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# A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid

B. Girisuta, L. P. B. M. Janssen and H. J. Heeres\*

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Levulinic acid (LA), accessible by the acid catalyzed degradation of biomass, is potentially a very versatile green intermediate chemical for the synthesis of various (bulk) chemicals for applications like fuel additives, polymers, and resin precursors. We report here a kinetic study on one of the key steps in the conversion of biomass to levulinic acid, *i.e.* the reaction of 5-hydroxymethylfurfural (HMF) to levulinic acid. The kinetic experiments were performed in a temperature window of 98–181 °C, acid concentrations between 0.05–1 M, and initial HMF concentrations between 0.1 and 1 M. The highest LA yield was 94% (mol/mol), obtained at an initial HMF concentration of 0.1 M and a sulfuric acid concentration of 1 M. The yield at full HMF conversion is independent of the temperature. An empirical rate expression for the main reaction as well as the side reaction to undesired humins was developed using the power law approach. Agreement between experimental and model data is good. The rate expressions were applied to gain insights into optimum process conditions for batch processing.

## 1. Introduction

Biomass has been identified as an important source for bio-fuels and chemical products.<sup>1</sup> Biomass is abundantly available, for instance in the form of waste from agricultural, forest and industrial activities (*e.g.* paper industry). A substantial amount of research activity is currently undertaken world-wide to identify attractive chemical transformations to convert biomass into organic (bulk) chemicals, and to develop economically feasible processes for these transformations on a commercial scale. An attractive option is the conversion of lignocellulosic biomass into levulinic acid (4-oxopentanoic acid) by acid treatment.<sup>2–6</sup>

Levulinic acid is a very versatile building block for the synthesis of (bulk) chemicals for applications like fuel additives, polymers, and resin precursors.<sup>7</sup> Several reviews have been published describing the properties and potential industrial applications of levulinic acid and its derivatives.<sup>8–12</sup>

On a molecular level, the conversion of a typical lignocellulosic biomass like wood or straw to levulinic acid follows a complicated reaction pathway,<sup>13</sup> involving several intermediate products (see Fig. 1). The simplified reaction scheme given in Fig. 1 does not explicitly show the reactions leading to undesired black insoluble polymeric materials also known as humins. As part of a larger project to develop efficient reactor configurations for the conversion of biomass to levulinic acid, we have initiated a study to determine the kinetics of all steps involved (Fig. 1). A stepwise approach was followed, starting with the conversion of 5-hydroxymethylfurfural (HMF) to levulinic acid (LA).

A number of experimental studies have been reported on the kinetics of the acid catalyzed HMF decomposition to levulinic acid. The first study was carried out by Teunissen in 1930.<sup>14</sup> Reactions were carried out at 100 °C using various acid catalysts with acid concentrations ranging between 0.1 and 0.5 N. Heimlich and Martin<sup>15</sup> studied the reaction in a temperature range of 100–140 °C using hydrochloric acid (0.35 N) as catalyst. McKibbins *et al.*<sup>16</sup> investigated the influence of sulfuric acid concentration (0.025–0.4 N) and temperature (160–220 °C) on the decomposition rate of HMF to levulinic acid. In all these studies, the effect of the initial concentration of HMF was not determined and first order kinetics was assumed. Kuster and van der Baan<sup>17</sup> studied the influence of the initial HMF concentration on the kinetics of HMF decomposition at 95 °C using various concentrations (0.5–2.0 N) of hydrochloric acid. The most recent kinetic study was reported by Baugh and McCarty,<sup>18</sup> who used dilute acid as catalyst at variable pH (2–4) and temperature (170–230 °C). Table 1 summarizes the results from previous kinetic studies on the acid catalysed reaction of HMF to levulinic acid.

On the basis of these data, it may be concluded that a general kinetic expression for a broad range of temperatures,

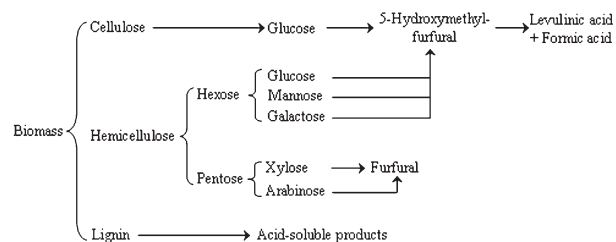


Fig. 1 Simplified reaction scheme for the conversion of lignocellulosic biomass into levulinic acid.

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**Table 1** Literature overview of rate of reaction for the acid catalysed decomposition of HMF

$T$	$C_{\text{acid}}$	$C_{\text{HMF},0}$	$R_{\text{HMF}}/\text{mol L}^{-1} \text{min}^{-1}$	Reference
100 °C	$C_{\text{H}_2\text{SO}_4} = 0.1\text{--}0.5 \text{ N}$ $C_{\text{HCl}} = 0.1\text{--}0.5 \text{ N}$	0.08–0.09 M	$R = 6.8 \times 10^{-3} C_{\text{H}^+} C_{\text{HMF}}$	14
100–140 °C	$C_{\text{HCl}} = 0.35 \text{ M}$	n.a.	$R = 1.1 \times 10^{11} \exp\left(-\frac{96000}{RT}\right) C_{\text{HMF}}$	15
160–220 °C	$C_{\text{H}_2\text{SO}_4} = 0.025\text{--}0.4 \text{ N}$	0.061–0.139 M	$R = 2.4 \times 10^{11} \alpha_{\text{H}} C_{\text{A}} \exp\left(-\frac{96800}{RT}\right) C_{\text{HMF}}^a$	16
95 °C	$C_{\text{HCl}} = 0.5\text{--}2.0 \text{ N}$	0.25–1 M	$R = 0.001(C_{\text{H}^+})^{1.2} C_{\text{HMF}}$	17
170–230 °C	pH = 2–4	0.024 M	$R = (1300 + 4.1 \times 10^6 C_{\text{H}^+}) \exp\left(-\frac{55900}{RT}\right) C_{\text{HMF}}$	18

<sup>a</sup>  $\alpha_{\text{H}}$  represents a correction factor given in the original paper and  $C_{\text{A}}$  is expressed in normality (N).

catalysts and initial HMF concentrations is lacking. In addition, all earlier studies focus on the overall decomposition of HMF without discriminating between the rates of the main reaction to LA and formic acid (FA) and the side reaction to humins. In this paper, the kinetics of the acid catalyzed decomposition of HMF in a broad range of process conditions will be reported, including the kinetics of the reactions leading to humin. The results will be applied to gain insights into the optimum process conditions to reduce humin formation and to achieve the highest LA yield. Furthermore, the results will also be used as input for a full kinetic model for the acid catalyzed hydrolysis of biomass to levulinic acid. These results will be reported in due course.

