Chapter 6

Experimental and Kinetic Modelling Studies on the Acid-Catalysed Hydrolysis of the Water Hyacinth Plant to Levulinic Acid

Abstract

Levulinic acid (LA) is considered as a versatile precursor for green fuel additives, polymers and resins. A comprehensive experimental and modelling study on the acid-catalysed hydrolysis of the water hyacinth plant to LA is reported (T = 150–175 °C, sulphuric acid concentrations between 0.1 and 1 M, water hyacinth intake between 1 and 5 wt %). At high catalyst concentrations (> 0.5 M), LA is the major organic acid whereas at low catalyst concentration (< 0.1 M) and high initial intakes of water hyacinth, the formation of propionic acid instead of LA is favoured. The highest yield of LA was 53 mol % (35 wt %) based on the amount of C6-sugars in the water hyacinth (175 °C, initial water hyacinth intake of 1 wt %, sulphuric acid concentration of 1 M). The LA yield as a function of the reaction conditions was modelled using a kinetic model originally developed for the acid-catalysed hydrolysis of cellulose and good agreement between the experimental and modelled data was obtained.

Keyword: Water hyacinth (*Eichhornia crassipes*), levulinic acid, acid hydrolysis, green chemicals.

6.1 Introduction

With an annual production of up to $1.7–2.0\times10^{11}$ tons, biomass has been identified as an important source for alternative fuels and added-value chemicals [1-3]. However, only 6×10^9 tons of biomass are currently used for food and non-food applications [4]. Food applications are by far the most important (96.5–97%). A substantial amount of research is currently carried out worldwide to identify attractive chemical transformations to convert biomass into organic (bulk) chemicals. Examples are the production of organic acids from biomass-based sugars through fermentation or thermochemical processes. A well known example is lactic acid, which is easily converted to polylactic acid, a green polymer with very interesting applications.

A wide variety of biomass sources is available for further conversion and utilisation. Selection of the biomass feedstock is of paramount importance from both techno- and socio-economical points of view. For ethical reasons, the biomass feedstock should not compete with the food chain. Waste streams with a low or even negative value, such as agricultural waste are preferred. Furthermore, it is also advantageous to select sources that are not prone to diseases, only require a limited amount of fertiliser, have a high growth rate per ha per year and are preferably available throughout the year. Based on these criteria, the water hyacinth could be an excellent biomass feedstock for further conversions and utilisation.

The water hyacinth plant (*Eichhornia crassipes*) is a free-floating aquatic plant originating from the Amazon River basin in South America [5,6]. Owing to its beautiful lavender flowers, the water hyacinth was introduced to various countries as an ornamental plant and has spread to more than 50 countries on five continents [7-9]. The plant tolerates extremes in water level fluctuations, seasonal variations in flow velocity, nutrient availability, pH, temperature and toxic substances [7]. It can even grow at salinity levels up to 0.24% as was shown in Indonesia [10]. Extremely high growth rates of up to 100–140 ton dry material ha^{-1} year^{-1} [11,12] have been reported, depending on the location and time of year. This enormous growth rate is among the highest reported for a wide range of biomass sources [11].

The coverage of waterways by water hyacinth has created various problems. Examples are the destruction of ecosystems (Victoria Lake in Africa), irrigation problems and an increase in mosquito populations. These negative effects have pinpointed the water hyacinth as one of the world's worst weeds [13] and stimulated the search for control measures. Chemical control of the water hyacinth using herbicides is very effective but the long-term effects of these chemical substances on the environment are unknown. Furthermore, the sprayed plants are left to rot in the water, leading to pollution and eutrophication. So far, control by manual and mechanical harvesting has been practised widely in countries suffering from water hyacinth. However, as removal of the weed by both means is extremely costly, the interest in valorisation of harvested water hyacinth plants

has grown rapidly. Commercial utilization of the water hyacinth as a whole or partly is considered to be a suitable method to reduce the cost of the removal.

A well-known approach to convert lignocellulosic material like the water hyacinth to bulk chemicals is treatment of the biomass with a mineral acid like sulphuric acid at elevated temperatures (100–250 °C). Upon this treatment, the various fractions of lignocellulosic materials (lignin, hemicellulose and cellulose) are converted to soluble low molecular weight components.

Hemicellulose, a polymeric material consisting of C5- and C6-sugars, is degraded to various organic chemicals, including oligomers of various sugars [14-16], monosaccharides [17-22], furfural generated from pentose dehydration [23-25], furfural-degradation products [26,27] and acetic acid [28].

The cellulose fraction is converted to a variety of interesting bulk chemicals [29-32]. An interesting example is levulinic acid (LA), a versatile building block for the synthesis of various organic compounds. The esters of LA can either be used in the flavouring and fragrance industries or as blending component in biodiesel [33]. The reaction of LA with phenol is known to produce diphenolic acid [34,35] that can serve as a replacement for Bisphenol A in the production of polycarbonates, epoxy resins and other polymers [36,37,33]. Other products derived from LA are δ-aminolevulinic acid, a biodegradable herbicide [38], succinic acid [39] and methyltetrahydrofuran [40], a gasoline oxygenate [36]. Details on the properties and potential industrial applications of LA and its derivatives are provided in several reviews [41-43].

The aim of this study was to identify whether the harvested water hyacinth plant is a useful biomass source for LA manufacture. The chemical composition of the water hyacinth plant was determined, followed by systematic studies to optimise the LA yield by altering the process conditions (temperature, water hyacinth intake and acid concentration). Subsequently, the LA yields were modelled using a recently developed kinetic model for cellulose.

6.2 Materials and Methods

6.2.1 Water hyacinth

Fresh water hyacinth plants were obtained from Intratuin B.V. (Groningen, Netherlands). The plants were washed with water to remove sand and dirt. The leaves were separated from the stems and the roots and were reduced in size to about 2–3 mm using a mini-chopper (TEFAL Rondo 500). These finely cut parts were dried overnight in an oven at 55 °C. The dried leave parts were chopped (TEFAL Rondo 500) and sieved through a 0.5 mm pore-size sieve before use. The leave parts with a size < 0.5 mm were used for this study.

6.2.2 Chemicals

All chemicals used in this study were of analytical grade and used without purification. Concentrated sulphuric acid 95–97 wt % [*7664-93-9*], glucose [*14431-43-7*] and formic acid [*64-18-6*] were purchased from Merck GmbH (Darmstadt, Germany); xylose [*58-86-6*], arabinose [*28697-53-2*], furfural [*98-01-1*], 5-hydroxymethylfurfural [*67-47-0*], propionic acid 99 wt % [*79-09-4*], acetic acid 96 wt % [*64-19-7*] and LA 98 wt % [*123-76-2*] were obtained from Acros Organics (Geel, Belgium). Deionised water was applied to prepare the various solutions.

6.2.3 Experimental procedures

6.2.3.1 Water hyacinth characterisation

Thermal gravimetric analysis (TGA) was used to determine the chemical composition (cellulose, hemicellulose, lignin and the inorganic ash content) of the water hyacinth plants used in this study. The elemental composition was determined by elemental analysis. Two-stage acid-catalysed hydrolysis was used to determine the type and amount of sugars and acetyl groups [44]. In the first-stage, the water hyacinth was hydrolyzed in a concentrated solution of sulphuric acid (72 wt %) at 30 °C for 120 min. After completion, the reaction mixture was diluted with water to obtain an acid concentration of 4 wt %, and was re-hydrolysed in the second-stage at 121 °C for 60 min. The liquid phase was separated from the solids using a micro-centrifuge (Omnilabo International B.V.) for approximately 15–20 minutes at 1200 rpm. Afterward, the sample was neutralised using $Ba(OH)_2$ until a pH of 5–7 was obtained and subsequently centrifuged to obtain a particle-free solution. The composition of the particle-free solution was determined using high performance liquid chromatography (HPLC) equipped with a BioRad sugars column Aminex HPX-87P.

6.2.3.2 Kinetic experiments

The reactions were carried out in glass ampoules with a length of 150 mm, an internal diameter of 3 mm and a wall thickness of 1.5 mm. The ampoules were filled with a predetermined amount of dried water hyacinth. Subsequently, an aqueous solution (0.2–0.5 cm³) of the sulphuric acid catalyst at the desired concentration was added. The ampoules were sealed with a torch. The sealed ampoules were placed in a constant temperature oven (± 1 °C). At various reaction times, ampoules were taken from the oven and quenched in an ice-water bath (4 °C) to stop the reaction. The ampoule was opened, and the liquid was separated from the solids using a micro-centrifuge (Omnilabo International B.V.) for approximately 15–20 minutes at 1200 rpm. A certain amount of the clear solution was taken (100–200 µL) and diluted with water (2 cm³). The composition of the solution was determined using HPLC equipped with a BioRad organic acids column Aminex HPX-87H.

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

6.2.4 Analytical equipment

The composition of the liquid phase was determined using an HPLC system consisting of a Hewlett Packard 1050 pump and a Waters 410 refractive index detector. Two different columns were applied. The mobile phase for Aminex HPX-87P Sugar column was HPLC-grade water at a flow rate of 0.55 cm^3 min^{-1}, and the column was operated at 80 °C. An aqueous solution of sulphuric acid (5 mM) at a flow rate of 0.55 cm^3 min^{-1} was used as the mobile phase for the Aminex HPX-87H Organic Acid column, which was operated at 60 °C. The concentration of each compound in the liquid phase was determined using calibration curves obtained by analysing standard solutions with known concentrations.

The gas composition was analysed with GC-MS, which consisted of a HP 5890 Series II gas chromatography with a HP 6890 detector. The composition of the gas phase was determined using a CP-Porabond-Q column (length = 25 m and I.D. = 0.25 mm). The oven temperature was set at 40 °C for 2 min and increased to 240 °C with an increment of 30 °C min^{-1}. Helium was used as the carrier gas with a flow rate of 1.5 cm^3 min^{-1}.

Elemental analyses were performed at the Analytical Department of the University of Groningen using an automated Euro EA3000 CHNS analyser. Thermal analysis of oven-dried water hyacinth was performed on a Mettler Toledo TGA/SDTA 851e with a heating rate of 10 °C min^{-1} in an inert atmosphere.

6.2.5 Modelling techniques and software

The kinetic parameters for the proposed kinetic model were estimated using a maximum-likelihood approach, which is based on minimization of errors between the experimental data and the kinetic model. Minimization of errors was initiated by providing initial guesses for each kinetic parameter. The best estimates were obtained using the MATLAB toolbox *fminsearch*, which is based on the Nelder-Mead optimization method.

The optimisation experiments were modelled using Design-Expert 7 software (Stat-Ease). The yield of LA was modelled using a standard expression as given in equation (6.1):

$$Y_{LA} = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} \sum_{j=1}^{3} b_{ij} x_i x_j \tag{6.1}$$

The operating variables (water hyacinth intake, temperature and acid catalyst concentration) are represented by the indices 1–3. The regression coefficients were obtained by statistical analyses of the data. Significance of factors was determined

by their *p*-value in the ANOVA analyses. A factor was considered significant if the *p*-value was lower than 0.05, meaning that the probability of noise causing the correlation between a factor and the response is lower than 0.05. Insignificant factors were eliminated using backward elimination, and the significant factors were used to model the data.

