Kinetics of Formic Acid-catalyzed Cellulose Hydrolysis

Laura Kupiainen, Juha Ahola,* and Juha Tanskanen

Hydrolysis is a reaction to produce sugars from lignocellulosic raw materials for biochemical production. The present study elucidates the hydrolysis of cellulose and formation of glucose decomposition products catalyzed by 5% to 20% (w/w) formic acid at 180 to 220 °C with an initial cellulose concentration of 10 to 100 g/L. Microcrystalline cellulose was used as a model compound. The experimental findings indicated that cellulose hydrolysis follows first-order kinetics in formic acid. A side reaction from cellulose to non-glucose products was required to explain the experimental results. A kinetic model was developed for the hydrolysis of microcrystalline cellulose in formic acid, based on a rate constant expression in accordance with the specific acid catalysis. The model showed good agreement with the experimental data. This study demonstrates how kinetic parameters can be fitted in a case-specific manner for the hydrolysis part of the kinetic model, while the well-established glucose decomposition model is utilized directly from literature.

Keywords: Dilute sulfuric acid; Cellulose hydrolysis; Kinetic modelling; Reaction kinetics

*Contact information: Department of Process and Environmental Engineering, University of Oulu, P.O. BOX 4300, FI-90014 University of Oulu, Finland; *Corresponding author: juha.ahola@oulu.fi*

INTRODUCTION

Despite great efforts in developing production methods for chemicals based on lignocellulosic biomass, only around 50 million tons of chemicals and polymers are produced from biomass, whereas the production of chemicals and polymers from petroleum is globally estimated at around 330 million tons (De Jong *et al*. 2012). Bio-based platform chemicals, such as hydroxymethylfurfural, levulinic acid, and succinic acid, can be produced from glucose, which is the basic unit of abundantly available cellulose (Bozell and Petersen 2010; Werpy and Petersen 2004). There already exist commercial production methods for upgrading some of platform chemicals, and the application of high-throughput reactor systems to chemical synthesis and catalysis research will likely accelerate the development of downstream processing (Lee *et al.* 2013; Tullo 2010). However, one of the bottlenecks is the production of low-cost sugars from inedible lignocellulose, especially from cellulose itself. The challenge is to break down intra- and inter-fibrillar bonds between cellulose chains as well as β-1,4-glycosidic bonds of cellulose polymer and produce glucose effectively with high selectivity and yield.

Hydrolysis, *i.e.*, the cleavage of chemical bonds by the addition of water, is a reaction to break down cellulose to glucose. Most effectively, hydrolysis of cellulose takes place under conditions in which high pressure (22 MPa) and temperature (374 °C) creates supercritical water (Sasaki *et al.* 1998), or a catalyst accelerates the reaction below the critical point. Metal salts, *e.g.*, $AlCl_3$ (Ma *et al*. 2012), heterogeneous solid acids, *e.g.*, sulfonated carbonaceous solid acids (Guo *et al.* 2012), mineral acids, *e.g.*, dilute sulfuric acid (Karimi *et al*. 2006), and enzymes (Taherzadeh and Karimi 2007) have been studied for cellulose hydrolysis; the last two examples are the most studied catalysts. In supercritical conditions, reaction times are of a few seconds, which hinders the control of processing solid raw material. Under milder conditions, *e.g.*, enzymatic hydrolysis, a pretreatment step, long reaction times, and a series of expensive and even enzymes derived from genetically modified organisms are required (Huan *et al*. 2011).

Acid-catalyzed cellulose hydrolysis has the advantage of simultaneously producing glucose, hydroxymethylfurfural (HMF), formic acid (FA), and levulinic acid (LA), which are versatile value-added chemicals. These chemicals are formed through serial reactions, which are illustrated in the simplified scheme shown in Fig. 1. The drawback is that the reaction conditions are harsh and the selectivity for glucose production is limited due to side reactions (Mok *et al*. 1992), transformations in cellulose (Bouchard *et al*. 1989), and decomposition reactions of glucose (Saeman 1945). The glucose yield is about 50% to 60% in a plug flow reactor (McParland *et al*. 1982; Thompson and Grethlein 1979) and 70% in a semi-batch reactor (Mok *et al*. 1992). The ideal reactor configuration is a countercurrent reactor with a theoretical glucose yield of 90% (Greenwald *et al.* 1983), but this reactor design is challenging to realize in practice. However, Kim *et al*. (2001) and Gurgel *et al*. (2012) have obtained significant glucose yields in a bed-shrinking flow-through reactor and in a batch reactor, respectively. These interesting results were achieved under extremely low acid conditions, *i.e.*, 0.07% to 0.28% H_2SO_4, although kinetic studies of cellulose hydrolysis have shown that glucose yield is enhanced under short reaction times by increasing temperature and acid concentration (Fagan *et al*. 1971; Malester *et al.* 1992; Saeman 1945). Therefore, the in-depth studies of reaction conditions that are atypical for acid-catalyzed cellulose hydrolysis would be valuable.

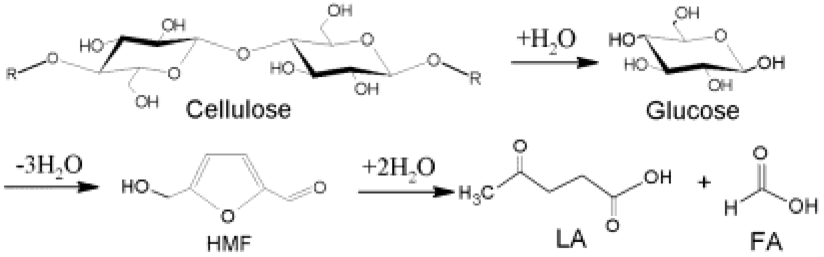

Fig. 1. Serial reaction pattern of cellulose hydrolysis catalyzed by acid

In the present study, formic acid is used as a cellulose hydrolysis catalyst under conditions comparable to extremely low sulfuric acid conditions. Formic acid, the strongest monocarboxylic acid, is formed during cellulose hydrolysis *via* glucose decomposition reactions. Unlike sulfuric acid, formic acid is a volatile compound that can be separated and recovered by thermal operations. Formic acid is an effective solvent for delignifying and fractionating biomass (Dapia *et al*. 2002; Zhang *et al.* 2010). Previously, formic acid has been studied as a pretreatment agent prior to enzymatic hydrolysis with (Sindhu *et al*. 2010) or without (Marzialetti *et al*. 2011) a mineral acid catalyst. It has also been used for cellulose hydrolysis in the presence of HCl at low temperature, *i.e.*, 55 to 65 °C (Sun *et al.* 2007), or in the absence of a mineral acid catalyst at high temperature, *i.e.*, 230 to 270 °C (Asaoka and Funazukuri 2011). However, a systematic kinetic study of cellulose hydrolysis in formic acid is lacking under reaction conditions corresponding to dilute sulfuric acid conditions at high temperature.

