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Experimental and kinetic modelling studies on the acid-catalysed hydrolysis of the water hyacinth plant to levulinic acid

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ABSTRACT

A comprehensive experimental and modelling study on the acid-catalysed hydrolysis of the water hyacinth plant (*Eichhornia crassipes*) to optimise the yield of levulinic acid (LA) is reported (T = 150–175 °C, $C_{H_2SO_4}$ = 0.1—1 M, water hyacinth intake = 1–5 wt%). At high acid concentrations (>0.5 M), LA was the major organic acid whereas at low acid concentrations (<0.1 M) and high initial intakes of water hyacinth, the formation of propionic acid instead of LA was favoured. The highest yield of LA was 53 mol% (35 wt%) based on the amount of C6-sugars in the water hyacinth (T = 175 °C, $C_{H_2SO_4}$ = 1 M, water hyacinth intake = 1 wt%). The LA yield as a function of the process 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.

1. Introduction

With an annual production of up to 1.7–2.0 × 10^{11} ton, biomass has been identified as an important source for alternative fuels and added-value chemicals (Huber et al., 2006; Kamm et al., 2006; Klass, 1998). However, only 6 × 10^9 ton of biomass are currently used for food and non-food applications (Zoebelin, 2001). 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 carbohydrates through fermentation and/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. Proper selection of the biomass feedstock is of paramount importance from both a techno- and socio-economical point of view. The biomass feedstock should not compete with the food chain and 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 limited amounts of fertilisers, 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 conversion and utilisation.

The water hyacinth plant (*Eichhornia crassipes*) is a free-floating aquatic plant originating from the Amazon River basin in South America. 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. The plant tolerates extremes in water level fluctuations, seasonal variations in flow velocity, nutrient availability, pH, temperature and toxic substances (Gopal, 1987). It can even grow at salinity levels up to 0.24% as was shown in Indonesia (Kikuchi et al., 1997). Extremely high growth rates of up to 100–140 ton dry material ha^{-1} $year^{-1}$ (Gunnarsson and Petersen, 2007; Nigam, 2002) were reported, depending on the location and time of the year. This growth rate is among the highest reported for a wide range of biomass sources (Nigam, 2002).

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 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 the water hyacinth. However, as removal of the weed

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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 hemicellulose and cellulose fractions of lignocellulosic materials are converted to soluble low molecular weight components.

Hemicellulose, a biopolymer consisting of C5- and C6-sugars, is degraded to various organic compounds, including oligo-saccharides (Garrote et al., 2003; Jacobsen and Wyman, 2002; Parajo et al., 2004), mono-saccharides (Gamez et al., 2004; Garrote et al., 2001; Herrera et al., 2003; Roberto et al., 2003; Schell et al., 2003), furfural from C5-sugars (Mansilla et al., 1998; Root et al., 1959), degradation products from furfural (Rose et al., 2000) and acetic acid (Jin et al., 2005).

The acid-catalysed hydrolysis of the cellulose fraction leads to a variety of (potentially) interesting bulk chemicals (Saeman, 1945; Xiang et al., 2003). An 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 industry or as blending component in biodiesel (Hayes et al., 2006). The reaction of LA with phenol is known to give diphenolic acid (Holmen, 1969) that can serve as a replacement for Bisphenol A in the production of polycarbonates, epoxy resins and other polymers (Bozell et al., 2000; Hayes et al., 2006; Werpy and Petersen, 2004). Other products derived from LA are δ-aminolevulinic acid, a biodegradable herbicide (Moens, 1999), succinic acid (Dunlop and Shelbert, 1954) and methyltetrahydrofuran (Elliott and Frye, 1999), a gasoline oxygenate (Bozell et al., 2000). Details on the properties and potential industrial applications of LA and its derivatives are provided in several reviews (Leonard, 1956; Timokhin et al., 1999).

The continuous production of LA from lignocellulosic biomass on (semi) commercial scale was initiated by the Biofine company (Bozell et al., 2000; Fitzpatrick, 1997; Hayes et al., 2006). To the best of our knowledge, the first commercial-scale plant for the conversion of lignocellulosic biomass to LA was built in Caserta, Italy (Ritter, 2006). The unit processes 3000 ton tobacco bagasse and paper mill sludge per year. The plant is applying the Biofine technology and the major products are LA and ethyl levulinate, the latter to be used as a fuel additive.

