

# Kinetic Study on the Acid-Catalyzed Hydrolysis of Cellulose to Levulinic Acid

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A variety of interesting bulk chemicals is accessible by the acid-catalyzed hydrolysis of cellulose. An interesting example is levulinic acid, a versatile precursor for fuel additives, polymers, and resins. A detailed kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid is reported in this paper. The kinetic experiments were performed in a temperature window of 150–200 °C, sulfuric acid concentrations between 0.05 and 1 M, and initial cellulose intakes between 1.7 and 14 wt %. The highest yield of levulinic was 60 mol %, obtained at a temperature of 150 °C, an initial cellulose intake of 1.7 wt %, and a sulfuric acid concentration of 1 M. A full kinetic model covering a broad range of reaction conditions was developed using the power-law approach. Agreement between the experimental data and the kinetic model is good. The kinetic expressions were used to gain insights into the optimum process conditions for the conversion of cellulose to levulinic acid in continuous-reactor configurations. The model predicts that the highest obtainable levulinic acid yield in continuous-reactor configurations is about 76 mol %, which was obtained when using reactors with a large extent of backmixing.

## 1. Introduction

Cellulose is a natural polymer consisting of glucose units. It is abundantly available on earth, and its annual production is estimated at  $2 \times 10^9$  tons.<sup>1</sup> Cellulose may be converted to interesting bulk chemicals by an acid-catalyzed hydrolysis reaction. During hydrolysis, the  $\beta$ -(1→4)-glycosidic bonds of cellulose are cleaved to give glucose, which can be converted further to various organic (bulk) chemicals. One attractive option is the conversion of glucose to levulinic acid (4-oxopentanoic acid) by acid treatment. Levulinic acid is a versatile building block for fuel additives, polymer precursors, and resin precursors.<sup>2</sup> Several reviews have been published describing the properties and potential industrial applications of levulinic acid and its derivatives.<sup>3–6</sup>

Two different approaches are commonly applied for the acid-catalyzed hydrolysis of cellulose. The first uses high concentrations of mineral acids (e.g., 15–16 N HCl or 31–70 wt % H<sub>2</sub>SO<sub>4</sub>) as catalysts and low operating temperatures (20–50 °C).<sup>7,8</sup> The major drawbacks are the high operating cost of acid recovery and the use of expensive construction material for both the hydrolyzer and the acid recovery system. The second approach uses highly diluted acids at high operating temperatures (170–240 °C). This method is favored, and research studies applying this approach are abundant.<sup>9–12</sup>

Various kinetic studies on the acid-catalyzed hydrolysis using a range of cellulosic materials have been reported in the literature. The first systematic kinetic study on biomass hydrolysis to glucose was performed in 1945 by Saeman,<sup>13</sup> who studied the hydrolysis reaction of Douglas fir in batch reactors. In this study, the hydrolysis reaction is modeled by the following two consecutive first-order reactions:



The reaction rate constants are represented by modified Arrhenius equations, including the effects of temperature ( $T$ ) and acid concentration ( $A$ ).

$$k_i = k_{i,0} A^{m_i} \exp^{-\frac{E_i}{RT}} \quad i = 1, 2 \quad (2)$$

Here,  $k_{i,0}$  is the frequency factor,  $m_i$  is the reaction order in acid,  $R$  is the ideal gas constant, and  $E_i$  is the activation energy.

Further investigations were conducted by Fagan and co-workers<sup>14</sup> on Kraft paper slurries. A nonisothermal plug-flow reactor was used to determine the kinetics of the hydrolysis reaction. Further studies were performed on Solka-Floc<sup>15</sup> and filter paper<sup>16</sup> in an isothermal plug-flow reactor. Malester and co-workers<sup>17,18</sup> carried out kinetic studies using municipal solid waste (MSW) as the cellulose source. The experiments were carried out in a 2 L batch steel reactor using sulfuric acid in low concentrations as the catalyst. All these kinetic studies applied the kinetic model developed earlier by Saeman<sup>13</sup> to analyze the kinetic data. An overview of kinetic studies including the range of process conditions and intakes is given in Table 1. For cellulose decomposition to glucose, the activation energy is between 172 and 189 kJ mol<sup>−1</sup>. However, large variations are observed in the order of acid concentration (1.0–1.78). A similar observation also holds for the decomposition of glucose to (nonidentified) products, where the order in acid concentration varies between 0.55 and 1.02.

The acid-catalyzed hydrolysis of cellulose is a heterogeneous reaction where mass-transfer effects may play an important role and, under some conditions, may even determine the overall reaction rate. As such, the dimensions of the cellulosic materials and their properties (e.g., crystallinity of the cellulose fraction) may have significant effects on the overall rate of the hydrolysis reaction. Mass-transfer effects on the overall rate of the hydrolysis reaction of cellulose were investigated by Saeman<sup>13</sup> by conducting the reaction with various cellulose particle sizes. The hydrolysis reaction rate was unaffected when using particle sizes in the range of 20–200 mesh (74–840  $\mu$ m). Similar results were obtained by Malester and co-workers.<sup>18</sup> These results imply that, under these conditions, the hydrolysis reaction of cellulose can be treated as a homogeneous reaction when the particle size of cellulose is <20 mesh (840  $\mu$ m). Sharples<sup>19,20</sup> proposed a kinetic model including the effects of the degree of crystallinity of the cellulose on the reaction rate. The cellulose applied in this study was pretreated with 18 wt % of sodium hydroxide

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**Table 1. Literature Overview of Kinetic Parameters for the Acid-Catalyzed Hydrolysis of Cellulose**

substrate	cellulose hydrolysis			glucose decomposition			reaction conditions
	$k_{1,o}$ (min <sup>-1</sup> )	$m_1$	$E_1$ (kJ mol <sup>-1</sup> )	$k_{2,o}$ (min <sup>-1</sup> )	$m_2$	$E_2$ (kJ mol <sup>-1</sup> )	
Douglas fir <sup>13</sup>	$1.73 \times 10^{19}$	1.34	179.5	$2.38 \times 10^{14}$	1.02	137.5	$T = 170\text{--}190\text{ }^\circ\text{C}$ $C_{\text{substrate}} = 10\text{ wt } \%$ $A = 0.4\text{--}1.0\text{ wt } \%$
Kraft paper slurries <sup>14</sup>	$28 \times 10^{19}$	1.78	188.7	$4.9 \times 10^{14}$	0.55	137.2	$T = 180\text{--}240\text{ }^\circ\text{C}$ $C_{\text{substrate}} = 2.5\text{ wt } \%$ $A = 0.2\text{--}1.0\text{ wt } \%$
Solca-Floc <sup>15</sup>	$1.22 \times 10^{19}$	1.16	177.8	$3.79 \times 10^{14}$	0.69	136.8	$T = 180\text{--}240\text{ }^\circ\text{C}$ $C_{\text{substrate}} = 10\text{ wt } \%$ $A = 0.5\text{--}2.0\text{ wt } \%$
filter paper <sup>16</sup>	$1.22 \times 10^{19}$	1.16	178.9	$3.79 \times 10^{14}$	0.69	137.2	$T = 200\text{--}240\text{ }^\circ\text{C}$ $C_{\text{substrate}} = 2\text{ wt } \%$ $A = 0.4\text{--}1.5\text{ wt } \%$
MSW <sup>18</sup>	$1.16 \times 10^{19}$	1.0	171.7	$4.13 \times 10^{15}$	0.67	142.4	$T = 200\text{--}240\text{ }^\circ\text{C}$ $C_{\text{substrate}} = 1\text{ wt } \%$ acid = 1.3–4.4 wt %

solution for 48 h at room temperature. A kinetic model with an inverse relation between the hydrolysis reaction rate constant and the mean length of the crystalline domains of the cellulose was proposed. Later investigations<sup>21,22</sup> have shown that the Sharples model is not valid for virgin, untreated cellulose.

All previous kinetic studies mainly focused on the optimization of glucose production. Only a few kinetic reports<sup>23–25</sup> are available for the acid-catalyzed hydrolysis of cellulose to levulinic acid. A complete kinetic model describing the acid-catalyzed hydrolysis of cellulose to levulinic acid, including byproduct formation and covering a broad range of reaction conditions and intakes, is lacking. In addition, the acid-catalyzed decomposition reactions of glucose and 5-hydroxymethylfurfural (HMF) produce an insoluble-solid product known as humins. These humins are expected to be formed as well when reacting cellulose with acids in an aqueous environment. However, humins formation has never been included in the kinetic models reported to date. In this paper, we report a systematic kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid using sulfuric acid as the catalyst. The effects of temperature, acid concentration, and initial intake of cellulose on the yield of levulinic acid were assessed, and a kinetic model including humin formation and covering a wide range of reaction conditions was developed. The results were applied to optimize the production of levulinic acid in various reactor configurations.

## 2. Materials and Methods

**2.1. Chemicals.** All chemicals used in this study were of analytical grade and used without purification. Microcrystalline cellulose [9004-34-6] with an average particle size of 20  $\mu\text{m}$  was purchased from Sigma-Aldrich. The elemental composition of the cellulose was determined by elemental analysis (C, 42.2%; H, 6.1%). The carbon content is less than the theoretical value for pure cellulose (C, 44.5%; H, 6.2%) because of the presence of water. On the basis of the elemental composition, the cellulose applied contains  $\sim 4\text{ wt } \%$  water. This was independently confirmed by thermogravimetric analysis (TGA). Concentrated sulfuric acid 95–97 wt % [7664-93-9], glucose [14431-43-7], and formic acid [64-18-6] were purchased from Merck GmbH (Darmstadt, Germany); 5-hydroxymethylfurfural [67-47-0] and levulinic acid 98 wt % [123-76-2] were obtained from Acros Organics (Geel, Belgium). Deionized water was applied to prepare the various solutions.

**2.2. Experimental Procedures. 2.2.1. Kinetic Experiments.** The reactions were carried out in two types of glass ampoules with a wall thickness of 1.5 mm and a length of 15 cm, differing

in internal diameter (3 and 5 mm). The ampoules were filled with the predetermined amount of cellulose. Subsequently, the acid-catalyst solution (0.2–0.5 cm<sup>3</sup>) was added. The ampoules were sealed with a torch. The sealed ampoules were placed in a constant-temperature oven ( $\pm 1\text{ }^\circ\text{C}$ ). At various reaction times, ampoules were taken from the oven and quenched in an ice-water bath (4  $^\circ\text{C}$ ) to stop the reaction. The ampoule was opened, and the liquid was separated from the solids using a microcentrifuge (Omnilab International BV) for  $\sim 15\text{--}20\text{ min}$  at 1200 rpm. A certain amount of the clear solution was taken (100–200  $\mu\text{L}$ ) and diluted with water (2 cm<sup>3</sup>). The composition of the solution was determined using high-performance liquid chromatography (HPLC).

