1} \tag{2}$$

$$\mathrm{F} \xrightarrow[k_3]{} \mathrm{D_2} \tag{3}$$

$$\mathrm{X} \equiv \text{xylose};\ \mathrm{F} \equiv \text{furfural};\ \mathrm{D_1}, \mathrm{D_2} \equiv \text{decomposition products.}$$

**Scheme 1** Xylose dehydration in a monophase system.

Other researchers have suggested that reaction 2 takes place between furfural and a xylose intermediate.[31,32] Root *et al.* based this claim by citing that the quantity of furfural added to a xylose solution did not affect its disappearance rate.[32] However, as shown in Fig. 4(a), there is a visible distinction between xylose disappearance in the monophase and biphasic systems. Qi *et al.*[9] postulated a side reaction which involves xylose; however it was defined as a unimolecular decomposition reaction.

The rate equations for xylose consumption and furfural production can be written as:

$$\frac{d[\mathrm{X}]}{dt} = -k_1'[\mathrm{X}][\mathrm{H_3O^+}] - k_2'[\mathrm{X}][\mathrm{F}][\mathrm{H_3O^+}] \tag{4}$$

$$\frac{d[\mathrm{F}]}{dt} = k_1'[\mathrm{X}][\mathrm{H_3O^+}] - k_2'[\mathrm{X}][\mathrm{F}][\mathrm{H_3O^+}] - k_3'[\mathrm{F}][\mathrm{H_3O^+}] \tag{5}$$

All three reactions are a function of the acid catalyst concentration and their rate constants have the appropriate dimensions. All experimental data for the monophasic reactions were fitted to the model to estimate the three rate parameters. The best correlated values with their standard errors are tabulated in Table 1. Fig. 6 shows the experimental data in a monophase reacting system with the fitted model.

The furfural decomposition data is plotted in Fig. 7 along with its kinetic model fit. The disappearance rate was relatively slow and was observed to follow a first order decomposition. TOC measurements were performed to predict the overall carbon balance. We accounted for over 90% of the carbon. This balance does not include formic acid which was detected as a by-product and not quantified. The correlated values for activation energy and pre-exponential factor for reaction 3 in our kinetic model are listed in Table 1. These results are consistent with previously reported values for unimolecular furfural degradation in a single phase.[7,9]

### 3.6 Kinetic model for xylose dehydration in a biphasic system

The suggested reaction scheme for dehydration of xylose in a biphasic system is shown in Fig. 8. This one is similar to our previously proposed scheme for a monophase system with

**Table 1** Estimated kinetic parameters for xylose dehydration in a monophase system

| | $\log_{10}A$ | $E_A$/kJ mol$^{-1}$ |
|---|---|---|
| [b]$k_1$(min$^{-1}$) | 13.17 ± 0.72[a] | 123.91 ± 6.00 |
| [b]$k_2$(M$^{-1}$ min$^{-1}$) | 7.63 ± 1.97 | 72.47 ± 16.28 |
| [b]$k_3$(min$^{-1}$) | 5.44 ± 1.18 | 67.58 ± 9.66 |

[a] 95% confidence interval in parameter estimation. [b] 1st and 2nd order rate parameters that are lumped with acid concentration; $k_n = k'_n\,[\mathrm{H_3O^+}]$.

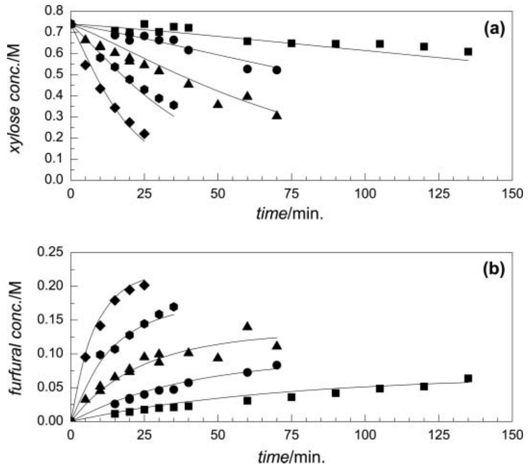

**Fig. 6** Kinetic model fit for (**a**) xylose decomposition and (**b**) furfural formation in a monophase system for 10 wt% xylose and 0.1 M HCl. $T/°\mathrm{C}$ = 130 (■), 140 (●), 150 (▲), 160 (⬢), 170 (◆); model prediction (—).

