

Alternative Sugar Sources for Biobased Chemicals

Ria Mayasari Abdilla-Santes



Alternative Sugar Sources for Biobased Chemicals

Ria Mayasari Abdilla-Santes

Alternative Sugar Sources for Biobased Chemicals

Ria Mayasari Abdilla-Santes

Doctoral thesis

University of Groningen

The Netherlands

The work described in this thesis was conducted at the Department of Chemical Engineering (ENgineering and TEchnology institute Groningen – ENTEG), Faculty of Science and Engineering, University of Groningen, the Netherlands.

This doctoral project was financially supported by the Directorate General of Higher Education of the Republic of Indonesia and University of Groningen.

Cover and layout design by: Iliana Boshoven- Gkini | www.AgileColor.com

Cover image by: Grafvision

Printing by: ProefschriftMaken

ISBN: 978-94-034-2781-2

ISBN: 978-94-034-2782-9 (electronic version)



**rijksuniversiteit
 groningen**

Alternative Sugar Sources for Biobased Chemicals

PhD thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on

Friday 26 June 2020 at 12:45 hours

by

Ria Mayasari Abdilla

born on 14 November 1984
In Martapura, Indonesia

Supervisor

Prof. H.J. Heeres

Assessment committee

Prof. F. Picchioni

Prof. P.P. Pescarmona

Prof. J.H. Bitter

Dedicated to my parents, husband and my children.

For your endless love, support and prayer.

Contents

1

11	General Introduction
12	1.1. The biobased economy and the biorefinery concept
21	1.2. Sugar based platform chemicals
27	1.3. Alternative sugar sources for platform chemicals
27	1.3.1. Pyrolytic sugars
29	1.3.2. Thick juice
30	1.4. Thesis outline
32	References

2

35	Kinetic Studies on the Conversion of Levoglucosan to Glucose in Water Using Brønsted Acids as the Catalysts
36	Abstract
37	2.1. Introduction
39	2.2. Experimental section
39	2.2.1. Chemicals
39	2.2.2. Experimental procedure
39	2.2.3. Analytical methods
40	2.2.4. Definition and determination of kinetic parameters
40	2.3. Results and discussion
40	2.3.1. Product distribution using sulfuric acid as the catalyst
42	2.3.2. Effect of process variables on the hydrolysis rate of LG
44	2.3.3. Kinetic model development for sulfuric acid
47	2.3.4. Kinetic model development for acetic acid
51	2.4. Application of the kinetic model
51	2.4.1. Comparison between sulfuric and acetic acid
51	2.4.2. Selectivity
52	2.4.3. Determination of optimum reaction conditions for highest yield
53	2.5. Conclusions
54	Acknowledgement
55	Nomenclature
56	References
58	Supporting information for Chapter 2

3

65	Conversion of Levoglucosan to Glucose Using an Acidic Heterogeneous Amberlyst 16 Catalyst: Kinetics and Packed Bed Measurements
66	Abstract
67	3.1. Introduction
68	3.2. Experimental section
68	3.2.1. Chemicals
69	3.2.2. Experimental procedures
69	3.2.3. Analytical methods
69	3.2.4. Definitions
70	3.3. Results and discussion
70	3.3.1. Batch experiments: Product distribution, mass balances and reproducibility
71	3.3.2. Assessment of mass transfer limitations in batch experiments
72	3.3.3. Effect of process conditions on the conversion of LG to GLC in batch
74	3.3.4. Catalyst stability
74	3.3.5. Kinetic model development
75	3.3.6. Modeling approach
76	3.3.7. Modeling results
79	3.3.8. Model Implications
79	3.4. Continuous experiments in a packed bed reactor
81	3.5. Conclusions
81	Acknowledgement
82	Nomenclature
83	References
85	Supporting information for Chapter 3

4

95	Valorization of Humins Type Byproducts from Pyrolytic Sugars Conversion to Biobased Chemicals
96	Abstract
97	4.1. Introduction
99	4.2. Experimental section
99	4.2.1. Chemicals
99	4.2.2. Humin synthesis
100	4.2.3. Synthesis of the Pt /CeO ₂ catalyst for catalytic liquefaction reactions

4

100	4.2.4. Experimental procedures
102	4.2.5. Analytical methods
104	4.2.6. Characterization of the Pt/CeO ₂ catalyst
105	4.3. Results and discussion
105	4.3.1. Synthesis and characterization of the pyrolytic sugar (PS)- derived humins
109	4.3.2. Thermal pyrolysis
109	4.3.2.1. TGA studies
110	4.3.2.2. Pyrolysis experiments
110	4.3.2.3. Catalytic pyrolysis
111	4.3.3. Catalytic liquefaction using Pt/CeO ₂ catalyst
113	4.4. Conclusions
114	Acknowledgement
115	References
117	Supporting information for Chapter 4

5

125	High-Yield 5-Hydroxymethylfurfural Synthesis from Crude Sugar Beet Juice in a Biphasic Microreactor
126	Abstract
127	5.1. Introduction
130	5.2. Experimental section
130	5.2.1. Chemicals
130	5.2.2. Experimental procedures
130	5.2.2.1. HMF formation in batch experiments
130	5.2.2.2. HMF formation in continuous microreactor experiments
131	5.2.3. Analytical methods
132	5.2.4. Determination of yield and conversion
133	5.3. Results and discussion
133	5.3.1. Thick juice and SUC biphasic reactions in a batch setup
136	5.3.2. Thick juice and SUC biphasic reactions in a continuous slug- flow microreactor setup
138	5.3.3. Comparison with literature data for HMF production from FRC and SUC
139	5.4. Conclusions
140	Acknowledgements
140	References
144	Supporting information for Chapter 5

6

155	5-Hydroxymethylfurfural synthesis from sugar beet thick juice: kinetic and modeling studies
156	Abstract
157	6.1. Introduction
159	6.2. Experimental section
159	6.2.1. Chemicals
159	6.2.2. Sugar content in thick juice
159	6.2.3. Batch experiment in water
160	6.2.4. Analytical methods
160	6.2.5. Definitions
161	6.2.6. Kinetic modeling approach
161	6.3. Results and discussion
161	6.3.1. Benchmark experiments in water with thick juice and pure SUC
162	6.3.2. Kinetic modeling
165	6.3.3. Model studies on the effects of minor components in the thick juice
167	6.3.3.1. pH effects
169	6.3.3.2. Effects of organic acids
170	6.3.3.3. Effects of salts
177	6.3.4. Discussion
178	6.4. Conclusions
178	Acknowledgements
178	References
180	Supporting information for Chapter 6

A

190	Summary
194	Samenvatting
198	Acknowledgement
201	List of Publication

1

General
Introduction

1.1. THE BIOBASED ECONOMY AND THE BIOREFINERY CONCEPT

The high consumption of fossil resources like crude oil, coal, gas and its derivatives, combined with diminishing reserves and high CO₂ emissions have caused considerable environmental and political concerns. This has led to a growing societal awareness that change is required, for instance by embracing the concept of a “biobased economy”. The biobased economy involves production methods based on renewable resources like biomass with a minimum of waste, resource optimization and low greenhouse gas (GHG) emissions [1].

Biomass is a collective term for all organic material derived from living or recently living organisms. Therefore, it encompasses both animal and plant-derived material. In the context of renewable energy, however, the term usually refers to plant based material [2], or in other words, plant material derived from the reaction between CO₂, water and sunlight via photosynthesis to produce carbohydrates – the main building blocks of biomass [3]. Biomass – with an estimated annual global production of 170x10⁹ ton [4], is considered the only naturally occurring carbon resource available in high enough quantities to substitute, at least partly, the fossil resources currently used for the production of heat and power, transportation fuels and chemicals [5, 6]. The International Energy Agency (IEA) forecasts that 10% of the world’s primary energy supply by 2035 will be from biomass, and that biofuels can replace up to 27% of the transportation fuels by 2050 [7]. Furthermore, biomass has great potential to replace the fossil resources currently used for the productions chemicals and materials.

Biomass is typically classified into a number of categories, namely; 1) virgin wood, forestry residues or residues from wood processing industries, 2) energy crops, high yield crops specifically grown to be used for the generation of heat and power, 3) agricultural residues, from harvesting or processing, 4) food waste, for example from the food and beverage industry, and post-consumer waste, 5) industrial waste and co-products, like the waste products from slaughter houses [1].

One of the cornerstones of a biobased economy is the so-called “biorefinery concept”. The National Renewable Energy Laboratory (NREL) defines a biorefinery as an integrated facility where biomass is processed efficiently to produce fuels, power and heat, and value-added chemicals. As such, there are strong analogies with today’s crude oil refineries [8], see Table 1 for details. The website biorefinery.nl describes biorefining as a process involving fractionation of biomass into various fractions that undergo further biological, (bio)chemical, physical and/or thermal chemical processing and separation [9].

Table 1. Comparison of crude oil refineries and biorefineries [1].

	Conventional refinery	Biorefinery
Feedstock	- o Feedstock relatively homogeneous - o Low in oxygen content - o The weight of the product generally increases with processing - o Some sulfur present - o Sometimes high in sulfur	- o Feedstock usually heterogeneous regarding bulk component (e.g., carbohydrates, lignin, proteins, oils, extractives, and/or ash. Most of the starting material present in polymeric form (cellulose, starch, proteins, lignin) - o High in oxygen content - o The weight of the product generally decreases with processing - o To perceive the functionality in the starting material is essential - o Low sulfur content - o Sometimes high in inorganics, especially silica
Building block composition	Main building blocks: ethylene, propylene, methane, benzene, toluene, xylene	Main building blocks: glucose, xylose, fatty acids (e.g., oleic, stearic, sebacic)
(Bio)chemical processes	- o Almost exclusively chemical processes - o Introduction of heteroatoms (O, N, S) - o Relative homogeneous processes to obtain the building blocks: steam cracking, catalytic reforming - o Wide range of conversion chemistry	- o Combination of chemical and biotechnological processes - o Removal of oxygen - o Relative homogeneous processes to obtain the building blocks - o Smaller range of conversion chemistry: dehydration, hydrogenation, fermentation
Chemical intermediates produced at commercial scale	Many	Few (but increasing, e.g., ethanol, furfural, biodiesel, succinic acid, etc)

From a technical point of view, almost all fuels and chemicals made from fossil resources can be substituted by their biobased counterparts [10], as illustrated in Figure 1.

According to IEA Bioenergy Task 42, biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy. This means that a biorefinery can be a facility, a process, a plant or even a cluster of facilities. The IEA Bioenergy Task 42 classifies biorefineries into four different categories based on possible biomass to end-product chains. These are; 1) platforms, 2) products (energy and biobased materials and chemicals), 3) feedstocks, and 4) conversion processes [1]. Figure 2 illustrates this biorefinery classification system.

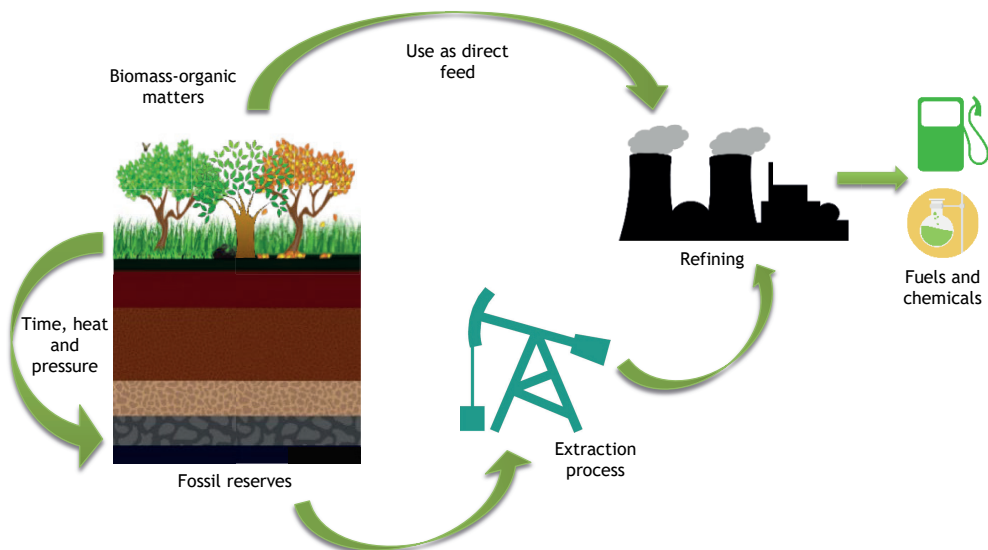


Figure 1. Productions of fuels and chemicals from fossil resources and biomass.

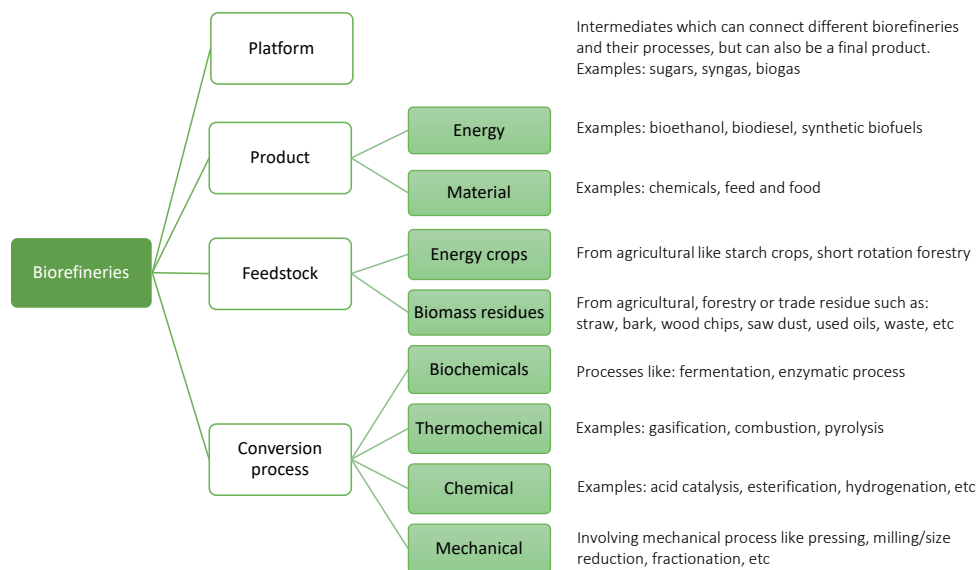


Figure 2. Biorefinery classification system according to IEA Bioenergy Task 42 [1].

Several examples of the biorefinery concept definition by IEA Bioenergy Task 42 are provided in Figure 3.

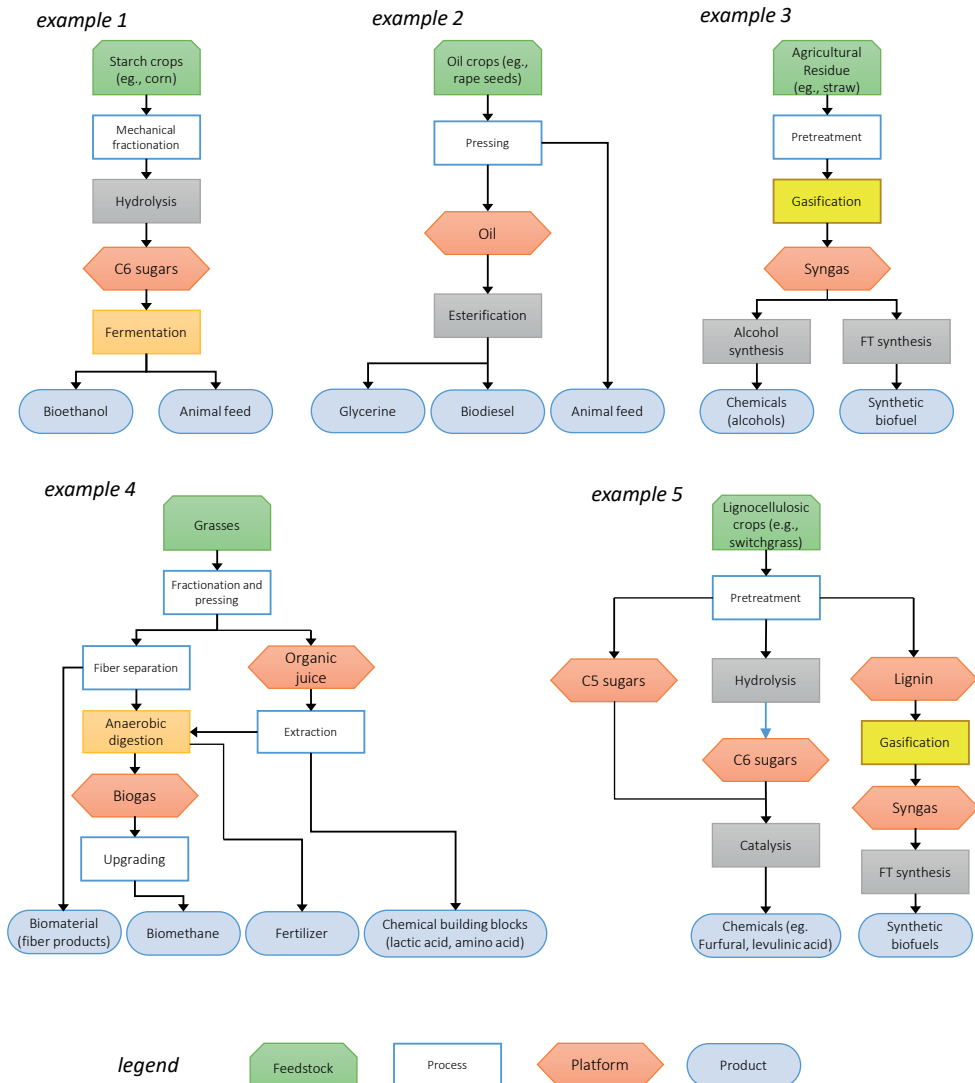


Figure 3. Examples of biorefineries according to the classification system of IEA Bioenergy Task 42 (adapted from [1, 11]).

Among the many types of biomass available, lignocellulosic (woody) biomass is considered a very attractive one. Lignocellulosic biomass consists mainly of cellulose (30-60%), hemicellulose (20-40%) and lignin (10-30%) [12]. Cellulose is a linear polymer consisting of hundreds to thousands of β -1,4-linked glucose units. Through inter- and intra-chain hydrogen bonding and van der Waals interactions, the cellulose chains self-assemble into microfibrils. Hemicellulose is a low molecular weight, highly branched polysaccharide composed of C_5 and C_6 sugars and sugar acids. Lignin is a complex and recalcitrant cross linked polymer with substituted aromatic rings connected by various linkages. It is comprised

of three building blocks, namely *p*-coumaryl, coniferyl, and sinapyl alcohol (see Figure 4 for details) [13]. The monomeric-unit distribution and molecular weight depend heavily on the type of plant and the plant part.

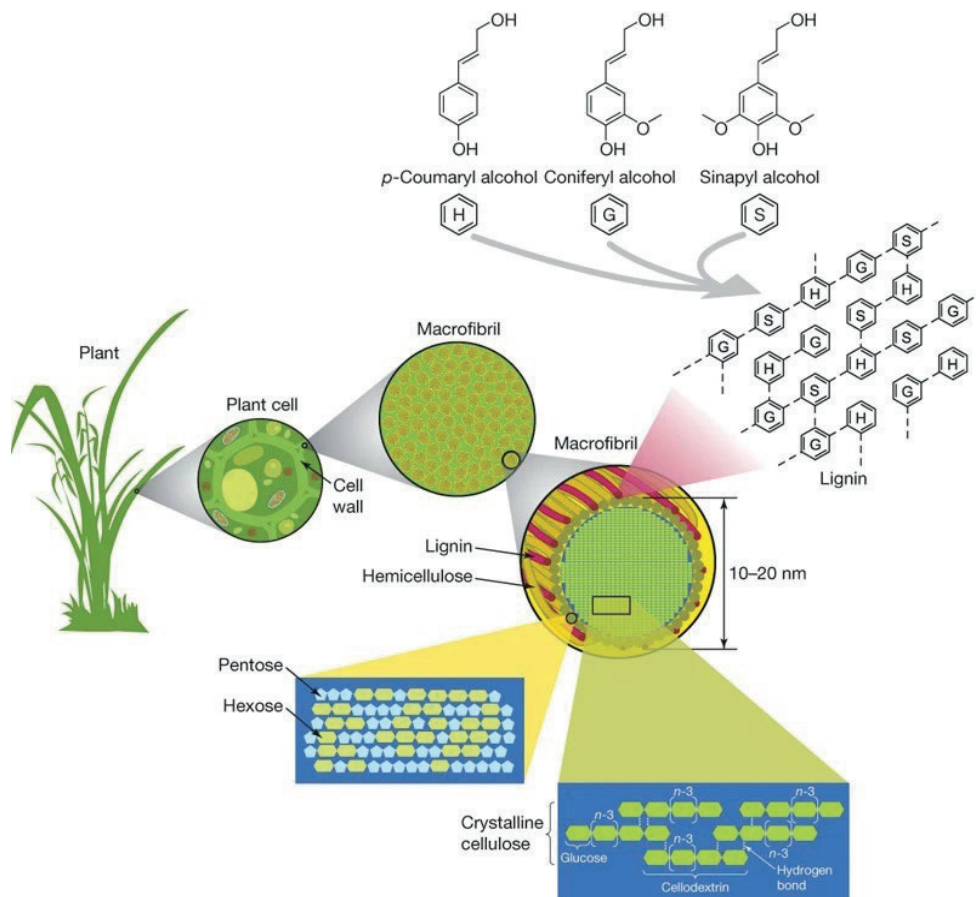


Figure 4. Illustration of the lignocellulosic biomass structure [14] (used with permission).

Lignocellulosic biomass is considered the most important feed for biorefineries due to its wide availability, relatively low costs (see Table 2 for representative examples), and limited direct competition with food and feed production [1]. A lignocellulosic biorefinery transforms lignocellulosic biomass into intermediates (cellulose, hemicellulose, and lignin) to be processed into a spectrum of products and bioenergy [11, 15]. At a cost level of ~\$60/dry ton, lignocellulosic biomass is competitive in price with petroleum at \$20/barrel on an equivalent energy content basis [16].

Table 2. Prices of lignocellulosic biomass sources (2016).

Type of Lignocellulosic biomass	Price	Ref
Forestry residues	\$20 – 30 /dry ton	[17]
	\$43 /ton	[18]
Wood waste (from saw mills, pulp and paper mills, bark, chip, sander dust, sawdust, etc)	\$20 /dry ton or less	[17]
Agricultural residue (e.g., corn stover, straw, sugarcane residue, etc)	\$40 – 50 /dry ton	[17]
Wood/timber	\$63 /ton	[18]
Energy crops (poplar, willow, switchgrass)	\$71 /ton	[18]

Large-scale biomass processing units exist already for centuries, though these focus mainly on the utilization of the carbohydrate fraction of lignocellulosic biomass. Examples are the production of pulp and paper, cellulose for viscose silk, fibers and guncotton via nitration, nylon from furfural, and sugars through saccharification. In the early 21st century, the focus is still on the processing of the carbohydrate fraction of the lignocellulosic biomass, though byproduct valorization is gaining more and more attention. New (potentially) attractive products from the carbohydrate fraction include biofuels (e.g., bioethanol) and the so-called platform chemicals (e.g., levulinic- and formic acid, γ -valerolactone, and a number of furan derivatives) [13].

To access the carbohydrate fraction, lignocellulosic biomass typically undergoes a pre-treatment process to release monosaccharides. Subsequently, these are processed by (catalytic) technology into platform chemicals (see Figure 5). These pre-treatment procedures are often quite energy intensive and have a major effect on the techno-economic viability (Table 3).

A Dutch company, Biomass Technology Group (BTG) has developed an innovative pyrolysis based biorefinery concept with lignocellulosic biomass as the feedstock. Their method involves fast pyrolysis technology as the primary pre-treatment process to convert the feedstock into a liquefied product (pyrolysis liquid or pyrolysis oil) that is subsequently fractionated in a secondary processing step. Finally, marketable products are produced via tertiary upgrading. A simplified scheme of the pyrolysis biorefinery is shown in Figure 6. In recent years, a commercial pyrolysis plant has been realized in Hengelo, the Netherlands (Empyro) and production started in 2015. As this process fractionates the biomass into various fractions, it may also be considered a pre-treatment technology.

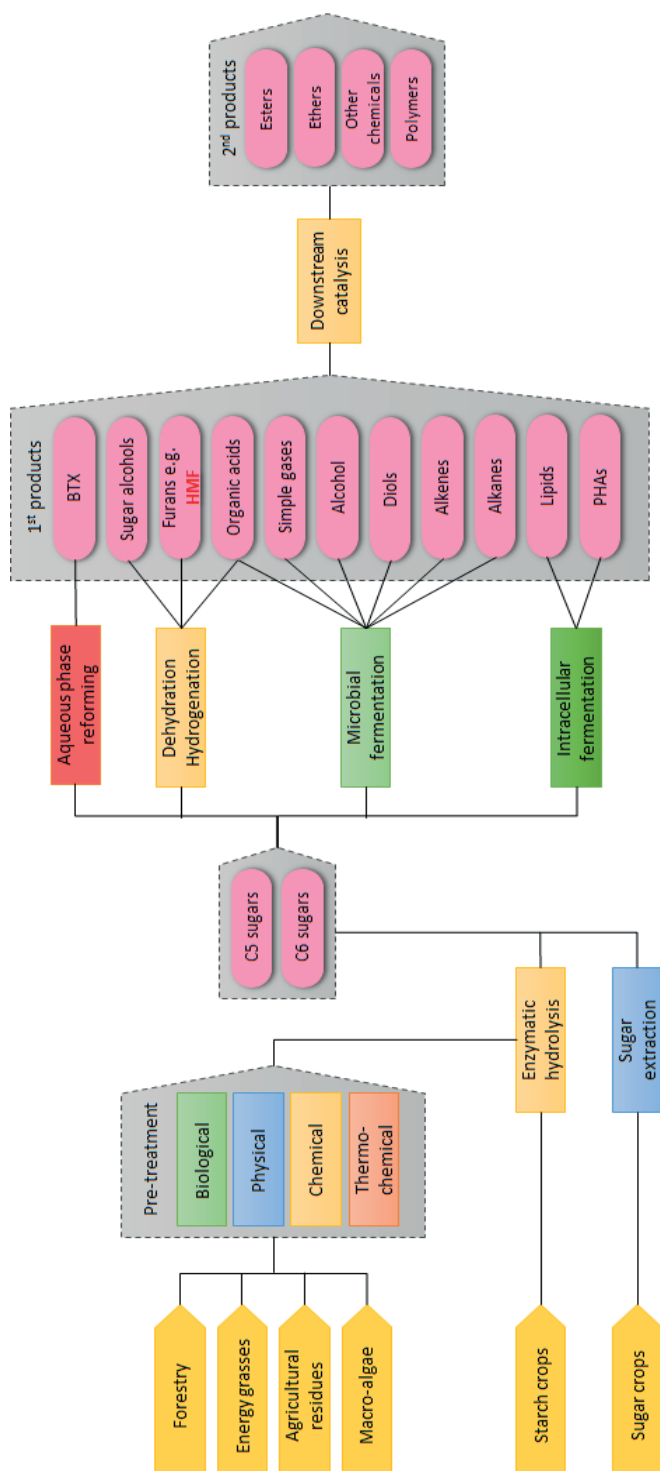


Figure 5. Sugar platform chemicals from lignocellulosic biomass [19].

Table 3. Available technologies for lignocellulosic biomass pre-treatment (taken from [19]).

Technology	Advantage	Barrier
Steam explosion	- o Cost-effective - o High glucose yields - o Lignin and hemicellulose removal - o Low environmental impact	- o Often a catalyst is needed to optimise the pre-treatment - o Formation of inhibitors and toxic compounds
Dilute acid pre-treatment	Good removal of the hemicellulose fraction	- o Degradation, byproducts (salts) and inhibitors - o Corrosion
Concentrated acid hydrolysis	- o No enzymes needed - o Good removal of hemicellulose fraction	- o High chemical use and CapEx - o Corrosion and toxic hazards - o Degradation, byproducts (salts) and inhibitors
Auto-catalysis/hydrothermal	- o No chemical use or residues - o High glucose yields	- o Higher operating temperature - o Inhibitor formation
Organosolv treatment	Causes lignin and hemicellulose hydrolysis	- o High capital and operating costs - o Solvent may inhibit cell growth
Alkaline pre-treatment (e.g., dilute ammonia, NaOH, lime)	- o Low capital costs - o Low inhibitor formation - o High glucose yields	- o Residue formation - o Need to recycle chemicals - o Enzyme adjustments needed
Ammonia fibre explosion (AFEX)	- o No need for small particles - o Low inhibitor formation - o High accessible surface area	o High cost due to solvent
Supercritical (CO ₂) pre-treatment	- o Increases accessible surface area - o Low amounts of inhibitors and residues	- o Does not affect lignin and hemicellulose fractions - o High pressure, high CapEx
Ionic liquid	- o Effective dissolution of all lignocellulose components - o Small amounts of degradation products	Expensive technology and recovery required
Microbial/biological (fungi)	- o Low energy requirement - o No corrosion - o Suitable for lignin and hemicelluloses removal	- o Time consuming - o Some saccharide losses
Mechanical milling	- o Reduces cellulose crystallinity - o No inhibitors or residues	- o High energy consumption - o Low sugar yields

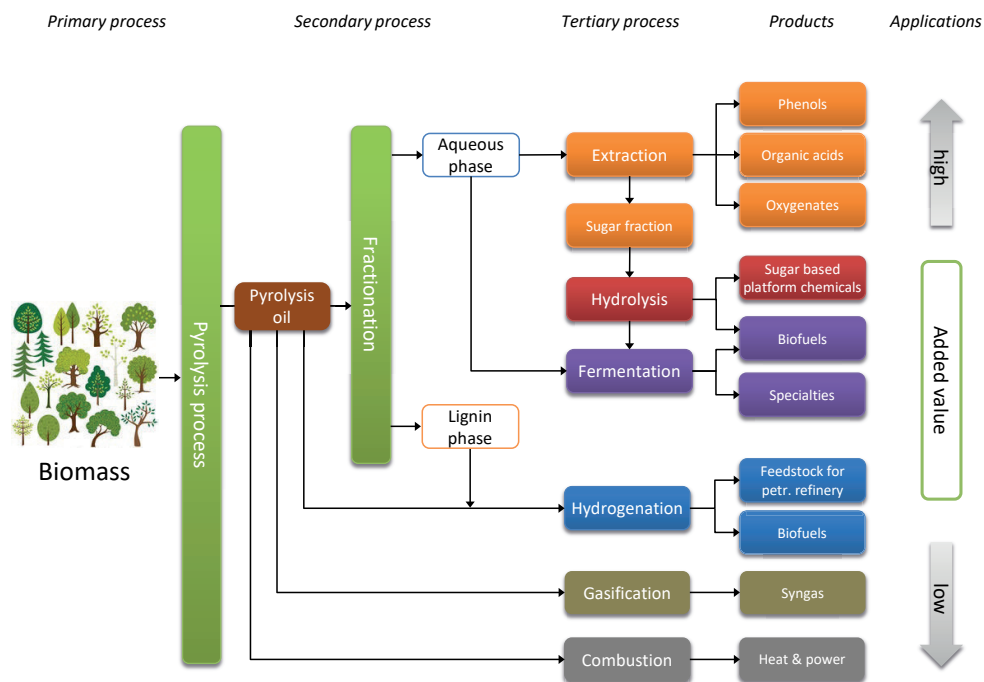


Figure 6. Schematic representation of a pyrolysis-based biorefinery.

