Chapter 4
A Kinetic Study on the Conversion of Glucose to Levulinic Acid*

Abstract
Levulinic acid has been identified as a promising 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 carried out in a broad temperature window (140–200 °C), using sulphuric acid as the catalyst (0.05–1 M) and an 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 by-products 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.

4.1 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-oxopentanoic 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 versatile building block for the synthesis of various organic (bulk) chemicals as shown in Figure 4.1 [1-5]. For instance, 2-methyltetrahydrofuran and various levulinate esters may be used as gasoline and biodiesel additives, respectively. δ-Aminolevulinic acid is a known herbicide, and the bisphenol derivative may be an interesting substitute for bisphenol A [6,7].

![Figure 4.1 Potentially interesting derivatives of levulinic acid.](image)

On a molecular level, the conversion of lignocellulosic biomass to levulinic acid is known to follow a complicated reaction scheme involving several intermediates and by-products (Figure 4.2) [8,9]. 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 [9]. Lignin, the third main constituent of lignocellulosic biomass,
is a resin-like polymer matrix with various substituted phenolics present. During the acid hydrolysis, various acid soluble lignin-derived components may be formed, increasing the product complexity. The simplified reaction scheme given in Figure 4.2 does not explicitly show the reactions leading to the undesired insoluble-polymeric materials known as humins.

**Figure 4.2** Possible pathways and products of the acid-catalysed hydrolysis of a typical lignocellulosic material.

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 [10]. 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.

The acid-catalysed decomposition of glucose has been studied by a number of authors [11-20]. 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 4.1). The development of a kinetic scheme for the conversion of glucose to levulinic acid, including the kinetics of by-product 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 concentration windows, whereas our study was performed in a large window for all variables.

Table 4.1 Overview of kinetic studies of glucose decomposition.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$C_{GLC,0}$</th>
<th>$C_{acid}$</th>
<th>Order in substrate and acid</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>170–190</td>
<td>5 wt %</td>
<td>H$_2$SO$_4$ (0.4–1.6 wt %)</td>
<td>$R \propto \left[w_{H_2SO_4}\right]^{0.02}C_{GLC}$</td>
<td>[11]</td>
</tr>
<tr>
<td>100–150</td>
<td>0.056 M</td>
<td>HCl (0.35 M)</td>
<td>$R \propto C_{GLC}$</td>
<td>[12]</td>
</tr>
<tr>
<td>160–240</td>
<td>0.278–1.112 M</td>
<td>H$_2$SO$_4$ (0.025–0.8 N)</td>
<td>$R \propto C_{acid}C_{GLC}$</td>
<td>[13]</td>
</tr>
<tr>
<td>180–244</td>
<td>0.4–6 wt %</td>
<td>H$_2$SO$_4$ (0.5–4 wt %)</td>
<td>$R \propto \left[w_{H_2SO_4}\right]^{1.8955}C_{GLC}$</td>
<td>[15]</td>
</tr>
<tr>
<td>100–144</td>
<td>4–12 wt %</td>
<td>H$_2$SO$_4$ (4–20 wt %)</td>
<td>$R \propto \left[C_{H^+}\right]^{3.33}C_{GLC}$</td>
<td>[16]</td>
</tr>
<tr>
<td>170–230</td>
<td>0.006–0.33 M</td>
<td>pH 1–4</td>
<td>$R \propto C_{H^+}C_{GLC}$</td>
<td>[17]</td>
</tr>
<tr>
<td>190–210</td>
<td>0.125 M</td>
<td>pH 1.5–2.2</td>
<td>$R \propto C_{H^+}C_{GLC}$</td>
<td>[20]</td>
</tr>
</tbody>
</table>

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

4.2 Experimental

4.2.1 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 ($V_{liquid}= 0.5 \text{ cm}^3$). 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).
4.2.2 Analytical methods

The composition of the liquid phase was determined using an HPLC system consisting of a Hewlett Packard 1050 pump, a Bio-Rad Organic Acid column Aminex HPX-87H and a Waters 410 differential refractive index detector. 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 minutes. A typical chromatogram is shown in Figure 4.3. The concentrations of each compound in the product mixture were determined using calibration curves obtained by analysing standard solutions of known concentrations.