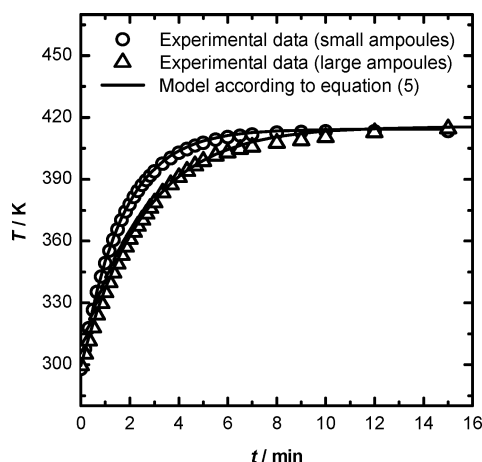
The composition of the gas phase after the reaction was determined using GC-MS. Gas samples were obtained by placing an ampoule in an airtight plastic bag. The plastic bag was flushed with helium and placed under vacuum. Subsequently, the glass ampoule was broken, and the released gas was mixed with 10 cm<sup>3</sup> of helium gas.

The solid products were washed with water several times and dried overnight in the oven at a temperature of 60  $^\circ\text{C}$ . The elemental composition of the dried solid products was determined using elemental analysis. The particle structure of the solid products was analyzed using a scanning electron microscope (SEM).

**2.2.2. Heat-Transfer Experiments.** At the start-up of the reaction, the ampoules were placed in a constant-temperature oven and the contents were heated up to the predetermined oven temperature. To determine the temperature profile at the start of the reaction and to compensate for this nonisothermal behavior in the kinetic modeling, the temperature inside the ampoule during the heating-up phase was determined experimentally. For this purpose, a special ampoule with a thermocouple was developed. The ampoule was filled with a representative reaction mixture (without catalyst) and closed tightly using a special bolt-and-screw system to prevent evaporation of the liquid. The ampoule was subsequently placed in the oven, and the temperature of the reaction mixture was followed in time. Before and after each experiment, the amount of liquid inside the ampoule was measured to determine the amount of evaporation. In all cases, the loss of water was  $< 1\text{ wt } \%$ , indicating that the results were not biased by water evaporation.

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

$$\frac{d(MC_p T)}{dt} = UA_i(T_{\text{oven}} - T) \quad (3)$$



**Figure 1.** Heating profile of the reaction mixture at  $T_{\text{oven}} = 140\text{ }^{\circ}\text{C}$  for both types of ampoules.

When assuming that the heat capacity of the reaction mixture is constant and not a function of temperature, rearrangement of eq 3 will give the following:

$$\frac{dT}{dt} = \frac{UA_t}{MC_p} (T_{\text{oven}} - T) = h(T_{\text{oven}} - T) \quad (4)$$

Solving the ordinary differential eq 4 with the initial value  $t = 0$ ,  $T = T_i$ , leads to

$$T = T_{\text{oven}} - (T_{\text{oven}} - T_i) \exp^{-ht} \quad (5)$$

The value of  $h$  was determined by fitting all experimental data at different oven temperatures ( $100\text{--}160\text{ }^{\circ}\text{C}$ ) using a nonlinear regression method and was found to be  $0.596\text{ min}^{-1}$  (for small ampoules) and  $0.359\text{ min}^{-1}$  (for large ampoules). Figure 1 shows experimental and modeled temperature profiles performed at an oven temperature of  $140\text{ }^{\circ}\text{C}$  using both types of ampoules. Equation 5 was incorporated in the kinetic model to describe the nonisothermal behavior of the system at the start-up of the reaction.

**2.3. Method of Analyses.** 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 refractive index detector. The mobile phase consisted of an aqueous solution of sulfuric acid ( $5\text{ mM}$ ) at a flow rate of  $0.55\text{ cm}^3\text{ min}^{-1}$ . The column was operated at  $60\text{ }^{\circ}\text{C}$ . The analysis for a sample was complete within 55 min. The concentration of each compound in the liquid phase was determined using calibration curves obtained by analyzing standard solutions with known concentrations.

The gas composition was analyzed with GC-MS, which consists of an HP 5890 Series II gas chromatograph and an HP 6890 detector. The composition of the gas phase was determined using a CP-Porabond-Q column (length =  $25\text{ m}$  and i.d. =  $0.25\text{ mm}$ ). The oven temperature was set at  $40\text{ }^{\circ}\text{C}$  for 2 min and increased to  $240\text{ }^{\circ}\text{C}$  with an increment of  $30\text{ }^{\circ}\text{C min}^{-1}$ . Helium was used as the carrier gas with a flow rate of  $1.5\text{ mL min}^{-1}$ . Elemental analyses were performed at the Analytical Department of the University of Groningen using an automated Euro EA3000 CHNS analyzer. Solid-products particles were analyzed using a field emission scanning electron microscope (FESEM) on a JEOL 6320F.

**2.4. Determination of 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. Minimization of errors was 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 calculation of errors was based on the concentrations of glucose ( $C_{\text{GLC}}$ ) and levulinic acid ( $C_{\text{LA}}$ ). To compensate for the large spread in concentrations, the concentrations were scaled and transformed to the yields of glucose ( $Y_{\text{GLC}}$ ) and levulinic acid ( $Y_{\text{LA}}$ ), respectively. By definition, these vary between 0 and 1 and are expressed as

$$Y_{\text{GLC}} = \frac{C_{\text{GLC}}}{C_{\text{CEL},0}} \quad (6)$$

$$Y_{\text{LA}} = \frac{C_{\text{LA}}}{C_{\text{CEL},0}} \quad (7)$$

Here, the  $C_{\text{CEL},0}$  is defined as the initial concentration of cellulose, expressed as the amount of glucose units present in cellulose and determined using the following relation:

$$C_{\text{CEL},0} = \frac{\text{mass of cellulose} \times \text{wt \% of glucose in cellulose}}{\text{molecular weight of glucose} \times \text{volume of reaction mixture}} \quad (8)$$

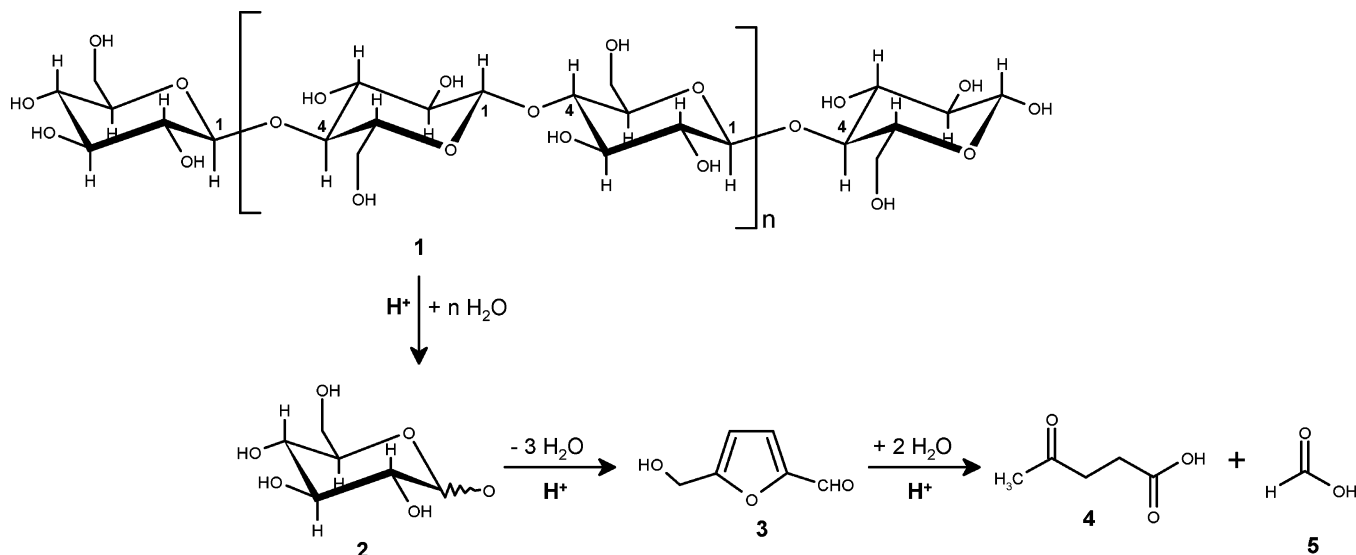
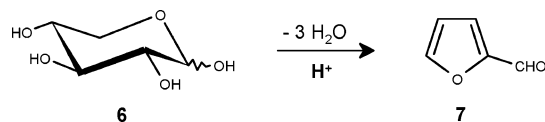
### 3. Results and Discussions

**3.1. Reaction Products.** The generally accepted reaction pathway for the acid-catalyzed hydrolysis of cellulose to levulinic acid is schematically given in Scheme 1.

In the first step, the polymer chains of cellulose (**1**) are broken down into low molecular weight fragments and ultimately to glucose (**2**) by the action of an acid catalyst. The glucose is decomposed to 5-hydroxymethylfurfural (HMF, **3**), which is further converted in a serial mode to levulinic acid (**4**) and formic acid (**5**). All anticipated products (**2–5**) were detected in this study and identified and quantified using HPLC analysis. A typical example of an HPLC chromatogram is given in Figure 2.

