

Hydrochloric Acid-Catalyzed Levulinic Acid Formation from Cellulose: Data and Kinetic Model to Maximize Yields

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In this study, the kinetics of the acid catalyzed hydrolysis of microcrystalline cellulose (Avicel PH101) to levulinic (LA) and formic (FA) acids was investigated in a batch reactor over the following range of conditions: 160–200°C, hydrochloric acid concentrations of 0.309–0.927 M (11.3–33.8 g/l), cellulose concentrations of 49.8–149 mM (8.06–24.1 g/l), and residence times of 0–50 min. The maximum LA yield of around 60% of theoretical was achieved for an initial cellulose concentration of 99.6 mM, acid concentration 0.927 M, and 180–200°C. A mathematical model and its analytical solution were developed to predict conversion of cellulose to LA and FA through glucose and hydroxymethyl-2-furfural based on an irreversible pseudo-first order reaction. Rate analysis of each reaction indicated that the rate-controlling step shifted from LA formation initially to HMF formation later. © 2011 American Institute of Chemical Engineers AIChE J, 00: 000–000, 2011

Keywords: cellulose, levulinic acid, hydrochloric acid, kinetics, model, rate control

Introduction

Levulinic acid ($\text{H}_8\text{C}_5\text{O}_3$, gamma-ketovaleric acid, LA) and formic acid (H_2CO_2 , FA) are short-chain fatty acids that can provide potentially important platforms for production of liquid fuels and chemicals.¹ LA can be produced from glucose,^{2,3} cellulose,^{4,5} 5-hydroxymethyl-2-furfural (HMF),⁶ normal corn starch,⁷ whole kernel grain sorghum,⁸ water hyacinth plant,⁹ bagasse and paddy straw,¹⁰ and wheat straw.¹¹ Although focus on cellulosic feedstocks is important in the long term to achieve low costs and make a substantial impact on fuel consumption, more information is needed on

avenues to achieve the highest possible yields from cellulosic materials. Development of robust kinetic models can serve this goal well by providing new insight into interplays among the various reaction steps that can help identify avenues that favor LA production.

Some mathematical models of LA formation have been developed, with the most common being based on that developed by Saeman in 1945.¹² In this case, the author assumed a two-step reaction from cellulose to decomposition products through glucose (Eq. 1) with the rate constant including the effect of acid concentration along with a modified Arrhenius equation for its temperature dependence:



A more detailed reaction mechanism of LA formation from cellulose through glucose and HMF as well as some parallel by-product reactions to humins was proposed by Girisuta

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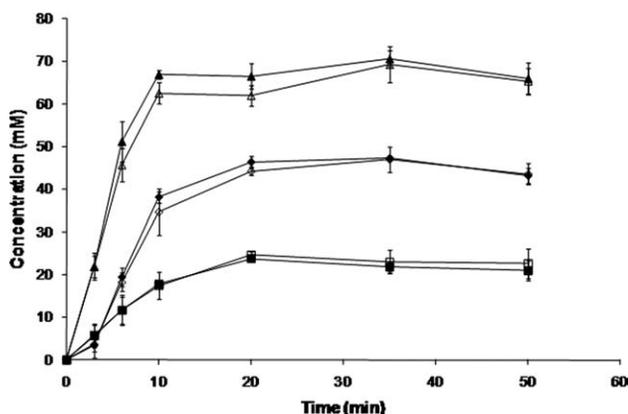


Figure 1. LA (solid) and FA (open) concentrations at three initial cellulose concentrations vs. reaction time: 49.8 mM (□), 99.6 mM ◇, and 149 mM (Δ).

Conditions: 200°C and acid 0.206 M HCl concentration.

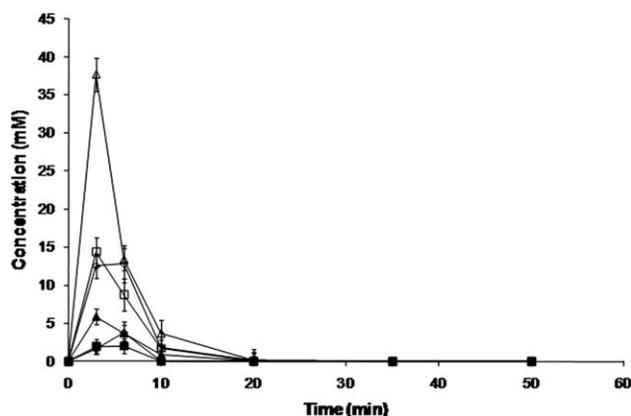


Figure 2. Glucose (solid) and HMF (open) concentrations at three initial cellulose concentrations vs. time: 49.8 mM (□), 99.6 mM ◇, and 149 mM (Δ).

Conditions were the same as Figure 1.

Materials and Methods

Materials

Avicel PH 101 microcrystalline cellulose (power with size 0.05 mm, Eluka BioChemika) and hydrochloric acid (Sigma-Aldrich) were the raw material and catalyst for LA production, respectively. LA (Sigma-Aldrich 98%), FA (Fisher Scientific, 99%), D-(+)-glucose (Sigma-Aldrich, 99.5%), and 5-hydroxymethyl-2-furaldehyde, (SAFC, 99%) were used as standards for HPLC analysis. Calcium carbonate (Fisher Scientific, 99.0%) was used to neutralize acid in samples before HPLC analysis.

Experimental methods

Tubular batch reactors [Hastelloys C-276, O.D. 1/2" (12.7 mm) of 6" length (152.4 mm)] were used for LA and FA production from Avicel PH 101. Appropriate amounts of Avicel PH 101, hydrochloric acid, and deionized water were added to the tubes for each experiment to give a total volume, including the solid cellulose, of 10 ml, thereby allowing for expansion of the contents on heating. The tubes were capped tightly with Swedgelock fittings. The tube reactors were heated using two 4 kW fluidized sand baths (Model SBL-2D, Techne Co., Princeton, NJ), and their internal temperature was monitored with a K type thermocouple probe (Omega CASS-18U-12, Omega Engineering Co., Stamford, CT). The tubes were submerged in the first sand bath that was set at 300°C to reduce the heat up time and held there until their internal temperature was within 5°C of the target value, with the time required being usually less than 1 min. At that point, the tubes were quickly moved to a second sand bath that was controlled at the target temperature, with this time being defined as time zero. At various time intervals, one of the tubes was removed from the sand bath and dropped into cool water to stop the reaction. When the temperatures had dropped to ambient levels, the tubes were opened, and the tube contents were filtered through filter paper of known weight. The filtrates were added to centrifugal tips for further preparation of samples for HPLC analysis. The tubes were washed three times with deionized water, and the wash water was passed through filter paper to trap as much of the solids from the reaction as possible. The filter paper was then dried at

105°C in an oven overnight. Then, the filter paper, including the residues, was weighed, and the residue weight was calculated. The washed solids remaining after reaction were analyzed.