In this study, the aim was to develop a kinetic model for cellulose hydrolysis and glucose formation in formic acid. Kinetic studies based on dilute sulfuric acid (Fagan *et al*. 1971; Girisuta *et al*. 2007; Gurgel *et al*. 2012; McParland *et al.* 1982) typically rely on the empirical power law model developed by Saeman (1945). Instead, we used a strategy in which the rate constant equation is based on specific acid catalysis theory and the hydrogen ion concentration is evaluated at the reaction temperature. Formation of HMF and levulinic acid, as well as humins by-products, was also incorporated into the kinetic model.

EXPERIMENTAL

Materials

Microcrystalline cellulose was purchased from Acros Organics. The average particle size of the cellulose was 90 µm. The crystallinity index of cellulose was in the range 0.72 to 0.75 (Kupiainen *et al.* 2012a). The calibration chemicals for HPLC were sourced from Merck and Alfa Aesar. The chemicals were used as supplied. Formic acid catalyst solutions of 5% to 20% (w/w) were prepared using purified water from a Milli-Q system.

Experimental Procedure

Cellulose hydrolysis experiments were conducted in batch reactors made of zirconium tubing. The inner volume of the reactor was about 40 mL. A PTFE-coated thermo element sensor was inserted into the reactor through a zirconium cap to enable the temperature measurement inside the reactor during the experiments. The average heating-up time was 2.9 min to a temperature of 200 °C. The temperature was dropped to below 100 °C in 0.5 min after the experiment using a cold water bath.

For the experiment, 3 g of cellulose was weighed and 30 mL of a catalyst solution was pipetted into the reactor. A preheating oven set at 440 to 470 °C and a fluidized sand bath (SBL-2D, Techne) set at the desired reaction temperature were used for rapid and precise temperature control. The experiment began when the reactor was placed in the preheating oven. After reaching the reaction temperature, the reactor was transferred into the sand bath. The experiment was stopped by quenching the reactor in a cold water bath. After the experiment, solids were separated from the liquid by filtration using a filter paper (Whatman 1). A sample was taken from the filtrate for HPLC analysis, and the cake was washed with about 80 mL of deionized water, dried overnight at 105 °C, and weighed.

HPLC Analysis

Concentrations of cellobiose, glucose, 5-hydroxymethyl-2-furfural, levulinic acid and furfural were analyzed by high-performance liquid chromatography (HPLC) using an ICSep ICE-Coregel 87H3 column (Transgenomic) and a refractive index detector (Agilent Technologies). A diode array detector (Agilent Technologies) with a wavelength of 280 nm was also used to detect smaller concentrations of HMF and furfural. The column was operated at 60 °C. The mobile phase was 5 mM H_2SO_4 with a flow rate of 0.8 mL/min.

A small peak was perceived after glucose in every sample. To elucidate the peak, individual xylose and fructose samples were analyzed. Their retention times were similar to the peak after glucose. Because furfural, a xylose decomposition product, is also present in every sample of cellulose hydrolysis, it is likely that the peak after glucose is xylose from a xylan impurity of the microcrystalline cellulose. Fructose, an isomerization product of glucose, is known to decompose quickly into HMF.

pH Measurements

The pH was measured using a SenTix 81 pH electrode (WTW) connected to an inoLab pH 720 meter (WTW). The pH meter was calibrated at three points (1.679, 4.006, and 6.865 pH).

Yield Calculation

For the molar cellulose concentration (C_c), cellulose is treated as glucan (anhydroglucose), *i.e.*, $MW_{glucan\ unit} = MW_g - MW_{H2O}$ = 180.2 g/mol – 18.0 g/mol = 162.2 g/mol. In this way, cellulose is converted to glucose equivalents, which represents the maximum theoretical glucose from cellulose. The cellulose concentration as glucose equivalents is calculated as follows:

$$C_c = m_c / (V * MW_{glucan\ unit}), \tag{1}$$

where m_c is the mass of cellulose or the mass of weighed cake from experiments, V is the liquid volume and MW is the molar mass. The glucose yield (Y_g) is defined in this study per initial cellulose concentration as glucose equivalents:

$$Y_g = 100 * C_g / C_{c,0}. \tag{2}$$

The yields of HMF and LA are defined in the same way.

RESULTS AND DISCUSSION

Effect of Reaction Conditions

The basis for the kinetic study of cellulose hydrolysis in formic acid was a three-level experimental design, which was executed by varying formic acid concentration (5% to 20% (w/w)), temperature (180 to 220 °C), and time. Furthermore, some additional data points were obtained at specific reaction conditions (*i.e.*, acid concentration and temperature) with longer reaction times, or an experimental datum point was replicated. The initial cellulose concentration was 100 g/L. In addition, a few experiments were conducted with lower initial cellulose concentrations at 200 to 220 °C.

The reaction time varied from 3 to 330 min, resulting in cellulose conversions of 7% to 78% (mol/mol). The main products of formic acid catalyzed cellulose hydrolysis were glucose, HMF, and levulinic acid (LA), where HMF is an intermediate product to forming LA. The maximum glucose yield, 22% (mol/mol) was achieved in 10 min at 220 °C in 20% HCOOH. Cellobiose and furfural were also detected in small amounts. The yield of cellobiose was between 0.02% and 0.67%. The cellobiose yield increased slightly with the temperature at high conversions. The furfural yield from initial cellulose was below 2.7%. The formation of furfural, a product from the decomposition of pentoses (C5 sugars), could be explained by a xylan impurity in the cellulose raw material.