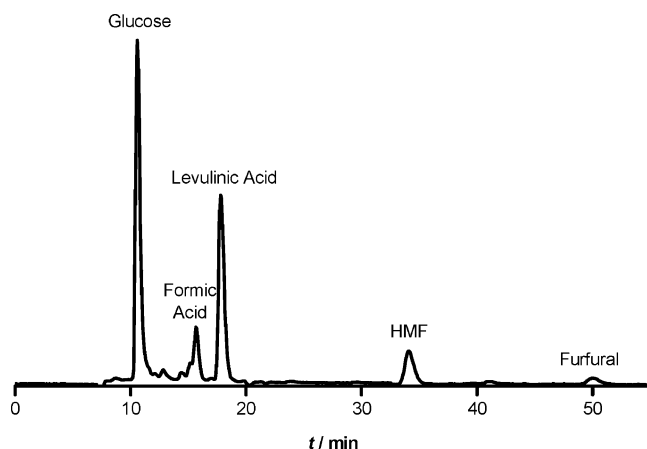
Besides the anticipated products, small amounts of glucose-reversion products (e.g., levoglucosan, isomaltose, or gentiobiose) and furfural were detected in the liquid phase. The formation of the reversion products was also observed in our previous study<sup>26</sup> on the acid-catalyzed decomposition of glucose. The maximum amount of glucose-reversion products was very low ( $<0.1\text{ wt \%}$ ). The presence of furfural in the reaction mixture is, at first sight, surprising. It is a known product of the acid-catalyzed decomposition of C5-sugars and particularly of xylose (**6**), as shown in Scheme 2.<sup>27–29</sup> It is likely that the cellulose applied in this study is contaminated with C5-sugars, producing furfural (**7**). On the basis of the intake of cellulose and the maximum experimentally observed concentration of furfural, the amount of C5-sugars in the cellulose applied in this study is  $\sim 1\text{ wt \%}$ .

During all experiments, dark-brown insoluble substances known as humins were formed. These are well-known products of side-reactions of the acid-catalyzed decompositions of glucose and HMF. The presence of these humins was confirmed by elemental analysis on the solid products present after the reaction. The elemental composition (in wt %) for a typical product (C, 55.2; H, 4.9) suggests that the solids are a mixture consisting mainly of humins (typical composition: C, 63.1; H, 4.2)<sup>30</sup> and some unreacted cellulose (C, 42.2; H, 6.1). Further

**Scheme 1. Acid-Catalyzed Hydrolysis Reaction of Cellulose to Levulinic Acid****Scheme 2. Acid-Catalyzed Decomposition of Xylose to Furfural**

evidence for the formation of substantial amounts of humins was obtained from SEM. Typical SEM images of the cellulose particles applied in this study and the solid products after the reaction are given in Figure 3. It shows round-shaped, agglomerated particles with particle sizes in the range of 5–10  $\mu m$ . On the basis of their visual appearance, the particles are likely composed of insoluble humins.<sup>30</sup> Furthermore, some unreacted cellulose appears to be present, in line with the elemental analysis data.

Other possible byproducts of the acid-catalyzed hydrolysis of cellulose are gas-phase components from thermal degradation reactions of reactants and/or products. To gain insights into the extent of these reactions, the gas phase after the reaction was analyzed using GC and GC-MS. Both CO and CO<sub>2</sub> could be detected; however, the amounts were <0.1 wt % of the cellulose intake. This implies that the formation of gas-phase compounds is only a minor reaction pathway under the reaction conditions applied in our experiments.



**Figure 2.** Typical HPLC chromatogram for the acid-catalyzed hydrolysis of cellulose ( $x_{CEL,0} = 7.7$  wt %,  $CH_2SO_4 = 0.05$  M,  $T = 200$  °C,  $t = 16$  min).

The product levulinic acid (LA) is stable at the conditions applied in this study and is not a source for byproducts (e.g., levoglucosan or  $\alpha$ -angelica lactone). This was independently checked by exposing a solution of levulinic acid (0.1 M) in a 1 M aqueous sulfuric acid solution for 2 h at 200 °C. After reaction, only LA was detected in the solution.

**3.2. Effects of Process Variables on the Yield of Levulinic Acid.** A total of 26 experiments were performed covering a wide range of reaction conditions. Three operating temperatures (150, 175, and 200 °C) were used. In all cases, sulfuric acid was used as the catalyst with concentrations varying between 0.05 and 1 M. The initial intake of cellulose ( $x_{CEL,0}$ ) was varied between 1.7 and 14 wt %.

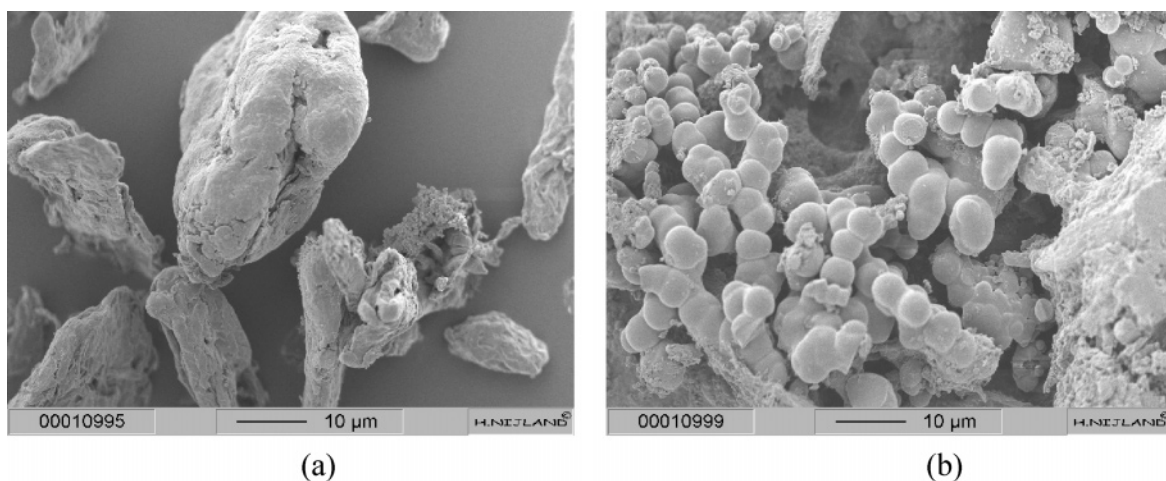
The composition of the reaction mixture was followed in time and a typical concentration profile is given in Figure 4. As anticipated on the basis of Scheme 1, the concentrations of both glucose and 5-hydroxymethylfurfural (HMF) displayed an optimum. The maximum  $C_{GLC}$  was 0.15 M, which equals a glucose yield ( $Y_{GLC}$ ) of 30 mol %. The maximum  $C_{HMF}$  obtained in all experiments were generally much lower than the maximum  $C_{GLC}$ , which indicates that the conversion of HMF to levulinic acid (LA) and formic acid (FA) is much faster than the conversion of glucose to HMF. In line with the reaction stoichiometry given in Scheme 1, LA and FA were always found in a 1:1 molar ratio. This finding also implies that these compounds are stable under the reaction conditions employed and do not decompose to other products.

The yield of levulinic acid ( $Y_{LA}$ ) is a clear function of the operating temperature, with high temperatures leading to reduced yields. This is illustrated in Figure 5, where the yields of levulinic acid are plotted as a function of reaction time at three different temperatures.

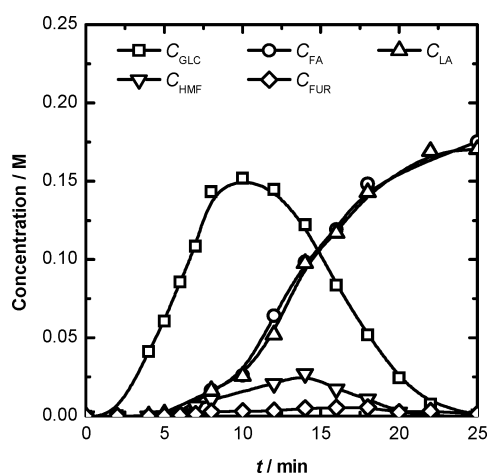
The yield of levulinic acid was improved when applying higher acid concentrations; see Figure 6 for details. This effect was substantial, and the yields increased from 31 to 54 mol % when increasing the acid concentration from 0.1 to 1 M.

A number of experiments were carried out using various initial intakes of cellulose (1.7–14 wt %) at  $T = 150$  °C and a catalyst concentration of 1 M. The initial intake of cellulose has a significant effect on the yields of levulinic acid (Figure 7). Lower intakes of cellulose resulted in higher yields of levulinic acid. These findings are in line with previous studies on the acid-catalyzed decompositions of HMF and glucose,

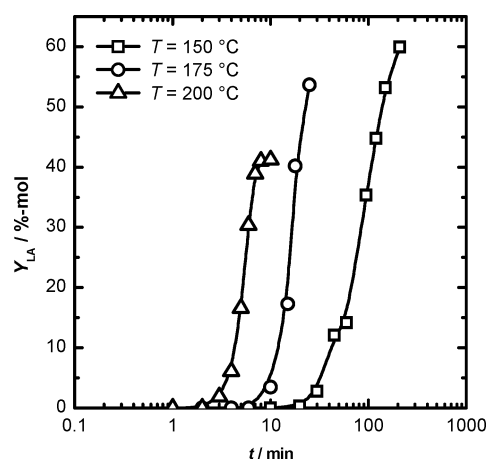




**Figure 3.** SEM image of cellulose particles used in this study (a) and the solid products obtained after the reaction (b).



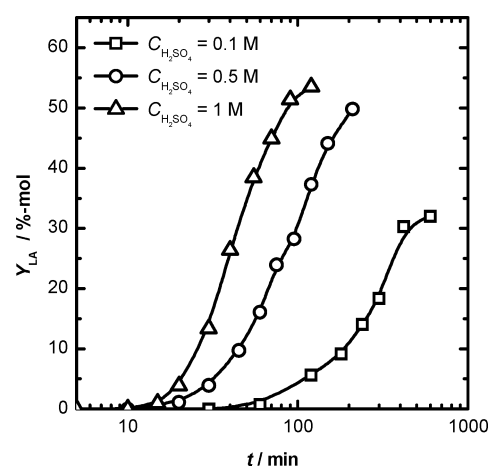
**Figure 4.** Typical concentration profile during acid-catalyzed hydrolysis of cellulose ( $x_{CEL,0} = 7.7$  wt %,  $C_{H_2SO_4} = 0.05$  M,  $T = 200$  °C).



