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GREEN CHEMICALS
A Kinetic Study on the Conversion of Glucose to Levulinic Acid

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Levulinic acid has been identified as a promising green, biomass derived platform chemical. A kinetic study on one of the key steps in the conversion of biomass to levulinic acid, *i.e.*, the acid catalysed decomposition of glucose to levulinic acid has been performed. The experiments were performed in a broad temperature window (140–200°C), using sulphuric acid as the catalyst (0.05–1 M) and a initial glucose concentration between 0.1 and 1 M. A kinetic model of the reaction sequence was developed including the kinetics for the intermediate 5-hydroxymethyl-2-furaldehyde (HMF) and humins byproducts using a power-law approach. The yield of levulinic acid is favoured in dilute glucose solution at high acid concentration. On the basis of the kinetic results, continuous reactor configurations with a high extent of back-mixing are preferred to achieve high levulinic acid yields.

Keywords: biomass; green chemistry; levulinic acid; kinetic studies; reactor configurations.

INTRODUCTION

A substantial amount of research activities is currently undertaken worldwide to identify attractive chemical transformations to convert biomass into organic (bulk)-chemicals and to develop economically feasible processes for these transformations on a commercial scale. Our research activities involve the acid-catalysed decomposition of lignocellulosic biomass into valuable chemicals. An attractive option is the conversion of lignocellulosic biomass into levulinic acid (4-oxo-pentanoic-acid) by acid treatment at relatively mild conditions. Levulinic acid contains a ketone group and a carboxylic acid group. These two functional groups make levulinic acid a potentially very versatile building block for the synthesis of various organic (bulk)-chemicals as shown in Figure 1 (Leonard, 1956; Kitano *et al.*, 1975; Thomas and Barile, 1985; Ghorpade and Hanna, 1997; Timokhin *et al.*, 1999). For instance, 2-methyl-tetrahydrofuran and various levulinate esters may be used as gasoline and biodiesel additives, respectively. δ-Aminolevulinate is a known herbicide and the bisphenol derivative may be an interesting substitute for bisphenol A (Bozell *et al.*, 2000).

On a molecular level, the conversion of lignocellulosic biomass to levulinic acid is known to follow a complicated reaction scheme (Grethlein, 1978; Danon *et al.*, 2005) involving several intermediates and byproducts (Figure 2). Hemicellulose and cellulose, two of the three main constituents of biomass, are carbohydrate-based polymers that can be broken down to low molecular weight sugars by hydrolysis using an acid catalyst. The acid-catalysed decomposition of the C6-sugar fragments (e.g., glucose) leads to 5-hydroxymethyl-2-furaldehyde as the intermediate product, which is subsequently rehydrated to give levulinic and formic acids as the final products. Hydrolysis of the C5 sugars of hemicellulose may lead to furfural. In addition, other constituents in the hemicellulose matrix may produce side products like acetic acid and galacturonic acid (Danon *et al.*, 2005). Lignin, the third main constituent of lignocellulosic biomass, is a resin-like polymer matrix with various substituted phenolics present. During acid hydrolysis, various acid soluble lignin-derived components may be formed, increasing the product complexity. The simplified reaction scheme given in Figure 2 does not explicitly show the reactions leading to undesired insoluble polymeric materials known as humins.

As part of a larger project to develop efficient reactor configurations for the conversion of biomass to levulinic acid, we have initiated a study to determine the kinetics of all steps involved in the process. A stepwise approach was followed, starting with the conversion of 5-hydroxymethyl-2-furaldehyde (HMF) to levulinic acid (Girisuta *et al.*, 2005). We here report our results of the kinetic study of the acid catalysed decomposition of glucose in a broad range of process conditions, including the kinetics of the reactions leading to humins.

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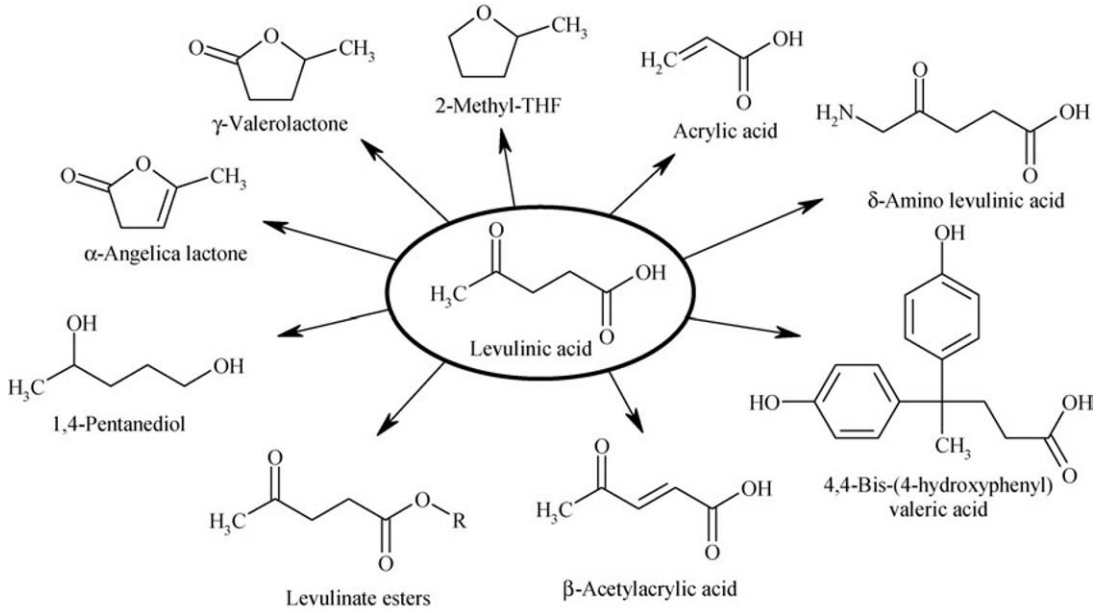


Figure 1. Potentially interesting derivatives of levulinic acid.

The acid-catalysed decomposition of glucose has been studied by a number of authors (Saeman, 1945; Heimlich and Martin, 1960; Mckibbins *et al.*, 1962; Fagan *et al.*, 1971; Smith *et al.*, 1982; Bienkowski *et al.*, 1987; Baugh and McCarty, 1988; Bergeron *et al.*, 1989; Mosier *et al.*, 2002; Xiang *et al.*, 2004). However, in all studies, only the rate of decomposition of glucose has been taken into account, often represented by a simple first order reaction (Table 1). The development of a kinetic scheme for the conversion of glucose to levulinic acid including the kinetics of byproduct formation and incorporation of HMF as an intermediate has not been reported to date. In addition, the rate-equations provided in the literature are often valid for small temperature, substrate and/or catalyst