Analytical methods

Glucose, FA, LA, and hydroxymethyl furfural concentrations were measured using a Waters model 2695 HPLC system equipped with a 2414 refractive detector and a Waters 2695 autosampler using Millennium32 chromatography manager 3.2 software (Waters Co., Milford, MA). A Bio-Rad Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA) was used for analyzing these compounds. The column temperature was 65°C, the mobile phase was 0.005 M H₂SO₄, the flow rate was 0.6 ml/min, and the HPLC was operated in the isocratic mode. The identities of the compounds were authenticated by comparing their retention times with those of pure compounds (Sigma-Aldrich, St. Louis, MO). Before analytical work, the acid in the filtrates was neutralized with calcium carbonate to a pH of 5 to 6, and then the suspensions were centrifuged at 15,000 rpm for

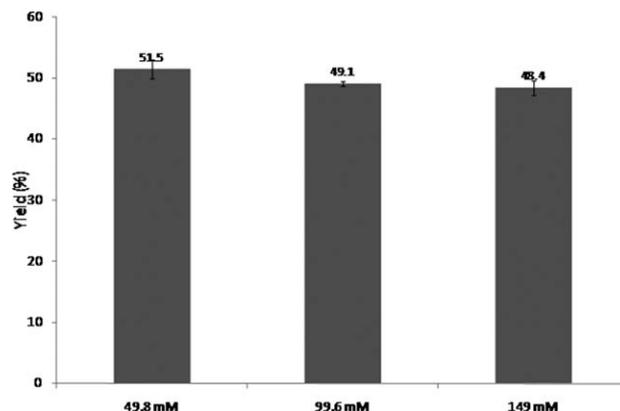


Figure 3. Maximum LA yields at three initial cellulose concentrations with other conditions the same as for Figure 1.

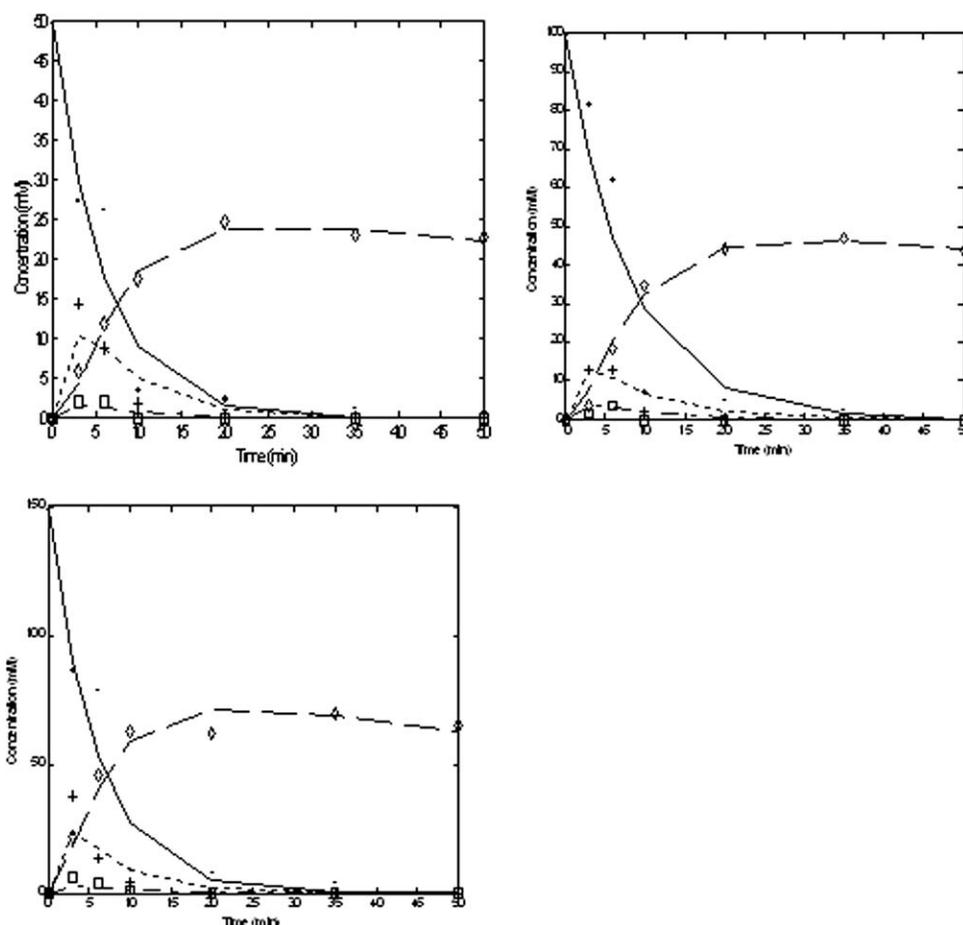


Figure 4. Fitted curves of concentration vs. time for three initial cellulose concentrations: top left, 49.8; top right, 99.6; and bottom left, 149 mM.

Experimental data (symbols) and kinetic model (lines) concentrations for cellulose decomposition to LA: cellulose (●, —), glucose (+, ---), HMF (□, ···), and LA (◇, -·-·). Conditions: 49.8 mM cellulose concentration, 200°C, and 0.206 M HCl concentration.

5 min through a 0.2 μm membrane filter. The supernatants were used for HPLC analysis.

The overall reactions from glucose to LA and from glucan in cellulose to LA can be, respectively, expressed as:



The average molecular weight of glucan, a unit of cellulose, is 162, and because glucose has a molecular weight of 180 and LA yields reported in the literature⁵ are based on glucose, LA and FA concentrations (g/l) measured from HPLC were converted to LA and FA yields as a percent of the theoretical maximum as follows:

$$\begin{aligned} \text{LA yield} &= \frac{\text{LA concentration (g/l)} \times \text{glucose MW}}{\text{Initial glucose concentration} \times \text{LA MW}} \\ &= \frac{\text{LA concentration (g/l)}}{\text{Initial glucose concentration} \times 0.664} \% \quad (15) \end{aligned}$$

$$\begin{aligned} \text{FA yield} &= \frac{\text{FA concentration (g/l)} \times \text{glucose MW}}{\text{Initial glucose concentration} \times \text{FA MW}} \\ &= \frac{\text{FA concentration (g/l)}}{\text{Initial glucose concentration} \times 0.236} \quad (16) \end{aligned}$$