![Typical chromatogram of a product mixture obtained from the acid-catalysed decomposition of glucose.](image)

**Figure 4.3** Typical chromatogram of a product mixture obtained from the acid-catalysed decomposition of glucose.

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

4.2.3 Heat transfer experiments

At the start-up of the reaction, the reaction takes place nonisothermally due to heating-up of the contents of the ampoule from the room temperature to the oven temperature. To gain insight into the time required for heating-up the reaction mixture and to compensate for this effect in the kinetic modelling studies, the temperature inside the ampoules as a function of the time during the heating-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. 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:

$$\frac{d(MC_pT)}{dt} = UA_i(T_{oven} - T) \quad (4.1)$$

When assuming that the heat capacity of the reaction mixture is constant and not a function of temperature, rearrangement of equation (4.1) will give:

$$\frac{dT}{dt} = \frac{UA_i}{MC_p} (T_{oven} - T) = h(T_{oven} - T) \quad (4.2)$$

Solving the ordinary differential equation (4.2) with the initial value $T = T_i$ at $t = 0$ leads to:

$$T = T_{oven} - (T_{oven} - T_i) \exp^{-ht} \quad (4.3)$$

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 4.4 shows an experimental and modelled temperature profile performed at an oven temperature of 100 °C. Equation (4.3) was incorporated in the kinetic model to describe the non-isothermal behaviour of the system at the start-up of the reaction.

![Figure 4.4](image)

**Figure 4.4** Heating profile of the reaction mixture at $T_{oven} = 100$ °C.
4.2.4 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:

\[ X_{\text{GLC}} = \frac{(C_{\text{GLC,0}} - C_{\text{GLC}})}{C_{\text{GLC,0}}} \]  

(4.4)

\[ Y_{\text{HMF}} = \frac{(C_{\text{HMF}} - C_{\text{HMF,0}})}{C_{\text{GLC,0}}} \]  

(4.5)

\[ Y_{\text{LA}} = \frac{(C_{\text{LA}} - C_{\text{LA,0}})}{C_{\text{GLC,0}}} \]  

(4.6)

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 [21,22]. 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 optimisation method.

4.3 Results and discussions

4.3.1 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, \( C_{\text{H2SO4}} \) ranging between 0.05 and 1 M and \( C_{\text{GLC,0}} \) between 0.1 and 1 M. A typical concentration profile is given in Figure 4.5. HMF was observed as an intermediate product in all experiments. The \( C_{\text{HMF}} \) showed a maximum with respect to reaction time, although its maximum value is generally very low and less than 5% of the \( C_{\text{GLC,0}} \). This observation indicates that the conversion of HMF to levulinic acid is much faster than the conversion of glucose to HMF.

![Figure 4.5 Typical concentration profile \( (C_{\text{GLC,0}} = 0.1 \text{ M}, C_{\text{H2SO4}} = 1 \text{ M}, T = 140 \text{ °C}) \).](image)
The rate of glucose decomposition is a strong function of the temperature, and the time to reach 99 mol % of glucose conversion ranged between 12 h at 140 °C ($C_{GLC,0} = 0.1 \text{ M}$, $C_{H_2SO_4} = 0.1 \text{ M}$) and 6 min at 200 °C ($C_{GLC,0} = 1 \text{ M}$, $C_{H_2SO_4} = 0.5 \text{ M}$). 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 black insoluble-products, also known as humins, was observed. The composition and the formation pathways of these polymeric sugar-derived compounds are poorly understood [23]. The yield of 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 % at $C_{GLC,0} = 0.1 \text{ M}$, $C_{H_2SO_4} = 1 \text{ M}$ and $T = 140 \text{ °C}$.

