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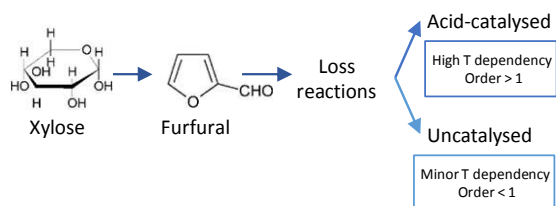
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Kinetics of furfural degradation in a formic acid catalyst was studied, and it was found out that the overall order of the reaction changes with the amount of acid catalyst.



## ARTICLE

## Kinetics of furfural destruction in formic acid medium

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Furfural is one of the key chemicals produced from hemicellulose pentosans in acidic conditions. In the same conditions, furfural also undergoes degradation reactions leading to yield loss. In this study, the kinetics of furfural degradation in formic acid medium containing 2 to 30% (w/w) formic acid and 0.05 to 0.16 mol/L furfural was studied in small batch reactors. The reaction temperatures were 160, 180, and 200°C. The results showed that the overall order of the reaction changes with the amount of formic acid catalyst: in high acid concentration (30%) the apparent order of reaction is over one and in low acid concentration (2%) the order of reaction is below one. The proposed kinetic model, which includes an uncatalysed and an acid-catalysed term, is capable of estimating this behaviour. The model and findings presented in this study can support the optimisation of furfural production conditions.

### Introduction

A biorefinery is a concept where multiple products are manufactured from renewable feedstock. Furfural has the potential to become one of the platform chemicals for the production of fuels and chemicals in a sustainable lignocellulosic biorefinery<sup>1</sup>. In the production process, biomass hemicellulose is first hydrolysed to monomeric sugars. Then furfural is formed by the dehydration of pentoses in acidic conditions. In the same conditions, furfural also undergoes side reactions, resulting in yield loss. These reactions can be divided into furfural degradation and furfural condensation, where furfural degradation includes self-polymerisation (furfural resinification)<sup>2</sup>, ring opening<sup>2</sup>, and decomposition<sup>3</sup> reactions, and furfural condensation denotes reactions with sugar intermediates. Furfural yields could be improved by removing furfural from the catalytically active aqueous phase soon after it forms<sup>4</sup>. Industrial furfural processes widely use steam stripping to remove furfural from the reactor and also partly to prevent furfural loss reactions. This leads to a problem with dilute water-furfural-acid solutions<sup>4</sup>. One option for steam stripping is the use of a two-phase system, where an organic phase, in which furfural is soluble but the water and acid catalyst are not, is introduced to the reactor. Using this system, good results have been achieved with both homogeneous<sup>5,6</sup> and heterogeneous catalysts<sup>6,7</sup>.

While new reactor systems, like biphasic reactors, can offer a great solution to the furfural degradation problem, it is still relevant to deepen the knowledge of furfural degradation in acidic conditions. Although the first kinetic studies of furfural degradation date back to the 1940s<sup>3</sup>, the reaction pathways

leading to furfural losses are still unclear<sup>8</sup> and comprehensive knowledge of furfural degradation is lacking<sup>9,10</sup>. The kinetic studies carried out so far mostly use mineral acid catalysts, sulphuric acid<sup>3,11,12</sup> or hydrochloric acid<sup>3,13</sup> and in one or two furfural concentrations with only small variation. In most cases, first-order kinetics fit the results well, even if there have been notifications that the reaction order might differ from unity<sup>9,10</sup>. In studies based on only one initial concentration of either furfural or acid catalyst, some of the phenomena that occur might not be seen. Therefore, more extensive studies concerning furfural loss reactions are needed. Such information would be beneficial in designing more optimal furfural production processes.

Mineral acids are effective and widely used furfural production catalysts. However, organic acids would be an attractive option especially if furfural production is integrated to organosolv techniques<sup>14,15</sup>. Formic acid is proved to be an effective catalyst for biomass processing.<sup>16,17</sup> It is released from hemicellulose in the furfural production process. Thus, it is readily available in the process. Furthermore, formic acid could be recovered from reaction medium by thermal operation and waste producing neutralisation linked to mineral acids could be avoided.