Cellulose contents in the residues were analyzed by converting the cellulose into glucose using the NREL-recommended

Table 1. Kinetic Model First-Order Rate Constants at Three Initial Cellulose Concentrations

Cellulose Concn. (mM)	k_1' (l/mol min)	k_2' (l/mol min)	k_3' (l/mol min)	k_4' (l/mol min)	k_5' (l/mol min)	k_6' (l/mol min)	C_{wp}
49.8	0.834 ± 0.010	2.23 ± 0.15	0	7.91 ± 0.75	6.94 ± 1.47	0.0200 ± 0.0033	2.04E-6
99.6	0.602 ± 0.033	3.17 ± 0.40	0	6.16 ± 0.43	5.45 ± 0.83	0.0218 ± 0.0068	1.47E-6
149.1	0.823 ± 0.059	3.25 ± 0.11	0	16.6 ± 0.92	13.9 ± 1.81	0.0290 ± 0.0061	2.01E-6
Average	0.753 ± 0.034	2.89 ± 0.22	0	10.2 ± 0.7	8.76 ± 1.37	0.0236 ± 0.0054	1.84E-6

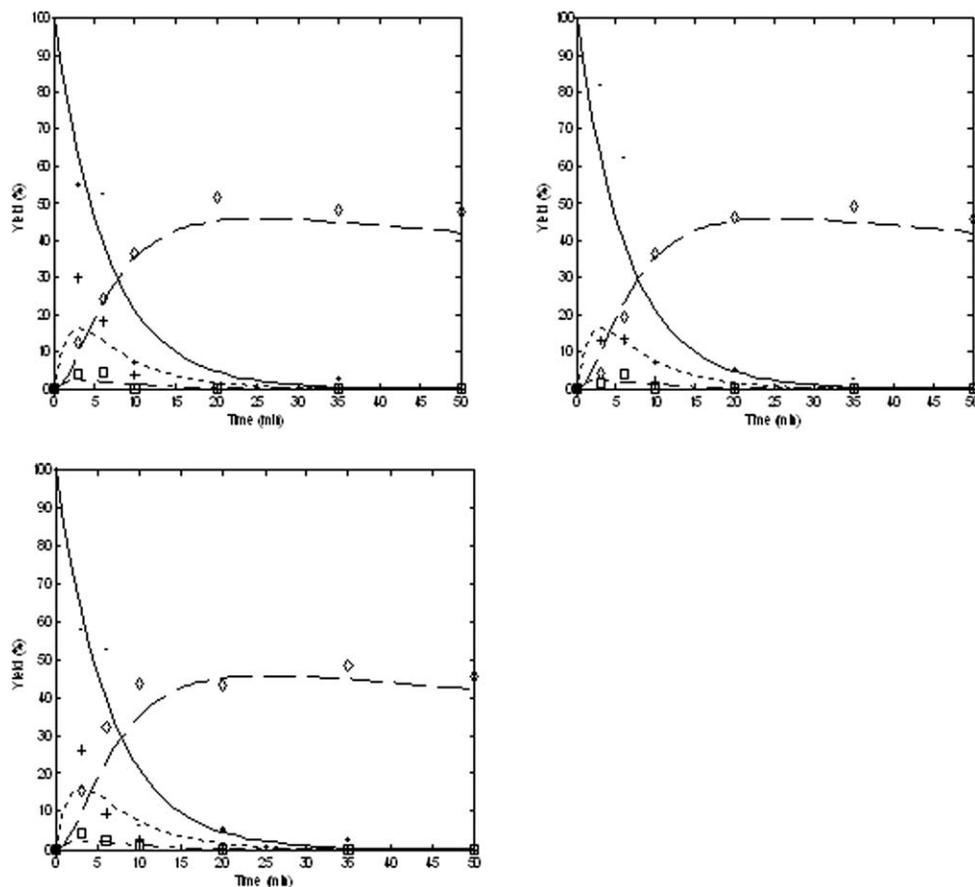


Figure 5. Smoothed curves of yields vs. time for three initial cellulose concentrations using the average rate constants in Table 1: top left, 49.8; top right, 99.6; and bottom left, 149 mM.

Experimental data (symbols) and kinetic model yields (lines) during cellulose decomposition: cellulose (●, —), glucose (+, ---), HMF (□, ···), and LA (◇, -·-). Conditions are the same as for Figure 4.

method.¹³ Briefly, about 0.3 g of residues was added to 3 ml of 72 wt % sulfuric acid, and the suspension was hydrolyzed at 50°C for 1 h. Then, the slurry was diluted to 4 wt % sulfuric acid by adding 84 ml deionized water and autoclaved at 121°C

for 1 h. After cooling, the slurry was filtered through a crucible. About 2 ml of filtrate were neutralized by calcium carbonate to a pH 5–6, and then the suspensions were centrifuged at 15,000 rpm for 5 min through the 0.2 μm membrane filter. The supernatants were used for HPLC analysis.

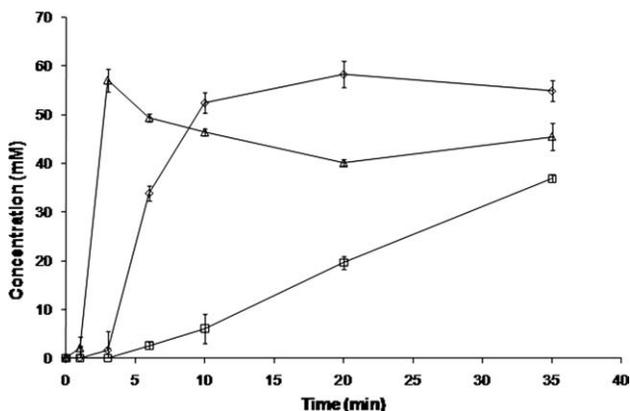


Figure 6. Experimental LA concentrations vs. time for three temperatures: 160°C (□), 180°C (◇), and 200°C (Δ).

Conditions: 99.6 mM initial cellulose concentration, and 0.927 M HCl concentration.

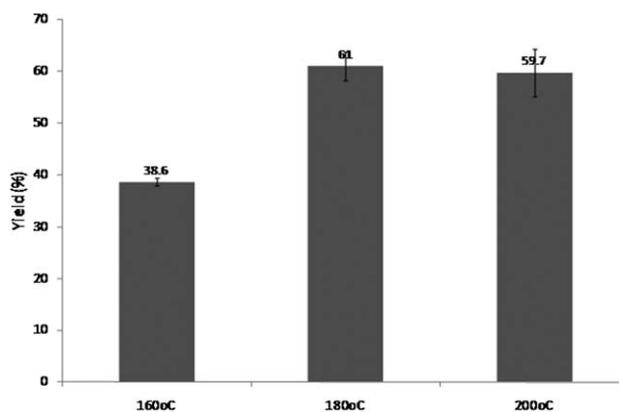


Figure 7. Maximum LA yields at three temperatures with other conditions the same as for Figure 6.