The aim of this study was to identify whether the 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.

2. Methods

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 23 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.

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 levulinic acid (98 wt%) [*123-76-2*] were obtained from Acros Organics (Geel, Belgium). Deionised water was applied to prepare the various solutions.

2.3. Experimental procedures

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 quantify the amounts of C5- and C6-sugars and acetyl groups (Sluiter et al., 2005). In the first stage, the water hyacinth was hydrolysed 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 (humins, insoluble lignin/lignin decomposition products and ash) using a micro-centrifuge (Omnilabo International B.V.) for approximately 15–20 min 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 Sugar column Aminex HPX-87P.

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 ($x_{WH,0}$). Subsequently, an aqueous solution (0.2–0.5 cm^3) 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 (humins, insoluble lignin/lignin decomposition products and ash) using a micro-centrifuge (Omnilabo International B.V.) for approximately 15–20 min at 1200 rpm. A certain amount of the clear solution was taken (100–200 μL) and diluted with water (2 cm^3). The composition of the solution was determined using HPLC equipped with a BioRad Organic Acid 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.

2.4. Analytical equipment

The composition of the liquid phase after the reaction was determined using an HPLC system consisting of a Hewlett Packard 1050 pump and a Waters 410 refractive index detector. Two different columns (Aminex HPX-87P and Aminex HPX-87H) were

applied. HPLC-grade water at a flow rate of 0.55 $cm^3\ min^{-1}$ was used as the mobile phase for the Aminex HPX-87P Sugar column 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 equipped with a CP-Porabond-Q column (length = 25 m and I.D. = 0.25 mm) and a HP 6890 detector. 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.

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 optimisation method.

2.6. Definitions of LA yield

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

$$Y_{LA}\ (\text{mol}\%) = \frac{C_{LA}}{C_{C6,0}} \times 100\% \quad (1)$$

In Eq. (1), $C_{C6,0}$ 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 of LA and the available C6-sugars in the water hyacinth:

$$Y_{LA,wt}\ (\text{wt}\%) = \frac{C_{LA} \times M_{LA}}{C_{C6,0} \times M_{C6\text{-sugars}}} \times 100\% \quad (2)$$

In Eq. (2), the terms M_{LA} and $M_{C6\text{-sugars}}$ 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 of the mass of LA and the total mass of the oven-dried water hyacinth ($Y_{LA,total}$):

$$Y_{LA,total}\ (\text{wt}\%) = \frac{C_{LA} \times M_{LA}}{m_{WH}} \times 100\% \quad (3)$$

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

3. Results and discussion

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 Fig. 1. Three distinct

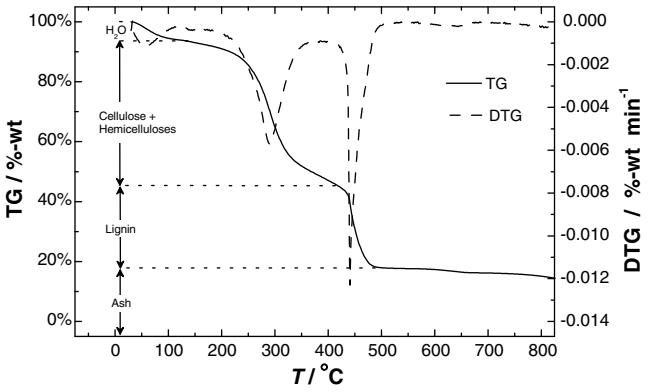


Fig. 1. Thermo Gravimetric (TG) and Differential Thermo Gravimetric (DTG) curves for oven-dried water hyacinth.

stages of weight losses were visible. The first-stage between 40 and 100 °C was attributed to evaporation of residual water (7.4 wt%), the second between 200–350 °C to cellulose and hemicelluloses degradation to volatiles (46.7 wt%) and the third between 420 and 500 °C for lignin decomposition (27.7 wt%). These temperature ranges are in line with a previous TGA study on lignocellulosic biomass (Negro et al., 2003). The residue (18.2 wt%) is non-combustible and is defined as the ash content of the water hyacinth. The composition of the ash fraction of the water hyacinth was reported by Gopal (1987) and consisted of K_2O (6.3–34.1%), Na_2O (1.8–1.88%), CaO (8.4–12.8%), Cl (3.9–21%) and $(PO_4)^3$ (2.8–8.2%), suggesting that the ash is basic in nature.