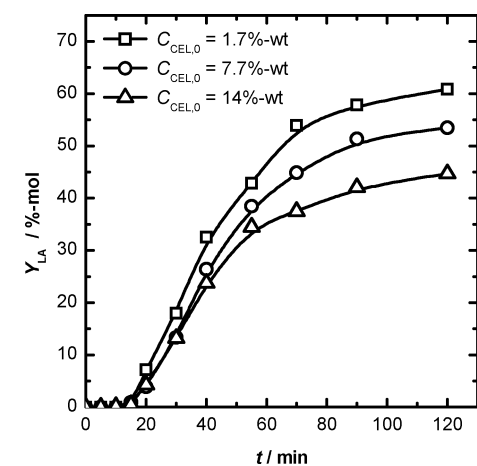
**Figure 5.** Effect of temperature on the yield of levulinic acid ( $x_{CEL,0} = 1.7$  wt % and  $C_{H_2SO_4} = 0.5$  M).

where low substrate concentrations favored high LA yields. The highest levulinic acid yield (60 mol %) at full cellulose conversion was obtained at a temperature of 150 °C, an initial cellulose intake of 1.7 wt %, and a sulfuric acid concentration of 1 M.

**3.3. Kinetic Modeling. 3.3.1. Development of a Kinetic Model.** We here propose a novel kinetic model for the acid-catalyzed hydrolysis of cellulose to levulinic acid, including the



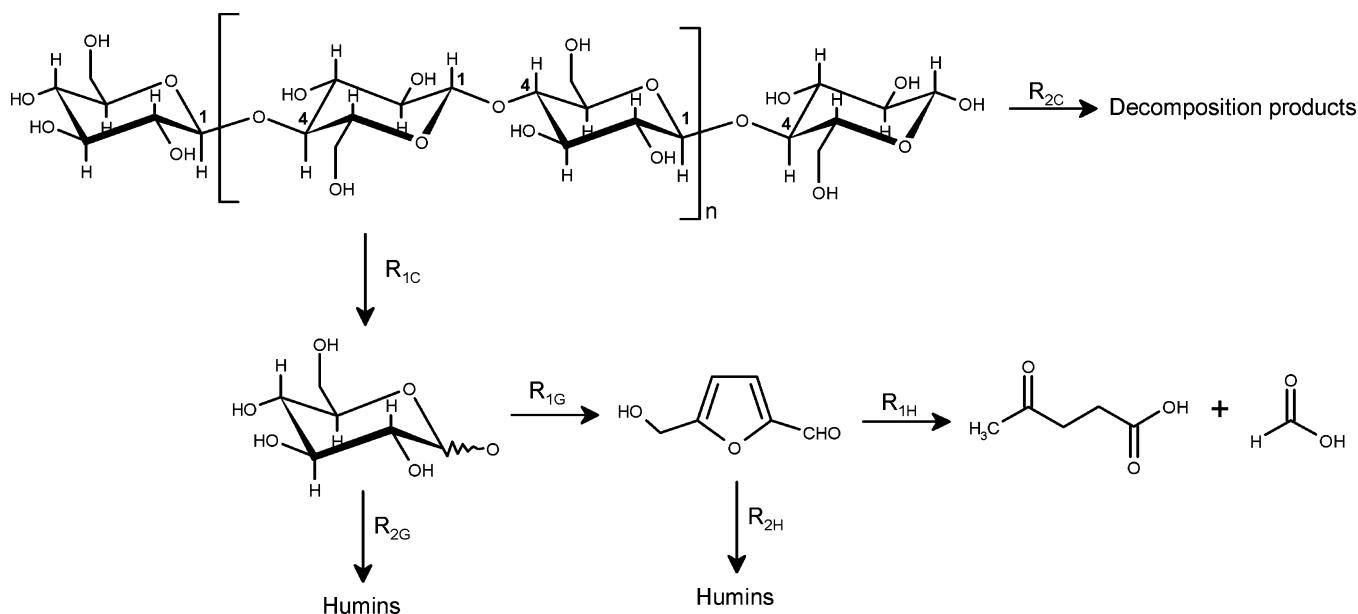
**Figure 6.** Effect of sulfuric acid concentration on yield of levulinic acid ( $T = 150$  °C and  $x_{CEL,0} = 7.7$  wt %).



**Figure 7.** Effect of initial intake of cellulose on yields of levulinic acid ( $T = 150$  °C and  $C_{H_2SO_4} = 1$  M).

main reactions and possible side reactions. It is based on the following considerations:

- (1) The reaction rate equations are quantified using the power-law approach instead of a pseudo-first-order approach.
- (2) The reaction rate constants are defined in term of modified Arrhenius equations that combine effects of both temperature and acid-catalyst concentration.
- (3) The first step in the acid-catalyzed hydrolysis of cellulose is cleavage of the  $\beta$ -(1 $\rightarrow$ 4)-glycosidic bond in cellulose to

**Scheme 3. Proposed Reaction Network for the Acid-Catalyzed Hydrolysis Reaction of Cellulose to Levulinic Acid**

glucose by an acid catalyst (see Scheme 3). The rate of this reaction is expressed by the following equations:

$$R_{1C} = k_{1C}(C_{CEL})^{a_C} \quad (9)$$

$$k_{1C} = k_{1RC} \exp\left[-\frac{E_{1C}}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right] (C_{H^+})^{a_C} \quad (10)$$

In this paper, the concentration of cellulose is defined in terms of the number of available glucose units in the cellulose.

(4) It is assumed that cellulose does not selectively react to glucose. We propose that decomposition products are formed in a parallel-reaction mode.<sup>31,32</sup> All side reactions are lumped in one overall reaction (Scheme 3) and modeled using the following relations:

$$R_{2C} = k_{2C}(C_{CEL})^{b_C} \quad (11)$$

$$k_{2C} = k_{2RC} \exp\left[-\frac{E_{2C}}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right] (C_{H^+})^{b_C} \quad (12)$$

(5) The main reaction of the acid-catalyzed decomposition of glucose is the formation of HMF with a reaction rate defined as follows:

$$R_{1G} = k_{1G}(C_{GLC})^{a_G} \quad (13)$$

$$k_{1G} = k_{1RG} \exp\left[-\frac{E_{1G}}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right] (C_{H^+})^{a_G} \quad (14)$$

In parallel, undesired products (humins) are produced for which the reaction rate is defined as follows:

$$R_{2G} = k_{2G}(C_{GLC})^{b_G} \quad (15)$$

$$k_{2G} = k_{2RG} \exp\left[-\frac{E_{2G}}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right] (C_{H^+})^{b_G} \quad (16)$$

The kinetic parameters for the acid-catalyzed reaction of glucose to HMF and humins have been determined independently, and the values of the kinetic constants are given in Table 2.<sup>26</sup>

(6) Levulinic acid and formic acid are formed when HMF is treated with sulfuric acid, and the rate of this reaction is expressed as follows:

$$R_{1H} = k_{1H}(C_{HMF})^{a_H} \quad (17)$$

$$k_{1H} = k_{1RH} \exp\left[-\frac{E_{1H}}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right] (C_{H^+})^{a_H} \quad (18)$$

Similar to that of glucose, the side reaction of the acid-catalyzed decomposition of HMF results in the formation of humins:

$$R_{2H} = k_{2H}(C_{HMF})^{b_H} \quad (19)$$

$$k_{2H} = k_{2RH} \exp\left[-\frac{E_{2H}}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right] (C_{H^+})^{b_H} \quad (20)$$

The kinetic parameters for both main and side reactions of the acid-catalyzed decomposition of HMF have been determined previously and are given in Table 3. Experimentally, it was observed that the acid-catalyzed decomposition of HMF was generally fast compared to the reaction of glucose to HMF (*vide supra*). Only at high temperatures (>200 °C), significant amounts of HMF were formed. In all other cases, the maximum HMF yield was <2.5 mol % on the basis of cellulose intake. Therefore, the acid-catalyzed decomposition of HMF was included in the kinetic model only for the high-temperature (200 °C) experiments.

**Table 2. Kinetic Parameters for the Acid-Catalyzed Decomposition of Glucose<sup>26</sup>**

parameter	estimate
$a_G$	$1.09 \pm 0.01$
$b_G$	$1.30 \pm 0.02$
$\alpha_G$	$1.13 \pm 0.01$
$\beta_G$	$1.13 \pm 0.02$
$E_{1G}$ (kJ mol <sup>-1</sup> )	$152.2 \pm 0.7$
$E_{2G}$ (kJ mol <sup>-1</sup> )	$164.7 \pm 0.6$
$k_{1RG}$ <sup>a</sup> (M <sup>1-<math>\alpha_G</math>-<math>\beta_G</math></sup> min <sup>-1</sup> )	$0.013 \pm 0.001$
$k_{2RG}$ <sup>a</sup> (M <sup>1-<math>b_G</math>-<math>\beta_G</math></sup> min <sup>-1</sup> )	$0.013 \pm 0.001$

<sup>a</sup> The values were determined at a reference temperature ( $T_R$ ) of 140 °C.

**Table 3. Estimated Kinetic Parameters for the Acid-Catalyzed Decomposition of HMF<sup>30</sup>**

parameter	estimate
$a_H$	$0.88 \pm 0.01$
$b_H$	$1.23 \pm 0.03$
$\alpha_H$	$1.38 \pm 0.02$
$\beta_H$	$1.07 \pm 0.04$
$E_{1H}$ (kJ mol <sup>-1</sup> )	$110.5 \pm 0.7$
$E_{2H}$ (kJ mol <sup>-1</sup> )	$111.3 \pm 2.0$
$k_{1RH}^a$ (M <sup>1-<math>a_H</math>-<math>\alpha_H</math></sup> min <sup>-1</sup> )	$0.340 \pm 0.010$
$k_{2RH}^a$ (M <sup>1-<math>b_H</math>-<math>\beta_H</math></sup> min <sup>-1</sup> )	$0.117 \pm 0.008$

<sup>a</sup> The values were determined at a reference temperature ( $T_R$ ) of 140 °C.

**Table 4. Estimated Kinetic Parameters for the Acid-Catalyzed Hydrolysis of Cellulose**

parameter	estimate
$a_C$	$0.98 \pm 0.02$
$b_C$	$1.01 \pm 0.08$
$\alpha_C$	$0.96 \pm 0.02$
$\beta_C$	$0.94 \pm 0.07$
$E_{1C}$ (kJ mol <sup>-1</sup> )	$151.5 \pm 1.2$
$E_{2C}$ (kJ mol <sup>-1</sup> )	$174.7 \pm 1.4$
$k_{1RC}^a$ (M <sup>1-<math>a_C</math>-<math>\alpha_C</math></sup> min <sup>-1</sup> )	$0.410 \pm 0.018$
$k_{2RC}^a$ (M <sup>1-<math>b_C</math>-<math>\beta_C</math></sup> min <sup>-1</sup> )	$0.065 \pm 0.014$

<sup>a</sup> The values were determined at a reference temperature ( $T_R$ ) of 175 °C.