The main driver so far for the transition from fossil based refineries to biorefineries is the need for sustainable energy and transportation fuels. However, the production of biobased chemicals is also of high interest, as the product price per ton is by far higher than for energy carriers and transportation fuels. Unfortunately, at the moment the production costs of most biobased products exceeds those of fossil counterparts. Also, performance should at least be as good as their petrochemical counterparts [20]. Therefore, major technological developments regarding biobased products are required. Two main strategies are currently pursued. The first comprises the modification of biopolymers like starch, cellulose and proteins while keeping the biopolymer intact. Examples are starch modification by e.g., acetylation, carboxymethylation to produce enhanced oil recovery chemicals, additives for the paper industry and components in biodegradable plastics [21]. The second approach involves the so-called “platform chemicals” concept. Here, the biopolymers are broken down into low molecular weight compounds, also known as building blocks or platform chemicals. These platform chemicals are subsequently converted via various methods to high value intermediates and final consumer products. A schematic illustration of the latter approach is given in Figure 7.

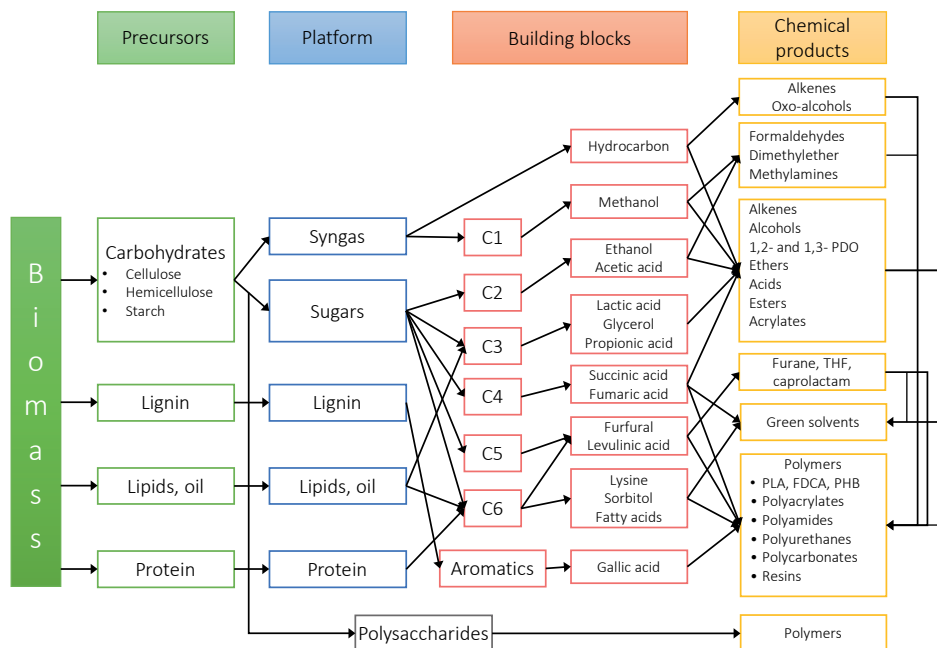


Figure 7. Biomass to biobased chemicals using the platform chemical concept (adapted from [22]).

1.2. SUGAR BASED PLATFORM CHEMICALS

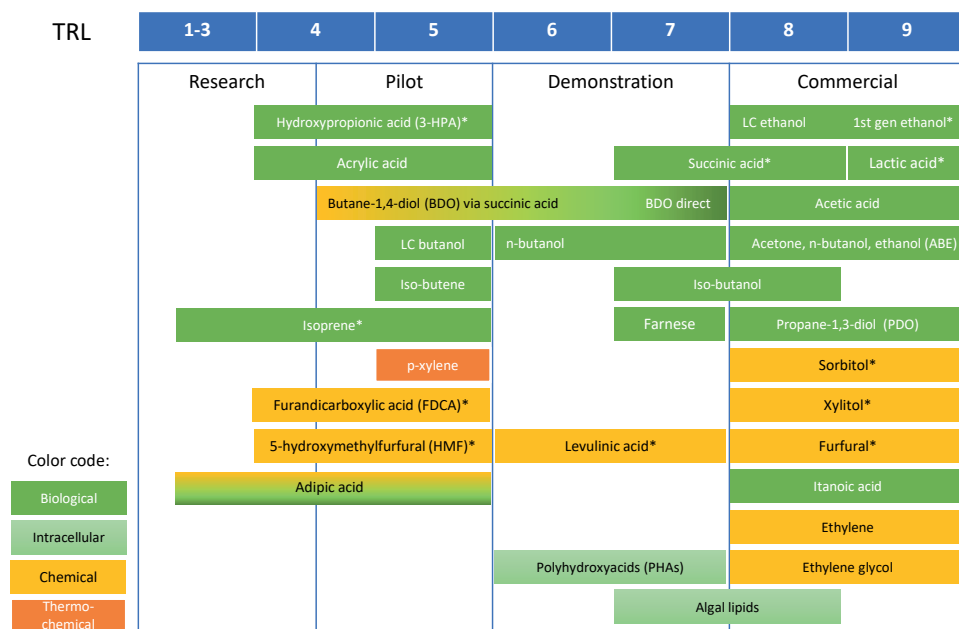
The term platform chemical is given to biobased chemicals which have high derivatization potential due to the presence of multiple functional groups and may be obtained from a suitable biomass source in high yields. These chemicals are also often addressed as building block chemicals. A good example of a platform chemical is bioethanol, which can be produced via sugar fermentation. Besides being a biofuel, it is an important precursor for other chemicals such as ethyl esters, diethyl ether, acetic acid, ethylene, ethyl amines, etc.

A wide variety of platform chemicals can be obtained from sugars. In 2004, researchers from the Pacific Northwest National Laboratory (PNNL), NREL, and the Office of Energy Efficiency and Renewable Energy (EERE) released a report containing a list with 12 most prospective sugar-derived platform chemicals. The list was made after an extensive identification and selection process involving about 300 possible platform chemicals accessible from biomass [23]. The list was updated in 2010 by Bozell and Petersen [24] by a comprehensive evaluation using the following criteria:

- 1) The compound or technology has received significant attention in the literature,
- 2) The compound has a high derivatization potential to multiple products,
- 3) The technology provides direct substitutes for existing petrochemicals,

- 4) The technology is applicable to produce high volume products,
- 5) The compound has high potential as a platform chemical,
- 6) Scale up of the product or a technology to pilot, demo, or full scale is underway,
- 7) The compound is an existing commercial product, prepared at intermediate or commodity levels,
- 8) The compound may serve as a primary building block of a biorefinery,
- 9) Commercial production of the compound from renewable carbon is well established.

In 2015, the European Commission released a list with 25 important sugar-derived products. The main selection criteria was the level of industry activity, as also considered by US DOE's and IEA Bioenergy Task 42 reports. All 25 compounds are primary products, made in one step from sugars [19], see Figure 8 for details. Out of the 25 compounds, 11 were proposed earlier as top sugar-derived platform chemicals by Bozell and Petersen [24] and 14 are currently at Technology Readiness Levels (TRL's) between 6 and 7.



*Also included in the top 12 sugar-derived platform chemicals proposed by Bozell and Petersen [24]. TRL (Technology readiness level): 1) Basic research 2) Technology formulation 3) Applied research 4) Small scale prototype 5) Large scale prototype 6) Prototype system 7) Demonstration system 8) First of a kind commercial system 9) Full commercial application. All compounds are derived from sugar or starch crops unless marked as LC (lignocellulosic).

Figure 8. Current development status of selected sugar based platform chemicals [19].

5-hydroxymethylfurfural (HMF). Among the various chemicals displayed in Figure 8, HMF is of our particular interest. HMF is a sugar derivative that contains both an aldehyde and alcohol group. Relevant properties of HMF and several attractive derivatives from HMF are presented in Table 4 and Figure 9, respectively. Although in theory HMF is easily accessible from sugar, its large scale production is hindered by several factors such as low yields (due to thermal decomposition), and high cost of production and product separation. The TRL of HMF production is estimated at around 4-5 at the moment. Swiss-based AVA Biochem and Avantium are leading companies regarding HMF commercialization [19, 25]. Reflecting on the current situation and considering the vast potential of HMF, intense research and development activities are required to assist the transition of HMF production from pilot to commercial stage.

Early reports on the synthesis of HMF are from 1895. At that time, Dull [26] and Kiermeyer [27] independently published a method for the synthesis of HMF (which they called óxymethylfurfural). Dull initially prepared HMF from inulin with oxalic acid as the catalyst, whereas Kiermayer used levulose as the sugar source. Soon after, other reports were released by Fenton [28], Gostling [29] and Robinson [30]. A detailed study regarding HMF synthesis, physical characterization and its chemical behavior was published in 1919 by Middendorp [31].

Table 4. Relevant properties of HMF.

Properties	Values
Molecular weight	126.11
Melting point	28-34 °C
Boiling point	114-116 °C (in 1 mmHg)
Density	1.243 g mL ⁻¹ (at 25 °C)
Refractive index	1.563 ± 0.02 g mL ⁻¹
Flash point	175 °F
Storage temperature	2-8 °C
Surface tension	50.0 ± 3.0 dyne cm ⁻¹
Sensitivity	Air and light sensitive

Research regarding HMF synthesis and its derivatives has since then been growing, particularly in the last 20 years. Recent developments regarding synthetic methodology and processing of HMF as well as subsequent conversions and applications have been extensively reviewed by our group [32].

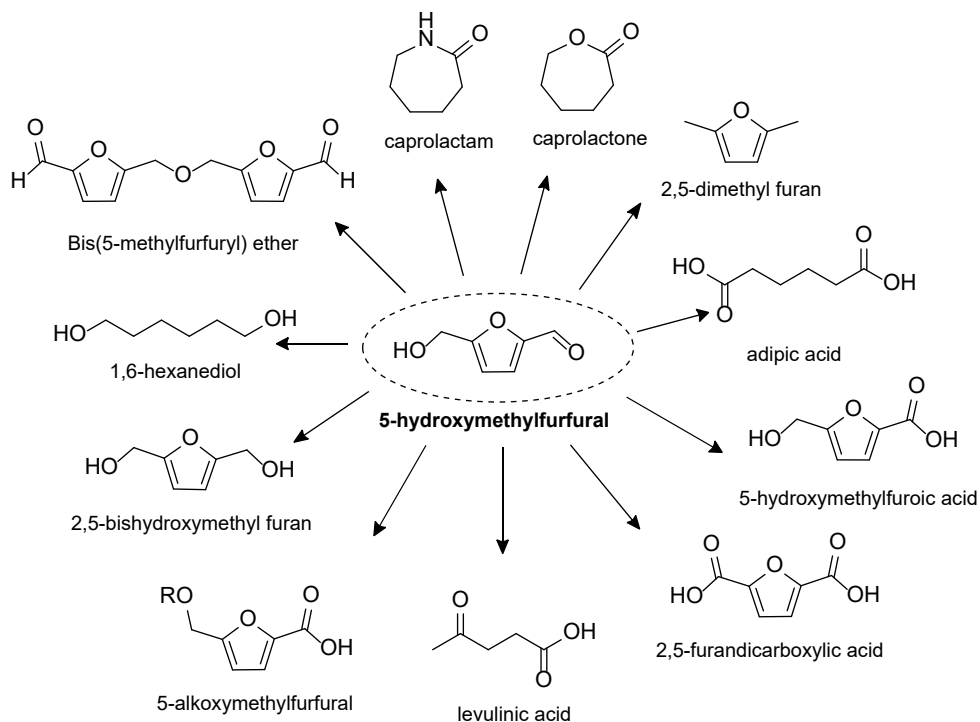
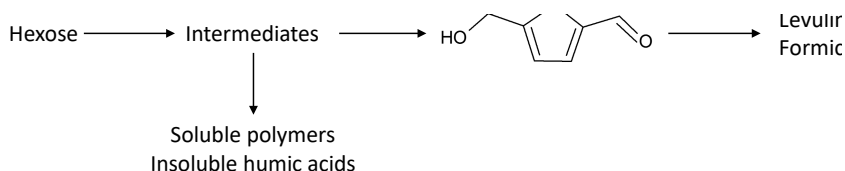


Figure 9. Potential derivatives of HMF (reproduced from [32] with permission).

The principle of HMF synthesis is based on the dehydration of hexoses (Scheme 1). Well known byproducts are levulinic acid and formic acid as well as soluble and insoluble condensation products known as humins. HMF synthesis routes are generally classified into solvent based and catalyst based routes. Three solvent categories are typically considered; 1) aqueous system, 2) mixed solvents (e.g., biphasic systems), and 3) non aqueous system (e.g., ionic liquids) whereas five catalyst subcategories are used; 1) organic acids, 2) mineral acids, 3) salts, 4) lewis acids and 5) solid catalysts, see Table 5 for examples.



Scheme 1. Simplified reaction scheme of HMF synthesis.

Table 5. Examples of catalysts used in the synthesis of HMF (taken from [33]).

Organic acids	Mineral acids	Salts	Lewis acids	Solid catalysts
Oxalic acid	H_3PO_4	$\text{Ag}_3\text{PW}_{12}\text{O}_{40}$	AlCl_3	Ion exchange resins
Levulinic acid	H_2SO_4		ZnCl_2	Zeolites
Maleic acid	HCl		BF_3	Metal oxides* :
Formic acid	HI		$\text{B}(\text{OH})_3$	
Acetic acid	HBr		Lanthanide salts	
p-toluenesulfonic acid				
Trifluoroacetic acid				

*TiP = titanium phosphate, $\text{C-ZrP}_2\text{O}_7$; cubic zirconium pyrophosphate, ZrP : $\text{Zr}(\text{HPO}_4)_2$, eHTiNbO₅: exfoliated HTiNbO₅, obtained by treating the H-compound with Bu_4NOH

In terms of HMF yield, D-fructose is a superior feedstock compared to D-glucose. However, D-glucose is preferable due to its low cost. Oligo- and polysaccharides, as well as lignocellulosic biomass, are potentially interesting feedstocks for HMF and could offer substantial economic and environmental benefits, though the HMF yield is lower compared to monosaccharides, particularly D-fructose (see Table 6 for selected examples).

As such, the identification of alternative cost-efficient substrates for HMF synthesis giving high yields of HMF is of high interest. Such substrates should be inexpensive, relatively abundant and require minimal/low cost pre-treatment or even no pre-treatment (before conversion to into HMF).

Table 6. Selected examples of oligo-, polysaccharide and lignocellulosic biomass feedstock for HMF synthesis.

Substrate	Solvent(s)	Catalyst	Temperature (°C)	Reaction time	HMF yield (%)	Ref
Inulin	Water	-	180	2 h	44	[34]
Cellulose	Water	-	280	4 min in cont. flow	11.9	[35]
Cellulose	Water	H ₂ SO ₄ , 20 mM	215	1 h	5	[36]
Corn starch	Water:dioxane 1:1 v/v	Pyridine:H ₃ PO ₄ 5:3 mol/mol	220-226	30 min excl. pre-heating	44	[37]
Inulin	Water	CO ₂ , 11 MPa	180	2 h	52	[34]
Oak wood chips	-	H ₂ SO ₄ , 0.6 wt% aq	286	90 s at 69 bar steam	50-80	[38]
Cassava waste	Water	Sulfonated carbon-based catalyst	250	1 min	11	[39]
Corn cob	Water	TiO ₂ -ZrO ₂	250	5 min	8.5	[40]
Rice husk					33	
Sugar cane baggase					66	
Cellobiose	DMF	Hydrotalcite/ Amberlyst 15 1:1 w/w	120	3 h	35	[41]
Sucrose	DMA	CrCl ₃ /NH ₄ Br	100	1 h	87	[42]
Sucrose	DMSO	LaCl ₃	120	2 h	47	[43]
Tapioca flour	Water/Acetone/DMSO	WO ₃ -ZrO ₂	230		22	[44]
Cellulose	Water:MIBK 1:5	TiO ₂	270	2 min	30	[45]
Inulin	Water/DMSO (5:5 w/w): MIBK/2-Bu-OH (7:3 w/w) 1:2 w/w	HCl, pH 1.5	170	5 min	75	[46]
Jerusalem artichoke	Water:MIBK 1:5	H-form Zeolite, Si/Al = 11	165	1 h	57	[47]
Cellulose	[EMIm]Cl	-	120	3 h	21	[48]
Inulin	[HMIIm][HSO ₄]	-	80	3 h	59	[49]
Starch	[OMIm]Cl/0.5 M HCl/EtOAc	-	120	1 h	30	[50]
Pine wood	[BMIm]Cl	CrCl ₃	200	3 min	35	[51]
Rice straw						

1.3. ALTERNATIVE SUGAR SOURCES FOR PLATFORM CHEMICALS

In this thesis, strategies to convert alternative sugar sources, namely **pyrolytic sugars** and **thick juice**, into platform chemicals via chemo-catalytic routes are described. The following section will provide details regarding these two sugar sources and their potential for platform chemical synthesis.

1.3.1. Pyrolytic sugars

A promising and versatile technology to acquire low molecular weight sugars from lignocellulosic biomass is fast pyrolysis, a process which is also considered a biomass pre-treatment step (*vide supra*). In the fast pyrolysis process, lignocellulosic biomass (e.g., forestry residue) is converted to a condensable vapor, gas and char by rapid heating of the biomass in an inert atmosphere (1-2 s, 450-600 °C). Cooling of the vapor stream gives a liquid product known as bio-oil, pyrolysis oil or pyrolysis liquid. Depending on the process parameters, a liquid yield of up to 70 wt% of initial dry biomass can be attained [52]. The obtained pyrolysis oil is a complex mixture of different compounds belonging to many chemical product classes. The oil can be conveniently fractionated into three product streams; a pyrolytic lignin (low and high mol-mass lignin), an aqueous phase containing smaller organic components like organic acids (e.g., acetic acid) and pyrolytic sugars. BTG has developed a pilot scale setup to fractionate the pyrolysis oil into these fractions. A simplified schematic illustration of the pyrolysis oil fractionation process is given in Figure 10. In their setup, the pyrolytic sugar phase is concentrated to a thick syrup (up to 30 wt% of the original pyrolysis oil) [53]. This syrup contains low molecular weight sugars like 1,6-anhydro- β -D-glucopyranose, commonly known as levoglucosan, 1,6-anhydro- β -D-glucose (cellobiosan) (see Figure 11 for chemical structure) and sugar molecules of higher molecular weight. When using pure cellulose as the pyrolysis feedstock, levoglucosan yields of up to 59 wt% have been reported [54]. Levoglucosan is readily hydrolyzed to glucose, a precursor for many biobased chemicals.

A number of studies have reported the conversion of the sugar fraction (pyrolytic sugars) of the pyrolysis oil into bioethanol via fermentation [55-58]. For the fermentation process, impurities in the pyrolytic sugars were shown to have a negative effect and adequate removal/separation of impurities is required. In subsequent steps in which the sugars are hydrolyzed into their respective monomers, the pH is adjusted to achieve an optimum pH for the yeast, followed by the actual fermentation process to bioethanol. In this thesis, the focus is on chemo-catalytic pathways to transform pyrolytic sugars into biobased chemicals, for instance HMF and/or others without prior pre-treatment of the pyrolytic sugars.

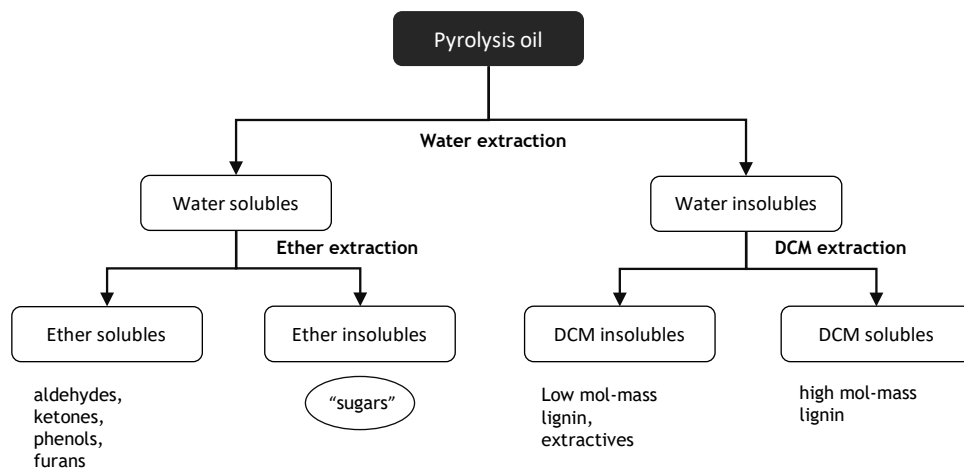


Figure 10. Simplified scheme for pyrolysis oil fractionation (adapted from [70]).

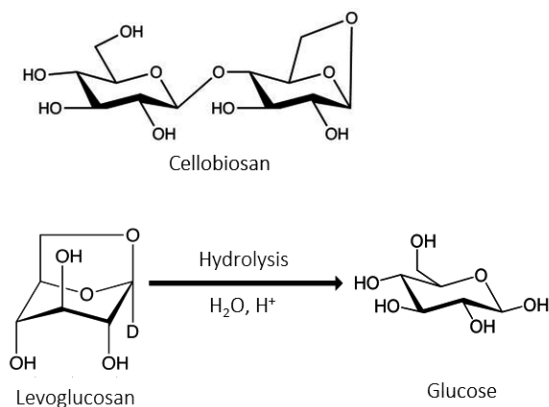


Figure 11. Chemical structure of cellobiosan and levoglucosan, which can be further hydrolyzed to glucose.

1.3.2. Thick juice

Thick juice is an intermediate sugar stream in a conventional sugar beet factory. The process of converting sugar beets into table sugar (sucrose) will be explained in detail in the following paragraph (see also Figure 12), followed by a rationale on the use of this stream for the synthesis of platform chemicals.

In a typical sugar beet factory, sugar beets are washed and cut into *cossettes* - thin strips resembling french fries, prior to the extraction of the sugars. The *cossettes* are passed through hot water to extract the sucrose. The remaining beet pulp is used as animal feed and other products, while the raw liquid extract is purified by adding Ca(OH)_2 and CO_2 to precipitate inorganic substances and proteins. The remaining low viscosity, pale yellow liquid is known as *thin juice*. Thin juice has a sugar content of approximately 12-14%. Thin juice is thickened by evaporating the excess of water, resulting in the formation of *thick juice* with a sugar content of approximately 60-70%. The thick juice is fed to a large boiling station where pulverized sugar is added to initiate the crystallization process. Subsequently, the thick, brown juice which is now called *massecuite*, is centrifuged in three stages to separate the white sugar crystals from the brown syrup. The syrup is then returned to the boiling station and re-processed till the sugar level is below a certain threshold value. The remaining syrup after this treatment is called *molasses* [59].

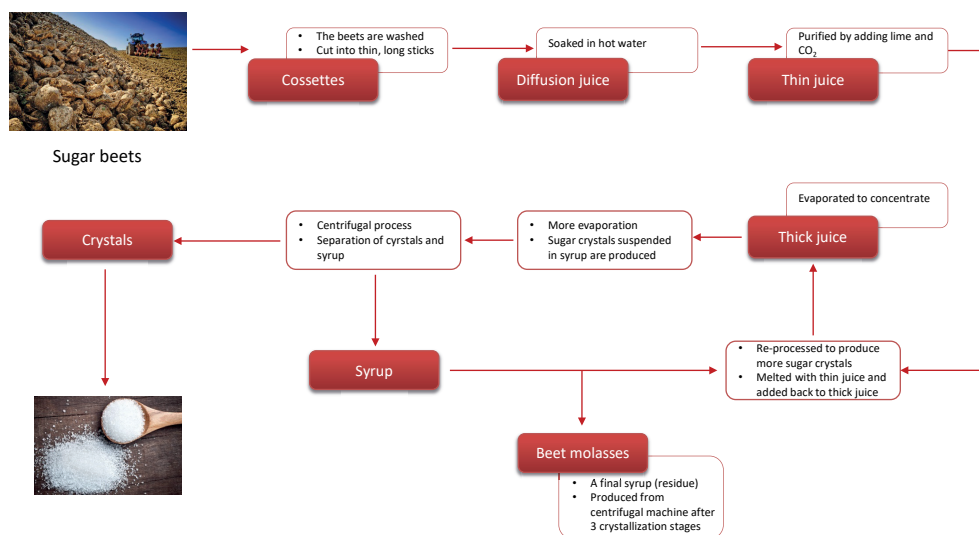


Figure 12. Schematic representation of sugar beet processing.

1

Until 2017, the production of sugar in the EU was strictly regulated by the European commission [60]. From 2017 onwards, restrictions were abandoned and it is expected that this will lead to increased production levels in the EU and lower sucrose prices on the long term [61]. As such, there is an incentive for sugar beet refiners to explore new markets and product outlets. Meanwhile, the European commission has targeted to replace 30% of fossil based chemicals and materials with biobased versions and to supply 25% of Europe's transport energy needs by sustainable advanced biofuels by 2030 [62]. As such, both from a price and legislation perspective, the co-production of biobased products like HMF in a sugar refinery is potentially of high interest. In addition, sugar beet has a high content of organics and sucrose, leading to high sucrose yields per unit area [63].

The conversion of thick juice to bioethanol [64-66] and biohydrogen [67, 68] via fermentation routes have been successfully demonstrated. However, studies on (chemo)-catalytic valorization routes of thick juice to platform molecules like HMF are limited [69]. Therefore, it is interesting to explore the potential of sugar beet juice as feedstock for platform chemicals.

1.4. THESIS OUTLINE

The research described in this thesis involves chemo-catalytic conversions of the two alternative sugar sources i.e., pyrolytic sugars and thick juice into biobased chemicals. The main objectives of this thesis were the development of synthetic methodologies for the conversion of such feeds into platform chemicals, particularly HMF, by experimental and modeling studies, exploring both the effects of process conditions and catalysts. In some cases, the studies were performed on model components to reduce complexity.

In **Chapter 1**, a general introduction on the biobased economy, the biorefinery concept and sugar based platform chemicals is provided. As a follow up, two sugar sources, pyrolytic sugars and thick juice, are introduced and proposed as alternative, cheap sugar feeds for HMF synthesis.

In **Chapter 2**, an experimental and kinetic modeling study on the conversion of levoglucosan (the major sugar in pyrolytic sugar) to glucose is described. Experiments were conducted in an aqueous-acidic medium in a batch reactor. Two Brønsted acids i.e., sulfuric acid and acetic acid, were explored as catalysts. Kinetic parameters were determined using a MATLAB optimization routine. The obtained kinetic parameters were then used to determine the optimum reaction conditions for the hydrolysis of levoglucosan to glucose.

In **Chapter 3**, the hydrolysis of levoglucosan with a solid catalyst (Amberlyst 16) was systematically studied in a batch and in a continuous fixed bed reactor. Mass transfer limitations in this heterogenous catalytic system were carefully examined and accounted for in the kinetic modeling. From the batch data, kinetic parameters were determined and these were successfully applied to model the performance in the continuous setup.

In **Chapter 4**, an experimental study on the (catalytic) pyrolysis and hydrotreatment of humins derived from pyrolytic sugars is described. Pyrolysis of the humins was carried out in a PTV-GC-MS at 550 °C in the absence and presence of a H-ZSM-5 catalyst. The catalytic hydrotreatment reaction was studied in a batch autoclave at 350 °C, for 4 h with two heterogeneous Pt catalysts (Pt/C and Pt/CeO₂) and iso-propanol as a solvent and hydrogen source. The liquid products from the reaction were characterized in detail using advanced analytical techniques (e.g., GCxGC-FID).

In **Chapter 5**, an experimental study on conversion of thick juice to HMF using sulfuric acid as the catalyst in a liquid-liquid system is provided. The reactions were carried out in a batch and in a continuous microreactor. Water was used as the reaction medium while methyl isobutyl ketone (MIBK) and 2-methyltetrahydrofuran (MTHF) were used as the organic extraction solvent. Addition of salts to the system to improve the partitioning of HMF was also considered. This study shows that thick juice is a better feed for HMF synthesis than sucrose in terms of yield and selectivity.

In the last chapter (**Chapter 6**), a comprehensive study on the conversion of thick juice to HMF is provided. The objective of this study was to identify the origin of the better performance of thick juice compared to pure sucrose. The experiments were carried out in water in a batch reactor using sucrose solutions with deliberately added contaminants such as salts and organic acids. The experimental concentration-time profiles were modeled using kinetic expressions for the individual reactions to quantify the observations and to conclude which of the contaminants in the thick juice are responsible for the improved performance of this feed for HMF synthesis.