The composition of the sugar monomers in the water hyacinth was determined using a two-stage acid hydrolysis procedure. The total amount of C6-sugars was 26.3 wt% and consisted of glucose (19.8 wt%) and galactose (6.5 wt%). Mannose could not be detected. Details on the composition of C6-sugars in the water hyacinth plant are scarce. In most cases only the total amounts of cellulose were reported, which vary between 17.8 and 19.5 wt% (Abdelhamid and Gabr, 1991; Chanakya et al., 1993; Patel et al., 1993).

Two C5-sugars (xylose and arabinose) in the water hyacinth leaves were detected by HPLC in amounts of 11.5 and 9.0 wt%, respectively. Nigam (2002) reported similar amounts for xylose (12.4 wt%), whereas their reported arabinose level (2.2 wt%) was considerably lower (Nigam, 2002).

Significant amounts of acetic acid (1.1 wt%) were detected in the reaction mixture after the two-stage hydrolysis process. This acid is likely formed by hydrolysis of acetyl groups present in the hemicellulose fraction (Garrote et al., 2002; Jin et al., 2005).

The elemental composition of the water hyacinth leaves (dry basis) was determined by elemental analysis giving a C-content of 42.18%, a H-content of 6.41% and a N content of 4.25%.

3.2. Exploratory experiments

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

3.2.1. Results for 1.0 M sulphuric acid

Typical concentration profiles for the various water-soluble compounds when hydrolysing the water hyacinth leaves in a strong acidic medium (1.0 M sulphuric acid) are given in Fig. 2.

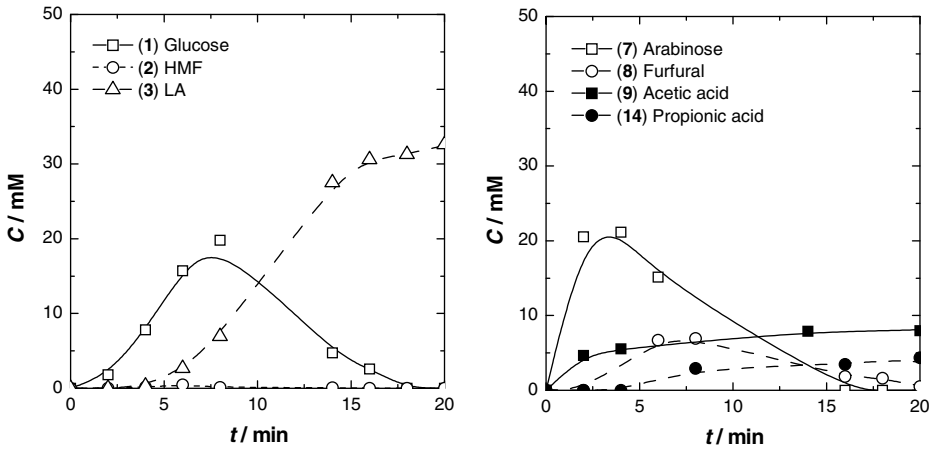


Fig. 2. Concentration profiles of reaction products from water hyacinth leaves (1.0 M sulphuric acid, $x_{WH,0}$ = 5 wt%, T = 175 °C).

At the end of the reaction, the amount of LA in the reaction mixture reached a constant level of about 32 mM, corresponding with a yield of 40 mol% on 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 found for LA.

A number of intermediate products arising from the cellulose and hemicellulose fraction of the water hyacinth leaves with clear maximum concentrations were detected (Fig. 2). These were identified as monomeric sugars (glucose and arabinose) as well as furan derivatives (5-hydroxymethylfurfural and furfural). The concentration profiles for galactose and xylose could not be obtained due to overlapping HPLC peaks (Aminex HPX-87H column). However, the combined peak areas of both sugars also showed a clear optimum, indicative for the occurrence of consecutive reaction pathways.

In all experiments, dark-brown insoluble products were formed. These are likely mixtures of humin type of by-products from the acid-catalysed decomposition of glucose and HMF (Girisuta et al., 2006a,b), the products of condensation reactions of C5-sugars and furfural (Root et al., 1959), residual insoluble lignin and ash.