The increasing temperature enhanced the glucose and HMF yields, whereas the decreasing temperature enhanced the LA yield (*vide infra* Fig. 8). The increasing formic acid concentration also slightly enhanced the glucose and HMF yields. The results of cellulose hydrolysis in formic acid are in accordance with the findings by Girisuta *et al*. (2007) for sulfuric acid.

Effect of Initial Cellulose Concentration

The maximum combined yield of the main products was 34% (mol/mol) with a cellulose conversion of 77% (mol/mol), which corresponds to a selectivity of 44%. The selectivity was above 50% when the initial cellulose concentration was lower than 100 g/L. Therefore, the effect of initial cellulose concentration on conversion and yield was investigated. Figure 2 illustrates that increasing initial cellulose concentration slightly decreased the hydrolysis reaction rate. A ten-fold increase in the initial cellulose concentration is needed for the small decrease in the hydrolysis rate. The result is consistent with the study by Saeman (1945), who noticed a slight decrease in reaction rate with liquid-to-solid ratios of 5 to 20. Generally speaking, scientific literature concerning the effect of initial cellulose concentration on hydrolysis rate is extremely limited. The assumption about pseudo-homogeneity is valid under broad circumstances. For example, cellulose hydrolysis can be modeled as pseudo-homogeneous reaction, when a particle size is below 840 μm (Girisuta *et al*. 2007; Saeman 1945).

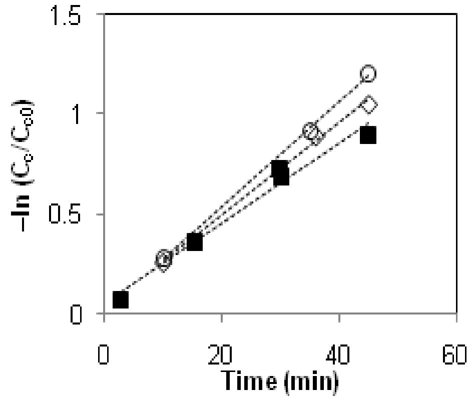

Fig. 2. First-order kinetics of cellulose hydrolysis at 200 °C in 10% HCOOH. Symbols: (■) 100 g/L (◊) 39 g/L (○) 10 g/L

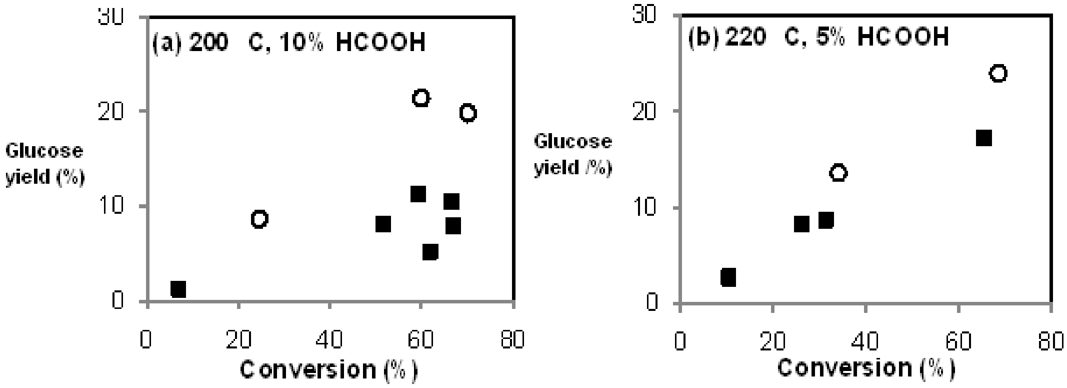

Fig. 3. The effect of initial cellulose concentration on glucose yield in formic acid. Symbols: (■) 100 g/L (○) 10 g/L

The effect of initial cellulose concentration on glucose yield has been considered in a few studies. For example, there was no correlation found between an initial slurry concentration (5% to 13.5%) and the glucose yield at 200 to 240 °C in the study by Thompson and Grethlein (1979). Contrary to that, glucose yields of this study were affected by the initial cellulose concentration. Figure 3 shows that glucose yield increased significantly with the decreasing initial cellulose concentration at the same conversion level. However, it was earlier found that glucose decomposes to an intermediate compound in formic acid with first-order kinetics (Kupiainen *et al*. 2011), and that the overall cellulose hydrolysis reaction in formic acid also follows first-order kinetics (Kupiainen *et al*. 2012a). This indicates that glucose yield cannot be affected by the initial cellulose concentration unless there is an additional side-reaction from cellulose. The results imply that a simplified reaction scheme of two consecutive reactions is an insufficient description of cellulose hydrolysis.

Kinetic Model

The kinetics of cellulose hydrolysis is classically modeled using two consecutive first-order reactions (Fagan *et al*. 1971; Franzidis *et al*. 1983; Malester *et al*. 1998; McParland *et al*. 1982; Ranganathan *et al*. 1985; Saeman 1945; Thompson and Grethlein 1979). The first reaction is for cellulose hydrolysis, and the second one is for glucose decomposition. Mok *et al.* (1992) experimentally found soluble non-glucose products from cellulose. Girisuta *et al.* (2007) included a side-reaction from cellulose to unknown by-products in their kinetic model.

In this study, a reaction scheme shown in Fig. 4 is used for cellulose hydrolysis and glucose decomposition. In the scheme, Y is soluble (non-glucose) by-products from cellulose hydrolysis and X is insoluble by-products (so-called humins) from glucose decomposition reactions. For glucose decomposition, the reaction scheme has been taken from our previous study with its kinetic parameters (Kupiainen *et al.* 2011).

