
Levulinic Acid from Lignocellulosic Biomass

Buana Girisuta



**university of
 groningen**

The author thanks the University of Groningen for the financial support through an Ubbo Emmius Scholarship.

RIJKSUNIVERSITEIT GRONINGEN

Levulinic Acid from Lignocellulosic Biomass

Proefschrift

ter verkrijging van het doctoraat in de
Wiskunde en Natuurwetenschappen
aan de Rijksuniversiteit Groningen
op gezag van de
Rector Magnificus, dr. F. Zwarts,
in het openbaar te verdedigen op
maandag 5 november 2007
om 14.45 uur

door

Buana Girisuta
geboren op 15 augustus 1975
te Bandung, Indonesië

Promotores : Prof. dr. ir. H. J. Heeres
Prof. dr. ir. L. P. B. M. Janssen

Beoordelingscommissie : Prof. dr. A. A. Broekhuis
Prof. dr. J. G. de Vries
Prof. ir. G. J. Harmsen

ISBN 978-90-367-3228-4

ISBN 978-90-367-3229-1 (electronic version)

To Rina and my beloved parents

Table of Contents

1 Introduction

1.1 Biomass applications for energy generation and chemicals production	2
1.2 Biomass: definitions, composition and sources	3
1.3 Biomass valorisation using the biorefinery concept	6
1.4 Conversion of biomass to levulinic acid	7
1.4.1 Preparation methods of LA	8
1.4.2 Continuous production of LA	10
1.4.3 Mechanistic studies	13
1.5 Potential applications of LA and its derivatives	15
1.5.1 Reactions involving the carboxylic group	15
1.5.2 Reactions involving the carbonyl group	15
1.5.3 Reactions involving the methyl group	16
1.5.4 Oxidation reactions	17
1.5.5 Reduction reactions	18
1.6 Thesis Outline	18
1.7 References	19

2 Exploratory Catalyst-Screening Studies on the Conversion of 5-Hydroxymethylfurfural and Glucose to Levulinic Acid

2.1 Introduction	28
2.2 Materials and methods	29
2.2.1 Chemicals	29
2.2.2 Solid acid catalysts	29
2.2.3 Experimental procedure for the acid-catalysed decompositions of glucose and HMF	30
2.2.4 Adsorption phenomena of LA and FA on the ZSM-5 zeolites	31
2.2.5 Analytical methods	31
2.2.6 Definitions	31
2.3 Results and discussions	32
2.3.1 Acid-catalysed hydration reaction of HMF to LA	32
2.3.1.1 Homogeneous Brønsted acid catalysts	32
2.3.1.2 Solid acid catalysts	34
2.3.2 Acid-catalysed dehydration reaction of glucose to LA	37
2.3.2.1 Homogeneous Brønsted acid catalysts	37
2.3.2.2 Solid acid catalysts	38
2.4 Conclusions	38
2.5 Nomenclature	39
2.6 References	40

3 A Kinetic Study on the Decomposition of 5-Hydroxymethylfurfural into Levulinic Acid

3.1	Introduction	44
3.2	Experimental	45
3.2.1	Experimental procedure	45
3.2.2	Analytical methods	46
3.2.3	Heat transfer experiments	47
3.2.4	Determination of the kinetic parameters	48
3.3	Results and discussions	49
3.3.1	Acid screening	49
3.3.2	Reaction products	49
3.3.3	Effects of temperature, acid concentration and initial HMF concentration on HMF conversions and LA yields	51
3.3.4	Development of a kinetic model	52
3.3.4.1	<i>Modelling results</i>	54
3.3.4.2	<i>Alternative models</i>	56
3.4	Application of the kinetic model	57
3.4.1	Comparisons with literature models	57
3.4.2	Batch simulation and optimisation	58
3.5	Conclusions	59
3.6	Nomenclature	60
3.7	References	61

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

4.1	Introduction	64
4.2	Experimental	66
4.2.1	Experimental procedure	66
4.2.2	Analytical methods	67
4.2.3	Heat transfer experiments	67
4.2.4	Determination of the kinetic parameters	69
4.3	Results and discussions	69
4.3.1	Effects of process variables on the decomposition reaction of glucose	69
4.3.2	Development of a kinetic model for glucose decomposition to levulinic acid	71
4.3.3	Modelling results	76
4.4	Application of the kinetic model	78
4.4.1	Batch simulation and optimisation	78
4.4.2	Optimisation of continuous reactor systems	79
4.5	Conclusions	81
4.6	Nomenclature	81
4.7	References	83

5 A Kinetic Study on the Acid Catalysed Hydrolysis of Cellulose to Levulinic Acid

5.1	Introduction	86
5.2	Materials and methods	88
5.2.1	Chemicals	88
5.2.2	Experimental procedures	88
5.2.2.1	<i>Kinetic experiments</i>	88
5.2.2.2	<i>Heat-transfer experiments</i>	89
5.2.3	Method of analyses	90
5.2.4	Determination of the kinetic parameters	90
5.3	Results and discussions	91
5.3.1	Reaction products	91
5.3.2	Effects of process variables on the yield of LA	93
5.3.3	Kinetic modelling	96
5.3.3.1	<i>Development of a kinetic model</i>	96
5.3.3.2	<i>Modelling results</i>	99
5.3.3.3	<i>Evaluation of mass-transfer effects</i>	101
5.3.3.4	<i>Model implications</i>	103
5.3.3.5	<i>Comparisons with previous kinetic studies</i>	103
5.4	Applications of the kinetic model for reactor optimisation	104
5.4.1	Optimisation of LA production in a batch reactor	104
5.4.2	Optimisation of LA production in continuous reactors	106
5.5	Conclusions	108
5.6	Nomenclature	108
5.7	References	111

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

6.1	Introduction	114
6.2	Materials and methods	115
6.2.1	Water hyacinth	115
6.2.2	Chemicals	116
6.2.3	Experimental procedures	116
6.2.3.1	<i>Water hyacinth characterisation</i>	116
6.2.3.2	<i>Kinetic experiments</i>	116
6.2.4	Analytical equipment	117
6.2.5	Modelling techniques and software	117
6.2.6	Definitions of LA yield	118
6.3	Results and discussions	118
6.3.1	Determination of the water hyacinth composition	118
6.3.2	Exploratory experiments	120
6.3.2.1	<i>Results for 1.0 M sulphuric acid</i>	120
6.3.2.2	<i>Results for 0.1 M sulphuric acid</i>	123
6.3.3	Optimisation experiments	125

6.4 Development of a kinetic model for the acid-catalysed hydrolysis of water hyacinth to LA	128
6.5 Conclusions	132
6.6 Nomenclature	134
6.7 References	135
Summary	139
Samenvatting (Dutch Summary)	143
Acknowledgements	147
List of Publications	149

Chapter 1

Introduction

Abstract

In this chapter, a general overview of the use of biomass for chemical production and energy generation will be provided. Valorisation of biomass using the biorefinery concept will be introduced. It will be shown that levulinic acid (LA) is an interesting biomass-derived chemical. The conversion technology developed for the conversion of biomass to LA is reviewed. Subsequently, an extensive overview of the reactions of LA to interesting derivatives is provided, categorised according to functional group transformations. Finally, an outline of this thesis is provided.

1.1 Biomass applications for energy generation and chemicals production

The world is highly dependent on the utilization of fossil resources (e.g., petroleum, natural gas and coal) to fulfil its energy needs. Furthermore, a wide range of modern products like polymers, resins, textiles, lubricants, fertilizers, etc. are also derived from fossil resources. The consumption rate of fossil resources in the world has increased 50% in the period 1980–2004, and it is projected that the world needs 600×10^{15} Btu of fossil resources in 2030 as shown in Figure 1.1.