In this paper, the furfural degradation reactions in aqueous acid medium, containing 2 to 30% (w/w) of formic acid, were examined using three different initial furfural concentrations (0.05, 0.10, and 0.16 mol/L). The temperature used was 160–200°C and the time varied from a few minutes to several hours. In the same conditions, furfural can be produced effectively (yield up to 60%) from xylose<sup>18</sup>. Furthermore, a kinetic model for furfural degradation is proposed in the present study. This

study also gives insights into possible furfural degradation mechanisms.

## Materials and methods

### Materials

Furfural and formic acid were purchased from Acros Organics and Riedel-de Haën, respectively. The formic acid was used without further purification. The furfural was distilled at atmospheric conditions before use. Initial solutions with different amounts of furfural (0.05, 0.10, or 0.16 mol/L) in 2, 10, or 30% (w/w) formic acid were prepared before the experiments. The pH of the formic acid solutions were 2.0, 1.5 and 0.89, respectively. MilliQ water was used in the solutions.

### Experimental

The experiments were carried out using zirconium batch reactors with a volume of approx. 40 mL. The temperature of the liquid in each reactor was monitored using a PTFE-coated K-type thermoelement sensor which was inserted into the reactor through a zirconium cap. Temperature data with respect to time was recorded. A two-oven system, described previously<sup>18</sup>, was used for fast heating and steady temperature control. The experimental procedure was the same as reported previously, except for the preheating which was done until the temperature inside the reactor was a few degrees below the desired reaction temperature. The reaction times used varied from 5 to 274 minutes. The furfural and formic acid concentrations in the experimental samples were analysed by HPLC and the pH was measured using the same methods as earlier<sup>18</sup>.

### Conversion calculations

The conversion of furfural,  $X_F$  (%), is calculated as follows:

$$X_F = 100([F_0] - [F])/[F_0], \quad (1)$$

where  $[F_0]$  is the initial furfural concentration and  $[F]$  is the furfural concentration after the reaction.

### Modelling

When modelling reaction kinetics, the amount of catalyst has to be taken into account. Furfural destruction is an acid-catalysed reaction. The acidity of a solution is caused by the release of hydrogen ions in the dissociation reaction of acid, which is temperature-dependent. The temperature dependence of the formic acid dissociation constant,  $K_a$ , can be taken into account in the kinetic modelling using the equation 2 obtained by Kim et al.<sup>19</sup>, as in earlier studies<sup>17,18</sup>:

$$\ln K_a = -57.528 + 27739/T + 9.1232 \ln T, \quad (2)$$

where  $T$  is temperature in K.

The initial formic acid concentration,  $[HCOOH]_0$ , was measured by HPLC and the hydrogen ion concentration at the reaction temperature was calculated using equation 2 and

equations 3-5 based on the equilibrium of dissociation reaction and material and ion balances of the system.

$$[H^+] + [HCOO^-] - [HCOOH] - K_a = 0 \quad (3)$$

$$[HCOOH]_0 - [HCOOH] - [HCOO^-] = 0 \quad (4)$$

$$[H^+] - [HCOO^-] = 0 \quad (5)$$

where  $[H^+]$ ,  $[HCOO^-]$  and  $[HCOOH]$  are concentrations (mol/l) in the equilibrium state of dissociation.

In the kinetic modelling, a total of 65 experiments were employed. The model equations were implemented in the MATLAB environment. The rate constants were represented in the Arrhenius form and reparameterisation was used to reduce the correlation between the activation energy and the pre-exponential factor. The equation for the reparameterised rate constant is shown in equation 6.

$$k = k' e^{\left[ \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]}, \quad (6)$$

where  $k'$  is the pre-exponential factor,  $T$  is the reaction temperature in K,  $E$  is the activation energy, and  $T_0$  is the reference temperature = 165°C (in K).

The recorded temperature data with respect to time was used in estimation. The system of ordinary differential equations was solved numerically by ode15s, a solver for stiff systems. The kinetic parameters were estimated using nonlinear regression analysis. The estimation was done using the Levenberg–Marquardt algorithm available within the MATLAB lsqcurvefit function. In the estimation, the experimental results were weighted to prevent the dominance of high concentrations, i.e. the experiments with initial concentrations of 0.05, 0.10, and 0.16 mol/L, obtained weighting coefficients of 3, 1.5 and 1, respectively. The quality of the model was monitored by multiple methods: residuals, correlation matrices, contour plots of parameter pairs, and figures showing the objective function as a function of each parameter value.