REFERENCES

- [1] E. de Jong and G. Jungmeier. *Biorefinery Concepts in Comparison to Petrochemical Refineries*. Industrial Biorefineries & White Biotechnology, Elsevier, (2015), pp.3-33.
- [2] What is BIOMASS, <https://www.forestresearch.gov.uk/tools-and-resources/biomass-energy-resources/general-biomass-information/what-is-biomass/>, 7-12-2018.
- [3] P. McKendry. Energy Production from Biomass (Part 1): Overview of Biomass. *Bioresource Technology*, 83 (2002), pp.37-46.
- [4] B. Kamm and M. Kamm. Principles of Biorefineries. *Applied Microbiology and Biotechnology*, 64 (2004), pp.137-145.
- [5] N. Sriram and M. Shahidehpour. Renewable Biomass Energy. Power Engineering Society General Meeting, 2005. IEEE (2005).
- [6] Key World Energy Statistics, <https://www.iea.org/publications/freepublications/publication/KeyWorld2017.pdf>.
- [7] S. Wang, G. Dai, H. Yang and Z. Luo. Lignocellulosic Biomass Pyrolysis Mechanism: A State-of-the-Art Review. *Progress in Energy and Combustion Science*, 62 (2017), pp.33-86.
- [8] What Is a Biorefinery? <http://www.nrel.gov/biomass/biorefinery.html>.
- [9] Biorefinery concepts, <http://www.biorefinery.nl/background-biorefinery/biorefinery-concepts/>.
- [10] A. Raschka and M. Carus. Industrial Material Use of Biomass Basic Data for Germany, Europe and the world. Nova-Institute for Ecology and Innovation, Hürth, 2012.
- [11] F. Cherubini, G. Jungmeier, M. Wellisch, T. Willke, I. Skiadas, R. Van Ree and E. de Jong. Toward A Common Classification Approach for Biorefinery Systems. *Biofuels, Bioproducts and Biorefining*, 3 (2009), pp.534-546.
- [12] A. Boisen, T.B. Christensen, W. Fu, Y.Y. Gorbanev, T.S. Hansen, J.S. Jensen, S.K. Klitgaard, S. Pedersen, A. Riisager and T. Ståhlberg. Process Integration for the Conversion of Glucose to 2, 5-Furandicarboxylic Acid. *Chemical Engineering Research and Design*, 87 (2009), pp.1318-1327.
- [13] M.V. Galkin and J.S. Samec. Lignin Valorization through Catalytic Lignocellulose Fractionation: A Fundamental Platform for the Future Biorefinery. *ChemSusChem*, 9 (2016), pp.1544-1558.
- [14] E.M. Rubin. Genomics of cellulosic biofuels. *Nature*, 454 (2008), pp.841-845.
- [15] E. de Jong and R.J.A. Gosselink. Lignocellulose-Based Chemical Products. *Bioenergy Research: Advances and Applications*, Elsevier, (2014), pp. 277-313.
- [16] B. Yang, L. Tao and C.E. Wyman. Strengths, Challenges, and Opportunities for Hydrothermal Pretreatment in Lignocellulosic Biorefineries. *Biofuels, Bioproducts and Biorefining*, 12 (2018), pp.125-138.
- [17] Matthew H. Langholtz, Bryce J. Stokes, Laurence M. Eaton, et al., 2016 Billion-Ton Report: Advancing Domestic Resources for A Thriving Bioeconomy, Volume 1: Economic Availability of Feedstocks (2016), Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States).
- [18] What Price Feedstock? <https://www.biofuelsdigest.com/bdigest/2016/05/02/what-price-feedstock/>, 11 December 2018.
- [19] R. Taylor, L. Natrass, G. Alberts, et al., From the Sugar Platform to Biofuels and Biochemicals: Final Report for the European Commission Directorate-General Energy, No. ENER/C2/423-2012/SI2.673791 (2015), E4tech/ReCORD/Wageningen UR - 183.
- [20] E. de Jong, A. Higson, P. Walsh and M. Wellisch. Bio-Based Chemicals Value Added Products from Biorefineries. IEA Bioenergy, Task 42 Biorefinery, (2012).
- [21] J.H. Clark, F.E.I. Deswarte and T.J. Farmer. The Integration of Green Chemistry into Future Biorefineries. *Biofuels, Bioproducts and Biorefining*, 3 (2009), pp.72-90.
- [22] B. Kamm and M. Kamm. *Biorefineries—Multi Product Processes*. White Biotechnology, Springer Berlin Heidelberg, (2007), pp. 175-204.
- [23] T. Werpy, G. Petersen, A. Aden, et al. Top Value Added Chemicals from Biomass: Volume 1—Results of Screening for Potential Candidates from Sugars and Synthesis Gas, NREL/TP-510-35523 (2004), DTIC Document.
- [24] J.J. Bozell and G.R. Petersen. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—the US Department of Energy's "Top 10" Revisited. *Green Chemistry*, 12 (2010), pp.539-554.

- [25] Avantium YXY Pilot Plant, <https://www.chemicals-technology.com/projects/avantiumxyx/>, 26 September 2018.
- [26] G. Dull. *Chem.Ztg.*, 19 (1895), pp.166-216.
- [27] J. Kiermayer. A Derivative of Furfuraldehyde from Laevulose. *Chem.Ztg.*, 19 (1895), pp.1003-1006.
- [28] H.J.H. Fenton and M. Gostling. XL1.—Bromomethylfurfuraldehyde. *Journal of the Chemical Society, Transactions*, 75 (1899), pp.423-433.
- [29] H.J.H. Fenton and M. Gostling. LXXXV.—Derivatives of Methylfurfural. *Journal of the Chemical Society, Transactions*, 79 (1901), pp.807-816.
- [30] H.J.H. Fenton and F. Robinson. CXLVIII.—Homologues of Furfuraldehyde. *Journal of the Chemical Society, Transactions*, 95 (1909), pp.1334-1340.
- [31] J.A. Middendorp. Sur L'oxyméthylfurfurol. *Recueil des Travaux Chimiques des Pays-Bas et de la Belgique*, 38 (1919), pp.1-71.
- [32] R. van Putten, van der Waal, Jan C, E. De Jong, C.B. Rasrendra, H.J. Heeres and J.G. de Vries. Hydroxymethylfurfural, a Versatile Platform Chemical Made from Renewable Resources. *Chemical Reviews*, 113 (2013), pp.1499-1597.
- [33] Boy Arief Fachri. Catalytic Inulin Conversions to Biobased Chemicals (Doctoral Dissertation), Groningen (2015).
- [34] S. Wu, H. Fan, Y. Xie, Y. Cheng, Q. Wang, Z. Zhang and B. Han. Effect of CO₂ on Conversion of Inulin to 5-Hydroxymethylfurfural and Propylene Oxide to 1, 2-Propanediol in Water. *Green Chemistry*, 12 (2010), pp.1215-1219.
- [35] K. Ehara and S. Saka. Decomposition Behavior of Cellulose in Supercritical Water, Subcritical Water, and Their Combined Treatments. *Journal of Wood Science*, 51 (2005), pp.148-153.
- [36] W.S. Mok, M.J. Antal Jr and G. Varhegyi. Productive and Parasitic Pathways in Dilute Acid-Catalyzed Hydrolysis of Cellulose. *Industrial & Engineering Chemistry Research*, 31 (1992), pp.94-100.
- [37] M. Mednick. The Acid-Base-Catalyzed Conversion of Aldohexose into 5-(Hydroxymethyl)-2-Furfural. *The Journal of Organic Chemistry*, 27 (1962), pp.398-403.
- [38] F.H. Snyder (Ed.). Preparation of Hydroxymethylfurfural from Cellulosic Materials, U.S. Patent No. 2,851,468. 9 Sep., 1958.
- [39] W. Daengprasert, P. Boonnoun, N. Laosiripojana, M. Goto and A. Shotipruk. Application of Sulfonated Carbon-Based Catalyst for Solvothermal Conversion of Cassava Waste to Hydroxymethylfurfural and Furfural. *Industrial & Engineering Chemistry Research*, 50 (2011), pp.7903-7910.
- [40] A. Chareonlimkun, V. Champreda, A. Shotipruk and N. Laosiripojana. Catalytic Conversion of Sugarcane Bagasse, Rice Husk and Corn cob in the Presence of TiO₂, ZrO₂ and Mixed-Oxide TiO₂-ZrO₂ under Hot Compressed Water (HCW) Condition. *Bioresource Technology*, 101 (2010), pp.4179-4186.
- [41] A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani. A One-Pot Reaction for Biorefinery: Combination of Solid Acid and Base Catalysts for Direct Production of 5-Hydroxymethylfurfural from Saccharides. *Chemical Communications*, (2009), pp.6276-6278.
- [42] C. Wang, L. Fu, X. Tong, Q. Yang and W. Zhang. Efficient and Selective Conversion of Sucrose to 5-Hydroxymethylfurfural Promoted by Ammonium Halides under Mild Conditions. *Carbohydrate Research*, 347 (2012), pp.182-185.
- [43] K. Seri, Y. Inoue and H. Ishida. Highly Efficient Catalytic Activity of Lanthanide (III) Ions for Conversion of Saccharides to 5-Hydroxymethyl-2-Furfural in Organic Solvents. *Chemistry Letters*, 29 (2000), pp.22-23.
- [44] W. Dedsukphon, K. Faungnawakij, V. Champreda and N. Laosiripojana. Hydrolysis/Dehydration/Aldol-Condensation/Hydrogenation of Lignocellulosic Biomass and Biomass-Derived Carbohydrates in the Presence of Pd/WO₃-ZrO₂ in a Single Reactor. *Bioresource Technology* 102 (2011), pp.2040-2046.
- [45] C.V. McNeff, D.T. Nowlan, L.C. McNeff, B. Yan and R.L. Fedie. Continuous Production of 5-Hydroxymethylfurfural from Simple and Complex Carbohydrates. *Applied Catalysis A: General*, 384 (2010), pp.65-69.
- [46] J.N. Chheda, Y. Román-Leshkov and J.A. Dumesic. Production of 5-Hydroxymethylfurfural and Furfural by Dehydration of Biomass-Derived Mono- and Poly-Saccharides. *Green Chemistry*, 9 (2007), pp.342-350.
- [47] C. Moreau, R. Durand, C. Pourcheron and S. Razigade. Preparation of 5-Hydroxymethylfurfural from Fructose and Precursors over H-form Zeolites. *Industrial Crops and Products*, 3 (1994), pp.85-90.
- [48] W. Hsu, Y. Lee, W. Peng and K.C. Wu. Cellulosic Conversion in Ionic Liquids (ILs): Effects of H₂O/Cellulose Molar Ratios, Temperatures, Times, and Different ILs on the Production of Monosaccharides and 5-Hydroxymethylfurfural (HMF). *Catalysis Today*, 174 (2011), pp.65-69.

- [49] X. Qi, M. Watanabe, T.M. Aida and R.L. Smith Jr. Efficient One-Pot Production of 5-Hydroxymethylfurfural from Inulin in Ionic Liquids. *Green Chemistry*, 12 (2010), pp.1855-1860.
- [50] J. Chun, J. Lee, Y. Yi, S. Hong and C. Chung. Direct Conversion of Starch to Hydroxymethylfurfural in the Presence of an Ionic Liquid with Metal Chloride. *Starch-Stärke*, 62 (2010), pp.326-330.
- [51] Y. Zhang, H. Du, X. Qian and E.Y. Chen. Ionic Liquid– Water Mixtures: Enhanced Kw for Efficient Cellulosic Biomass Conversion. *Energy & Fuels*, 24 (2010), pp.2410-2417.
- [52] N.M. Bennett, S.S. Helle and S.J. Duff. Extraction and Hydrolysis of Levoglucosan from Pyrolysis Oil. *Bioresource Technology*, 100 (2009), pp.6059-6063.
- [53] Bio-Materials & Chemicals, <http://www.btgworld.com/en/rtd/technologies/bio-materials-chemicals>, 04 May 2016.
- [54] N. Kuzhiyil, D. Dalluge, X. Bai, K.H. Kim and R.C. Brown. Pyrolytic Sugars from Cellulosic Biomass. *ChemSusChem*, 5 (2012), pp.2228-2236.
- [55] J. Lian, S. Chen, S. Zhou, Z. Wang, J. O'Fallon, C. Li and M. Garcia-Perez. Separation, Hydrolysis and Fermentation of Pyrolytic Sugars to Produce Ethanol and Lipids. *Bioresource Technology*, 101 (2010), pp.9688-9699.
- [56] M.R. Rover, P.A. Johnston, T. Jin, R.G. Smith, R.C. Brown and L. Jarboe. Production of Clean Pyrolytic Sugars for Fermentation. *ChemSusChem*, 7 (2014), pp.1662-1668.
- [57] L. Luque, R. Westerhof, G. Van Rossum, S. Oudenhoven, S. Kersten, F. Berruti and L. Rehmann. Pyrolysis Based Bio-Refinery for the Production of Bioethanol from Demineralized Ligno-Cellulosic Biomass. *Bioresource Technology*, 161 (2014), pp.20-28.
- [58] H. Wang, D. Livingston, R. Srinivasan, Q. Li, P. Steele and F. Yu. Detoxification and Fermentation of Pyrolytic Sugar for Ethanol Production. *Applied Biochemistry and Biotechnology*, 168 (2012), pp.1568-1583.
- [59] How Sugar is Produced from Sugar Beet, <http://www.dansukker.co.uk/uk/about-sugar/how-sugar-is-produced-from-sugar-beet.aspx>, 17 September 2017.
- [60] EU Sugar Quota System Comes to an End, http://europa.eu/rapid/press-release_IP-17-3487_en.htm, 18-01-2018.
- [61] EU Set for Big Sugar Beet Crops as EU Drops Quotas, <https://uk.reuters.com/article/europe-sugar-crops/eu-set-for-big-sugar-beet-crop-as-eu-drops-quotas-idUKL8N1LO4U8>, 22-01-2018.
- [62] <http://biconsortium.eu/library/bic-documents>, 18-01-2018.
- [63] F. Barbir and S. Ulgiati, *Energy Options Impact on Regional Security*, Springer, 2010.
- [64] L. Tan, Z. Sun, S. Okamoto, M. Takaki, Y. Tang, S. Morimura and K. Kida. Production of Ethanol from Raw Juice and Thick Juice of Sugar Beet by Continuous Ethanol Fermentation with Flocculating Yeast Strain KF-7. *Biomass and Bioenergy*, 81 (2015), pp.265-272.
- [65] S. Dodić, S. Popov, J. Dodić, J. Ranković, Z. Zavargo and R.J. Mućibabić. Bioethanol Production from Thick Juice as Intermediate of Sugar Beet Processing. *Biomass and Bioenergy*, 33 (2009), pp.822-827.
- [66] R. Razmovski and V. Vučurović. Bioethanol Production from Sugar Beet Molasses and Thick Juice using *Saccharomyces Cerevisiae* Immobilized on Maize Stem Ground Tissue. *Fuel*, 92 (2012), pp.1-8.
- [67] E. Boran, E. Özgür, M. Yücel, U. Gündüz and I. Eroglu. Biohydrogen Production by *Rhodobacter capsulatus* in Solar Tubular Photobioreactor on Thick Juice Dark Fermenter Effluent. *Journal of Cleaner Production* 31 (2012), pp.150-157.
- [68] D. Foglia, W. Wukovits, A. Friedl, M. Ljunggren, G. Zacchi, K. Urbaniec and M. Markowski. Effects of Feedstocks on the Process Integration of Biohydrogen Production. *Clean Technologies and Environmental Policy*, 13 (2011), pp.547-558.
- [69] I. van Zandvoort. *Towards the Valorization of Humin By-Products: Characterization, Solubilization and Catalysis* (Doctoral Dissertation), Utrecht (2015).
- [70] Oasmaa, E. Kuoppala, A. Ardiyanti, R. Venderbosch and H. Heeres. Characterization of Hydrotreated Fast Pyrolysis Liquids. *Energy & Fuels*, 24 (2010), pp.5264-5272.

2

Kinetic Studies on the Conversion of Levoglucosan to Glucose in Water Using Brønsted Acids as the Catalysts

This chapter is published as:

Kinetic Studies on the Conversion of Levoglucosan to Glucose in Water Using Brønsted Acids as the Catalysts

R.M. Abdilla, C.B. Rasrendra and H.J. Heeres

Ind. Eng. Chem. Res. 2018, 57, 9, 3204-3214

DOI: 10.1021/acs.iecr.8b00013

Fast pyrolysis is a promising and versatile technology to depolymerize and concentrate sugars from lignocellulosic biomass. The produced pyrolysis oils contain considerable amounts of levoglucosan (1,6-anhydro- β -D-glucopyranose), which is an interesting source for glucose (GLC). Here, we report a kinetic study on the conversion of levoglucosan (LG) to GLC in water using sulfuric and acetic acid as the catalysts under a wide range of conditions in a batch setup. The effects of the initial LG loading (0.1–1 M), sulfuric and acetic acid concentrations (0.05–0.5 M and 0.5–1 M, respectively), and reaction temperatures (80–200 °C) were determined. Highest GLC yields were obtained using sulfuric acid (98 mol %), whereas the yields were lower for acetic acid (maximum 90 mol%) due to the formation of byproducts such as insoluble polymers (humins). The experimental data were modeled using MATLAB software, and relevant kinetic parameters were determined. Good agreement between experimental data and model was obtained when assuming that the reaction is first order with respect to LG. The activation energies were 123.4 kJ mol⁻¹ and 120.9 kJ mol⁻¹ for sulfuric and acetic acid, respectively.

2.1. INTRODUCTION

Biomass is considered the only sustainable carbon source for the production of carbonbased fuels and chemicals with low carbon emissions [1-3]. A particularly interesting biomass source is lignocellulosic biomass, the most abundant and renewable biomass on earth [4]. Particularly the cellulose and hemicellulose fraction in lignocellulosic biomass may be used as a renewable source for the production of biofuels and biobased chemicals by catalytic conversions, often after a pre-treatment to obtain monomeric sugars [4, 5].

A promising and versatile technology for the pre-treatment of lignocellulosic biomass is fast pyrolysis [6-8]. Fast pyrolysis is an alternate method to acid and enzymatic hydrolysis of lignocellulosic biomass to obtain (monomeric) sugars from biomass [9]. In fast pyrolysis, lignocellulosic biomass (e.g., forestry residue) is rapidly heated (typically, <2 s, 450–600 °C) in the absence of oxygen under atmospheric pressure [10-13]. The vapors formed are rapidly cooled into a liquid product known as pyrolysis oils (also known as bio-oils or pyrolysis liquids). Typical liquid yields are reported to be up to 75–85 wt% of the initial biomass feed [5, 6, 13]. Generally, pyrolysis oils are complex mixtures of numerous oxygenated compounds of various organic groups such as carboxylic acids, alcohols, ketones, aldehydes, phenolics, and sugars [14]. Compared to other biomass conversion technologies, pyrolysis offers a number of advantages such as; i) low capital investment and operating costs [15], ii) possibility to use a wide variety of biomass feed, including agricultural wastes, grasses, and woody biomass [16-18] and iii) pyrolysis is a fast process compared to biological approaches [17, 19].

Levoglucosan (1,6-anhydro- β -D-glucopyranose) is known to be among the major products found in pyrolysis oil and is actually the primary degradation product of cellulose [5, 9]. The yield of levoglucosan (LG) in pyrolysis oil varies and is depending, among others, on the type of feedstock and the operating conditions. LG yield up to 33 wt% has been reported when using cotton as the biomass feed [20]. When pure cellulose is used as the starting material, the yield can be as high as 60 wt% [7, 21]. LG is an example of an anhydrosugar and is readily converted to glucose (GLC) by an acid-catalyzed hydrolysis [5]. GLC is a known precursor for biofuels (bioethanol) and biobased chemicals. Examples of the latter are 5-hydroxymethylfurfural (HMF), levulinic acid and lactic acid, which are versatile platform chemicals and precursors for biodegradable polymers [22]. As such, isolation and valorization of the sugar fraction and particularly LG from pyrolysis oils could improve the techno-economic feasibility of the pyrolysis process (Figure 1). Various approaches have been identified to separate the sugar fraction in the pyrolysis oil from the pyrolytic lignin fraction, of which liquid-liquid extraction combined with destillative workup is considered the most promising [5, 23-25]. It allows isolation of the sugar fraction as a liquid in good yields (up to 34 wt% of the original oil) [26]. The composition has been determined in detail, and it typically consists of LG (16 wt%), glycoaldehyde (11 wt%), acids (2.5 wt%), ketones (1.4 wt%) and phenolics (0.4 wt%) [27].

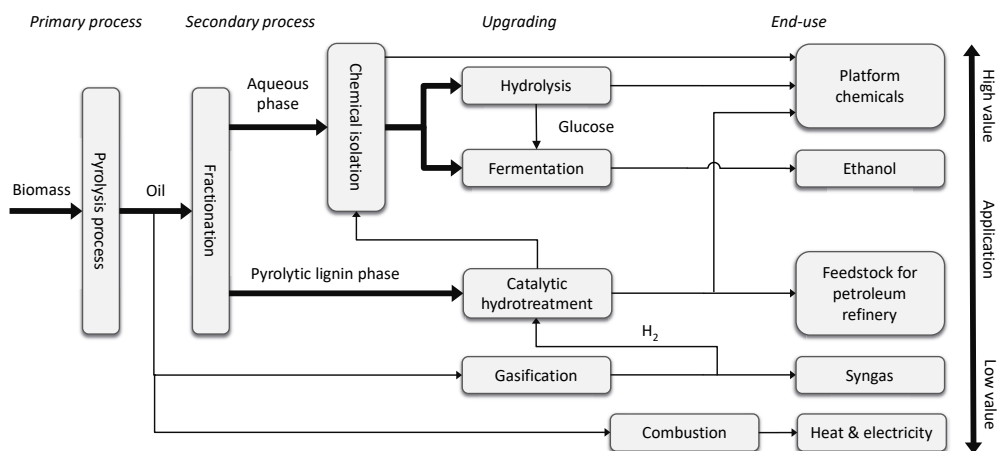


Figure 1. Biorefinery concept for pyrolysis technology [28] (reproduced with permission).

For the development of technology to convert the sugar fraction of pyrolysis oils for further use, it is essential to gain insights in the rate of hydrolysis reactions. We here report a model study on the conversion of LG, a main component in the sugar fraction of pyrolysis oil, to GLC. To the best of our knowledge, a limited number of kinetic studies on LG conversion to GLC have been reported. LG hydrolysis in water with hydrochloric acid catalyst was investigated by Vidrio [29]. The reactions were carried out at low temperature (25–50 °C) over a six-week period. The activation energy found in this study was 97 kJ mol⁻¹. Helle et al. [9] studied the reaction of LG in water, in spent sulfite liquor and/or pyrolysis oil extract using sulfuric acid as the catalyst in a temperature range between 50 and 130 °C. Activation energies of 114 kJ mol⁻¹ and 87 kJ mol⁻¹ were found for the hydrolysis of LG in dilute sulfuric acid and in spent sulfite liquor or pyrolysis oil extract, respectively. In both studies, first order kinetics were assumed and the effect of the initial concentration of LG on reaction kinetic was not determined.

In the following, an experimental and modeling study on the conversion of LG to GLC under acidic conditions in aqueous solutions is discussed. Sulfuric acid and acetic acid were used as the catalyst under broad range of reaction conditions. Acetic acid was selected as it is abundantly available in pyrolysis oils with concentrations up to 10 wt% [30]. The effects of reaction parameters (acid concentration, temperature, initial LG loading) on the reaction rates were measured and the relevant kinetic parameters were determined from the experimental data using MATLAB software. Differences on the catalytic activity between sulfuric acid and acetic acid will be highlighted and the implications of the models regarding GLC yield will be discussed.

2.2. EXPERIMENTAL SECTION

2.2.1. Chemicals

LG was purchased from Carbosynth, UK. Sulfuric acid (96–98 wt %), HMF, formic acid and GLC (≥ 99.5 wt %) were obtained from Sigma-Aldrich (Steinheim, Germany). Levulinic acid was purchased from Alfa Aesar. Acetic acid (glacial) was acquired from Merk Millipore (Darmstadt, Germany). All chemicals were used without further purification. For all experiments, Milli-Q water was used to prepare the solutions.

2.2.2. Experimental procedure

The experimental methods are based on published work by Girisuta et al. [31]. The hydrolysis reactions were carried out in glass ampules (i.d. 3 mm, wall thickness of 1.5 mm, and length of 15 cm). The ampules were filled with approximately 0.3 mL of the reaction mixture consisting of a pre-determined amount of LG (0.1–1 M) and catalyst (0.05–0.5 M sulfuric acid, 0.5–1 M acetic acid). After filling, the ampules were sealed with a torch. The ampules were placed in an aluminum rack and subsequently placed in a temperature-controlled oven (GC oven, Hewlett Packard 5890A) at $T_{\text{oven}} = 80\text{--}160$ °C for experiments using sulfuric acid and at $T_{\text{oven}} = 160\text{--}200$ °C for experiments using acetic acid. At different reaction times, an ampule was removed from the oven and quickly quenched in cold water to stop the reaction. Typically, at least 8 ampules were used for one series of experiments. An overview of experimental data of all individual experiments is given in the Supporting Information. After reaction, the ampules were opened and the reaction mixture was withdrawn. Subsequently, the mixture was filtered with a 0.45 μm PTFE filter to remove any insoluble matter. An amount of the clear solution was then diluted with Milli-Q water, and the resulting mixture was subjected to analysis by high performance liquid chromatography (HPLC).

2.2.3. Analytical methods

The composition of the reaction mixture was determined by HPLC. The HPLC device consists of an Agilent 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87H), a refractive index detector, and an ultraviolet detector. The mobile phase was 5 mM aqueous sulfuric acid at a flow rate of 0.55 mL min⁻¹. The HPLC column was operated at 60 °C. The concentration of compounds in the product mixture was determined using calibration curves obtained by analyzing standard solutions with known concentrations. A typical HPLC chromatogram of a sample is shown in Figure 2.

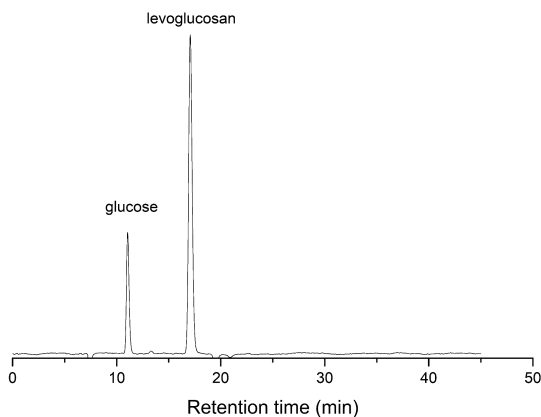


Figure 2. Typical HPLC chromatogram for a product mixture of LG hydrolysis in water.

2.2.4. Definition and determination of kinetic parameters

The concentrations of the relevant compounds as measured by HPLC were used to calculate the conversion of LG (X_{LG}) and the yield of GLC (Y_{GLC}). The conversion and yield definitions are given in eqs 1 and 2.

$$X_{LG} = \frac{(C_{LG,0} - C_{LG})}{C_{LG,0}} \quad (1)$$

$$Y_{GLC} = \frac{(C_{GLC})}{C_{LG,0}} \quad (2)$$

The kinetic parameters of the reactions were obtained using MATLAB R2016a software package based on with minimization of the error between the measured/experimental values and the model. Details on this procedure can be found elsewhere [32, 33]. Reaction rate equations used for the modeling are given in the following section (see section 2.3.3).

2.3. RESULTS AND DISCUSSION

2.3.1. Product distribution using sulfuric acid as the catalyst

A total of 38 experimental series were conducted in a broad range of reaction conditions (80–160 °C, $C_{LG,0} = 0.1$ –1 M) using sulfuric acid as the catalyst (0.05–0.5 M). A typical example of a reaction profile (160 °C, $C_{LG,0} = 1$ M, $C_{H_2SO_4} = 0.1$ M) is given in Figure 3 (left side). At these

conditions, LG is converted within 10 min to GLC. At prolonged reaction times, the concentration of GLC is reduced and HMF, levulinic acid (LA) and formic acid (FA) are formed. These are known products from the subsequent dehydration reactions of GLC in acidic conditions [31]. In addition, the color of the solution changes from colorless to light yellow and finally to brown with the concomitant formation of solids, indicative for the formation of humins. These are known to consist of oligomeric-polymeric condensed structures and are inevitably formed upon the treatment of GLC in acidic conditions at elevated temperatures [31].

Mass balance calculations were performed based on the total amount of HPLC detectables (LG, GLC, HMF, LA, FA) and the LG intake and the results are given in Figure 3 (right side). It is evident that, particularly in the initial stage of the reaction, mass balance closure is not quantitative, meaning that small amounts of other components are formed. This is also clear when considering the profile after about 10 minutes (Figure 3, left side), showing quantitative LG conversion whereas the amount of GLC is at maximum about 85% of the initial LG concentration. Indeed, some unknown components are visible at the initial stage of the reaction in the HPLC chromatograms. A possibility is the formation of dihydroxyacetone (DHA) [34], a known degradation product of LG at acidic conditions. These findings are of interest for the development of the kinetic models as they imply the existence of a parallel pathway for LG hydrolysis not leading to GLC but to unknown components.

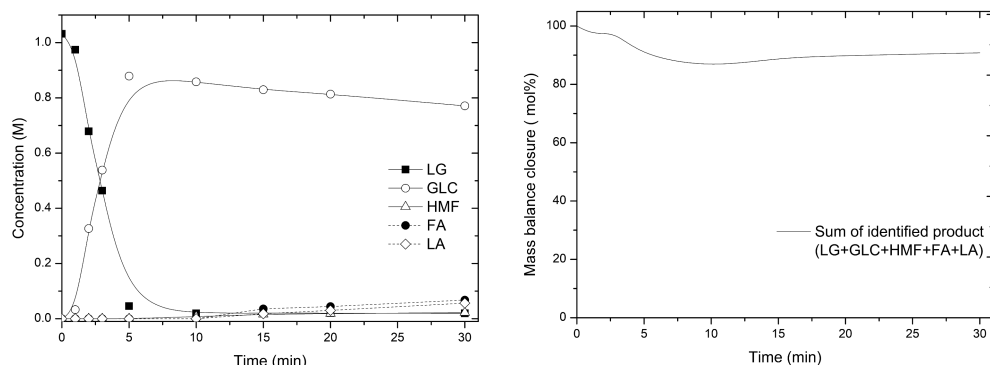


Figure 3. Representative example of a concentration profile (left) and the mass balance closure (right) at 160 °C, $C_{\text{LG},0} = 1 \text{ M}$ and $C_{\text{H}_2\text{SO}_4} = 0.1 \text{ M}$.

To test the reproducibility of the experiments, 10 randomly selected experimental series (from 38 batch experiments in total) were performed twice and the result of a representative experiment is given in Figure 4. It implies that the reproducibility of the experiments is good.

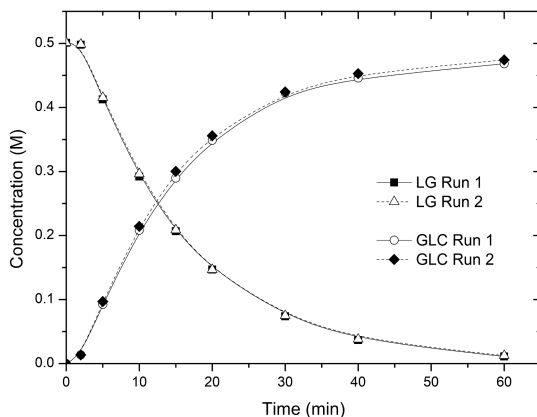


Figure 4. Reproducibility experiment for the acid-catalyzed conversion of LG (120°C , $C_{\text{LG},0} = 0.5 \text{ M}$, $C_{\text{H}_2\text{SO}_4} = 0.1 \text{ M}$).

2.3.2. Effect of process variables on the hydrolysis rate of LG

The temperature has a major effect on the conversion of LG, as clearly shown in Figure 5. For example, at a temperature of 140°C , 94 mol% of LG conversion (X_{LG}) was obtained after 10 min, whereas quantitative conversion is not attainable within 100 min batch time when the temperature is below 120°C .

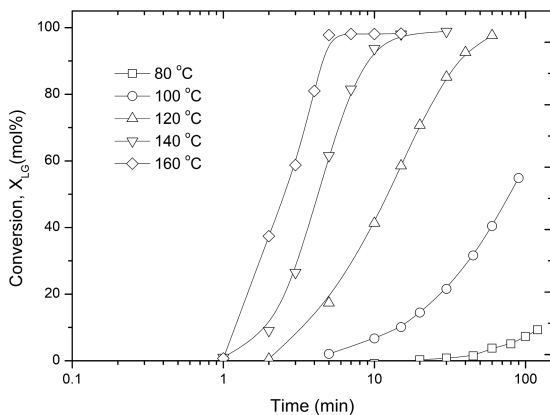


Figure 5. Effect of temperature on the conversion of LG ($C_{\text{LG},0} = 0.5 \text{ M}$, $C_{\text{H}_2\text{SO}_4} = 0.1 \text{ M}$).