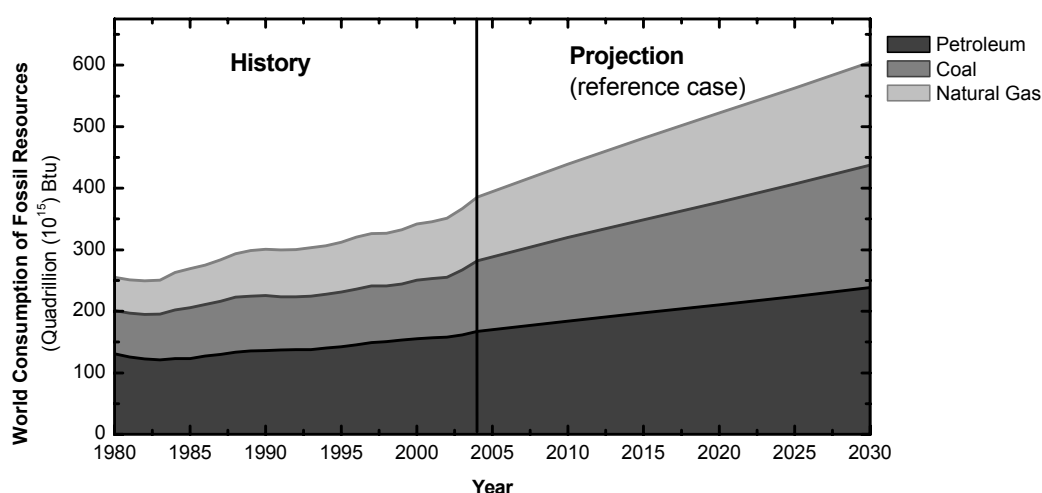


Figure 1.1 World consumption of fossil resources 1980–2030 (taken from [1]).

However, fossil resources are not-renewable and its availability is irrevocably decreasing. Due to high demands, a dramatic increase in the oil price was observed in the last decade (Figure 1.2). CO₂ emissions from burning of fossil resources have resulted in a major increase in the CO₂ concentration in the earth atmosphere. There is more and more evidence available that this will have a major impact on our global climate. These issues have stimulated the development of alternative renewable resources to substitute fossils. Biomass is a prime candidate because it is the only renewable resource of fixed carbon, which is essential for the production of conventional hydrocarbon liquid transportation fuel [2-7] and petrochemicals products [8,9].

To stimulate the transition from a fossil-based economy to renewable alternatives, active government participation is required. For example, the U.S. Department of Energy has set goals to replace 20% of the liquid petroleum transportation fuel with biofuels and to replace 25% of industrial organic chemicals with biomass-derived chemicals by 2025 [10]. Meanwhile, the European Union has targeted 2% of all petrol and diesel transport fuels to be biomass-derived by December 2005 and 5.75% by December 2010 [11].

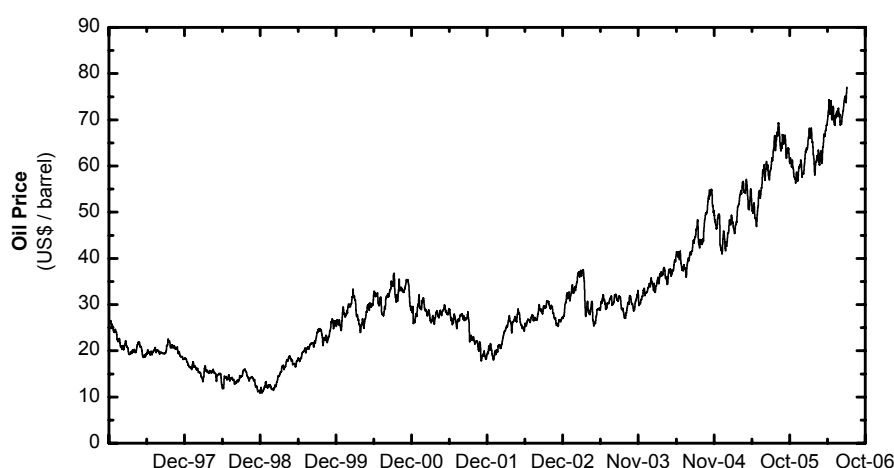


Figure 1.2 NYMEX Light Sweet Crude Oil price in the period 1997–2006 (taken from [12]).

1.2 Biomass: definitions, composition and sources

The term biomass is defined as any organic matter that is available on a renewable basis, including dedicated energy crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes and other waste materials [13]. The annual production of biomass is about $1.7\text{--}2.0 \times 10^{11}$ tons [14]; however, only 6×10^9 tons are currently used for food and non-food applications. Food applications are by far the most important (96.5–97%). The remainder is used in non-food applications, for example as a feedstock for the chemical industry.

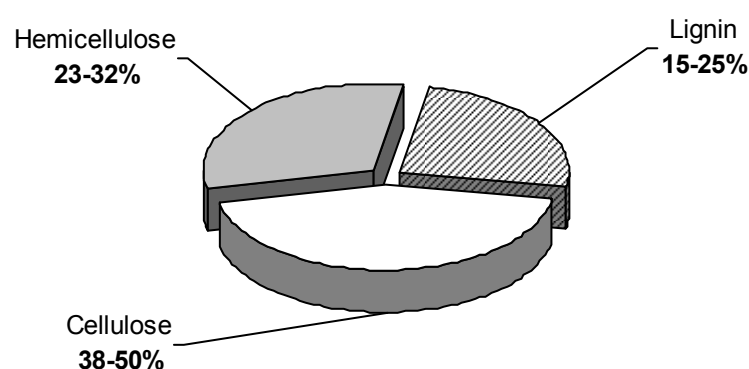


Figure 1.3 Distribution of important organic constituents in biomass (taken from [15]).

The chemical composition of biomass depends strongly on its source. Generally biomass consists of 38–50% of cellulose, 23–32% hemicellulose and 15–25% lignin (see Figure 1.3). Cellulose is a non-branched water-insoluble polysaccharide consisting of several hundred up to tens of thousands of glucose units. Cellulose is

the most abundant biopolymer synthesised by nature, its amount is estimated at approximately 2×10^9 tons year⁻¹ [16]. Hemicellulose is a polymeric material, although lower in molecular weight than cellulose, consisting of C6-sugars (glucose, mannose and galactose) and C5-sugars (mainly arabinose and xylose). The third component (lignin) is a highly cross-linked polymer made from substituted phenylpropene units (see Figure 1.4). It acts as glue, holding together the cellulose and hemicellulose fibres.

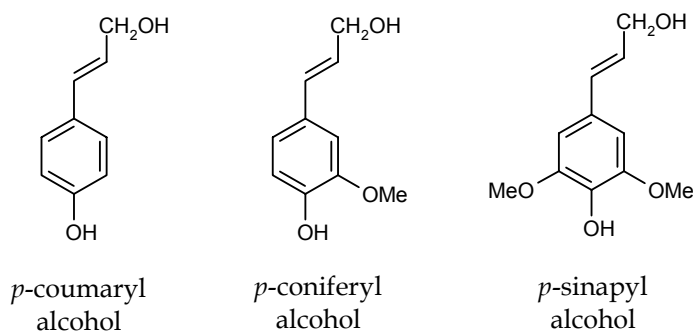


Figure 1.4 Molecular structures of the building blocks of lignin [17].

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 and has been selected as the biomass feedstock of choice for this thesis.

Water hyacinth (*Eichhornia crassipes*) is a free-floating aquatic plant originating from the Amazon River basin in South America. It was brought from its native habitat into the United States at the World's Industrial and Cotton Centennial Exposition of 1884–1885 in New Orleans, Louisiana [18,19]. Owing to its beautiful lavender flower, the water hyacinth was subsequently introduced to various countries as an ornamental plant and has spread to more than 50 countries on five continents [20–22]. The plant can be cultivated in various places (e.g., shallow temporary ponds, wetlands, marshes, sluggish flowing waters, large lakes, reservoirs and rivers) because it can tolerate extremes in water level fluctuations, seasonal variations in flow velocity and extremes with respect to nutrient availability, pH, temperature and toxic substances [20]. It can even tolerate salinity levels up to 0.24% as was shown in Indonesia [23].