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.

On the basis of the product composition and literature precedents for other biomass sources (Baugh and Mccarty, 1988; Grethlein, 1978; Khajavi et al., 2005; Mansilla et al., 1998), a simplified reaction pathway for the acid-catalysed hydrolysis of the cellulose and hemi-cellulose fraction of the water hyacinth is proposed (Scheme 1).

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 Fig. 3.

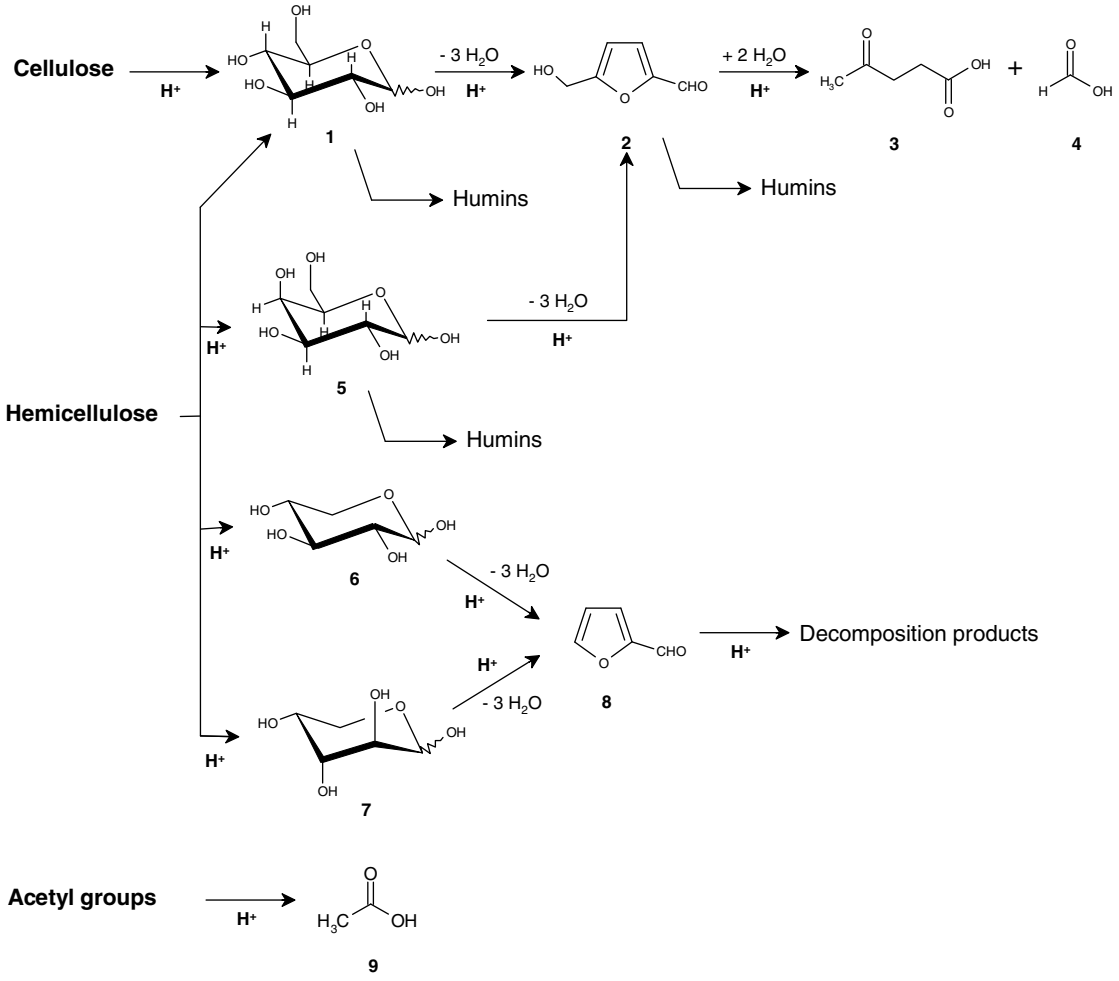
The amounts of LA at the end of the reaction when using 0.1 M sulphuric acid were considerably lower (1 mol%) than found for 1 M acid (40 mol%). One possible explanation for this observation is a reduction in the rate of formation of monomeric C6-sugars at low acid catalyst concentrations. Indeed, the maximum glucose concentration (8 mM) at 0.1 M was considerably lower than at 1 M sulphuric acid (20 mM).