In Figure 6 (left side), the effect of the catalyst concentration ($C_{\text{H}_2\text{SO}_4}$) on LG conversion versus time (at 140°C and $C_{\text{LG},0} = 0.5 \text{ M}$) is given. The reaction rate is evidently enhanced at higher acid concentrations, and higher conversions at lower batch times are attained at higher catalyst concentrations. The GLC yields are also a function of the acid concentration. However, this effect is only pronounced at high conversions and acid concentrations, see

Figure 6 (right side) for details. Apparently, at these extremes, the consecutive reaction of GLC to HMF and LA takes place to a significant extent.

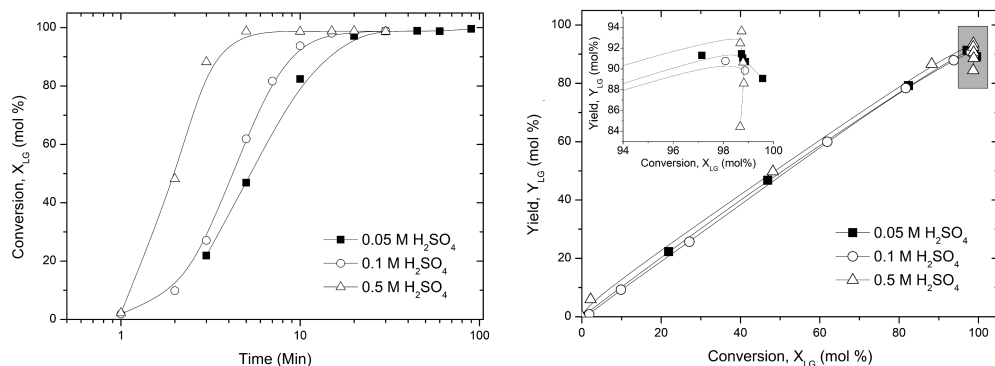


Figure 6. Effect of acid concentration on LG conversion, X_{LG} (left) and yield of GLC, Y_{GLC} (right). Reaction conditions: 140 °C and $C_{LG,0} = 0.5$ M.

The effect of the initial concentration of LG was investigated ($C_{LG,0}$ 0.1–1 M, 120 °C and $C_{H_2SO_4} = 0.05$ M) and the conversion of LG was found to be independent on the initial concentration of LG (Figure 7, left side). This is a strong indication that LG hydrolysis is first order in LG. Moreover, the initial concentration of LG has a small though significant influence on the GLC yield (Figure 7, right side). At higher LG loading, the yield of GLC is slightly reduced at prolonged batch times. This might be due to a higher rate of formation of soluble and insoluble polymers at higher GLC concentrations, resulting a decrease in the yield of GLC.

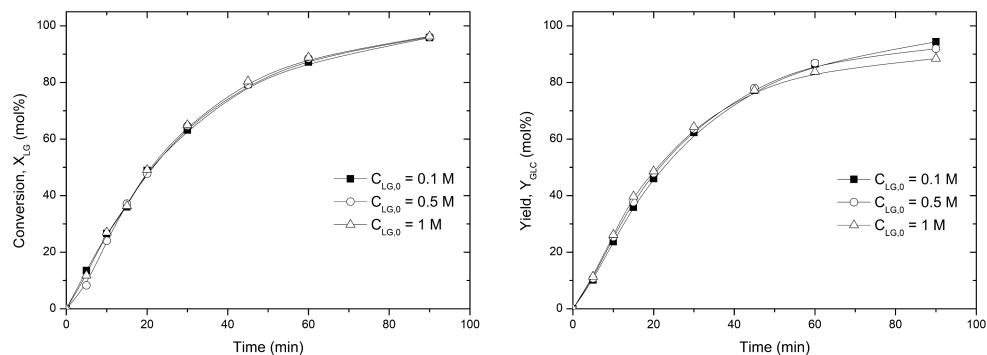
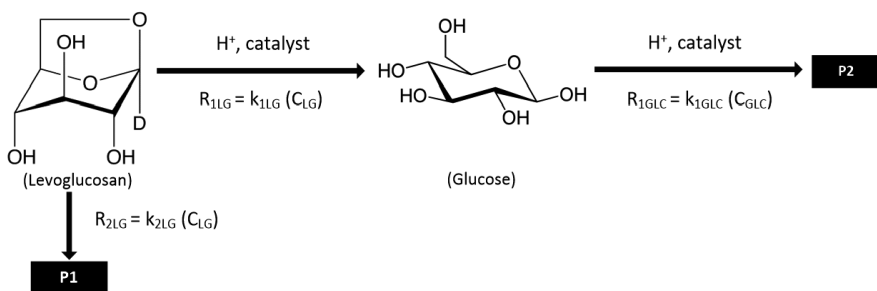


Figure 7. Effect of LG initial loading on its conversion, X_{LG} (left) and yield of GLC, Y_{GLC} (right) at reaction conditions: 120 °C, $C_{H_2SO_4} = 0.05$ M.

2.3.3. Kinetic model development for sulfuric acid

A kinetic model for the reaction of LG in water with sulfuric acid as the catalyst was developed involving a sequence of reactions based on the products formed (Scheme 1). It initially involves two parallel reactions for LG, viz. the main hydrolysis reaction to GLC and a reaction to other products. This reaction has to be considered based on mass balance (Figure 3), particularly at high temperatures. In addition, GLC is assumed to react further to, among others, HMF, LA and FA, and soluble and insoluble humins. The latter reactions are lumped into one overall reaction involving GLC as the starting material. Based on the experiments with variable LG intakes, it was shown that the reaction is first order in LG and this characteristic was also used as the input in the kinetic model.



Scheme 1. Proposed scheme for LG hydrolysis in acidic solutions.

Using the first order reaction assumption, the reaction rates of the three individual reactions are defined in eqs 3-5.

$$R_{1LG} = k_{1LG} (C_{LG}) \quad (3)$$

$$R_{2LG} = k_{2LG} (C_{LG}) \quad (4)$$

$$R_{1GLC} = k_{1GLC} (C_{GLC}) \quad (5)$$

The temperature and acid concentration dependence of the kinetic constants was introduced using modified Arrhenius equations (eqs 6-8).

$$k_{1LG} = (C_{H^+}) k_{1RLG} \exp \left[\frac{E_{1LG}}{R} \left(\frac{T - T_R}{T_R T} \right) \right] \quad (6)$$

$$k_{2LG} = (C_{H^+}) k_{2RLG} \exp \left[\frac{E_{2LG}}{R} \left(\frac{T - T_R}{T_R T} \right) \right] \quad (7)$$

$$k_{1GLC} = (C_{H^+}) k_{1GLC} \exp \left[\frac{E_{1GLC}}{R} \left(\frac{T - T_R}{T_R T} \right) \right] \quad (8)$$

Where T is a function of time (see the Supporting Information for more details), and T_R is reference temperature (115 °C). The order in acid is also assumed to be one, and this is incorporated in eqs 6–8.

The reaction is assumed to be catalyzed by protons, of which the concentration was calculated using eq 9.

$$C_{H^+} = C_{H_2SO_4} + \frac{1}{2} \left(- \left(K_{a,HSO_4^-} + C_{H_2SO_4} \right) + \sqrt{\left(K_{a,HSO_4^-} + C_{H_2SO_4} \right)^2 + 4 \left(C_{H_2SO_4} K_{a,HSO_4^-} \right)} \right) \quad (9)$$

The term K_{a,HSO_4^-} in eq 9 represents the dissociation constant of (HSO_4^-) . This value is temperature dependent and given by eqs 10 and 11 [35].

$$pK_{a,HSO_4^-} = 0.0152T - 2.636 \quad (10)$$

$$pK_{a,HSO_4^-} = -\log_{10} \left(K_{a,HSO_4^-} \right) \quad (11)$$

where T is temperature in K.

In a batch system, the concentrations of LG and GLC versus time are represented by the differential equations given in eqs 12 and 13.

$$\frac{dC_{LG}}{dt} = - (R_{1LG} + R_{2LG}) \quad (12)$$

$$\frac{dC_{GLC}}{dt} = R_{1LG} - R_{1GLC} \quad (13)$$

In total, 38 concentration-time profiles at different temperatures, acid concentrations and LG intakes were determined experimentally, giving a total of 684 data points (9 samples per experiment, concentrations of LG and GLC for each sample). The best estimates of the kinetic parameters and their standard deviations, as determined by minimization of the errors between all experimental data and the kinetic model, are shown in Table 1.

Comparison of the experimental data and the output of the kinetic model demonstrates a good fit for a broad range of reaction conditions (Figure 8). A parity plot (Figure 9) shows the goodness-of-fit between the experimental and model data.

Table 1. Kinetic parameters for the reactions of LG to products with sulfuric acid as the catalyst.

Parameters	Estimated value	Unit	Description
k_{1RLG}	0.599 ± 0.009	$M^{-1} min^{-1}$	Reaction rate constant of k_{1LG} at reference temperature*
E_{1LG}	123.4 ± 1.1	$kJ mol^{-1}$	Activation energy of k_{1LG}
k_{2RLG}	0.023 ± 0.008	$M^{-1} min^{-1}$	Reaction rate constant of k_{2LG} at reference temperature*
E_{2LG}	166.5 ± 14.9	$kJ mol^{-1}$	Activation energy of k_{2LG}
k_{1RGLC}	0.005 ± 0.001	$M^{-1} min^{-1}$	Reaction rate constant of k_{1GLC} at reference temperature*
E_{1GLC}	97.2 ± 9.9	$kJ mol^{-1}$	Activation energy of k_{1GLC}

* $T_R = 115 \text{ } ^\circ C$

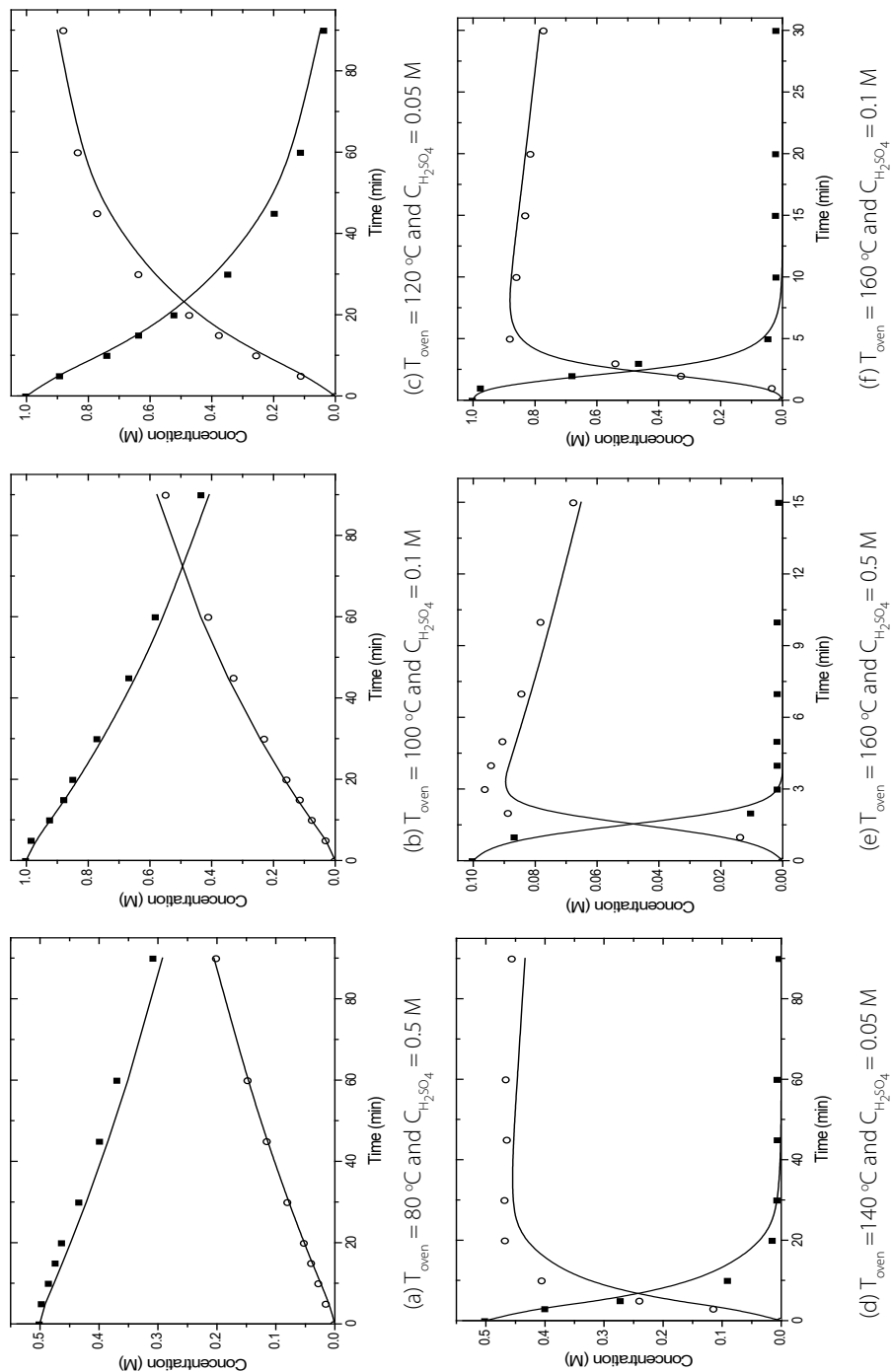


Figure 8. Comparison of experimental data (■: C_{IG} and ○: C_{GLC}) and predicted data from the kinetic model (solid lines) for experiments with sulfuric acid as the catalyst.

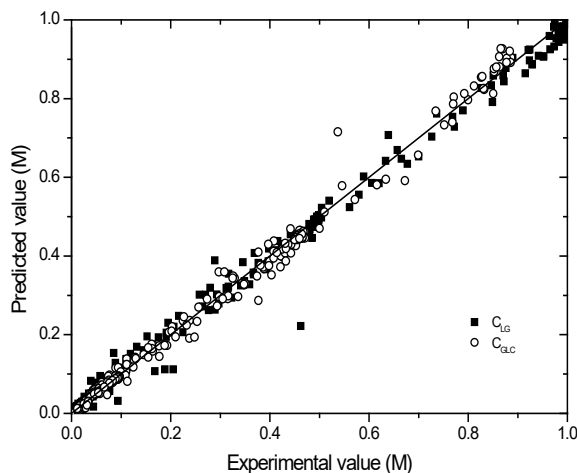


Figure 9. Parity plot for all experimental and model data-points with sulfuric acid as the catalyst.

The activation energy obtained in this study ($123.4 \text{ kJ mol}^{-1}$) is comparable to the one found in the literature (114 kJ mol^{-1}) using sulfuric acid catalyst at lower temperatures ($50\text{--}130^\circ\text{C}$) [9]. However, it is considerably higher than the value found using hydrochloric acid (97 kJ mol^{-1}) at lower temperatures ($25\text{--}50^\circ\text{C}$) [29]. The difference in the activation energy might be attributed by the intrinsic feature of HCl or due to the large difference in the temperatures between ours and the HCl catalyzed study.

2.3.4. Kinetic model development for acetic acid

A variety of acids have been identified in crude pyrolysis oils. Examples are acetic acid, formic acid, glycolic acid and propionic acid [10]. Acetic acid is reported to be the major organic acid, and, depending on the conditions applied during the pyrolysis process, its concentration can be up to 10 wt% [30]. As such, it is also of interest to determine the effects of acetic acid on the rate of LG hydrolysis as this will also give insights in the rate of LG conversion in the pyrolysis process (e.g., in the condenser systems) and during storage. This is of high importance when the objective of the pyrolysis process is to optimize LG concentrations, and as such to reduce the rate of LG hydrolysis to GLC. In addition, this information will also be essential to determine possible anion effects on catalysis, i.e., whether acetate or sulfate anions play a role or that only the proton concentration is determining the rate of the reactions.

The experimental procedure applied was similar to the experiments using sulfuric acid as the catalyst (see section 2.2.2), with only slight differences in the experimental condition ranges ($C_{\text{LG},0} = 0.1\text{--}1 \text{ M}$ at $T = 160\text{--}200^\circ\text{C}$ and $C_{\text{CH}_3\text{COOH}} = 0.5\text{--}1 \text{ M}$). A total of 10 concentration

versus time profiles were obtained each consisting of 16 data points representing the LG and GLC concentration at certain reaction times. A higher temperature range was applied compared to sulfuric acid to compensate for the by far lower proton concentration in solution when using acetic acid. At the end of the reactions, the reaction mixture was dark brown–black in color and contained significant amounts of solid (humins) byproducts.

Typical concentration-time profiles for LG and the main product GLC at two temperatures (160, 180 °C) are provided in Figure 10 and show that the temperature has a large effect on the LG conversion rates. However, the yields of GLC are lower than for sulfuric acid, indicating a higher rate for the degradation of GLC to among others soluble and insoluble (humins) byproducts. In line with the result from sulfuric acid-catalyzed experiments, GLC decomposition products were HMF, LA and FA (results not shown for brevity). It is worth to note that the conversion rate of LG when using acetic acid as catalyst is significantly lower than for sulfuric acid (see Figure 3 for comparison).

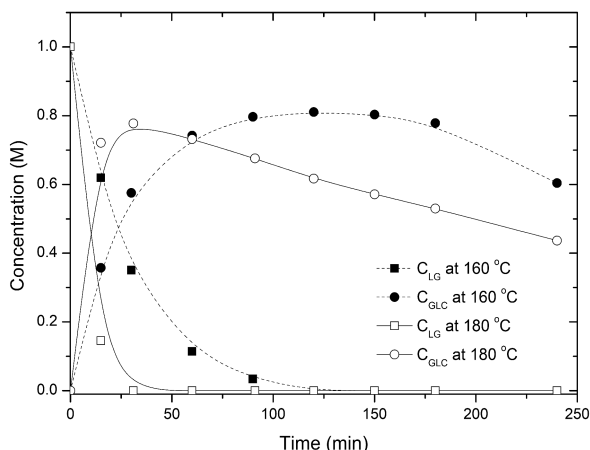


Figure 10. Typical concentration profiles for the reaction of LG in an acetic acid–water system ($C_{LG,0} = 1$ M, $C_{CH_3COOH} = 0.5$ M, 160 and 180 °C).

Typically, the maximum yields of GLC are lower when using acetic acid than sulfuric acid as catalyst, viz. 90 mol % at 0.1 M LG, an acetic acid concentration of 1 M, and a temperature of 160 °C compared to 98 mol % at 0.1 M LG, a sulfuric acid concentration of 0.1 M, and a temperature of 140 °C. As such, the parallel decomposition of LG to other products than GLC seems to occur with a higher rate for acetic acid. The kinetic model development for acetic acid is based on the reaction network given in Scheme 1. Eqs 3–8 and eqs 12 and 13 were applied to express the rate, kinetic rate constants, and concentrations of LG and GLC as a function of time, respectively. The concentration of H^+ was calculated using the acid dissociation constant (eq 14), which was corrected for the temperature by using eqs 15 and 16.

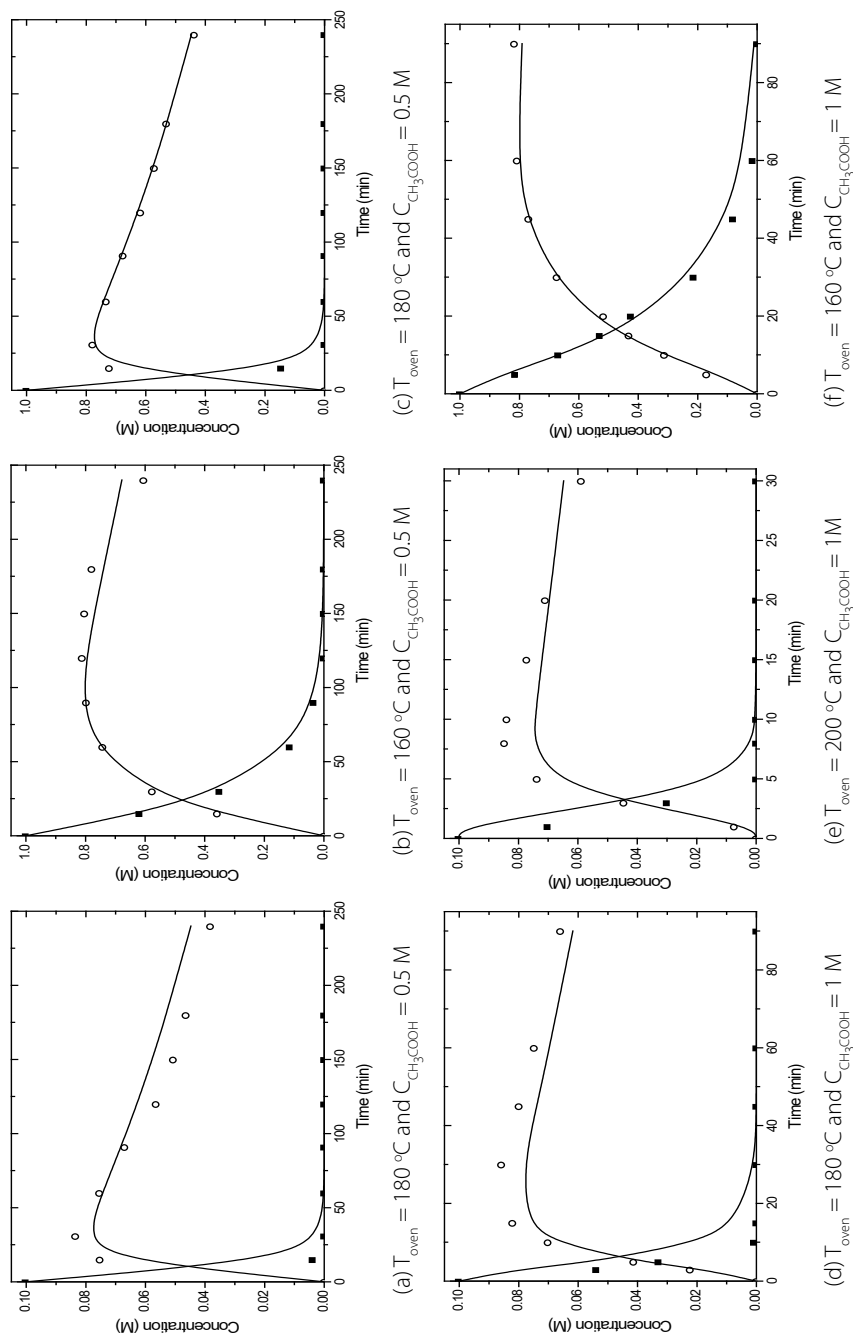


Figure 11. Comparison of experimental data ($\blacksquare$ C_{GL} and $\circ$ C_{GL_2}) and predicted data using the kinetic model (solid lines) for experiment with acetic acid as the catalyst

$$C_{H^+} = \frac{1}{2} \left(-K_{a,CH_3COO^-} + \sqrt{K_{a,CH_3COO^-}^2 + 4 \left(C_{CH_3COOH} K_{a,CH_3COO^-} \right)} \right) \quad (14)$$

$$\Delta G = -RT \ln K_{a,CH_3COO^-} \approx 2.303RTpK_{a,CH_3COO^-} \quad (15)$$

$$\Delta G = \Delta H - T\Delta S \quad (16)$$

where R is the universal gas constant, T is temperature and the value of H and S for acetic acid in water are reported to be $-0.41 \text{ kJ mol}^{-1}$ and $-0.0925 \text{ kJ mol}^{-1}\text{K}^{-1}$, respectively [36].

The kinetic parameters were determined using MATLAB optimization routines, and the best estimations including their standard deviations are given in Table 2.

Table 2. Kinetic parameters for LG hydrolysis acetic acid as the catalyst.

Parameters	Estimated value	Unit	Description
k_{1RLG}	0.610 ± 0.063	$\text{M}^{-1} \text{min}^{-1}$	Reaction rate constant of k_{1LG} at reference temperature*
E_{1LG}	120.9 ± 3.7	kJ mol^{-1}	Activation energy of k_{1LG}
k_{2RLG}	0.01 ± 0.006	$\text{M}^{-1} \text{min}^{-1}$	Reaction rate constant of k_{2LG} at reference temperature*
E_{2LG}	189.0 ± 18.0	kJ mol^{-1}	Activation energy of k_{2LG}
k_{1RGLC}	0.116 ± 0.028	$\text{M}^{-1}\text{min}^{-1}$	Reaction rate constant of k_{1GLC} at reference temperature*
E_{1GLC}	60.9 ± 7.2	kJ mol^{-1}	Activation energy of k_{1GLC}

* $T_R = 115^\circ\text{C}$.

A good fit between experimental data and the kinetic model was observed, see Figure 11 for details. This is confirmed by the parity plot between experimental and modeled data (Figure 12).

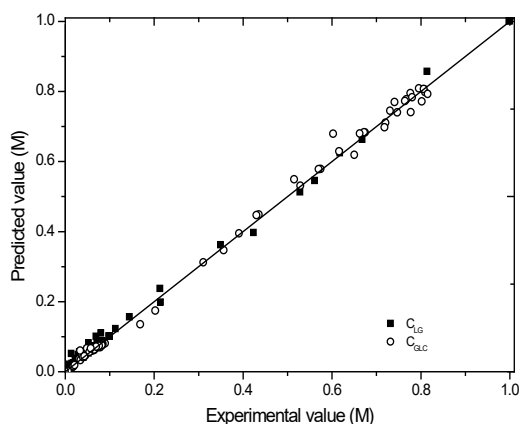


Figure 12. Parity plot for all experimental and model point with acetic acid as the catalyst.

2.4. APPLICATION OF THE KINETIC MODEL

2.4.1. Comparison between sulfuric and acetic acid

With the kinetic models for both acid catalysts available, it is possible to gain insight into LG conversion, selectivity and yield of GLC as a function of the type of acid catalyst and process conditions. For instance, a simulation of the typical batch time needed to achieve 90 mol% LG conversion using sulfuric acid and acetic acid as catalysts at various temperatures is given in Figure 13.

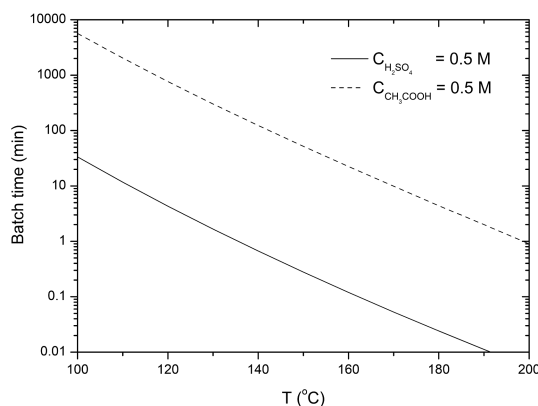


Figure 13. Required batch time for $X_{GLC} = 90$ mol% as a function of T and type of acid ($C_{LG,0} = 0.1 M$).

Thus, it is clear that sulfuric acid is by far more effective than acetic acid and the batch times required for 90% conversion at various temperatures are typically a factor of 170–180 lower.

2.4.2. Selectivity

Quantitative information on the effect of reaction conditions on the selectivity of the reaction can be obtained from the kinetic model. For this purpose, a rate selectivity parameter (S) is used, which is defined as the ratio between the rate of the desired reactions and the rate of undesired reactions (eq 17). As such, S considers the conversion of LG to GLC and to byproducts, without considering subsequent reactions of GLC. As such, this approach is only valid at relatively short batch times.

$$S = \frac{(\text{rate of glucose formation})}{(\text{rate of levoglucosan to decomposition product})} = \frac{R_{1LG}}{R_{2LG}} \quad (17)$$

Substitution of the rate expressions and kinetic constants equations as given in eq 6 and 7 leads to eq 18.

$$S = \frac{k_{1RLG}}{k_{2RLG}} \exp \left[\frac{(E_{1LG} - E_{2LG})}{R} \left(\frac{T - T_R}{T_R T} \right) \right] \quad (18)$$

The latter equation shows that the value of S is independent of the C_{LG} and $C_{H_2SO_4}$ or C_{CH_3COOH} and only a function of the temperature. The activation energies of the main reaction, $E_{1LG} = 123.4$ (for sulfuric acid) and $120.9 \text{ kJ mol}^{-1}$ (for acetic acid), are lower than the side reaction, $E_{2LG} = 166.5$ (for sulfuric acid) and 189 kJ mol^{-1} (for acetic acid, see Tables 1 and 2). Hence, to achieve high selectivity in the initial stage of the reaction, it is best to perform the reaction at the lower temperatures. However, this goes at the expense of reaction rates and thus the space time yields. Therefore, a compromise between a high reaction rate, for which higher temperatures are preferred, and a good GLC selectivity, which is favored at lower temperatures, is required.

It is also of interest to compare the activation energies for the lumped decomposition reaction of GLC to P2 for both acids. The activation energy for acetic acid is 60.9 kJ mol^{-1} , which is significantly lower than for sulfuric acid (97.2 kJ mol^{-1}). In line with this finding is the formation of significantly higher amounts of insoluble humins during the reaction with acetic acid. These observations are in agreement with a previous study by Girisuta et al. [31] where various Brønsted acids (H_3PO_4 , oxalic acid, HCl, H_2SO_4 , and HI) were tested as the catalyst for HMF conversion to LA. Here, the organic acid in the series (oxalic acid) gave a lower yield of LA and significantly higher amounts of humins than the mineral acids.

2.4.3. Determination of optimum reaction conditions for highest yield

The kinetic model also allows for determination of the optimum reaction conditions to achieve the highest Y_{GLC} . For this purpose, eq 1 is differentiated to give:

$$dX_{LG} = - \frac{dC_{LG}}{C_{LG,0}} \quad (19)$$

The combination of eqs 12 and 13 and eq 19 leads to eq 20.

$$\frac{dC_{GLC}}{dX_{LG}} = \frac{R_{1LG} - R_{1GLC}}{R_{1LG} + R_{2LG}} C_{LG,0} \quad (20)$$

Eq 20 was solved from 0 to 90 mol % LG conversion for the reactions using sulfuric acid and acetic acid as the catalyst. The GLC yield is subsequently calculated using eq 2. Figure 14 shows the GLC yield as a function of temperature and acid concentration at an initial LG concentration of 0.1 M and a X_{LG} of 90 mol %. Within this range of process conditions, the yield of GLC is almost independent of the acid concentration for both sulfuric and acetic acid.

Also, it is evident that the GLC yield is highest at the lowest temperatures in the range for sulfuric acid (Figure 14, left side), while it is highest at intermediate temperatures for acetic acid (Figure 14, right side). This simulation is in line with the experimental results (*vide supra*).

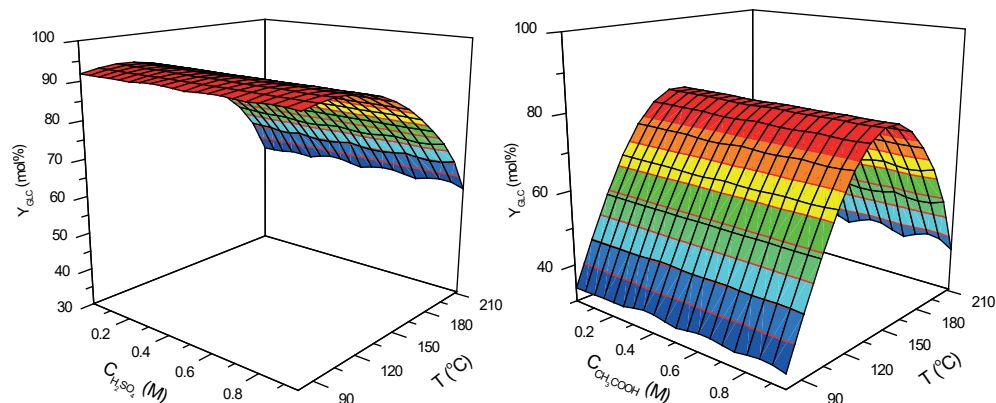


Figure 14. Effects of acid concentration and temperature on yield of GLC using sulfuric acid (left) and acetic acid (right) (at 0.1 M LG loading and 90 mol% LG conversion).