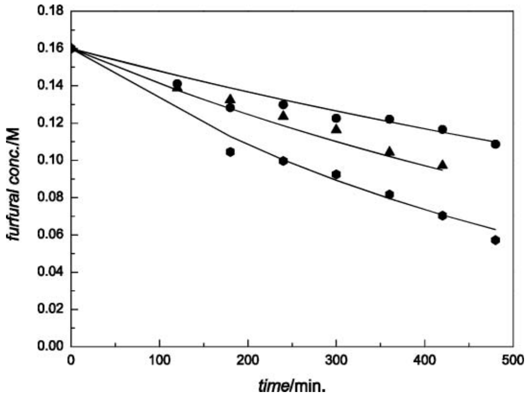

**Fig. 7** Kinetic model fit for furfural decomposition in a monophase system for 1.5 wt% furfural and 0.1 M HCl. $T/°\mathrm{C}$ = 140 (●), 150 (▲), 160 (⬢); model prediction (—).

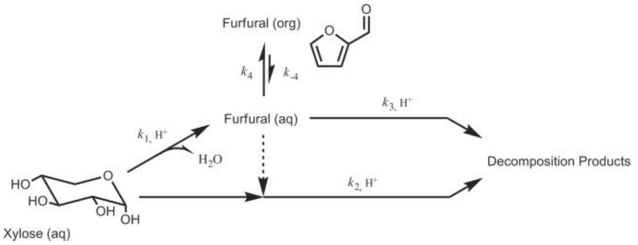

**Fig. 8** Overall reaction scheme including furfural extraction to the organic phase in a biphasic system.

the exception that the furfural can be extracted into a separate organic phase.

Based on experimental observation, a kinetic model was established to depict xylose decomposition in the two-phased system, as shown in Scheme 2.

In this model estimation, the same values estimated from monophase experiments were used for the rate parameters of $k_1$, $k_2$, and $k_3$. Reaction 4 depicts furfural transport between the organic and aqueous layers. The mass transfer coefficients, $k_4$ and $k_{-4}$, were assumed constant values, as the furfural distribution between aqueous and organic phases was considered to be constant and not temperature dependent of the Arrhenius equation under the reaction conditions (Table 2). In the modeling, it was assumed that the furfural distribution was solely dependent on the bidirectional mass transfer rates, and other kinetics or paths were not disturbed by thermodynamic instability.

**Table 2** Estimated mass transfer coefficients derived for a biphasic system

| | |
|---|---|
| $k_4/k_{-4}$ | 7.1 |

$$X(aq) \xrightarrow[k_1]{} F(aq) + 3H_2O \tag{6}$$

$$X(aq) + F(aq) \xrightarrow[k_2]{} D_1 \tag{7}$$

$$F(aq) \xrightarrow[k_3]{} D_2 \tag{8}$$

$$F(aq) \xrightarrow[k_4]{} F(org) \tag{9}$$

$$F(org) \xrightarrow[k_{-4}]{} F(aq) \tag{10}$$

**Scheme 2** Xylose dehydration in a biphase system.

Additional tests showed that the organic phase served solely as "storage" for furfural where no additional decomposition reactions occurred. This is most likely due to the negligible solubility of the acid catalyst in this phase. The organic phase only contained furfural and MIBK.

The overall rate equations for a biphasic system are:

$$\frac{d[\mathrm{X}]}{dt} = -k_1'[\mathrm{X}][\mathrm{H_3O^+}] - k_2'[\mathrm{X}][\mathrm{F}]_{aq}[\mathrm{H_3O^+}] \tag{11}$$

$$\frac{d[\mathrm{F}]_{aq}}{dt} = k_1'[\mathrm{X}][\mathrm{H_3O^+}] - k_2'[\mathrm{X}][\mathrm{F}]_{aq}[\mathrm{H_3O^+}] - k_3'[\mathrm{F}]_{aq}[\mathrm{H_3O^+}] - k_4[\mathrm{F}]_{aq} + k_{-4}[\mathrm{F}]_{org} \tag{12}$$

$$\frac{d[\mathrm{F}]_{org}}{dt} = k_4[\mathrm{F}]_{aq} - k_{-4}[\mathrm{F}]_{org} \tag{13}$$

When the rates of mass transfer are much faster than the rate of furfural formation, their parameters can be related by the distribution coefficient of furfural at equilibrium:

$$k_4/k_{-4} \approx K_{\mathrm{eq}} = \frac{[\mathrm{F}]_{org}}{[\mathrm{F}]_{aq}} = 7.1 \tag{14}$$

The best fit was achieved when log($k_4$) was approximately 7.4, which is much larger than the other kinetic parameters ($k_4$ or $k_{-4} \gg k_1$, $k_2$, or $k_3$).