On the contrary, the rates of formation and decomposition reactions involving the C5-sugars (xylose, arabinose) were not affected by the amount of acid catalyst. In both cases, significant amounts of C5-sugars (xylose and arabinose) were formed as well as furfural (Figs. 2 and 3). Furthermore, the maximum concentration of arabinose was about equal to the value observed at high acid catalyst concentrations. These observations indicate that breakdown of the hemicellulose fraction at low acid concentrations is still very facile. This is in line with earlier investigations on the acid-catalysed decomposition reactions of hemicellulose and is ascribed to the low crystallinity of this fraction (Parajo et al., 2004).

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.* Figs. 2 and 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 catalyst concentrations (Fig. 2) and was actually the major organic acid in the reaction mixture. Propionic acid likely originates from the C5-sugars of the hemicellulose fraction. Oeffner et al. studied the degradation of xylose in aqueous media at different pH values and found substantial amounts of propionic acid (Oefner et al., 1992). 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 was (partly) neutralised by the basic components in the (high) ash fraction of the water hyacinth (*vide supra*) (Malester et al., 1988; Springer and Harris, 1985). This explanation is also supported by the fact that the water hyacinth intake also had a profound effect on the organic acid 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 (Fig. 4). In strong acidic medium, the formation of levulinic acid was favoured, whereas propionic acid was the major acid formed at lower acidity.



Scheme 1. Simplified reaction network for the acid-catalysed hydrolysis reaction of the water hyacinth plant (1: Glucose, 2: 5-Hydroxymethylfurfural, 3: Levulinic acid, 4: Formic acid, 5: Galactose, 6: Xylose, 7: Arabinose, 8: Furfural, 9: Acetic acid).

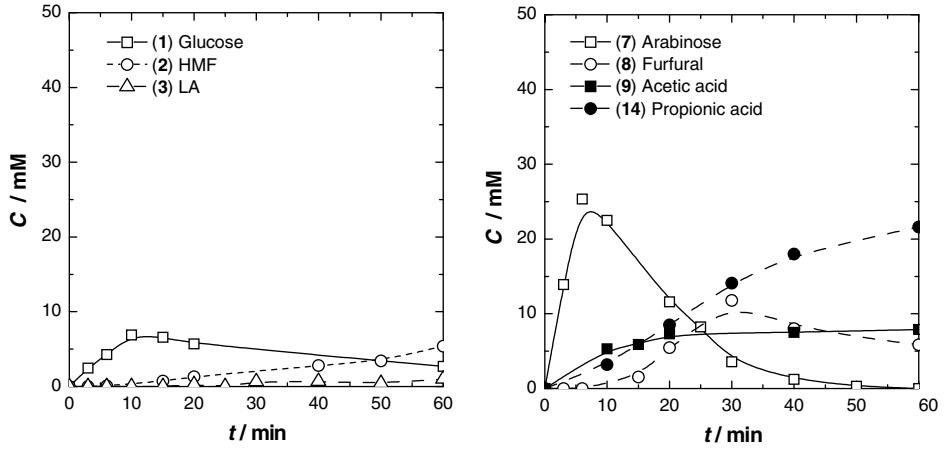


Fig. 3. Concentration profiles of reaction products from water hyacinth leaves (0.1 M sulphuric acid, $x_{WH,0}$ = 5 wt%, T = 175 °C).

3.3. Optimisation experiments

A total of 12 experiments were performed, differing in temperature, sulphuric acid concentration and intake of water hyacinth leaves. The results are given in Table 1. The highest experimental Y_{LA} was 53 mol% (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. The acid concentration had a profound effect on the Y_{LA}, with higher concentrations leading to higher yields. The temperature had a small but significant effect on the LA yield. The yield was reduced when performing the reaction at higher temperatures. These findings are in line with the experimental and model-