## Results

The experimentation to investigate furfural degradation in formic acid was performed using three different acid concentrations (2, 10, and 30% (w/w)) and three initial furfural concentrations (0.05, 0.1, and 0.16 mol/L). The furfural conversions were between 2 and 52%. The experimental data is illustrated in Figure 1.

Figure 1 shows differences in furfural degradation behaviour with respect to initial furfural and formic acid concentrations. Figure 1a presents the experiments conducted in 2% formic acid. It can be seen that in low acid concentration (2%), furfural degradation increases when the low initial furfural concentration (0.05 mol/L, white markers) is used compared to the high initial furfural concentration (0.16 mol/L, black markers), which indicates that the reaction order is below one.

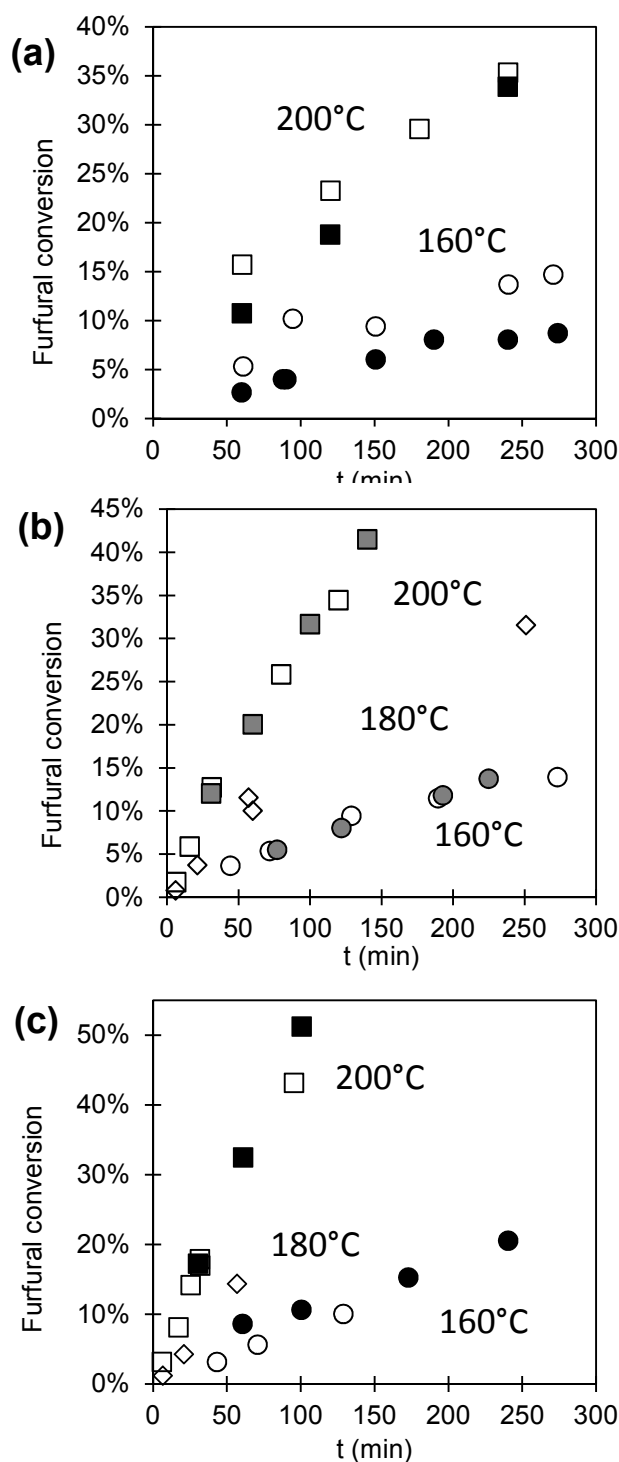


Figure 1. Experimental data of furfural degradation in a) 2% (w/w), b) 10% (w/w), and c) 30% (w/w) formic acid using three initial concentrations of 0.05 mol/L (white markers), 0.10 mol/L (grey markers), and 0.16 mol/L (black markers) at three temperatures 160°C (circles), 180°C (diamonds), and 200°C (squares).