Fig. 9 exhibits the biphasic model used to fit the experimental data for xylose decomposition and furfural formation. The model shows a good fit for all temperatures apart from 170 °C. The model underestimates the xylose degradation rate at this temperature, as well as the furfural presence in the organic phase.

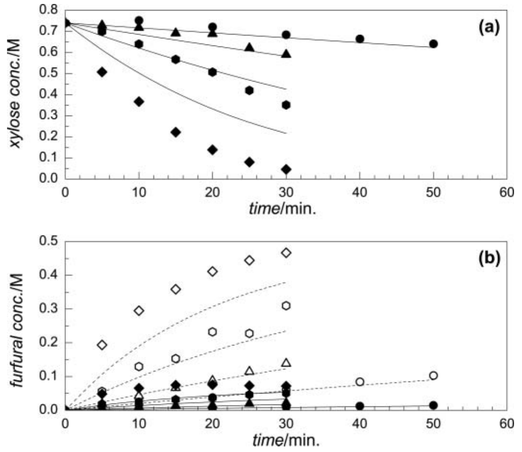

**Fig. 9** Kinetic model fit for (**a**) xylose decomposition and (**b**) furfural formation in a biphase system for 10 wt% xylose and 0.1 M HCl. The biphase system consisted of 1 : 1 wt/wt aqueous solution and MIBK. *T*/°C = 140 (●), 150 (▲), 160 (⬢), 170 (◆). Open and closed symbols denote furfural concentrations in the organic and aqueous phases respectively. Dashed (---) and solid (—) lines represent model predictions for furfural in the organic and aqueous phases respectively.

## 4. Discussion

### 4.1 Kinetic model calculations

The apparent rate parameters introduced here allow for theoretical calculations of furfural yield in both a single and two-phase system. Fig. 10 plots the calculated values at various temperatures as a function of reaction time for both systems. These results show that a biphasic reaction system is essential to maximize the yield of furfural. The optimal yield also occurs at high temperatures and short reaction times. The kinetic parameters in Table 1 show that the dehydration of xylose to furfural is the highest activation energy step. As this is the desired reaction, a higher yield is expected at increased temperatures since the ratios of $k_1$ to $k_2$ and $k_1$ to $k_3$ increase with elevated temperatures. Likewise, shorter reaction times are preferred to maximize the furfural yield. Implementing a biphasic system presents a distinct advantage with a theoretical furfural yield of 85% at 170 °C compared to a single aqueous phase system which yields only 30% at the same temperature.

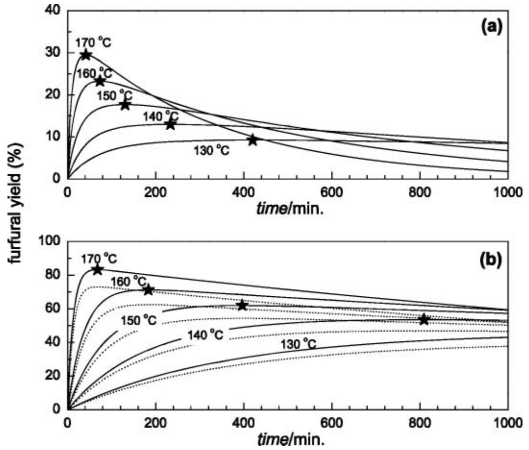

**Fig. 10** Calculated furfural yield as a function of reaction time and temperature for (**a**) a monophase and (**b**) a biphase system at 10 wt% xylose and 0.1 M HCl. Biphasic system consisted of 1 : 1 wt/wt aqueous solution and MIBK. Dotted lines (···) represent furfural yield in the organic phase. Solid lines (—) represent total furfural yield. Symbols (★) represent maximum furfural yields.