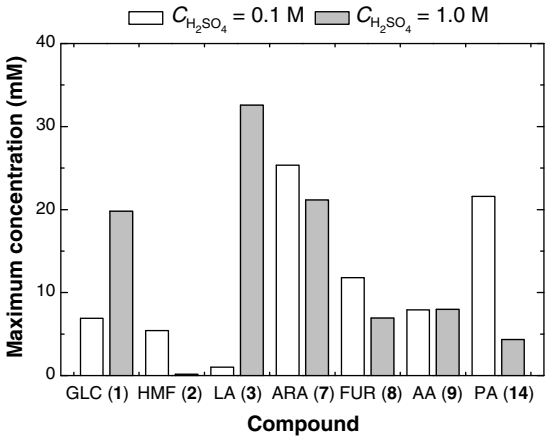


Fig. 4. Maximum concentrations of selected reaction products as a function of the acid catalyst concentration ($x_{WH,0}$ = 5 wt% and T = 175 °C).

Table 1
Experimental conditions and LA yield for the optimisation experiments[a]

No.	T (°C)	$C_{H_2SO_4}$ (M)	$x_{WH,0}$ (wt%)	t (min)	Y_{LA}[b] (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.
[b] Y_{LA} is defined in Eq. (2).

ling studies on the acid-catalysed hydrolysis of cellulose to LA (Girisuta et al., 2007).

Table 2 shows a comparison between the LA yields from earlier studies on a variety of lignocellulosic biomass sources with the results provided here for the water hyacinth leaves. Clearly, the yields of LA are depending on the biomass source and reaction conditions. High LA yields were 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 was relatively low and comparable with wood sawdust. This is the consequence of the relatively low amounts of C6-sugars in the water hyacinth leaves (26.3%, Table 2) compared to other lignocellulosic biomass sources (>40%).

The water hyacinth plant is a fast growing plant and growth rates up to ~100 dry ton ha^{-1} year^{-1} have been reported (Nigam, 2002). With the yield data reported in Table 2, the annual LA production rate can be as high as 9 ton ha^{-1}.

3.4. Development of a kinetic model for the acid-catalysed hydrolysis of water hyacinth leaves to LA

We recently published a kinetic model for the acid-catalysed hydrolysis of cellulose to LA (Girisuta et al., 2007). The model was validated in a 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 to the cellulose model were 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 based biopolymers 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 acid-catalysed hydrolysis of water hyacinth leaves is based on the following considerations and assumptions:

1. Among the sugars present in the water hyacinth leaves, 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. The formation of undesirable by-products in the form of humins is also taken into account (Girisuta et al., 2006a,b, 2007).
2. The reaction rates 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 were determined in previous studies in our laboratory (Table 3) and were used as input in the kinetic model (Girisuta et al., 2006a,b, 2007).
3. The first step in the acid-catalysed hydrolysis of water hyacinth leaves is the depolymerisation of the cellulose and hemicellulose fractions into their respective sugar monomers, and these reaction rates are represented as R_{1WH}, R_{2WH} and R_{3WH}. It is assumed that the lignin fraction is inert. To compensate for the fact that the properties of the cellulose fraction in the water hyacinth differs from that of pure cellulose (e.g. crystallinity), a correction factor (c_{1WH}) was applied:

$$R_{1WH} = c_{1WH} R_{CEL \rightarrow GLC} \quad (4)$$

where $R_{CEL \rightarrow GLC}$ represents the reaction rate of glucose formation from pure cellulose (Table 3, Girisuta et al., 2007).
4. The hemicellulose fraction is known to be more easily hydrolysed than cellulose. Unfortunately, no data are available for the rate of hydrolysis of the C6-sugars in the hemicellulose fraction of the water hyacinth leaves. Therefore, the depolymerisation

Table 2
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%)	References
Wood sawdust	190	20	50	1.5	HC1	0.5	9	36	Sassenrath and Shilling (1966)
Cane sugar	100	10	100	16	HC1	24	15	15	McKenzie (1929)
Bagasse	25–195	10	40	1.3	H_2SO_4	2	18	45	Ramos-Rodriguez (1972)
Corn starch	162	29	90	6.5	HC1	1	26	37	Thomas and Schuette (1931)
Starch	200	31	90	1.7	HC1	0.5	35	49	Moyer (1942)
Pulp slurry	160	10	60	6	HC1	1	41	68	Carlson (1962)
Water hyacinth	175	1	26.3	9.5	H_2SO_4	0.5	9	35 (53)[a]	This study

[a] The yield of LA defined on a molar base (Y_{LA}).