## 2. Experimental

### 2.1 Experimental procedure

All chemicals used in this study were of analytical grade and used without purification. HMF was obtained from Fisher Scientific BV (Netherlands). All acid catalysts were purchased from Merck GmbH (Darmstadt, Germany). Milli-Q water was used to prepare the various solutions.

The reactions were carried out in glass ampoules (inside diameter of 3 mm, wall thickness of 1.5 mm, and length of 15 cm). The ampoules were filled with approximately 0.5 cm<sup>3</sup> of reaction mixture and sealed using a torch. The sealed ampoules were placed in a special rack that can hold up to 20 ampoules, and placed in a constant temperature oven ( $\pm 1$  °C). At different reaction times, ampoules were taken from the oven and quenched into an ice-water bath (4 °C) to stop the reaction. The reaction mixture was taken out of the ampoule and diluted with water to 10 cm<sup>3</sup>. Insoluble humins were separated using a 0.2  $\mu\text{m}$  cellulose acetate filter (Schleicher & Schuell MicroScience GmbH, Dassel, Germany). The particle-free solution was subsequently analyzed using High Performance Liquid Chromatography (HPLC).

### 2.2 Analytical methods

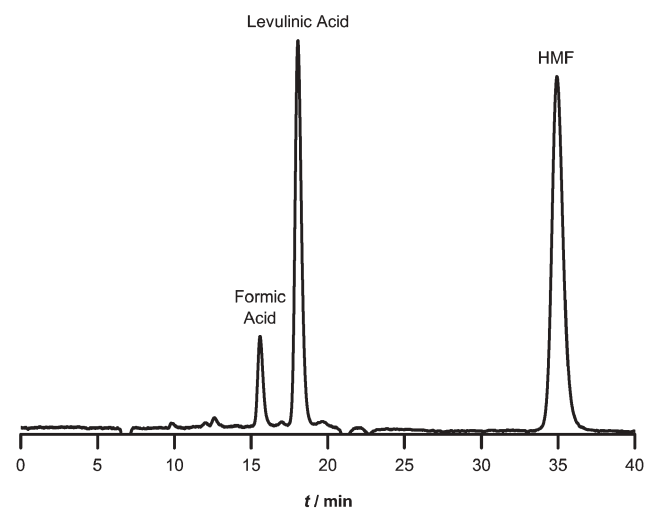
The composition of the liquid phase was determined using an HPLC system consisting of a Hewlett Packard 1050 pump, a Bio-Rad organic acid column Aminex HPX-87H, and a Waters 410 differential refractometer. The mobile phase consisted of an aqueous solution of sulfuric acid (5 mM) at

flow rate of 0.55 cm<sup>3</sup> min<sup>-1</sup>. The column was operated at 60 °C. The analysis for a sample was complete within 40 minutes. A typical chromatogram is shown in Fig. 2. The concentrations of each compound in the product mixture were determined using calibration curves obtained by analysing standard solutions with known concentrations.

The gas composition was analyzed with gas chromatography (Varian Micro GC CP-2003) equipped with a TCD cell using a Porapak Q column operated at 75 °C. Helium was used as the carrier gas. Humin particles were analyzed using Field Emission Scanning Electron Microscopy (FESEM) on a JEOL 6320F. C and H elemental analyses were performed at the Analytical Department of the University of Groningen using an automated Euro EA3000 CHNS analyser.

### 2.3 Heat transfer experiments

At the start of the reaction, the reaction takes place non-isothermally due to heating-up of the contents of the ampoule from room temperature to the oven temperature. To gain insights in the time required to heat up the reaction mixture and to compensate for this effect in the reaction modelling studies, the temperature inside the ampoules as a function of the time during the heat up process were determined experimentally. For this purpose, an ampoule equipped with

**Fig. 2** HPLC chromatogram for HMF decomposition.

a thermocouple was filled with a representative reaction mixture (1 M HMF in water without acid). The ampoule was then closed tightly using a special bolt and screw system to prevent evaporation of the liquid. The ampoule was subsequently placed in the oven at a specified temperature and the temperature of the reaction mixture was followed in time. Before and after an experiment, the amount of liquid inside the ampoule was measured to ensure that evaporation of the liquid did not occur.

The experimental profiles at different temperatures were modelled using a heat balance for the contents in an ampoule:

$$\frac{d(MC_p T)}{dt} = UA_t(T_{\text{oven}} - T) \quad (1)$$

When assuming that the heat capacity of reaction mixture is constant and not a function of temperature, rearrangement of eqn (1) will give:

$$\frac{dT}{dt} = \frac{UA_t}{MC_p}(T_{\text{oven}} - T) = h(T_{\text{oven}} - T) \quad (2)$$

Solving the ordinary differential eqn (2) with the initial values  $t = 0$ ,  $T = T_i$  leads to:

$$T = T_{\text{oven}} - (T_{\text{oven}} - T_i)\exp^{-ht} \quad (3)$$

The value of  $h$  was determined by fitting all experimental data at different oven temperatures (100–160 °C) using a non-linear regression method, and was found to be 0.596 min<sup>-1</sup>. Fig. 3 shows an experimental and modelled temperature profile performed at an oven temperature of 100 °C. Eqn (3) was incorporated in the kinetic model to describe the non-isothermal behaviour of the system at the start of the reaction.

The effect of the chemical reaction on the heating profiles was modelled using the mass and energy balance (eqn (1) with an additional term for the chemical reaction) for a batch reactor. The heating profiles did not change significantly when taking into account an additional term for chemical reaction. Therefore, the heating profiles were not compensated for the occurrence of chemical reaction.

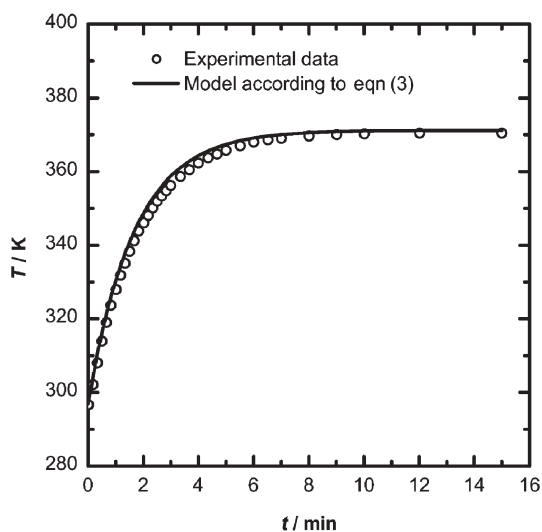


Fig. 3 Heating profile of the reaction mixture at  $T_{\text{oven}} = 100$  °C.

## 2.4 Determination of the kinetic parameters

The kinetic parameters were estimated using a maximum likelihood approach, which is based on minimization of errors between the experimental data and the kinetic model. Details about this procedure can be found in the literature.<sup>19,20</sup> Minimization of objective function is initiated by providing initial guesses for each kinetic parameter. The best estimates were obtained using the MATLAB toolbox `fminsearch`, which is based on the Nelder–Mead optimization method.