However, the behaviour changes when stronger acid is used. Figure 1b indicates that, in 10% acid, the order of reaction is one, because there is no difference in furfural conversion between the initial furfural concentrations (0.05 and 0.1 mol/L, white and grey markers, respectively). On the other hand, in

30% acid, furfural degradation slightly increases when the initial furfural concentration is higher. This means that the reaction order is over one. Thus, based on Figures 1a-c, it can be concluded that the overall order of furfural degradation reaction is not unity, and that the order is somehow dependent on the acid concentration.

In our previous study<sup>18</sup>, furfural degradation followed first-order kinetics and the model used was based on the specific acid-base catalysis (equation 7), where the base term,  $k_{OH}[OH^-]$ , was removed because it was assumed that  $[H^+] \gg [OH^-]$ . Independent activation energies for the uncatalysed term,  $k_0$ , and the acid catalysed term,  $k_H[H^+]$ , were used.

$$k = k_0 + k_H [H^+] + k_{OH} [OH^-], \quad (7)$$

where  $k_0$  is the rate constant for the uncatalysed reaction,  $k_H$  and  $k_{OH}$  are the rate constants for catalysis by hydrogen ions and hydroxide ions, respectively,  $[H^+]$  is the hydrogen ion concentration, and  $[OH^-]$  is the hydroxide ion concentration.

In the present study, the kinetic model was modified to the power law model shown in equation 8 to take into account the effect of initial furfural concentration.

$$d[F]/dt = -k_0 [F]^n - k_1 [H^+] [F]^m, \quad (8)$$

where  $k_0$  is the rate constant for an uncatalysed reaction in the water solvent,  $k_1$  is the rate constant for an acid-catalysed reaction,  $[H^+]$  is the hydrogen ion concentration at the reaction temperature, and  $n$  and  $m$  are the order of uncatalysed and acid-catalysed reactions, respectively.

The estimated values for kinetic parameters are shown in Table 1 with a 95% confidence interval based on the  $t$ -distribution. The residuals (not shown) and parity plot (Figure 3) revealed that the model fitted the experimental results well. The coefficient of determination ( $R^2$  value) was 99.6%.

Table 1. Kinetic parameters for furfural degradation. The values are given with a 95% confidence interval based on the  $t$ -distribution.

Parameter	Estimated value	
	Model 1	Model 2
$k'_0$ (1/min)*	$1.34e-04 \pm 0.05e-04$	$1.35e-04 \pm 0.02e-04$
$E_0$ (kJ/mol)	$9.63 \pm 0.5$	0
$n$	$0.668 \pm 0.015$	$0.655 \pm 0.041$
$k'_1$ (1/min)*	$0.0612 \pm 0.0037$	$0.568 \pm 0.001$
$E_1$ (kJ/mol)	$110.3 \pm 1.1$	$113.6 \pm 0.1$
$m$	$1.087 \pm 0.014$	$1.082 \pm 0.003$

\* Rate constants are given for a reference temperature of 165°C.

All the parameters were identified well except for the activation energy of the uncatalysed reaction,  $E_0$ , which was identified only from the upper side (Fig. 2). Thus, the temperature dependency of the uncatalysed reaction formulated using equation 6 was removed by setting  $E_0$  to zero, and the parameters were re-estimated. The new model (model 2) gave an equally good fit as the original (model 1). The parity plots of

the model with and without temperature dependency for the uncatalysed reaction are given in Figure 3. Kinetic model 2 is used for further examination.