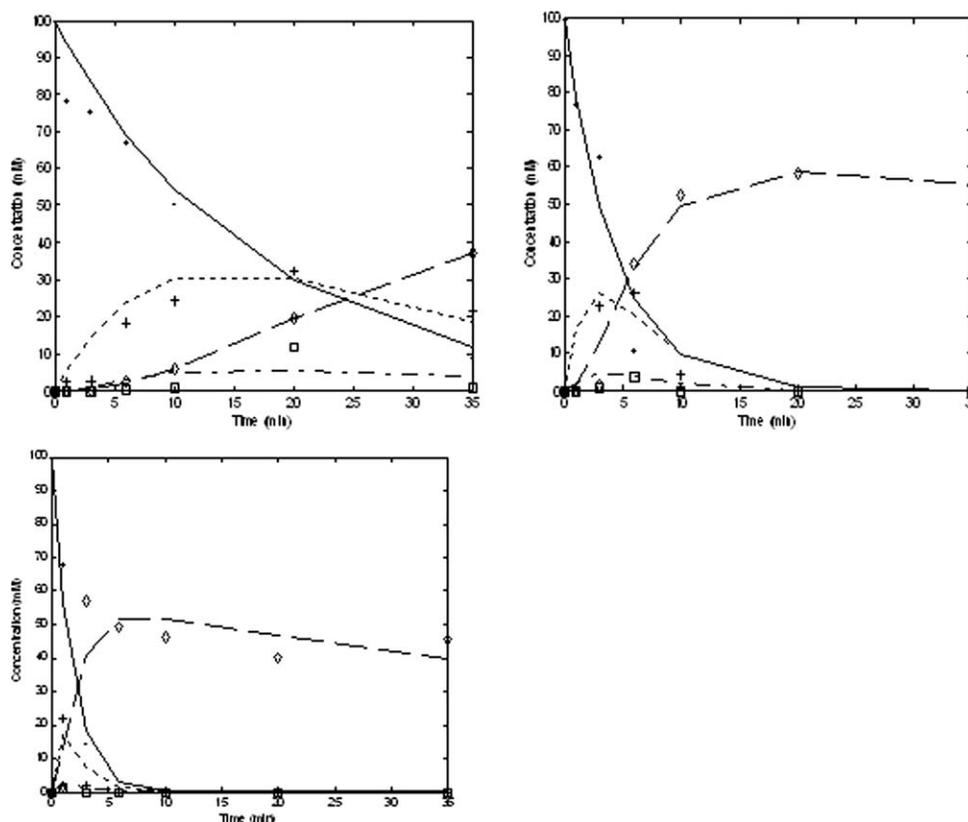


Figure 8. Fitted curves of concentrations vs. time for three temperatures: top left 160°C, top right 180°C, and bottom left 200°C.

Experimental data (symbols) and kinetic model concentrations (lines) results for cellulose decomposition to LA: cellulose (●, —), glucose (+, - - -), HMF (□, - · -), and LA (◇, - - -). Conditions: 99.6 mM cellulose concentration and 0.927 M HCl concentration.

Results and Discussion

Effect of initial cellulose concentration on LA production

Kinetic experiments were conducted at the following conditions: 200°C, acid concentration of 0.206 M, and cellulose concentrations of 49.8 mM, 99.6 mM, and 149 mM. Plots of concentrations and yields for LA, FA, glucose, and HMF vs. time are shown in Figures 1–3, respectively. Thus, we see that increasing the initial cellulose concentration from 49.8 mM to 149 mM increased the LA concentration from 24.6 mM to 69.3 mM (Figure 1). Furthermore, the LA concentration increased by almost the same multiple (2.82 times) as the cellulose concentration (2.99 times). With increasing reaction time, LA and FA concentrations increased rapidly initially, reached the maximum values, and dropped somewhat at the end reaction period. Figure 1 also shows that the concentrations of LA and FA were almost the same because glucose decomposition produced equal numbers of LA and FA mole-

cules. The two concentration peaks observed for glucose and HMF resulted from the fact that both are intermediates in the series of reactions from cellulose to LA and FA (Figure 2). Figure 3 reveals that increasing the initial cellulose concentration decreased the maximum LA yield slightly from 51.5% to 48.4% (a 5.8% decrease). Although large decreases in LA yield have been reported as the initial cellulose concentration increased, our smaller drop in yields may be due to our lower cellulose concentrations (49.8 to 149 mM) than those (105 to 864 mM) of Girisuta et al.'s experiments.⁵

A MATLAB program was used to fit the parameters in Eqs. 8 to 11 to best match the experimental concentrations of cellulose, glucose, HMF, and LA, with the resulting curves presented in Figure 4 and the corresponding rate constants k_i' reported in Table 1. These fitted curves facilitate following trends in reactant, intermediate, and product concentrations over the reaction time. The model nearly perfectly followed the LA concentration data over time, but deviations were found

Table 2. Kinetic Model First-Order Rate Constants at Three Temperatures

Temperature (°C)	k_1' (l/mol min)	k_2' (l/mol min)	k_3' (l/mol min)	k_4' (l/mol min)	k_5' (l/mol min)	k_6' (l/mol min)
160	0.0665 ± 0.0033	0.0845 ± 0.020	0	0.271 ± 0.057	0.187 ± 0.041	0.00296 ± 0.00077
180	0.251 ± 0.007	0.464 ± 0.057	0	1.63 ± 0.16	0.856 ± 0.206	0.00648 ± 0.00160
200	0.615 ± 0.005	2.10 ± 0.09	0	7.87 ± 0.13	5.92 ± 0.26	0.0118 ± 0.0007
Ratio of $k_{i,200}/k_{i,160}$	9.25	24.9	N/A	29.0	31.7	3.99

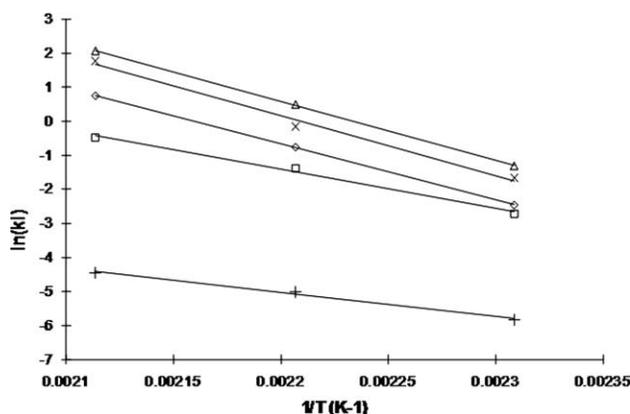


Figure 9. Experimental points (symbols) and best fit lines for plot of \ln of rate constants vs. inverse absolute temperature: k_1 (\square , $-$), k_2 (\diamond , $-$), k_4 (Δ , $-$), k_5 (\times , $-$), and k_6 ($+$, $-$).