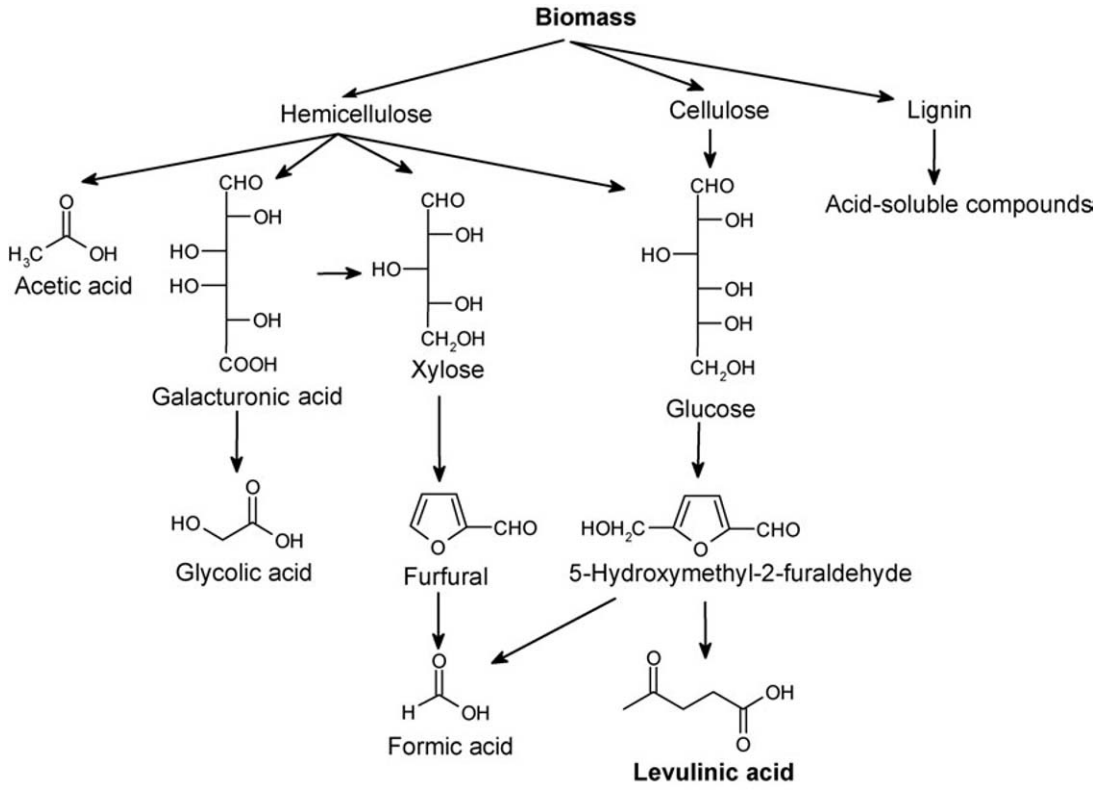


Figure 2. Possible pathways and products of the acid-catalysed hydrolysis of a typical lignocellulosic material.

Table 1. Overview of kinetic studies of glucose decomposition.

T (°C)	$C_{GLC,0}$	C_{Acid}	Order in substrate and acid	Reference
170–190	5 %-w	H_2SO_4 0.4–1.6 %-w	$R \propto (w_{H_2SO_4})^{1.02} C_{GLC}$	Saeman, 1945
100–150	0.056 M	HCl 0.35 M	$R \propto C_{GLC}$	Heimlich and Martin, 1960
160–240	0.278–1.112 M	H_2SO_4 0.025–0.8 N	$R \propto C_{Acid} C_{GLC}$	Mckibbins *et al.*, 1962
180–244	0.4–6 %-w	H_2SO_4 0.5–4 %-w	$R \propto (w_{H_2SO_4})^{0.8955} C_{GLC}$	Smith *et al.*, 1982
100–144	4–12 %-w	H_2SO_4 4–20 %-w	$R \propto (C_{H^+})^{1.33} C_{GLC}$	Bienkowski *et al.*, 1987
170–230	0.006–0.33 M	pH 1–4	$R \propto C_{H^+} C_{GLC}$	Baugh and McCarty, 1988
190–210	0.125 M	pH 1.5–2.2	$R \propto C_{H^+} C_{GLC}$	Xiang *et al.*, 2004

concentration windows, whereas our study was performed in a large window for all variables.

The results of this kinetic study will be used as input to obtain a full kinetic model for the acid-catalysed hydrolysis of a lignocellulosic biomass to levulinic acid. In addition, it allows selection and the development of efficient continuous reactor technology, in which the yield of levulinic acid is optimized and the amount of undesired, humin-like, byproducts is reduced.

METHODS AND ANALYSIS

Experimental Procedure

All chemicals (analytical grade) were purchased from Merck (Darmstadt, Germany) and used without further purification. The reactions were carried out in glass ampoules with an internal diameter of 3 mm, a wall thickness of 1.5 mm, and a length of 15 cm. An ampoule was filled at room temperature with a solution of glucose and sulphuric acid in the predetermined amounts ($V_{liquid} = 0.5\ cm^3$). The ampoule was sealed with a torch. A series of ampoules was placed in a special rack and subsequently positioned in a constant temperature oven (± 0.1°C) which was pre-set at the desired reaction temperature. At different reaction times, an ampoule was taken from the oven and directly quenched into an ice-water bath (4°C) to stop the reaction. The ampoules were opened, the reaction mixture was taken out and subsequently diluted with water to 10 ml. Insoluble humins, formed during the decomposition reaction, were separated from the solution by filtration over a 0.2 μm cellulose acetate filter (Schleicher & Schuell MicroScience, Dassel, Germany). The particle-free solution was then analysed using High Performance Liquid Chromatography (HPLC).

METHOD OF ANALYSIS

The composition of the liquid phase was determined using a HPLC system consisting of a Hewlett Packard 1050 pump, a Bio-Rad Organic Acid column Aminex HPX-87H, and a Waters 410 differential refractometer. The mobile phase consisted of aqueous sulphuric acid (5 mM) which was set at a flow rate of 0.55 $cm^3\ min^{-1}$. The column was operated at 60°C. The analysis for a sample was complete in 40 min. A typical chromatogram is shown in Figure 3. The concentrations of each compound in the product mixture were determined using calibration curves obtained by analysing standard solutions of known concentrations.

Identification of side-products of glucose decomposition (i.e., reversion products) was performed by connecting the HPLC system to a API3000 triple quadrupole LC/MS/MS mass spectrometer (Perkin-Elmer Sciex Instruments, Boston, MA, USA). The mass spectrometer was supplied with an atmospheric pressure ionization source at a temperature of 400°C.

Heat Transfer Experiments

At the start-up of the reaction, the reaction takes place non-isothermally due to heating-up of the contents of the ampoule from room temperature to the oven temperature. To gain insight in the time required to heat up the reaction mixture and to compensate for this effect in the reaction modelling studies, the temperature inside the ampoules as a function of the time during the heat up process was determined experimentally. For this purpose, an ampoule equipped with a thermocouple was filled with a representative reaction mixture. The ampoule was then closed tightly using a special bolt and screw system to prevent evaporation of the liquid. The ampoule was subsequently placed in the oven at a specified temperature and the temperature of reaction mixture was followed in time. A typical profile is given in Figure 4. Before and after an experiment, the amount of liquid inside the ampoule was measured to ensure that evaporation of the liquid did not occur.