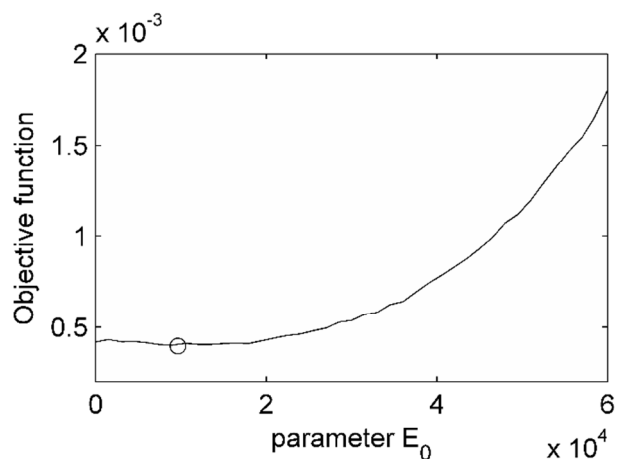


Figure 2. Parameter  $E_0$  vs. objective function. The estimated value for  $E_0$  is marked with a circle.

The experimental data and kinetic model 2 at two temperatures, 200°C and 160°C, are shown in Figures 4 and 5, respectively. It can be seen in the figures that the overall reaction order of furfural degradation changes with the amount of acid catalyst. At 200°C (Figure 4), the overall reaction order is one in 2% acid, i.e. the initial furfural concentration does not influence furfural conversion. Whereas, in 10% and 30% acid, the overall reaction order is slightly higher than one, which means that conversion increases when a higher initial furfural concentration is used.

However, Figure 5 reveals that the overall reaction order changes also with the temperature. At 160°C, contrary to 200°C, the modelled conversion increases when a lower initial furfural concentration is used. This behaviour is clearly seen in the experimental data for 2% acid and partly for the 10% acid, but for the 30% acid and short reaction times, the behaviour is opposite and the conversion is higher in a higher initial furfural concentration.

The results show that the kinetic model used is capable of estimating the change in the overall reaction order in the experimental conditions used and describes the experimental data quite well in a wide acid concentration range.

## Discussion

The estimated activation energy for the acid-catalysed reaction,  $E_1$ , is lower than in our earlier study (135 kJ/mol) using formic acid<sup>18</sup> or the value (125 kJ/mol) obtained by Marcotullio et al. using H<sub>2</sub>SO<sub>4</sub> medium<sup>12</sup>, but in the same area as the activation energies (102 or 115 kJ/mol) obtained by Danon et al.<sup>10</sup> using 50 mM HCl and 500 mM NaCl medium with a first- or second-order model. Lower activation energies have also been reported, ranging from 48 kJ/mol to 92 kJ/mol<sup>9</sup>. However, all

the activation energies reported in the recent literature are in the same magnitude.

Moreover, it has been stated recently that the difference between activation energies in the earlier study of Williams and Dunlop<sup>3</sup> (83.7 kJ/mol) and that of Marcotullio lies in the modelling differences<sup>8</sup>: Dunlop did not take into account the variation in the second dissociation constant of sulphuric acid, whereas in the Marcotullio study, hydronium ion activities instead of molar concentrations were used. Thus, the differences in activation energies might be partly caused by the acid catalyst used and the handling of acidity in the model. Therefore, the dissociation reaction of the acid catalyst and its temperature dependency are essential for accurate kinetic models with a wide working area. In our model, the temperature dependency of acid dissociation was taken into account with the empirical equation reported by Kim et al.<sup>19</sup> The equation is valid for a diluted solution. Thus, if a more accurate model for a high formic acid concentration is needed, high concentration experimental data on formic acid dissociation will be needed in addition to kinetic data.