Conditions: 99.6 mM initial cellulose concentration, 0.927 M HCl concentration, and 473 K.

between the model predictions and experimental data for glucose concentrations at initial cellulose concentrations of 49.8 mM (Figure 4 top left) and 149 mM (Figure 4 bottom left). Because the rate constants k'_i in Table 1 did not change monotonically with increasing initial cellulose concentration, the rate constants appeared to be independent of the initial cellulose concentration. On this basis, average values (Table 1) of the rate constants k'_i calculated for the three initial cellulose concentrations were used in Eq. 12 to predict yield changes with time, as shown for cellulose, glucose, HMF, and LA in Figure 5. In this case, the LA yield was predicted to be around 42% over the range of initial cellulose concentrations for this model that did not include internal and external mass transfer effects.

Effect of temperature on LA concentration

Figure 6 shows the concentrations of LA for a cellulose concentration of 99.6 mM and an acid concentration of 0.926 M for temperatures of 160, 180, and 200°C. As temperature was increased from 160 to 200°C, the maximum LA concentration increased from 36.9 to 67.1 mM. Although the LA concentration at 160°C was the lowest among the three temperatures, the reaction was incomplete as shown in Figure 6 with about 22 mM of glucose that could be further reacted to higher LA concentrations left at the end of this experiment. Because the rate of reaction increased with temperature, the time to achieve the maximum LA concentration dropped considerably with increasing temperature, as expected. For example, the time to reach the maximum LA concentration was

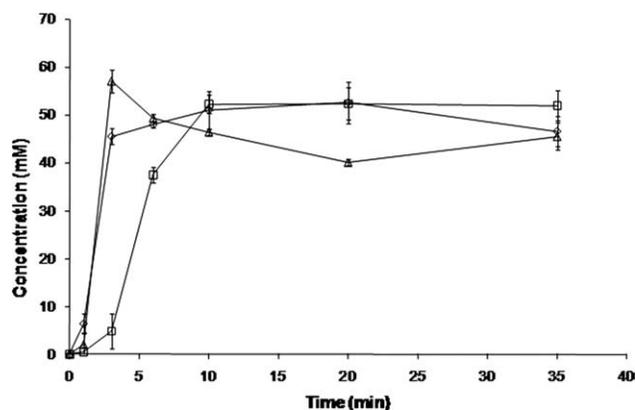


Figure 10. Experimental LA concentrations vs. time for three acid concentrations: 0.309 M (\square), 0.618 M \diamond , and 0.927 M (Δ).

Conditions: 99.6 mM initial cellulose concentration and 200°C.

about 20 min at 180°C but only 3 min at 200°C. After 3 min at 200°C, the LA concentration dropped, implying that the maximum LA concentration depended strongly on both temperature and time. However, of greatest importance, the LA yield shown in Figure 7 did not change significantly over the temperature range of 180 to 200°C but held essentially constant at about 60%, with a possibly slightly higher value of 61% at 180°C for an acid concentration 0.927 M, an initial cellulose concentration 99.6 mM, and a reaction time 20 min.

By contrast, Girisuta et al.⁵ reported that the LA yield decreased from 61% at 150°C to 42% at 200°C. This difference might be explained by two factors: (1) our lower cellulose concentrations reduced the effect of temperature on LA yield as intrinsic kinetics were approached due to less mass transfer resistance and (2) hydrochloric acid is a stronger catalyst than the sulfuric acid used by Girisuta et al.

Cellulose, glucose, HMF, and LA concentrations based on the experimental data and kinetic model are shown in Figure 8, with the rate constants k'_i for the model listed in Table 2. Although the LA data display linear behavior in Figure 8 (top left) and nonlinear curves in Figure 8 (top right and bottom left), the model from Eqs. 8 through 11 follows both trends well. Unlike the nonmonotonic change in k'_i at various initial cellulose concentrations described in the last Section, all of the rate constants k'_i increased with increasing temperature in the following order: $k'_4 > k'_5 > k'_2 > k'_1 > k'_6$. Thus, reaction 5 describing humins formation from HMF had the highest rate constant except for reaction 4, implying that a very large portion of the solid residues/humins resulted from that reaction. Furthermore, the ratio $k'_{5,200}/k'_{5,160}$ for reaction 5 in Table 2 is largest (31.7) among all ratios of $k'_{i,200}/k'_{i,160}$, suggesting that humins formation from HMF was most

Table 3. Kinetic Model Pre-exponent Factors and Activation Energies

	k'_1 (l/mol min)	k'_2 (l/mol min)	k'_3 (l/mol min)	k'_4 (l/mol min)	k'_5 (l/mol min)	k'_6 (l/mol min)
A_i (l/mol.min)	2.36E10	2.80E15	N/A	5.62E16	8.57E16	3.95E4
A_i (l/mol.s)	3.93E8	4.67E13	N/A	9.37E14	14.3E14	658
E_{ai} (J/mol)	9.56E4	13.7E4	N/A	14.4E4	14.7E4	5.90E4
R_i^2	0.992	1.000	N/A	1.000	0.991	0.996

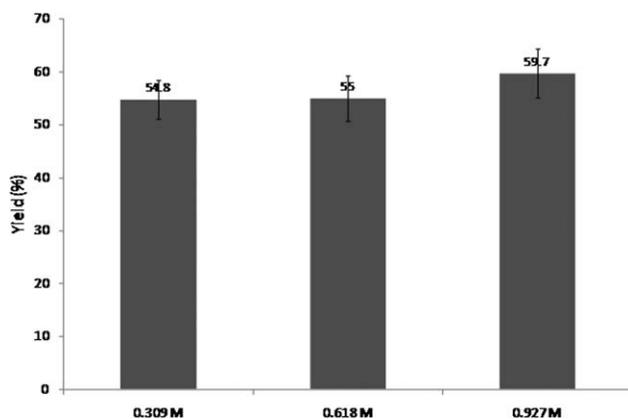


Figure 11. Maximum LA yields at acid concentrations with other conditions the same as for Figure 10.