The water hyacinth leaves (about 10–20 cm in diameter) are thick, waxy, rounded and glossy, and rise well above the water surface on stalks. The stalk is about 50 cm long, and carries about 8–15 flowers at the top (see Figure 1.5). The

flowers have six petals, purplish blue or lavender to pinkish, the uppermost petal with a yellow, blue-bordered central splotch. About 50% of the water hyacinth's biomass consists of the roots, which are fibrous (10–300 cm in length), feathery and purplish black. A typical chemical composition of water hyacinth is given in Table 1.1.



Figure 1.5 Water hyacinth (*Eichhornia crassipes*) (taken from [24]).

Table 1.1 Typical chemical composition of water hyacinth. ^a

Component	wt %
Moisture	85–95
Organic matter (dry basis)	
Cellulose	18–31
Hemicelluloses	18–43
Lignin	7–26
Ash (dry basis)	15–26
Elemental composition (dry basis)	
C	41.1– 43.7
H	5.3–6.4
O	27.5–28.8
N	1.5–4.3

^a Values are collected from [25-29,2].

The water hyacinth reproduces itself vegetatively through stolons and sexually by seeds [30]. Vegetative reproduction is more important than sexual reproduction and allows the plant to quickly cover large areas of water in relatively short periods of time. It doubles its population every 6 to 18 days, depending on the location and time of year. Extremely high growth rates of up to 100–140 ton dry material ha⁻¹ year⁻¹ have been reported [31,32], depending on the location and time

of the year. This enormous growth rate is among the highest reported for a wide range of biomass sources [31].

The coverage of waterways by water hyacinth has created various problems. Examples are destructions 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 [33] 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 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 as a suitable method to reduce the cost of the removal.

1.3 Biomass valorisation using the biorefinery concept

The utilisation of biomass for the production of non-food products has fostered research and development activities in various countries. To steer the research and development activities and to enhance market introduction, a novel concept was introduced: biorefining [34-36,13]. According to the American National Renewable Energy Laboratory (NREL) a biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass [37].

Biorefining aims for a complete valorisation of the biomass source by performing the overall processes with a minimum loss of energy and mass and to maximize the overall value of the production chain. It consists of an efficient fractionation of the biomass into various value-added products and energy using physical separation processes in combination with (bio-) chemical and thermo-chemical conversion steps. In that sense, the biorefinery concept has similar objectives as today's petroleum refineries.

Large-scale biorefinery systems are already operational; however, these existing systems deliver predominantly food products such as soy oil and soy protein, wheat starch and gluten, potato starch and protein. With the biorefinery concept, these existing biomass based production processes may be optimised and novel processes may be developed that are more energy and cost effectively so that they can also be applied for non-food uses.

Typically, three stages may be defined in a biorefinery:

1. Separation of the biomass into its components (cellulose, hemicellulose, lignin, proteins, amino acids, pure plant oil (PPO), minerals, fine chemicals and pharmaceutical compounds) in a primary fractionation/depolymerization unit. Typical technologies applied in this stage are

traditional separation processes like filtration, solvent extraction and distillation. However, novel concepts like supercritical CO₂ extractions and catalytic de-polymerization may also be explored.

2. Conversion of the intermediate fractions to valuable end products (e.g., bio-fuels) and chemical intermediates is performed in a secondary refinery process. Examples of chemical intermediates are conventional intermediates, such as alcohols or acids, and platform chemicals (*vide infra*) like levulinic acid, lactic acid or phenolic compounds. The secondary conversion processes may be distinguished into thermo-chemical processes (e.g., gasification, liquefaction) and biochemical processes (e.g., fermentation).
3. Further (catalytic) processing of the chemical intermediates to high added value end-products.

The residues of all process steps are applied for the production of power and heat. A schematic representation of a biorefinery process is given in Figure 1.6.

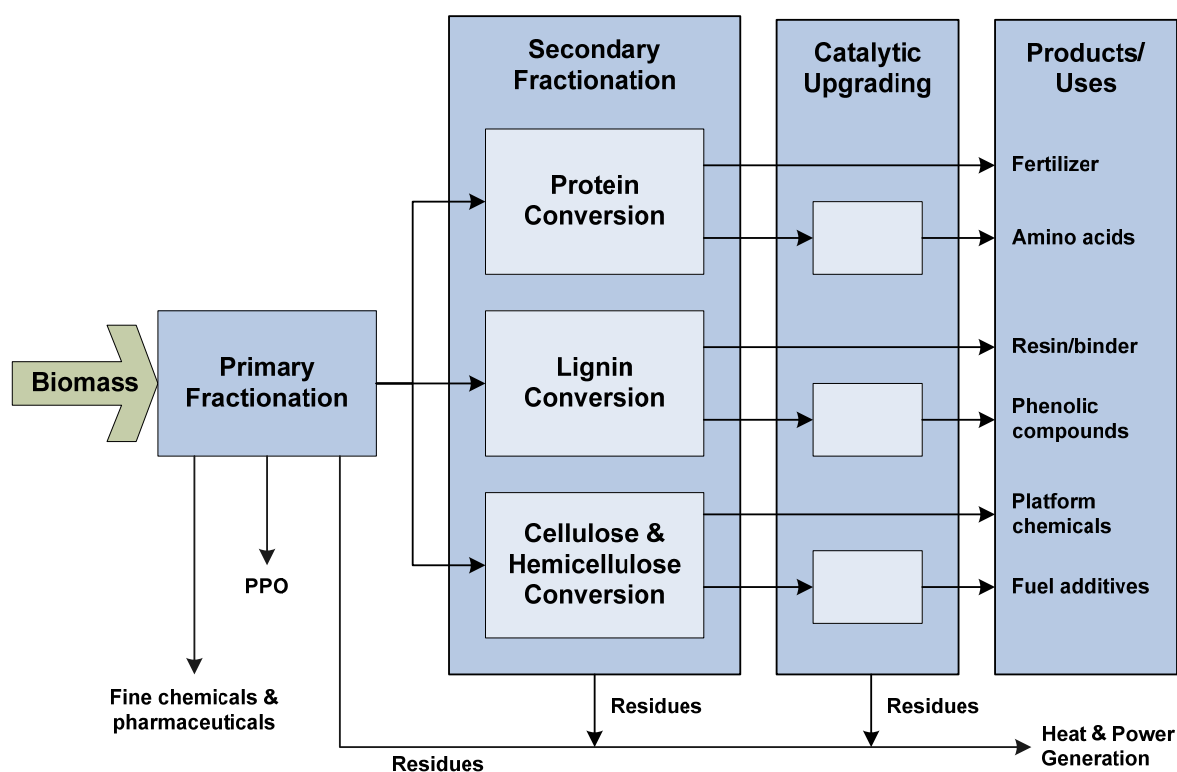


Figure 1.6 A simplified scheme of a biorefinery concept.

1.4 Conversion of biomass to levulinic acid

Researchers from NREL and PNNL (Pacific Northwest National Laboratory) have recently conducted an extensive study to identify valuable sugar-based building blocks for lignocellulosic biomass [38]. Of 300 initially selected

candidates, a long list of thirty-interesting-chemicals was obtained through an iterative process. The list was further reduced to twelve by evaluating the potential markets of the building blocks and their derivatives and the complexity of the synthetic pathways. One of these promising top-twelve building blocks is levulinic acid that is accessible from lignocellulosic biomass using an acid catalyst. The conversion of a typical lignocellulosic biomass to LA is shown in Figure 1.7.