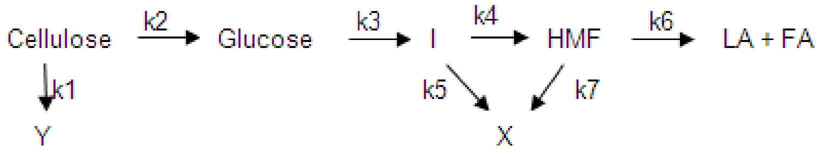

Fig. 4. Proposed reaction scheme for cellulose hydrolysis

Cellulose hydrolysis is modeled assuming that the reaction is pseudo-homogeneous and that all reaction steps follow first-order kinetics. The rate equations are then in the form of $R_i = k_i C_j$, where *i* is the number of the reaction step and *j* is the component.

Instead of the classical power-law model, the so-called Saeman's equation, the rate constant can be calculated according to specific acid catalysis both for cellulose hydrolysis (Kupiainen *et al*. 2012a) and glucose decomposition (Kupiainen *et al*. 2010). In this model, the rate constant is directly proportional to hydrogen ion concentration, as shown in Eq. (3):

$$k_i = \left(k_{H_2O} + k_{H^+} C_{H^+,T}\right) e^{-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{mean}}\right)} . \qquad (3)$$

The hydrogen ion concentration, $C_{H^+,T}$, is calculated here at the reaction temperature due to the characteristics of weak organic acids (Kupiainen *et al*. 2010). This was done by estimating the temperature dependence of the dissociation constant, $K_{a,FA}$, based on the literature (Kim *et al*. 1996). First, the initial acid concentration, $C_{HCOOH,0}$, was calculated based on the pH measured at room temperature ($C_{H^+} = 10^{-pH,25°C}$) by solving a system of nonlinear equations (Eq. 4) in Matlab 7.5.0. The initial acid concentration was then used to calculate the hydrogen ion concentration at the reaction temperature ($C_{H^+,T}$). The equations are:

$$\begin{aligned} &C_{H^+} C_{HCOO^-} - K_{a,FA}\, C_{HCOOH} = 0 \\ &C_{HCOOH,0} - C_{HCOOH} - C_{HCOO^-} = 0 \\ &C_{H^+} - C_{HCOO^-} = 0 \end{aligned} \tag{4}$$

where $pK_{a,FA}$= -57.528+2773.9/T+9.1232ln(T) (Kim *et al*. 1996).

The kinetic parameters, k_{H_2O}, k_{H^+}, and E_a, were estimated in Matlab 7.5.0 using a non-linear least square method that utilized the Levenberg-Marquardt algorithm. The differential mass balance equation for a non-isothermal batch reactor model (Eq. 5) was solved with an ode15s solver in Matlab 7.5.0:

$$\frac{dC_j}{dt} = \sum_{i=1} \nu_{ji} R_i \tag{5}$$

The non-isothermalicity, *i.e.*, the temperature data measured with respect to time, was incorporated in the model through Eq. 3.

Estimated Parameters

A total of 51 experiments with an initial cellulose concentration of 100 g/L were used in the parameter estimation. It was assumed that glucose decomposition is similar in the presence and absence of cellulose.

Table 1. Best Estimates of the Kinetic Parameters (Confidence Interval of 95%, N-distribution)

Reaction i	k_{H_2O} [a] (min^{-1})	k_{H^+} [a] (M^{-1}min^{-1})	E_a (kJ/mol)
1 (C → Y)	0.0047 ± 0.0006	0.63 ± 0.07	161 ± 9
2 (C → G)	0.0026 ± 0.0004	0.74 ± 0.06	201 ± 9
3[b] (G → I)	0.018 ± 0.000	2.6 ± 0.0	153 ± 2
4[b] (I → HMF)	0.109 ± 0.001	8.6 ± 0.1	110 ± 5
5[b] (I → X)	0.058 ± 0.002	2.9 ± 0.1	117 ± 4
6[b] (HMF → LA)	0	5.5 ± 0.2	107 ± 5
7[b] (HMF → X)	0.031 ± 0.005	2.5 ± 0.2	127 ± 9

[a] The values are at the reference temperature of 200 °C.

[b] The parameter values taken from study by Kupiainen *et al*. (2011).

The model for independent glucose decomposition was developed earlier by the authors (Kupiainen *et al*. 2011), and thus the kinetic parameters were estimated solely for two reactions of cellulose hydrolysis.

The best estimates of the parameters for cellulose hydrolysis are presented in Table 1. The R^2 value was 99.4%. As presented in Fig. 5, the sensitivity analysis shows that the parameters are well-defined. Furthermore, the parity plot in Fig. 6 indicates that the model is in good agreement with the data for both cellulose conversion and glucose yield.