The yield of levulinic acid as a function of the reaction time and $C_{GLC,0} (0.1–1\text{M})$ is given in Figure 4.6. 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 4.7. 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 4.8).

![Figure 4.6 Yield of levulinic acid versus time for different $C_{GLC,0}$ ($T = 140 \text{ °C}$, $C_{H_2SO_4} = 1 \text{ M}$).](image)
4.3.2 Development of a kinetic model for glucose decomposition to levulinic acid

The acid-catalysed decomposition of glucose (1) to levulinic acid (LA, 3) and formic acid (FA, 4) is schematically given in Scheme 4.1. In line with literature data and our experimental findings, HMF (2) is considered as an intermediate product.
Scheme 4.1 Acid-catalysed decomposition of glucose to LA.

This simplified scheme does not take into account the formation of humins and other possible 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 [13,17]. LA is not a source for humins. This was checked independently by reacting LA with 1 M sulphuric acid at 150 °C for 6 hours. It was found out that the concentration of LA was constant during the reaction. The rate of formation of humins from glucose and HMF was included in the kinetic model.

Fructose (5) is a known intermediate in the acid-catalysed decomposition of glucose [24-26]. It is likely formed from glucose (1) according to a reaction mechanism given in Scheme 4.2 [27,28]. Here, 1,2-enediol (6) is proposed as the common intermediate. However, fructose could not be detected in our reaction mixtures. This is not surprising, as previous studies [29,30] have already shown that the dehydration of fructose to HMF is much faster than that of glucose. Therefore, any fructose formed from glucose is expected to be converted to HMF rapidly.

Scheme 4.2 Reaction mechanisms for the acid-catalysed decomposition of glucose to LA.
Other possible by-products are so-called reversion products, like levoglucosan or 1,6-anhydro-β-D-glucopyranose (9), 1,6-anhydro-β-D-glucofuranose (10), isomaltose (11) and gentiobiose (12), is shown in Scheme 4.3. In acidic solutions, the acyclic form of D-glucose (1) exists in equilibrium with its anomeric forms, i.e., α-D-glucopyranose (7) and β-D-glucopyranose (8). The anomeric forms may be involved in a number of reactions leading to reversion products [27,31]. Intra-molecular condensation reactions produce 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 [32,33] have also found and isolated other type of disaccharides, i.e., (1→2)-linked and (1→3)-linked dimers. Most studies [33,31] revealed that the yields of anhydro sugars were higher than the yields of disaccharides, although other investigator [32] found opposite results.

**Scheme 4.3** Reversion reactions of glucose in acid solutions.

Some of the reversion products were detected in our experiments (Figure 4.9). 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.

![Figure 4.9](attachment:image.png) Identification of reversion products ($C_{GLC,0} = 1 \text{ M}, C_{H_2SO_4} = 0.1 \text{ M}, T = 170 \degree C, t = 10 \text{ min}$).

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 (Scheme 4.4) was applied to model the acid-catalysed decomposition of glucose.

![Scheme 4.4](attachment:scheme.png) Reaction network for the acid-catalysed decomposition of HMF to LA.

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

$$R_{1G} = k_{1G} (C_{GLC})^{a_1}$$  \hspace{1cm} (4.7)

$$R_{2G} = k_{2G} (C_{GLC})^{b_1}$$  \hspace{1cm} (4.8)
A Kinetic Study on the Conversion of Glucose to Levulinic Acid

\[ R_{1H} = k_{1H}(C_{HMF})^{\alpha_H} \]  \hspace{1cm} (4.9)

\[ R_{2H} = k_{2H}(C_{HMF})^{\beta_H} \]  \hspace{1cm} (4.10)