sensitive to temperature and has the largest activation energy among these reactions. If the rate constants follow the Arrhenius expression of Eq. 7, $\ln k'_i$ should be a linear function of $1/T$ as shown in Eq. 17 and confirmed in Figure 9 for each rate constant:

$$\ln k'_i = \ln A_i - \frac{E_a}{RT} \quad i = 1 - 6 \quad (17)$$

From this plot, the activation energies and pre-exponential factors given in Table 3 were determined for each reaction from the slopes and intercepts of the straight lines for the three temperatures covered. Thus, we see that the activation energies E_{a1} and E_{a6} for reactions 1 and 6 were much smaller than those for reactions 2, 4, and 5, and E_{a4} and E_{a5} had almost same values. As a result, increasing temperature would cause approximately the same increase in reaction rates for reactions 4 and 5, resulting in little change in LA yields with temperature. In parallel with this observation, the pre-exponential factors A_1 and A_6 were much smaller than A_4 and A_5 , and analyzing them in terms of reaction rate collision theory gives¹⁴:

$$A = pz \quad (18)$$

in which A is the pre-exponential factor in the Arrhenius equation, z is the frequency factor, and p is the steric factor. Steric factors for reactions between polyatomic molecules are less than those for reactions involving a single-atomic molecule.¹⁴ Against this, a polymer, cellulose, is the reactant in reaction 1, two polyatomic molecules take part in reaction 6, and only one polyatomic molecule is reacted in each of the other reactions. Therefore, the steric factors and pre-exponential factors of reactions 1 and 6 would be expected to be smaller than for the other reactions, consistent with the model predictions.

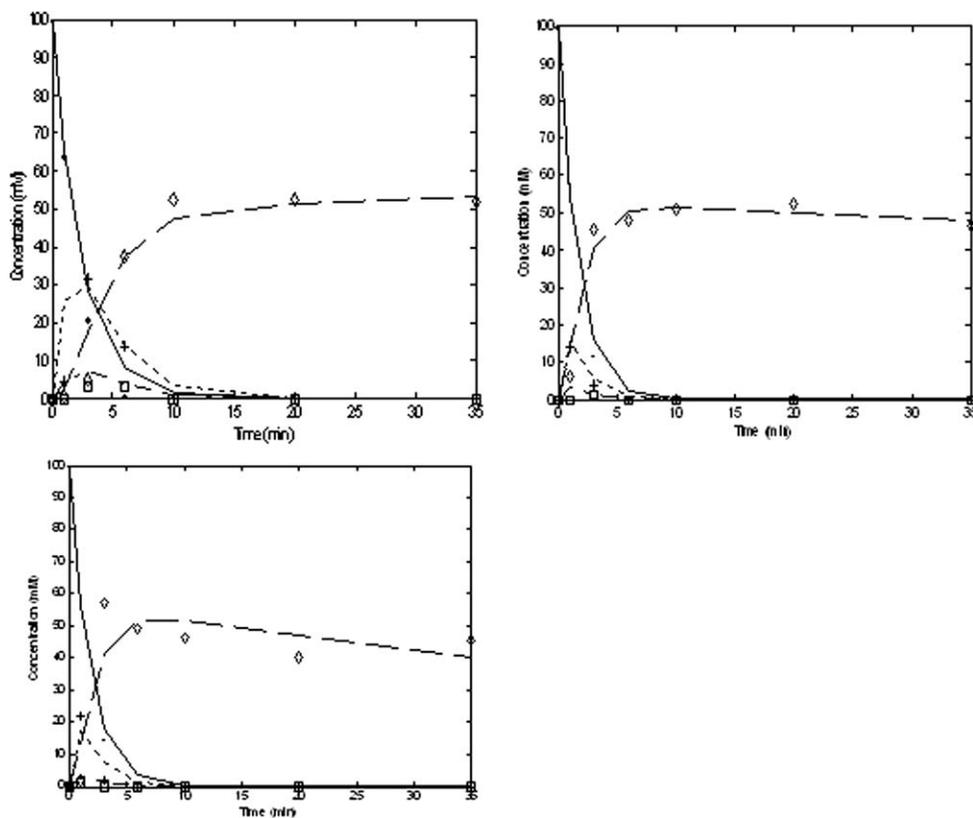


Figure 12. Fitted curves of concentrations vs. time for reaction with three concentrations of hydrochloric acid: top left 0.309, top right 0.618, and bottom left 0.927 M.

Experimental data (symbols) and kinetic model concentration (lines) for cellulose decomposition to LA: cellulose (●, -), glucose (+, -), HMF (□, -), and LA (◇, -). Conditions: 99.6 mM cellulose concentration and 200°C.

Table 4. Kinetic Model First-Order Rate Constants at Three Acid Concentrations

Acid Concn. (M)	k_1' (l/mol min)	k_2' (l/mol min)	k_3' (l/mol min)	k_4' (l/mol min)	k_5' (l/mol min)	k_6' (l/mol min)
0.309	1.35 ± 0.01	1.80 ± 0.23	0	3.17 ± 1.09	3.08 ± 0.98	0 ± 0.0016
0.618	0.984 ± 0.034	3.81 ± 0.58	0	10.0 ± 0.4	8.76 ± 0.83	0.00526 ± 0.00030
0.927	0.615 ± 0.005	2.10 ± 0.09	0	7.87 ± 0.13	5.92 ± 0.25	0.0118 ± 0.0007

Effect of hydrochloric acid concentration on levulinic acid

The effect of HCl acid concentration on LA concentrations and yields are summarized in Figures 10 and 11 at the following conditions: cellulose concentration of 99.6 mM, 200°C, and acid concentrations of 0.309, 0.618, and 0.927 M. Thus, we see that increasing acid concentration caused a slight increase in the maximum LA concentration and yield from 52.3 mM and 54.8% at acid concentration 0.309 M to 57.1 mM and 59.7% at acid concentration 0.927 M, respectively. This outcome is consistent with the role of hydrochloric acid as a catalyst not changing chemical equilibrium under ideal conditions even though the chemical reaction rate would increase with increasing acid concentration. As a result, the maximum LA concentration and yield changed little for the three acid concentrations applied. However, increasing acid concentration reduced the time needed to attain the maximum LA concentration and yield: for the conditions tested, the time to the highest LA concentrations was about 20 min with an acid concentration 0.309 M but only 6 min at 0.926 M. This result confirmed that acid accelerated the reactions. Moreover, LA concentrations and yields dropped if the solution was held beyond the optimum time due to by-product formation.