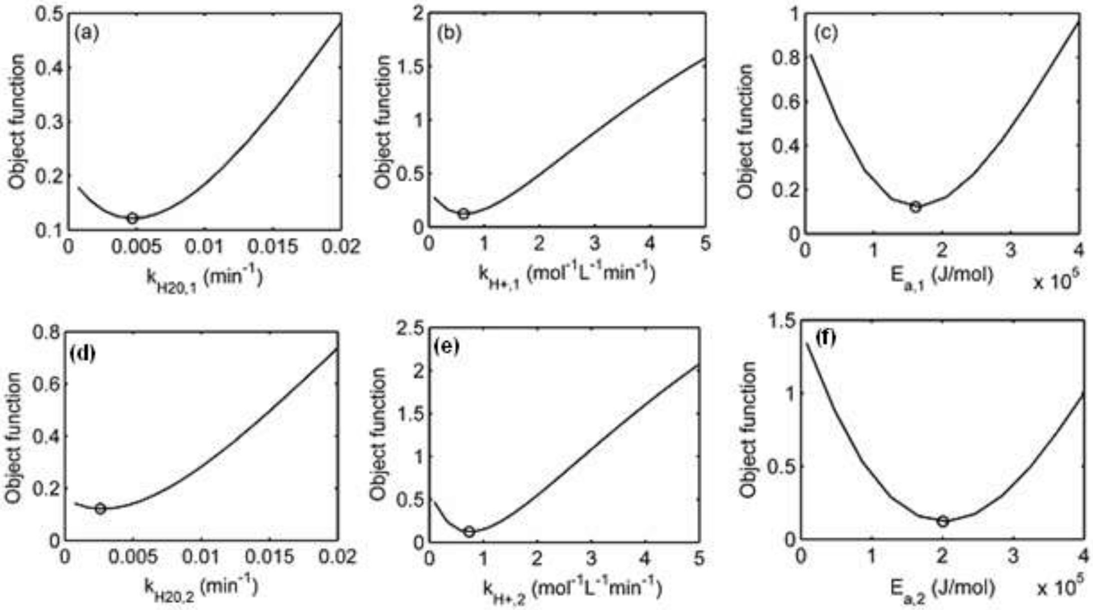

Fig. 5. Sensitivity of parameters; (o) Estimated parameter value

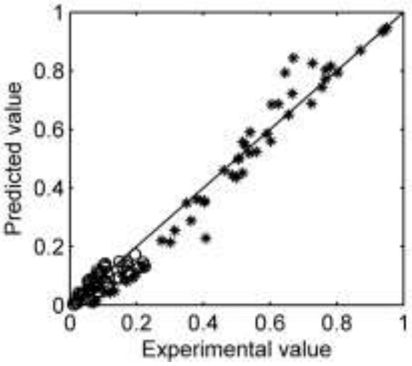

Fig. 6. Parity plot; (*) Cellulose conversion; (o) Glucose yield

Performance of the Model

Figures 7 and 8 show the cellulose and product concentrations, respectively, at different reaction conditions. As stated previously, the model shows good accordance with the experimental data from cellulose hydrolysis and product formation. However, in Fig. 7b, suspicious cellulose data points are seen for the longest reaction times in 10% to 20% HCOOH. Experimental cellulose is actually defined here as solids by filtering. Therefore, it is likely that humins, *i.e.*, solid by-products (X) from glucose decomposition reactions, interfere with the cellulose gravimetric analysis, which is a common way to determine unreacted cellulose (Gurgel *et al*. 2012; Mok *et al*. 1992). The kinetic model was then used to study the data points. Figure 9 shows how cellulose data points are corrected by subtracting the amount of humins estimated by the model from the experimental cellulose values. It can be seen from Fig. 9 that within short reaction times, original cellulose data points equal to the corrected ones. This indicates that there are no humins formed at the beginning of the reaction, as expected, but the formation of humins had a clear effect on the determination of cellulose conversion at the longest reaction time points at 200 °C (20% HCOOH) and at 220 °C (10% to 20% HCOOH). These suspicious values at the longest reaction times were excluded from the data set when the kinetic parameters were estimated.

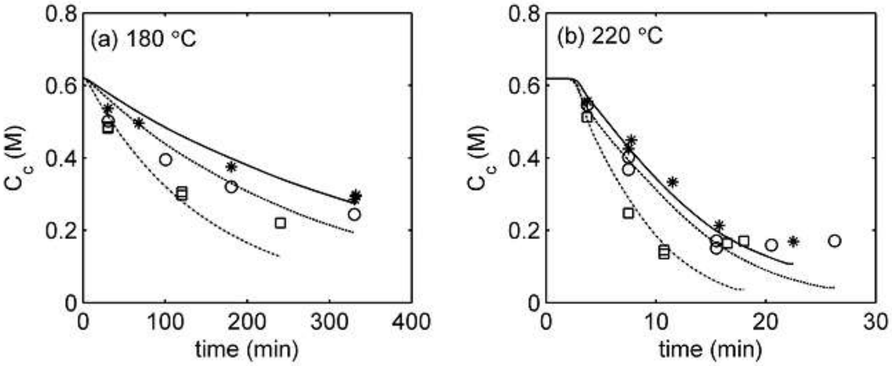

Fig. 7. Cellulose hydrolysis in formic acid (symbols) and the model prediction (lines); Symbols: (*) 5%, (○) 10%, (□) 20% HCOOH

Experimental uncertainty is detected in glucose data based on the replicated experiments shown in Fig. 8. However, the general trend shows that prolonged reaction times are needed for cellulose hydrolysis before the glucose maximum is reached in a serial reaction.

The kinetic model makes it possible to explain the behavior of cellulose hydrolysis phenomena. The activation energy of cellulose hydrolysis to glucose (E_{a2} = 201 kJ/mol) is higher than the activation energy to soluble by-products (E_{a1} = 161 kJ/mol) and the activation energy of glucose decomposition (E_{a3} = 153 kJ/mol). This means that the glucose yield in formic acid is enhanced at higher temperatures. The result is consistent with the observed cellulose hydrolysis catalyzed by dilute sulfuric acid (Gurgel *et al*. 2012; Malester *et al*. 1992; Mok *et al*. 1992; Saeman 1945), and the experimental data of this study. On the other hand, Girisuta *et al*. (2007) reported that the activation energy of cellulose hydrolysis to glucose was lower than that to unknown by-products; this may be due to the low temperature range (140 to 200 °C) employed by these authors.

Increasing the acid concentration favors glucose formation over formation of soluble by-products from cellulose ($k_{H^+,2} > k_{H^+,1}$), but the effect is minor. However, the acid factor for glucose decomposition reaction at the liquid phase, $k_{H^+,3} = 2.6\ M^{-1}min^{-1}$ (Kupiainen *et al*. 2011), is higher than the acid factors for cellulose hydrolysis.

The ratio of k_1 to k_2 was calculated to assess the role of the parallel reaction route. At the temperature range studied, the ratio k_1/k_2 was >1. This indicates that the reaction rate from cellulose to soluble by-products is higher than the reaction rate from cellulose to glucose. This leads to a higher selectivity toward unwanted by-products. On the other hand, reaction step 2 is more sensitive to temperature than reaction steps 1 and 3 ($E_{a,2} > E_{a,1} > E_{a,3}$), which enhances the glucose yield at higher temperatures. However, the amount of material lost in the side reaction is still significant based on the model.