6.2.6 Definitions of LA yield

The yield of LA on a molar base (Y_{LA}) is defined as the ratio between the LA concentration in the reaction product (C_{LA}) and the concentration of the available C6-sugars in the water hyacinth ($C_{C6,0}$):

$$Y_{LA}\left(\text{mol }\%\right) = \frac{C_{LA}}{C_{C6,0}} \times 100\% \tag{6.2}$$

In equation (6.2), the $C_{C6,0}$ is the sum of the available C6-sugar monomers (glucose and galactose) in the cellulose and hemicellulose fraction.

It is also possible to define the yield of LA on a weight base ($Y_{LA,wt}$), which is defined as the mass ratio between the LA and the available C6-sugars in the water hyacinth:

$$Y_{LA,wt}\left(\text{wt }\%\right) = \frac{C_{LA} \times M_{LA}}{C_{C6,0} \times M_{\text{C6-sugars}}} \times 100\% \tag{6.3}$$

In equation (6.3), the terms M_{LA} and $M_{\text{C6-sugars}}$ represent the molecular weight of LA (116 g mol^{-1}) and C6-sugars (180 g mol^{-1}), respectively.

The yield of LA can also be defined as the ratio between the mass of LA and the total mass of the oven-dried water hyacinth:

$$Y_{LA,total}\left(\text{wt }\%\right) = \frac{C_{LA} \times M_{LA}}{m_{WH}} \times 100\% \tag{6.4}$$

where m_{WH} represent the mass of the oven-dried water hyacinth.

6.3 Results and discussion

6.3.1 Determination of the water hyacinth composition

Detailed knowledge of the water hyacinth composition is essential to gain insights into the highest theoretically possible LA yield and to rationalise the product composition after the acid-catalysed hydrolysis reaction. The results of a thermo gravimetric analysis (TGA) of water hyacinth leaves are given in Figure 6.1. Three distinct stages of weight losses are visible. The first-stage between 40 and 100 °C is due to evaporation of residual water. Cellulose and hemicelluloses are degraded between 200–350 °C. Finally lignin decomposes between 420 and 500 °C. These temperature ranges are in line with a previous study [45] on the characterisation of lignocellulosic biomass using TGA analysis. The residue is non-

combustible and is defined as the ash content of water hyacinth. Gopal [7] has reported a typical composition of the ash fraction of the water hyacinth: K_2O: 6.3–34.1%; Na_2O: 1.8–1.88%; CaO: 8.4–12.8%; Cl^-: 3.9–21%; $(PO_4)^{3-}$: 2.8–8.2%, suggesting that the ash is basic in nature. The results of our analysis for the organic and inorganic content, including the elemental composition, are given in Table 6.1.
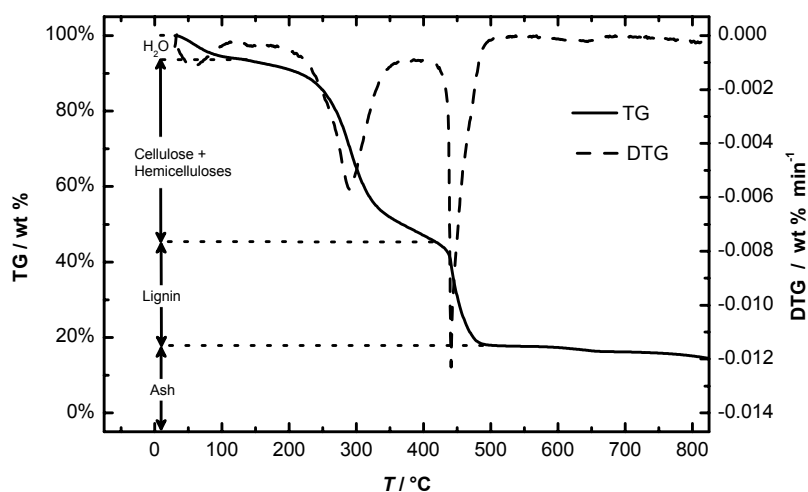
Figure 6.1 Thermo Gravimetric (TG) and Differential Thermo Gravimetric (DTG) curves of the oven-dried water hyacinth.

Table 6.1 Chemical composition of oven-dried water hyacinth leaves.

	wt %
Thermal gravimetric analysis	
Cellulose + Hemicellulose	46.74
Lignin	27.69
Ash	18.20
Water	7.37
Elemental analysis (dry basis)	
C	42.18
H	6.41
O	27.52
N	4.25
Ash	19.65
Two-stage acid hydrolysis	
Glucose	19.8
Galactose	6.5
Xylose	11.5
Arabinose	9.0
Acetyl groups	1.1

The type and amounts of sugar monomers in the water hyacinth were determined using a two-stage acid hydrolysis procedure. The total amount of C6-sugars was 26.3 wt %, being glucose (19.8 wt %) and galactose (6.5 wt %). Mannose could not be detected. Details about the amount and type of C6-sugars in the water hyacinth plant are scarce. Most studies only reported the amount of cellulose, which varies between 17.8 and 19.5 wt % [46-48]. Our analysis reveals the presence of two C5-sugars, xylose and arabinose, in the water hyacinth leaves in amounts of 11.5 and 9.0 wt %, respectively. Nigam (2002) reported similar amounts for xylose (12.4 wt %), whereas their arabinose levels (2.2 wt %) were considerably lower [11].

Considerable amounts of acetic acid (1.1 wt %) were detected in the reaction mixture after the two-stage hydrolysis process. The presence of this acid is likely the result of hydrolysis of acetyl groups in the hemicellulose fraction [49,28].

6.3.2 Exploratory experiments

Exploratory experiments on the acid-catalysed hydrolysis of the water hyacinth plant to gain insights into the type and amount of reaction products were carried at T = 175 °C, using a water hyacinth intake of 5 wt % and two sulphuric acid concentrations (1.0 and 0.1 M).

6.3.2.1 Results for 1.0 M sulphuric acid

Typical concentration profiles for the various water-soluble compounds when hydrolysing the water hyacinth plant in a strong acidic medium (1.0 M sulphuric acid) are given in Figure 6.2.
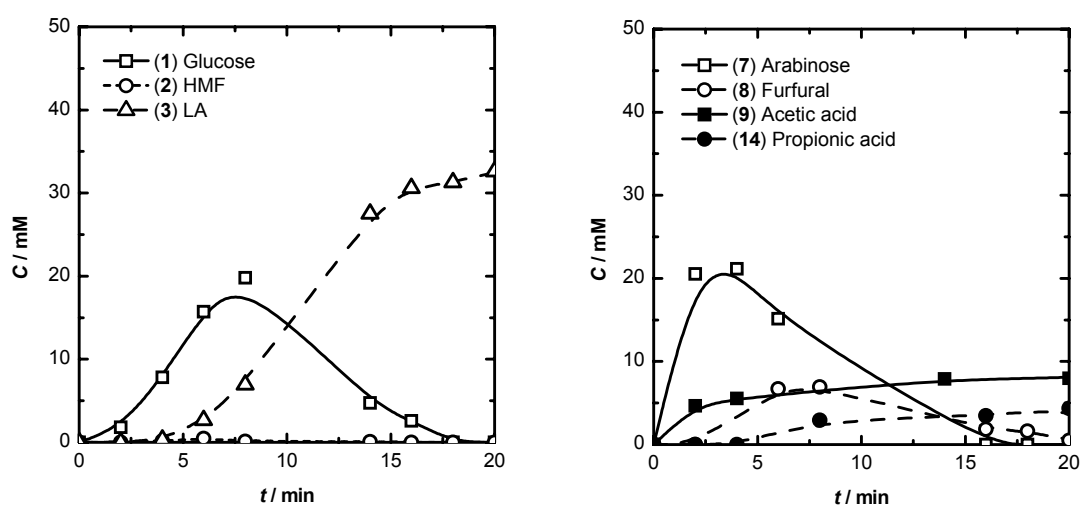

Figure 6.2 Concentration profiles of various compounds present when hydrolysing water hyacinth leaves ($C_{H_2SO_4}$ = 1.0 M, $x_{WH,0}$ = 5 wt %, T = 175 °C).

The amount of LA in the reaction mixture after 20 min was about constant and reached a maximum level of 32 mM, corresponding with a yield of 40 mol % on the available C6-sugars in the water hyacinth. Besides LA, considerable amounts of other organic acids (formic acid, acetic acid and propionic acid) were present after 20 min of reaction time, although the concentrations were significantly lower than that of LA.

A number of intermediate products with clear maximum concentrations were observed (Figure 6.2). These were identified as monomeric sugars (glucose and arabinose) as well as furan derivatives (5-hydroxymethylfurfural and furfural). The concentration profiles of galactose and xylose cannot be presented individually because of overlapping peaks in the HPLC analysis using the Aminex HPX-87H column, which hampered the quantitative analysis. However, the combined peak area of both sugars also showed a clear optimum, indicative for the existence of consecutive reaction pathways.

On the basis of the product composition and literature precedents for other biomass sources [50,51], a simplified reaction pathway for the acid-catalysed hydrolysis of the water hyacinth is proposed in Scheme 6.1.
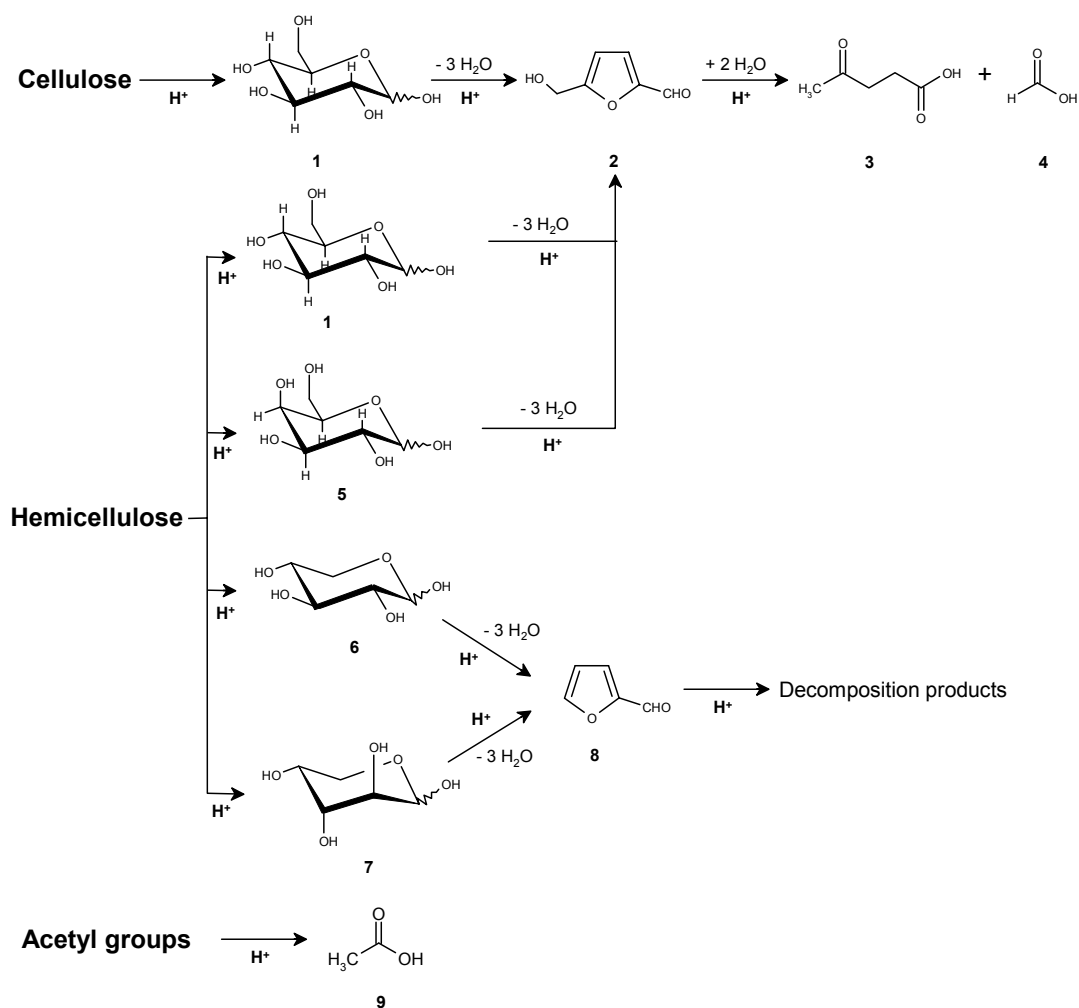

Scheme 6.1 Simplified reaction scheme for the acid-catalysed hydrolysis reaction of water hyacinth.