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

\[ k_{1G} = (C_{1G})^{\gamma_c} k_{1RG} \exp \left( \frac{E_{1R}}{R} \left( \frac{T-T_R}{T_R} \right) \right) \]  \hspace{1cm} (4.11)

\[ k_{2G} = (C_{1G})^{\gamma_c} k_{2RG} \exp \left( \frac{E_{2R}}{R} \left( \frac{T-T_R}{T_R} \right) \right) \]  \hspace{1cm} (4.12)

\[ k_{1H} = (C_{1H})^{\gamma_H} k_{1RH} \exp \left( \frac{E_{1H}}{R} \left( \frac{T-T_R}{T_R} \right) \right) \]  \hspace{1cm} (4.13)

\[ k_{2H} = (C_{1H})^{\gamma_H} k_{2RH} \exp \left( \frac{E_{2H}}{R} \left( \frac{T-T_R}{T_R} \right) \right) \]  \hspace{1cm} (4.14)

where \( T \) is a function of time defined in equation (4.3), 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 follow:

\[ C_{H^+} = C_{H_3SO_4} + \frac{1}{2} \left( K_{a,HSO_4^-} + \sqrt{K_{a,HSO_4^-}^2 + 4C_{H_3SO_4} K_{a,HSO_4^-}} \right) \]  \hspace{1cm} (4.15)

The term \( K_{a,HSO_4^-} \) in equation (4.15) represents the dissociation constant of \( (HSO_4^-) \), which ranges between \( 10^{-4.5} \)–\( 10^{-3.6} \) in the temperature window of 140–200 °C [34].

The kinetic constants and the reaction orders for the decomposition to HMF to LA and FA have been determined earlier in our previous study [10]. The results are given in Table 4.2. These values were used as input for the kinetic model for glucose decomposition.

**Table 4.2** Kinetic parameter estimates for the HMF decomposition to LA.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{1RH} ) (M(^{-1})a(^{-1})H \ min(^{-1}) (a ))</td>
<td>0.340 ± 0.010</td>
</tr>
<tr>
<td>( E_{1H} ) (kJ mol(^{-1}))</td>
<td>110.5 ± 0.7</td>
</tr>
<tr>
<td>( k_{2RH} ) (M(^{-1})a(^{-1})H \ min(^{-1}) (a ))</td>
<td>0.117 ± 0.008</td>
</tr>
<tr>
<td>( E_{2H} ) (kJ mol(^{-1}))</td>
<td>111 ± 2.0</td>
</tr>
<tr>
<td>( a_{1H} ) (--)</td>
<td>0.88 ± 0.01</td>
</tr>
<tr>
<td>( b_{1H} ) (--)</td>
<td>1.23 ± 0.03</td>
</tr>
<tr>
<td>( a_{2H} ) (--)</td>
<td>1.38 ± 0.02</td>
</tr>
<tr>
<td>( \beta_{1H} ) (--)</td>
<td>1.07 ± 0.04</td>
</tr>
</tbody>
</table>

\(a \) \( T_R = 140 \) °C
In a batch system, the concentrations of the compound involved in decomposition reaction can be represented as follow:

\[
\frac{dC_{GLC}}{dt} = -(R_{1G} + R_{2G}) \tag{4.16}
\]

\[
\frac{dC_{HMF}}{dt} = R_{1H} - (R_{1H} + R_{2H}) \tag{4.17}
\]

\[
\frac{dC_{LA}}{dt} = R_{1H} \tag{4.18}
\]

### 4.3.3 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 4.3. The experimental data consisted of 660 data points (22 experiments, 10 samples per experiment, concentrations of LA, 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 4.10). A parity chart (Figure 4.11) shows the goodness-of-fit between the experimental and model data.