2.5. CONCLUSIONS

A comprehensive experimental and modeling study on the acid-catalyzed reaction of LG to GLC in a batch reactor has been performed. A broad range of reaction conditions was tested, including variation in initial LG intake (0.1–1 M), temperature (80–200 °C), and acid catalysts (sulfuric acid, 0.05–0.5 M and acetic acid, 0.5–1 M). In the temperature range used in this study, sulfuric acid gave the highest GLC yield (max. 98 mol %), while the use of acetic acid as catalyst gave a lower yield (max. 90 mol %) due to byproduct formation. Furthermore, a broadly applicable kinetic model for the acid-catalyzed hydrolysis of LG for both the sulfuric and acetic acid catalysts has been developed, assuming first order dependencies in substrates and acid. A maximum-likelihood approach has been applied to estimate the kinetic parameters, and a good fit between experimental data and modeling results was obtained. The model implies that the GLC yield is essentially independent of the LG loading. Within the investigated range of reaction conditions, the GLC yield is at the highest when the reaction temperature is between 100 and 120 °C (with sulfuric acid) and between 140 and 160 °C (with acetic acid).

ACKNOWLEDGEMENT

R.M.A. would like to thank the Directorate General of Higher Education, Ministry of Education and Culture, Indonesia for funding of her Ph.D. program. The authors also thank Jan Henk Marsman, Léon Rohrbach, Erwin Wilbers, Marcel de Vries, and Anne Appeldoorn for analytical and technical support and Henk van de Bovenkamp for invaluable discussions about MATLAB programming.

NOMENCLATURE

ΔH	:	Change in enthalpy (kJ mol^{-1})
ΔG	:	Gibbs free energy (kJ mol^{-1})
ΔS	:	Change in entropy ($\text{kJ mol}^{-1}\text{K}^{-1}$)
A_t	:	Heat transfer area (m^2)
C_{H^+}	:	Concentration of H^+ (M)
C_{GLC}	:	Concentration of GLC (M)
$C_{\text{GLC},0}$	:	Initial concentration of GLC (M)
C_{LG}	:	Concentration of LG (M)
$C_{\text{LG},0}$	:	Initial concentration of LG (M)
C_p	:	Heat capacity of reaction mixture ($\text{J g}^{-1}\text{K}^{-1}$)
E_{1GLC}	:	Activation energy of the decomposition of GLC to P2 (kJ mol^{-1})
E_{1LG}	:	Activation energy of the main reaction of LG to GLC (kJ mol^{-1})
E_{2LG}	:	Activation energy of the side reaction of LG to P1 (kJ mol^{-1})
h	:	Lump heat transfer term (min^{-1})
k_{1GLC}	:	Reaction rate constant of the decomposition of GLC (M min^{-1})
k_{1LG}	:	Reaction rate constant of the main reaction of LG to GLC (M min^{-1})
k_{1RLGC}	:	Reaction rate constant k_{1GLC} at reference temperature (M min^{-1})
k_{1RLG}	:	Reaction rate constant k_{1LG} at reference temperature (M min^{-1})
k_{2LG}	:	Reaction rate constant of LG for the side reaction to X (M min^{-1})
k_{2RLG}	:	Reaction rate constant k_{2LG} at reference temperature (M min^{-1})
K_a	:	Acid dissociation constant (–)
M	:	Mass of the reaction mixture (g)
R	:	Universal gas constant, $8.3144 \text{ J mol}^{-1}\text{K}^{-1}$
R_{1GLC}	:	Reaction rate of GLC to P2 ($\text{mol L}^{-1}\text{min}^{-1}$)
R_{1LG}	:	Reaction rate of LG to GLC ($\text{mol L}^{-1}\text{min}^{-1}$)
R_{2LG}	:	Reaction rate of LG to P1 ($\text{mol L}^{-1}\text{min}^{-1}$)
S	:	Rate selectivity parameter (–)
t	:	Time (min)
T	:	Reaction temperature ($^{\circ}\text{C}$)
T_i	:	Temperature of reaction mixture at $t = 0$ ($^{\circ}\text{C}$)
T_{oven}	:	Temperature of oven ($^{\circ}\text{C}$)
T_R	:	Reference temperature ($^{\circ}\text{C}$)
U	:	Overall heat transfer coefficient ($\text{W m}^{-2}\text{K}^{-1}$)
X_{LG}	:	Conversion of LG (mol %)
Y_{GLC}	:	Yield of GLC (mol %)

REFERENCES

- [1] G.W. Huber, S. Iborra and A. Corma. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chemical Reviews*, 106 (2006), pp.4044-4098.
- [2] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr, J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski. The Path Forward for Biofuels and Biomaterials, *Science*, 311 (2006), pp.484-489.
- [3] J. Lian, M. Garcia-Perez, R. Coates, H. Wu and S. Chen. Yeast Fermentation of Carboxylic Acids Obtained from Pyrolytic Aqueous Phases for Lipid Production. *Bioresource technology*, 118 (2012), pp.177-186.
- [4] F.H. Isikgor and C.R. Becer. Lignocellulosic Biomass: A Sustainable Platform for the Production of Bio-Based Chemicals and Polymers. *Polymer Chemistry*, 6 (2015), pp.4497-4559.
- [5] N.M. Bennett, S.S. Helle and S.J. Duff. Extraction and Hydrolysis of Levoglucosan from Pyrolysis Oil. *Bioresource Technology*, 100 (2009), pp.6059-6063.
- [6] J. Lian, S. Chen, S. Zhou, Z. Wang, J. O'Fallon, C. Li and M. Garcia-Perez. Separation, Hydrolysis and Fermentation of Pyrolytic Sugars to Produce Ethanol and Lipids. *Bioresource Technology*, 101 (2010), pp.9688-9699.
- [7] M.S. Mettler, A.D. Paulsen, D.G. Vlachos and P.J. Dauenhauer. Pyrolytic Conversion of Cellulose to Fuels: Levoglucosan Deoxygenation via Elimination and Cyclization Within Molten Biomass. *Energy & Environmental Science*, 5 (2012), pp.7864-7868.
- [8] S. Czernik and A. Bridgwater. Overview of Applications of Biomass Fast Pyrolysis Oil. *Energy & Fuels*, 18 (2004), pp.590-598.
- [9] S. Helle, N.M. Bennett, K. Lau, J.H. Matsui and S.J. Duff. A Kinetic Model for Production of Glucose by Hydrolysis of Levoglucosan and Cellobiosan from Pyrolysis Oil. *Carbohydrate Research*, 342 (2007), pp.2365-2370.
- [10] K. Sipilä, E. Kuoppala, L. Fagernäs and A. Oasmaa. Characterization of Biomass-Based Flash Pyrolysis Oils. *Biomass and Bioenergy*, 14 (1998), pp.103-113.
- [11] A. Oasmaa and S. Czernik. Fuel Oil Quality of Biomass Pyrolysis Oils. State of the Art for the End Users. *Energy & Fuels*, 13 (1999), pp.914-921.
- [12] A. Bridgwater and G. Peacocke. Fast Pyrolysis Processes for Biomass. *Renewable and Sustainable Energy Reviews*, 4 (2000), pp.1-73.
- [13] Fast pyrolysis, <http://www.btgworld.com/en/rtd/technologies/fast-pyrolysis>, 7 December 2016.
- [14] E. Hoekstra, S.R. Kersten, A. Tudos, D. Meier and K.J. Hogendoorn. Possibilities and Pitfalls in Analyzing (Upgraded) Pyrolysis Oil by Size Exclusion Chromatography (SEC). *Journal of Analytical and Applied Pyrolysis*, 91 (2011), pp.76-88.
- [15] R.P. Anex, A. Aden, F.K. Kazi, J. Fortman, R.M. Swanson, M.M. Wright, J.A. Satrio, R.C. Brown, D.E. Dugaard and A. Platon. Techno-Economic Comparison of Biomass-to-Transportation Fuels via Pyrolysis, Gasification, and Biochemical Pathways. *Fuel*, 89 (2010), pp.529-535.
- [16] T.R. Carlson, G.A. Tompsett, W.C. Conner and G.W. Huber. Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks. *Topics in Catalysis*, 52 (2009), pp.241-252.
- [17] D.M. Alonso, J.Q. Bond, J.C. Serrano-Ruiz and J.A. Dumesic. Production of Liquid Hydrocarbon Transportation Fuels by Oligomerization of Biomass-Derived C9 Alkenes. *Green Chemistry*, 12 (2010), pp.992-999.
- [18] B. Digman, H.S. Joo and D. Kim. Recent Progress in Gasification/Pyrolysis Technologies for Biomass Conversion to Energy. *Environmental Progress & Sustainable Energy*, 28 (2009), pp.47-51.
- [19] B. Yang and C.E. Wyman. Pretreatment: the Key to Unlocking Low-Cost Cellulosic Ethanol. *Biofuels, Bioproducts and Biorefining*, 2 (2008), pp.26-40.
- [20] L. Li and H. Zhang. Preparing Levoglucosan Derived from Waste Material by Pyrolysis. *Energy Sources*, 26 (2004), pp.1053-1059.
- [21] N. Kuzhiyil, D. Dalluge, X. Bai, K.H. Kim and R.C. Brown. Pyrolytic Sugars from Cellulosic Biomass. *ChemSusChem*, 5 (2012), pp.2228-2236.
- [22] J.J. Bozell and G.R. Petersen. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—the US Department of Energy's "Top 10" Revisited. *Green Chemistry*, 12 (2010), pp.539-554.

- [23] A. Oasmaa, E. Kuoppala, A. Ardiyanti, R. Venderbosch and H. Heeres. Characterization of Hydrotreated Fast Pyrolysis Liquids. *Energy & Fuels*, 24 (2010), pp.5264-5272.
- [24] M.R. Rover, P.A. Johnston, T. Jin, R.G. Smith, R.C. Brown and L. Jarboe. Production of Clean Pyrolytic Sugars for Fermentation. *ChemSusChem*, 7 (2014), pp.1662-1668.
- [25] H. Abou-Yousef and P. Steele. Increasing the Efficiency of Fast Pyrolysis Process Through Sugar Yield Maximization and Separation from Aqueous Fraction Bio-Oil. *Fuel Processing Technology*, 110 (2013), pp.65-72.
- [26] R. Venderbosch, A. Ardiyanti, J. Wildschut, A. Oasmaa and H. Heeres. Stabilization of Biomass-Derived Pyrolysis Oils. *Journal of Chemical Technology and Biotechnology*, 85 (2010), pp.674-686.
- [27] Yin Wang. Catalytic Hydrotreatment of Pyrolysis Liquids and Fractions: Catalyst Development and Process Studies, (Doctoral Dissertation). Groningen, (2017).
- [28] A. Kloekhorst, J. Wildschut and H.J. Heeres. Catalytic Hydrotreatment of Pyrolytic Lignins to Give Alkylphenolics and Aromatics using A Supported Ru Catalyst. *Catalysis Science & Technology*, 4 (2014) , pp.2367-2377.
- [29] E. Vidrio. Study of the Kinetics of the Acid-Catalyzed Hydrolysis of Levoglucosan. *McNair Scholars J*, 5 (2004), pp.90-103.
- [30] F. Mahfud, F. Van Geel, R. Venderbosch and H. Heeres. Acetic Acid Recovery from Fast Pyrolysis Oil. An Exploratory Study on Liquid-Liquid Reactive Extraction using Aliphatic Tertiary Amines. *Separation Science And Technology*, 43 (2008), pp.3056-3074.
- [31] B. Girisuta, L.P.B.M. Janssen and H.J. Heeres. Green Chemicals: A Kinetic Study on the Conversion of Glucose to Levulinic Acid. *Chemical Engineering Research and Design*, 84 (2006), pp.339-349.
- [32] Y. Bard. *Nonlinear Parameter Estimation*. Academic Press, (1974), pp.61-71.
- [33] C.D. Knights and C.A. Peters. Statistical Analysis of Nonlinear Parameter Estimation for Monod Biodegradation Kinetics Using Bivariate Data. *Biotechnology And Bioengineering*, 69 (2000), pp.160-170.
- [34] X. Hu, L. Wu, Y. Wang, Y. Song, D. Mourant, R. Gunawan, M. Gholizadeh and C. Li. Acid-Catalyzed Conversion of Mono-and Poly-Sugars into Platform Chemicals: Effects of Molecular Structure of Sugar Substrate. *Bioresource Technology*, 133 (2013), pp.469-474.
- [35] A.G. Dickson, D.J. Wesolowski, D.A. Palmer and R.E. Mesmer. Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250 °C, *Journal of Physical Chemistry*, 94 (1990) , pp.7978-7985.
- [36] R.N. Goldberg, N. Kishore and R.M. Lennen. Thermodynamic Quantities for the Ionization Reactions of Buffers. *Journal of Physical and Chemical Reference Data*, 31 (2002), pp.231-370.

SUPPORTING INFORMATION FOR CHAPTER 2

Heat transfer experiments

At the start of a reaction, the reaction occurs non-isothermally due to the heating-up of the glass ampoule and its content from room temperature to oven temperature. To incorporate this non-isothermal regime in the kinetic modeling study, the temperature inside the ampoule as a function of time during the heating-up process was experimentally determined. For this purpose, an ampoule was equipped with thermocouple and filled with glycerol. The ampoule was then placed inside the oven at a specified temperature (from 80–200 °C) and the temperature of the ampoule's content was followed in time. The obtained temperature profiles at different oven temperatures were modeled using a heat balance equation (eq S1).

$$\frac{d(MC_p T)}{dt} = UA_t (T_{\text{oven}} - T) \quad (\text{S1})$$

Using an assumption that the heat capacity of ampoule's content is not a function of temperature, the above equation can be rearranged to give eq S2.

$$\frac{dT}{dt} = \frac{UA_t}{MC_p} (T_{\text{oven}} - T) = h(T_{\text{oven}} - T) \quad (\text{S2})$$

Solving the ordinary differential equation (eq S2) with an initial value of $T = T_i$ at $t = 0$, gives:

$$T = T_{\text{oven}} - (T_{\text{oven}} - T_i) \exp^{-ht} \quad (\text{S3})$$

The value of h was determined by fitting the experimental data at different oven temperatures using a non-linear regression method. The obtained values for different oven temperatures (80–200 °C) are presented in Table S1.

Table S1. Lumped heat transfer term (h) for different oven temperatures.

T_{oven} (°C)	h (min ⁻¹)
80	1.3702
100	1.4077
120	1.4179
140	1.4292
160	1.4893
180	1.5114
200	1.5273

A good fit between the experimental data and modeled temperature profile was obtained, see Figure S1 for a representative example. Eq S3 was incorporated in the kinetic model to compensate the initial, non-isothermal stage of the reaction.

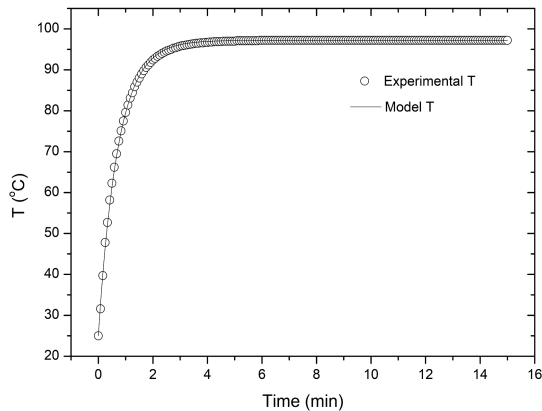


Figure S1. Heating profile of the reaction mixture at $T_{oven} = 100\text{ }^{\circ}\text{C}$.

Experimental data: Concentration versus time profiles

Table S2. Experimental data for reactions with sulfuric acid at various conditions.

Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)	Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)
1	80	0.05	0	0.101	0	20	120	0.1	0	0.101	0
			15	0.100	0.001				2	0.099	0.003
			30	0.100	0.002				5	0.084	0.017
			45	0.100	0.002				10	0.061	0.040
			60	0.099	0.003				15	0.044	0.056
			90	0.097	0.005				20	0.031	0.070
			120	0.096	0.006				30	0.015	0.084
			150	0.095	0.007				40	0.008	0.091
2	80	0.1	180	0.093	0.009	21	120	0.5	60	0.002	0.097
			0	0.101	0				1	0.100	0
			10	0.100	0.001				3	0.098	0.002
			20	0.100	0.002				5	0.064	0.036
			30	0.100	0.003				8	0.031	0.068
			45	0.099	0.004				10	0.010	0.087
			60	0.097	0.006				15	0.006	0.093
			80	0.095	0.008				20	0.001	0.096
			100	0.093	0.009				30	0.001	0.097
			120	0.092	0.011				30	0.000	0.096

Table S2 (continued). Experimental data for reactions with sulfuric acid at various conditions.

Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)	Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)
3	80	0.5	0	0.100	0	22	120	0.05	0	0.501	0
			5	0.098	0.003				5	0.452	0.053
			10	0.096	0.006				10	0.378	0.126
			15	0.095	0.008				15	0.318	0.184
			20	0.092	0.010				20	0.266	0.234
			30	0.086	0.016				30	0.177	0.317
			45	0.080	0.022				45	0.102	0.388
			60	0.074	0.029				60	0.057	0.431
4	80	0.05	90	0.062	0.040	23	120	0.1	90	0.020	0.457
			0	0.501	0				0	0.501	0
			15	0.501	0.004				2	0.498	0.014
			30	0.500	0.008				5	0.414	0.095
			45	0.499	0.012				10	0.294	0.211
			60	0.495	0.016				15	0.208	0.295
			90	0.492	0.024				20	0.147	0.352
			120	0.481	0.031				30	0.074	0.424
5	80	0.1	150	0.475	0.038	24	120	0.5	40	0.037	0.449
			180	0.466	0.045				60	0.012	0.471
			0	0.501	0				0	0.501	0
			10	0.505	0.005				1	0.498	0.009
			20	0.500	0.010				3	0.318	0.179
			30	0.497	0.015				5	0.154	0.337
			45	0.494	0.021				8	0.049	0.432
			60	0.482	0.029				10	0.027	0.452
6	80	0.5	80	0.476	0.038	25	120	0.05	15	0.006	0.463
			100	0.465	0.047				20	0.003	0.461
			120	0.455	0.056				30	0.003	0.459
			0	0.501	0				0	1.001	0
			5	0.497	0.015				5	0.891	0.110
			10	0.485	0.027				10	0.738	0.255
			15	0.473	0.039				15	0.635	0.375
			20	0.463	0.052				20	0.521	0.472
7	80	0.05	30	0.434	0.080	26	120	0.1	30	0.347	0.635
			45	0.398	0.115				45	0.196	0.770
			60	0.369	0.147				60	0.111	0.832
			90	0.307	0.200				90	0.036	0.879
			0	1.001	0				0	1.001	0
			15	0.999	0.010				2	0.983	0.026
			30	0.993	0.016				5	0.828	0.178
			45	0.990	0.024				10	0.591	0.401
8	80	0.5	60	0.987	0.032	27	120	0.5	15	0.417	0.573
			90	0.984	0.048				20	0.281	0.701
			120	0.966	0.062				30	0.133	0.801
			150	0.953	0.078				40	0.066	0.854
			180	0.931	0.090				60	0.021	0.885

Conversion of Levoglucosan to Glucose with Brønsted Acids catalyst

Table S2 (continued). Experimental data for reactions with sulfuric acid at various conditions.

Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)	Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)
8	80	0.1	0	1.001	0	27	120	0.5	0	1.000	0
			10	0.999	0.011				1	0.976	0.018
			20	0.998	0.022				3	0.641	0.378
			30	0.996	0.031				5	0.290	0.674
			45	0.995	0.047				8	0.087	0.852
			60	0.975	0.060				10	0.041	0.853
			80	0.943	0.076				15	0.012	0.871
			100	0.930	0.096				20	0.008	0.867
9	80	0.5	120	0.917	0.113	28	140	0.1	30	0.006	0.864
			0	1.000	0				0	0.101	0
			5	0.987	0.030				1	0.100	0.001
			10	0.979	0.058				3	0.068	0.035
			15	0.925	0.084				5	0.033	0.069
			20	0.925	0.112				10	0.005	0.096
			30	0.874	0.165				15	0.002	0.099
			45	0.791	0.229				25	0.001	0.098
10	100	0.05	60	0.728	0.299	29	140	0.05	45	0.001	0.096
			90	0.607	0.409				60	0.001	0.096
			0	0.101	0				0	0.501	0
			10	0.096	0.004				3	0.399	0.114
			20	0.092	0.008				5	0.272	0.239
			30	0.088	0.013				10	0.090	0.405
			45	0.082	0.019				20	0.015	0.467
			60	0.076	0.024				30	0.007	0.468
11	100	0.1	80	0.069	0.031	30	140	0.1	45	0.006	0.464
			100	0.066	0.040				60	0.006	0.465
			120	0.057	0.044				90	0.002	0.455
			0	0.101	0				0	0.501	0
			5	0.097	0.003				1	0.496	0.004
			10	0.093	0.007				2	0.456	0.047
			15	0.089	0.011				3	0.368	0.131
			20	0.085	0.015				5	0.193	0.306
12	100	0.5	30	0.078	0.022	31	140	0.5	7	0.093	0.400
			45	0.067	0.032				10	0.032	0.448
			60	0.059	0.041				15	0.010	0.463
			90	0.045	0.055				30	0.006	0.458
			0	0.100	0				0	0.501	0
			2	0.097	0.003				1	0.490	0.030
			5	0.085	0.015				2	0.260	0.249
			10	0.067	0.033				3	0.059	0.434
12	100	0.5	15	0.053	0.046	31	140	0.5	5	0.006	0.469
			20	0.038	0.061				10	0.007	0.463
			30	0.023	0.077				15	0.006	0.454
			40	0.014	0.086				20	0.006	0.444
			60	0.005	0.095				30	0.007	0.423

Table S2 (continued). Experimental data for reactions with sulfuric acid at various conditions.

Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)	Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)
13	100	0.05	0	0.501	0	32	160	0.05	0	0.101	0
			10	0.480	0.021				1	0.099	0.002
			20	0.457	0.042				3	0.045	0.055
			30	0.438	0.063				5	0.014	0.085
			45	0.430	0.101				10	0.002	0.096
			60	0.394	0.127				15	0.002	0.094
			80	0.361	0.167				25	0.002	0.090
			100	0.324	0.198				45	0.002	0.084
14	100	0.1	120	0.291	0.226				60	0.001	0.079
			0	0.501	0	33	160	0.5	0	0.100	0
			5	0.491	0.015				1	0.087	0.014
			10	0.467	0.037				2	0.010	0.089
			15	0.450	0.057				3	0.002	0.096
			20	0.429	0.077				4	0.002	0.094
			30	0.393	0.113				5	0.002	0.090
			45	0.343	0.163				7	0.002	0.084
			60	0.298	0.205				10	0.002	0.078
15	100	0.5	90	0.226	0.275				15	0.001	0.067
			0	0.501	0	34	160	0.1	0	0.501	0
			2	0.490	0.017				1	0.497	0.016
			5	0.425	0.075				2	0.314	0.194
			10	0.350	0.164				3	0.207	0.299
			15	0.278	0.239				4	0.095	0.398
			20	0.193	0.317				5	0.011	0.467
			30	0.112	0.389				7	0.009	0.461
			40	0.067	0.433				10	0.010	0.456
16	100	0.05	60	0.022	0.469				15	0.009	0.444
			0	1.001	0	35	160	0.1	0	0.501	0
			10	0.965	0.042				1	0.492	0.015
			20	0.954	0.090				2	0.317	0.189
			30	0.872	0.130				3	0.190	0.310
			45	0.850	0.203				5	0.024	0.456
			60	0.774	0.258				10	0.010	0.451
			80	0.701	0.330				15	0.010	0.439
			100	0.622	0.379				20	0.010	0.427
17	100	0.1	120	0.562	0.443				30	0.009	0.409
			0	1.001	0	36	160	0.5	0	0.501	0
			5	0.983	0.030				1	0.443	0.073
			10	0.922	0.074				2	0.055	0.434
			15	0.877	0.113				3	0.009	0.466
			20	0.848	0.156				4	0.009	0.461
			30	0.770	0.228				5	0.009	0.432
			45	0.667	0.327				7	0.009	0.416
			60	0.581	0.409				10	0.008	0.382
17	100	0.1	90	0.432	0.547				15	0.008	0.349

Conversion of Levoglucosan to Glucose with Brønsted Acids catalyst

Table S2 (continued). Experimental data for reactions with sulfuric acid at various conditions.

Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)	Exp No.	T (°C)	C _{H₂SO₄} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)
18	100	0.5	0	1.000	0	37	160	0.05	0	1.001	0
			2	0.992	0.032				1	0.999	0.013
			5	0.852	0.156				3	0.486	0.511
			10	0.659	0.350				5	0.169	0.793
			15	0.506	0.502				10	0.019	0.887
			20	0.370	0.617				15	0.020	0.864
			30	0.218	0.753				25	0.019	0.827
			40	0.120	0.833				45	0.019	0.772
			60	0.078	0.888				60	0.018	0.736
19	120	0.05	0	0.101	0	38	160	0.1	0	1.001	0
			5	0.087	0.010				1	0.974	0.033
			10	0.074	0.024				2	0.679	0.326
			15	0.064	0.036				3	0.464	0.539
			20	0.051	0.046				5	0.046	0.879
			30	0.037	0.063				10	0.019	0.858
			45	0.021	0.078				15	0.021	0.830
			60	0.013	0.087				20	0.020	0.814
			90	0.004	0.095				30	0.020	0.771

Table S3. Experimental data for reaction with acetic acid catalyst at various condition.

Exp No.	T (°C)	C _{CH₃COOH} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)	Exp No.	T (°C)	C _{CH₃COOH} (M)	Time (min)	C _{LG} (M)	C _{GLC} (M)
1	160	0.5	0	0.100	0	6	160	1	0	0.100	0
			15	0.050	0.033				5	0.085	0.020
			30	0.024	0.062				10	0.066	0.036
			60	0	0.082				15	0.053	0.047
			90	0	0.087				20	0.042	0.056
			120	0	0.087				30	0.020	0.075
			150	0	0.086				45	0.007	0.084
			180	0	0.084				60	0.001	0.089
2	180	0.5	240	0	0.080	7	180	1	90	0	0.091
			0	0.100	0				0	0.100	0
			15	0.004	0.075				3	0.054	0.022
			31	0	0.083				5	0.033	0.041
			60	0	0.076				10	0.001	0.070
			91	0	0.067				15	0	0.082
			120	0	0.056				30	0	0.086
			150	0	0.051				45	0	0.080
3	200	0.5	180	0	0.046	8	200	1	60	0	0.075
			240	0	0.038				90	0	0.066
			0	0.100	0				0	0.100	0
			2	0.072	0.018				1	0.070	0.007
			5	0.016	0.067				3	0.030	0.045
			10	0	0.082				5	0	0.074
			15	0	0.078				8	0	0.085
			20	0	0.074				10	0	0.084
4	160	0.5	30	0	0.061	9	160	1	15	0	0.077
			40	0	0.050				20	0	0.071
			60	0	0.035				30	0	0.059
			0	1.000	0				0	1.000	0
			15	0.619	0.357				5	0.815	0.170
			30	0.351	0.576				10	0.670	0.312
			60	0.114	0.742				15	0.529	0.431
			90	0.034	0.797				20	0.425	0.516
5	180	0.5	120	0	0.811	10	180	1	30	0.214	0.673
			150	0	0.803				45	0.081	0.769
			180	0	0.778				60	0.015	0.807
			240	0	0.604				90	0	0.817
			0	1.000	0				0	1.000	0
			15	0.146	0.721				5	0.808	0.204
			31	0	0.777				10	0.215	0.664
			60	0	0.732				15	0.060	0.766
6	160	0.5	91	0	0.676	7	160	1	30	0	0.781
			120	0	0.617				45	0	0.748
			150	0	0.571				60	0	0.719
			180	0	0.530				90	0	0.651
			240	0	0.436						

3

Conversion of Levoglucosan to Glucose Using an Acidic Heterogeneous Amberlyst 16 Catalyst: Kinetics and Packed Bed Measurements

This chapter is published as:

Conversion of Levoglucosan to Glucose Using an Acidic Heterogeneous Amberlyst 16 Catalyst: Kinetics and Packed Bed Measurements

R.M. Abdilla-Santes, C.B. Rasrendra, J.G.M. Winkelman and H.J. Heeres

Chemical Engineering Research and Design 152 (2019): 193-200.

DOI: 10.1016/j.cherd.2019.09.016

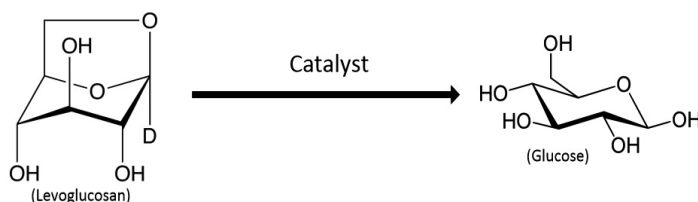
Levoglucosan (1,6-anhydro- β -D-glucopyranose) is an anhydrosugar found in significant amounts in pyrolysis oils obtained from lignocellulosic biomass. Levoglucosan (LG) is an attractive source for glucose (GLC), which can be used as a feedstock for biofuels (e.g., bioethanol) and biobased chemicals. Here, we report a kinetic study on the conversion of LG to GLC in water using Amberlyst 16 as the solid acid catalyst at a wide range of conditions in a batch setup. The effects of the reaction temperature (352–388 K), initial LG intake (100–1000 mol m⁻³), catalyst loading (1–5 wt%), and stirring rate (250–1000 rpm) were determined. The highest GLC yield was 98.5 mol% (388 K, 5 wt% Amberlyst 16, $C_{LG,0}$ = 500 mol m⁻³ at 500 rpm stirring rate and t = 60 min). The experimental data were modeled and relevant kinetic parameters were determined using a first order approach including diffusion limitations of LG inside the Amberlyst particles. Good agreement between experiments and kinetic model was obtained. The activation energy was found to be 132.3 ± 10.1 kJ mol⁻¹. Experiments in a continuous packed bed setup for up to 30 h show that catalyst stability is good. In addition, the steady state LG conversion (73 mol%) and the GLC selectivity were in line with the kinetic model obtained in the batch reactor

3.1. INTRODUCTION

Lignocellulosic biomass is an abundant, sustainable and carbon-neutral renewable resource for the generation of biofuels and valuable biobased chemicals. Extensive research activities are currently commenced globally to identify techno-economically viable routes [1-3]. Pyrolysis is an attractive method among other approaches for the conversion of lignocellulosic biomass to a liquid energy carrier, referred to as bio-oil or pyrolysis liquid or pyrolysis oil. Typical liquid yields are up to 75–85 wt% of the initial biomass feed [4-6] and the composition depends on the type of feedstock (biomass) and the pyrolysis conditions [7].