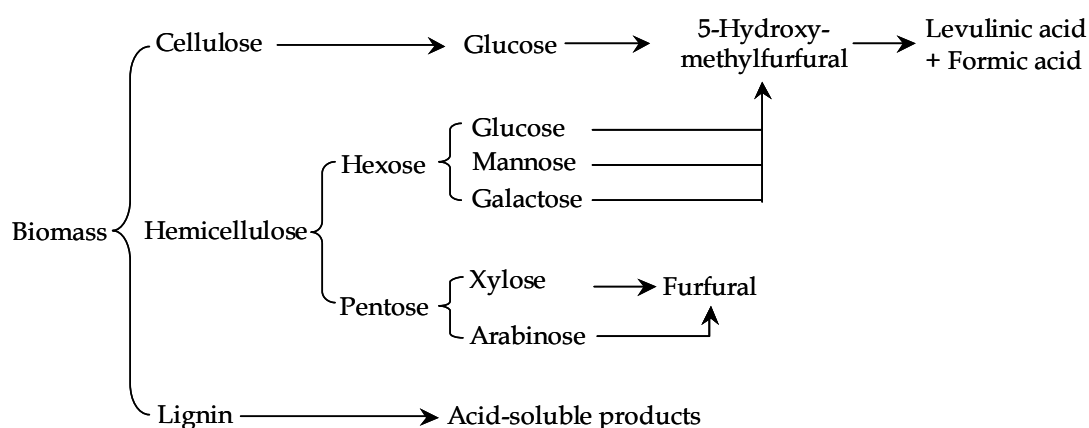


Figure 1.7 Simplified reaction scheme for the conversion of lignocellulosic biomass to LA.

Levulinic acid (**1**, LA), also known as 4-oxopentanoic acid or γ -ketovaleric acid, is a C5-chemical with a ketone and a carboxylic group. The presence of both groups results in interesting reactivity patterns [16]. LA is readily soluble in water, ethanol, diethyl ether, acetone and many other organic solvents. The dissociation constant (pK_a) of LA is 4.59 [39], which is comparable with low molecular weight aliphatic carboxylic acids. Some selected physical properties of LA are given in Table 1.2.

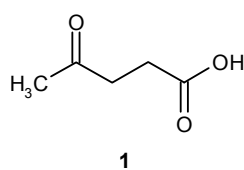
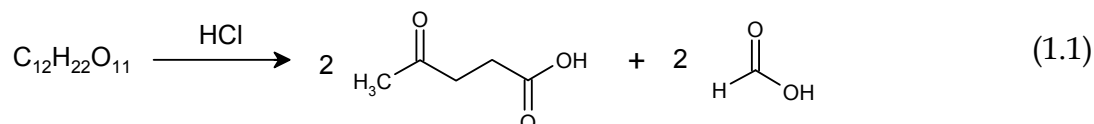


Table 1.2 Selected physical properties of LA [39].

Physical properties	Values
pK_a	4.59
Melting point	37 °C
Boiling point	246 °C
Density	1.14
Refractive index (20 °C)	1.1447
Surface tension (25 °C)	39.7 dyne cm ⁻¹
Heat of vapourisation (150 °C)	0.58 kJ mol ⁻¹
Heat of fusion	79.8 kJ mol ⁻¹

1.4.1 Preparation methods of LA

The first study on the preparation of LA was reported in the 1840s by the Dutch professor G. J. Mulder [40], who prepared LA by heating sucrose with mineral acids at high temperature (equation 1.1) [Note: Unfortunately, details on the reaction conditions and the LA yield are unknown].



The controlled degradation of hexose (C6-sugars) by acids is still the most widely used approach to prepare LA from lignocellulosic biomass. The theoretical yield of LA from C6-sugars is 100 mol %, or 64.5 wt % due to the co-production of formic acid [41]. Commonly, LA yields of about two thirds (or even less) than the theoretical value are attained. These lower yields are due to the formation of undesired black insoluble-materials called humins. Another possible by-product of biomass hydrolysis is furfural, formed by the decomposition reactions of C5-sugars. Table 1.3 gives an overview of LA synthesis using various types of feedstock and acid catalysts.

Table 1.3 Overview of acid catalysed production methods for LA.

Feedstock	C_0 (wt %) ^a	Acid	C_{acid} (wt %)	T (°C)	t (h)	Y_{LA} (wt %) ^b	Ref.
Cane sugar	28	HCl	18	100	24	15	[42]
Glucose	32	HCl	20	R.T. ^c	24	15	[43]
Corn starch	29	HCl	6.5	162	1	26	[44]
Sucrose	29	HCl	6.5	162	1	29	[44]
Glucose	29	HCl	6.5	162	1	24	[44]
Fructose	29	HCl	6.5	162	1	25	[44]
Hydrol ^d	42	HCl	7.4	R.T. ^c	22	25	[45]
Corn starch	33	HCl	1.8	200	0.5	35	[46]
Starch	26.5	HCl	5.2	R.T. ^c	24	19	[47]
Rice hulls	14	HCl	1	160	3	10.3	[48]
Rice straw	14	HCl	1	160	3	5.5	[48]
Corn stalks	14	HCl	1	160	3	7.5	[48]
Cotton linters	14	HCl	1	160	3	7.4	[48]
Sucrose	6	H ₂ SO ₄	9	125	16	30	[49]
Sucrose	6	HCl	9.7	125	16	43	[49]
Sucrose	6	HBr	9	125	16	50	[49]
Sucrose	27	Amberlite IR-120	19	R.T.	41	15.6	[50]
Fructose	27	Amberlite IR-120	19	R.T.	27	23.5	[50]
Glucose	27	Amberlite IR-120	19	R.T.	124	5.8	[50]
Glucose	5-20	H ₂ SO ₄	0.1-4	160-240	$f(T)$ ^e	35.4	[51]

Table 1.3 (continued)

Feedstock	C_0 (wt %) ^a	Acid	C_{acid} (wt %)	T (°C)	t (h)	Y_{LA} (wt %) ^b	Ref.
Pulp slurry	10	HCl	6	160	1	40.5	[52]
Glucose	10	HCl	6	160	0.25	41.4	[52]
Cotton stems	n.a. ^f	H ₂ SO ₄	5	180–190	2	6.13	[53]
Wood sawdust	20	HCl	1.5	190	0.5	9	[54]
Oakwood	n.a.	H ₂ SO ₄	3	180	3	17.5	[55]
Bagasse	9	H ₂ SO ₄	1.3	25–195	2	17.5	[56]
Fructose	4.5-18	HCl	2–7.5	100	24	52	[57]
Sucrose	20	Resin-Dowex	6.25	100	24	17	[58]
Sawdust	n.a.	HCl	8	n.a.	n.a.	6.9	[59]
Shredded paper	n.a.	HCl	8	n.a.	n.a.	17.2	[59]
Fructose	50	LZY-zeolite	50	140	15	43.2	[60]
Glucose	12	Clay-catalyst ^g	3	150	24	12	[61]
Glucose	12	HY-zeolite	3	150	24	6	[62]
Cellulose	10	H ₂ SO ₄	3	250	2	25.2	[63]
Various woods ^h	10-20	H ₂ SO ₄	5	200–240	2–4	13–18	[63]
Cellulose	10	H ₂ SO ₄	1–5	150–250	2–7	≤ 25.2	[64]
Cellulose	10	HCl	1–5	150–250	2–7	≤ 28.8	[64]
Cellulose	10	HBr	1–5	150–250	2–7	≤ 26.9	[64]
Aspen wood	10	H ₂ SO ₄	1–5	150–250	2–7	≤ 15.5	[64]
Aspen wood	10	HCl	1–5	150–250	2–7	≤ 12.4	[64]
Aspen wood	10	HBr	1–5	150–250	2–7	≤ 13.0	[64]
Newspaper	30	H ₂ SO ₄	10	150	8	12.8	[65]
Sorghum grain	10	H ₂ SO ₄	8	200	0.67	32.6	[66]
Extruded starch	25	H ₂ SO ₄	4	200	0.67	47.5	[67]
Wheat straw	6.4	H ₂ SO ₄	3.5	209.3	0.63	19.8	[68]

^a C_0 is the initial concentration of feedstock and defined as the ratio between the mass of feedstock and the total mass; ^b Y_{LA} is defined as the ratio between the mass of LA and the mass of feedstock; ^c R.T. = Refluxed Temperature; ^d Mother liquor of crystalline corn starch; ^e Time is a function of temperature; ^f n.a. = data is not available; ^g Fe-pillared montmorillonite; ^h Types of wood are beech, aspen, pine and spruce.