The concentrations of HMF and LA vary considerably from experiment to experiment and within an experimental run. As a result, the high concentrations will dominate the error calculation when minimizing the objective function. To solve this problem, the concentrations of HMF and LA were scaled and transformed to the HMF conversion and the LA yield, respectively. By definition,<sup>21</sup> the HMF conversion ( $X_{\text{HMF}}$ ) and LA yield ( $Y_{\text{LA}}$ ) vary between 0–1, and are expressed as:

$$X_{\text{HMF}} = \frac{(C_{\text{HMF},0} - C_{\text{HMF}})}{C_{\text{HMF},0}} \quad (4)$$

$$Y_{\text{LA}} = \frac{(C_{\text{LA}} - C_{\text{LA},0})}{C_{\text{HMF},0}} \quad (5)$$

## 3. Results and discussion

### 3.1 Acid screening

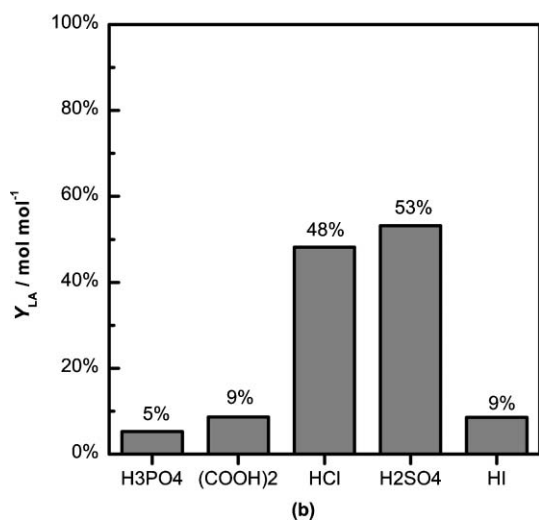
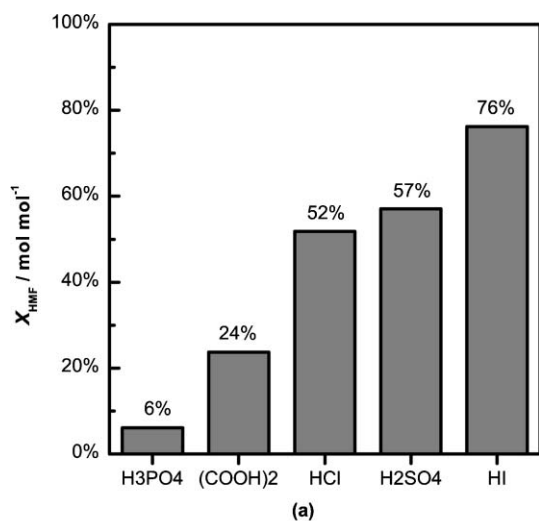
At the start of the research, a number of acid catalysts were screened ( $\text{H}_3\text{PO}_4$ , oxalic acid, HCl,  $\text{H}_2\text{SO}_4$ , and HI) to determine the preferred acid for further studies. All screening experiments were conducted at 98 °C and 1 hour reaction time using a  $C_{\text{HMF},0}$  of 0.1 M and acid concentrations of 1 M. The results are shown in Fig. 4.  $\text{H}_3\text{PO}_4$  and oxalic acid gave very low HMF conversions (<25%). In addition, the LA yields were also very low (5–9%). The application of HI resulted in very high HMF conversion, unfortunately accompanied with very low LA yields. Major by-products were humins and some as yet unidentified soluble products. Of all acids screened, HCl and  $\text{H}_2\text{SO}_4$  gave the best results. Conversions were between 52–57%, and the yields between 48–53%.  $\text{H}_2\text{SO}_4$  showed a slightly better performance than HCl and was used in subsequent experiments.

### 3.2 Reaction products

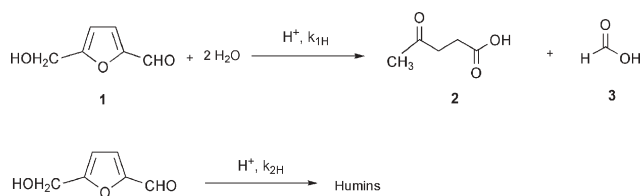
The acid catalysed decomposition of 5-hydroxymethylfurfural (HMF, **1**) to levulinic acid (LA, **2**) and formic acid (FA, **3**) is schematically presented in Scheme 1.

A typical reaction profile of the acid catalysed HMF decomposition reaction is given in Fig. 5. In line with the reaction stoichiometry, the LA and FA co-product were always produced in a 1 : 1 molar ratio. This implies that both LA and FA are stable under the reaction conditions employed and do not decompose to other products (*vide infra*).

Possible by-products, other than FA, are insoluble dark-brown substances, known as humins, and gas-phase components due to thermal degradation of reactants/products. Humins were formed in all experiments. The elemental

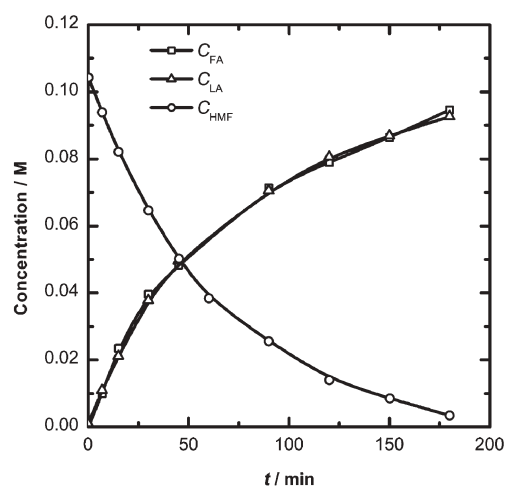


**Fig. 4** Effects of acid type on (a) HMF conversion and (b) LA yield.

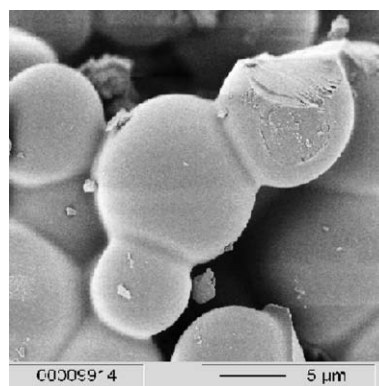


composition of a typical humin sample was determined and contained 61.2 wt% of carbon and 4.5 wt% of hydrogen. These values are close to the elemental composition given in the literature<sup>22</sup> (C, 63.1; H, 4.2) for the humins obtained by reacting HMF with 0.3 wt% oxalic acid at 130 °C for 3 hours. To gain insights in the average particle size and particle morphology, a number of humin samples were analysed using SEM. A typical example is given in Fig. 6. The humins appear as round, agglomerated particles with a diameter between 5–10 μm.