Pyrolysis oils are complex mixtures of low molecular weight acids, alcohols, furanics, aldehydes, ketones, sugar derivatives and phenolics as well as higher molecular weight sugar oligomers and lignin fragments [8-10]. However, upon the addition of water, phase separation of the pyrolysis oil is observed leading to a water phase enriched in polar low molecular weight molecules including the sugar derivatives (sugar fraction) and a lignin rich phase (pyrolytic lignin fraction) [8, 11-13]. Both fractions can be further refined by solvent extraction protocols, among others giving a sugar fraction with high amounts of sugar derivatives [6, 8, 14-16]. The composition of the sugar fraction has been determined in detail, and it typically consists of levoglucosan (16 wt%), glycolaldehyde (11 wt%), acids (2.5 wt%), ketones (1.4 wt%) and phenolics (0.4 wt%) [17], though the exact amounts are a function of the processing conditions and composition of the biomass feed.

The sugar fraction has the potential to be an interesting feed for the production of value-added biobased chemicals. Levoglucosan (1,6-anhydro- β -D-glucopyranose, LG), the primary degradation product of cellulose [6, 18], has been identified as the main component in the sugar fraction of pyrolysis oils. LG can be converted into a wide variety of chemicals, among others by an initial conversion to glucose (GLC) using an acid-catalyzed hydrolysis reaction (Scheme 1). GLC is an interesting starting material for value-added furan derivatives such as 5-hydroxymethylfurfural (HMF) as well as levulinic acid (LA) and lactic acid (LAC). The latter is the precursor for polylactic acid, a biodegradable biopolymer [19].



Scheme 1. Levoglucosan (LG) hydrolysis to glucose (GLC).

The research described in this work is aimed to explore the use of a solid acid catalyst for the reaction of LG to GLC and to optimize the reaction conditions to obtain high GLC yields. For proper reactor design, kinetic expressions in the form of rate equations are required,

which to the best of our knowledge are not reported in the literature for solid acid catalysts. The only examples involve the use of mineral acids like HCl and sulfuric acid. A kinetic study using hydrochloric acid catalyst at relatively low temperature (298–323 K) was performed by Vidrio [20] and an activation energy of 97 kJ mol⁻¹ was reported. Helle et al. [18] conducted a kinetic study using sulfuric acid as the catalyst in a temperature range between 323 and 403 K and found an activation energy of 114 kJ mol⁻¹. In both studies, the effect of the initial concentration of LG was not determined and first order kinetics were assumed. Recently, we have reported a systematic experimental and modeling study of the conversion of LG to GLC in aqueous sulfuric and acetic acid solutions with good results [21].

The use of mineral acids as catalysts for the reaction has severe drawbacks when considering the green principles of chemistry and technology. Recycle of such acids is energy and capital intensive and often the acids are neutralized in the workup section to produce large amounts of inorganic salts. As such, the use of solid acid catalysts is highly desirable, allowing operation in for instance packed bed configurations without the need of recycle. We here report an experimental and modeling study of the hydrolysis of LG in aqueous solution using a heterogeneous solid catalyst in the form of Amberlyst 16. To the best of our knowledge, detailed studies on LG hydrolysis in water with a solid acid catalyst and accompanying kinetic models have not been reported in the literature. This particular solid acid was selected as it is commercially available, relatively cheap compared to other ion exchange resins and has a good thermal stability of up to 403 K. The active sites are composed of sulfonic acid groups and in combination with the porous, open structure, it was shown to be an excellent catalyst for various transformations. The effects of reaction parameters (temperature, stirring rate, LG intake and catalyst loading) on the reaction rate were investigated and the relevant kinetic parameters were determined from the experimental data. The implications of the models regarding GLC yield will be discussed and finally the stability of the catalyst was investigated in a continuous setup for extended run-times.

3.2. EXPERIMENTAL SECTION

3.2.1. Chemicals

LG was purchased from Carbosynth, UK. GLC (≥99.5 wt%) was obtained from Sigma-Aldrich (Steinheim, Germany). Both chemicals were used without further purification. Amberlyst 16 (wet) was acquired from Dow Chemicals (Chauny, France). The catalyst was washed three times with Milli-Q water and dried overnight at 50 °C (323 K) prior to use. Milli-Q water was used for all experiments.

3.2.2. Experimental procedures

The batch experiments were carried out in pressure tubes (Ace pressure tube bushing type, front seal, volume ~ 9 mL with a length of 10.2 cm and an outer diameter of 19 mm). The tubes were loaded with 5 mL LG solution ($100\text{--}1000\text{ mol m}^{-3}$) containing the appropriate amounts of the Amberlyst 16 catalyst (1, 2 and 5 wt% of the mass of reaction solution (LG solution)). After filling, the tubes were subsequently submerged in a temperature-controlled heating bath (352–388 K). During reaction, the mixture was stirred at 500 rpm using a Teflon-coated magnetic stir bar. At various reaction times, a tube was taken and quickly immersed in cold water to stop the reaction. Subsequently, an aliquot of the reaction mixture was taken, diluted with Milli-Q water and analyzed by high performance liquid chromatography (HPLC).

The continuous experiments were performed in a packed-bed reactor. The setup was equipped with a pre-heater to heat the feed liquid and an air pump to feed the solution to the reactor and a back pressure valve to set the pressure, see Figure S1 in the Supporting Information for details. The reactor (length of 14.3 cm and an internal diameter of 6 mm) was filled with 1.33 g of Amberlyst 16. The pre-heater has approximately the same dimensions as the reactor. The experiments were carried out at a set-point of 393 K with a feed consisting of 100 mol m^{-3} of LG loading at a liquid flowrate of 2.2 mL min^{-1} and the outlet pressure was set at 5 bar. At different runtimes, samples were taken from the reactor outlet, diluted with Milli-Q water and subjected to analysis by HPLC.

3.2.3. Analytical methods

The amounts of LG and GLC in the reaction mixtures were quantified by HPLC. The HPLC instrument was equipped with Agilent 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87 H) operated at $60\text{ }^{\circ}\text{C}$, a refractive index detector and an ultraviolet detector. The mobile phase consisted of aqueous sulfuric acid (5 mol m^{-3}) at a flow rate of 0.55 mL min^{-1} . The Injection volume of the sample was set at $5\text{ }\mu\text{L}$. Calibration curves of standard solutions with known concentrations were used to determine the concentration of compounds in the product mixture. A typical HPLC chromatogram of a sample is shown in the Supporting Information (Figure S2).

3.2.4. Definitions

The concentrations of the relevant compounds involved in the reaction were determined by HPLC. These concentrations were used to calculate the conversion of LG (X_{LG}) and the yield of GLC (Y_{GLC}) according to the definitions given in eqs 1 and 2.

$$X_{\text{LG}} = \frac{(C_{\text{LG},0} - C_{\text{LG}})}{C_{\text{LG},0}} \quad (1)$$

$$Y_{\text{GLC}} = \frac{C_{\text{GLC}}}{C_{\text{LG},0}} \quad (2)$$

3.3. RESULTS AND DISCUSSION

3.3.1. Batch experiments: Product distribution, mass balances and reproducibility

The conversion of LG with Amberlyst 16 as the solid acidic catalyst in water was performed in a batch setup in a broad range of reaction conditions (352–388 K, $C_{\text{LG},0} = 100\text{--}1000 \text{ mol m}^{-3}$ and a catalyst loading between 1 and 5 wt% on LG solution) at various stirring speeds. An example of a concentration versus time profile for LG and GLC ($C_{\text{LG},0} = 1000 \text{ mol m}^{-3}$, 5 wt% catalyst, 500 rpm at 388 K) is shown in Figure 1 (left). At these conditions, LG is nearly fully converted to GLC within 60 min. At prolonged reaction times, the concentration of GLC is slightly reduced. This is most likely due to subsequent reactions of GLC to for instance HMF, LA, formic acid (FA) and insoluble polymers (humins) [22]. In our case, the formation of LA, FA (by HPLC) and/or humins (by visual observations) was not observed for all experiments. HMF was detected in a very small amount when $T > 370 \text{ K}$. However, the amounts were too limited to allow accurate quantification.

Furthermore, mass (carbon) balance calculations were conducted based on the total amount of HPLC detectables (LG and GLC, excluding HMF, as it is only detected as traces) and the LG intake. The results are given in Figure 1 (right) and show that carbon balance closure is quantitative from the beginning of the reaction until about 90 min. Above 90 min, a slight decrease in the carbon balance closure is apparent. This is due to limited decomposition of GLC, also visible in the GLC concentration versus time profile at extended batch times (Figure 1, left). The level of decomposition of GLC is by far lower than found in our previous study using sulfuric acid [21], implying that Amberlyst 16 is more preferred than sulfuric acid when aiming for high GLC yields from LG.

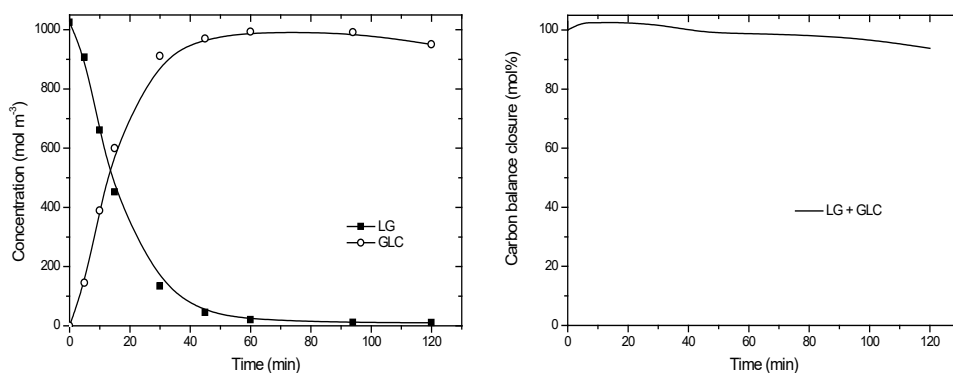


Figure 1. Representative example of a concentration-time profile in batch (left) and carbon balance closure (right) at 388 K, $C_{\text{LG},0} = 1000 \text{ mol m}^{-3}$ and 5 wt% catalyst at 500 rpm.

The reproducibility of the experiments was tested by performing a number of duplicate experiments. The results are given in Figure S3 (Supporting Information) and indicate that reproducibility of the experiments is good.

3.3.2. Assessment of mass transfer limitations in batch experiments

The conversion of LG to GLC in water using a solid Amberlyst 16 catalyst is an example of a heterogeneous reaction system. As such, diffusion limitations of LG, both externally and inside the porous Amberlyst particles, may occur and affect the conversion and yield of the process. To test the possibility of external mass-transfer limitations of LG from the liquid bulk to the catalyst surface, the effect of stirring rate on the LG conversion was determined and the results are presented in Figure 2. It is evident that within the tested range of stirring speeds (250–1000 rpm), the conversion of LG does not depend on the stirring rate. From this observation, we conclude that external mass-transfer limitation of LG is absent.

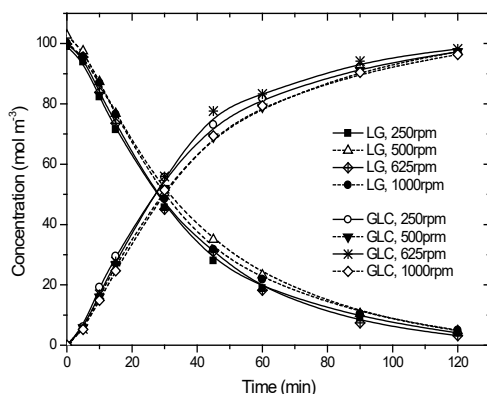


Figure 2. Effect of stirring rate on LG conversion to GLC with Amberlyst 16 ($C_{\text{LG},0} = 100 \text{ mol m}^{-3}$, 388 K and 2 wt% catalyst).

To investigate whether intra-particle mass transfer limitations are of importance, the Weisz-Prater criterion [23] ($N_{\text{W-P}}$) was determined for a number of representative experiments (Table 1, see Supporting Information for calculation details). According to this criterion, a value of ≤ 0.3 implies the absence of intra-particle mass transfer limitations.

The Weisz-Prater criterion was found in the range between 0.25 and 2.77, indicating that most experiments were performed in a regime where the overall rate is affected by intra-particle diffusion limitation of LG. As such, this effect was considered in the kinetic modeling studies (*vide infra*).

Table 1. Calculated values for the Weisz-Prater criterion (N_{W-P}) for a number of representative experiments.

T, K	W_{cat}^* (g)	$C_{LG,0}$ (mol m ⁻³)	N_{W-P}
388	0.1	100	1.64
352	0.05	100	0.26
370	0.05	100	0.78
388	0.05	100	2.59
370	0.05	500	0.98
388	0.05	500	2.77
352	0.1	100	0.16
370	0.1	100	0.79
370	0.1	500	0.83
388	0.1	500	1.75
370	0.25	100	0.63
388	0.1	1000	1.69
388	0.25	1000	0.48

*Catalyst intakes of 0.05, 0.1 and 0.25 g correspond to catalyst loadings of 1, 2 and 5 wt% (on reaction solution) respectively.

3.3.3. Effect of process conditions on the conversion of LG to GLC in batch

The effects of various process conditions on the conversion of LG and the GLC yield were determined experimentally. The temperature has a major effect on the rate of the reaction, see Figure 3 for details. For instance, at a temperature of 388 K, 96 mol% of LG conversion (X_{LG}) was obtained after 2 h and it dropped to 45 mol% at lower temperature (370 K). The LG conversion versus time curve follows the trend of the GLC yield versus time curve, indicating that the reaction is very selective with GLC as the sole product.

The effect of the catalyst loading (wt% on reaction solution) on the LG conversion vs time (370 K and $C_{LG,0} = 100 \text{ mol m}^{-3}$, 500 rpm) is given in Supporting Information (see Figure S4, left side). A linear relation between the initial reaction rate and the catalyst loading was observed (see Figure S4, right side), indicating a first order dependency in catalyst.

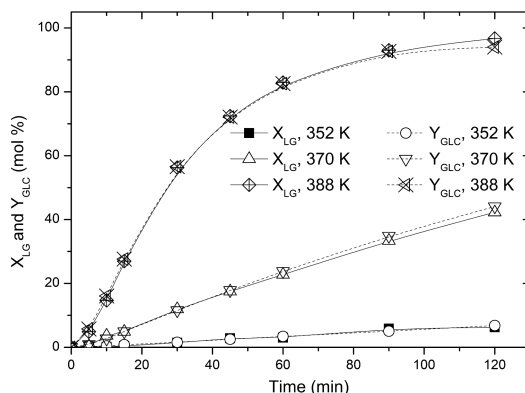


Figure 3. Conversion of LG and yield of GLC versus time at different temperatures ($C_{LG,0} = 1 \text{ M}$, 2 wt% catalyst, at stirring speed of 500 rpm).

The effect of the initial concentrations of LG on the conversion of LG was determined ($C_{LG,0} = 100\text{--}1000 \text{ mol m}^{-3}$, 388 K and 5 wt% catalyst) and the results are given in Figure 4 (left). The conversion of LG is essentially independent on the initial concentration of LG, indicating that the reaction order in LG is close to one. The rate of the undesired decomposition reaction of GLC, however, seems a function of the LG concentration, with high concentrations leading to a lower GLC yield (see Figure 4 (right)). This implies that the rate of the decomposition reaction is concentration depending and has an order higher than 1. The maximum yield of GLC was close to quantitative (98.5 mol%) when the reaction was carried out with 5 wt% of Amberlyst 16, an initial LG concentration of 500 mol m^{-3} , 388 K, 500 rpm and a batch time of 60 min.

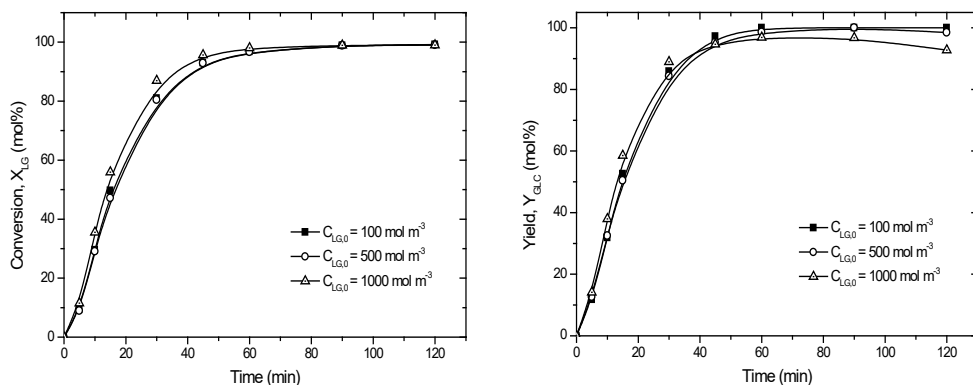


Figure 4. Effect of initial LG concentration on LG conversion, X_{LG} (left) and yield of GLC, Y_{GLC} (right) at reaction conditions: 388 K, 5 wt% catalyst and stirring speed of 500 rpm.

3.3.4. Catalyst stability

Catalyst stability was tested in the batch setup by performing three successive experimental runs (388 K, $C_{LG,0} = 100 \text{ mol m}^{-3}$, 2 wt% catalyst and a stirring speed of 500 rpm). After each run, the Amberlyst 16 catalyst was collected, washed with Milli-Q water and dried at 323 K for 4 h before a next run. The results are compiled in Figure 5. Clearly, the LG conversion and GLC yield are not affected after 3 runs, indicating that catalyst stability is good.

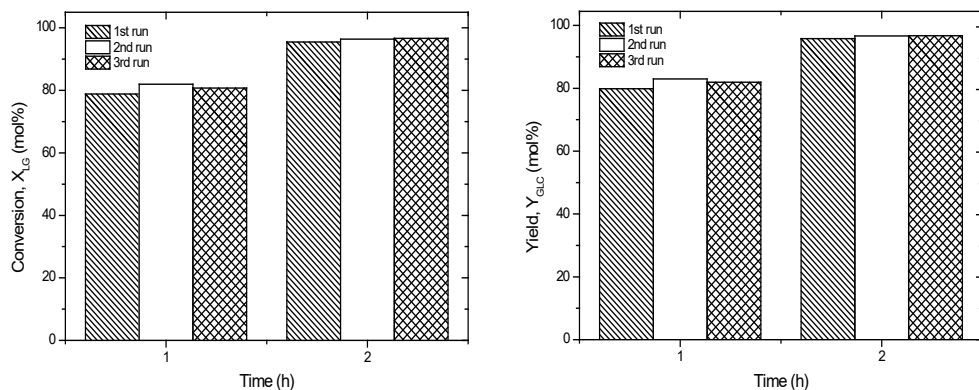


Figure 5. Determination of catalyst stability by successive batch experiments showing X_{LG} (left) and yield of GLC, Y_{GLC} (right) vs the number of runs at 388 K, $C_{LG,0} = 100 \text{ mol m}^{-3}$, 2 wt% catalyst and a stirring speed of 500 rpm.

3.3.5. Kinetic model development

A kinetic model for the reaction of LG in water with Amberlyst 16 as the catalyst was developed based on a simplified mechanism where LG is converted to GLC as a sole product (Scheme 1), justified by the very good carbon balance closures and excellent selectivity of the reaction. The LG and GLC component balances for the batch reactor with the assumption of a constant liquid volume are given in eqs 3 and 4.

$$V_{\text{liquid}} \frac{dC_{LG}}{dt} = -R'_{LG} W_{\text{cat}} \quad (3)$$

$$V_{\text{liquid}} \frac{dC_{GLC}}{dt} = R'_{LG} W_{\text{cat}} \quad (4)$$

where R'_{LG} denotes the LG reaction rate based on the weight of catalyst. The reaction is taken as first order in LG, as confirmed by experiments with different initial LG concentrations (Figure 4), and proceeds in the catalyst particles. The LG concentration in the catalyst particles can differ from the aqueous phase concentrations if the rate of diffusion of LG cannot keep up with the reaction rate. In that case the actual reaction rate is lower than the reaction rate based on bulk concentrations. Indeed, assessment of the WP criterion for the system reveals

that intra-particle diffusion limitation of LG play a role (*vide supra*). To incorporate this effects the reaction rate is expressed as:

$$R'_{LG} = k' C_{LG} \eta_{cat} \quad (5)$$

where η_{cat} denotes the catalyst effectiveness factor ($\eta_{cat} \leq 1$).

The reaction rate constant varies with the temperature according to an Arrhenius equation (eq 6) that depends on two parameters, the reaction rate constant at the reference temperature of 373 K, k'_{373} , and the activation energy, E_a :

$$k' = k'_{373} \exp \left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{373} \right) \right] \quad (6)$$

The temperature in the batch reactor increases over time from the initial, T_i to the set point value of the heating bath, $T_{setpoint}$ as given by eq 7 (for details see the Supporting Information).

$$T_{bulk} = T_{setpoint} - (T_{setpoint} - T_{bulk,i}) e^{-ht} \quad (7)$$

The reactor temperatures calculated from eq 7 are shown in the Supporting Information (Figure S5). It shows that the set-point is reached within a couple of minutes. As such, for reaction performed at particularly the highest temperature where the reaction rates are highest, the non-isothermal trajectory may have to be considered in the kinetic modeling (*vide infra*). The temperature of the catalyst particles is expected to closely follow the liquid bulk temperature and any difference between the two and any temperature gradients inside the catalyst particles are assumed negligible. For first order reactions the effectiveness factor of the catalyst is given by the well-known equation [24].

$$\eta_{cat} = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \quad (8)$$

where the Thiele modulus, ϕ , is defined as:

$$\phi = R \sqrt{\frac{k' \rho_{cat}}{D_{eff}}} \quad (9)$$

3.3.6. Modeling approach

Experimental data were obtained at the conditions given in Table 2. For each of the possible 27 combinations of reaction conditions a sequence of 8 batch experiments was performed with reaction times ranging from 5 to 120 minutes (300 to 7200 s). Concentration-time profiles of all the batch experiments are available in the Supporting Information (Figure S6).

Table 2. Experimental conditions employed for the kinetic measurements.

Parameter	Values
$C_{LG,0}$ (mol m ⁻³)	100, 500, 1000
Catalyst loading (wt%)	1, 2, 5
T_{setpoint} (K)	352, 370, 388

The model, consisting of eqs 3-9, was fitted to the experimental data using MATLAB software. The diffusion coefficient of LG was obtained from the Wilke-Chang equation (see Supporting Information). The effective diffusivity of LG in the catalyst particle was estimated as: $D_{\text{eff}} = (\varepsilon/\tau)D_{LG}$ with $(\varepsilon/\tau) = 0.1$. The objective function in the optimization of the reaction rate was the sum of squared relative residuals, SSR, according to:

$$SSR = \sum_i \left(\frac{C_{\text{model}} - C_{\text{experimental}}}{C_{\text{experimental}}} \right)_i^2 \quad (10)$$

where the summation is over all of the experimental data. Using relative residuals here ensures that more or less equal weights are attributed to the data points despite the variation in the magnitude of the concentrations. The 95% parameter confidence intervals were obtained by adjusting the parameters until the SSR increases to a value given by eq 11:

$$SSR_{0.95} = SSR_{\min} \left[1 + \frac{m}{N-m} F(m, N-m, 0.95) \right] \quad (11)$$

where $F(m, N-m, 0.95)$ is the value of the Fisher distribution at a 95% confidence level with $(m, N-m)$ degrees of freedom [25].

3.3.7. Modeling results

The values of the parameters k'_{373} and E_a in eq 6 were fitted to all experimental data simultaneously. The resulting equation for the reaction rate is given as:

$$k' = (6.08 \pm 0.51) \times 10^{-6} \exp \left[\frac{-(132.3 \pm 10.1) \times 10^3}{R} \left(\frac{1}{T} - \frac{1}{373} \right) \right] \quad (12)$$

The activation energy for the reaction is 132.3 ± 10.1 kJ mol⁻¹ and this value is somewhat higher compared to the ones found in the literature for soluble mineral acids. For instance, the activation energy for the conversion of LG to GLC using sulfuric acid as the catalyst in the temperature range of 323–403 K was reported to be 114 kJ mol⁻¹ [18], whereas we recently obtained a value of 123.4 kJ mol⁻¹ for a temperature range of 353–433 K [21].

The reaction rate according to eq 12 is plotted in Figure 6 (solid line). The influence of the non-isothermal conditions (Figure S7, Supporting Information) on the final outcome is

small as shown by small deviation of the dotted line in Figure 6. The latter was obtained by assuming that the reactor temperature was always equal to the setpoint temperature. This approach was inspired by Figure S7 where the reactor temperatures are shown to deviate from the setpoint temperatures only for the first 2 to 3 min, compared to a total reaction time of 2 h. Also shown in Figure 6 are the results obtained by neglecting any diffusion limitation in the catalyst particles. The observed values of the rate constants, equal to $\eta_{cat} k'$, are shown as squares and the dashed line. Specifically at the highest temperature applied here the difference between the observed and intrinsic values of the reaction rate is substantial: 1.55×10^{-5} vs $3.16 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$ respectively.

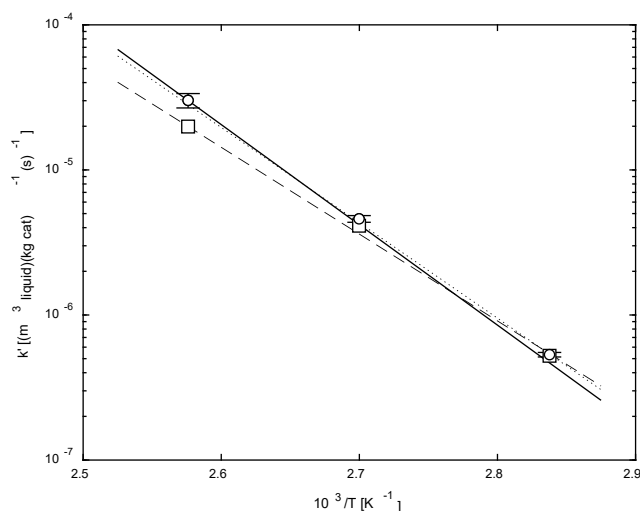


Figure 6. Arrhenius plot of the conversion rate constant of LG to GLC. Solid line: fitted through all the data, see eq 12). Circles and horizontal bars: average and standard deviation of 9 sequences consisting of 8 batch experiments each. Dotted line: isothermal conditions assumed. Dashed line and squares: diffusion limitations assumed absent.

The effectiveness factors from eq 8 show that the experiments at the highest temperature applied suffered from significant diffusion limitation, with an effectiveness factor as low as 0.68. The variation of the catalyst effectiveness factor as a function of the temperature is illustrated in Figure S8, (Supporting Information).

The assumption of a first order dependency of the reaction rate on the LG concentration is very plausible because of the excellent fit of the Arrhenius plot, see Figure 6. The first order kinetics are further substantiated by considering the plot of the relative concentrations vs the time multiplied with the amount of catalyst in the reactor. Figure 7 and 8 show these plots for all the experimental results obtained at 388 K. The data plotted in Figure 7 and 8 converge on a single curve. This type of behavior is obtained only with a first order reaction. With other reaction orders the results plotted according to this method cannot be represented by a single line.

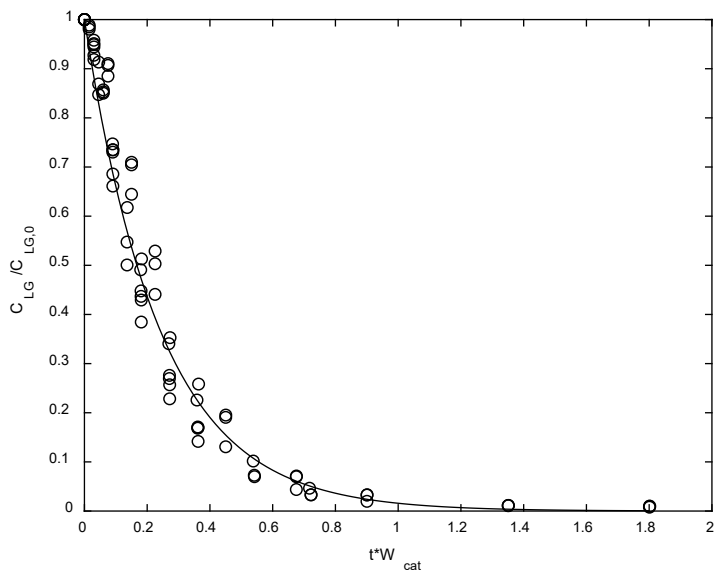


Figure 7. Relative LG concentrations vs $t \times W_{cat}$ at 388 K. Symbols: experimental data obtained with 9 sequences where $C_{LG,0} = 100, 500$ and 1000 mol m^{-3} , and the catalyst loading is 1, 2 and 5 wt%. Line: model calculations using the result of eq 12.

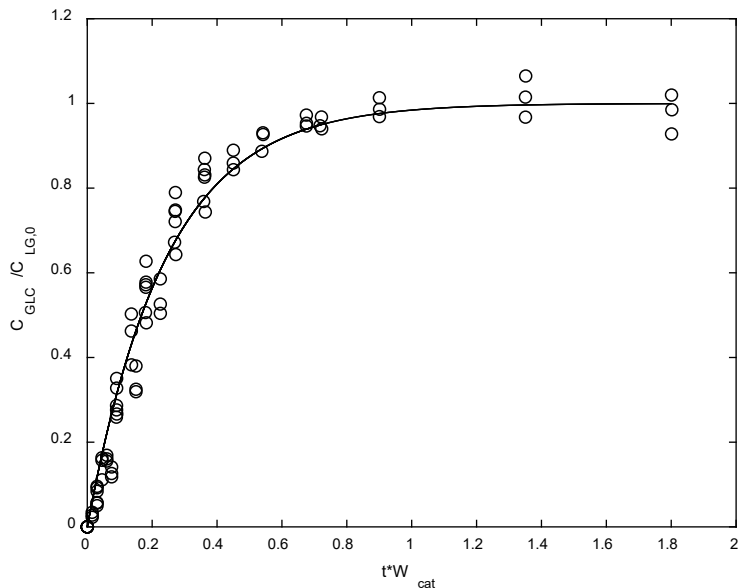


Figure 8. Relative GLC concentrations vs $t \times W_{cat}$ at 388 K. Symbols and line: see Figure 7.

3.3.8. Model Implications

With the kinetic models available, it is possible to gain insight into LG conversion, selectivity and yield of GLC as a function of the process conditions. For instance, a simulation of the typical batch time needed to achieve 90 mol% LG conversion with 0.1 g Amberlyst 16 as catalysts at various temperatures is given in Figure 9.