Other starting materials and reagents have also been applied. Examples are the hydrolysis of acetyl succinate ester [69], the acid hydrolysis of furfuryl alcohol [70,71] and the oxidation of ketones [72-74]. LA can also be prepared by a Pd-catalysed carbonylation of ketones [75] and by the alkylation of nitroalkanes [76]. However, all these methods result in relatively high amounts of various by products and require expensive feedstocks.

1.4.2 Continuous production of LA

Most of the studies provided in Table 1.3 were exploratory in nature and carried out in typical laboratory batch reactors. Evidently, continuous processing

for larger scale applications is advantageous. A continuous process for the production of LA from corncob furfural residue at atmospheric pressure was proposed by Dunlop and Wells (1957) [77] and is shown schematically in Figure 1.8. In this process, the carbohydrate feedstock (corncob furfural residue) is mixed with sulphuric acid and water to reach a concentration of corncob furfural residue of 21 wt % and an acid concentration of 3 wt %. Subsequently, the mixture is continuously passed through a reactor maintained at an elevated temperature (169 °C). Typical residence times are 2 h. The insoluble humins are separated from the product mixture in a filter unit. The aqueous mixture containing the acid catalyst and LA is then contacted with a water-immiscible solvent (methyl isobutyl ketone) to obtain an extract containing LA and an aqueous solution containing the acid catalyst. The latter is recycled to the mixer prior to the reactor. In an evaporator, the extraction solvent is separated from the LA and is recycled to the extraction column. Further concentration and purification of LA is carried out in a fractionation unit (vacuum distillation). With this process, a LA yield of 19.9 wt % based on the weight of the dry feedstock charged to the process was obtained.

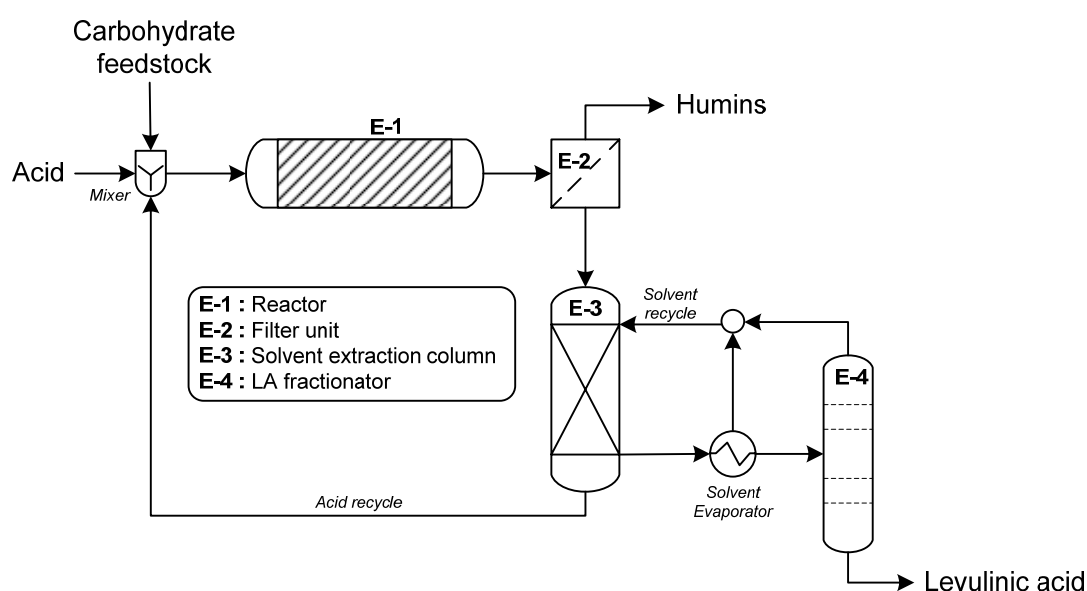


Figure 1.8 Continuous process for producing LA from corncob furfural residue [77].

Ghorpade and Hanna (1999) [78] proposed a concept based on reactive extrusion for the continuous production of LA. A simplified diagram of the process is shown in Figure 1.9. Corn starch, water and sulphuric acid are mixed in a pre-conditioner unit, and the slurry is then fed to a twin-screw extruder with a variable temperature profile of 80–100 °C, 120–150 °C and 150 °C. The product is filtered to separate the LA from the humins. The filtrate is then fed to a vacuum distillation unit to purify the LA. By feeding 820 kg h⁻¹ of corn starch, 40 kg h⁻¹ of sulphuric acid 5 wt % and 290 kg h⁻¹ of water, the yield of LA was about 48 wt %.

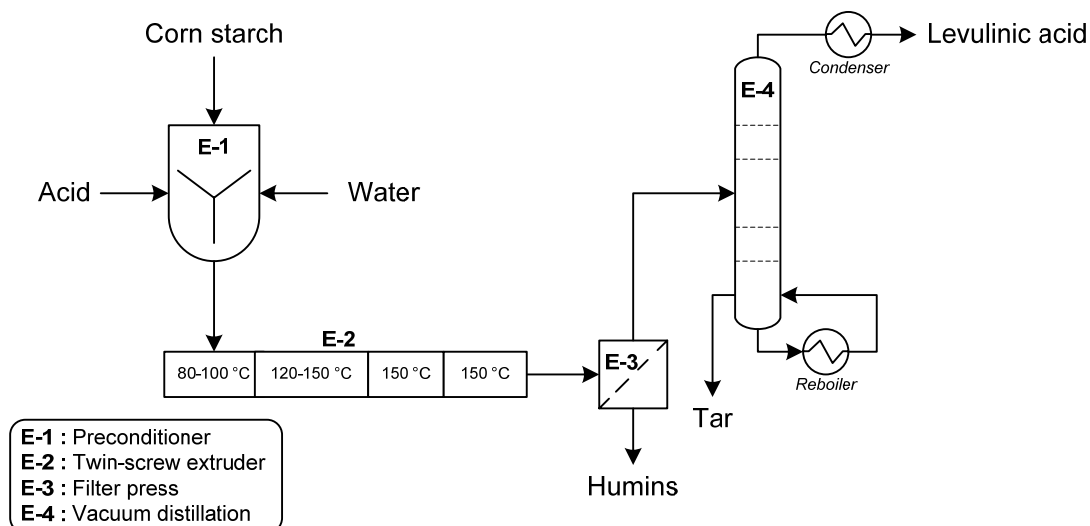


Figure 1.9 Production of LA using reactive extrusion [78].