**Table 4.3** Kinetic parameter estimates for the glucose decomposition to LA.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{1G}) (M(^{-1})G min(^{-1})) (^a)</td>
<td>0.013 ± 0.001</td>
</tr>
<tr>
<td>(E_{1G}) (kJ mol(^{-1}))</td>
<td>152.2 ± 0.7</td>
</tr>
<tr>
<td>(k_{2G}) (M(^{-1})G min(^{-1})) (^a)</td>
<td>0.013 ± 0.001</td>
</tr>
<tr>
<td>(E_{2G}) (kJ mol(^{-1}))</td>
<td>164.7 ± 0.6</td>
</tr>
<tr>
<td>(\alpha_G) (–)</td>
<td>1.09 ± 0.01</td>
</tr>
<tr>
<td>(\beta_G) (–)</td>
<td>1.30 ± 0.02</td>
</tr>
<tr>
<td>(\alpha_C) (–)</td>
<td>1.13 ± 0.01</td>
</tr>
<tr>
<td>(\beta_C) (–)</td>
<td>1.12 ± 0.02</td>
</tr>
</tbody>
</table>

\(^a\) \(T_R = 140^\circ C\)
A Kinetic Study on the Conversion of Glucose to Levulinic Acid

Figure 4.10 Comparison of experimental data (□: C_{GLC}, ○: C_{HMF}, Δ: C_{LA}) and kinetic model (solid lines).

Figure 4.11 Parity plot of all experimental data and model prediction.
4.4 Application of the kinetic model

4.4.1 Batch simulation and optimisation

With the model available, it is possible to gain insight into the conversion, selectivity and yield of LA as a function of the process conditions. A typical batch time for 90 mol % glucose conversion as a function of the temperature is given in Figure 4.12.

![ Figure 4.12 Reaction time to achieve 90 mol % of glucose conversion in isothermal batch reactor as a function of temperatures (C_{GLC,0} = 0.1 M, C_{H2SO4} = 1 M). ]

The kinetic model also allows the determination of the optimum reaction conditions to achieve the highest selectivity of LA. For this purpose equation (4.4) is differentiated to give:

\[
\frac{dX_{GLC}}{dC_{GLC}} = -\frac{dC_{GLC}}{C_{GLC,0}} \tag{4.19}
\]

Combination of equations (4.16)–(4.19) leads to the following expressions:

\[
\frac{dC_{GLC}}{dX_{GLC}} = -C_{GLC,0} \tag{4.20}
\]

\[
\frac{dC_{HMF}}{dX_{GLC}} = \frac{R_{IG} - R_{IH} - R_{2H}}{R_{1G} + R_{2G}} C_{GLC,0} \tag{4.21}
\]

\[
\frac{dC_{LA}}{dX_{GLC}} = \frac{R_{IH}}{R_{1G} + R_{2G}} C_{GLC,0} \tag{4.22}
\]

Equations (4.20)–(4.22) were solved using the numerical integration toolbox ode45 in the MATLAB software package from 0 to 90 mol % glucose conversion. The selectivity of LA (\(\sigma_{LA}\)) is defined as the ratio of the amount of the desired product (LA) formed and the key reactant (glucose) converted.
\[ \sigma_{LA} = \frac{C_{LA} - C_{LA,0}}{C_{GLC,0} - C_{GLC}} = \frac{Y_{LA}}{X_{GLC}} \] (4.23)

Figure 4.13 shows the predicted \( \sigma_{LA} \) as a function of the \( T \) and \( C_{GLC,0} \) at 90 mol % glucose conversion and a \( C_{H2SO4} \) of 0.5 M. The experimental data points are also given, demonstrating the good fit between experiments and model.

Figure 4.13. Temperature effect on \( \sigma_{LA} \) at \( X_{GLC} = 90 \) mol % and \( C_{H2SO4} = 0.5 \) M. Symbols (□), (○) and (△) represent experimental values of \( \sigma_{LA} \) at \( C_{GLC,0} = 0.1, 0.5 \) and 1.0 M respectively.

The \( \sigma_{LA} \) 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 humins formation from glucose (Table 4.3) 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 humins formation, reactions at low temperature are favoured. It is also evident that higher \( C_{GLC,0} \) will lead to lower \( \sigma_{LA} \). This may be rationalised 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 \( \sigma_{LA} \).