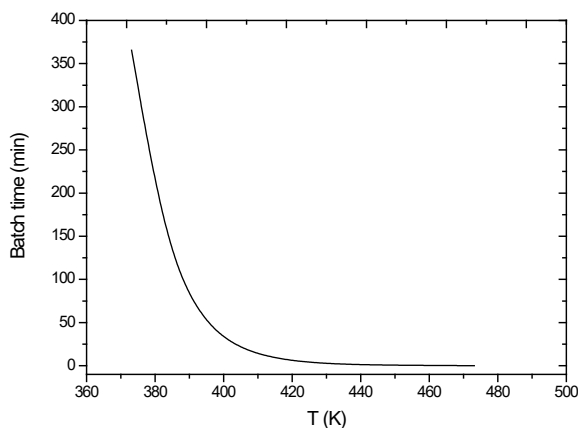


Figure 9. Required batch time for $X_{LG} = 90$ mol% as a function of T ($C_{LG,0} = 100 \text{ mol m}^{-3}$, $W_{cat} = 0.1 \text{ g}$).

3.4. CONTINUOUS EXPERIMENTS IN A PACKED BED REACTOR

The Amberlyst catalyst was tested for its performance in the hydrolysis of LG over extended time periods in a packed bed reactor (Figure S1, Supporting Information). In total, three runs with up to 30 hours run time were performed with a feed consisting of 100 mol m^{-3} of LG with a flow rate of 2.2 ml min^{-1} over 1.33 g of catalyst bed (Weight hourly space velocity, WHSV = 99 h^{-1}). The results of the three runs are given in Figure 10. The system reaches a steady state within 30 minutes, where the conversion of LG reached 73 mol% on average. Higher LG conversions were not aimed at, as very high conversions hamper determination of catalyst stability. Selectivity is close to quantitative and other byproducts were not identified (HPLC). Moreover, it is apparent from the three runs that the reproducibility of the system is good. In addition, catalyst stability of the three runs also seems on par to each other, at least for 30 h runtimes, in line with the batch recycle experiments.

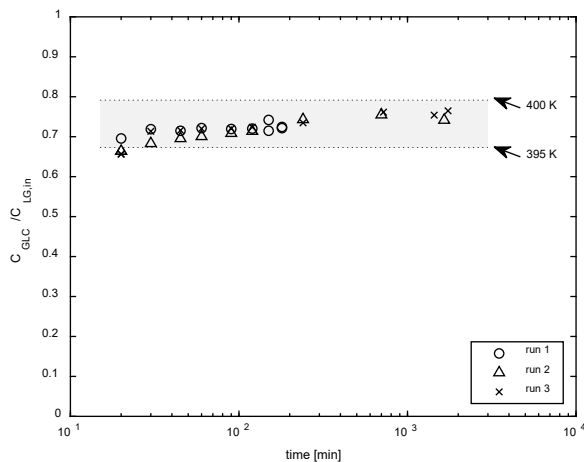


Figure 10. GLC yields versus runtime for triplicate packed bed experiments. Symbols: measured data points. Grey area: calculated from eq 15 over the temperature range of 395–400 K.

The packed bed reactor was modeled as an ideal plug flow reactor. The component balance for a plug flow reactor reads:

$$v_s \frac{dC_{LG}}{dx} = -k' \eta_{cat} C_{LG} \frac{W_{cat}}{V_R} \quad (13)$$

In eq 13 any effects due to diffusion limitation in the catalyst is taken into account via the catalyst effectiveness factor η_{cat} . Any external (gas-to-liquid) mass transfer limitations are assumed negligible here. Integration of eq 13 gives:

$$\frac{C_{LG}}{C_{LG,0}} = \exp \left[-\frac{\eta_{cat} W_{cat} k'}{\phi_v} \right] \quad (14)$$

and:

$$\frac{C_{GLC}}{C_{LG,0}} = 1 - \frac{C_{LG}}{C_{LG,0}} = 1 - \exp \left[-\frac{\eta_{cat} W_{cat} k'}{\phi_v} \right] \quad (15)$$

Experimentally some difficulties in controlling the temperature were encountered, resulting in some variation of the operating temperature of the reactor around the set point. The inlet reactor temperature was found to be 398 K, the exit temperature was 388 K. This difference is likely due to heat losses to the environment due to insufficient isolation. Therefore, in Figure 10, we compare the experimental results of the packed bed reactor with modeling results over the temperature range of 395–400 K. It can be concluded that the kinetic model derived in batch including intra-particle mass transfer limitations describes the experimental runs in the packed bed reactor well and confirms its validity.

3.5. CONCLUSIONS

An experimental study on the conversion of LG to GLC with a solid Amberlyst 16 catalyst in water was performed in a batch setup using a wide range of process conditions (250–1000 rpm, initial LG concentration between 100–1000 mol m⁻³, 352–388 K and a catalyst loading between 1–5 wt%) The highest GLC yield was 98.5 mol% (388 K, 5 wt% Amberlyst 16, $C_{LG,0} = 500 \text{ mol m}^{-3}$ at 500 rpm stirring rate and $t = 60 \text{ min}$). The data were successfully modeled assuming a first order reaction in LG and incorporation of intra-particle diffusion limitation of LG. The activation energy was found to be $132.3 \pm 10.1 \text{ kJ mol}^{-1}$. Catalyst stability was assessed by recycle runs in batch and continuous experiments in a packed bed reactor. Catalyst activity was stable for runtimes up to 30 h, indicating good catalyst stability, supported by the batch recycle experiments. The steady state conversion levels in the packed bed reactor were successfully modeled using the kinetic model from the batch data.

ACKNOWLEDGEMENT

R.M. Abdilla-Santes express gratitude to the Directorate General of Higher Education, Ministry of Education and Culture, Indonesia for funding of her PhD program. C.B. Rasrendra acknowledges ITB for receiving a WCU-ITB grant. The authors also thank Jan Henk Marsman, Léon Rohrbach, Erwin Wilbers, Marcel de Vries, and Anne Appeldoorn for analytical and technical support, and Henk van de Bovenkamp for input in the reactor modeling.

NOMENCLATURE

A_t	:	Heat transfer area (m^2)
C_{GLC}	:	Aqueous phase concentration of GLC ($mol\ m^{-3}$)
$C_{GLC,0}$	:	Initial aqueous phase concentration of GLC ($mol\ m^{-3}$)
C_{LG}	:	Aqueous phase concentration of LG ($mol\ m^{-3}$)
$C_{LG,0}$	:	Initial aqueous phase concentration of LG ($mol\ m^{-3}$)
C_p	:	Heat capacity of reaction mixture ($J\ g^{-1}\ K^{-1}$)
D_{eff}	:	Effective diffusivity of LG in the catalyst particle, $m^2\ s^{-1}$
D_{LG}	:	Aqueous diffusivity of LG, $m^2\ s^{-1}$
d_p	:	Catalyst average particle diameter, m
E_a	:	Activation energy of LG reaction to GLC ($kJ\ mol^{-1}$)
h	:	Heat transfer coefficient from the oven to the reaction mixture (min^{-1})
k'	:	Reaction rate constant based on weight of catalyst ($(m^3\ liquid)^{-1}\ (kg\ catalyst)^{-1}\ s^{-1}$)
k'_{373}	:	Reaction rate constant at the reference temperature of 373 K, $(m^3\ liquid)^{-1}\ (kg\ catalyst)^{-1}\ s^{-1}$
M	:	Mass of the reaction mixture (g)
r	:	Catalyst particles average radius (m)
R	:	Universal gas constant, $8.3144\ J\ mol^{-1}\ K^{-1}$
R_0	:	Initial rate of reaction ($mol\ m^{-3}\ min^{-1}$)
R_{LG}	:	LG reaction rate based on weight of catalyst ($mol\ (kg\ catalyst)^{-1}\ s^{-1}$)
SSR	:	Sum of squared residuals (–)
t	:	Time (min or s)
T_{bulk}	:	Bulk or aqueous phase temperature (K)
$T_{bulk,i}$	:	Initial bulk temperature (K)
$T_{setpoint}$	:	Temperature of heating bath, setpoint for the steady state temperature (K)
T_R	:	Reference temperature (K)
U	:	Overall heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
v_s	:	Superficial velocity ($m\ s^{-1}$)
V_{liquid}	:	Volume of liquid in the reactor ($m^3\ liquid$)
V_R	:	Volume of the reactor (m^3)
W_{cat}	:	Weight of catalyst (g)
X_{LG}	:	Conversion of LG (mol %)
Y_{GLC}	:	Yield of GLC (mol %)
ε/τ	:	Porosity-tortuosity ratio of the catalyst (–)
ϕ	:	Thiel modulus (–)
ϕ_v	:	Volumetric flow rate ($m^3\ s^{-1}$)
η_{cat}	:	(Internal) catalyst effectiveness factor (–)
ρ_{cat}	:	Density of the catalyst ($kg\ m^{-3}$)

REFERENCES

- [1] A. Corma, S. Iborra and A. Velty. Chemical Routes for the Transformation of Biomass into Chemicals. *Chemical Reviews*, 107 (2007), pp.2411-2502.
- [2] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr, J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski. The Path Forward for Biofuels and Biomaterials. *Science*, 311 (2006), pp.484-489.
- [3] R. van Putten, van der Waal, Jan C, E. De Jong, C.B. Rasrendra, H.J. Heeres and J.G. de Vries. Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources. *Chemical reviews*, 113 (2013), pp.1499-1597.
- [4] Fast pyrolysis, <http://www.btgworld.com/en/rtd/technologies/fast-pyrolysis>, 7 December 2016.
- [5] J. Lian, S. Chen, S. Zhou, Z. Wang, J. O'Fallon, C. Li and M. Garcia-Perez. Separation, Hydrolysis and Fermentation of Pyrolytic Sugars to Produce Ethanol and Lipids. *Bioresource technology*, 101 (2010), pp.9688-9699.
- [6] N.M. Bennett, S.S. Helle and S.J. Duff. Extraction and Hydrolysis of Levoglucosan from Pyrolysis Oil. *Bioresource Technology*, 100 (2009), pp.6059-6063.
- [7] M. Bykova, D.Y. Ermakov, V. Kaichev, O. Bulavchenko, A. Saraev, M.Y. Lebedev and V. Yakovlev. Ni-Based Sol–Gel Catalysts as Promising Systems for Crude Bio-Oil Upgrading: Guaiacol Hydrodeoxygenation Study. *Applied Catalysis B: Environmental*, 113 (2012), pp.296-307.
- [8] A. Oasmaa, E. Kuoppala, A. Ardiyanti, R. Venderbosch and H. Heeres. Characterization of Hydrotreated Fast Pyrolysis Liquids. *Energy & Fuels*, 24 (2010), pp.5264-5272.
- [9] H. Wang, J. Male and Y. Wang. Recent Advances in Hydrotreating of Pyrolysis Bio-Oil and Its Oxygen-Containing Model Compounds. *ACS Catalysis*, 3 (2013), pp.1047-1070.
- [10] A.H. Zacher, M.V. Olarte, D.M. Santosa, D.C. Elliott and S.B. Jones. A Review and Perspective of Recent Bio-Oil Hydrotreating Research. *Green Chemistry*, 16 (2014), pp.491-515.
- [11] A. Ardiyanti, S. Khromova, R. Venderbosch, V. Yakovlev and H. Heeres. Catalytic Hydrotreatment of Fast-Pyrolysis Oil Using Non-Sulfided Bimetallic Ni-Cu Catalysts On A δ - Al_2O_3 Support. *Applied Catalysis B: Environmental*, 117 (2012), pp.105-117.
- [12] D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness and A.H. Zacher. Catalytic Hydroprocessing of Biomass Fast Pyrolysis Bio-Oil to Produce Hydrocarbon Products. *Environmental Progress & Sustainable Energy*, 28 (2009), pp.441-449.
- [13] B. Scholze and D. Meier. Characterization of the Water-Insoluble Fraction from Pyrolysis Oil (Pyrolytic Lignin). Part I. PY–GC/MS, FTIR, and Functional Groups. *Journal of Analytical and Applied Pyrolysis*, 60 (2001), pp.41-54.
- [14] R. Venderbosch, A. Ardiyanti, J. Wildschut, A. Oasmaa and H. Heeres. Stabilization of Biomass-Derived Pyrolysis Oils. *Journal of Chemical Technology and Biotechnology*, 85 (2010), pp.674-686.
- [15] M.R. Rover, P.A. Johnston, T. Jin, R.G. Smith, R.C. Brown and L. Jarboe. Production of Clean Pyrolytic Sugars for Fermentation. *ChemSusChem*, 7 (2014), pp.1662-1668.
- [16] H. Abou-Yousef and P. Steele. Increasing the Efficiency of Fast Pyrolysis Process Through Sugar Yield Maximization and Separation From Aqueous Fraction Bio-Oil. *Fuel Processing Technology*, 110 (2013), pp.65-72.
- [17] Yin Wang. Catalytic Hydrotreatment of Pyrolysis Liquids and Fractions: Catalyst Development and Process Studies (Doctoral Dissertation), Groningen (2017).
- [18] S. Helle, N.M. Bennett, K. Lau, J.H. Matsui and S.J. Duff. A Kinetic Model for Production of Glucose by Hydrolysis of Levoglucosan and Cellobiosan from Pyrolysis Oil. *Carbohydrate research*, 342 (2007), pp.2365-2370.
- [19] J.J. Bozell and G.R. Petersen. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—the US Department of Energy's "Top 10" Revisited. *Green Chemistry*, 12 (2010), pp.539-554.
- [20] E. Vidrio. Study of the Kinetics of the Acid-Catalyzed Hydrolysis of Levoglucosan. *McNair Scholars J*, 5 (2004), pp.90-103.
- [21] R. Abdilla, C. Rasrendra and H. Heeres. Kinetic Studies on the Conversion of Levoglucosan to Glucose in Water Using Brønsted Acids as the Catalysts. *Industrial & Engineering Chemistry Research*, 57 (2018), pp.3204-3214.

- [22] B. Girisuta, L.P.B.M. Janssen and H.J. Heeres. Green chemicals: A kinetic study on the Conversion of Glucose to Levulinic Acid. *Chemical Engineering Research and Design*, 84 (2006), pp.339-349.
- [23] M.A. Vannice and W.H. Joyce. *Kinetics of Catalytic Reactions*. Springer, 2005.
- [24] H. Fogler. *Elements of Chemical Reaction Engineering*, 3rd ed. Prentice Hall, 1999.
- [25] N.R. Draper and H. Smith. *Applied Regression Analysis*. John Wiley & Sons, 2014.

SUPPORTING INFORMATION FOR CHAPTER 3

Figures

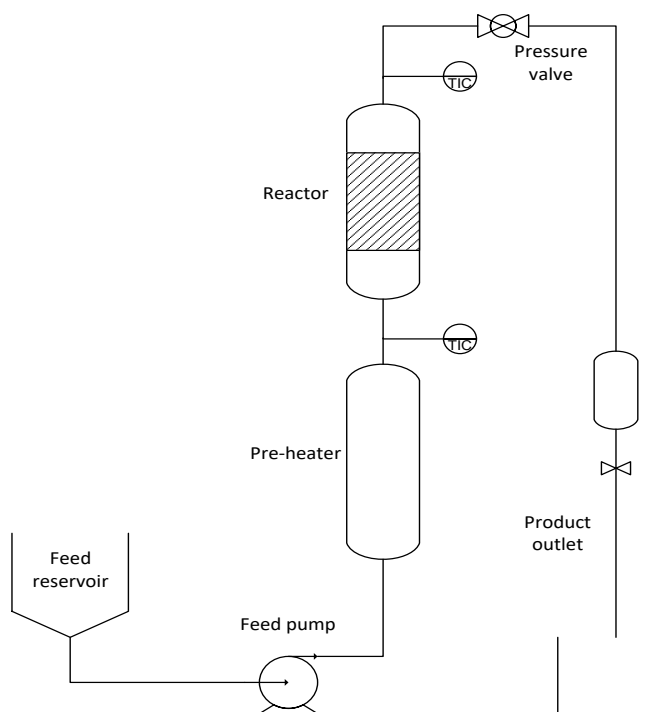


Figure S1. Schematic representation of the continuous setup.

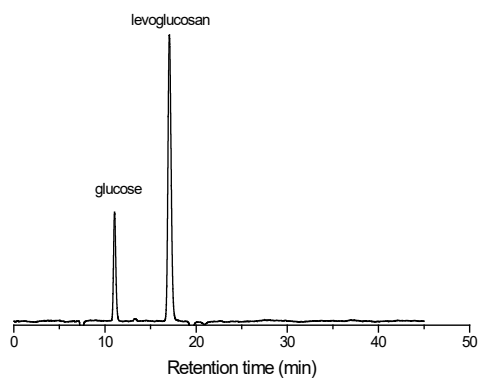


Figure S2. Typical HPLC chromatogram for a product mixture of LG hydrolysis in water.

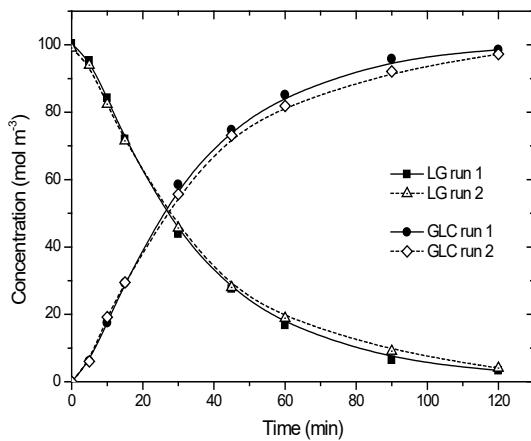


Figure S3. Representative example of a duplicate experiment with Amberlyst 16 ($C_{LG,0} = 100 \text{ mol m}^{-3}$, 388 K, 2 wt% catalyst and 250 rpm).

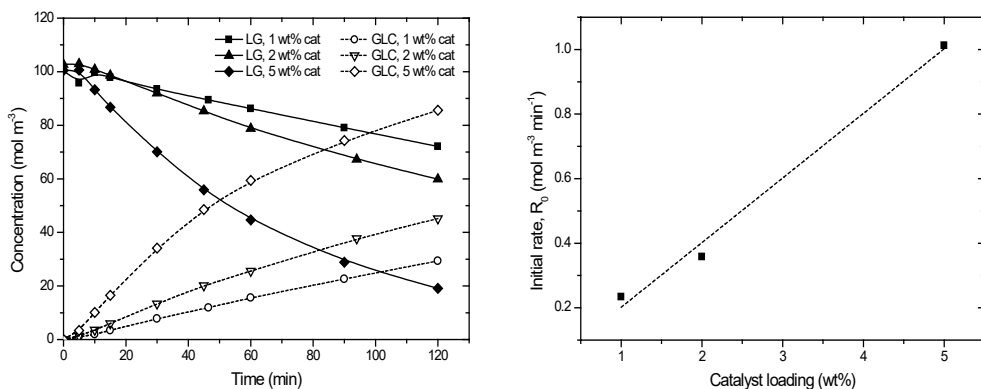


Figure S4. Effect of catalyst loading (wt%) on LG conversion and yield of GLC (left) and relation between catalyst loading and initial reaction rate (right). Reaction condition: 370 K, $C_{LG,0} = 100 \text{ mol m}^{-3}$ at 500 rpm.

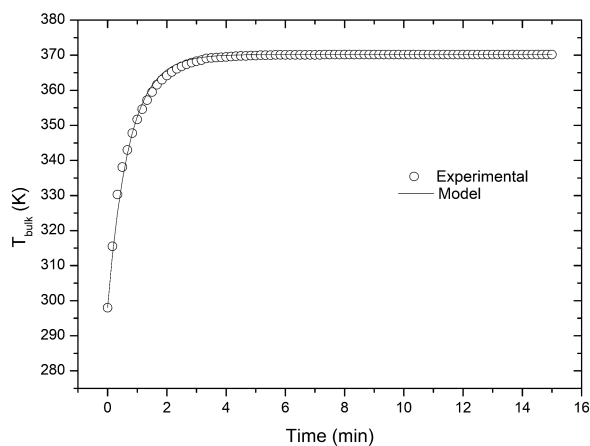


Figure S5. Heating profile of the reaction mixture at $T_{\text{setpoint}} = 370 \text{ K}$.

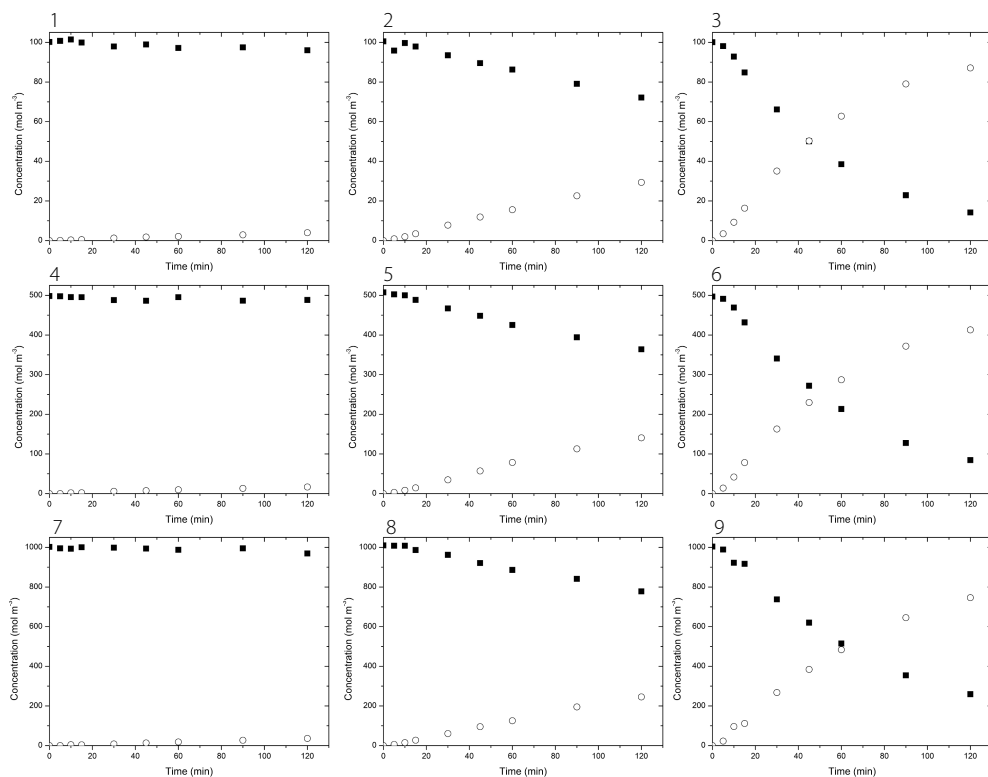


Figure S6. Concentration time profiles of the batch reactions which were included in the kinetic modeling (see Table S1 for details on reaction conditions). Filled square: LG concentration, circle: GLC concentration.

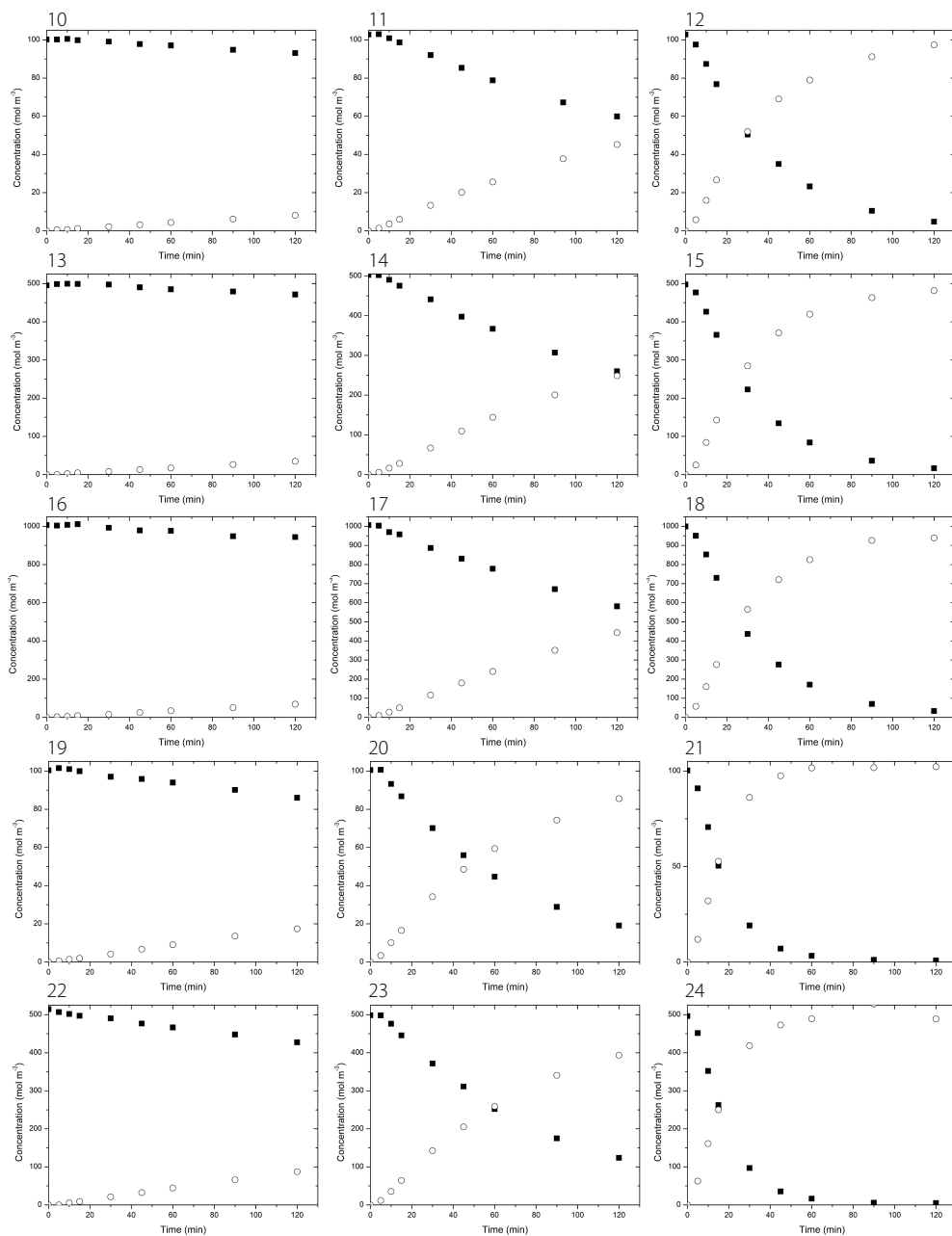


Figure S6 (Continued). Concentration time profiles of the batch reactions which were included in the kinetic modeling (see Table S1 for details on reaction conditions). Filled square: LG concentration, circle: GLC concentration.

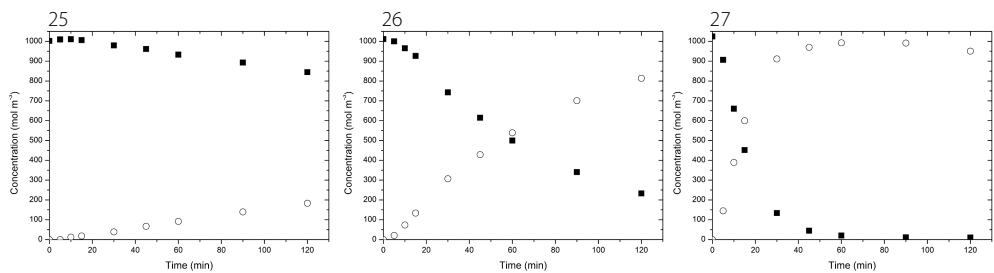


Figure S6 (Continued). Concentration time profiles of the batch reactions which were included in the kinetic modeling (see Table S1 for details on reaction conditions). Filled square: LG concentration, circle: GLC concentration.

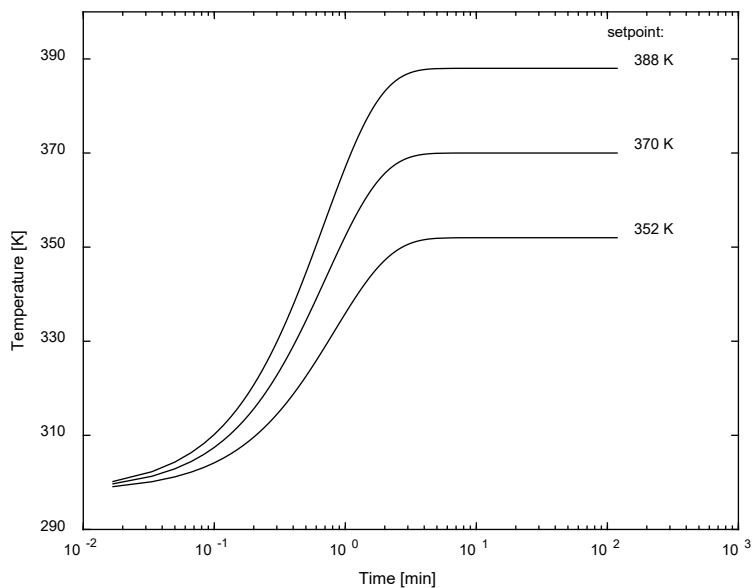


Figure S7. The reactor temperature vs time as calculated from eq 7.

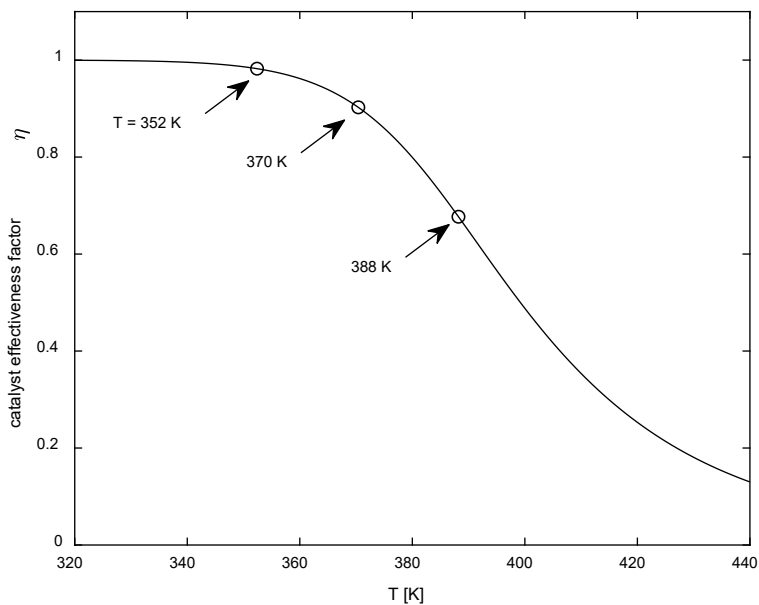


Figure S8. The catalyst effectiveness factor vs the temperature. Symbols indicate the experimental conditions.

Tables

Table S1. Overview of experiments as shown in Figure S6.

C _{LG,0} (mol m ⁻³)	Catalyst loading (wt%)	Temperature (K)		
		352	370	388
Entry*				
100	1	1	2	3
500	1	4	5	6
1000	1	7	8	9
Entry*				
100	2	10	11	12
500	2	13	14	15
1000	2	16	17	18
Entry*				
100	5	19	20	21
500	5	22	23	24
1000	5	25	26	27

*performed at stirring speed of 500 rpm.