(7) Previously, we have shown that both levulinic and formic acids are stable under the reaction conditions employed and do not decompose to humins or other organic compounds in the wide range of reaction conditions applied.<sup>30</sup> Therefore, the kinetic model does not include decomposition reactions of levulinic acid and formic acid.

(8) The amount of gaseous products formed during the acid-catalyzed hydrolysis of cellulose and the acid-catalyzed decompositions of glucose and HMF are negligible (*vide infra*). Therefore, these decomposition reactions were not included in the kinetic model.

For a batch reactor setup, the concentration of the individual species as a function of time, using the proposed kinetic model given in Scheme 3, may be represented by the following ordinary differential equations.

$$\frac{dC_{CEL}}{dt} = -R_{1C} - R_{2C} \quad (21)$$

$$\frac{dC_{GLC}}{dt} = R_{1C} - R_{1G} - R_{2G} \quad (22)$$

$$\frac{dC_{HMF}}{dt} = R_{1G} - R_{1H} - R_{2H} \quad (23)$$

$$\frac{dC_{LA}}{dt} = R_{1H} \quad (24)$$

The rate expressions (eqs 9–20) in combination with the mass balances (eqs 21–24) and the temperature profile (eq 5) were applied to model the experimental batch data.

**3.3.2. Modeling Results.** A total of 26 experiments gave 280 sets of experimental data, where each set consists of the concentrations of glucose, HMF, and levulinic acid 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 4.

The modeling results indicate that both the main reaction of cellulose to glucose and the side reaction to the decomposition

product are first order with respect to cellulose. These results confirm the assumption of Saeman's kinetic model<sup>13</sup> that the reaction of cellulose to glucose is first order in cellulose. Furthermore, the orders in acid concentration for both the main and side reactions are also close to 1. For the main reaction, orders between 1.0 and 1.78 were reported in the literature (Table 1).

Figure 8 shows a good fit between the experimental concentrations of glucose, HMF, and levulinic acid and the kinetic model for a broad range of reaction conditions. This is also confirmed by the parity plot as shown in Figure 9.

**3.3.3. Evaluation of Mass-Transfer Effects.** The kinetic data for the acid-catalyzed hydrolysis of cellulose were determined with the assumption that the overall reaction rate is not affected by mass-transfer effects. The existence of internal-particle mass-transfer limitations may be evaluated using the Weisz modulus ( $M_W$ ), which represents the ratio of the reaction rate and diffusion rate:

$$M_W = \frac{r_{GLC}}{C_{H^+,cel}} \frac{(d_{cel}/6)^2}{D_{H^+,cel}} \quad (25)$$

In eq 25, the term  $r_{GLC}$  is the reaction rate of glucose ((mol of glucose)/(m<sup>3</sup> of cellulose particle)/s),  $d_{cel}$  is the typical diameter of a cellulose particle, and  $C_{H^+,cel}$  and  $D_{H^+,cel}$  are the concentration and the diffusion coefficient of H<sup>+</sup> in the solid phase, respectively. Mass-transfer effects on the overall reaction rate are negligible when the  $M_W$  value is <0.15.<sup>33</sup>

To evaluate the value for  $M_W$ , a typical reaction rate at the high end of the temperature range (200 °C) was determined, because the effects of mass transfer on overall reaction are generally more profound at high temperatures. About  $6 \times 10^{-3}$  mmol of glucose was obtained from 8.2 mg of cellulose after 3 min. In combination with a bulk density of the microcrystalline cellulose of 500 kg m<sup>-3</sup>, this leads to an  $r_{GLC}$  of  $\sim 2$  mol m<sub>cellulose</sub><sup>-3</sup> s<sup>-1</sup>.

The concentration of H<sup>+</sup> in the cellulose particle may be estimated by the following equation:

$$m = \frac{C_{H^+,cel}}{C_{H^+,water}} \quad (26)$$

The value for  $m$  was calculated using literature data<sup>34</sup> and was estimated to be  $\sim 8$ . When applying a 0.5 M sulfuric acid concentration, the value of  $C_{H^+,cel}$  is  $\sim 4$  kmol m<sub>cellulose</sub><sup>-3</sup>.

Microcrystalline cellulose has a high capacity to retain water, and it swells to almost 100% of its initial particle size at 20 °C.<sup>35</sup> The diffusion coefficient of sulfuric acid in the swollen cellulose can be estimated as the diffusion coefficient in a porous medium:

$$D_{H^+,cel} = D_{H^+,w} \epsilon^{1.5} \quad (27)$$

The diffusion coefficient of sulfuric acid in water,<sup>37</sup>  $D_{H^+,w}$ , is  $\sim 1.8 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>, and the void fraction ( $\epsilon$ ) of 0.5 was obtained from the swelling properties of cellulose in water. Therefore, the diffusion coefficient of H<sup>+</sup> in cellulose was estimated to be  $6.4 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>. With these data and by using an average particle size of a cellulose particle of 20  $\mu$ m, an  $M_W$  value of  $3.1 \times 10^{-6}$  is calculated. This value is  $\ll 0.15$  and indicates that diffusion limitations are absent. Experimental verification was obtained by performing experiments with larger cellulose particles ( $d_{cel}$  between 45 and 55  $\mu$ m), obtained by sieving the cellulose particles through two successive sieves (55

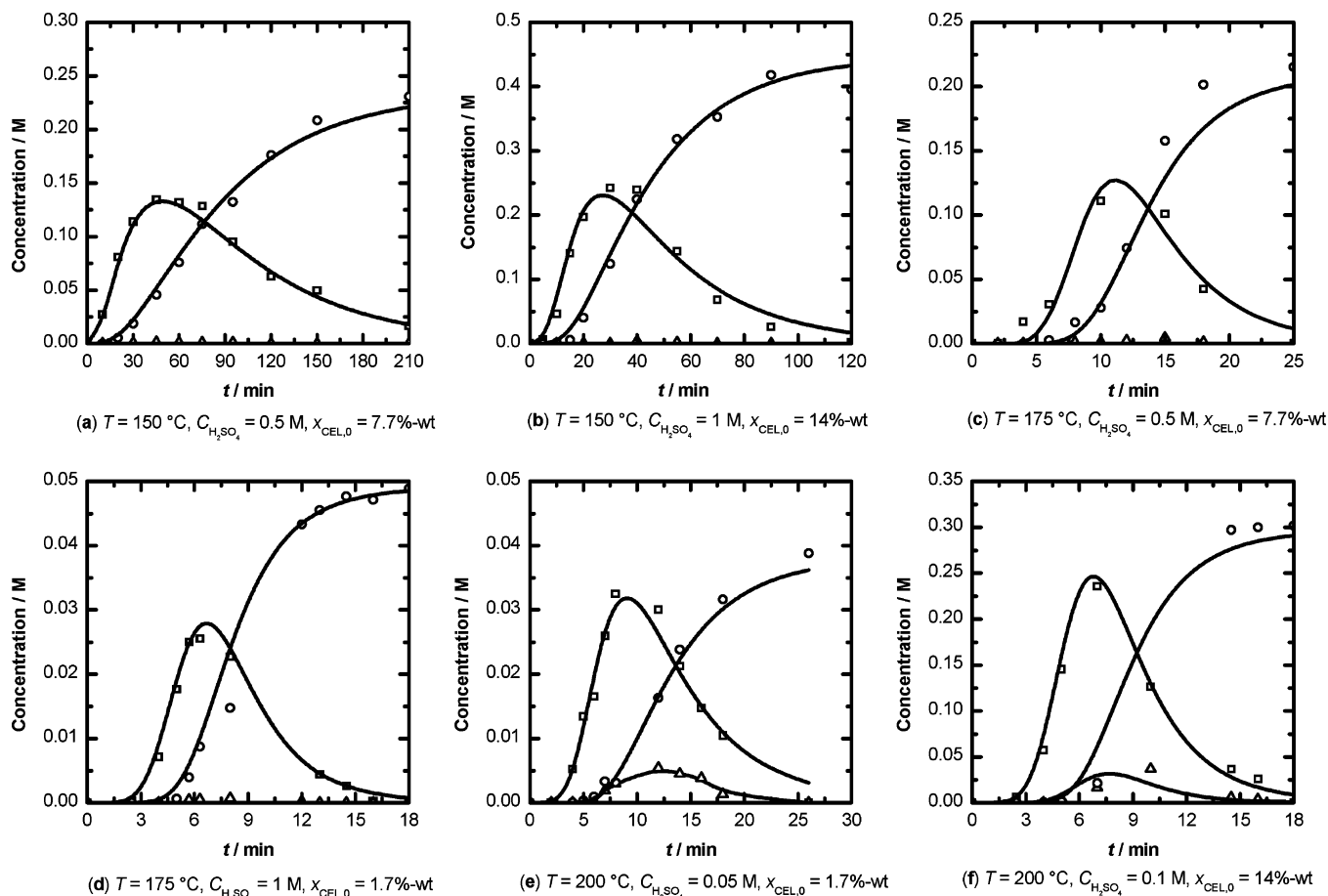


Figure 8. Comparison of experimental data ( $\square$ ,  $C_{GLC}$ ;  $\Delta$ ,  $C_{HMF}$ ;  $\circ$ ,  $C_{LA}$ ) and kinetic model (solid lines).

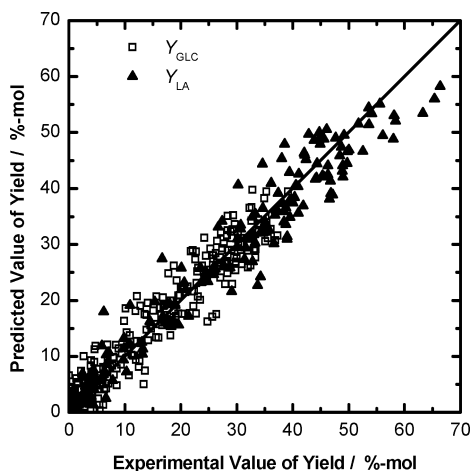


Figure 9. Parity plot for the experimental and modeled yield of glucose and levulinic acid.