Figure 1.10 shows the Biofine technology for the continuous production of LA [79], and typical yields of LA for the Biofine technology at different reaction conditions and intakes are given in Table 1.4. Carbohydrate feedstock and sulphuric acid catalyst solution are mixed, and the slurry is supplied continuously to a tubular reactor. This reactor is operated at a typical temperature of 210–220 °C and a residence time of only 12 s in order to hydrolyse the carbohydrate polysaccharide into their soluble monomers (hexose and pentose). This hydrolysis reaction is rapid according to their invention. The outflow of the first reactor is fed to a continuously stirred tank reactor operated at a lower temperature (190–200 °C) but with a longer residence time of 20 min. LA is removed by drawing-off liquid from the second reactor. The reaction conditions in the second reactor are chosen as such to vaporise formic acid and furfural, and the vapour is externally condensed to collect these side products. Solid by-products are removed from the LA solution in a filter-press unit.

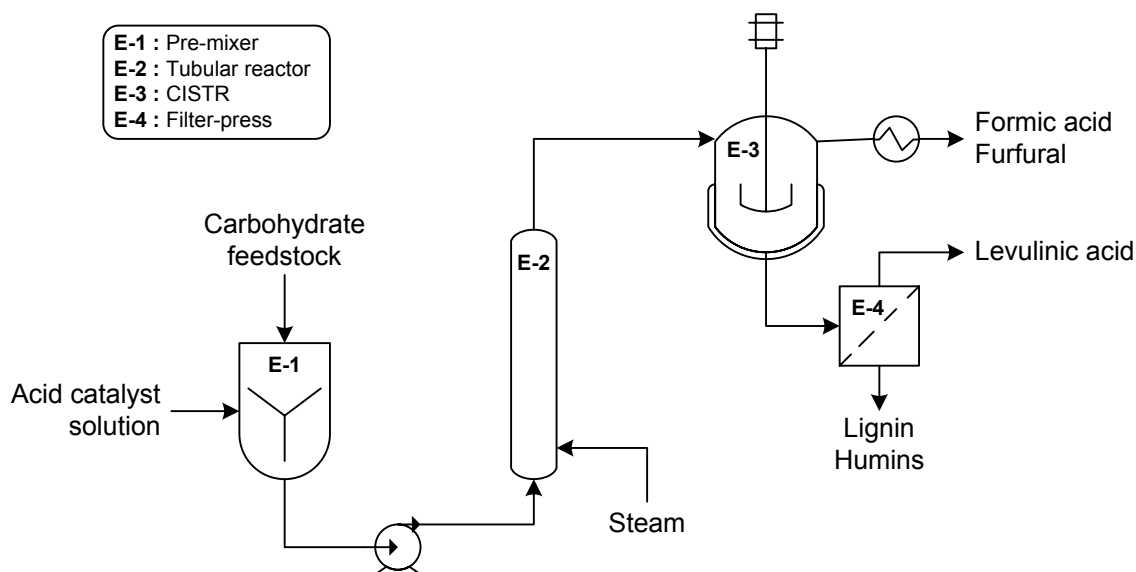


Figure 1.10 Continuous production of LA by the Biofine technology [79].

Table 1.4 Typical conditions for the Biofine process.

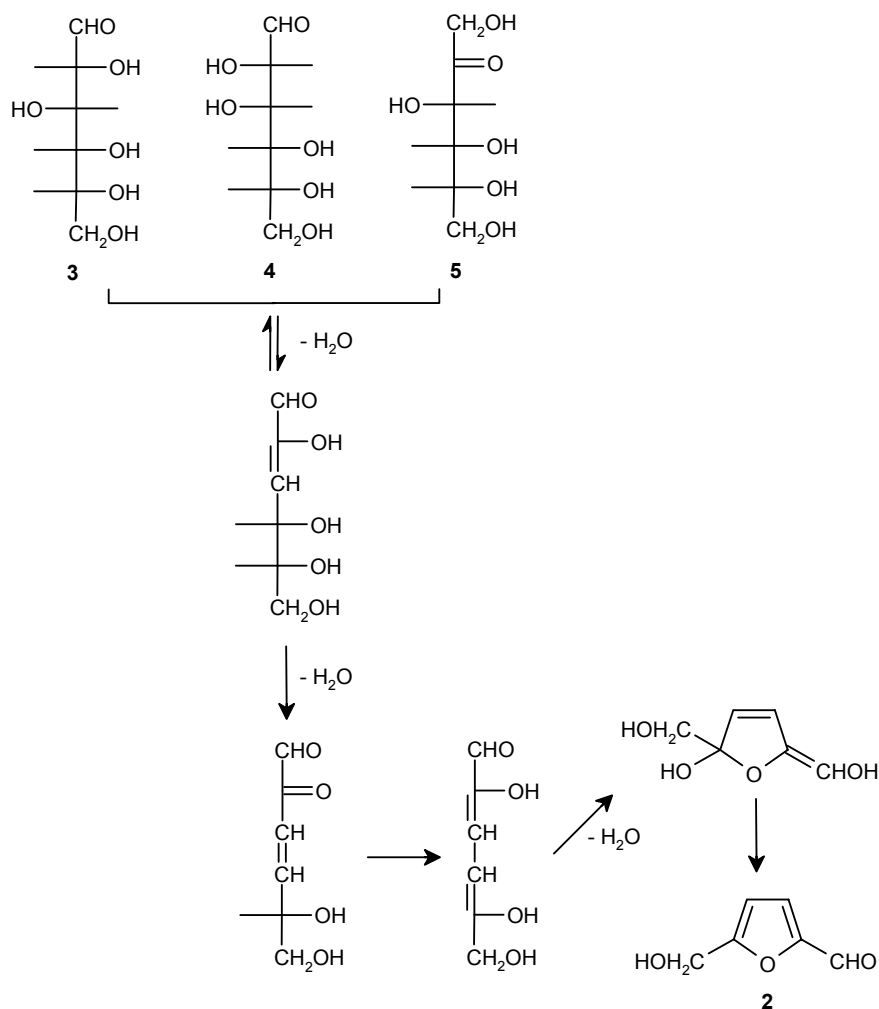
Feedstock (wt %) ^a	Feed (L min ⁻¹)	C ₀ ^b (wt %)	C _{H₂SO₄} (wt %)	T ₁ ^c (°C)	τ ₁ ^c (s)	T ₂ ^c (°C)	τ ₂ ^c (min)	LA outflow (kg min ⁻¹)	Y _{LA} ^d (wt %)
A (44 wt %)	0.945	4	3.5	232	14	196	30	0.0088	23
A (44 wt %)	0.96	2	1.9	215	14	200	20	0.0061	32
A (44 wt %)	0.32	10	3	232	23.3	206	29.8	0.0048	15
B (80 wt %)	1.02	1	1.15	220	14	200	20	0.0040	39
B (80 wt %)	1.04	2	1.5	215	14	200	25	0.0085	41
C (42 wt %)	0.70	10	5	220	15.7	210	20	0.0121	17

^a Feedstock A is a sludge of bleached kraft paper that contains 44 wt % of cellulose, feedstock B is a sludge of partially or non-bleached kraft paper that contains 80 wt % of cellulose and feedstock C is raw wood flour that contains 42 wt % of cellulose. ^b C₀ is the initial concentration of feedstock and defined as the ratio between the mass of the feedstock and the total mass. ^c T₁, τ₁, T₂ and τ₂ are the temperature in the 1st reactor, the residence time of the 1st reactor, the temperature in the 2nd reactor and the residence time of the 2nd reactor, respectively. ^d Y_{LA} is LA yield and defined as the ratio between the mass of LA and the mass of feedstock.