### 4.2 Biphasic model at high temperatures

The biphasic model shows an inconsistency with the experimental data at 170 °C. The experimental data shows an unpredicted increase in xylose decomposition, as well as an increased presence of furfural in the organic phase. Hence, a modified kinetic model is necessary to accurately represent the biphasic system at higher temperatures. An additional kinetic term(s) which is prominent at higher temperatures is required to explain this behavior. One of the simplest, for instance, would be an additional term that depicts the decomposition of xylose to produce furfural directly in the organic phase. This would explain the observed rate increase of xylose decomposition and the elevated furfural concentration in the organic layer. However, this concept is difficult to realize, for xylose is not found in the upper phase under these reaction conditions. Nonetheless, it would be reasonable to conceive that this term describes the chemistry that occurs in the interfacial region between the aqueous and organic phases.

For clarification purposes, a comparable term was indeed proposed to the existing kinetic model and the revised version appeared to be consistent with the experimental data at all temperatures. The activation energy for this additional theoretical term was found to be threefold of $E_{A_1}$. Hence, this high energy barrier step becomes relevant only at higher temperatures. Pressure limitations in the reaction vessel prohibited further studies at elevated temperatures to attempt to validate this hypothesis. Furthermore, sensitivity analysis has shown a minor deviation in the calculated rate parameters for the biphasic system compared to the monophase values. This difference is within the estimated error, but an improvement in the model fit for 170 °C was observed.

### 4.3 Microwave effect on rate parameters

The kinetic parameters derived from our model (Table 1) are in good agreement with those obtained in previous studies that used conventional heating methods. The literature reports activation energies for xylose dehydration in the range 111 to 125 kJ mol$^{-1}$.[9,10,33] Values for furfural degradation range from 48 to 90 kJ mol$^{-1}$.[7–10] These comparable rate parameters confirm the lack of any considerable effects arising from microwave heating. Our finding is contrary to others who report enhanced results due to microwave irradiation.[21,22] A plausible cause for the discrepancy lies in the nature of the catalyst. The enhanced microwave effects were reported for reaction systems with solid acid catalysts. Accordingly, it has been emphasized that microwave absorption at the solid interface can advantageously influence the overall reaction kinetics.[34]

### 4.4 Kinetic model comparison to proposed mechanism

Antal *et al.* proposed a detailed mechanism of the formation of furfural from xylose.[35] According to this work, it can be assumed that the rate-determining step for xylose dehydration is the formation of the protonated xylopyranose intermediate (step no. 5 in Scheme 2[35]). To determine the credibility of our kinetic model, a comparison was made between their reported rate constant of step no. 5 and our rate constant $k'_1$ calculated at their reaction temperature of 250 °C. The calculated rate constant from our model (1.04 $M^{-1}$ $s^{-1}$) was found to be comparable to that cited in the literature by Antal *et al.* (5.58 $M^{-1}$ $s^{-1}$). Different reaction conditions (temperature, catalyst) are a probable cause for the slight dissimilarity.

## 5. Conclusion

In this paper we have developed a kinetic model for the dehydration of xylose in a biphasic reaction system using microwave heating. Microwave heating shows no prominent effect on the dehydration chemistry and therefore it is likely that our model can also be valid for conventional heating. Our kinetic model involves three reactions and a phase equilibrium relationship. They consist of xylose dehydration to form furfural, formation of degradation products *via* reaction of xylose with furfural, and furfural degradation. In a two-phase system, the furfural is extracted into the organic phase.

The proposed kinetic model is consistent with the experimental data and can be used for both monophase and biphasic systems. An inconsistency exists at 170 °C for the two-phase system and further studies at elevated temperatures are necessary to deduce the source of this discrepancy.

The biphasic system does not alter the fundamental kinetics of its monophase analogue. The only role of the second phase is to extract the furfural.

Unequivocally, it has been demonstrated that a two-phase system is favorable with the calculated product yield being more than two-fold of that obtained in the single aqueous phase system. Theoretical calculations have allowed us to recognize optimal conditions to achieve maximum furfural yield in this system. These maximum yields are obtained in a biphasic system, at high temperature, and short reaction times. Furfural yields of over 80% should be achieved in this type of system which is significantly higher than industrially obtained furfural yields of 45–50%.[11]

Equilibrium between furfural in the organic and aqueous phases is not sustained throughout the reaction. The mass transfer between the phases is limiting compared to furfural formation. As the reaction proceeds and the rate of product formation decreases, the relative rate of mass transfer consequently intensifies and the system approaches phase equilibrium. This indicates that reactor design is also critical in obtaining high yields of furfural. This study demonstrates that furfural production can be significantly more efficient compared to the current industrial process.

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