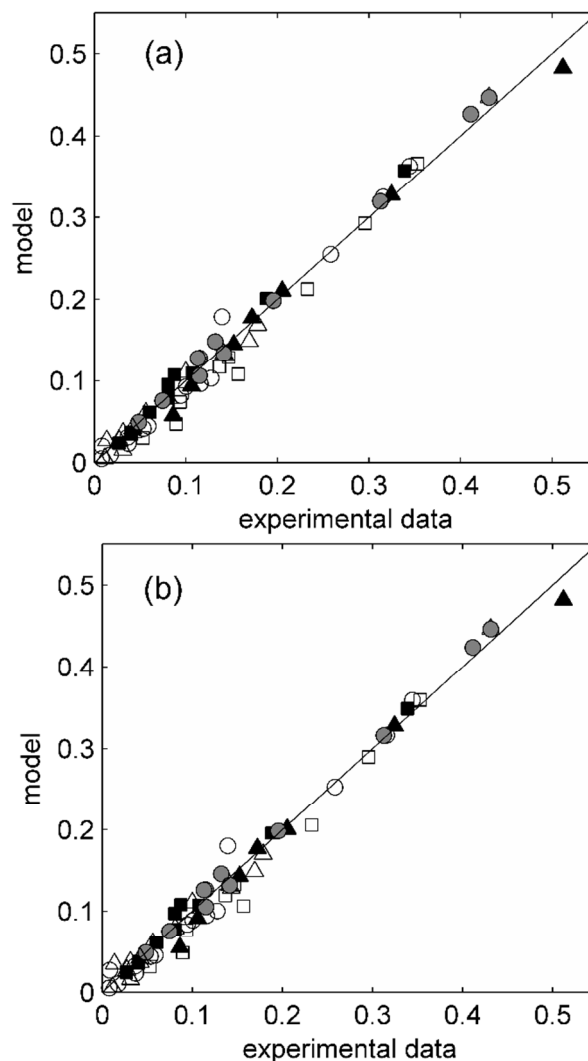


Figure 3. Parity plots of furfural concentration a) with or b) without temperature dependency for the uncatalysed reaction.

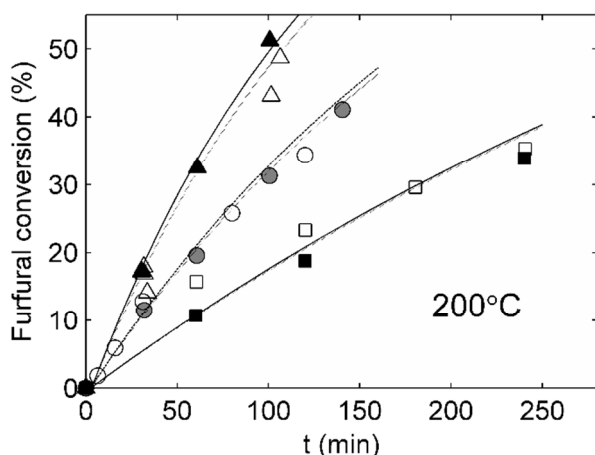


Figure 4. Furfural degradation in 2% (squares), 10% (circles) and 30% (triangles) formic acid at 200°C: kinetic model and experimental data in three furfural concentrations: 0.05 mol/L (white markers, dotted line), 0.10 mol/L (grey markers, dashed line) and 0.16 mol/L (black markers, straight line).

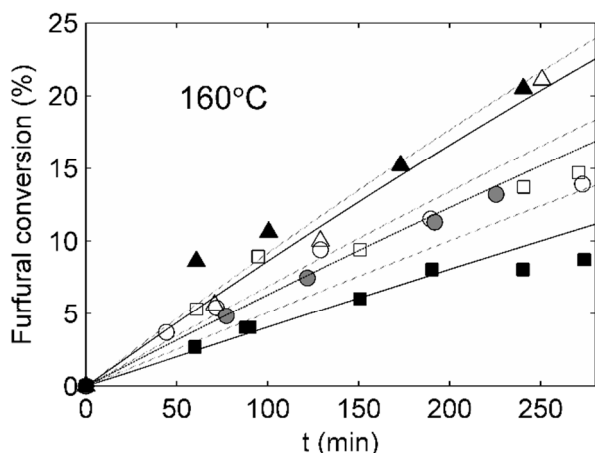


Figure 5. Furfural degradation in 2% (squares), 10% (circles) and 30% (triangles) formic acid at 160°C: kinetic model and experimental data in three furfural concentrations: 0.05 mol/L (white markers, dotted line), 0.10 mol/L (grey markers, dashed line) and 0.16 mol/L (black markers, straight line).