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

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

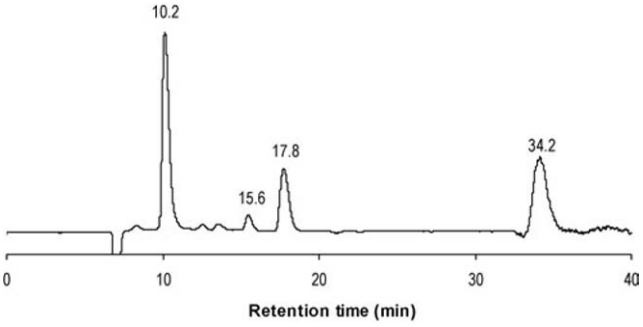


Figure 3. Typical chromatogram of a product mixture obtained from the acid-catalysed decomposition of glucose. The product mixture consists of glucose (RT = 10.2 min), formic acid (RT = 15.6 min), levulinic acid (RT = 17.8 min), and HMF (RT = 34.2 min).

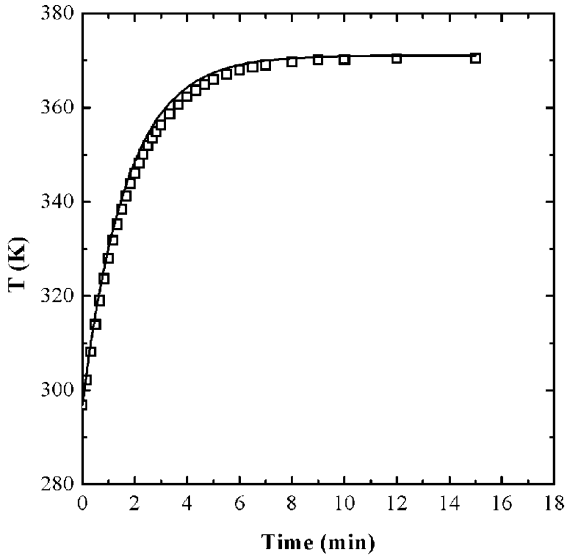


Figure 4. Heating profile of the reaction mixture at $T_{oven} = 100^{\circ}C$ [□: experimental data; solid curve: modelled profile according to equation (3)].

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

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

Solving the ordinary differential equation (2) with the initial value $t = 0$, $T = T_i$ leads to

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

The value of h was determined by fitting all experimental data at different oven temperatures (100–160°C) using a non-linear regression method and was found to be 0.596 min^{-1}. Figure 4 shows an experimental and modelled temperature profile performed at an oven temperature of 100°C. Equation (3) was incorporated in the kinetic model to describe the non-isothermal behaviour of the system at the start-up of the reaction.

Determination of the Kinetic Parameters

The concentrations of all compounds involved in the decomposition reaction of glucose were obtained from HPLC analysis. All concentrations were normalized with respect to the initial concentration of glucose as follows:

$$X_{GLC} = \frac{(C_{GLC,0} - C_{GLC})}{C_{GLC,0}} \tag{4}$$

$$Y_{HMF} = \frac{(C_{HMF} - C_{HMF,0})}{C_{GLC,0}} \tag{5}$$

$$Y_{LA} = \frac{(C_{LA} - C_{LA,0})}{C_{GLC,0}} \tag{6}$$

The kinetic parameters were determined using a maximum likelihood approach, which is based on minimization of errors between the experimental data and the kinetic model. Details about this procedure can be found in the literature (Bard, 1974; Knightes and Peters, 2000). Error minimization to determine the best estimate of the kinetic parameters was performed using the MATLAB toolbox fminsearch, which is based on the Nelder–Mead optimization method.

RESULTS AND DISCUSSION

Effects of Process Variables on the Decomposition Reaction of Glucose

A total of 22 experiments were performed in a temperature window of 140–200°C, $C_{H_2SO_4}$ ranging between 0.05 and 1 M, and $C_{GLC,0}$ between 0.1 and 1 M. A typical concentration profile is shown in Figure 5. HMF was observed as an intermediate product in all experiments. The C_{HMF} showed a maximum with respect to reaction time, although its maximum value is generally very low and less than 5% of the $C_{GLC,0}$. This observation indicates that the conversion of HMF to levulinic acid is much faster than the conversion of glucose to HMF.

The rate of glucose decomposition is a strong function of the temperature and the time for 99% conversion ranged between 12 h at 140°C ($C_{GLC,0} = 0.1$ M, $C_{H_2SO_4} = 0.1$ M) and only 6 min at 200°C ($C_{GLC,0} = 1$ M, $C_{H_2SO_4} = 0.5$ M) The reaction rate is also considerably higher at higher acid concentrations. At 200°C, only dilute solutions of sulphuric acid (0.05–0.1 M) could be used as catalyst. Due to the very fast reaction rates at these conditions, representative sampling and analysis proved not possible.

In all reactions, the formation of substantial amounts of insoluble dark-brown products, also known as humins, was observed. The composition and the formation pathways of these polymeric, sugar derived compound is poorly understood (Horvat *et al.*, 1985). The yield of

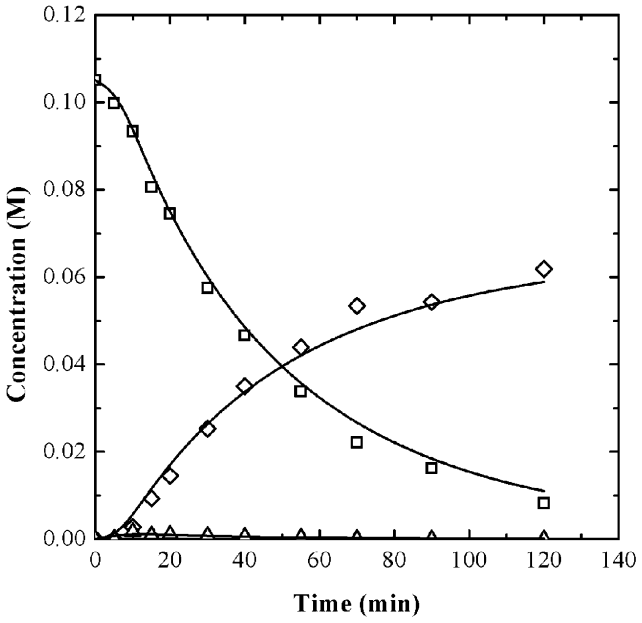
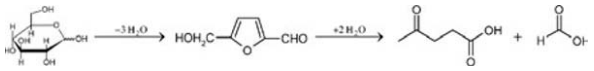


Figure 5. Typical concentration profile ($C_{GLC,0} = 0.1$ M, $C_{H_2SO_4} = 1$ M, $T = 140^{\circ}C$, □: C_{GLC}, △: C_{HMF}, ◇: C_{LA}).

levulinic acid is a function of the reaction time, temperature, $C_{GLC,0}$ and $C_{H_2SO_4}$. The highest yield was about 60% (mol mol^{-1}) at $C_{GLC,0} = 0.1$ M, $C_{H_2SO_4} = 1$ M, and $T = 140$°C. The yield of levulinic acid as a function of the reaction time and $C_{GLC,0}$ (0.1–1 M) is given in Figure 6. It is evident that more dilute solutions of glucose results in higher yields of levulinic acid. The effect of temperature on the yield is given in Figure 7. The maximum yield decreases when operating at the high end of the temperature window. The concentration of sulphuric acid only has a small effect on the yield of levulinic acid (Figure 8).