$\mu\text{m}$  and  $45\ \mu\text{m}$ ). The experimental results are shown in Figure 10. Evidently, similar results were obtained for both particle sizes, a clear indication that mass-transfer limitations are absent and do not bias the kinetic data.

**3.3.4. Model Implications.** The yields of levulinic acid ( $Y_{LA}$ ) were considerably reduced at high temperatures, as has been discussed in Section 3.2. The effects of temperature on  $Y_{LA}$  may be explained using the kinetic model (see Figure 11).

The hydrolysis reaction of cellulose to decomposition products has the largest activation energy ( $174.7\ \text{kJ mol}^{-1}$ ), which implies that this reaction is the most sensitive to the temperature. The second-largest activation energy ( $164.7\ \text{kJ mol}^{-1}$ ) was observed for the decomposition reaction of glucose to humins.

Conducting the reaction at high temperatures favors these side reactions, and as a result, more side products (i.e., the decomposition products and humins) are produced and the formation of levulinic acid is suppressed.

Experimentally, it has been observed that the yield of levulinic acid is higher when applying higher acid concentrations; see Figure 6 for details. These findings may be explained by assessing the reactions orders in acid concentrations for the various reactions. For the hydrolysis reaction of cellulose, the reaction orders in acid are similar for both the main ( $\alpha_C = 0.96$ ) and side ( $\beta_C = 0.94$ ) reactions, and no effects of the acid concentration are expected. Also, the orders in acid for glucose decompositions to HMF ( $\alpha_G = 1.13$ ) and humins ( $\beta_G = 1.13$ ) are similar. However, the reaction order in acid for the hydration reaction of HMF to LA has a slightly higher value ( $\alpha_H = 1.38$ ) than the side reaction ( $\beta_H = 1.07$ ). Therefore, high acid concentrations favor the hydration reaction of HMF to LA and lead to increased  $Y_{LA}$ .

Experimentally, it was found that low cellulose intakes lead to higher  $Y_{LA}$ . The reaction orders in cellulose for the reactions involving cellulose (see Figure 11) are similar ( $a_C = 0.98$  and  $b_C = 1.01$ ). Therefore, no loading effects are expected on the selectivity of this reaction. However, low cellulose loadings and subsequently low glucose concentrations favor the formation of LA and suppress humins formation. This is evident from the reaction orders of glucose (1.09) and HMF (0.88) for the main reactions, which are smaller than those of the undesired side reactions (1.30 and 1.23 for glucose and HMF, respectively).

**3.3.5. Comparisons with Previous Kinetic Studies.** A number of kinetic studies have been reported in the literature for the hydrolysis of cellulose to glucose (Table 1). However,



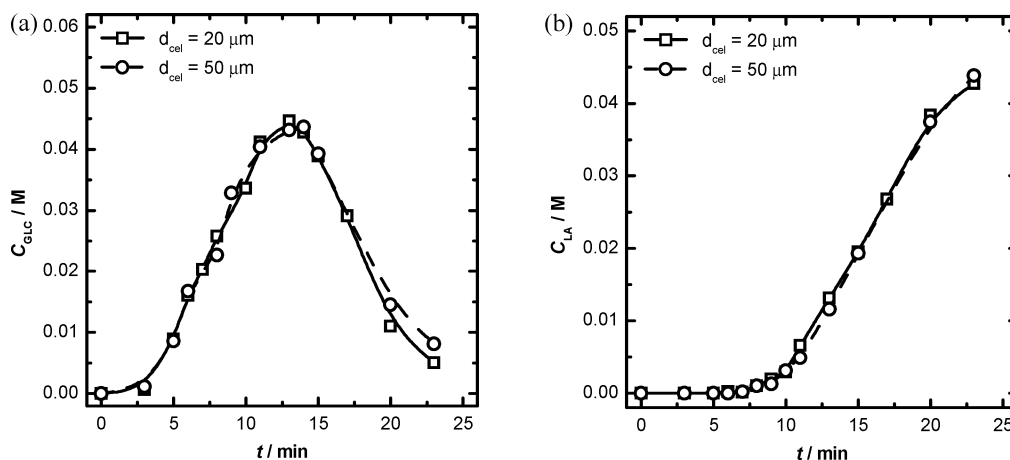


Figure 10. Effects of cellulose particle size on the concentrations of glucose (a) and levulinic acid (b).

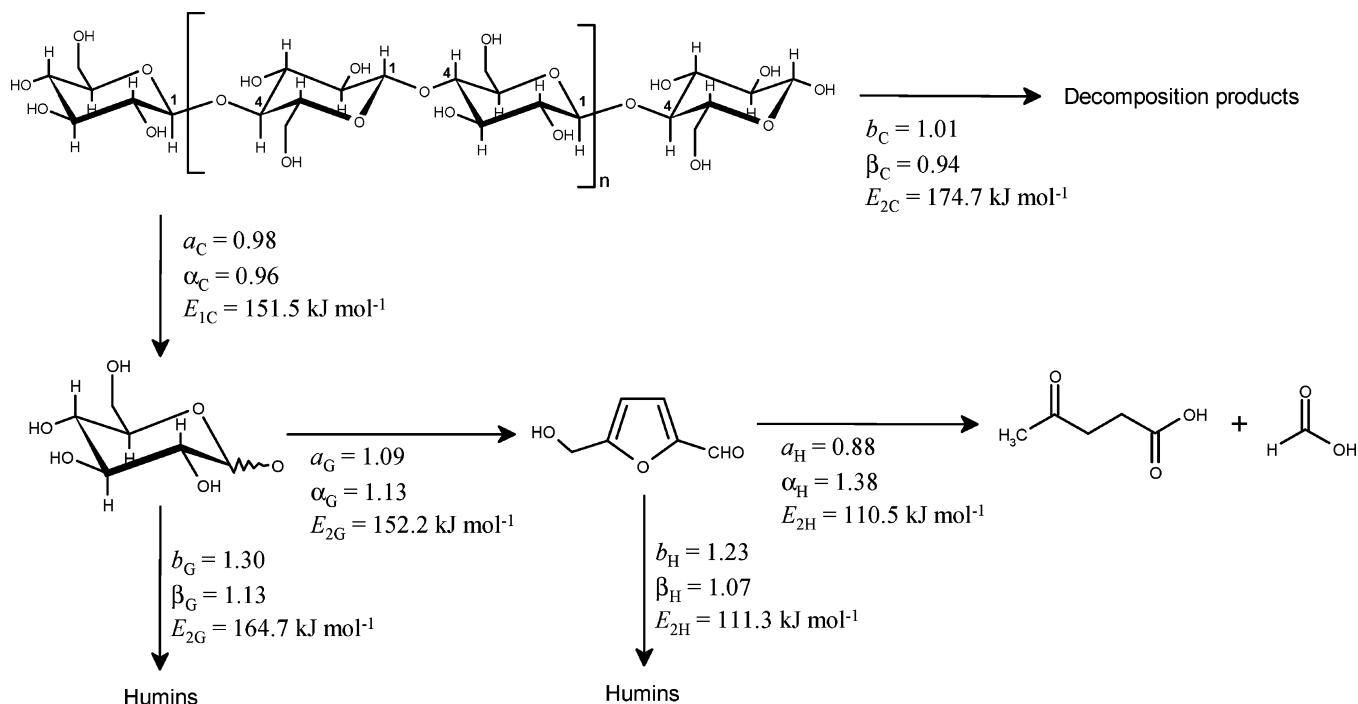


Figure 11. Schematic overview of reaction network and estimated kinetic parameters for cellulose hydrolysis to levulinic acid.

the range of process conditions and substrate intakes is generally rather limited; for instance, the intake of lignocellulosic material was not varied within each study. The kinetic study reported in this paper has been set up and validated for a much wider range of conditions. To investigate the broad applicability of the kinetic model presented in this paper, the modeled reaction rate constants ( $k_{CEL,model}$ ) for a set of experimental conditions were compared with the various literature models. For this purpose, a set of reaction conditions ( $T$ ,  $C_{H_2SO_4}$ , and  $x_{CEL,0}$ ) was selected within the validity range of our model ( $150^\circ C < T < 200^\circ C$ ,  $0.05 \text{ M (0.5 wt \%)} < C_{H_2SO_4} < 1 \text{ M (9.8 wt \%)}$ ,  $1.7 \text{ wt \%} < x_{CEL,0} < 14 \text{ wt \%}$ ). The reaction rate constants of cellulose hydrolysis at various reaction conditions were calculated using eqs 10 and 12, by taking into account that  $k_{CEL,model} = k_{1C} + k_{2C}$ . Similarly, the reaction rate constants of cellulose hydrolysis from the literature models ( $k_{CEL,lit}$ ) were calculated using the data provided in Table 1. The literature studies were performed using a feedstock with various cellulose contents. For a proper comparison, the actual cellulose content was calculated and used to determine the  $k_{CEL,lit}$ . The  $k_{CEL,lit}$  were compared with  $k_{CEL,model}$ , and the results are given in Figure 12. A good fit

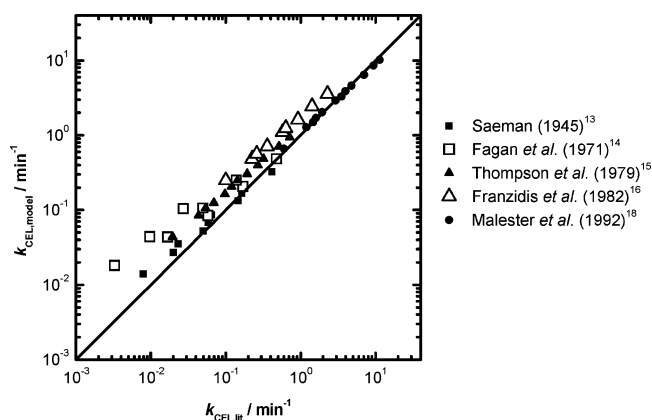
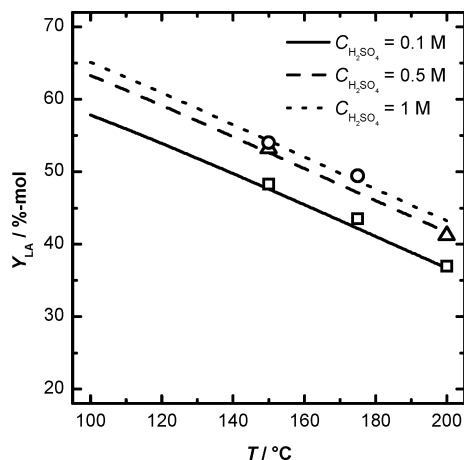


Figure 12. Comparisons between literature models and the kinetic model provided here.

between the  $k_{CEL,lit}$  and  $k_{CEL,model}$  was observed, especially for the kinetic models derived by Saeman<sup>13</sup> and Malester et al.,<sup>18</sup> indicating the broad applicability of our kinetic model.