In the literature, it is often mentioned that furfural is lost through resinification, which produces a black, insoluble resin, but the mechanism of the resinification reaction remains unclear.<sup>2,3,4,13</sup> Nevertheless, resinification, where two furfural molecules react with each other, is likely to be a second-order reaction. However, in many previous studies of furfural degradation<sup>11-13,20</sup>, the furfural loss reaction has been successfully modelled as a first-order reaction. This has led to the assumption that furfural self-polymerisation reactions leading to resins seem unlikely<sup>12</sup> or that the extent of these reactions is small<sup>10</sup>. Another explanation for this behaviour could lie in the mechanism of resinification. It is plausible that the second-order reaction where two furfural molecules react with each other is the initiation step of a polymer-forming reaction scheme, and after the initiation, the polymer chain

grows by adding one furfural molecule at a time. Thus, if the growth of polymers is dominant compared to the initiation, the overall reaction would be near one. Furthermore, it was proposed recently that two furfural molecules undergo the Diels-Alder reaction resulting in second-order kinetics<sup>10</sup>. This reaction could be the initiation step of furfural polymerisation and could even continue in the same manner as larger molecules, as proposed in Figure 6.

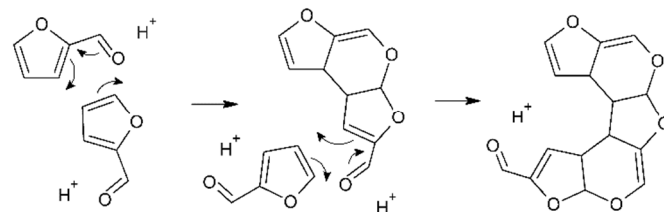


Figure 6. Proposed reaction mechanism for furfural polymerisation by the Diels-Alder reaction.

Besides resinification, furfural undergoes hydrolytic ring opening in aqueous acidic medium resulting in an aliphatic open-chain product<sup>2</sup>. Furfural is the only initial reactant in this reaction, and thus the reaction is first order as for furfural. It is likely that the products of the hydrolytic ring opening react with each other or furfural molecules, forming larger molecules. This mechanism would also lead to a reaction order of one. This theory is strengthened by the studies made with 5-hydroxymethylfurfural (HMF). HMF degrades in acidic conditions through two reactions: 1) HMF to humins, and 2) HMF to levulinic acid and formic acid. This reaction scheme, including the two reactions, is reliably modelled with first-order kinetics<sup>21,22</sup>. Horvat et al.<sup>23</sup> proposed a mechanism where 2,5-dioxo-6-hydroxyhexanal is the intermediate leading to humin formation from HMF. The hydrolytic ring opening reaction mechanism<sup>2</sup> for HMF leads to the same product, 2,5-dioxo-6-hydroxyhexanal. In a later study, Patil & Lund<sup>21</sup> proved that humin growth is possible by means of aldol addition/condensation of HMF with 2,5-dioxo-6-hydroxyhexanal. The suggested product from the hydrolytic ring opening of furfural, i.e. 1,2,5-tripentanone, has eno and keto forms. Thus, it is plausible that furfural can undergo the same kind of reaction scheme through aldol addition/condensation.

From the present results, it can be concluded that the first-order reactions are dominant compared to the second-order reactions in the studied reaction conditions. It seems likely that resinification occurs because solid matter is present in the reaction medium. Moreover, the results indicate that the second-order polymerisation reaction could be more important in high acidic conditions (pH 0.9 or less) and high temperatures. This could mean that in more severe conditions, furfural degradation would result in low molecular weight molecules rather than large polymers. This is in accordance with the conclusion of Zeitsch<sup>4</sup> where he proposed, based on the experiments of Root et al.<sup>11</sup>, that resinification plays only a minor role at high temperatures (>200°C). This was attributed

to the “entropy effect”, where increasing temperature favours the disintegration of molecules.

Additionally, Danon et al.<sup>10</sup> raised the possibility that furfural degradation comprises both a first- and a second-order reaction, because they could fit their experimental results with both a first- and a second-order model. On the other hand, it must be noted that Danon et al. carried out their experiments with one initial furfural concentration (50 mmol/L), so all the changes in the reaction order might not have been seen. They also formulated a hypothesis that the higher acidity resulting from glucose dehydration would favour Diels-Alder reactions. Nevertheless, the results represented in this paper strengthen their conclusion. The present results show that the overall reaction order changes in the experimental conditions used, and that the reaction order is slightly over one in more severe conditions. Moreover, the proposed kinetic model is capable of estimating the change in reaction order and describes the experimental data well in a wide acid concentration range.