The gas phase composition after reaction was analysed using GC. Only CO<sub>2</sub> could be detected. However, the amount of CO<sub>2</sub> formed was always less than 2 wt% of the HMF intake,



**Fig. 5** Typical concentration profile of HMF decomposition reaction ( $T = 98$  °C,  $C_{\text{HMF},0} = 0.1$  M,  $C_{\text{H}_2\text{SO}_4} = 1$  M).



**Fig. 6** Scanning electron microscope image of the insoluble humin product.

implying that this is only a minor reaction pathway under these conditions.

### 3.3 Effects of temperature, acid concentration and initial HMF concentration on HMF conversion and LA yield

A total of 11 batch experiments were performed in a broad range of process conditions ( $T = 98$ – $181$  °C,  $C_{\text{HMF},0} = 0.1$ – $1$  M) using sulfuric acid as the catalyst ( $0.05$ – $1$  M). The reaction rate is very sensitive to the temperature. For instance, essentially quantitative HMF conversion ( $X_{\text{HMF}}$ ) can be achieved in 10 minutes at 181 °C ( $C_{\text{H}_2\text{SO}_4} = 0.1$  M). However, the rate is reduced dramatically at lower temperatures, and a 10 h reaction time was required to obtain  $X_{\text{HMF}} = 80\%$  at 98 °C ( $C_{\text{H}_2\text{SO}_4} = 0.25$  M, see Fig. 7).

The effect of the  $C_{\text{H}_2\text{SO}_4}$  on HMF conversion and LA yield is shown graphically in Fig. 8. Evidently, higher acid concentrations result in higher reaction rates (Fig. 8(a)). At 181 °C, the highest temperature in our study, only dilute solutions of sulfuric acid could be applied. Due to the occurrence of very fast reactions at this temperature, regular sampling to obtain concentration–time profiles proved not possible. At similar conversion levels, the LA yield is slightly improved when using higher acid concentrations (Fig. 8(b)).

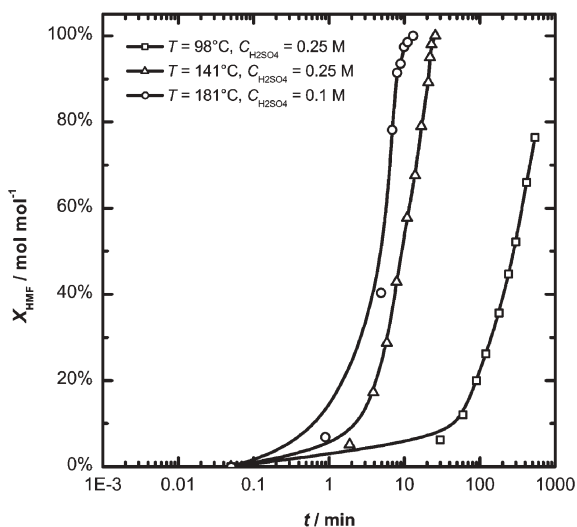


Fig. 7 Effect of temperature on HMF conversion ( $C_{\text{HMF},0} = 0.1 \text{ M}$ ).

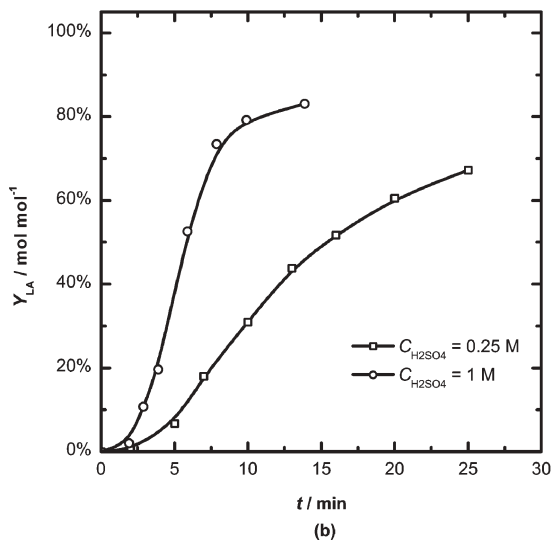
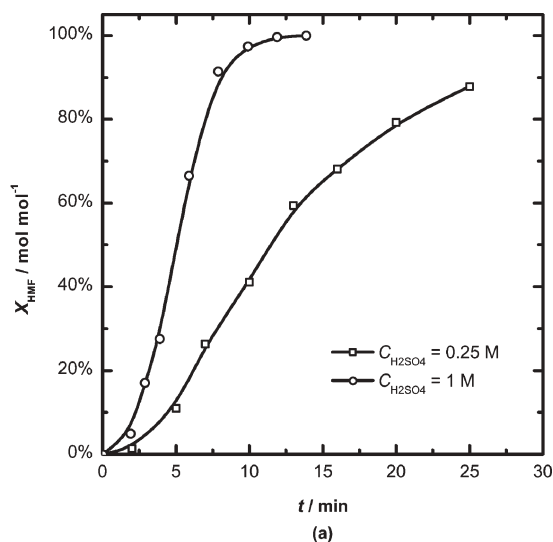


Fig. 8 Effect of acid concentration on (a)  $X_{\text{HMF}}$  and (b)  $Y_{\text{LA}}$ , at  $T = 141 \text{ }^\circ\text{C}$  and  $C_{\text{HMF},0} = 1 \text{ M}$ .

A number of experiments were performed with variable initial concentrations of HMF (0.1–1.7 M) at  $T = 98 \text{ }^\circ\text{C}$ , and  $C_{\text{H}_2\text{SO}_4} = 1 \text{ M}$ . The conversion of HMF is only slightly dependent on the initial concentration of HMF (Fig. 9(a)), an indication that the reaction order in HMF is close to 1. The initial concentration of HMF has a dramatic effect on the LA yield (Fig. 9(b)). The LA yield was significantly higher when using a low initial concentration of HMF (84% vs. 50%).

### 3.4 Development of a kinetic model

The kinetic model is based on the equations given in Scheme 1. It is assumed that HMF decomposes to LA and humins in a parallel reaction mode.<sup>16,17</sup> It cannot be excluded *a priori* that LA and FA are also a source for humins and decompose under the reaction conditions employed. A number of experiments were conducted using pure LA and FA (at  $141 \text{ }^\circ\text{C}$  and  $C_{\text{H}_2\text{SO}_4} = 1 \text{ M}$ ). Decomposition of both compounds did not occur under these conditions, implying that HMF is the sole source of humins.