Table 3
Rate equations for the acid-catalysed decomposition of cellulose, glucose and 5-hydroxymethylfurfural (HMF)

Reaction	Reaction rate (M min^{-1})[a]	References
Cellulose hydrolysis to glucose	$R_{CEL\rightarrow GLC} = 0.410\exp^{\left[\frac{151.5}{R}\left(\frac{1}{T}-\frac{448}{4487}\right)\right]}(C_{H^+})^{0.96}(C_{CEL})^{0.98}$	Girisuta et al. (2007)
Cellulose hydrolysis to humins	$R_{CEL\rightarrow HUM} = 0.065\exp^{\left[\frac{174.7}{R}\left(\frac{1}{T}-\frac{448}{4487}\right)\right]}(C_{H^+})^{0.94}(C_{CEL})^{1.01}$	Girisuta et al. (2007)
Glucose decomposition to HMF	$R_{1GLC} = 0.013\exp^{\left[\frac{152.2}{R}\left(\frac{1}{T}-\frac{413}{4137}\right)\right]}(C_{H^+})^{1.13}(C_{GLC})^{1.09}$	Girisuta et al. (2006a)
Glucose decomposition to humins	$R_{2GLC} = 0.013\exp^{\left[\frac{164.7}{R}\left(\frac{1}{T}-\frac{413}{4137}\right)\right]}(C_{H^+})^{1.13}(C_{GLC})^{1.30}$	Girisuta et al. (2006a)
HMF decomposition to LA	$R_{1HMF} = 0.340\exp^{\left[\frac{110.5}{R}\left(\frac{1}{T}-\frac{413}{4137}\right)\right]}(C_{H^+})^{1.38}(C_{HMF})^{0.88}$	Girisuta et al. (2006b)
HMF decomposition to humins	$R_{2HMF} = 0.117\exp^{\left[\frac{111.3}{R}\left(\frac{1}{T}-\frac{413}{4137}\right)\right]}(C_{H^+})^{1.07}(C_{HMF})^{1.23}$	Girisuta et al. (2006b)

[a] Activation energies are given in kJ/mol.

rates of hemicellulose to glucose (R_{2WH}) and galactose (R_{3WH}) were correlated to the rate of depolymerisation of pure cellulose ($R_{CEL\rightarrow GLC}$) by the following relations:

$$R_{2WH} = c_{2WH}R_{CEL\rightarrow GLC} \quad (5)$$

$$R_{3WH} = c_{3WH}R_{CEL\rightarrow GLC} \quad (6)$$

5. Part of the cellulose and hemicellulose fraction of the water hyacinth leaves is decomposed to humin type by-products (R_{4WH}):

$$R_{4WH} = c_{4WH}R_{CEL\rightarrow HUM} \quad (7)$$

In equation (7), $R_{CEL\rightarrow HUM}$ represents the decomposition rate of pure cellulose to the undesired humins (Table 3, Girisuta et al., 2007) and c_{4WH} is a correction factor to account for the differences in properties between the cellulose and water hyacinth matrix.

6. It is assumed that galactose decomposes in a similar fashion as glucose and forms HMF and subsequently LA and FA. The reaction rates of galactose to HMF (R_{1GAL}) and humins (R_{2GAL}) are assumed to be equal to the reaction rate of glucose (R_{1GLC} and R_{2GLC}):

$$R_{1GAL} = R_{1GLC} \quad (8)$$

$$R_{2GAL} = R_{2GLC} \quad (9)$$

Several additional experiments using pure galactose were 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 M). The experimental data were compared with the kinetic model developed earlier for the acid-catalysed decomposition of glucose (Fig. 5). Clearly, the rate of the acid-catalysed galactose decomposition is similar to that of glucose, proving the validity of this assumption.

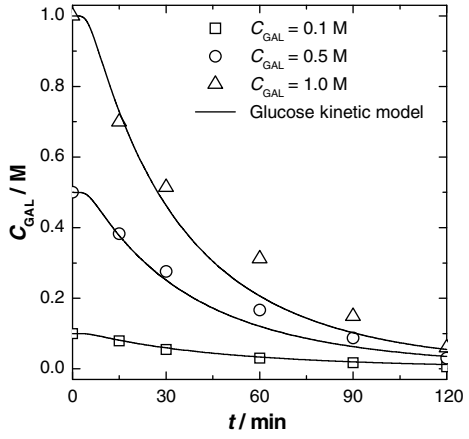


Fig. 5. Comparison of experimental data for galactose decomposition to LA with a kinetic model developed for glucose (T = 140 °C and $C_{H_2SO_4}$ = 1.0 M).