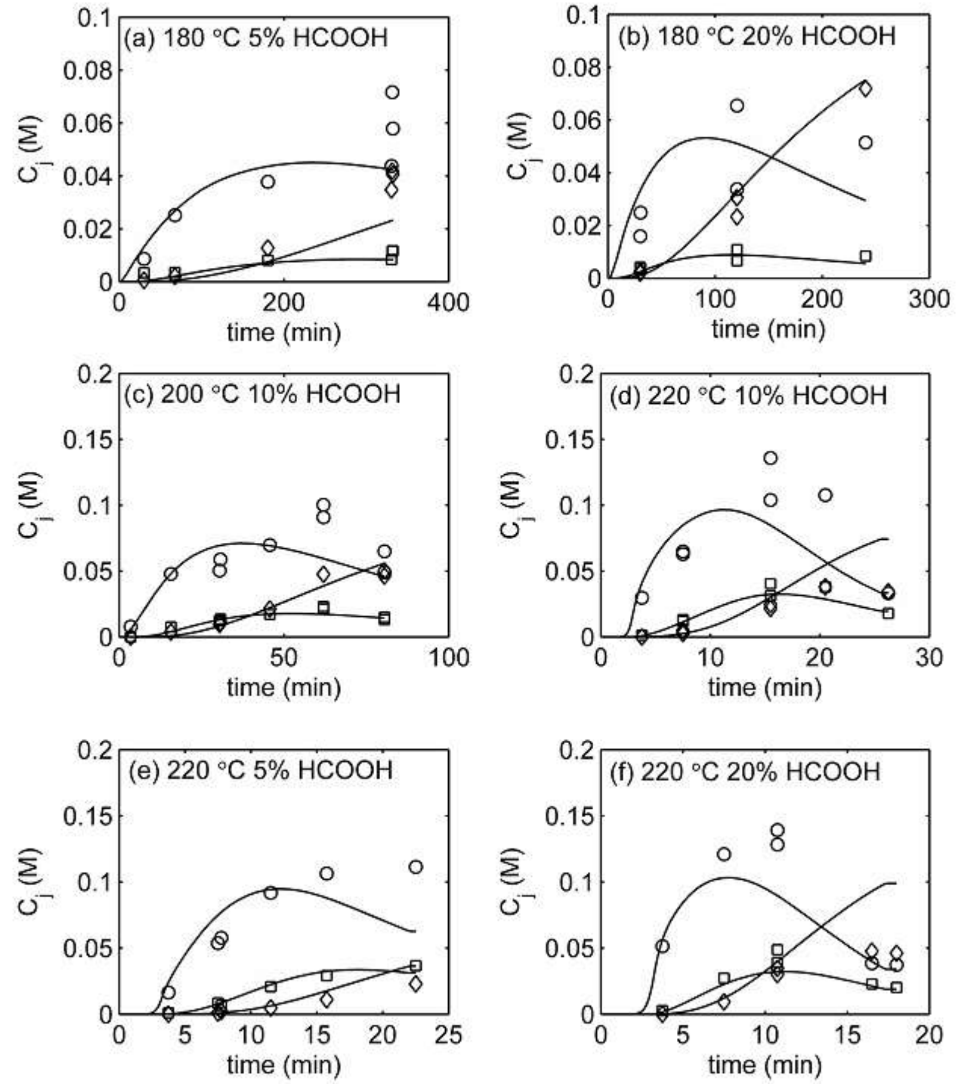

Fig. 8. Product formation in formic acid (symbols) and the model prediction (lines); Symbols: (o) Glucose (□) HMF (◊) LA

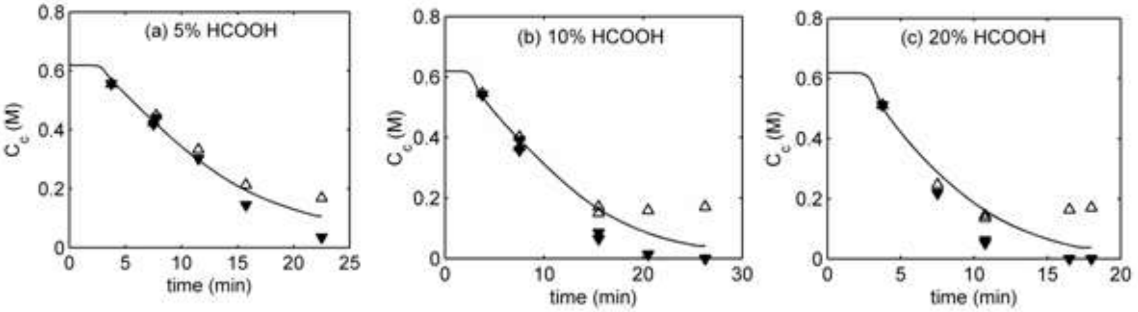

Fig. 9. Cellulose hydrolysis with experimental data points corrected by the model estimate of forming solids; Symbols: (∆) Original cellulose, (▼) Cellulose – solids

DISCUSSION

The model was used to predict the maximum glucose yield from hydrolysis of microcrystalline cellulose in 20% formic acid. Figure 10 shows the effect of temperature and time on glucose yield. The model predicts that the maximum glucose yield, 24% (mol/mol), is achieved in 1 min at 240 °C, which is outside the studied temperature range. However, the predicted condition area with formic acid corresponds to the optimum condition area with sulfuric acid (Fagan *et al*. 1971; Gurgel *et al*. 2012; McParland *et al*. 1982).

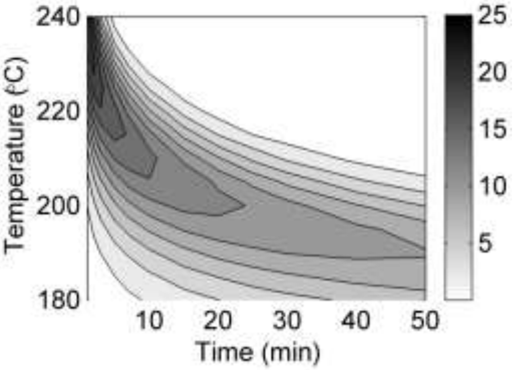

Fig. 10. Contour plot prediction for glucose yield (%) from microcrystalline cellulose in 20% HCOOH.