Furthermore, the results on formic acid medium indicate that the reaction mechanism includes some reaction schemes where the apparent reaction order is smaller than one. These are best seen in very dilute acidic conditions and low temperatures. Thus, more detailed research should be conducted in dilute H<sup>+</sup> concentrations and in water medium to reveal the mechanism of furfural degradation.

## Conclusions

In this study, formic acid catalysed furfural degradation was studied and the possible reaction mechanisms were discussed. The results show that, in the relatively large range of conditions used, the overall order of the reaction changes: in high acid concentration (30%), the order of reaction is over one and in low acid concentration (2%) the order of reaction is below one, and the kinetic model used is capable of following this behaviour. It can be concluded that there are several degradation reaction possibilities, and the reaction conditions determine which are favoured. In the future, more detailed research should be conducted to reveal the mechanism of the main furfural degradation reactions, which could open up new ideas for enhancing furfural yields in industrial processes.

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## Notes and references

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- 1 J. J. Bozell and G. R. Petersen, *Green Chem*, 2010, **12**, 539.
- 2 A. Gandini and M. N. Belgacem, *Prog Polym Sci*, 1997, **22**, 1203.

- 3 D. L. Williams and A.P. Dunlop, *Ind Eng Chem*, 1948, **40**, 239.
- 4 K. J. Zeitsch, The chemistry and technology of furfural and its many by-products. In: Sugar series, Elsevier, 2000, vol.13.
- 5 T. Zhang, R. Kumar and C. E. Wyman, *RSC Adv*, 2013, **3**, 9809.
- 6 R. Weingarten, J. Cho, J. Conner, Wm. Curtis and G. W. Huber, *Green Chem*, 2010, **12**, 1423.
- 7 B. Pholjaroen, N. Li, Z. Wang, A. Wang and T. Zhang, *J Energy Chem* 2013, **22**, 826.
- 8 C. M. Cai, T. Zhang, R. Kumar and C. E. Wyman, *J Chem Technol Biotechnol*, 2014, **89**, 2.
- 9 B. Danon, G. Marcotullio and W. de Jong, *Green Chem*, 2014, **16**, 39.
- 10 B. Danon, L. van der Aa and W. de Jong, *Carbohydr Res*, 2013, **375**, 145.
- 11 D. F. Root, J. F. Saeman, J. F. Harris and W. K. Neill, *For Prod J* 1959, **9**, 158.
- 12 G. Marcotullio, M. A. Tavares Cardoso, W. de Jong and A. H. M. Verkooijen, *Int J Chem React Eng* 2009, **7**, A67.
- 13 I. C. Rose, N. Epstein and A. P. Watkinson, *Ind Eng Chem Res*, 2000, **39**, 843.
- 14 X. Zhao, K. Cheng and D. Liu, *Appl Microbiol Biotechnol*, 2009, **82**, 815.
- 15 G. Yu, B. Li, C. Liu, Y. Zhang, H. Wang and X. Mu, *Ind Crop Prod*, 2013, **50**, 750.
- 16 O. Yemiş and G. Mazza, *Bioresource Technol*, 2011, **102**, 7371.
- 17 L. Kupiainen, Dilute acid catalysed hydrolysis of cellulose – extension to formic acid. Acta Univ. Oul. C Technica 438, 2012.
- 18 K. Lamminpää, J. Ahola and J. Tanskanen, *Ind Eng Chem Res*, 2012, **51**, 6297.
- 19 M. H. Kim, C. S. Kim, H. W. Lee and K. Kim, *J Chem Soc, Faraday Trans*, 1996, **92**, 4951.
- 20 Q. Jing, and X. Lü, *Chin J Chem Eng*, 2007, **15**, 666.
- 21 S. K. R. Patil and C. R. F. Lund, *Energy Fuels*, 2011, **25**, 4745.
- 22 L. Kupiainen, J. Ahola and J. Tanskanen, *Chem Eng Res Des* 2011, **89**, 2706.
- 23 J. Horvat, B. Klaić, B. Metelko and V. Sunjic, *Tetrahedron Letters*, 1985, **26**, 2111.