Development of a Kinetic Model for Glucose Decomposition to Levulinic Acid

The acid catalysed decomposition of glucose to levulinic acid is schematically given in equation (7). In line with literature data and our experimental findings, HMF is considered as an intermediate product.



(7)

This simplified scheme does not take into account the formation of humins and possible other by-products. Substantial amounts of insoluble humins are formed in the course of the reaction. There are strong indications that the humins may be formed from both glucose and HMF (Mckibbins *et al.*, 1962; Baugh and McCarty, 1988). Levulinic acid is not a source for humins. This was checked independently by reacting levulinic acid with 1 M sulphuric acid at 150°C for 6 h. It was found out that the concentration of levulinic acid was constant during the reaction. The rate of formation of humins from glucose and HMF was included in the kinetic model.

Fructose is a known intermediate in the acid catalysed glucose decomposition (Harris and Feather, 1973, 1974, 1975). It is likely formed from glucose according to a reaction mechanism given in Figure 9 (van Dam *et al.*, 1986; Moreau *et al.*, 1996). Here a 1,2-enediol is proposed as the common intermediate. However, fructose could not be detected in our reaction mixtures. This is not surprising as previous studies have already shown that the dehydration of fructose to HMF is much faster than that of glucose (Kuster and van der Baan, 1977; Kuster, 1990). Therefore, any fructose formed from glucose is expected to be converted to HMF rapidly.

Other possible byproducts are so-called reversion products like levoglucosan (1,6-anhydro-β-D-glucopyranose), 1,6-anhydro-β-D-glucofuranose, isomaltose and gentiobiose (Figure 10). In acidic solutions, the acyclic form of D-glucose exists in equilibrium with its anomeric forms (α-D-glucopyranose and β-D-glucopyranose). The anomeric forms may be involved in a number of reactions leading

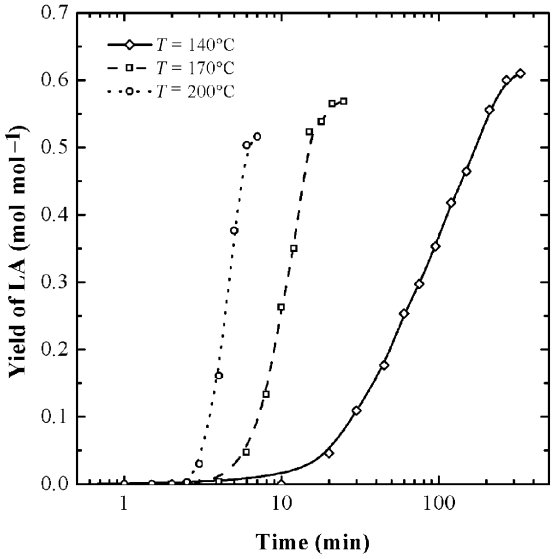


Figure 7. Yield of levulinic acid versus time at different temperatures ($C_{GLC,0} = 0.1$ M, $C_{H_2SO_4} = 0.5$ M).

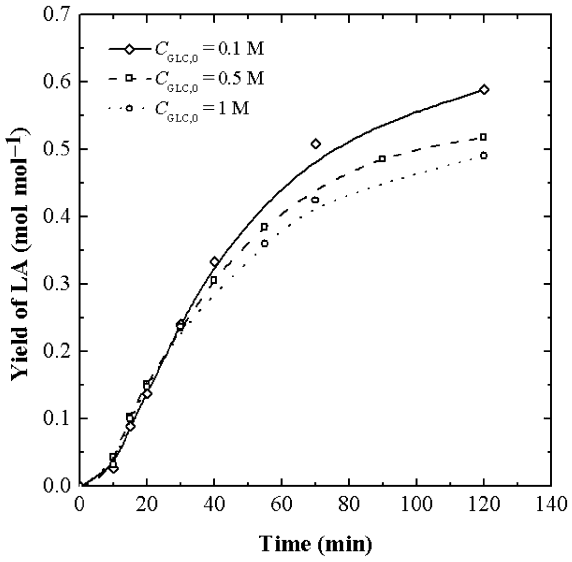


Figure 6. Yield of levulinic acid versus time for different $C_{GLC,0}$ ($T = 140$°C, $C_{H_2SO_4} = 1$ M).

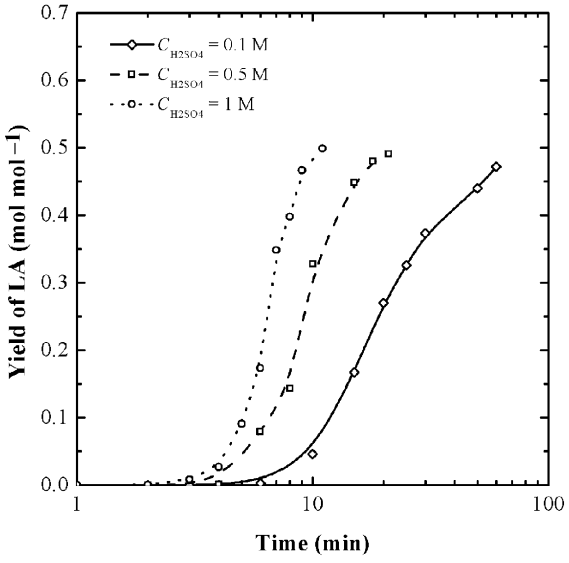


Figure 8. Yield of levulinic acid versus time at different $C_{H_2SO_4}$ ($C_{GLC,0} = 0.5$ M, $T = 170$°C).

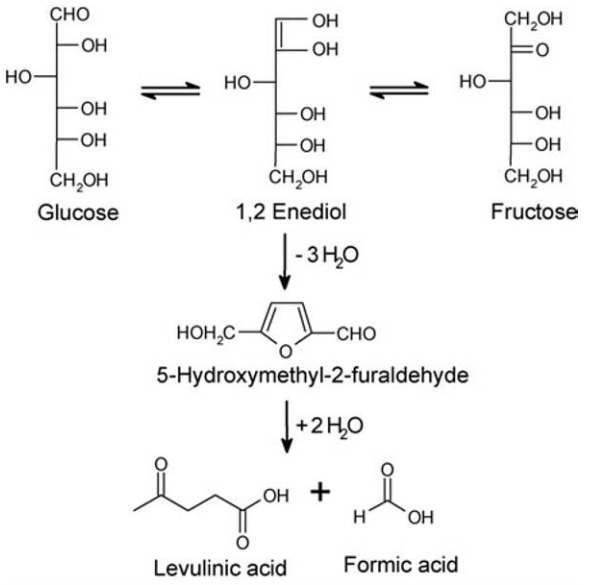


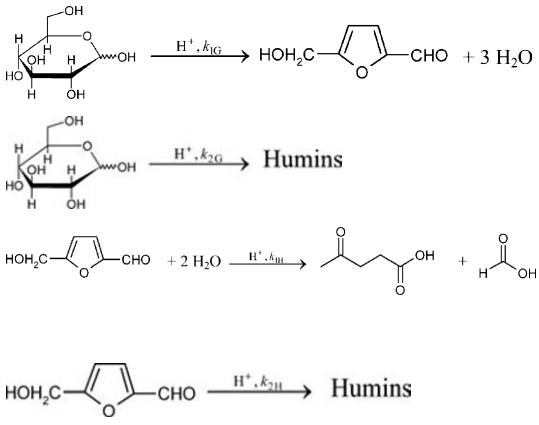
Figure 9. Reaction mechanism for the acid catalysed decomposition of glucose to levulinic acid.