Figure 11 shows the contour plot for the yield of soluble non-glucose compounds from cellulose. The model predicts a significant yield of soluble by-products even under reaction conditions appropriate for glucose production. Under these conditions, the yield of soluble by-products from cellulose was higher than the yield of insoluble by-products from glucose decomposition. Based on the model presented in this study, the main reason for the low glucose yield is the side reaction from microcrystalline cellulose to non-glucose products, and not the glucose decomposition reactions. In addition, the cellulose hydrolysis reaction has to proceed almost to completion before the rate of glucose decomposition exceeds the rate of glucose formation from the cellulose. These findings are consistent with Mok *et al*. (1992) concerning non-hydrolyzable oligomers, which were found in substantial amounts from cellulose hydrolysis in water. In dilute hydrogen ion concentrations used in this study, a significant side reaction is possible from cellulose to non-glucose products.

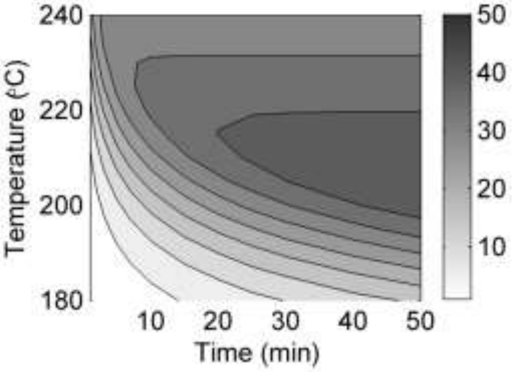

Fig. 11. Contour plot prediction for the yield of soluble by-products (%) from microcrystalline cellulose in 20% HCOOH

Because the kinetic parameters from independent glucose decomposition experiments can be successfully applied in the modeling of the whole cellulose hydrolysis system, it can be concluded that there are neither major interactions between cellulose and glucose nor its decomposition products. This gives advantages for those modeling cellulosic systems. Experiments can be performed only for different cellulosic raw materials instead of an extensive series of both hydrolysis and glucose decomposition experiments. The kinetic parameters have to be fitted to the hydrolysis part of the model, while the kinetic parameters for glucose decomposition are already available in the scientific literature. It has already been shown that the kinetic model for formic-acid-catalyzed glucose decomposition is applicable to predict glucose decomposition in 0.09% to 0.50% sulfuric acid at 180 to 220 °C (Kupiainen 2012). However, lignin and metal impurities contained in lignocellulosic raw materials may have an influence on glucose reactions.

Despite the low glucose yield afforded in this study, there is a potential to intensify cellulose hydrolysis in formic acid. For example, we found glucose yield to be two-fold higher from organosolv pulp than from microcrystalline cellulose (Kupiainen *et al*. 2012b). In addition, Gurgel *et al*. (2012) achieved glucose yields (defined as in this study) of up to 48% from cellulosic bagasse pulp under extremely low sulfuric acid conditions, which are similar to formic acid conditions used in this study. However, in order to maximize the glucose yield, a challenging optimization task has to be solved under reaction conditions of high temperature and a short reaction time. With reliable kinetics, it is possible to evaluate these complicated phenomena taking place in the reaction system and to design an appropriate reactor for the production of chemicals.

CONCLUSIONS

1. A kinetic model with a rate constant expression derived from specific acid catalysis theory was developed for the formic acid-catalyzed hydrolysis of microcrystalline cellulose. In addition, hydrogen ion concentrations were calculated at the reaction temperature. The model showed good agreement with experimental data.
2. A previously established glucose decomposition model was successfully incorporated into the cellulose hydrolysis model, indicating that there are no interactions between glucose decomposition and cellulose hydrolysis.
3. Based on the model, substantial amounts of raw material are lost in side reactions from cellulose to by-products in a batch reactor under reaction conditions similar to those for very dilute sulfuric acid. Glucose decomposition reactions have a minor effect on the glucose selectivity.
4. The model also has an ability to explain the formation of hydroxymethylfurfural and levulinic acid from glucose.

ACKNOWLEDGMENTS

The authors would like to thank the Emil Aaltonen Foundation and Oulu University Apuraharahasto for their financial support.

REFERENCES CITED

Asaoka, Y., and Funazukuri, T. (2011). “Hydrothermal saccharification of cotton cellulose in dilute aqueous formic acid solution,” *Res. Chem. Intermed.* 37(2-5), 233-242.

Bouchard, J., Abatzoglou, N., Chornet, E., and Overend, R. P. (1989). “Characterization of depolymerized cellulosic residues. Part 1: Residues obtained by acid hydrolysis processes,” *Wood Sci. Technol.* 23(4), 343-355.

Bozell, J., and Petersen, G. (2010). “Technology development for the production of biobased products from biorefinery carbohydrates – the US Department of Energy’s “Top 10” revisited,” *Green Chem*. 12(4), 539-554.

Dapía, S., Santos, V., and Parajó, J. C. (2002). “Study of formic acid as an agent for biomass fractionation,” *Biomass Bioenergy* 22(3), 213-221.

De Jong, E., Higson, A., Walsh, P., and Wellisch, M. (2012). “Bio-based chemicals value added products from biorefineries. IEA bioenergy – Task42 biorefinery,” (http://ieabioenergy.com/LibItem.aspx?id=7311).

Fagan, R., Grethlein, H., Converse, A., and Porteous, A. (1971). “Kinetics of the acid hydrolysis of cellulose found in paper refuse,” *Environ. Sci. Technol*. 5(6), 545-547.

Franzidis, J.-P., Porteous, A., and Anderson, J. (1983). “The acid hydrolysis of cellulose in refuse in a continuous reactor,” *Conserv. Recycling* 5(4), 215-225.

Girisuta, B., Janssen, L. P. B. M., and Heeres, H. J. (2007). “Kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid,” *Ind. Eng. Chem. Res*. 46(6), 1696-1708.

Greenwald, C. G., Nystrom, J. M., and Lee, L. S. (1983). “Yield predictions for various types of acid hydrolysis reactors,” *Biotechnol. Bioen. Symp*. 13(5), 27-39.

Guo, F., Fang, Z., Xu, C. C., Smith R. L. Jr. (2012). “Solid acid mediated hydrolysis of biomass for producing biofuels,” *Prog. Energ. Combust*. 38(5), 672-690.