The cellulose in the water hyacinth is broken down into low molecular weight fragments and ultimately to glucose (GLC, **1**) by the action of the acid catalyst [52]. Subsequently, the glucose is decomposed to 5-hydroxymethylfurfural (HMF, **2**), which is further converted in a serial mode to LA (**3**) and formic acid (**4**) [53,54].

The anticipated products of hemicellulose hydrolysis are glucose, galactose (**5**), xylose (**6**) and arabinose (ARA, **7**) and these were indeed detected in the reaction mixtures. The C6-sugars from the hemicellulose fraction (glucose and galactose) are expected to be converted to HMF and subsequently to LA [51,55]. Both C5-sugars (xylose and arabinose) are known to be decomposed to furfural (FUR, **8**) [23-25]. The furfural concentration also shows an optimum with respect to reaction time (Figure 6.2), indicating subsequent reactions under these conditions. Acetic acid (AA, **9**) is most likely formed from the hydrolysis of the acetyl groups present in the hemicellulose [49,28].

Besides these products, small amounts of other organic acids, i.e. lactic acid (**10**) and propionic acid (**14**, less than 0.2 wt %) were detected in the liquid phase. Further analysis by ion exchange chromatography (IEC) also revealed the presence of minor amounts (less than 0.1 wt %) of pyruvic acid (**11**) and glycolic acid (**12**). The presence of these acids is in line with previous study on C5-sugar decomposition [23], which proposed that **10**, **11** and **12** are, among others, the decomposition products of C5-sugars and particularly of xylose in neutral or low acidic media. A reaction scheme for the catalysed degradation of xylose is given in Scheme 6.2.
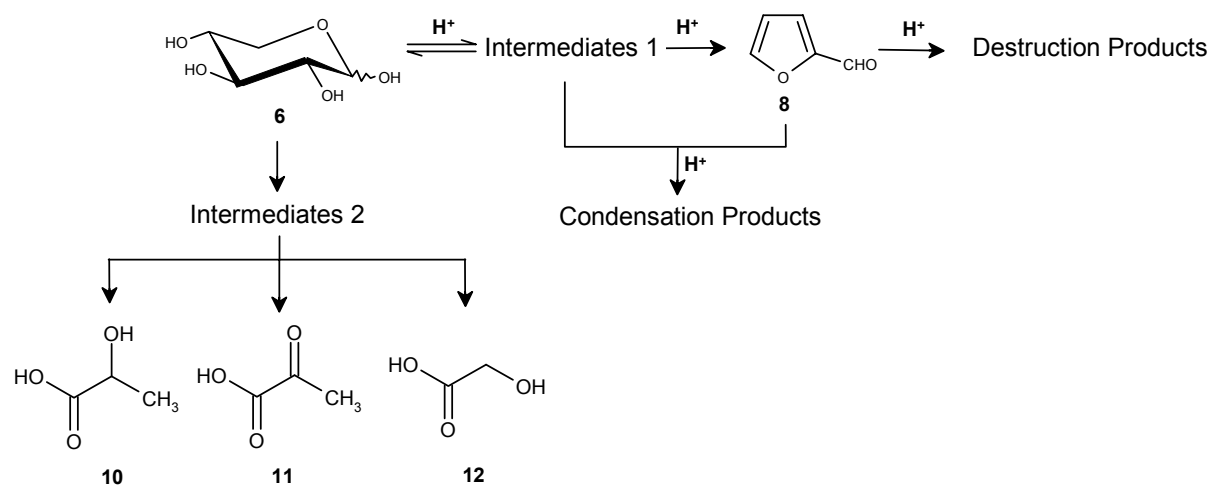
Scheme 6.2 Products of the catalysed-degradation of xylose [23].

Previous studies [56,57,28] have reported that propionic acid (PA, **14**) is a product of consecutive reactions of lactic acid via acrylic acid (**13**) as the intermediate (see Scheme 6.3). In the first step, the hydroxyl group of lactic acid is dehydrated to give acrylic acid. The latter is supposed to be hydrogenated to propionic acid.
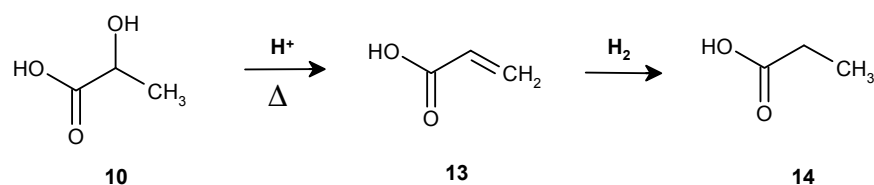
Scheme 6.3 Proposed reaction pathway for the conversion of lactic acid to propionic acid at elevated temperature [56,57,28].

In all experiments, dark-brown insoluble-products were formed. These are likely humins-type by-products from the acid-catalysed decomposition of glucose and HMF, as well as from the condensation reactions of C5-sugars and furfural [23].

Other possible by-products of the acid-catalysed hydrolysis of water hyacinth are gas-phase components from thermal degradation reactions of reactants and/or products. To gain insights into the extent of these reactions, the gas phase after the reaction was analysed using GC and GC-MS. Both CO and CO_2 could be detected; however, the amounts were less than 0.1 wt % of the water hyacinth intake. This implies that the formation of gas-phase compounds is only a minor reaction pathway under the reaction conditions applied in our experiments.

6.3.2.2 Results for 0.1 M sulphuric acid

To gain insights into the effects of the acid catalyst concentration on the product profiles, a series of experiments was carried out at low sulphuric acid concentrations (0.1 M). The results are shown in Figure 6.3.
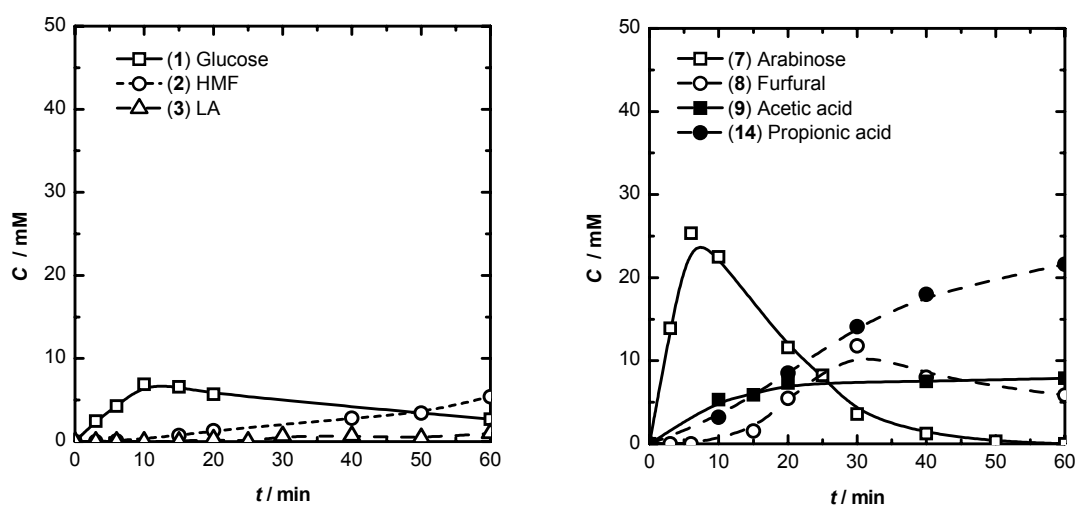
Figure 6.3 Concentration profile of various compounds present when hydrolysing water hyacinth leaves ($C_{H_2SO_4}$ = 0.1 M, $x_{WH,0}$ = 5 wt %, T = 175 °C).

The amount of LA at the end of the reaction is considerably lower (1 mol %) at 0.1 M when compared to 1 M sulphuric acid (40 mol %), see also Figure 6.4. This suggests that the amount of available monomeric C6-sugars in the reaction mixture is reduced considerably at low acid catalyst concentrations. This is clearly supported by Figure 6.3, which shows that the maximum glucose concentration (8 mM) is considerably lowered when compared with a hydrolysis experiment in the presence of 1 M sulphuric acid (20 mM). Glucose originates from both the cellulose and hemicellulose fraction of the water hyacinth leaves. It is well possible that glucose formation from the cellulose fraction is suppressed at low acid catalyst concentration due to a slower rate of break down of the glycosidic bonds in crystalline cellulose. In addition, the reaction rates of the subsequent reactions of glucose to HMF and LA are also reduced at lower acid concentrations. Consequently, only small amounts of LA are produced at these conditions.

On the contrary, the formation and decomposition reactions involving the C5-sugars were not affected by the amount of acid catalyst present in the reaction mixture. Significant amounts of C5-sugars (xylose and arabinose) were formed as well as furfural. These observations indicate that breakdown of the hemicellulose fraction at low acid concentrations is still very facile. This is further supported by the observation that the maximum concentration of arabinose, a main component in the hemicellulose fraction, is about equal to value observed at high acid catalyst concentrations. All observations suggest that hemicellulose breakdown is still facile at low acid catalyst concentrations. This is in line with earlier investigations on hemicellulose decomposition and is ascribed to the low crystallinity of the hemicellulose fraction [16].

The concentration of acetic acid in the mixture at the end of the reaction was essentially similar to that at higher acid catalyst concentration (*cf*. Figures 6.2 and 6.3). Apparently, the acetyl groups in the hemicellulose fraction are easily hydrolysed to acetic acid, even when using a dilute mineral acid catalyst.

Propionic acid was formed in larger amounts than found at higher acid concentrations (Figure 6.4). Oeffner *et al*. (1992) studied the degradation of xylose in aqueous media at different pH values and found substantial amounts of propionic acid [58]. The formation of propionic acid was highest in neutral and alkaline solutions, whereas furfural was the major product in acid media. This suggests that our experiments were actually carried out at very low acidic or even neutral conditions. We assume that the acid catalyst is neutralised by the basic components present in the (high) ash fraction of the water hyacinth (*vide supra*) [59,60]. This explanation is also supported by the fact that the water hyacinth intake also has a profound effect on the selectivity. When using a constant sulphuric acid catalyst concentration of 0.1 M and varying the water hyacinth intake, higher intakes led to larger amounts of propionic acid (*vide infra*).