### 4.4.2 Optimisation of continuous reactor systems

The yield of LA in continuous reactors will be a function of typical process parameters (\( T, C_{GLC,0} \) and \( C_{H2SO4} \)) and the extent of mixing in the reactor. In Figure 4.14, the yield of LA as a function of the glucose conversion at different temperatures (140 and 200 °C) is provided for the two extremes with respect to mixing, i.e., a plug-flow reactor (PFR) and a continuous ideal stirred tank reactor (CISTR).
Figure 4.14 Comparison of LA yields in two ideal continuous reactors at different temperatures ($C_{GLC,0} = 0.1$ M, $C_{H^+} = 0.5$ M).

Here the yield of LA, $\Psi_{LA}$, is defined as the ratio between the amounts of LA formed during the reaction and of glucose fed into the reactor.

$$\Psi_{LA} = \frac{C_{LA}^{out} - C_{LA}^{in}}{C_{GLC}^{in}}$$  \hspace{1cm} (4.24)

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 (4.19)–(4.22)). The general reactor design equation for a CISTR reads:

$$\tau_{CISTR} = \frac{C_{i}^{out} - C_{i}^{in}}{R_i}$$ \hspace{1cm} (4.25)

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

$$\tau_{CISTR} = \frac{X_{GLC}C_{GLC}^{in}}{R_{1G} + R_{2G}}$$ \hspace{1cm} (4.26)

Substitution of equation (4.26) into equation (4.25) and executing some rearrangement gives:

$$C_{HMF}^{out} = \left( \frac{R_{1G} - R_{1H} - R_{2H}}{R_{1G} + R_{2G}} \right) C_{GLC}^{in} X_{GLC}$$ \hspace{1cm} (4.27)

$$C_{LA}^{out} = \left( \frac{R_{1H}}{R_{1G} + R_{2G}} \right) C_{GLC}^{in} X_{GLC}$$ \hspace{1cm} (4.28)
Based on the results shown in Figure 4.14 it is clear that the LA 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 LA from the glucose/humins/sulphuric acid mixture is difficult, it might be advantageous to apply a reactor with a high extent of backmixing (Figure 4.14). 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, humins by-products. 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 back-mixing (Figure 4.14) and other reactor configurations may be applied as well.

4.5 Conclusions

A kinetic model for the acid-catalysed decomposition of glucose in a broad operating window \( \left( C_{\text{H}_2\text{SO}_4} = 0.05–1 \text{ M}, C_{\text{GLC,0}} = 0.1–1 \text{ M}, T = 140–200 \, ^\circ\text{C} \right) \) has been developed. Glucose decomposes in a consecutive reaction mode to give LA 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 by-product. The model implies that the highest yield of LA 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.

4.6 Nomenclature

\( a_G \) : Reaction order of \( C_{\text{GLC}} \) in the decomposition of glucose to HMF (−)
\( a_C \) : Reaction order of \( C_{\text{H}^+} \) in the decomposition of glucose to HMF (−)
\( a_H \) : Reaction order of \( C_{\text{HMF}} \) in the decomposition of HMF to LA and FA (−)
\( a_l \) : Reaction order of \( C_{\text{H}^+} \) in the decomposition of HMF to LA and FA (−)
\( A_t \) : Heat transfer area (m²)
\( b_G \) : Reaction order of \( C_{\text{GLC}} \) in the decomposition of glucose to humins (−)
\( b_C \) : Reaction order of \( C_{\text{H}^+} \) in the decomposition of glucose to humins (−)
\( b_H \) : Reaction order of \( C_{\text{HMF}} \) in the decomposition of HMF to humins (−)
\( b_l \) : Reaction order of \( C_{\text{H}^+} \) in the decomposition of HMF to humins (−)
\( C_{\text{GLC}} \) : Concentration of glucose (M)
\(C_{\text{GLC},0}\) : Initial concentration of glucose (M)