to reversion products (van Dam *et al.*, 1986; Helm *et al.*, 1989). Intra-molecular condensation reactions produces anhydro sugars, mainly levoglucosan and 1,6-anhydro-β-D-glucofuranose. Inter-molecular condensation reactions between two glucose units will give disaccharides such as isomaltose and gentiobiose. Several investigators (Thompson *et al.*, 1954; Peat *et al.*, 1958) have also found and isolated other type of disaccharides i.e., $(1 \rightarrow 2)$-linked and $(1 \rightarrow 3)$-linked dimers. Most studies (Peat *et al.*, 1958; Helm *et al.*, 1989) revealed that the yields of anhdyro sugars were higher than the yields of disaccharides, although other investigator (Thompson *et al.*, 1954) found opposite results.

Some of the reversion products were detected in our experiments (Figure 11). Gentiobiose and levoglucosan were identified in the product mixture from the retention times of their pure compound, i.e., 8.4 min (gentiobiose) and 13.6 min (levoglucosan). Isomaltose (7.7 min) and 1,6-anhydro-β-D-glucofuranose (12.6 min) were identified using LC-MS.

The reversion products were observed at the initial stage of the reactions. At full glucose conversion, reversion products were absent. The maximum concentrations of the reversion products in the course of the reaction were very low which made it very difficult to determine the concentrations of every component accurately. Therefore, we have not incorporated the reversion products in the kinetic model.

On the basis of these considerations, the following kinetic model was applied to model the acid-catalysed decomposition of glucose.



The reaction rates were defined using a power-law approach:

$$R_1 = k_{1G}(C_{GLC})^{aG}(C_{H^+})^{\alpha G} \quad (12)$$

$$R_2 = k_{2G}(C_{GLC})^{bG}(C_{H^+})^{\beta G} \quad (13)$$

$$R_3 = k_{1H}(C_{HMF})^{aH}(C_{H^+})^{\alpha H} \quad (14)$$

$$R_4 = k_{2H}(C_{HMF})^{bH}(C_{H^+})^{\beta H} \quad (15)$$

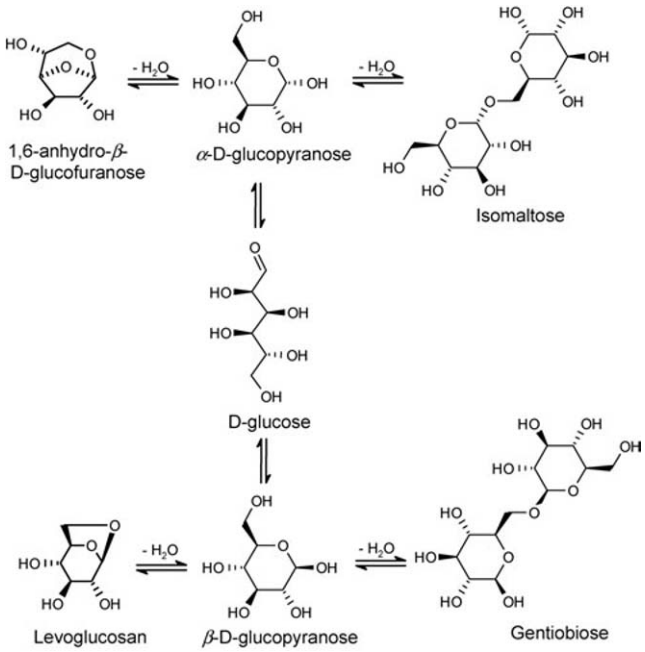


Figure 10. Reversion reactions of glucose in acid solutions.

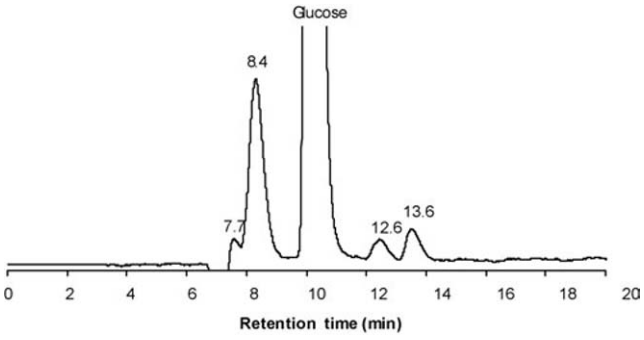


Figure 11. Identification of reversion products ($C_{GLC,0} = 1$ M, $C_{H_2SO_4} = 0.1$ M, $T = 170$°C, $t = 10$ min).

The kinetic constants and the reaction orders for the decomposition to HMF to levulinic acid and formic acid [equations (14) and (15)] have been determined earlier in our group (Girisuta *et al.*, 2005). The results are given in Table 2. These values were used as input for the kinetic model for glucose decomposition.

The temperature dependence of the kinetic constants was defined in term of modified Arrhenius equations:

$$k_{1G} = k_{1RG} \exp^{[-(E_{1G}/R)(1/T-1/T_R)]} \quad (16)$$

$$k_{2G} = k_{2RG} \exp^{[-(E_{2G}/R)(1/T-1/T_R)]} \quad (17)$$

$$k_{1H} = k_{1RH} \exp^{[-(E_{1H}/R)(1/T-1/T_R)]} \quad (18)$$

$$k_{2H} = k_{2RH} \exp^{[-(E_{2H}/R)(1/T-1/T_R)]} \quad (19)$$

where T is a function of time [equation (3)] and T_R is the reference temperature (140°C).

The catalytic effect of sulphuric acid is included in reaction rates in term of C_{H+}, which can be calculated as follows:

$$C_{H^+} = C_{H_2SO_4} + \frac{1}{2}\left(-K_{a,HSO_4^-} + \sqrt{K^2_{a,HSO_4^-} + 4C_{H_2SO_4}K_{a,HSO_4^-}}\right) \quad (20)$$

where K_{a,HSO_4^-} represents the dissociation constant of HSO_4^- which ranges between $10^{-4.5}$–$10^{-3.6}$ in the temperature window 140–200°C (Dickson *et al.*, 1990).

In a batch system, the concentrations of the compound involved in decomposition reaction can be represented as follows:

$$\frac{dC_{GLC}}{dt} = -(R_1 + R_2) \quad (21)$$

$$\frac{dC_{HMF}}{dt} = R_1 - (R_3 + R_4) \quad (22)$$

$$\frac{dC_{LA}}{dt} = R_3 \quad (23)$$

Modelling Results

The best estimates of the kinetic parameters, as determined by minimization of the errors between all experimental data and the kinetic model, are shown in Table 2. The experimental data consisted of 660 datapoints (22 experiments, 10 samples per experiment, concentrations of levulinic acid, HMF and glucose for each sample). Comparisons of the experimental data and the output of the kinetic model demonstrate a good fit for a broad range of reaction condition (Figure 12). A parity chart (Figure 13) shows the goodness of fit between the experimental and model data.