**Figure 13.** Effects of temperature and acid concentration on  $Y_{LA}$  evaluated at  $X_{CEL} = 99$  mol % and  $x_{CEL,0} = 1.7$  wt %. (□), (Δ), and (○) represent the experimental  $Y_{LA}$  at  $C_{H_2SO_4} = 0.1, 0.5$ , and  $1$  M, respectively.

#### 4. Applications of the Kinetic Model for Reactor Optimization

##### 4.1. Optimization of LA Production in a Batch Reactor.

With the model available, it is possible to optimize the yields of levulinic acid in a batch reactor as a function of reaction conditions. The yields of levulinic acid were evaluated at 99 mol % cellulose conversion ( $X_{CEL}$ ), which is defined as follows:

$$X_{CEL} = 1 - \frac{C_{CEL}}{C_{CEL,0}} \quad (28)$$

The combination of eqs 21–24 with the differentiated form of eq 28 leads to the following expressions:

$$\frac{dC_{CEL}}{dX_{CEL}} = -C_{CEL,0} \quad (29)$$

$$\frac{dC_{GLC}}{dX_{CEL}} = \frac{R_{1C} - R_{1G} - R_{2G}}{R_{1C} + R_{2C}} C_{CEL,0} \quad (30)$$

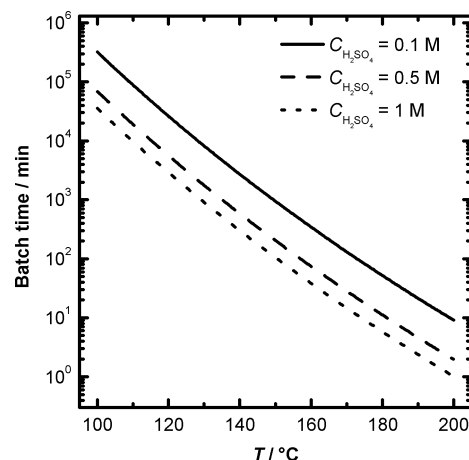
$$\frac{dC_{HMF}}{dX_{CEL}} = \frac{R_{1G} - R_{1H} - R_{2H}}{R_{1C} + R_{2C}} C_{CEL,0} \quad (31)$$

$$\frac{dC_{LA}}{dX_{CEL}} = \frac{R_{1H}}{R_{1C} + R_{2C}} C_{CEL,0} \quad (32)$$

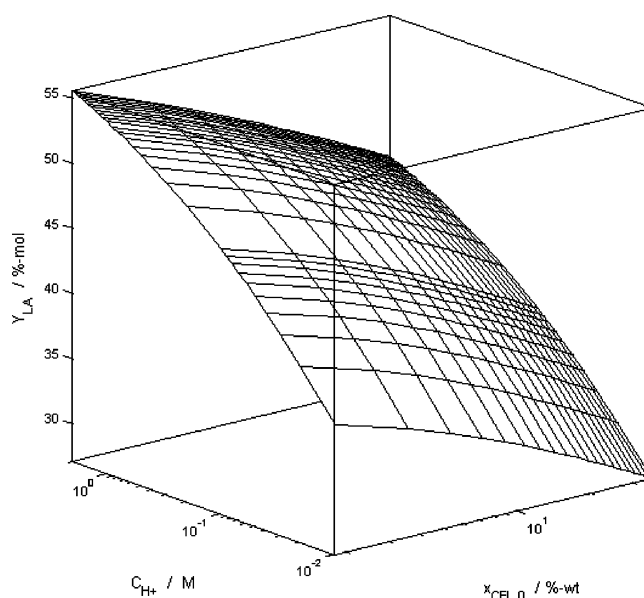
Equations 29–32 were solved simultaneously using the numerical integration toolbox *ode45* in MATLAB software package. The yields of levulinic acid were subsequently calculated using eq 7.

By using the solutions of ordinary differential eqs 29–32, it is possible to optimize the reaction conditions to obtain the highest  $Y_{LA}$ . For example, the modeled  $Y_{LA}$  obtained at various temperatures and acid concentrations at 99% conversion of cellulose is given in Figure 13. A number of experimental data points are also given, demonstrating the goodness-of-fit between the experimental data and the model.

Figure 13 confirms the experimental trends (Section 3.2) that low operating temperatures lead to higher  $Y_{LA}$ . However, the volumetric production rate of LA ( $\text{mol m}^{-3} \text{h}^{-1}$ ) will decrease dramatically when operating at low temperature. Figure 14 shows the reaction time needed to reach 99 mol % conversion



**Figure 14.** Modeled batch time for  $X_{CEL} = 99$  mol % as a function of temperature and acid concentration ( $x_{CEL,0} = 1.7$  wt %).



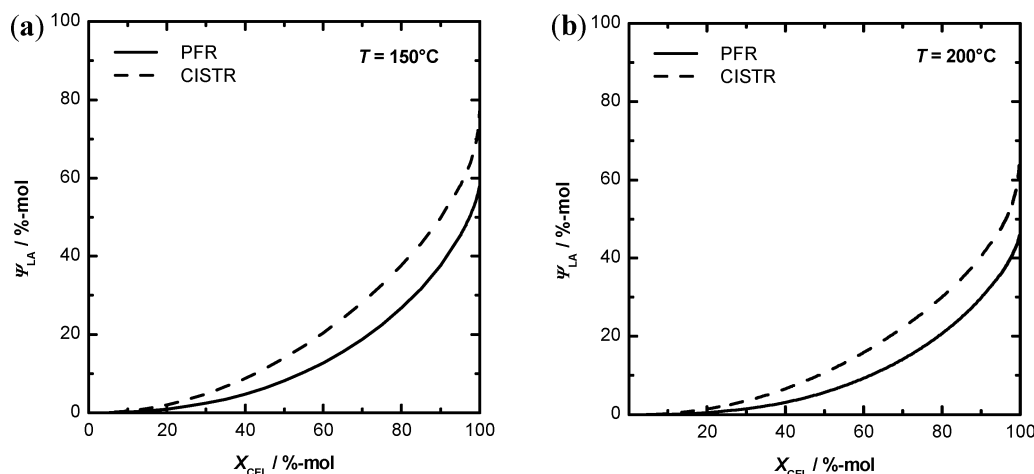
**Figure 15.** Modeled effects of  $x_{CEL,0}$  and  $C_{H^+}$  on  $Y_{LA}$  ( $T = 150$  °C and  $X_{CEL} = 99$  mol %).

of cellulose in a batch reactor as a function of the temperature and acid concentration.

Figure 15 shows the modeled  $Y_{LA}$  as a function of  $x_{CEL,0}$  and  $C_{H^+}$  evaluated at  $150$  °C and a cellulose conversion of 99 mol %. It is evident that the highest  $Y_{LA}$  is obtained at high acid concentrations and low initial cellulose intakes, in line with the experimental results (Section 3.2).

**4.2. Optimization of LA Production in Continuous Reactors.** The yields of levulinic acid in continuous reactors will be a function of reaction conditions ( $T$ ,  $C_{H_2SO_4}$ , and  $x_{CEL,0}$ ) and the extent of mixing in the reactor. The kinetic model derived in this paper was used to model the performance of two extremes with respect to mixing, i.e., a plug-flow reactor (PFR) and a continuous ideal stirred tank reactor (CISTR). The reactor design equations of a PFR are similar to the one for a batch reactor (eqs 29–32) provided that the time  $t$  is replaced by the residence time  $\tau_{PFR}$ . The reactor design equation for a CISTR reads as follows:

$$\tau_{CISTR} = \frac{C_i^{out} - C_i^{in}}{R_i} \quad (33)$$



**Figure 16.** Comparisons of  $\Psi_{LA}$  in two ideal continuous reactors (PFR and CISTR) at 150 °C (a) and 200 °C (b) ( $x_{CEL,0} = 1.7$  wt % and  $C_{H_2SO_4} = 1$  M).

Applying eq 33 for cellulose and combining it with the definition of cellulose conversion (eq 28) leads to

$$\tau_{CISTR} = \frac{C_{CEL}^{out} - C_{CEL}^{in}}{-R_{1C} - R_{2C}} = \frac{X_{CEL} C_{CEL}^{in}}{R_{1C} + R_{2C}} \quad (34)$$

Substitution of eq 34 into the design eq 33 for glucose, HMF, and LA leads to

$$C_{GLC}^{out} = \frac{R_{1C} - R_{1G} - R_{2G}}{R_{1C} + R_{2C}} X_{CEL} C_{CEL}^{in} \quad (35)$$

$$C_{HMF}^{out} = \frac{R_{1G} - R_{1H} - R_{2H}}{R_{1C} + R_{2C}} X_{CEL} C_{CEL}^{in} \quad (36)$$

$$C_{LA}^{out} = \frac{R_{1H}}{R_{1C} + R_{2C}} X_{CEL} C_{CEL}^{in} \quad (37)$$

The system of algebraic eqs 35–37 was solved numerically using a MATLAB toolbox *fsolve*, which gives the concentrations of glucose, HMF, and LA in the outlet of the reactor. The yield of LA in the continuous reactors ( $\Psi_{LA}$ ) is calculated as follows:

$$\Psi_{LA} = \frac{C_{LA}^{out}}{C_{CEL}^{in}} \quad (38)$$

Figure 16 shows the yields of LA as a function of cellulose conversion at different temperatures (150 and 200 °C) for both the PFR and CISTR. It is clear that the yield of LA increases with the cellulose conversion, and that, at any conversion level, the LA yield in a CISTR is always higher than that in a PFR. The highest obtainable yield is  $\sim 76$  mol % at  $T = 150^\circ\text{C}$ ,  $x_{CEL,0} = 1.7$  wt %, and  $C_{H_2SO_4} = 1$  M using a CISTR. This implies that continuous-reactor configurations with a high extent of backmixing are preferred with respect to the yield of LA. The yields of LA at low temperature are higher than at high temperature for both reactor configurations.