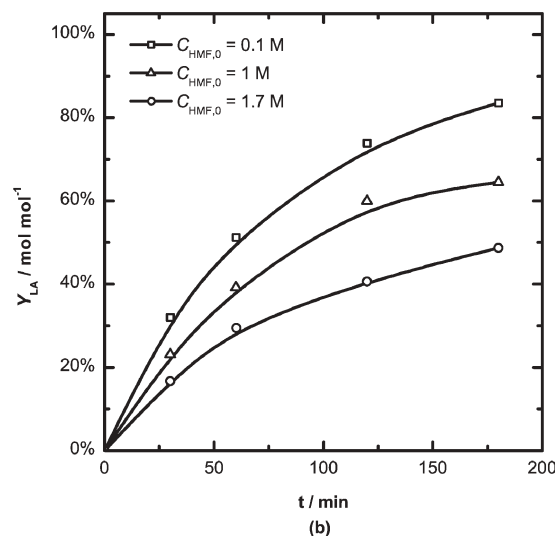
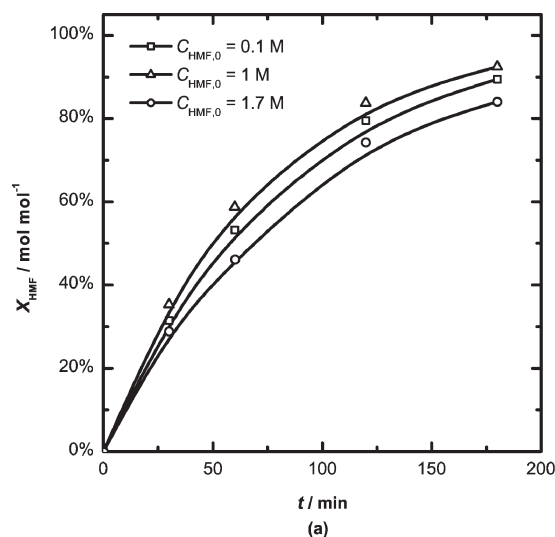
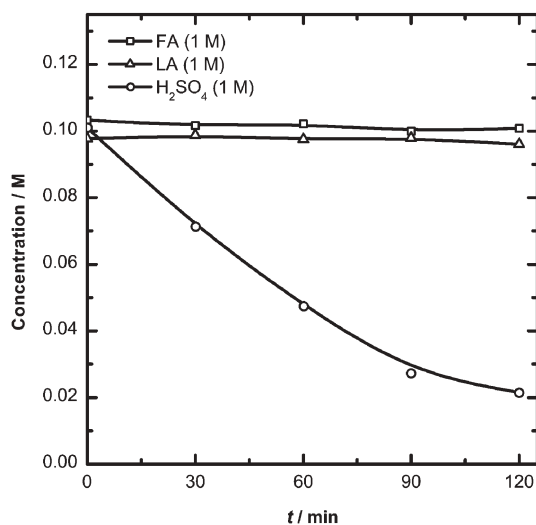


Fig. 9 Influence of initial concentration of HMF on (a)  $X_{\text{HMF}}$  and (b)  $Y_{\text{LA}}$ , at  $T = 98 \text{ }^\circ\text{C}$  and  $C_{\text{H}_2\text{SO}_4} = 1 \text{ M}$ .





**Fig. 10** HMF decomposition using FA, LA, and sulfuric acid as catalyst ( $T = 98\text{ }^{\circ}\text{C}$  and  $C_{\text{HMF},0} = 0.1\text{ M}$ ).

Both FA and LA are acidic compounds that potentially could also catalyse the decomposition of HMF. To investigate possible autocatalytic effects of the reaction products, a number of experiments were performed using FA or LA as catalysts ( $C_{\text{acids}} = 1\text{ M}$ ) to probe this possibility. The results are given in Fig. 10. It may be concluded that both LA and FA do not catalyse the decomposition of HMF, excluding autocatalytic effects in the kinetic scheme. Apparently, the  $\text{p}K_{\text{a}}$  values of both acids (FA = 3.74 and LA = 4.59) are too low to catalyse the reaction.

When applying the kinetic scheme as given in Scheme 1 and applying a power law approach instead of first-order reactions to express rate equations, the following relations hold:

$$R_1 = k_{1\text{H}}(C_{\text{HMF}})^{a\text{H}}(C_{\text{H}^+})^{z\text{H}} \quad (6)$$

$$R_2 = k_{2\text{H}}(C_{\text{HMF}})^{b\text{H}}(C_{\text{H}^+})^{\beta\text{H}} \quad (7)$$

The temperature dependencies of the kinetic rate constants are defined in terms of modified Arrhenius equations:

$$k_{1\text{H}} = k_{1\text{RH}} \exp \left[ -\frac{E_{1\text{H}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{R}}} \right) \right] \quad (8)$$

$$k_{2\text{H}} = k_{2\text{RH}} \exp \left[ -\frac{E_{2\text{H}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{R}}} \right) \right] \quad (9)$$

where  $T_{\text{R}}$  is the reference temperature, set at  $140\text{ }^{\circ}\text{C}$ .

In a batch system, the concentrations of HMF and LA as a function of time are represented by the following differential equations:

$$\frac{dC_{\text{HMF}}}{dt} = -(R_1 + R_2) \quad (10)$$

$$\frac{dC_{\text{LA}}}{dt} = R_1 \quad (11)$$

**3.4.1 Modelling results.** A total of 11 batch experiments gave 106 sets of experimental data, where each set consists of the

**Table 2** Kinetic parameters of HMF decomposition using sulfuric acid as catalyst

Parameter	Estimate
$k_{1\text{RH}}/\text{M}^{1-a\text{H}-z\text{H}}\text{ min}^{-1}$ <sup>a</sup>	$0.340 \pm 0.010$
$E_{1\text{H}}/\text{kJ mol}^{-1}$	$110.5 \pm 0.7$
$k_{2\text{RH}}/\text{M}^{1-b\text{H}-\beta\text{H}}\text{ min}^{-1}$ <sup>a</sup>	$0.117 \pm 0.008$
$E_{2\text{H}}/\text{kJ mol}^{-1}$	$111 \pm 2.0$
$a\text{H}$	$0.88 \pm 0.01$
$b\text{H}$	$1.23 \pm 0.03$
$z\text{H}$	$1.38 \pm 0.02$
$\beta\text{H}$	$1.07 \pm 0.04$
<sup>a</sup> $T_{\text{R}} = 140\text{ }^{\circ}\text{C}$	

concentrations of HMF and LA at a certain reaction time. The best estimates of the kinetic parameters and their standard deviations were determined using a MATLAB optimization routine, and the results are given in Table 2. A good fit between experimental data and the kinetic model was observed, as shown in Fig. 11. This is confirmed by a parity plot (Fig. 12).