On the basis of the experimental data at different acid concentrations, it may be concluded that the product composition at the end of the reaction and the maximum concentration of intermediate products are a strong function of the

acidity of the reaction medium (see Figure 6.4). In strong acidic medium, the formation of LA is favoured, whereas propionic acid is the major acid formed at lower acidity.
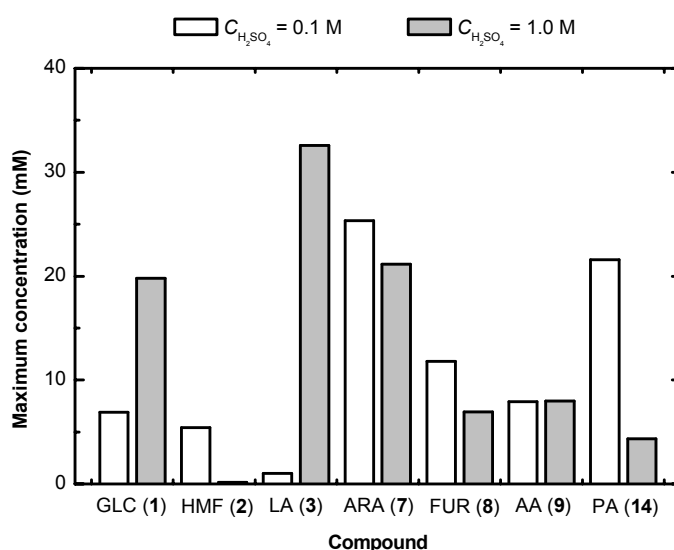
Figure 6.4 Maximum concentration of selected products as a function of the acid catalyst concentration ($x_{WH,0}$ = 5 wt % and T = 175 °C).

6.3.3   Optimisation experiments

A total of 12 experiments were performed, differing in temperature, sulphuric acid concentration and initial intake of water hyacinth (see Table 6.2). The effects of the process conditions on the LA yield (Y_{LA}) will be discussed in the following section.

Table 6.2 Experimental conditions and LA yield for the optimisation experiments.

No.	T (°C)	$C_{H_2SO_4}$ (M)	$x_{WH,0}$ (wt %)	t (min)	Y_{LA} [a] (mol %)
1	150	0.1	1	0 – 720	38
2	150	0.1	5	0 – 720	2
3	150	0.5	1	0 – 240	47
4	150	0.5	5	0 – 240	49
5	150	1.0	1	0 – 240	51
6	150	1.0	5	0 – 240	51
7	175	0.1	1	0 – 60	34
8	175	0.1	5	0 – 60	1
9	175	0.5	1	0 – 30	46
10	175	0.5	5	0 – 30	41
11	175	1.0	1	0 – 30	53
12	175	1.0	5	0 – 30	46

[a] The yields were evaluated at the final reaction time and Y_{LA} is defined in equation (6.2).

The highest experimental Y_{LA} is 53 mol % (or 9 wt % based on the mass of oven-dried water hyacinth), and was obtained at T = 175 °C, $x_{WH,0}$ = 1 wt % and $C_{H_2SO_4}$ = 1 M. To quantify the effect of process conditions on the LA yield, the data were analysed using the Design-Expert software. As anticipated on the basis of the screening experiments, the experiments carried out at a low acid catalyst concentration in combination with a high water hyacinth intake favoured the formation of propionic acid. These experiments (2 and 8) were excluded from the statistical analysis. The following model, including the quadratic and interaction terms, fits the experimental data well (R^2 = 0.9998):

$$Y_{LA} = 50.176 + (-0.109)T + (-4.762)C_{H_2SO_4} + (11.347)x_{WH,0}$$
$$+ (0.260)C_{H_2SO_4}T + (-0.069)x_{WH,0}T + (-1.0)C_{H_2SO_4}x_{WH,0} \tag{6.5}$$
$$+ (-16.944)C_{H_2SO_4}^2$$

Analysis of variance of the model is given in Table 6.3. A good agreement between the empirical model and the experimental data was observed as shown in the parity plot provided in Figure 6.5.

The model predicts that particularly the acid concentration has a profound effect on the Y_{LA}. This is clearly illustrates in Figure 6.6 and supported by the experiments (Table 6.2). For example, an increase in the acid concentration from 0.1 to 1 M ($x_{WH,0}$ = 1 wt % and T= 150 °C), the Y_{LA} increases from 38 to 51 mol %.

Within the limited temperature window (150–175 °C), the reaction temperature has a small but significant effect on the LA yield (Figure 6.6). The Y_{LA} is generally reduced when performing the reaction at higher temperatures. This is in line with the experimental and modelling studies on the acid-catalysed hydrolysis of cellulose to LA [52].

To increase the Y_{LA}, it seems preferable to conduct the hydrolysis reaction in a dilute solution (Figure 6.6).

Table 6.3 Analysis of variance of the preferred model.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	p-value Prob > F
Model	340.34	7	48.62	1723.33	0.0006
T (A)	42.11	1	42.11	1492.62	0.0007
$C_{H_2SO_4}$ (B)	118.10	1	118.10	4186.01	0.0002
$x_{WH,0}$ (C)	20.73	1	20.73	734.82	0.0014
AB	11.19	1	11.19	396.75	0.0025
AC	25.87	1	25.87	917.08	0.0011
BC	2.00	1	2.00	70.89	0.0138
B²	15.25	1	15.25	540.53	0.0018
Residual	0.056	2	0.028		
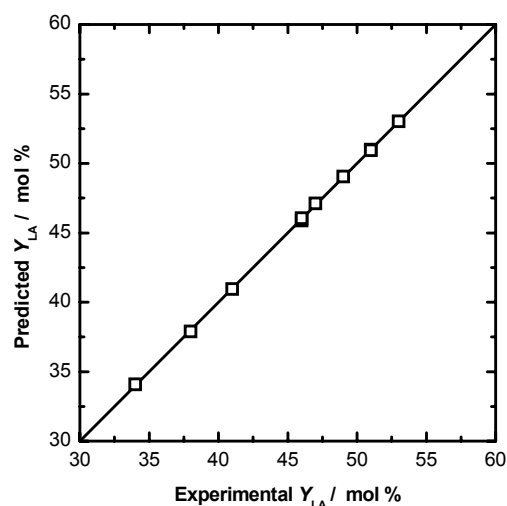
Figure 6.5 Parity plot between the experimental data and the predicted data from the empirical model.
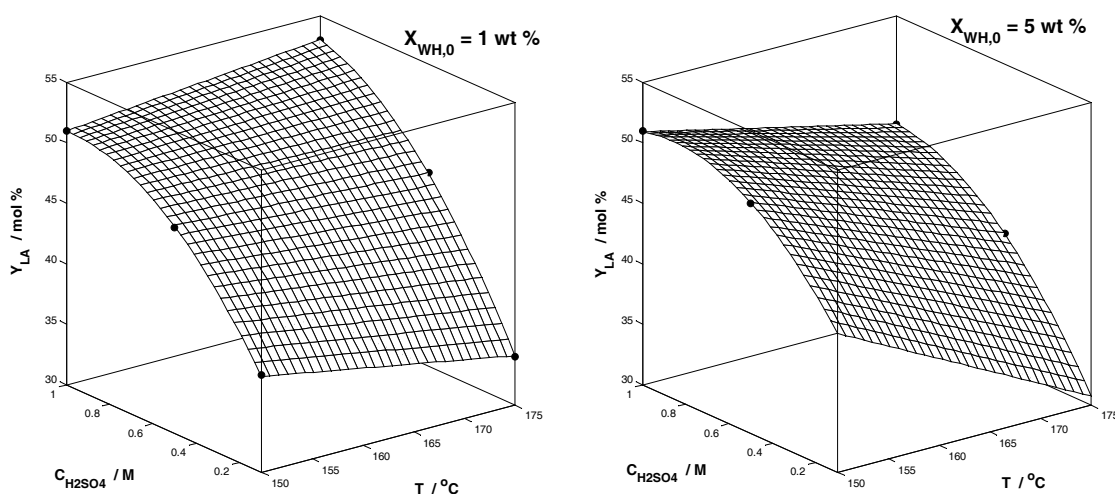
Figure 6.6 Optimisation studies using the empirical model on the effects of temperature and acid concentration at two water hyacinth intakes ($x_{WH,0}$ = 1 and 5 wt %). Symbols (•) represent the experimental data.

Table 6.4 shows a comparison between the LA yields from earlier studies on a variety of biomass sources with the results reported here for the water hyacinth leaves. Clearly, the yields of LA depend strongly on the type of biomass feedstock and reaction conditions. High LA yields are usually obtained by hydrolysing biomass feedstock with a high content of C6-sugars, such as starch or pulp slurry, at high temperatures. The LA yield from the water hyacinth is relatively low and comparable with that found for wood sawdust. This low LA yield is the consequence of the relatively low amounts of C6-sugars in the water hyacinth leaves compared to other feedstocks.

Table 6.4 Various methods to prepare LA from biomass feedstock.

Feedstocks	T (°C)	Biomass intake (wt %)	C6-sugars (wt %)	C_{acid} (wt %)	Acid	t (h)	$Y_{LA,total}$ (wt %)	$Y_{LA,wt}$ (wt %)	Reference
Wood sawdust	190	20	50	1.5	HCl	0.5	9	36	[61]
Cane sugar	100	10	100	16	HCl	24	15	15	[62]
Bagasse	25-195	10	40	1.3	H_2SO_4	2	18	45	[63]
Corn starch	162	29	90	6.5	HCl	1	26	37	[64]
Starch	200	31	90	1.7	HCl	0.5	35	49	[65]
Pulp slurry	160	10	60	6	HCl	1	41	68	[66]
Water hyacinth	175	1	26.3	9.5	H_2SO_4	0.5	9	35 (53)[a]	This study

[a] The value in parentheses is the yield of LA in defined on a molar base (Y_{LA}).