## 5. Conclusions

This study describes an in-depth experimental and modeling study on the acid-catalyzed hydrolysis of cellulose into levulinic acid. A broad range of reaction conditions were applied, including variations in temperature between 150 and 200 °C, sulfuric acid concentrations between 0.05 and 1 M, and initial cellulose intakes between 1.7 and 14 wt %. A power-law

approach was used to develop a novel kinetic model for the reaction, including side reactions to humins. A good fit between the experimental data and the modeling results was obtained. The highest yield of levulinic acid may be obtained at the low end of the temperature window, a low initial cellulose concentration, and a high sulfuric acid concentration. Modeling of the reactions in continuous-reactor systems revealed that reactor configurations with a high extent of back-mixing (e.g., a CISTR) give better yields of levulinic acid. The results of this study will be applicable for the rational design and operation of dedicated reactors for the conversions of various types of biomass feedstock to levulinic acid.

## Acknowledgment

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## Nomenclature

- $a_C$  = reaction order of  $C_{CEL}$  in the cellulose hydrolysis to glucose
- $\alpha_C$  = reaction order of  $C_{H^+}$  in the cellulose hydrolysis to glucose
- $a_G$  = reaction order of  $C_{GLC}$  in the glucose decomposition to HMF
- $\alpha_G$  = reaction order of  $C_{H^+}$  in the glucose decomposition to HMF
- $a_H$  = reaction order of  $C_{HMF}$  in the HMF decomposition to levulinic acid
- $\alpha_H$  = reaction order of  $C_{H^+}$  in the HMF decomposition to levulinic acid
- $A$  = acid concentration in Saeman's model, wt %
- $A_t$  = heat-transfer area,  $\text{m}^2$
- $b_C$  = reaction order of  $C_{CEL}$  in the cellulose hydrolysis to the decomposition products
- $\beta_C$  = reaction order of  $C_{H^+}$  in the cellulose hydrolysis to the decomposition products
- $b_G$  = reaction order of  $C_{GLC}$  in the glucose decomposition to humins
- $\beta_G$  = reaction order of  $C_{H^+}$  in the glucose decomposition to humins
- $b_H$  = reaction order of  $C_{HMF}$  in the HMF decomposition to levulinic acid
- $\beta_H$  = reaction order of  $C_{H^+}$  in the HMF decomposition to levulinic acid

$C_{\text{CEL}}$  = cellulose concentration, M  
 $C_{\text{CEL},0}$  = initial concentration of cellulose, M  
 $C_{\text{FUR}}$  = furfural concentration, M  
 $C_{\text{GLC}}$  = glucose concentration, M  
 $C_{\text{HMF}}$  = HMF concentration, M  
 $C_{\text{H}_2\text{SO}_4}$  = concentration of  $\text{H}_2\text{SO}_4$ , M  
 $C_{\text{H}^+}$  = concentration of proton, M  
 $C_{\text{H}^+,\text{cel}}$  = concentration of proton in the solid phase, M  
 $C_i^{\text{in}}$  = concentration of the  $i$ th compound at the inflow of continuous reactors, M  
 $C_i^{\text{out}}$  = concentration of the  $i$ th compound at the outflow of continuous reactors, M  
 $C_{\text{LA}}$  = levulinic acid concentration, M  
 $C_p$  = heat capacity of reaction mixture,  $\text{J g}^{-1} \text{K}^{-1}$   
 $d_{\text{cel}}$  = diameter of cellulose particle, m  
 $D_{\text{H}^+,\text{cel}}$  = diffusion coefficient of proton in the solid phase,  $\text{m}^2 \text{s}^{-1}$   
 $D_{\text{H}^+,\text{w}}$  = diffusion coefficient of proton in the aqueous phase,  $\text{m}^2 \text{s}^{-1}$   
 $E_1$  = activation energy of  $k_1$  in Saeman's model,  $\text{kJ mol}^{-1}$   
 $E_{1\text{C}}$  = activation energy of  $k_{1\text{C}}$ ,  $\text{kJ mol}^{-1}$   
 $E_{1\text{G}}$  = activation energy of  $k_{1\text{G}}$ ,  $\text{kJ mol}^{-1}$   
 $E_{1\text{H}}$  = activation energy of  $k_{1\text{H}}$ ,  $\text{kJ mol}^{-1}$   
 $E_2$  = activation energy of  $k_2$  in Saeman's model,  $\text{kJ mol}^{-1}$   
 $E_{2\text{C}}$  = activation energy of  $k_{2\text{C}}$ ,  $\text{kJ mol}^{-1}$   
 $E_{2\text{G}}$  = activation energy of  $k_{2\text{G}}$ ,  $\text{kJ mol}^{-1}$   
 $E_{2\text{H}}$  = activation energy of  $k_{2\text{H}}$ ,  $\text{kJ mol}^{-1}$   
 $h$  = heat-transfer coefficient from the oven to the reaction mixture,  $\text{min}^{-1}$   
 $k_1$  = reaction rate constant of cellulose hydrolysis in Saeman's model,  $\text{min}^{-1}$   
 $k_{1,0}$  = frequency factor of  $k_1$  in Saeman's model,  $\text{min}^{-1}$   
 $k_{1\text{C}}$  = reaction rate constant of cellulose hydrolysis to glucose,  $\text{M}^{1-a_{\text{C}}} \text{min}^{-1}$   
 $k_{1\text{RC}}$  = reaction rate constant  $k_{1\text{C}}$  at reference temperature,  $\text{M}^{1-a_{\text{C}}-\alpha_{\text{C}}} \text{min}^{-1}$   
 $k_{1\text{G}}$  = reaction rate constant of glucose decomposition into HMF,  $\text{M}^{1-a_{\text{G}}} \text{min}^{-1}$   
 $k_{1\text{RG}}$  = reaction rate constant  $k_{1\text{G}}$  at reference temperature,  $\text{M}^{1-a_{\text{G}}-\alpha_{\text{G}}} \text{min}^{-1}$   
 $k_{1\text{H}}$  = reaction rate constant of HMF decomposition to levulinic acid,  $\text{M}^{1-a_{\text{H}}} \text{min}^{-1}$   
 $k_{1\text{RH}}$  = reaction rate constant  $k_{1\text{H}}$  at reference temperature,  $\text{M}^{1-a_{\text{H}}-\alpha_{\text{H}}} \text{min}^{-1}$   
 $k_2$  = reaction rate constant of glucose decomposition in Saeman's model,  $\text{min}^{-1}$   
 $k_{2,0}$  = frequency factor of  $k_2$  in Saeman's model,  $\text{min}^{-1}$   
 $k_{2\text{C}}$  = reaction rate constant of cellulose hydrolysis to decomposition products,  $\text{M}^{1-b_{\text{C}}} \text{min}^{-1}$   
 $k_{2\text{RC}}$  = reaction rate constant  $k_{2\text{C}}$  at reference temperature,  $\text{M}^{1-b_{\text{C}}-\beta_{\text{C}}} \text{min}^{-1}$   
 $k_{2\text{G}}$  = reaction rate constant of glucose decomposition into humins,  $\text{M}^{1-b_{\text{G}}} \text{min}^{-1}$   
 $k_{2\text{RG}}$  = reaction rate constant  $k_{2\text{G}}$  at reference temperature,  $\text{M}^{1-b_{\text{G}}-\beta_{\text{G}}} \text{min}^{-1}$   
 $k_{2\text{H}}$  = reaction rate constant of HMF decomposition into humins,  $\text{M}^{1-b_{\text{H}}} \text{min}^{-1}$   
 $k_{2\text{RH}}$  = reaction rate constant  $k_{2\text{H}}$  at reference temperature,  $\text{M}^{1-b_{\text{H}}-\beta_{\text{H}}} \text{min}^{-1}$   
 $m$  = distribution coefficient of proton in bulk and solid phases  
 $m_1$  = reaction order of acid concentration of  $k_1$  in Saeman's model  
 $m_2$  = reaction order of acid concentration of  $k_2$  in Saeman's model

$M$  = mass of the reaction mixture, g  
 $M_{\text{W}}$  = Weisz modulus  
 $r_{\text{GLC}}$  = production rate of glucose,  $\text{mol m}_{\text{cellulose}}^{-3} \text{s}^{-1}$   
 $R$  = universal gas constant,  $8.3144 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1}$   
 $R_i$  = reaction rate of the  $i$ th compound in the continuous-reactor configurations,  $\text{M min}^{-1}$   
 $R_{1\text{C}}$  = reaction rate of cellulose hydrolysis to glucose,  $\text{M min}^{-1}$   
 $R_{1\text{G}}$  = reaction rate of glucose decomposition to HMF,  $\text{M min}^{-1}$   
 $R_{1\text{H}}$  = reaction rate of HMF decomposition to levulinic acid,  $\text{M min}^{-1}$   
 $R_{2\text{C}}$  = reaction rate of cellulose hydrolysis to decomposition products,  $\text{M min}^{-1}$   
 $R_{2\text{G}}$  = reaction rate of glucose decomposition to humins,  $\text{M min}^{-1}$   
 $R_{2\text{H}}$  = reaction rate of HMF decomposition to humins,  $\text{M min}^{-1}$   
 $t$  = time, min  
 $T$  = temperature, K  
 $T_i$  = temperature of reaction mixture at  $t = 0$ , K  
 $T_{\text{oven}}$  = oven temperature, K  
 $T_{\text{R}}$  = reference temperature, K  
 $U$  = overall heat-transfer coefficient,  $\text{W m}^{-2} \text{K}^{-1}$   
 $x_{\text{CEL},0}$  = initial intake of cellulose, wt %  
 $X_{\text{CEL}}$  = conversion of cellulose, mol %  
 $Y_{\text{GLC}}$  = yield of glucose, mol %  
 $Y_{\text{LA}}$  = yield of levulinic acid, mol %

#### Greek Symbols

$\epsilon$  = void fraction  
 $\tau_{\text{CISTR}}$  = residence time in a CISTR, min  
 $\tau_{\text{PFR}}$  = residence time in a PFR, min  
 $\Psi_{\text{LA}}$  = yield of LA in continuous reactors, mol %

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