With the model available, it is possible to gain quantitative information on the effects of the process conditions and input variables on the selectivity of the reaction. For this purpose, it is convenient to use the rate selectivity parameter ( $S$ ),<sup>23</sup> which is defined as the ratio between the rate of the desired reaction and the rate of undesired reaction.

$$S = \left( \frac{\text{rate of LA formation}}{\text{rate of humin formation}} \right) = \frac{R_1}{R_2} \quad (12)$$

Substitution of the rate expressions and kinetic constants equations as given in eqn (6)–(9) gives:

$$S = \frac{k_{1\text{RH}}}{k_{2\text{RH}}} \exp \left[ -\frac{(E_{1\text{H}} - E_{2\text{H}})}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{R}}} \right) \right] (C_{\text{HMF}})^{a\text{H} - b\text{H}} (C_{\text{H}^+})^{z\text{H} - \beta\text{H}} \quad (13)$$

Using eqn (13), it is possible to maximise  $S$  by selection of the  $C_{\text{HMF}}$ ,  $C_{\text{H}_2\text{SO}_4}$  and the temperature. The activation energies of the main reaction ( $E_{1\text{H}} = 110.5\text{ kJ mol}^{-1}$ ) and the side reaction ( $E_{2\text{H}} = 111\text{ kJ mol}^{-1}$ ) are similar (Table 2). This means that the selectivity of the reaction is independent on the temperature. Thus, to achieve high conversion rates in combination with high selectivity, it is attractive to perform the reaction at high temperatures.

Higher acid concentrations will speed up both the main and side reactions. The reaction order in acid of the main reaction ( $z\text{H} = 1.38$ ) is higher than that of the side reaction ( $\beta\text{H} = 1.07$ ), which means that higher acid concentrations will have a positive effect on the selectivity of the reaction. Hence, both from a conversion and selectivity point of view, it is advantageous to work at high acid concentrations. Eqn (13) predicts that the selectivity will be higher when working at low  $C_{\text{HMF}}$  because the order in HMF is negative ( $a\text{H} - b\text{H} = -0.35$ ). Here, a compromise between a high reaction rate (high HMF concentration favoured) and a good selectivity (low HMF concentration favoured) needs to be established (*vide infra*).

**3.4.2 Alternative models.** We have applied the power-law approach to define the reaction rates of the two reactions

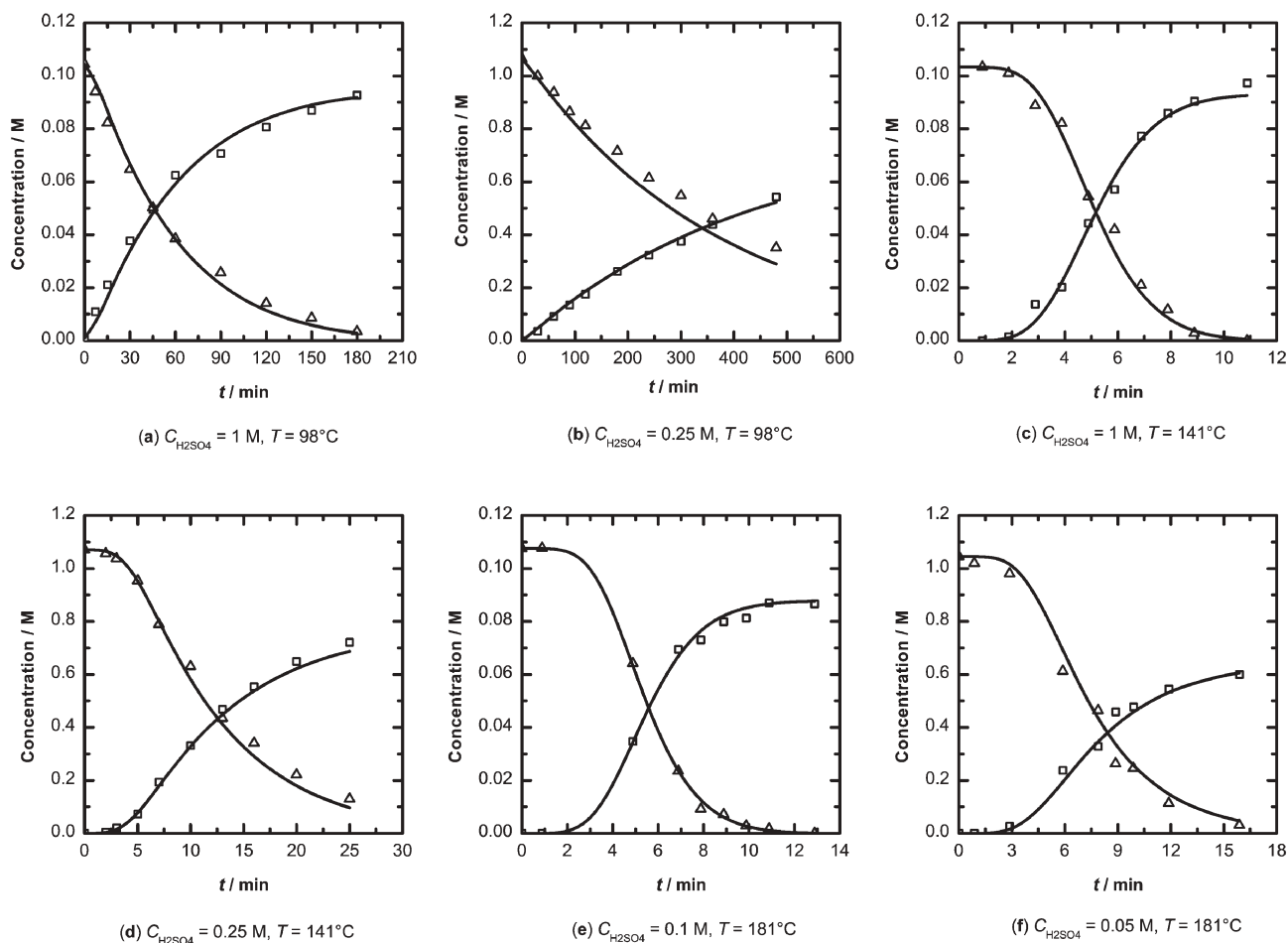


Fig. 11 Comparison of experimental data ( $\square$ :  $C_{\text{LA}}$ ;  $\triangle$ :  $C_{\text{HMF}}$ ) and kinetic model (solid lines).

(Scheme 1). With the experimental data set available, it is also possible to test other reaction models and particularly those models where all reactant orders are set to 1. To compare the quality of the models, the goodness-of-fit approach was

applied. The goodness-of-fit for a response of a model can be represented by fit-percentages such as:

$$\% \text{FIT}_{\text{HMF}} = \left[ 1 - \frac{\text{norm}(C_{\text{HMF}} - \hat{C}_{\text{HMF}})}{\text{norm}(C_{\text{HMF}} - \bar{C}_{\text{HMF}})} \right] \times 100\% \quad (14)$$

$$\% \text{FIT}_{\text{LA}} = \left[ 1 - \frac{\text{norm}(C_{\text{LA}} - \hat{C}_{\text{LA}})}{\text{norm}(C_{\text{LA}} - \bar{C}_{\text{LA}})} \right] \times 100\% \quad (15)$$

Table 3 shows the results for a number of possible models. It is clear that the power law model described in this report including humin formation shows the highest goodness-of-fit.