The water hyacinth plant has an enormously high growth rate and values up to ~100 dry ton ha^{-1} year^{-1} have been reported [11]. With the yield data reported in Table 6.4, a hectare of water hyacinth has the potential to produce 9 ton LA year^{-1}.
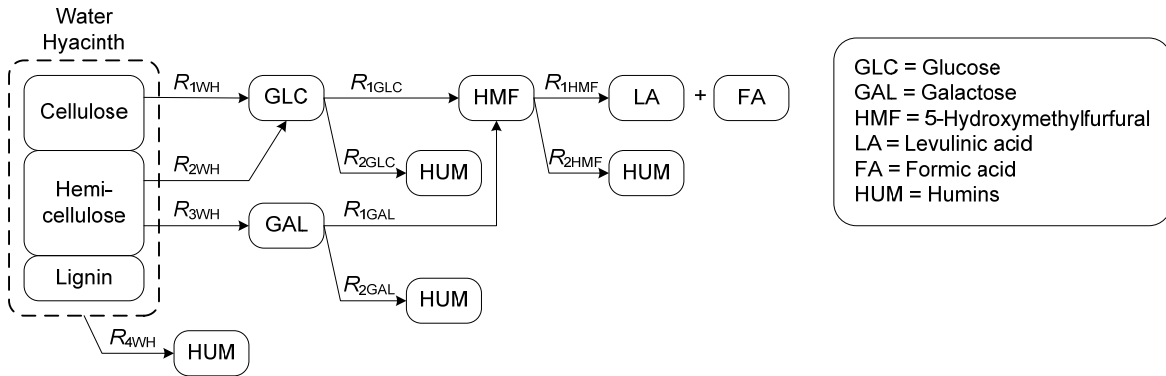
6.4 Development of a kinetic model for the acid-catalysed hydrolysis of water Hyacinth to LA

We recently published a kinetic model for the acid-catalysed hydrolysis of cellulose to LA [52]. The model has been validated in the temperature range of 150–200 °C, sulphuric acid concentrations between 0.05 and 1 M and initial cellulose intakes between 1.7 and 14 wt %. This kinetic model is the basis for the kinetic model presented here to predict the LA yields and the amounts of glucose for the acid-catalysed hydrolysis of the water hyacinth at different reaction conditions. Adjustments of the cellulose model are required to compensate for the fact that the water hyacinth is by far a more complex matrix than pure cellulose and consists of different sugar-polymers together with lignin. The acid-catalysed hydrolysis of this complex material is evidently not the same as for pure cellulose.

The kinetic model for the water hyacinth leaves is based on the following considerations and assumptions:

1. Among the sugars present in the water hyacinth, only the C6-sugars are converted to the desired product LA. These C6-sugars are glucose monomers from the cellulose and hemicellulose fraction and galactose monomers from the hemicellulose fraction. Scheme 6.4 shows the reaction network of acid-catalysed hydrolysis of water hyacinth. Undesirable by-products are humins and these are formed in each of the reactions within the network [53,54,52].

Scheme 6.4 Proposed reaction network for the acid-catalysed hydrolysis reaction of water hyacinth to LA.

2. The reaction rate equations are quantified using the power law approach, and the reaction rate constants are defined in term of modified Arrhenius equations. The kinetic parameters for the conversion of cellulose, glucose and HMF to LA have been determined in previous studies in our laboratory and are used as input in the kinetic model [53,54,52].

3. The first step in the acid-catalysed hydrolysis of water hyacinth is the depolymerisation of the cellulose and hemicellulose fractions into their sugar monomers, and the reaction rates are represented as R_{1WH}, R_{2WH} and R_{3WH} (Scheme 6.4). To compensate for the fact that the cellulose fraction in the water hyacinth differs from that of pure cellulose (e.g., crystallinity, particle size), a correction factor is applied:

$$R_{1WH} = c_{1WH} R_{CEL \to GLC} \tag{6.6}$$

where $R_{CEL \to GLC}$ represents the reaction rate of glucose formation from pure cellulose.

4. Hemicellulose fraction is more easily hydrolysed than cellulose. Unfortunately, no data are available for the rate of hydrolysis of the C6-sugars in the hemicellulose fraction. Therefore, the depolymerisation rates of glucose and galactose present in the hemicellulose are taken as follows:

$$R_{2WH} = c_{2WH} R_{CEL \to GLC} \tag{6.7}$$

$$R_{3WH} = c_{3WH} R_{CEL \to GLC} \tag{6.8}$$

5. Simultaneously, part of the water hyacinth is also decomposed to humin byproducts (R_{4WH}):

$$R_{4WH} = c_{4WH} R_{CEL \to HUM} \tag{6.9}$$

In equation (6.9), $R_{CEL \to HUM}$ represents the decomposition rate of pure cellulose to the undesired humins.

6. It is assumed that galactose decomposes in a similar fashion as glucose and forms HMF and subsequently LA and FA. The reaction rate of galactose

decomposition are assumed to be the same as the reaction rate of glucose decomposition:

$$R_{1GAL} = R_{1GLC} \tag{6.10}$$

$$R_{2GAL} = R_{2GLC} \tag{6.11}$$

Several additional experiments using pure galactose have been performed to validate this assumption. The experiments were carried out at 140 °C, 1.0 M sulphuric acid and variable galactose intakes (0.1–1.0 M). The experimental data were compared with the kinetic model developed for the acid-catalysed decomposition of glucose (Figure 6.7). Clearly, the rate of the acid-catalysed galactose decomposition is similar to that of glucose, proving the validity of this assumption.
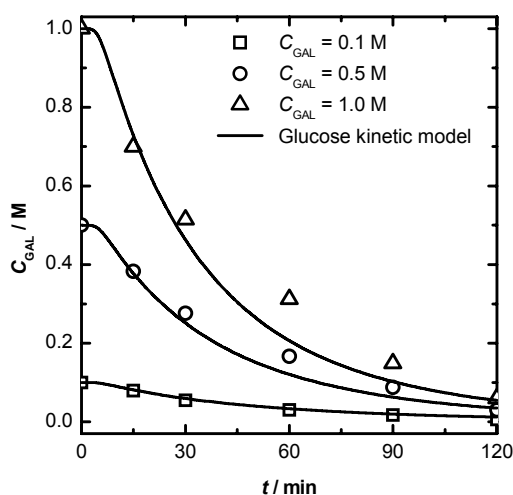
Figure 6.7 Comparisons of experimental data for galactose decomposition to LA with a kinetic model developed for glucose (T = 140 °C and $C_{H_2SO_4}$ = 1.0 M).

7. Considering that the decomposition rates of galactose and glucose are equal (*vide supra*), the proposed reaction network (Scheme 6.4) can be simplified to:
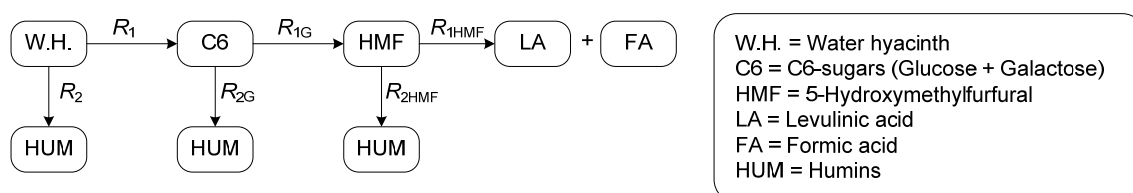
Scheme 6.5 Simplified reaction scheme of water hyacinth hydrolysis.

Here, the production rates of C6-sugars from the water hyacinth are lumped as follows:

$$R_1 = R_{1WH} + R_{2WH} + R_{3WH} = (c_{1WH} + c_{2WH} + c_{3WH})R_{CEL \to GLC} = c_1 k_{1C}(C_{CEL})^{a_C} \quad (6.12)$$

Meanwhile, the production rate of humins from the water hyacinth is given by:

$$R_2 = R_{4WH} = c_{4WH} R_{CEL \to HUM} = c_2 k_{2C}(C_{CEL})^{b_C} \quad (6.13)$$

The values for k_{1C}, k_{2C}, a_C and b_C were determined earlier in our group [52].

8. The initial concentration of C6-sugars fraction in the water hyacinth ($C_{C6,0}$) is determined using the following equation:

$$C_{C6,0} = \frac{\text{mass of water hyacinth} \times \text{wt\% of C6 - sugars in water hyacinth}}{\text{molecular weight of C6 - sugar} \times \text{volume of reaction mixture}} \quad (6.14)$$

9. At the start-up of the reaction, the temperature in the reactor is not constant and the reaction proceeds non-isothermal. Additional experiments according to a published procedure [53,54] were carried out to obtain a model to compensate for this effect. This model was subsequently incorporated into the kinetic model for the water hyacinth to describe the non-isothermal behaviour of the system at the start-up of the reaction.

For a batch reactor set-up with no density- and volume-changes, the concentrations of the individual species as a function of time, using the proposed kinetic model given in Scheme 6.5, may be represented by the following ordinary differential equations:

$$\frac{dC_{WH}}{dt} = -R_1 - R_2 \quad (6.15)$$

$$\frac{dC_{C6}}{dt} = R_1 - R_{1G} - R_{2G} \quad (6.16)$$

$$\frac{dC_{HMF}}{dt} = R_{1G} - R_{1HMF} - R_{2HMF} \quad (6.17)$$

$$\frac{dC_{LA}}{dt} = R_{1HMF} \quad (6.18)$$

The rate expressions of water hyacinth hydrolysis in equations (6.12) and (6.13) are combined with the mass balance equations (6.15)–(6.18) to model the experimental data. A total of 10 experiments gave 96 sets of experimental data, where each set consists of the concentrations of glucose and LA at a certain reaction time. The best estimates of the correction factor c_1 and c_2 were determined using a MATLAB optimisation routine, and the results are given in Table 6.5.

Table 6.5 Estimated correction factors for the acid-catalysed hydrolysis of water hyacinth.
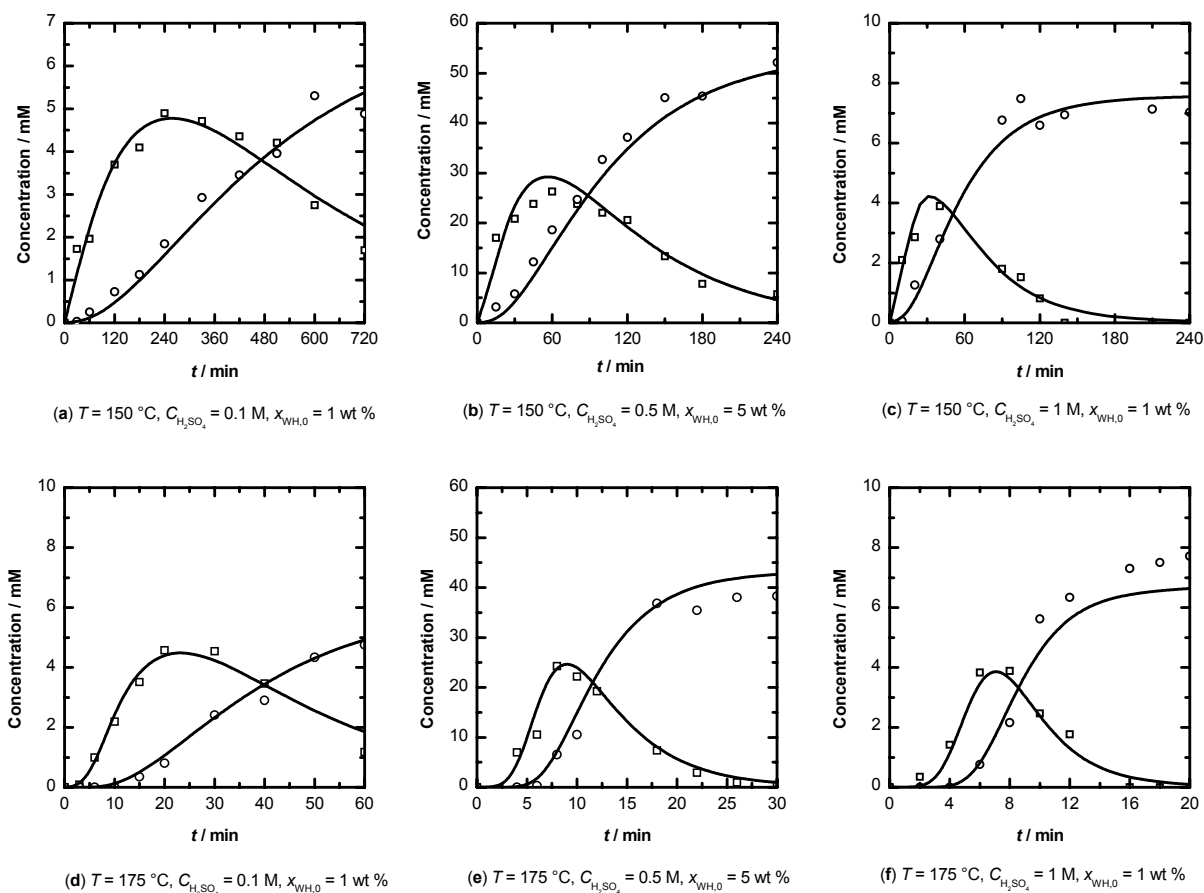
Parameter	Estimate
c_1 [−]	0.74 ± 0.04
c_2 [−]	1.94 ± 0.18