APPLICATION OF THE KINETIC MODEL

Batch Simulation and Optimization

With the model available, it is possible to gain insight in the conversion, selectivity, and yield of levulinic acid as a function of the process conditions. A typical batch time for 90% glucose conversion as a function of the temperature is given in Figure 14.

The kinetic model also allows determination of the optimum reaction conditions to achieve the highest selectivity of levulinic acid. For this purpose equation (4) is differentiated to give

$$dX_{GLC} = -\frac{dC_{GLC}}{C_{GLC,0}} \quad (24)$$

Combination of equations (21)–(23) and equation (24) leads to the following expressions:

$$\frac{dC_{GLC}}{dX_{GLC}} = -C_{GLC,0} \quad (25)$$

$$\frac{dC_{HMF}}{dX_{GLC}} = \frac{R_1 - R_3 - R_4}{R_1 + R_2} C_{GLC,0} \quad (26)$$

$$\frac{dC_{LA}}{dX_{GLC}} = \frac{R_3}{R_1 + R_2} C_{GLC,0} \quad (27)$$

Equations (25)–(27) were solved using the numerical integration toolbox ode45 in the MATLAB software package from 0% to 90% glucose conversion. The selectivity of levulinic acid (σ_{LA}) is defined as the ratio of the amount of desired product (levulinic acid) formed and the key reactant (glucose) converted.

$$\sigma_{LA} = \frac{C_{LA} - C_{LA,0}}{C_{GLC,0} - C_{GLC}} = \frac{Y_{LA}}{X_{GLC}} \quad (28)$$

Figure 15 shows the predicted σ_{LA} as a function of the T and $C_{GLC,0}$ at 90% glucose conversion and a $C_{H_2SO_4}$ of

Table 2. Estimated kinetic parameters for the acid-catalysed decomposition of glucose.

Parameter	Estimate	Parameter[a]	Estimate
aG	1.09 ± 0.01	aH	0.88 ± 0.01
bG	1.30 ± 0.02	bH	1.23 ± 0.03
αG	1.13 ± 0.01	αH	1.38 ± 0.02
βG	1.13 ± 0.02	βH	1.07 ± 0.04
E_{1G} (kJ mol^{-1})	152.2 ± 0.7	E_{1H} (kJ mol^{-1})	110.5 ± 0.7
E_{2G} (kJ mol^{-1})	164.7 ± 0.6	E_{2H} (kJ mol^{-1})	111.2 ± 2.0
k_{1RG} (M$^{1-aG-\alpha G}$ min^{-1})[b]	0.013 ± 0.001	k_{1RH} (M$^{1-aH-\alpha H}$ min^{-1})[b]	0.340 ± 0.010
k_{2RG} (M$^{1-bG-\beta G}$ min^{-1})[b]	0.013 ± 0.001	k_{2RH} (M$^{1-bH-\beta H}$ min^{-1})[b]	0.117 ± 0.008

[a]The kinetic parameters of HMF hydration to levulinic acid have been reported in previous work (Girisuta *et al.*, 2005).
[b]The values were determined at a reference temperature (T_R) of 140°C.

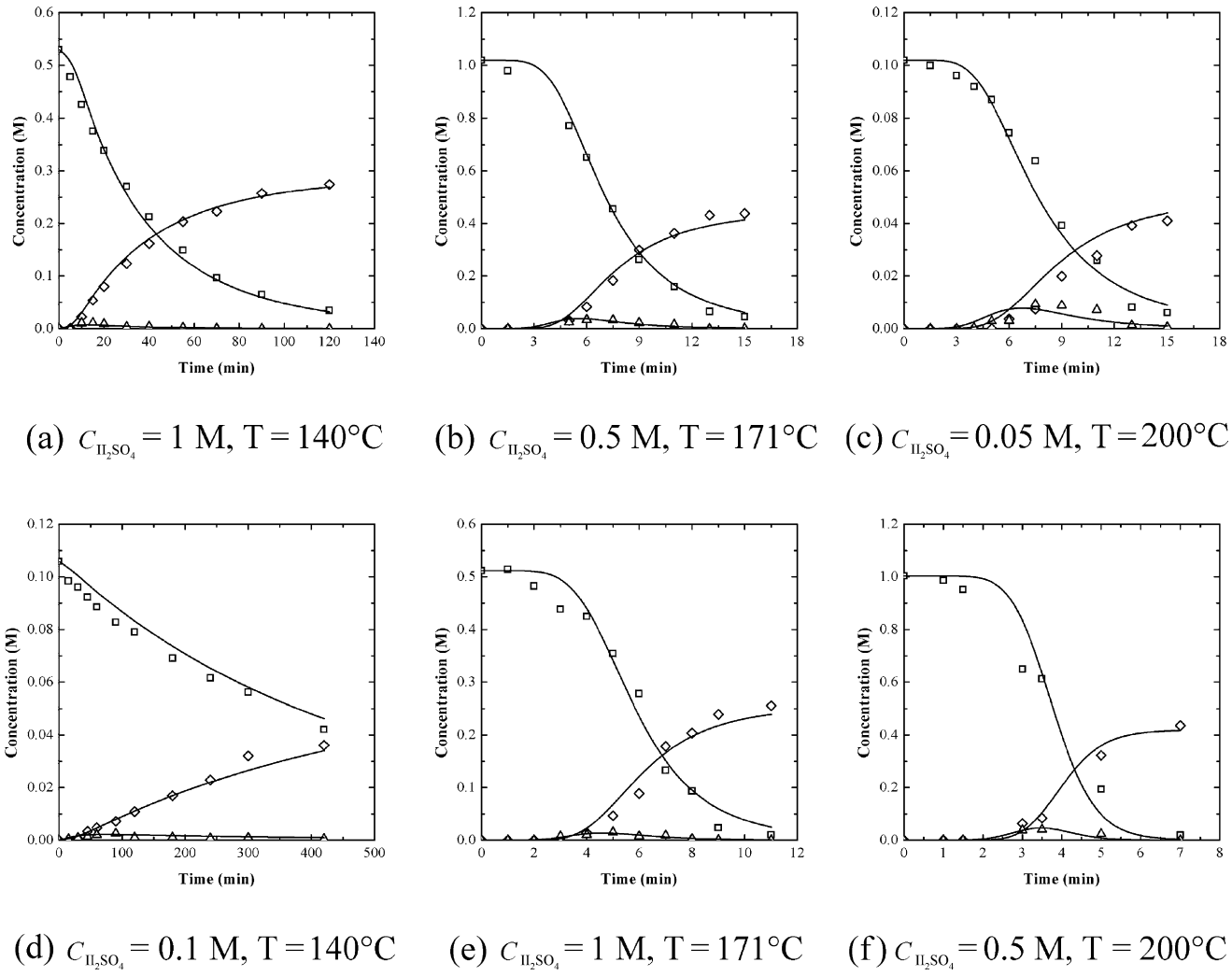


Figure 12. Comparison of experimental data (□: C_{GLC}, △: C_{HMF} and ◇: C_{LA}) and kinetic model (solid lines).