## 4. Application of the kinetic model

### 4.1 Comparisons with literature models

Various kinetic models for the sulfuric acid catalysed decomposition of HMF have been reported in the literature (Table 1). To demonstrate the broad applicability of the model presented in this paper, the predicted HMF reaction rates according to this model were compared to the various literature models. For this purpose, a set of reaction conditions ( $T$ ,  $C_{\text{H}_2\text{SO}_4}$ , and  $C_{\text{HMF}}$ ) was selected within the validity range of our model ( $100^\circ\text{C} < T < 180^\circ\text{C}$ ,  $0.05 \text{ M} < C_{\text{H}_2\text{SO}_4} < 1 \text{ M}$ ,

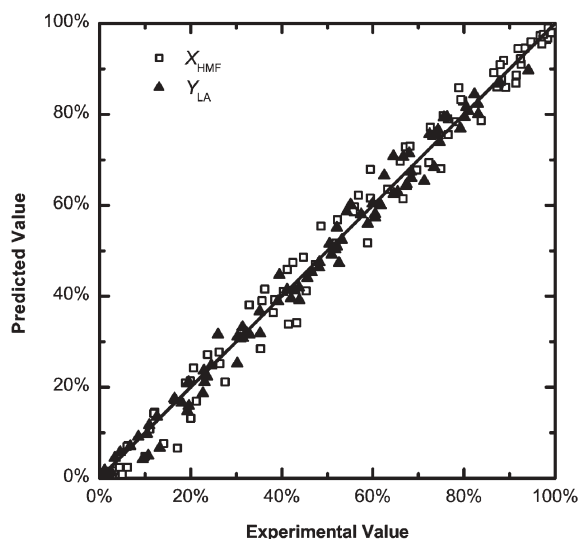


Fig. 12 Parity plot for all experimental and model points.



**Table 3** Goodness-of-fit of several kinetic models

Main reaction	Side reaction	%FIT <sub>HMF</sub>	%FIT <sub>LA</sub>
$R_1 = k_{1H}C_{HMF}C_{H^+}$	—	53%	41%
$R_1 = k_{1H}(C_{HMF})^{0.97}(C_{H^+})^{1.33}$	—	58%	48%
$R_1 = k_{1H}C_{HMF}C_{H^+}$	$R_2 = k_{2H}C_{HMF}C_{H^+}$	70%	62%
$R_1 = k_{1H}(C_{HMF})^{0.88}(C_{H^+})^{1.38}$	$R_2 = k_{2H}(C_{HMF})^{1.23}(C_{H^+})^{1.07}$	89%	87%

0.1 M <  $C_{HMF,0}$  < 1 M). The reaction rates of HMF ( $R_{HMF,power}$ ) at various reaction conditions were calculated using eqn (6) and eqn (7), by taking into account that  $R_{HMF,power} = R_1 + R_2$ . Similarly, the  $R_{HMF}$  for the literature models ( $R_{HMF,lit}$ ) were calculated using the data provided in Table 1. The  $R_{HMF,lit}$  were compared with  $R_{HMF,power}$  and the results are given in Fig. 13. A good fit between the  $R_{HMF,lit}$  and  $R_{HMF,power}$  was observed, indicating the broad applicability of our power law model.

#### 4.2 Batch simulation and optimization

With the model available, it is possible to calculate the  $X_{HMF}$  and  $Y_{LA}$  as a function of the batch time and process conditions. As an example, the modelled batch time required for  $X_{HMF} = 90\%$  at various temperatures and acid concentrations is given in Fig. 14.

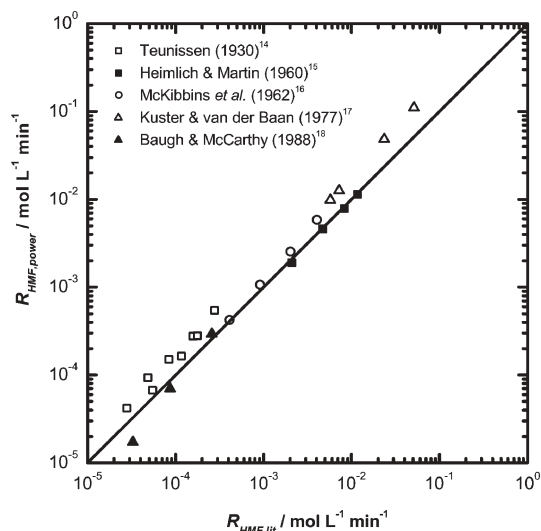
The kinetic model also allows determination of the optimum reaction conditions to achieve the highest  $Y_{LA}$ . For this purpose, eqn (4) is differentiated to give:

$$dX_{HMF} = - \frac{dC_{HMF}}{C_{HMF,0}} \quad (16)$$

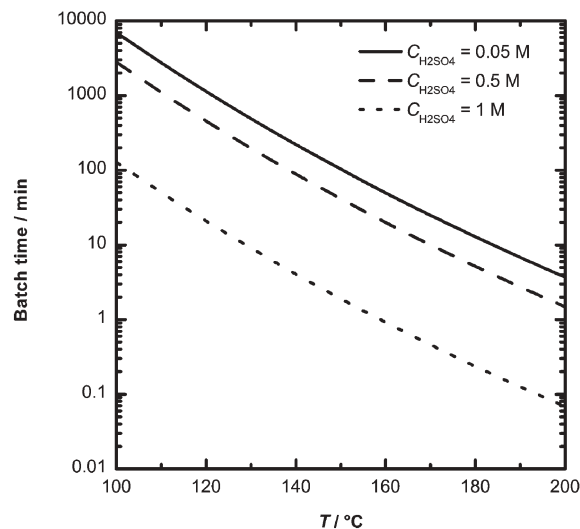
Combination of eqn (10), eqn (11) and eqn (16) leads to the following expressions:

$$\frac{dC_{HMF}}{dX_{HMF}} = -C_{HMF,0} \quad (17)$$

$$\frac{dC_{LA}}{dX_{HMF}} = \frac{R_1}{R_1 + R_2} C_{HMF,0} \quad (18)$$

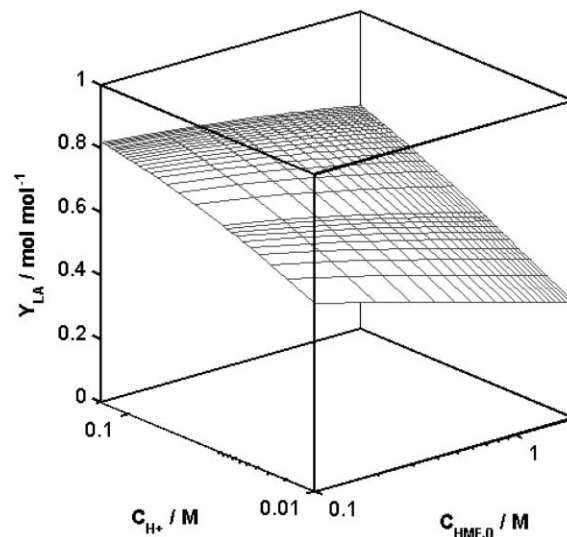


**Fig. 13** Comparison between the kinetic model provided here and previous kinetic studies.



**Fig. 14** Batch time for  $X_{HMF} = 90\%$  as a function of temperature and acid concentration ( $C_{HMF,0} = 0.1$  M).