The term c_1 is the summation of three individual rate constants, see equation (6.12) for details. The value of c_1 is less than 1, meaning that the rate of depolymerisation of C6-sugars from the water hyacinth matrix is slower than that of pure cellulose. The rate of decomposition of the hemicellulose fraction to C6-sugars is expected to be much faster than that of cellulose. This implies that the rate of formation of glucose from the water hyacinth matrix is slower than that from pure cellulose. Pure cellulose is usually produced from cotton and has gone through several treatments to remove the hemicellulose and lignin fractions. The presence of these fractions in the water hyacinth, especially lignin as the binder, and the differences in the cellulose structure likely reduces the rate of depolymerisation of the cellulose fraction in the water hyacinth to glucose monomers.

Figure 6.8 shows a good fit between the experimental concentrations of glucose and LA and the kinetic model for a broad-range of reaction conditions. This is also confirmed by the parity plot as shown in Figure 6.9.

6.5 Conclusions

The acid-catalysed hydrolysis of the water hyacinth to LA was carried out in a broad range of reaction conditions, including variations in temperature (150 and 175 °C), sulphuric acid concentrations (between 0.1 and 1 M) and initial water hyacinth intakes (1 and 5 wt %). The product distribution depends strongly on the reaction condition applied, and two distinct reaction pathways may be discriminated. At high sulphuric acid concentration, LA is the major organic acid formed, whereas propionic acid is preferentially formed at low acid concentrations. The highest yield of LA observed in this study was 53 mol % based on the available C6-sugars in the water hyacinth or 9 wt % based on dried water hyacinth. This value is at the low end when compared to other biomass sources, due to the relatively low amounts of C6-sugars in the water hyacinth. Based on this maximum yield of LA, it can be estimated that a hectare of lake occupied by water hyacinth has the potential to produce LA at a rate of ~ 9 ton year^{-1}. Finally, a kinetic model originally developed for the acid-catalysed cellulose hydrolysis was adapted and applied to model the LA yield from the water hyacinth plant. A good fit between the experimental data and the kinetic model was obtained.

(a) T = 150 °C, $C_{H_2SO_4}$ = 0.1 M, $x_{WH,0}$ = 1 wt %

(b) T = 150 °C, $C_{H_2SO_4}$ = 0.5 M, $x_{WH,0}$ = 5 wt %

(c) T = 150 °C, $C_{H_2SO_4}$ = 1 M, $x_{WH,0}$ = 1 wt %

(d) T = 175 °C, $C_{H_2SO_4}$ = 0.1 M, $x_{WH,0}$ = 1 wt %

(e) T = 175 °C, $C_{H_2SO_4}$ = 0.5 M, $x_{WH,0}$ = 5 wt %

(f) T = 175 °C, $C_{H_2SO_4}$ = 1 M, $x_{WH,0}$ = 1 wt %

Figure 6.8 Comparison of experimental data ($\square$: C_{GLC}; $\bigcirc$: C_{LA}) and kinetic model (solid lines).
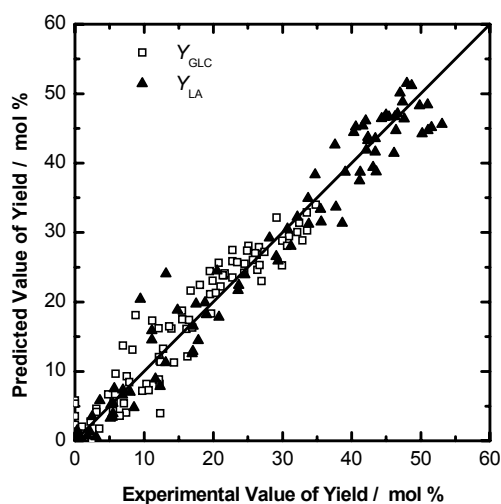
Figure 6.9 Parity plot for the experimental and modelled yield of glucose and LA.

6.6 Nomenclature

a_C	:	Reaction order for pure cellulose hydrolysis to glucose, [–]
b_C	:	Reaction order for pure cellulose decomposition to humins, [–]
c_1	:	Correction factor for the hydrolysis of water hyacinth to C6-sugars, [–]
c_{1WH}	:	Correction factor for R_{1WH}, [–]
c_2	:	Correction factor for the hydrolysis of water hyacinth to humins, [–]
c_{2WH}	:	Correction factor for R_{2WH}, [–]
c_{3WH}	:	Correction factor for R_{3WH}, [–]
c_{4WH}	:	Correction factor for R_{4WH}, [–]
C_{AA}	:	Acetic acid concentration, M
C_{ARA}	:	Arabinose concentration, M
C_{C6}	:	C6-sugars concentration, M
C_{CEL}	:	Cellulose concentration, M
C_{FUR}	:	Furfural concentration, M
C_{GLC}	:	Glucose concentration, M
$C_{C6,0}$	:	Initial concentration of C6-sugars in water hyacinth, M
C_{C6}	:	C6-sugars concentration, M
C_{HMF}	:	HMF concentration, M
$C_{H_2SO_4}$	:	Concentration of H_2SO_4, M
C_{LA}	:	LA concentration, M
C_{PA}	:	Propionic acid concentration, M
C_{WH}	:	Water hyacinth concentration, M
k_{1C}	:	Reaction rate constant for pure cellulose hydrolysis to glucose, min^{-1}
k_{2C}	:	Reaction rate constant for pure cellulose decomposition to humins, min^{-1}
$M_{C6\text{-sugars}}$	:	Molecular weight of C6-sugars, g mol^{-1}
M_{LA}	:	Molecular weight of LA, g mol^{-1}
m_{WH}	:	Mass of the oven-dried water hyacinth, g
R_1	:	Reaction rate of water hyacinth hydrolysis to C6-sugars, M min^{-1}
$R_{CEL \rightarrow GLC}$	:	Reaction rate of glucose formation from pure cellulose, M min^{-1}
$R_{CEL \rightarrow HUM}$	:	Reaction rate of humins formation from pure cellulose, M min^{-1}
R_{1G}	:	Reaction rate of C6-sugars decomposition to HMF, M min^{-1}
R_{1GAL}	:	Reaction rate of galactose decomposition to HMF, M min^{-1}
R_{1GLC}	:	Reaction rate of glucose decomposition to HMF, M min^{-1}
R_{1HMF}	:	Reaction rate of HMF decomposition to LA, M min^{-1}
R_{1WH}	:	Reaction rate of decomposition of cellulose fraction to glucose, M min^{-1}
R_2	:	Reaction rate of water hyacinth hydrolysis to humins, M min^{-1}
R_{2G}	:	Reaction rate of C6-sugars decomposition to humins, M min^{-1}
R_{2GAL}	:	Reaction rate of galactose decomposition to humins, M min^{-1}
R_{2GLC}	:	Reaction rate of glucose decomposition to humins, M min^{-1}
R_{2HMF}	:	Reaction rate of HMF decomposition to humins, M min^{-1}
R_{2WH}	:	Reaction rate of decomposition of hemicellulose fraction to glucose, M min^{-1}
R_{3WH}	:	Reaction rate of decomposition of hemicellulose fraction to galactose, M min^{-1}

R_{4WH}	:	Reaction rate of decomposition of water hyacinth to humins, M min^{-1}
t	:	Time, min
T	:	Temperature, K
$x_{WH,0}$	:	Initial intake of water hyacinth, wt %
Y_{GLC}	:	Yield of glucose, mol %
Y_{LA}	:	Yield of LA on a molar base, mol %
$Y_{LA,wt}$	:	Yield of LA on a weight base, mol %
$Y_{LA,total}$	:	Yield of LA based on the total mass of water hyacinth, mol %

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Summary

A substantial amount of research activities is currently carried out worldwide to identify attractive chemical transformation for the conversion of biomass to bio-fuels and green added-value chemicals. This research specifically focuses on the conversion of the C6-sugars in the water hyacinth plant (*Eichhornia crassipes*) to levulinic acid (LA) through an acid-catalysed hydrolysis reaction. LA has been identified as a platform chemical for the synthesis of various organic chemicals (see Figure A) with applications in the polymer, fuel additive and organic solvent industries.
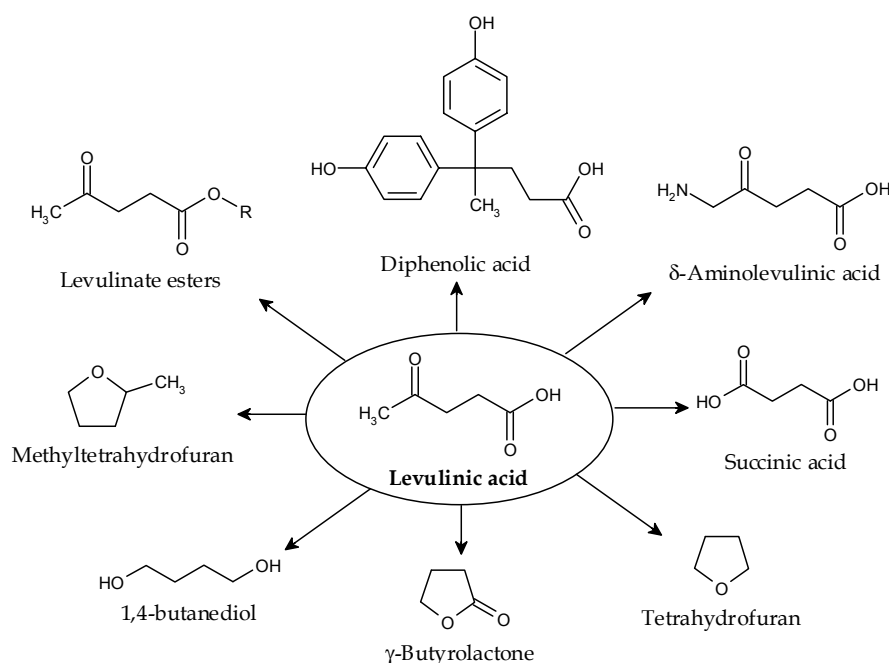
Figure A Potentially interesting derivatives of LA.