\(C_{\text{H}^+}\) : Concentration of H\(^+\) (M)

\(C_{\text{H}_{2}\text{SO}_4}\) : Concentration of sulphuric acid (M)

\(C_{\text{HMF}}\) : Concentration of HMF (M)

\(C_{\text{HMF},0}\) : Initial concentration of HMF (M)

\(C_{i}^{\text{in}}\) : Concentration of the \(i\)th compound at the inflow (M)

\(C_{i}^{\text{out}}\) : Concentration of the \(i\)th compound at the outflow (M)

\(C_{\text{LA}}\) : Concentration of LA (M)

\(C_{\text{LA},0}\) : Initial concentration of LA (M)

\(C_{\text{P}}\) : Heat capacity of reaction mixture (J g\(^{-1}\) 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 to HMF (M\(^{1-a_{G}}\) min\(^{-1}\))

\(k_{1RC}\) : Reaction rate constant \(k_{1C}\) at reference temperature (M\(^{1-a_{C}}\) min\(^{-1}\))

\(k_{1H}\) : Reaction rate constant of HMF for the main reaction (M\(^{1-a_{H}}\) min\(^{-1}\))

\(k_{1RH}\) : Reaction rate constant \(k_{1H}\) at reference temperature (M\(^{1-a_{H}}\) min\(^{-1}\))

\(k_{2G}\) : Reaction rate constant of glucose decomposition to humins (M\(^{1-b_{G}}\) min\(^{-1}\))

\(k_{2RC}\) : Reaction rate constant \(k_{2C}\) at reference temperature (M\(^{1-b_{C}}\) min\(^{-1}\))

\(k_{2H}\) : Reaction rate constant of HMF for the side reaction to humins (M\(^{1-b_{H}}\) min\(^{-1}\))

\(k_{2RH}\) : Reaction rate constant \(k_{2H}\) at reference temperature (M\(^{1-b_{H}}\) min\(^{-1}\))

\(K_{a,\text{HSO}_4}^{-}\) : Dissociation constant of (HSO\(_4\))\(^{-}\) (\(\text{mol L}^{-1}\))

\(M\) : Mass of the reaction mixture (g)

\(R\) : Universal gas constant, 8.3144 J mol\(^{-1}\) K\(^{-1}\)

\(R_{1G}\) : Reaction rate of glucose decomposition to HMF (mol L\(^{-1}\) min\(^{-1}\))

\(R_{1H}\) : Reaction rate of HMF decomposition to LA and FA (mol L\(^{-1}\) min\(^{-1}\))

\(R_{2G}\) : Reaction rate of glucose decomposition to humins (mol L\(^{-1}\) min\(^{-1}\))

\(R_{2H}\) : Reaction rate of HMF decomposition to humins (mol L\(^{-1}\) min\(^{-1}\))

\(t\) : Time (min)

\(T\) : Reaction temperature (°C)

\(T_{i}\) : Temperature of reaction mixture at \(t = 0\) (°C)

\(T_{\text{oven}}\) : Temperature of oven (°C)

\(T_{R}\) : Reference temperature (°C)

\(U\) : Overall heat transfer coefficient (W m\(^{-2}\) K\(^{-1}\))

\(w_{\text{H}_{2}\text{SO}_4}\) : Weight percentage of sulphuric acid (%)

\(X_{\text{GLC}}\) : Conversion of glucose (mol %)

\(Y_{\text{HMF}}\) : Yield of HMF (mol %)

\(Y_{\text{LA}}\) : Yield of LA (mol %)
A Kinetic Study on the Conversion of Glucose to Levulinic Acid

Greek symbols

\( \sigma_{\text{LA}} \) : Selectivity of LA (mol %)

\( \tau_{\text{CISTR}} \) : Residence time of CISTR (min)

\( \Psi_{\text{LA}} \) : Yield of LA in continuous reactors (mol %)

4.7 References


Chapter 4