Eqn (17) and eqn (18) were solved using the numerical integration toolbox ode45 in MATLAB software package from 0 to 90% HMF conversion. The LA yield was subsequently calculated using eqn (5). Fig. 15 shows the LA yield as a function of  $C_{HMF,0}$  and  $C_{H^+}$  at  $T = 180$  °C and 90% HMF conversion. It is evident that the LA yield is highest at high acid concentrations and low initial HMF concentrations, in line with the experimental results (*vide supra*).



**Fig. 15** Effects of  $C_{HMF,0}$  and  $C_{H^+}$  on  $Y_{LA}$  ( $T = 180$  °C and  $X_{HMF} = 90\%$ ).

## 5. Conclusions

This study describes an in-depth experimental and modelling study on the acid catalysed decomposition of HMF into LA and FA and humins by-products in a batch reactor. Acid screening studies show that H<sub>2</sub>SO<sub>4</sub> and HCl are the catalysts of choice with respect to LA yield. The LA yield is highest at high acid concentrations and low initial HMF concentrations and essentially independent of the temperature.

A broadly applicable kinetic model for the acid catalysed HMF decomposition at sulfuric acid concentrations between 0.05 and 1 M, initial concentrations of HMF between 0.1 and 1 M and a temperature window of 98–181 °C using a power law approach has been developed. The reaction rates for the main reaction to LA and FA and the side reaction to humins were modelled as a function of C<sub>HMF</sub>, C<sub>H<sup>+</sup></sub> and T. A maximum likelihood approach has been applied to estimate the kinetic parameters. A good fit between experimental data and modelling results was obtained. The highest LA yield at short batch times is obtained at high temperature, a low initial HMF concentration and a high acid concentration.

## 6. Nomenclature

<i>a</i> <sub>H</sub>	Reaction order of HMF in the main reaction to LA and FA
<i>z</i> <sub>H</sub>	Reaction order of H <sup>+</sup> in the main reaction to LA and FA
<i>A</i> <sub>t</sub>	Heat transfer area (m <sup>2</sup> )
<i>b</i> <sub>H</sub>	Reaction order of HMF in the side reaction to humins
<i>β</i> <sub>H</sub>	Reaction order of H <sup>+</sup> in the side reaction to humins
<i>C</i> <sub>H<sup>+</sup></sub>	Concentration of H <sup>+</sup> (M)
<i>C</i> <sub>HMF</sub>	Concentration of HMF (M)
<i>C</i> <sub>HMF,0</sub>	Initial concentration of HMF (M)
<i>C</i> <sub>p</sub>	Heat capacity of reaction mixture (J g <sup>-1</sup> K <sup>-1</sup> )
<i>C</i> <sub>LA</sub>	Concentration of levulinic acid (M)
<i>C</i> <sub>LA,0</sub>	Initial concentration of levulinic acid (M)
<i>E</i> <sub>1H</sub>	Activation energy of the main reaction to LA and FA (kJ mol <sup>-1</sup> )
<i>E</i> <sub>2H</sub>	Activation energy of the side reaction to humins (kJ mol <sup>-1</sup> )
<i>h</i>	Heat transfer coefficient from the oven to the reaction mixture (min <sup>-1</sup> )
<i>k</i> <sub>1H</sub>	Reaction rate constant of HMF for the main reaction (M <sup>1-<i>a</i><sub>H</sub>-<i>z</i><sub>H</sub></sup> min <sup>-1</sup> )
<i>k</i> <sub>1RH</sub>	Reaction rate constant <i>k</i> <sub>1H</sub> at reference temperature (M <sup>1-<i>a</i><sub>H</sub>-<i>z</i><sub>H</sub></sup> min <sup>-1</sup> )
<i>k</i> <sub>2H</sub>	Reaction rate constant of HMF for the side reaction to humins (M <sup>1-<i>b</i><sub>H</sub>-<i>β</i><sub>H</sub></sup> min <sup>-1</sup> )
<i>k</i> <sub>2RH</sub>	Reaction rate constant <i>k</i> <sub>2H</sub> at reference temperature (M <sup>1-<i>b</i><sub>H</sub>-<i>β</i><sub>H</sub></sup> min <sup>-1</sup> )
<i>M</i>	Mass of the reaction mixture (g)
<i>R</i>	Universal gas constant, 8.3144 J mol <sup>-1</sup> K <sup>-1</sup>
<i>R</i> <sub>1</sub>	Reaction rate of HMF to LA and FA (mol L <sup>-1</sup> min <sup>-1</sup> )
<i>R</i> <sub>2</sub>	Reaction rate of HMF to humins (mol L <sup>-1</sup> min <sup>-1</sup> )
<i>S</i>	Rate selectivity parameter
<i>t</i>	Time (min)
<i>T</i>	Reaction temperature (K)

<i>T</i> <sub>i</sub>	Temperature of reaction mixture at <i>t</i> = 0 (K)
<i>T</i> <sub>oven</sub>	Temperature of oven (K)
<i>T</i> <sub>R</sub>	Reference temperature (K)
<i>U</i>	Overall heat transfer coefficient (W m <sup>-2</sup> K <sup>-1</sup> )
<i>X</i> <sub>HMF</sub>	Conversion of HMF (mol mol <sup>-1</sup> )
<i>Y</i> <sub>LA</sub>	Yield of levulinic acid (mol mol <sup>-1</sup> )
Special symbols	
$\hat{C}_i$	Estimated value of matrix <i>C</i> <sub><i>i</i></sub> ( <i>i</i> = HMF, LA)
$\bar{C}_i$	Average value of matrix <i>C</i> <sub><i>i</i></sub> ( <i>i</i> = HMF, LA)
norm(C)	Norm. of matrix C
%FIT <sub><i>i</i></sub>	Fit percentage of the <i>i</i> th compound ( <i>i</i> = HMF, LA)

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