The water hyacinth plant grows extremely fast and growth rates up to 100–140 ton dry material per ha per year have been reported. As such, the water hyacinth plant is as an excellent biomass feedstock for further conversions, for example to LA. To define optimum reaction conditions and to develop efficient reactor configurations for the conversion of the C6-sugars in the water hyacinth plant to LA, the kinetics of the various chemical reactions involved should be determined.

The water hyacinth plant, like all lignocellulosic biomass sources, is a complex material consisting of cellulose and hemicellulose polymers that are bound together by lignin. Cellulose and hemicellulose are both involved in the

conversion of the water hyacinth plant to LA according to a complex reaction network (Figure B). A number of side reactions also produce by-products (*e.g.* insoluble humin compounds), increasing the complexity of the reaction network. Both the intermediates and by-products complicate the development of a kinetic model for the conversion of the C6-sugars in the water hyacinth plant to LA considerably. Therefore, a stepwise approach was applied by investigating the kinetics of the individual reactions separately, starting with 5-hydroxymethyl-furfural (HMF).
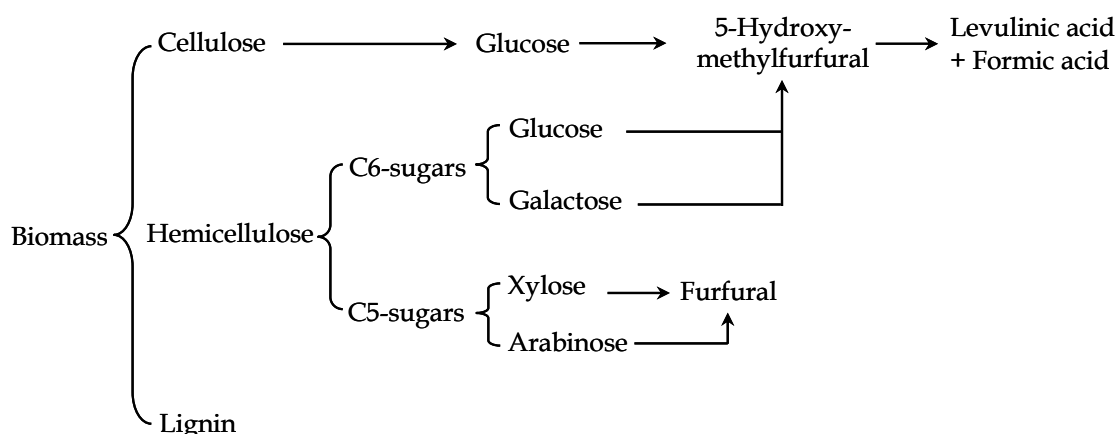
Figure B Simplified reaction scheme for the conversion of the water hyacinth plant to LA.

The first step was to select the optimal acid catalyst with respect to activity and selectivity towards LA. A catalyst-screening study on the conversions of 5-hydroxymethylfurfural (HMF) and glucose to LA is reported in *Chapter 2*. The catalytic activities of various types of acids (homogeneous and heterogeneous Brønsted acids) were tested. In the case of the reaction of HMF to LA, sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and hydrobromic acid (HBr) showed the highest catalytic activities and LA yields. The HMF conversion and the LA yield are correlated with the concentration of H^+ in solutions, indicating the absence of anion effects. When using glucose, H_2SO_4 and HCl showed the highest catalytic activities and LA yields. It was proven that the products LA and formic acid neither auto-catalyse the decomposition reactions of glucose to LA nor that of HMF to LA. Of the solid acid catalysts tested, ZSM–5 gave very promising result for the conversion of HMF to LA. With ZSM–5, catalyst recycle may be more facile than with sulphuric acid, leading to simplified catalyst recycling strategies. However, further optimisation studies will be required to identify whether it can be a replacement for sulphuric acid.

Chapter 3 describes an in-depth experimental and modelling study on the acid-catalysed decomposition of HMF to LA in a batch reactor. Earlier studies generally focused only on the overall decomposition rate of HMF without discriminating between the rates of the main reaction to LA and the side reaction to humins. Therefore, a general kinetic expression for a broad range of temperatures, catalyst

concentration and initial concentration of HMF for the main reaction as well as the side reaction was developed using the power law approach. The kinetic experiments were performed in a temperature window of 98–181 °C, acid concentrations between 0.05–1 M and initial HMF concentrations between 0.1 and 1 M. The highest LA yield is obtained (94 mol %) at high acid concentrations (1 M) and low initial HMF concentrations (0.1 M) and is essentially independent of the temperature. Agreement between experimental data and kinetic model is good. The rate expressions were applied to gain insights in optimum process conditions for batch processing. The highest LA yield at a short batch times is obtained at high temperature, a low initial concentration of HMF and a high acid concentration.

A kinetic study on one of the key steps in the conversion of biomass to LA, i.e., the acid-catalysed dehydration of glucose to LA, is reported in *Chapter 4*. Glucose decomposes in a consecutive reaction mode to give LA as the final product with HMF as the intermediate. Glucose as well as HMF decomposes in parallel reaction modes to give insoluble humins as the by-products. The kinetic 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. The highest yield was about 60 mol % at an initial glucose concentration of 0.1 M, a sulphuric acid concentration of 1 M and a temperature of 140 °C. A kinetic model using the power law approach was developed. Comparison of the experimental data and the output of the kinetic model showed a good fit for a broad range of reaction conditions. Optimisation for a batch reactor revealed that the yields of LA are highest when applying low temperature, high sulphuric acid concentration and low initial concentrations of glucose. The kinetic model also 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 (e.g., a continuously ideally stirred tank reactor, CISTR).

A systematic kinetic study on the acid-catalysed hydrolysis of cellulose to LA using sulphuric acid as the catalyst is reported in *Chapter 5*. A broad range of reaction conditions was applied, including variations in temperature between 150 and 200 °C, sulphuric acid concentrations between 0.05 and 1 M and initial cellulose intakes between 1.7 and 14 wt %. The kinetic models of HMF and glucose decomposition were used as input to develop a novel kinetic model for the reaction, including the side reactions to humins. A good-fit between experimental data and modelling results was obtained. The highest yield of LA (60 mol %) may be obtained at the low end of the temperature window (150 °C), a low initial cellulose concentration (1.7 wt %) and a high sulphuric acid concentration (1 M). The kinetic expressions were also used to gain insights into the optimum process condition for the conversion of cellulose to LA in continuous-reactor configurations. The model predicts that the highest attainable LA yield in continuous reactor configurations is about 76 mol %, which is obtained when using reactors with a large extent of back-mixing (e.g., a CISTR). The acid-

catalysed hydrolysis of cellulose is a heterogeneous reaction where mass transfer effects may play an important role and under some conditions may even determine the overall reaction rate. However, at our conditions, mass transfer limitations were shown to be absent by performing reactions with different cellulose particle sizes.

Experimental and modelling studies on the conversion of the C6-sugars in the water hyacinth plant to LA are described in *Chapter 6*. The chemical composition of the water hyacinth plant was determined, followed by systematic studies to optimise the LA yield by altering the reaction conditions (temperature, water hyacinth intake and acid concentration). The product distribution shows a strong dependency on the reaction conditions, and two distinct reaction pathways may be discriminated. At high acid-catalyst concentrations (> 0.5 M), LA is the major organic acid whereas at low catalyst concentration (< 0.1 M) and high initial intakes of water hyacinth, the formation of propionic acid instead of LA is favoured. The highest yield of LA was 53 mol % based on the available C6-sugars in the water hyacinth or 9 wt % based on dried water hyacinth. This value is at the low end when compared to other biomass sources, due to the relatively low amounts of C6-sugars in the water hyacinth plant. Based on this maximum yield of LA, it can be estimated that a hectare of lake occupied by the water hyacinth has the potential to produce LA at a rate of ~ 9 ton per year. Finally, a kinetic model originally developed for the acid-catalysed cellulose hydrolysis was adapted and applied to model the LA yield from the water hyacinth plant. A good fit between the experimental data and the kinetic model was obtained.

Samenvatting (Dutch Summary)

Er is wereldwijd grote belangstelling voor de inzet van biomassa voor het opwekken van energie en het maken van groene chemicaliën. Het onderzoek beschreven in dit proefschrift concentreert zich op de conversie van de C6-suikers in de water hyacint plant (*Eichornia crassipes*) naar levuline zuur (LA) door een zuur gekatalyseerde hydrolyse reactie. LA is geïdentificeerd als een zeer aantrekkelijk platform chemicalie, mede omdat het omgezet kan worden in een breed scala aan interessante derivaten (zie Figuur A) met toepassingen in de polymeer, brandstof additieven en oplosmiddelen industrie.
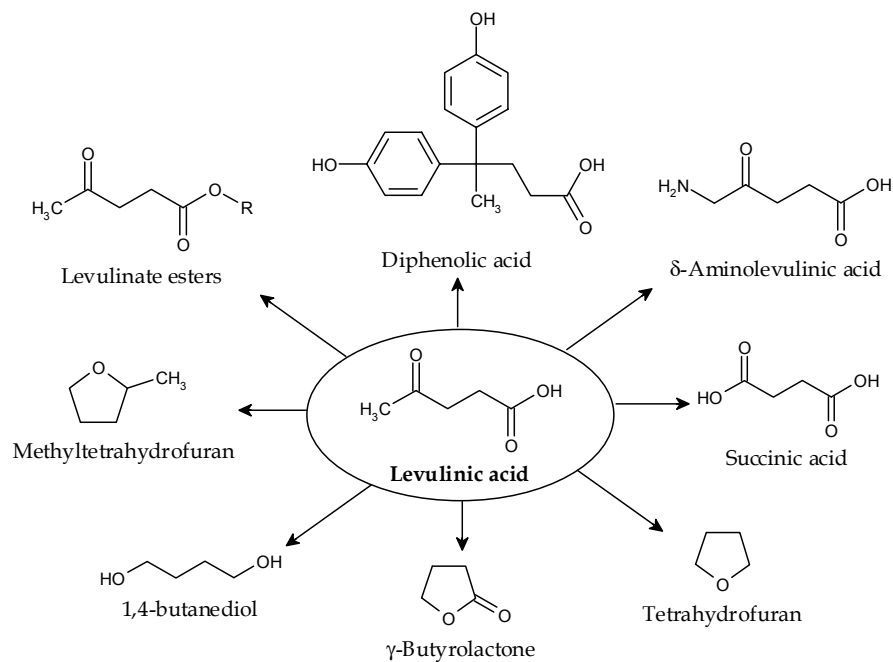
Figuur A Potentieel interessante derivaten van levuline zuur.

De water hyacint plant heeft vanwege de enorme groeisnelheid wereldwijd grote problemen gecreëerd op meren en waterwegen. Het blijkt dat de plant 100–140 ton droog materiaal per hectare per jaar kan aanmaken. Mede daarom is de water hyacint een potentieel zeer interessante lignocellulosische biomassa bron voor verdere conversie naar chemicaliën als LA.