Gurgel, L., Marabezi, K., Zanbom, M., and Curvelo, A. (2012). “Dilute acid hydrolysis of sugar cane bagasse at high temperatures: A kinetic study of cellulose saccharification and glucose decomposition. Part I: Sulfuric acid as the catalyst,” *Ind. Eng. Chem. Res*. 51(3), 1173-1185.

Huan, R., Su, R., Qi, W., and He, Z. (2011). “Bioconversion of lignocellulose into bioethanol: Process intensification and mechanism research,” *Bioenerg. Res*. 4(4), 225-245.

Karimi, K., Kheradmandinia, S., and Taherzadeh, M. J. (2006). “Conversion of rice straw to sugars by dilute-acid hydrolysis,” *Biomass Bioenergy* 30(3), 247-253.

Kim, M. H., Kim, C. S., Lee, H. W., and Kim, K. (1996). “Temperature dependence of dissociation constants for formic acid and 2,6-dinitrophenol in aqueous solutions up to 175°C,” *J. Chem. Soc. Faraday Trans*. 92(24), 4951- 4956.

Kim, J. S., Lee, Y. Y., and Torget, R. W. (2001). “Cellulose hydrolysis under extreme low sulfuric acid and high-temperature conditions,” *Appl. Biochem. Biotechnol*. 91-93(1-9), 331-340.

Kupiainen, L. (2012). *Dilute Acid Catalysed Hydrolysis of Cellulose - Extension to Formic Acid*, Ph.D. Dissertation, University of Oulu, Tampere, Finland.

Kupiainen, L., Ahola, J., and Tanskanen, J. (2010). “Comparison of formic and sulfuric acids as a glucose decomposition catalyst,” *Ind. Eng. Chem. Res*. 49(18), 8444-8449.

Kupiainen, L., Ahola, J., and Tanskanen, J. (2011). “Kinetics of glucose decomposition in formic acid,” *Chem. Eng. Res. Des*. 89(12), 2706-2713.

Kupiainen, L., Ahola, J., and Tanskanen, J. (2012a). “Distinct effect of formic and sulfuric acids on cellulose hydrolysis at high temperature,” *Ind. Eng. Chem. Res*.

51(8), 3295-3300.

Kupiainen, L., Ahola, J., and Tanskanen J. (2012b). "Hydrolysis of organosolv wheat pulp in formic acid at high temperature for glucose production," *Bioresour. Technol.* 116(7), 29-35.

Lee, J., Xu, Y., and Huber, G. W. (2013). "High-throughput screening of monometallic catalysts for aqueous-phase hydrogenation of biomass-derived oxygenates," *Appl. Catal. B-Environ*. 140-141(8-9), 98-107.

Ma, Y., Ji, W., Zhu, X., Tian, L., and Wan, X. (2012). "Effect of extremely low $AlCl_3$ on hydrolysis of cellulose in high temperature liquid water," *Biomass Bioenergy* 39(4), 106-111.

Malester, I., Green, M., and Shelef, G. (1992). "Kinetics of dilute acid hydrolysis of cellulose originating from municipal solid wastes," *Ind. Eng. Chem. Res*. 31(8), 1998-2003.

Marzialetti, T., Miller, S. J., Jones, C. W., and Agarwal, P. K. (2011). "Switchgrass pretreatment and hydrolysis using low concentrations of formic acid," *J. Chem. Technol. Biotechnol*. 86(5), 706-713.

McParland, J. J., Grethlein, H. E., and Converse, A. O. (1982). "Kinetics of acid hydrolysis of corn stover," *Sol. Energy* 28(1), 55-63.

Mok, W., Antal, M., and Varhegyi, G. (1992). "Productive and parasitic pathways in dilute acid-catalyzed hydrolysis of cellulose," *Ind. Eng. Chem. Res*. 31, 94-100.

Ranganathan, S., Macdonald, D., and Bakhshi, N. (1985). "Kinetic study of wheat straw hydrolysis using sulphuric acid," *Can. J. Chem. Eng*. 6(1), 840-844.

Saeman, J. F. (1945). Kinetics of wood saccharification. "Hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature," *Ind. Eng. Chem*. 37(1), 43-52.

Sasaki, M., Kabyemela, B., Malaluan, R., Hirose, S., Takeda, N., Adschiri, T., and Arai, K. (1998). "Cellulose hydrolysis in subcritical and supercritical water," *J. Supercrit. Fluid.* 13(1-3), 261-268.

Sindhu, R., Binod, P., Satyanagalakshmi, K., Janu, K. U., Sajna, K. V., Kurien, N., Sukumaran, R. K., and Pandey, A. (2010). "Formic acid as a potential pretreatment agent for the conversion of sugarcane bagasse to bioethanol," *Appl. Biochem. Biotechnol.* 162(8), 2313-2323.

Sun, Y., Lin, L., Pang, C., Deng, H., Peng, H., Li, J., He, B., and Liu, S. (2007). "Hydrolysis of cotton fiber cellulose in formic acid," *Energ. Fuel* 21(4), 2386-2389.

Taherzadeh, M., and Karimi, K. (2007). "Enzyme-based hydrolysis processes for ethanol from lignocellulosic materials: A review," *BioResources* 2(4), 707-738.

Thompson, D. R., and Grethlein, H. E. (1979). "Design and evaluation of a plug flow reactor for acid hydrolysis of cellulose," *Ind. Eng. Chem. Prod. R. D.* 18(3), 166-169.

Tullo, A. H. (2010). "Catalyzing biobased chemicals," *Chem. Eng. News* 88(38), 15-17.

Werpy, T., and Petersen, G. (ed.) (2004). "Top value added chemicals from biomass. Volume I – Results of screening for potential candidates from sugars and synthesis gas," National Renewable Energy Laboratory, Golden, CO.

Zhang, M., Qi, W., Liu, R., Su, R., Wu, S., and He, Z. (2010). "Fractionating lignocellulose by formic acid: Characterization of major components," *Biomass Bioenergy* 34(4), 525-532.

Article submitted: January 3, 2014; Peer review completed: March 16, 2014; Revised version received and accepted: March 18, 2014; Published: March 25, 2014.