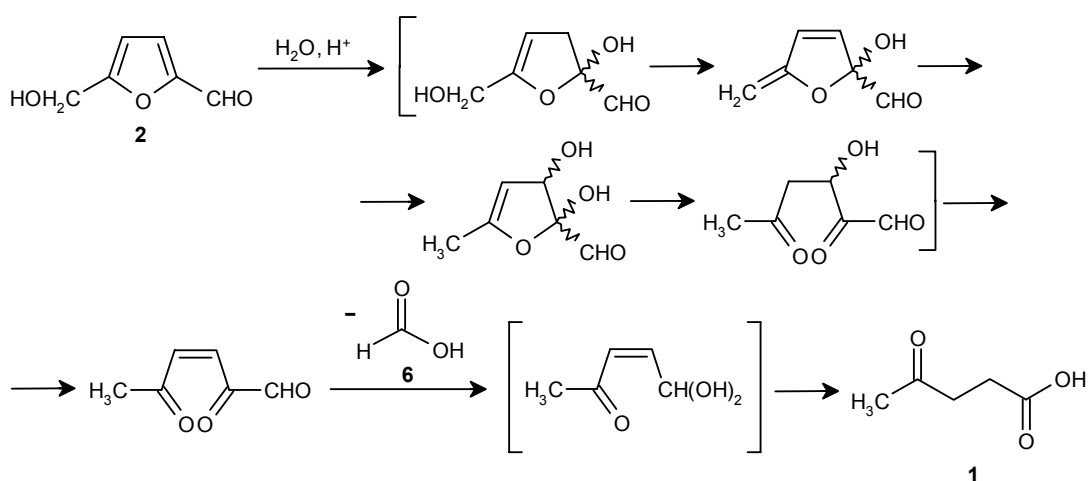
To the best of our knowledge, the first commercial-scale plant for the conversion of lignocellulosic biomass to LA has been built in Caserta, Italy [80,81]. This unit will process 3,000 ton of feedstock per year, originating from local tobacco bagasse and paper mill sludge. The plant is applying the Biofine technology and the major products will be LA and ethyl levulinate, the latter to be used as a fuel additive.

1.4.3 Mechanistic studies

The acid catalysed degradation of hexoses into LA has been extensively studied; however, only a limited amount of information is available on the underlying reaction mechanism [82-89]. The available information implies that hexose sugars initially dehydrate to form the intermediate product 5-hydroxymethylfurfural (HMF, **2**), which is subsequently hydrated to give the final product LA. Scheme 1.1 shows the proposed mechanism for the conversion of hexose sugars, such as D-glucose (**3**), D-mannose (**4**) or D-fructose (**5**) to HMF. The conversion of HMF into LA is the result of water addition to the C₂ - C₃ bond of the furan ring to give the final products LA and formic acid (**6**) (see Scheme 1.2).



Scheme 1.1 Dehydration reactions of hexose sugars to HMF [87,90].



Scheme 1.2 Proposed reaction mechanism for the conversion of HMF to LA [86].

1.5 Potential applications of LA and its derivatives

LA has been identified as a platform chemical for various interesting derivatives [41,39]. The applications of LA and its derivatives have been reviewed extensively [91,59,92,93]. In this overview, a number of interesting chemical reactions of LA will be provided. Functional group transformations involving the carboxylic-, carbonyl- and methyl-group as well as typical oxidation and reduction reactions will be reported

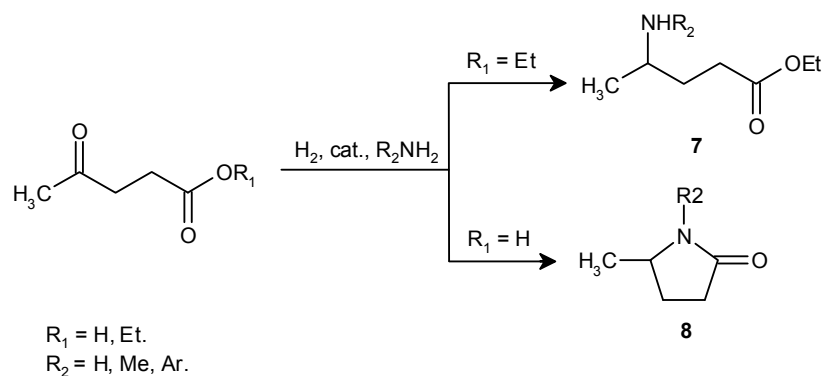
1.5.1 Reactions involving the carboxylic group

One of important reactions involving the carboxylic group of LA is esterification to produce various esters of LA. To obtain high yields of levulinate esters, the reaction is usually carried out in the presence of an acid catalyst, for example sulphuric, polyphosphoric acid or *p*-toluenesulfonic acid [94,95]. Recently, a novel technique to produce levulinate esters has been proposed. It involves the reaction of LA with an organic alcohol in a reactive-extraction mode. Here, the organic alcohol phase acts both as the esterifying agent and the extractant phase [96].

Ethyl levulinate, made by esterifying LA with ethanol, can be used as an oxygenate additive. A research by Tecaxo and Biofine Inc. showed that a mixture of 20% ethyl levulinate, 1% of co-additive and 79% diesel can be used in regular diesel engines [97]. Ethyl levulinate is also used in the flavouring and fragrance industries. Levulinate esters from high boiling alcohols can be used as plasticizer for cellulose plastics [98-100]. Another potential application of levulinate esters is to replace kerosene as a fuel for the direct firing of gas turbines [101].

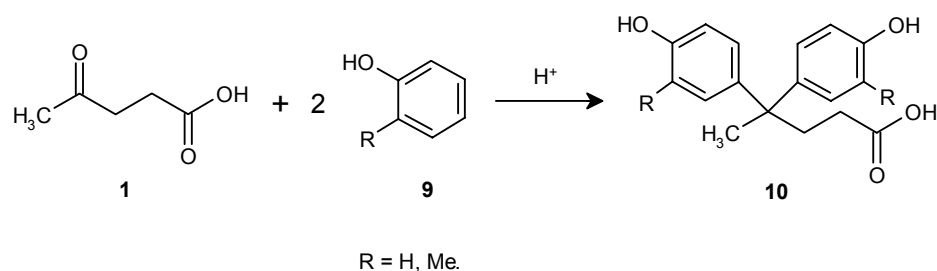
1.5.2 Reactions involving the carbonyl group

A wide range of interesting LA derivatives is available by nucleophilic additions to the carbonyl group. As an example, reactions of LA with nitrogen-containing nucleophiles give either amides (7) or the cyclodehydration products of the amides, depending on whether the carboxyl group of LA is protected or not [102,103] (see Scheme 1.3). The amides formed by the reaction of LA with various amines are attractive because of their biological activity. In the presence of a metal catalyst and hydrogen gas, LA can react with ammonia or ammonium hydroxide to give 5-methyl-2-pyrrolidone (8) [104], which is a useful intermediate for the pharmaceutical industry.



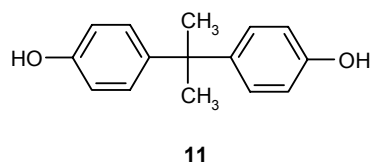
Scheme 1.3 Reductive amination of LA.

The carbonyl group of LA can also undergo through an acid-catalysed condensation reaction with aromatic or heterocyclic alcohols to give 4,4-diaryl-substituted valeric acids [105-107]. A typical example is diphenolic acid (**10**) (or 4,4-bis-(4'-hydroxyphenyl)pentanoic acid) that is prepared by reacting one mol of LA with two moles of phenol (**9**) (see Scheme 1.4).



Scheme 1.4 Preparation of diphenolic acid.

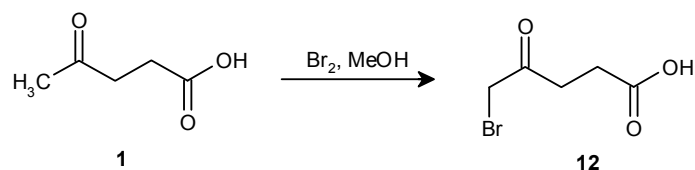
Diphenolic acid **10** has several uses, such as in the production of various polymers [108-111], lubricants [112], fire-retardant materials [113] and paints [107]. It can copolymerise with bisphenol A (BPA, **11**) [114] or directly replaces BPA in the production of polycarbonates, epoxy resins and other polymers [93,38,115]. In contrast to BPA, diphenolic acid contains a carboxyl group, which offers more functionality in the polymer synthesis. A recent study has estimated that diphenolic acid could capture a market of 4.5×10^4 tons year⁻¹ as a BPA replacement and also another 2.3×10^3 tons year⁻¹ as a coating material [93].