De water hyacint plant bestaat, net als vele andere vormen van lignocellulosische biomassa, uit cellulose en hemicellulose in een lignine matrix. De C6-suikers in deze matrix zijn de bron voor LA (Figuur B). Voor het bepalen van de optimale reactie condities en voor de ontwikkeling van efficiënte reactor

configuraties, moet de kinetiek van de chemische reacties als weergegeven in Figuur B bekend zijn. Helaas is dit niet het geval. Het bepalen van de kinetiek van de afzonderlijke stappen is dan ook een van de belangrijkste doelstellingen van het onderzoek beschreven in dit proefschrift. Vanwege de complexiteit is een stapsgewijze aanpak toegepast, startende met de conversie van 5-hydroxymethylfurfural (HMF) naar LA.
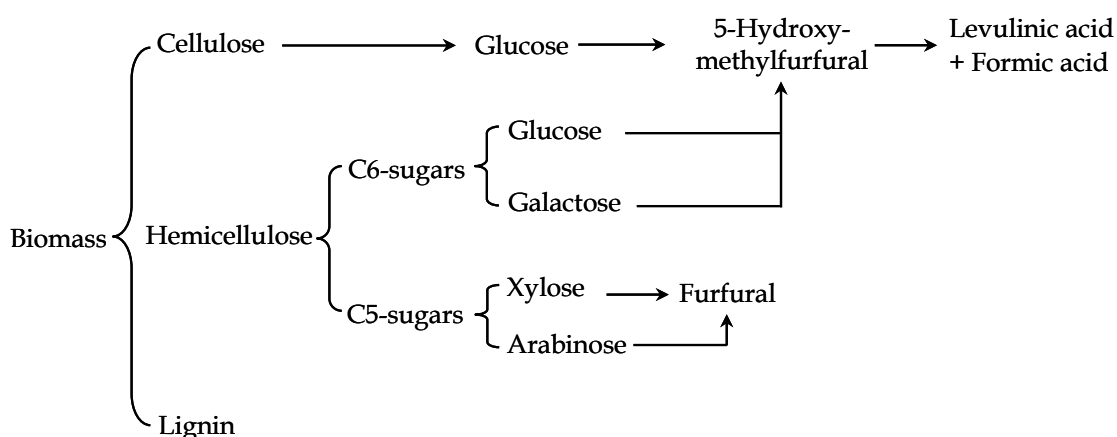
Figuur B Gesimplifeerd reactie schema voor de zuur gekatalyseerde hydrolyse van de water hyacint

In eerste instantie is onderzoek verricht naar de beste katalysator voor de reacties. Een katalysator screening studie voor de conversie van 5-hydroxymethylfurfural (HMF) en glucose naar LA wordt beschreven in *Hoofdstuk 2*. De katalytische activiteit van verschillende typen zuren (homogene en heterogene Brønsted zuren) is bepaald. In het geval van de reactie van HMF naar LA laten zwavelzuur (H_2SO_4), zoutzuur (HCl) en waterstof bromide (HBr) de hoogste katalytische activiteit en LA opbrengst zien. De conversie van HMF en de LA opbrengst zijn gerelateerd aan de concentratie H^+ in oplossing, een indicatie voor de afwezigheid van anion effecten. Voor glucose laten H_2SO_4 en HCl de grootste katalytische activiteit en LA opbrengst zien. De reactieproducten, LA en mierenzuur, blijken de reacties van glucose naar LA niet te katalyseren. Van een serie vaste zure katalysatoren geeft ZSM-5 de meest belovende resultaten voor de conversie van HMF naar LA. Bij het gebruik van vaste zuren als ZSM-5 is katalysator recycling veel makkelijker dan met zwavelzuur.

Hoofdstuk 3 beschrijft een diepgaand experimenteel en modellering onderzoek naar de zuur gekatalyseerde reactie van HMF naar LA in een batch reactor. Eerdere studies concentreerden zich alleen op de ontledingssnelheid van HMF, zonder verschil te maken tussen de snelheden van de hoofdreactie naar LA en de zijreacties naar humines. In *Hoofdstuk 3* is een algemene kinetische vergelijking opgesteld met gebruik van de 'power-law' benadering. De kinetische experimenten zijn uitgevoerd in een temperatuursgebied van 98–181 °C, zuur concentraties van 0.05–1 M en initiële HMF concentraties van 0.1 and 1 M. De hoogste LA opbrengst (94 mol %) is behaald bij hoge zuur concentraties (1 M), lage

initiële HMF concentraties (0.1 M) en is relatief onafhankelijk van de temperatuur. De overeenkomst tussen de experimentele data en het kinetisch model is goed. De snelheids vergelijkingen zijn toegepast om inzicht te krijgen in de optimale proces condities voor een batch systeem. De hoogste LA opbrengst bij korte batch tijden is behaald bij een hoge temperatuur, een lage initiële HMF concentratie en een hoge zuur concentratie.

Hoofdstuk 4 beschrijft een kinetische studie naar de zuur gekatalyseerde dehydratie van glucose naar LA. Deze reactie verloopt via het intermediaire HMF (Figuur B). Zowel glucose als HMF kunnen ontleden naar onoplosbare humines. De kinetische experimenten zijn uitgevoerd in een breed temperatuur gebied (140–200 °C), met zwavelzuur als katalysator (0.05–1 M) en een initiële glucose concentratie tussen 0.1 en 1 M. De hoogste LA opbrengst was rond 60 mol % bij een initiële glucose concentratie van 0.1 M en een temperatuur van 140 °C. Vergelijking van de experimentele data en het kinetische model laten een goede fit zien voor een brede range aan temperaturen en reactie condities. Modelberekeningen laten zien dat de LA opbrengst in een batch reactor een maximum heeft bij lage temperaturen, hoge zwavelzuur concentratie en een lage initiële glucose concentratie. In het geval van continue reactor configuraties laat het kinetisch model zien dat de hoogste opbrengst kan worden behaald bij toepassing van verdunde glucose oplossingen, een hoge concentratie van zwavelzuur als katalysator en het gebruik van een reactor configuratie met een hoge mate van menging (bv. een geroerde tank reactor, CSTR).

Een systematische kinetische studie van de zuur gekatalyseerde hydrolyse van cellulose naar levuline zuur met zwavelzuur als katalysator wordt beschreven in *Hoofdstuk 5*. Een brede range aan reactie condities is toegepast (variaties in temperatuur tussen 150 en 200 °C, zwavelzuur concentraties tussen 0.05 en 1 M en initiële glucose concentraties tussen de 1.7 en 14 wt %). Het kinetisch model voor de reactie van glucose naar LA is gebruikt als uitgangspunt voor de ontwikkeling van een nieuw model voor de reactie van cellulose naar LA. De hoogste opbrengst aan levuline zuur (60 mol %) is behaald bij de 150 °C, een lage initiële cellulose concentratie (1.7 wt %) en een hoge zwavelzuur concentratie (1 M). De kinetische vergelijking is ook gebruikt om inzicht te krijgen in de optimale proces condities voor de conversie van cellulose naar levuline zuur in continue reactor configuraties. Het model voorspelt dat de hoogst haalbare opbrengst voor levuline zuur ongeveer 76 mol % is bij het gebruik van een reactor met een hoge mate van menging (bv. CSTR). De zuur gekatalyseerde hydrolyse van cellulose is een heterogene reactie waar massa transport effecten een grote rol kunnen spelen en voor sommige condities zelfs volledig de overall reactie snelheid kunnen bepalen. Experimenten met cellulose van verschillende deeltjesgroottes laten geen verschillen in de LA opbrengsten zien, een indicatie dat de reacties in het kinetische regime zijn uitgevoerd en dat de intrinsieke kinetiek bepaald is.

Een experimentele studie naar de conversie van de C6-suikers in de waterhyacinth plant naar LA wordt beschreven in *Hoofdstuk 6* met als doel om na te gaan of geoogste water hyacint planten een geschikte biomassa bron zijn voor

de productie van LA. De chemische samenstelling van de water hyacint plant is bepaald, gevold door een systematische experimentele studie waar het effect van procescondities (temperatuur, water hyacint intake en zuur concentratie) op de LA opbrengst bepaald is. De product distributie is sterk afhankelijk van de katalysator concentratie en twee reactie wegen kunnen worden onderscheiden. Bij hoge zuurconcentraties (>0.5 M) wordt voornamelijk LA gevormd, bij lage zuur concentraties (<0.1 M) en hoge initiële intakes van de water hyacint plant is de vorming van propionzuur dominant. De hoogste opbrengst van LA was 53 mol % gebaseerd op de beschikbare C6-suikers in de water hyacint plant ofwel 9 wt % gebaseerd op gedroogde water hyacint. Deze waarde is aan de lage kant vergeleken met andere biomassa bronnen. Dit is voornamelijk het gevolg van de relatief lage hoeveelheden aan C6-suikers in de water hyacint plant. Gebaseerd op deze opbrengst kan er ~ 9 ton LA per hectare per jaar geproduceerd worden. De experimentele resultaten zijn gemodelleerd op basis van een kinetisch model ontwikkelt voor de zuur gekatalyseerde cellulose hydrolyse naar LA (*Hoofdstuk 5*). Het model blijkt de experimentele data goed te voorspellen.

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List of Publications

1. Schaap, A. P.; **Girisuta, B.**; Heeres, H. J., The water hyacinth as a renewable feedstock for green (bulk) chemicals. *NPT Procestechnologie* **2004**, *11*, 10-11.

2. **Girisuta, B.**; Janssen, L. P. B. M.; Heeres, H. J., Green chemicals: From cellulose waste to levulinic acid. *Proceeding of the 6th Netherlands' Catalysis and Chemistry Conference* **2005**, Noordwijkerhout (the Netherlands), 7-9 March 2005 (*oral presentation*).

3. **Girisuta, B.**; Janssen, L. P. B. M.; Heeres, H. J., Green bulk chemicals: kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid. *Proceeding of the 7th World Congress of Chemical Engineering* **2005**, Glasgow (Scotland), 10-14 July 2005 (*oral presentation*).

4. **Girisuta, B.**; Janssen, L. P. B. M.; Heeres, H. J., Green chemicals: conversion of biomass to levulinic acid. *Proceeding of the 6th International Conference on Process Intensification* **2005**, Delft (the Netherlands), 27-29 September 2005 (*oral presentation*).

5. **Girisuta, B.**; Janssen, L. P. B. M.; Heeres, H. J., Green chemicals: A kinetic study on the conversion of glucose to levulinic acid. *Chem. Eng. Res. Des.* **2006**, *84*, 339-349.

6. **Girisuta, B.**; Janssen, L. P. B. M.; Heeres, H. J., A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid. *Green Chem.* **2006**, *8*, 701-709.

7. **Girisuta, B.**; Janssen, L. P. B. M.; Heeres, H. J., Dehydration of glucose to 5-hydroxymethylfurfural using aluminium salts as novel Lewis acid catalyst. *Proceeding of the 4th Asia Pacific Congress on Catalysis* **2006**, Singapore, 6-8 December 2006 (*oral presentation*).

8. **Girisuta, B.**; Janssen, L. P. B. M.; Heeres, H. J., Kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid. *Ind. Eng. Chem. Res.* **2007**, *46*, 1969-1708.

9. **Girisuta, B.**; Danon, B.; Manurung, R.; Janssen, L. P. B. M.; Heeres, H. J., Experimental and kinetic modelling studies on the acid-catalysed hydrolysis of the water hyacinth plant to levulinic acid. **2007** (*submitted to Bioresource Technology*).