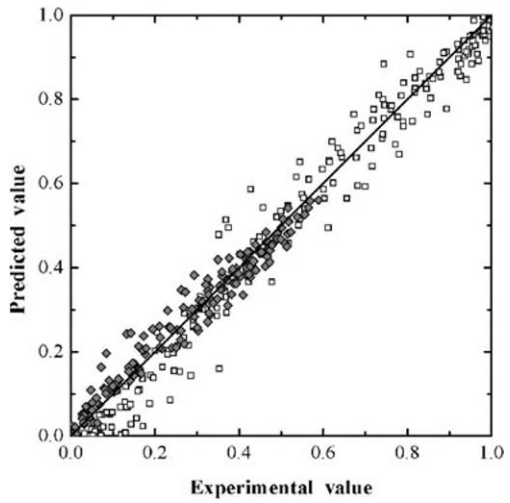


Figure 13. Parity plot of all experimental data and model prediction (□: X_{GLC}, ◆: Y_{LA}).

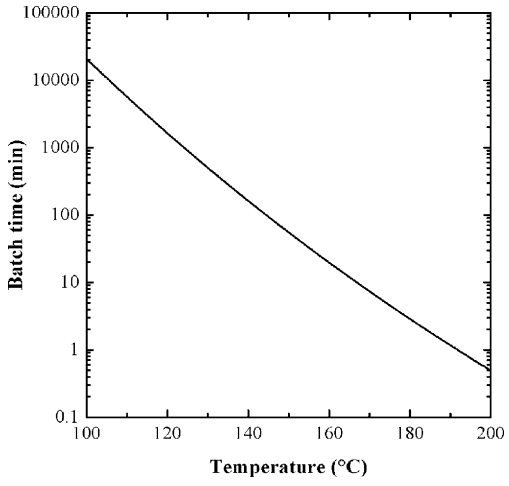


Figure 14. Reaction time to achieve 90% glucose conversion in an isothermal batch reactor as a function of the temperature ($C_{GLC,0}$ = 0.1 M, $C_{H_2SO_4}$ = 1 M).

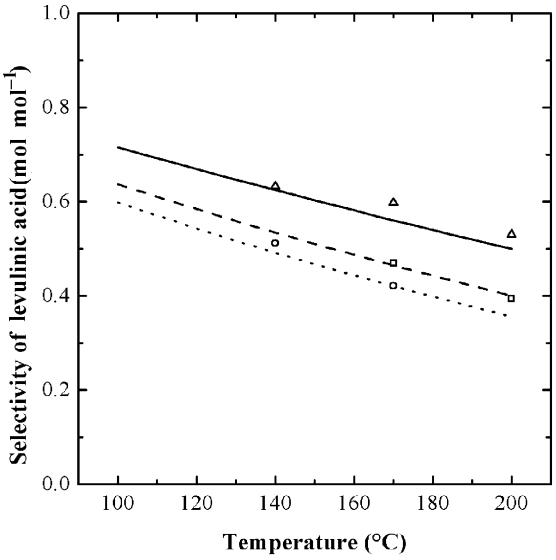


Figure 15. Temperature effect on σ_{LA} at $X_{GlC} = 90\%$ and $C_{H_2SO_4} = 0.5$ M. (—): $C_{GLC,0} = 0.1$ M; (----): $C_{GLC,0} = 0.5$ M; (····): $C_{GLC,0} = 1$ M. △, □ and ○ represent experimental σ_{LA} at $C_{GLC,0} = 0.1$, 0.5 and 1 M, respectively.

0.5 M. The experimental data points are also given, demonstrating the good fit between experiments and model.

σ_{LA} is strongly temperature depending, with high temperatures leading to lower selectivity. This is in line with the observed activation energies for the main and side reactions. The activation energy for humin formation from glucose (Table 2) is significantly higher (164.7 kJ mol^{-1}) than all other activation energies, implying that the kinetics of this reaction is the most sensitive to temperature. To reduce humin formation, reactions at low temperature are favoured. It is also evident that higher $C_{GLC,0}$ will lead to lower σ_{LA}. This may be rationalized when looking at the orders in substrate for the various reactions involved. The order of glucose for the desired reaction to HMF (1.09) is lower than that of the side reaction to humins (1.30), hence a higher $C_{GLC,0}$ will lead to reduced σ_{LA}.

Optimization of Continuous Reactor Systems

The yield of levulinic acid in continuous reactors will be a function of typical process parameters (T, $C_{GLC,0}$, $C_{H_2SO_4}$) and the extent of mixing in the reactor. In Figure 16, the yield of levulinic acid as a function of the glucose conversion at different temperatures (140 and 200°C) is provided for the two extremes with respect to mixing (PFR and CISTR).

Here the yield of levulinic acid is defined as the ratio between the amounts of levulinic acid formed during the reaction and of glucose fed into the reactor.

$$Y_{LA} = \frac{C_{LA}^{out} - C_{LA}^{in}}{C_{GLC}^{in}} \tag{29}$$

The graphs were constructed from the mass balance design equations for the two model reactors in combination with the rate equations for the reactions. The reactor design equations of the PFR are similar to the design equations for the batch reactor [equations (24)–(27)]. The general reactor design equation for a CISTR reads:

$$\tau_{CISTR} = \frac{C_i^{out} - C_i^{in}}{R_i} \tag{30}$$

The relationship between glucose conversion (X_{GLC}) and τ_{CISTR} is given by the following equation:

$$\tau_{CISTR} = \frac{X_{GLC} C_{GLC}^{in}}{R_1 + R_2} \tag{31}$$

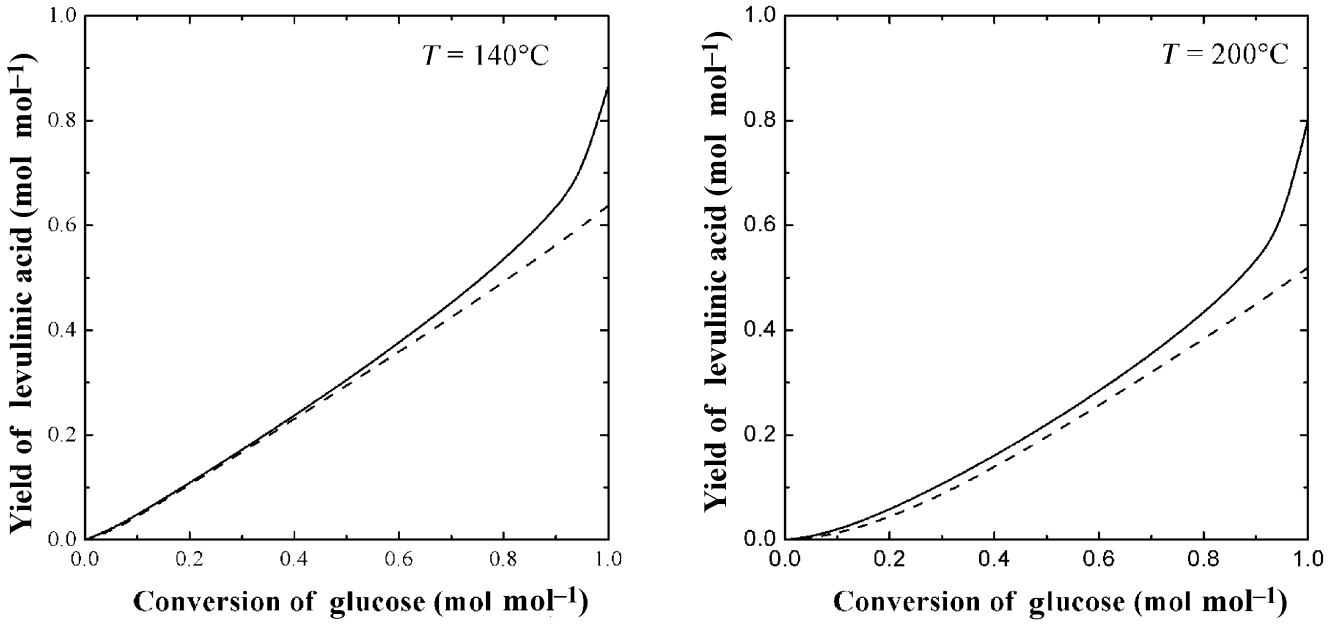


Figure 16. Comparison of levulinic acid yields in two ideal continuous reactors [(—): CISTR; (----): PFR] at different temperatures $C_{GLC,0} = 0.1$ M, $C_{H^+} = 0.5$ M).

Substitution of equation (31) into equation (30) and executing some rearrangement gives:

$$C_{HMF}^{out} = \left(\frac{R_1 - R_3 - R_4}{R_1 + R_2}\right) C_{GLC}^{in} X_{GLC} \quad (32)$$

$$C_{LA}^{out} = \left(\frac{R_3}{R_1 + R_2}\right) C_{GLC}^{in} X_{GLC} \quad (33)$$

Based on the results shown in Figure 16 it is clear that the levulinic acid yields increases with the glucose conversion and that the yields in a CISTR are higher than in a PFR, particularly at high conversion levels. The yields at low temperature are higher than the yields at high temperature for both reactor configurations.

To select the optimum operating conditions for the reactor, it is also necessary to consider the full process configuration. If a high glucose conversion is desired, e.g., when the separation of the levulinic acid from the glucose/humin/sulphuric acid mixture is difficult, it might be advantageous to apply a reactor with a high extent of backmixing (Figure 16). A number of options are available like a stirred tank reactor equipped with an impeller or a recycle reactor with a high recycle ratio. An important feature will be the scaling properties of the insoluble, humin byproducts. However, information on this topic is lacking and further research will be required. In case separation of the product mixture is simple and cheap, it might be advantageous to operate at relatively low conversions of glucose to reduce reactor volume and associated costs. At low conversions, the yield is not a strong function of the extent of backmixing (Figure 16) and other reactor configurations may be applied as well.

CONCLUDING REMARKS

A kinetic model for the acid catalysed decomposition of glucose in a broad operating window ($C_{H_2SO_4}$: 0.05–1 M, $C_{GLC,0}$: 0.1–1 M, T: 140–200°C) has been developed. Glucose decomposes in a consecutive reaction mode to give levulinic acid as the final product through HMF as the intermediate. Glucose as well as HMF decomposes in parallel reaction modes to give insoluble humins as the byproduct. The model implies that the highest yield of levulinic acid in continuous reactor configurations may be achieved by applying dilute solution of glucose, a high concentration of sulphuric acid as the catalyst and using a reactor configuration with a high extent of back-mixing.

NOMENCLATURE

aG	reaction order of C_G in the decomposition of glucose into HMF
αG	reaction order of C_{H^+} in the decomposition of glucose into HMF
aH	reaction order of C_{HMF} in the decomposition of HMF into main products
αH	reaction order of C_{H^+} in the decomposition of HMF into main products
A_t	heat transfer area, m^2
bG	reaction order of C_G in the decomposition of glucose into humins
βG	reaction order of C_{H^+} in the decomposition of glucose into humins
bH	reaction order of C_{HMF} in the decomposition of HMF into humins
βH	reaction order of C_{H^+} in the decomposition of HMF into humins
C_{GLC}	glucose concentration, M
$C_{GLC,0}$	initial concentration of glucose, M
C_{HMF}	HMF concentration, M
$C_{HMF,0}$	initial concentration of HMF, M
$C_{H_2SO_4}$	concentration of H_2SO_4, M
C_{H^+}	concentration of hydrogen ion, M
C_i^{in}	concentration of the ith compound at the inflow, M
C_i^{out}	concentration of the ith compound at the outflow, M
C_{LA}	levulinic acid concentration, M
$C_{LA,0}$	initial concentration of levulinic acid, M
C_p	heat capacity of reaction mixture, $Jg^{-1}K^{-1}$
E_{1G}	activation energy of k_{1G}, kJ mol^{-1}
E_{1H}	activation energy of k_{1H} kJ mol^{-1}
E_{2G}	activation energy of k_{2G} kJ mol^{-1}
E_{2H}	activation energy of k_{2H} kJ mol^{-1}
h	heat transfer coefficient from the oven to the reaction mixture, min^{-1}
k_{1G}	reaction rate constant of glucose decomposition into HMF, $M^{1-aG-\alpha G}$ min^{-1}
k_{1H}	reaction rate constant of HMF decomposition into main products, $M^{1-aH-\alpha H}$ min^{-1}
k_{1RG}	reaction rate constant $k_{1,G}$ at reference temperature, $M^{1-aG-\alpha G}$ min^{-1}
k_{1RH}	reaction rate constant $k_{1,H}$ at reference temperature, $M^{1-aH-\alpha H}$ min^{-1}
k_{2G}	reaction rate constant of glucose decomposition into humins, $M^{1-bG-\beta G}$ min^{-1}
k_{2H}	reaction rate constant of HMF decomposition into humins, $M^{1-bH-\beta H}$ min^{-1}
k_{2RG}	reaction rate constant k_{2G} at reference temperature, $M^{1-bG-\beta G}$ min^{-1}
k_{2RH}	reaction rate constant k_{2H} at reference temperature, $M^{1-bH-\beta H}$ min^{-1}
K_{a,HSO_4^-}	dissociation constant of HSO_4^-
M	mass of the reaction mixture, g
R	universal gas constant, 8.3144 J $mol^{-1}K^{-1}$
R_1	reaction rate of glucose decomposition to HMF, M min^{-1}
R_2	reaction rate of glucose decomposition to humins, M min^{-1}
R_3	reaction rate of HMF decomposition to levulinic acid, M min^{-1}
R_4	reaction rate of HMF decomposition to humins, M min^{-1}
t	time, min
T	temperature, K
T_i	temperature of reaction mixture at $t = 0$, K
T_{oven}	temperature of oven, K
T_R	reference temperature, K
U	overall heat transfer coefficient, W m^{-2} K^{-1}
$w_{H_2SO_4^-}$	weight percentage of H_2SO_4
X_{GLC}	conversion of glucose, mol mol^{-1}
Y_{HMF}	yield of HMF, mol mol^{-1}
Y_{LA}	yield of levulinic acid, mol mol^{-1}

Greek symbols

σ_{LA}	selectivity of levulinic acid, mol mol^{-1}
τ_{CISTR}	residence time of CISTR, min

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