Figure 12 presents cellulose, glucose, HMF, and LA concentrations vs. time based on the kinetic model, with the rate constants determined by the MATLAB program for each reaction shown in Table 4. Thus, we can see that the rate constants k_1' and k_6' in Table 4, respectively, decreased and increased monotonically with increasing acid concentration, but the rate constants k_2' , k_4' , and k_5' did not.

Application of the Nelder-Mead approach in MATLAB to the proposed model with the fitted constants in Table 2 predicted that a maximum LA yield of 59.2% would occur at a time of 20.4 min and acid concentration of 0.899 M at 180°C (Figure 13). This predicted LA yield is somewhat less than that determined experimentally (59.7% in Figure 11) but is in the range of experimental error. Figure 13 also shows that the LA yield is insensitive to both reaction time and acid concentration: the LA yield changed by only about 0.2% when the reaction time and acid concentration were increased from 20 min and 0.85 M to 21 min and 0.95 M, respectively.

Identification of probable rate-limiting factors

The hydrolysis of acid-catalyzed cellulose to glucose is a heterogamous reaction that may be controlled by external and internal mass transfer and surface reaction. The relationship between the observed process rate and temperature can be used to identify the rate-limiting step. The rate would change linearly with temperature if external mass transfer were limiting and change exponentially if internal mass

transfer and surface reaction controlled.¹⁵ The fact that the changes in rate constant with temperature followed the Arrhenius equation in Figure 9 demonstrated that acid-catalyzed reaction of cellulose to glucose is not controlled by external mass transfer. The importance of internal mass transfer limitations in heterogamous chemical kinetics can be judged by the Weis-Prater (Eq. 19) criterion¹⁵:

$$C_{wp} = \eta\phi^2 \quad (19)$$

where C_{wp} is the Weis-Prater parameter (dimensionless) and η is the effectiveness factor of internal mass transfer (dimensionless). For an irreversible first-order reaction η is

$$\eta = \frac{3}{\phi} \left(\frac{1}{\tan h\phi} - \frac{1}{\phi} \right) \quad (20)$$

where ϕ is the Thiele modulus. For a first-order reaction in spherical particles, ϕ is equal to

$$\phi = \frac{R}{3} \sqrt{\frac{k_1}{D_e}} \quad (21)$$

where k_1 is the reaction rate constant (s^{-1}), D_e is the effective diffusion coefficient (m/s), and R is the particle radius (0.025 × 10⁻³ m for Avicel particles) (m). The diffusion coefficient of protons in water at 298 K is 9.311 × 10⁻⁹ m².¹⁶ The value at 473 K was corrected with Eq. 22¹⁷:

$$D_{e\ 473} = \frac{D_{e\ 298} \mu_{298} T_{473}}{T_{298} \mu_{473}} \quad (22)$$

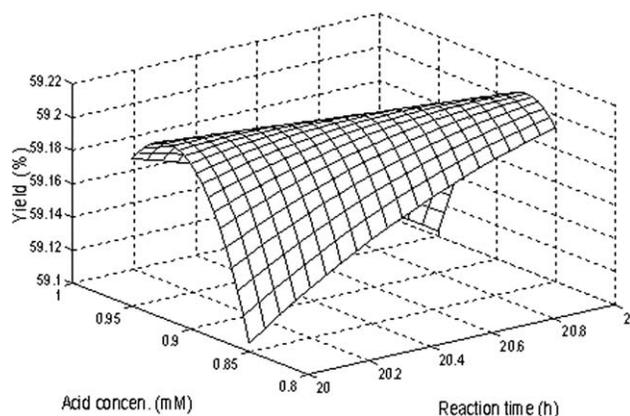


Figure 13. Simulated LA yield surface with respect to reaction time and acid concentration applying the model with the fitted constants in Table 2.

Conditions: cellulose concentration 99.6 mM and temperature 180°C.

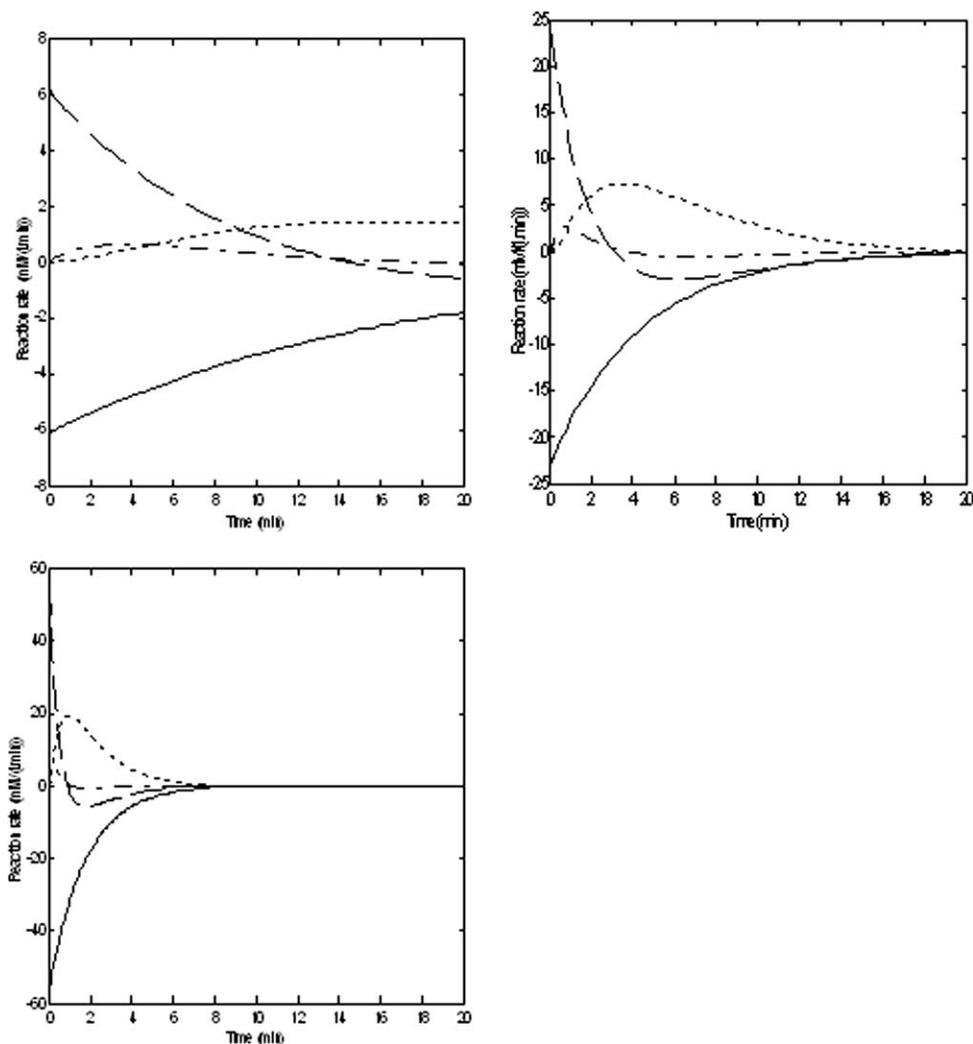


Figure 14. Reaction rates vs. time from the kinetic models for cellulose decomposition to LA at three temperatures: top left 160°C, top right 180°C, and bottom left 200°C.