7. In case the rates of the decomposition reaction of galactose and glucose are equal (*vide supra*), the proposed reaction network can be simplified considerably by introduction of an overall reaction rate of C6-sugar monomers from the water hyacinth leaves (R_1):

$$R_1 = R_{1WH} + R_{2WH} + R_{3WH} = (c_{1WH} + c_{2WH} + c_{3WH})R_{CEL\rightarrow GLC} = c_1R_{CEL\rightarrow GLC} \quad (10)$$

The reaction rate of humins from the water hyacinth leaves (R_2) is given by:

$$R_2 = R_{4WH} = c_{4WH}R_{CEL\rightarrow HUM} = c_2R_{CEL\rightarrow HUM} \quad (11)$$

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

$$C_{C6,0} = \frac{\text{mass of water hyacinth} \times \text{ wt\% of C6-sugars in water hyacinth}}{\text{molecular weight of C6-sugar} \times \text{ volume of reaction mixture}} \quad (12)$$

9. At the start-up of the reaction, the temperature in the reactor was not constant and the reaction proceeded non-isothermal. Additional experiments according to a published procedure (Girisuta et al., 2006a,b) 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 the concentrations of the individual species as a function of time may be represented by the following set of ordinary differential equations:

$$\frac{dC_{WH}}{dt} = -R_1 - R_2 \quad (13)$$

$$\frac{dC_{C6}}{dt} = R_1 - R_{1GLC} - R_{2GLC} \quad (14)$$

$$\frac{dC_{HMF}}{dt} = R_{1GLC} - R_{1HMF} - R_{2HMF} \quad (15)$$

$$\frac{dC_{LA}}{dt} = R_{1HMF} \quad (16)$$

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 experimental data were modelled using the mass balances (Eqs. (13)–(16)) and rate equations (Eqs. (10) and (11) and data provided in Table 3). With this information, the reaction rates of monomeric C6-sugar formation (R_1) and humin formation (R_2) from the water hyacinth leaves may be determined and correlated with the known reaction rates for pure cellulose using the factors c_1 and c_2 (Eqs. (10) and (11)). The best estimates of the factors c_1 and c_2 were 0.74 ± 0.04 and 1.94 ± 0.18, respectively. A good fit between the experimental concentrations of glucose and LA and the kinetic model for a broad-range of reaction conditions was observed and confirmed

by a parity plot of the experimental and modelled concentrations of glucose and LA (relative errors of 6.9% and 2.8% for glucose and LA, respectively).

The factor c_1 is the summation of three constants, see Eq. (10) for details, and correlates the rate of formation of C6-sugars from both the cellulose and hemicellulose fraction of the water hyacinth with that of pure cellulose. The value of c_1 is less than 1, meaning that the rate of depolymerisation of C6-sugars from the water hyacinth matrix is lower than that of pure cellulose. The rate of decomposition of the hemicellulose fraction to C6-sugars (R_{2WH} and R_{3WH}) 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 lower than that from pure cellulose. This may be related to matrix effects (e.g. the presence of lignin) and/or difference in the cellulose properties (e.g. crystallinity).

4. Conclusions

The acid-catalysed hydrolysis of the water hyacinth to levulinic acid 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 water hyacinth intakes (1 and 5 wt%). The organic acid product distribution is a clear function of the reaction conditions and two distinct reaction pathways may be discriminated. At high sulphuric acid concentrations, LA is the major organic acid formed, whereas propionic acid is preferentially formed at low acid concentrations. The highest yield of levulinic acid 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 of the range when compared to other lignocellulosic biomass sources and is due to the relatively low amounts of C6-sugars in the water hyacinth leaves. Based on this maximum LA yield, an annual production rate of $\sim$9 ton ha^{-1} may be estimated. Finally, a kinetic model originally developed for the acid-catalysed hydrolysis of cellulose was adapted to model the LA yield from the water hyacinth plant. A good fit between the experimental data and the kinetic model was obtained.

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