1.5.3 Reactions involving the methyl group

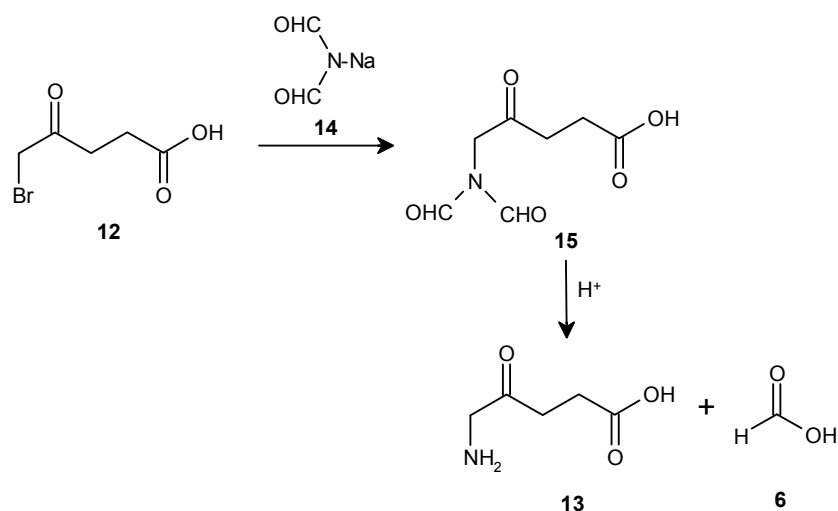
The methyl group of LA can be easily halogenated using bromide or chloride to yield organic halides. For example, 5-bromolevulinic acid (**12**) may be obtained by the bromination of LA in methanol [116,117] (see Scheme 1.5). 5-Bromolevulinic acid is a precursor for δ -aminolevulinic acid (DALA). The latter is an active

ingredient of a biodegradable herbicide, with a projected market of $9.1\text{--}13.6 \times 10^4$ tons year⁻¹ [38]. In the pharmaceutical industry, DALA has also been used in limited quantities as an active component in photodynamic cancer treatment [118].



Scheme 1.5 Bromination reactions for LA.

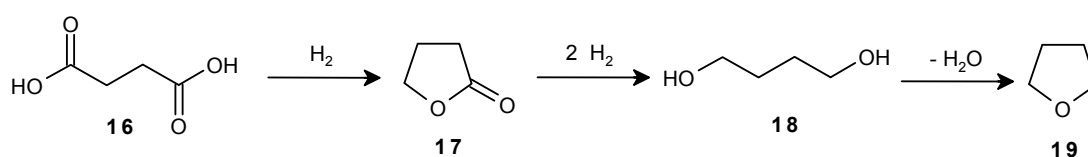
DALA (13) is prepared by reacting 5-bromolevulinic acid with nitrogen-containing nucleophiles, such as sodium azide [117] or potassium phthalimide [119]. Recently, the use of sodium diformylamide (14) [120] as the N-nucleophile to give an intermediate product (15) has been reported (see Scheme 1.6). Using 14, DALA was obtained in high yields (> 80 mol %) and purity (> 90%) [121].



Scheme 1.6 Synthesis of DALA.

1.5.4 Oxidation reactions

LA can be oxidised to various interesting derivatives. The chemoselectivity is highly depending on the type of oxidant. High-temperature (365–390 °C) oxidations of LA using oxygen in the presence of a V_2O_5 catalyst give succinic acid (16) with a typical yield of about 80% [122]. Succinic acid (1,4-butanedioic acid) is a versatile compound, and its production uses and reactions are reviewed in the literature [123]. In 2004, the market potential for products based on succinic acid is estimated to be 2.7×10^5 tons year⁻¹ [124].

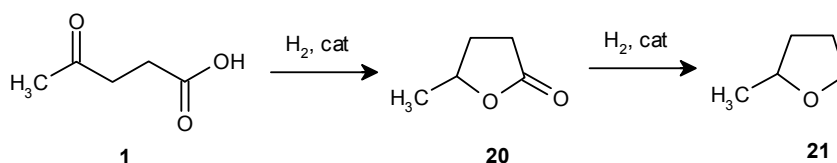


Scheme 1.7 Conversion of succinic acid into several derivatives.

Several well-known derivatives of succinic acid (see Scheme 1.7) are γ -butyrolactone (GBL, **17**), 1,4-butanediol (BDO, **18**) and tetrahydrofuran (THF, **19**). Hydrogenation of succinic acid leads to the formation of GBL that is used as an intermediate for agrochemicals and pharmaceuticals [115]. BDO is a compound of great interest as a starting material for the production of important polymers such as polyesters, polyurethanes and polyethers [125]. A major BDO-based polymer is polybutylene terephthalate, which is mainly used for engineering plastics, fibers, films and adhesives. Other relevant BDO applications are in the formation of THF, which is obtained by homogeneous dehydration of BDO. THF is a solvent for poly-(vinyl chloride) (PVC) and is used as a monomer in the manufacture of polytetramethylene glycol, which is used as an intermediate for Spandex fibers and polyurethanes [125].

1.5.5 Reduction reactions

LA may be reduced by catalytic hydrogenation to γ -valerolactone (GVL, **20**). Typical catalysts are platinum oxide [126], Raney nickel [127,128], copper-chromite [128], rhenium catalysts [129], rhodium complexes [130] and ruthenium complexes [131-133]. GVL is used as a solvent for lacquers, insecticides and adhesives [134].



Scheme 1.8 Reduction of LA to MTHF through GVL as the intermediate.

One of the important derivatives of GVL is methyltetrahydrofuran (MTHF, **21**), which has potential as a gasoline oxygenate and has a predicted [93] market potential as high as 2.6×10^5 m³ year⁻¹. Yields as high as 83 mol % (63 wt %) were reported [135].

1.6 Thesis Outline

The primary objective of this thesis is to define optimum catalysts, reaction conditions and reactor configurations for the conversion of water hyacinth to LA. The conversion of the C₆-sugars present in the water hyacinth plant to LA involves several reactions that together form a complex reaction network. A number of side reactions giving rise to by-products formation (e.g., insoluble humin compounds) significantly complicate the catalyst selection and the development of kinetic models. Therefore, a stepwise approach was applied by investigating the individual reactions in the overall reaction scheme separately.

In *Chapter 2*, the results of an experimental screening study using a wide variety of acid catalysts for the conversion of glucose and HMF to LA is reported. The optimum catalyst was selected and applied in subsequent studies.

Chapter 3 describes an experimental and modelling study on the conversion of HMF to LA. The kinetics of the main and side reactions were determined and optimum reaction conditions were defined on the basis of the kinetic model.

The results of Chapter 3 together with additional experiments were applied to determine the kinetics for the desired and side-reactions for the reaction of glucose to LA. The resulting kinetic models and the implication for reactor design are provided in *Chapter 4*.

Extensions of the kinetic schemes when using cellulose as the reactant are reported in *Chapter 5*. Combined with the result of Chapter 3 and 4, this has led to kinetic expressions for all main and side reactions taking place when converting cellulose to LA. The kinetic expressions are used to determine the optimum reaction conditions and reactor configurations for the conversion of cellulose to LA.

An experimental and modelling study on the acid catalysed hydrolysis of the water hyacinth plant to LA is reported in *Chapter 6*. The kinetic models described in Chapters 3-5 are applied to determine the optimum conditions to obtain high LA yields.

1.7 References

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