Cellulose (—), glucose (---), HMF (-.-), and LA (---). Conditions: 99.6 mM cellulose concentration and 0.927 M HCl concentration.

where μ is the water viscosity at T (Pa s) (9×10^{-4} for 298 K and 1.36×10^{-4} Pa s for 473 K). Applying these values to Eqs. 19–22, the Weisz-Prater parameters are much less than 1 for reaction 1 at the three initial cellulose concentrations in Table 1. Therefore, the internal mass transfer is predicted to be negligible.

Rate-controlling step in the reaction of cellulose to LA

Equations 3–6 are rate expressions for consumption of cellulose and formation of glucose, HMF, and LA. After the rate constants in these equations were determined by the MATLAB program, the reaction rates were calculated to determine the rate-controlling step. The rates of cellulose decomposition at 160, 180, and 200°C shown in Figure 14 are always negative because it is consumed. On the other hand, the net reaction rate to LA changed from positive to negative as LA was initially produced and then consumed, whereas the reaction rates of glucose and HMF quickly increased before decreasing (except for Figure 14 top left)

but remained positive. Initially, glucose formation controlled the rate of the entire series of reactions because it had the smallest reaction rate among all the absolute reaction rates. However, as shown in the figures, HMF formation soon had the smallest absolute reaction rate, with the result that the reaction from glucose to HMF became rate controlling in the series of reactions. This change in the rate-controlling step was dependent on reaction temperature, with the transition occurring earlier at higher temperatures. For example, this shift occurred after about 5 min at 160°C but less than 1 min at 200°C.

Conclusions

Data were developed on the effects of initial cellulose concentration, hydrochloric acid concentration, and temperature on LA concentrations and yields from cellulose in a batch system. The highest LA yield of about 60% was observed at an initial cellulose concentration of 99.6 mM, an acid concentration of 0.927 M, and 180–200°C in our experiments. Higher acid concentrations and temperatures

accelerated the reaction rate and allowed the maximum LA yield to be reached sooner, but the maximum LA yield varied little with changing acid concentration and temperature. This outcome is consistent with acid acting as a catalyst to accelerate the reaction rate but not change chemical equilibrium. The maximum LA concentration was approximately proportional to the initial cellulose concentration, showing that cellulose concentration had little impact on yields.

A kinetic model that included a series of pseudo-first order reactions producing LA and FA from cellulose through glucose and HMF as well as parallel reactions for humins formation successfully replicated the time history of concentrations and yields for cellulose, glucose, HMF, and LA. All of the rate constants increased with increasing temperature, in a manner consistent with Arrhenius dependence. The fact that LA formation (reaction 4) from HMF had the same activation energy as humins formation (reaction 5) from HMF suggests that LA yield is less affected by temperature, consistent with our experimental data. Over most of the reaction time, HMF formation was the slowest step in the series of reactions and controlled overall reaction progress.

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Literature Cited

1. Bozell JJ, Moens L, Elliott DC, Wang Y, Neuenschwander GG, Fitzpatrick SW, Bilski RJ, Jarnefeld JL. Production of levulinic acid and use as a platform chemical for derived products. *Resour Conserv Recycl.* 2000;28:227–239.
2. Girisuta B, Janssen LPBM, Heeres HJ. A kinetic study on the conversion of glucose to levulinic acid. *Chem Eng Res Des.* 2006;84:339–349.
3. Jing Q, Lu XY. Kinetics of non-catalyzed decomposition of glucose in high-temperature liquid water. *Chin J Chem Eng.* 2008;16:890–894.
4. Seri K, Sakaki T, Shibata M, Inoue Y, Ishida H. Lanthanum(III)-catalyzed degradation of cellulose at 250 degrees C. *Bioresour Technol.* 2002;81:257–260.
5. Girisuta B, Janssen LPBM, Heeres HJ. Kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid. *Indus Eng Chem Res.* 2007;46:1696–1708.
6. Girisuta B, Janssen LPBM, Heeres HJ. A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid. *Green Chem.* 2006;8:701–709.
7. Cha JY, Hanna MA. Levulinic acid production based on extrusion and pressurized batch reaction. *Ind Crops Prod.* 2002;16:109–118.
8. Fang Q, Hanna MA. Experimental studies for levulinic acid production from whole kernel grain sorghum. *Bioresour Technol.* 2002;81:187–192.
9. Girisuta B, Danon B, Manurung R, Janssen LPBM, Heeres HJ. Experimental and kinetic modelling studies on the acid-catalysed hydrolysis of the water hyacinth plant to levulinic acid. *Bioresour Technol.* 2008;99:8367–8375.
10. Yan LF, Yang NK, Pang H, Liao B. Production of levulinic acid from bagasse and paddy straw by liquefaction in the presence of hydrochloride acid. *Clean-Soil Air Water* 2008;36:158–163.
11. Chang C, Cen PL, Ma XJ. Levulinic acid production from wheat straw. *Bioresour Technol.* 2007;98:1448–1453.
12. Saeman JF. Kinetics of wood saccharification hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature. *Ind Eng Chem.* 1945;37:43.
13. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, Crocker D. Determination of structural carbohydrates and lignin in biomass. *Lab Anal Proced. (LAP)* 2008; 4/25.
14. Upadhyay SK. *Chemical Kinetics and Reaction Dynamics.* New York: Springer, 2006:93–99.
15. Fogler SH. *Elements of Chemical Reaction Engineering,* 4th ed. Upper Saddle River, NJ: Prentice Hall, 2005:838–849.
16. *CRC Handbook of Chemistry and Physics,* 74th ed. In: Section 5 Thermochemistry, Electrochemistry, and Kinetics-90. Lide DR, editor. Boca Raton, FL: CRC press, Inc. 2000:5–90.
17. Poling BE, Prausnitz JM, O'Connell JP. In: Lide DR, editor. *Properties of Gases and Liquids,* 5th ed. New York: McGraw-Hill, 2001:11.39.

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