Heat transfer experiments

At the beginning of the reaction, the pressure tube and its content need to be heated up from room temperature to bath/reaction temperature. At this stage, the reaction occurs non-isothermally and therefore need to be incorporated in our kinetic modeling study. To do this, the temperature inside the tube as a function of time during the heating-up process was experimentally determined and by filling a thermocouple equipped pressure tube with appropriate amount of glycerol. The tube was then immersed in the heating bath at specified temperature (from 352–388 K) and the temperature of the content was followed in time. Afterwards, the temperature-time profiles obtained at different heating bath temperatures were modeled using a heat balance equation presented in eq S1.

$$\frac{d(MC_p T_{\text{bulk}})}{dt} = UA_t (T_{\text{setpoint}} - T_{\text{bulk}}) \quad (\text{S1})$$

When assuming that the heat capacity of tube's content is not a function of temperature, eq 1 can be rearranged to give eq S2.

$$\frac{dT_{\text{bulk}}}{dt} = \frac{UA_t}{MC_p} (T_{\text{setpoint}} - T_{\text{bulk}}) = h (T_{\text{setpoint}} - T_{\text{bulk}}) \quad (\text{S2})$$

Solving the ordinary differential equation (eq S2) with an initial value of $T_{\text{bulk}} = T_{\text{bulk},i}$ at $t = 0$, gives:

$$T_{\text{bulk}} = T_{\text{setpoint}} - (T_{\text{setpoint}} - T_{\text{bulk},i}) \exp^{-ht} \quad (\text{S3})$$

Using a non-linear regression method, the value of h was determined by fitting the experimental data at different heating bath temperatures 352–388 K and the results are given in Table S2.

Table S2. Heat transfer coefficients for different heating bath temperature.

Heating bath temperature, T_{setpoint} (K)	h (min^{-1})
352	1.211
370	1.4049
388	1.4554

The fitting between experimental data and modeled temperature profile was excellent and representative example can be seen in Figure S5.

Weisz-prater assessment

Introduction

The extent of intraparticle diffusion limitation for a component may be evaluated by Weisz-Prater criterion (N_{W-P}) [23]. According to this criterion (see eq S1 for detail), mass transfer limitation of a component is negligible when the value of $N_{W-P} \leq 0.3$. This is valid for a reaction order in substrate of 2 or less. In our case, the reaction order is one for LG.

$$N_{W-P} = \frac{-R_0 \times r_p^2}{C_s \times D_{eff}} \leq 0.3 \quad (S1)$$

where:

R_0 = initial reaction rate, $\text{mol m}^{-3} \text{cat}^{-1} \text{s}^{-1}$

r_p = radius of catalyst particle, m

C_s = concentration of the component at the catalyst surface, mol m^{-3}

D_{eff} = effective diffusion coefficient of the component, $\text{m}^2 \text{s}^{-1}$

Assessment of the Weisz-Prater criterion for LG

The values for the individual contributions in the N_{W-P} (eq S1) determination will be discussed in the following section.

Radius of the catalyst particle

According to the supplier, the particle size distribution of the catalyst Amberlyst 16 is between 0.6 – 0.8 mm. An average value of 0.7 mm is taken for the diameter. Therefore, r_p is set at $3.5 \times 10^{-4} \text{m}$.

Concentration of the component at the catalyst surface

In our case, it is assumed that the concentration of substances at catalyst surface is equal to the bulk concentration of substances ($C_s = C_b$). This assumption based on our experiments which at stirring speed of 250 to 1000 rpm, no difference in LG conversion was observed. The bulk concentration of LG at the start of the reaction is known for all experiments.

Effective diffusion coefficients

The diffusion coefficient for LG in water can be estimated using the Wilke-Chang equation (eq S2):

$$D_{AB} = \frac{7.4 \times 10^{-8} \times T \times (\Phi_B M_B)^{1/2}}{V_{bA}^{0.6} \times \mu} \quad (S2)$$

where:

D_{AB} = diffusivity of solute (in this case, LG) in very dilute solution in H_2O , $m^2 s^{-1}$

T = temperature, K

ϕ_B = association factor of H_2O (2.26)

M_B = molecular weight of H_2O , $g mol^{-1}$

V_{bA} = molar volume of solute (in this case, LG) at its normal boiling point, $cm^3 mol^{-1} = 96.03 cm^3 mol^{-1}$

μ = viscosity of H_2O , cP

The effective diffusion coefficient (D_{eff}) was taken as 10 % from the diffusion coefficient (D_{AB}), calculated from Wilke Chang equation $((\epsilon/\tau)D_{LG})$ with $(\epsilon/\tau) = 0.1$. This consideration is based on literature review on diffusion coefficient of Amberlyst 15 – which has similar properties like Amberlyst 16 used in this study. The results on diffusion coefficients at the operating reaction temperature are given in Table S3.

Table S3. Effective diffusion coefficient of LG in water at different temperature.

T (K)	μ (cP)	$D_{LG-water}$ ($m^2 s^{-1}$)	$D_{eff(LG-water)}$ ($m^2 s^{-1}$)
352	0.355	6.80×10^{-11}	3.25×10^{-10}
370	0.288	9.04×10^{-11}	4.3×10^{-10}
388	0.241	1.17×10^{-10}	5.28×10^{-10}

Initial rates

The initial rates were obtained from the experimental data and an overview of a number of representative experiments at a range of process conditions is given in Table S4.

Table S4. Assessment of the Weisz-Prater criterion for LG for selected representative experiments.

Entry ^(a)	T (K)	W_{cat} ^(b) (g)	$C_{LG,0}$ ($mol m^{-3}$)	R_0 ($mol m^{-3} cat^{-1} s^{-1}$)	$D_{eff(LG-water)}$ ($m^2 s^{-1}$)	r_p^2 (m^2)	N_{W-P}
12	388	0.1	100	0.7085	5.28×10^{-10}	1.23×10^{-7}	1.64
1	352	0.05	100	0.0676	3.247×10^{-10}	1.23×10^{-7}	0.26
2	370	0.05	100	0.2717	4.294×10^{-10}	1.23×10^{-7}	0.78
3	388	0.05	100	1.118	5.28×10^{-10}	1.23×10^{-7}	2.59
5	370	0.05	500	1.716	4.294×10^{-10}	1.23×10^{-7}	0.98
6	388	0.05	500	5.98	5.28×10^{-10}	1.23×10^{-7}	2.77
10	352	0.1	100	0.043095	3.247×10^{-10}	1.23×10^{-7}	0.16
11	370	0.1	100	0.2782	4.294×10^{-10}	1.23×10^{-7}	0.79
14	370	0.1	500	1.4625	4.294×10^{-10}	1.23×10^{-7}	0.83
15	388	0.1	500	3.77	5.28×10^{-10}	1.23×10^{-7}	1.75
20	370	0.25	100	0.221	4.294×10^{-10}	1.23×10^{-7}	0.63
18	388	0.1	1000	7.605	5.528×10^{-10}	1.23×10^{-7}	1.69
27	388	0.25	1000	2.158	5.528×10^{-10}	1.23×10^{-7}	0.48

(a) All experiments has volume of 5 ml. (b) Catalyst weight of 0.05, 0.1 and 0.25 g corresponds to 1, 2 and 5 wt% catalyst loading respectively.

4

Valorization of Humin Type Byproducts from Pyrolytic Sugars Conversion to Biobased Chemicals

This chapter is submitted to Journal of Analytical and Applied Pyrolysis as:
Valorization of Humin Type Byproducts from Pyrolytic Sugar Conversions to Biobased Chemicals

R.M. Abdilla-Santes, S. Agarwal, X. Xi, H. Heeres, P.J. Deuss and H.J. Heeres

Pyrolytic sugar fraction, obtained by aqueous extraction of pyrolysis oil, are an attractive source for sugar-derived platform chemicals. However, solids (humin) formation occurs to a significant extent during its hydrolysis and subsequent conversion processes. In this study, we report investigations on possible conversion routes (pyrolysis, liquefaction) of such humin byproducts obtained from pyrolytic sugars conversions to biobased chemicals. Experiments were carried out with a model humin made from a representative technical, unpurified pyrolytic sugar and the product was characterized by elemental analysis, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), high performance liquid chromatography (HPLC), gas chromatography–mass spectrometry (GC-MS), fourier-transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR). The obtained humin is soluble in organic solvents (dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), isopropanol (IPA)), in contrast to typical humins obtained from glucose and fructose, allowing characterization using NMR and GPC. All analyses reveal that the humins are oligomer in nature (M_w of about 900 g mol⁻¹) and consist of sugar and furanic fragments linked with among others (substituted) aliphatic, ester units and, in addition, phenolic fragments with methoxyl groups. The humins were used as a feed for catalytic pyrolysis and catalytic liquefaction experiments. Catalytic pyrolysis experiments (mg scale, programmable temperature vaporizer (PTV)-GC-MS, 550 °C) with HZSM-5-50 as the catalyst gave benzene-toluene-xylene-naphthalene-ethylbenzene mixtures (BTXNE) in 5.1 wt% yield based on humin intake. Liquefaction experiments (batch reactor, 350 °C, 4 h, IPA as both the solvent and hydrogen donor and Pt/CeO₂ (4.43 wt% Pt) catalyst) resulted in 80 wt% conversion of the humin feed to a product oil with considerable amounts of phenolics and aromatics (ca. 24.7% based on GC detectables in the humin oil). These findings imply that the techno-economic viability of pyrolysis oil biorefineries can be improved by converting humin type byproducts to high value, low molecular weight biobased chemicals.

4.1. INTRODUCTION

Lignocellulosic biomass is considered a promising alternative feedstock for renewable carbon-based transportation fuels (e.g., bioethanol, biodiesel) and biobased chemicals [1-3]. In the last decade, major breakthroughs have been realized regarding the conversion of the carbohydrate fraction from lignocellulosic biomass. For example, an attractive valorization route involves the conversion into biobased platform chemicals like 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) [4, 5].

The cellulose and hemicellulose fractions in lignocellulosic biomass typically need to be depolymerized/pre-treated to obtain monomeric sugars like glucose and xylose before further conversion into biobased chemicals and biofuels [6]. Well known approaches are enzymatic and acid-catalyzed depolymerization. A less developed route is the use of fast pyrolysis technology as a pre-treatment process. In fast pyrolysis processes, the biomass is rapidly heated to 450 – 600 °C in the absence of oxygen, leading to significant deconstruction and depolymerization. The main product is a liquid known as pyrolysis oil or bio-oil and depending on the process parameters, the oil yield can be as high as 70-80 wt% on a dry-feed basis [7, 8]. Pyrolysis oils are composed of several hundreds of small organic compounds in combination with considerable amounts of higher molecular weight (non GC detectable) compounds [9, 10]. A main disadvantage is its low thermal stability, which precludes separation by distillation. However, pyrolysis oils are easily fractionated into three product fractions using a combination of precipitation, extraction and fractionation approaches [11]. The following fractions are obtained, i) an organic so-called pyrolytic lignin fraction (products mostly derived from lignin), ii) an aqueous phase containing mostly monomeric and oligomeric sugars and iii) a low molecular weight oxygenate stream containing among others acetic acid. The aqueous sugar-rich phase can be concentrated to obtain a thick syrup, commonly addressed as pyrolytic sugars (PS), in yields up to 30 wt% of the original pyrolysis oil [11]. This separation procedure is the basis for a pyrolysis biorefinery, where the pyrolysis oil is separated into fractions, followed by tailored, dedicated conversions of each fraction into value added products.

The PS contains a number of sugars and sugar-derived chemicals. When using pure cellulose as the fast pyrolysis feedstock, the main product is 1,6-anhydro-β-D-glucopyranose, commonly known as levoglucosan, and the yield can be as high as 59 wt% [12]. It is also the main component in the PS fraction when using a typical lignocellulosic biomass as the feed (Table 1). Other products are 1,6-anhydro-β-cellobiose (cellobiosan) and higher molecular weight sugars. Levoglucosan is readily hydrolyzed to glucose using acid catalysts [13, 14], which subsequently can be converted to numerous biobased chemicals including HMF and LA.

Examples on the use of PS as a feed for LA and HMF synthesis are scarce. In a recent study, Zhang et al. [15] reported the hydrolysis of the water soluble fraction (WSF) of pyrolysis oil using H₂SO₄ (1 wt%) as the catalyst at 170 °C giving LA in low yields (2.3 mol%). We have

recently investigated the acid-catalyzed conversion of pine wood-derived PS (see Table 1 for its chemical composition) with 0.5 M H_2SO_4 catalyst at 180 °C [16]. HMF was detected in the earlier stage of the reaction (around 5 min, 1 wt% yield) whereas LA was the main detectable product (10 wt%) after 60 min. However, considerable amounts of insoluble brown products (humins) were formed. In addition, heating of the pine wood-derived PS in the absence of a catalyst also leads to significant amounts of such humins (32 wt% based on the initial PS feed). As such, the use of such PS fractions to obtain biobased chemicals has been hampered by the fact that significant amounts of humins are formed. Evidently, optimization studies to obtain higher yields of HMF/LA are required (catalyst and solvent selection, biphasic systems), although it is unlikely that humin formation can be avoided completely. As such, there is an incentive to convert these humins into valuable chemicals.

Table 1. Low molecular weight components detected in PS fractions.

Type	Component	Concentration (wt%)
Pine wood-derived pyrolytic sugar feed used in this study [17]	Levogluconan	16
	Glycoaldehyde	10.8
	Acids	2.5
	Ketones	1.4
	Phenolics	0.4
	Water	14.5
Type	Component	Concentration (mg g ⁻¹)
Water soluble fraction of pyrolysis oil from the fast pyrolysis of rice husk [15]	Levogluconan	28.9
	Cellobiosan	10.2
	Xylose	3.7
	Arabinose	1.2
	Glucose	2.6

It has been shown in the literature that humins from monomeric sugars (fructose, glucose) are carbonaceous, heterogeneous, polydisperse and typically highly insoluble materials consisting of a furan-rich polymer network with different oxygen containing functional groups [6, 18-20]. A number of valorization routes for such humins have been suggested in the literature. Examples are the use as an energy source by combustion [20], use in composites based on PFA (poly-furfuryl alcohol) [21] and valorization approaches involving depolymerization of the humin structure to low-molecular weight-components, which are subsequently transformed into biobased chemicals (Figure S1, Supporting Information) [22].

In this work, we describe experimental studies on the conversion of humins obtained from the technical, unpurified PS (acquired from pyrolysis oil) by catalytic pyrolysis and liquefaction approaches. The main objective was to obtain high amounts of monomeric products from the humin byproducts. All reactions were carried out using a humin sample derived from PS obtained from a pine-based pyrolysis oil. This humin was characterized in detail by various analytical techniques to gain insights in its chemical structure and rationalize its reactivity.

4.2. EXPERIMENTAL SECTION

4.2.1. Chemicals

All chemicals used in this work were of analytical purity and used without further purification, unless stated otherwise. Gases used in this study were supplied by Linde Gas (Schiedam, the Netherlands) and were of analytical grade. Tetrahydrofuran (THF), toluene and acetone were supplied by Boom B.V. (Meppel, the Netherlands). Isopropanol (IPA, anhydrous, 99.5 %), di-n-butylether (DBE), deuterated dimethyl sulfoxide (DMSO- d_6) and CeO_2 (Sigma No. 544841-50G) were obtained from Sigma Aldrich. Platinum(II) acetylacetonate was acquired from Merck (8.14689.0001).

4.2.2. Humin synthesis

The pyrolysis oil was provided by Biomass Technology Group (BTG, Enschede) and obtained from the fast pyrolysis of pine wood. The pyrolysis oil was fractionated by the addition of water, resulting in phase separation and the formation of an insoluble fraction (mostly lignin-derived) and a water phase (containing sugars, see Figure 1 for details). The water phase was concentrated using a rotavapor (100 mbar, at 80 °C) until water evaporation ceased, to give a thick PS syrup. Subsequently, the PS was thermally treated for 22 h in an oven at 130 °C under atmospheric pressure. The resulting dark brown product (designated as *raw PS-humins* in this study) was extracted with Milli-Q water (2.5 g sample in 80 mL water) at 100 °C for 5 h to remove (trapped) solubles. After water extraction, the insoluble part of the sample was filtered and dried overnight at 50 °C in an oven at atmospheric pressure. This residue was ground into a powder and used as the feed in this study (*PS-humins*).

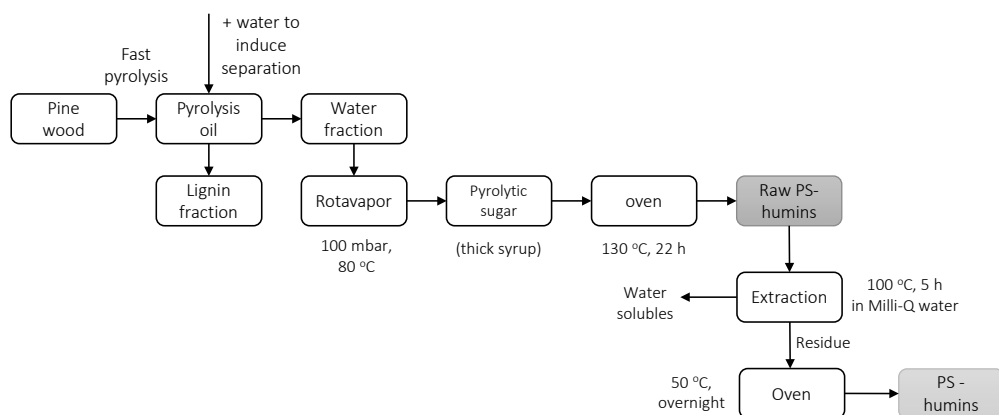


Figure 1. Schematic illustration of the synthesis of PS-humins.

4.2.3. Synthesis of the Pt /CeO₂ catalyst for catalytic liquefaction reactions

The Pt/CeO₂ (with a target content of 5 wt% Pt) catalyst was synthesized by a wet impregnation procedure. Pt(Acac)₂ (0.404 g, 0.0218 g Pt) was dissolved in acetone (78 mL) under stirring and the appropriate amount of pre-calcined (500 °C) CeO₂ (4.004 g) was added. The acetone was then slowly removed from the suspension by heating the suspension at 40 °C under atmospheric pressure (about 8 h). The remaining solid was collected and calcined in a muffle furnace under air (heating profile: from room temperature to 300 °C with a heating rate of 5 °C min⁻¹ for 2 h followed by heating to 500 °C with a rate of 5 °C min⁻¹ for 1 h followed by cooling to 50 °C). After calcination, the catalyst was reduced in a tubular glass oven with a sweep gas consisting of 7 vol% hydrogen and 93 vol% nitrogen (heating profile: room temperature to 400 °C with a heating rate of 5 °C min⁻¹, 6 h at 400 °C and then cooled to 50 °C).

4.2.4. Experimental procedures

Thermal and catalytic pyrolysis. Pyrolysis and catalytic pyrolysis of the PS-humins were performed following a procedure described by Agarwal, et al. [23]. The experiments were conducted using a PTV injector (programmable temperature vaporizer, Model: Optic2 from Atlas) placed on a HP 5890 GC Series II system in combination with a HP 5972 MS detector (PTV-GC-MS) controlled by an Optic 2 device. Typically, for thermal pyrolysis 0.6–0.8 mg of the humin sample was used. For catalytic pyrolysis, a humin to catalyst ratio of 0.05 w/w was used, loading first the PS-humins followed by the catalyst. The (catalytic) pyrolysis temperature was set at 550 °C. The oven was programmed to ramp from 40 °C to 550 °C with a rate of 16 °C min⁻¹ and kept at 550 °C for 60 s. After (catalytic) pyrolysis in the injector was completed, the products were transferred to a capillary column (Agilent Technologies VF–5 ms, 30 m × 0.25 mm × 1.0 μm film thickness, split ratio of 50:1). Helium was used as the carrier gas at a flow rate of 1 mL min⁻¹. The initial temperature was set at 40 °C and kept for 60 s followed by heating to 250 °C with a rate of 10 °C min⁻¹. MS detector was operated in the scan range of m/z 35–400 using ionization mode (70 eV) with an interface temperature of 280 °C. The NIST-05a mass spectra library was used to identify the pyrolysis products. Subsequently, the total ion chromatogram (TIC) peak areas acquired from MS detector were used as a semi-quantitative estimation of the concentration of GC-MS detectable compounds, assuming a linear correlation between the concentration and the TIC peak area percentage as often applied when reporting the composition of biomass-derived pyrolysis product streams. The semi-quantitative yields of each compound/group of compounds were calculated by dividing the corresponding TIC peak area percentage to the total TIC peak area of all the GC detectables. For simplicity, except BTXNE, the compounds were classified based on chemical functionalities, e.g., aromatic derivatives (substituted benzene and polycyclic aromatics), furans and derivatives, naphthalenes (naphthalene and substituted naphthalenes), (substituted) phenolic derivatives, and others (mainly alkanes, alkenes, acetic acid, indanes, etc). An external

standard solution with known quantities of BTXNE was used to calculate the response factor of BTXNE to determine the yields of BTXNE. Again, it was assumed that the concentration of the compounds is linearly related to the TIC peak area. A measurement using an external standard solution was performed prior to each set of experiments. A schematic representation of the PTV-GC-MS setup is provided in the Supporting Information (Figure S2).

Catalytic liquefaction experiments. The catalytic liquefaction of the PS-humins were performed in a 100 mL batch autoclave (Parr reactor system) with maximum operating conditions of 350 °C and 200 bar, surrounded with an electrically heated metal block and equipped with an overhead stirrer (Rushton type turbine with a gas induced impeller). Prior to an experiment, the reactor was weighed and then charged with a humin sample (5.0 g), IPA (15 g), and the metal catalyst (0.6 g, 12 wt% on humin intake). The reactor was closed and tested for leakage by pressurizing it with 50-80 bar of nitrogen. The pressure was released and the reactor was subsequently flushed twice with nitrogen gas. Subsequently, the stirring was started (1300 rpm) and the reactor was heated to 350 °C at a rate of about 5 °C min⁻¹, giving a final pressure of typically 80-90 bar. After reaction (4 h), the reactor was cooled to room temperature, the pressure was recorded and the gas phase collected in a 3 L plastic gas bag (SKC Tedlar, with polypropylene septum fitting) for GC analysis. The reactor was weighed and the reactor content was transferred to a centrifuge tube and weighed again. The product mixture was centrifuged at 4500 rpm for 45 min and the liquid phase (product oil) was separated from the solid phase (unreacted humins and catalyst). The reactor and the stirrer were thoroughly rinsed with acetone several times to collect the remaining solids. The combined acetone fraction (containing small amount of remaining product oil, unreacted humins and catalyst) was passed through a filter paper (to collect the solids) and collected in a beaker. The acetone in the mixture was then removed by evaporation in air and the resulting product (the remaining product oil) was weighted and added to the previously obtained product oil. The solid residue of unreacted humins and catalyst (from filter paper and centrifuge tube) was dried at 70 °C, under vacuum for overnight and also weighted for mass balance calculations. The obtained product oil is in one phase and designated as *humin oil* in this study. An overview of the product workup is shown in Figure 2.

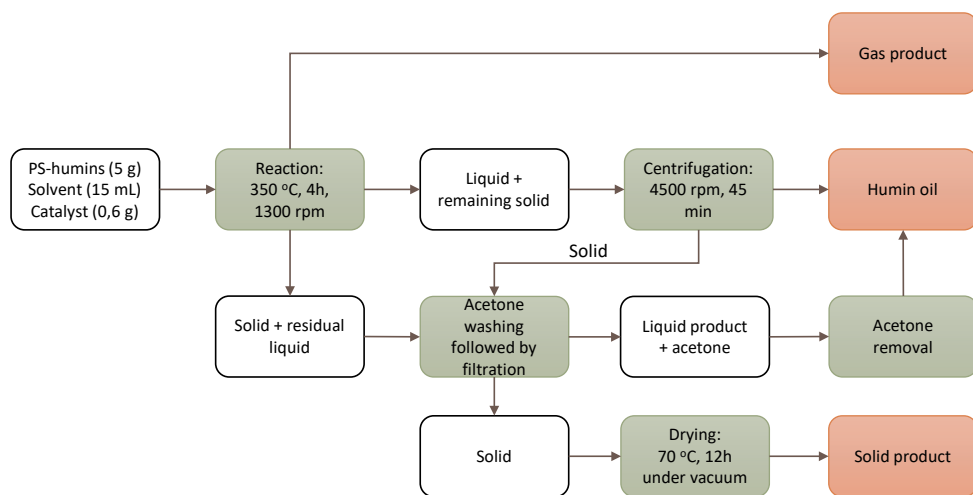


Figure 2. Schematic representation of the catalytic liquefaction procedure.

The conversion of humins and yields of humin oils are reported on a mass basis and were calculated using equations 1-3. In eq 3, the total feed intake represents the humin and solvent intake excluding catalyst.

$$\text{Humin conversion} = \frac{\text{Humin}_{\text{in}} - (\text{Total solid}_{\text{out}} - \text{catalyst intake})}{\text{Humin}_{\text{in}}} \times 100 \% \quad (1)$$

$$\text{Humin oil yield (based on humin intake)} = \frac{\text{Total humin oil}}{\text{humin intake}} \times 100 \% \quad (2)$$

$$\text{Humin oil yield (based on total intake)} = \frac{\text{Total humin oil}}{\text{Total feed intake}} \times 100 \% \quad (3)$$

4.2.5. Analytical methods

Thermogravimetric analysis (TGA). TGA data of the humins (raw PS-humins and PS-humins) were obtained using a Mettler–Toledo analyzer (TGA/SDTA851e). The samples were heated in a nitrogen atmosphere from 30 to 900 °C with a heating rate of 10 °C min⁻¹.

Elemental analysis. The elemental composition (C, H, N, O, and S content) of the humins (raw PS-humins and PS-humins) were analyzed using an automated Euro Vector EA3000 CHNS analyzer with acetanilide as the calibration reference. The oxygen content was determined by the difference of CHNS. Each sample was analyzed at least in duplicate and the average value is reported.

Heteronuclear single quantum coherence (HSQC) NMR. NMR spectra of the humins samples were acquired at 25 °C using an Agilent 400 MHz spectrometer. Approximately 0.3 g

of each sample was dissolved in 0.7 g of DMSO- d_6 . ^1H - ^{13}C HSQC spectra were acquired using a standard pulse sequence with a spectral width of 160 ppm, 16 scans and 512 increments in the F1 dimension. The data were processed using the MestReNova software.

Fourier-transform infrared spectroscopy (FTIR). FTIR spectra of the humins samples were recorded on a Shimadzu IR Tracer-100 by attenuated total reflection (ATR) method in the range of 4000 – 600 cm^{-1} . Small amount of samples were placed on the sample unit (Graseby Specac Golden Gate with diamond crystal top with 45 degree angle) and the IR-spectra were recorded.

High performance liquid chromatography (HPLC). Components in the water phase (after water extraction of raw PS-humins) were identified by an HPLC system consisting of an Agilent 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87H), a refractive index detector and an ultraviolet detector. The HPLC column was operated at 60 °C and aqueous sulfuric acid (5 mM) was used as the mobile phase with a flow rate of 0.55 $mL\ min^{-1}$. Identification of compounds in the mixture were determined by comparison of retention time of known, pure compounds.

Gas phase analysis. The composition of the gas phase obtained after reaction was determined by a Hewlett Packard 5890 Series II gas chromatography with a thermal conductivity detector (GC-TCD) equipped with a CP Poraplot Q Al_2O_3/Na_2SO_4 column (50 m x 0.5 mm, 10 μm film thickness) and a CP molecular sieve 5 Å column (25 m x 0.53 mm, 50 μm film thickness). Both columns were maintained at the same temperature. The injector and detector temperature were set at 150 °C and 90 °C respectively. The injector and detector temperature were set at 150 °C and 90 °C respectively. The oven temperature was kept at 40 °C for 2 min, heated up to 90 °C at a rate of 20 °C min^{-1} and kept at this temperature for another 2 min. Helium was used as the carrier gas. The columns were flushed for 30 s with reference and sample gas prior the measurement. For peak identification and quantification, a reference gas mixture containing H_2 , CH_4 , CO , CO_2 , ethylene, ethane, propylene and propane with known concentration (55.19% H_2 , 19.70% CH_4 , 3.00% CO , 18.10% CO_2 , 0.51% ethylene, 1.49% ethane, 0.51% propylene and 1.50% propane) was used.

Gas chromatography–mass spectrometry (GC-MS). GC-MS analyses of the humin oil were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a quadrupole Hewlett-Packard 6890 MSD selective detector and a 30 m x 0.25 mm, i.d. and 0.25 μm film sol-gel capillary column. The injector temperature was set at 250 °C. The oven temperature was kept at 60 °C for 5 min, then increased to 250 °C at a rate of 3 °C min^{-1} , and then held at 250 °C for 10 min.

Two-dimensional gas chromatography-flame ionization detector (GCxGC-FID). GCxGC-FID analyses of the humin oil were performed on a Trace GCxGC system from Interscience

equipped with a cryogenic trap and two columns (RTX-1701 capillary column, 30 m x 0.25 mm i.d. and 0.25 μm film thickness connected by Meltfit to a Rxi-5Sil MS column, 120 cm x 0.15 mm i.d. and 0.15 μm film thickness). A flame ionization detector (FID) was used. A dual-jet modulator was applied using carbon dioxide to trap the samples. The lowest possible operating temperature for the cold trap was 60 $^{\circ}\text{C}$. Helium was used as the carrier gas (flow rate of 0.6 mL min^{-1}). The injector temperature and FID temperature were set at 250 $^{\circ}\text{C}$. The oven temperature was kept at 60 $^{\circ}\text{C}$ for 5 min and then increased to 250 $^{\circ}\text{C}$ with a rate of 3 $^{\circ}\text{C min}^{-1}$. The pressure was set at 0.7 bar and the modulation time was 6 s. For these measurements, certain amount of humin oil was mixed with THF solution in a 1:1 v/v ratio. The THF solution contained 500 mg L^{-1} of di-n-butyl ether (DBE) as the internal standard (IS). From the GCxGC-FID spectra, the yields of aromatics, phenolics, ketones, alkanes, naphthenes and acids were calculated based on the humin intake. Quantification was performed by using an average relative response factor (RRF) per component group with DBE as the IS. Details of the procedure can be found elsewhere [22].

Gel permeation chromatography (GPC). GPC analyses of the humins (raw PS-humins and PS-humins) and the humin oil were performed using an Agilent HPLC 1100 system equipped with three MIXED-E columns (length 300 mm, i.d. 7.5 mm, PLgel 3 mm) in series and a GBC LC 1240 refractive index (RI) detector. The average molecular weights were determined using the PSS WinGPC Unity software from Polymer Standards Service. Polystyrene samples with different molecular weights were used as a calibration standard. For the measurements, the system was operated at 140 bar pressure, a column temperature of 42 $^{\circ}\text{C}$, with THF as eluent at a flow rate of 1 mL min^{-1} and injection volume of 20 μL with sample concentrations of circa 10 mg mL^{-1} . For the analyses purpose, the samples were diluted with THF and two drops of toluene were added as a flow marker prior to injection. For analyses of the humin oil, the residual solvent (IPA) as well as low molecular products derived thereof (e.g., acetone) were removed by heating the sample at 70 $^{\circ}\text{C}$, 50 mbar, for 2 h prior to dissolution in THF.

4.2.6. Characterization of the Pt/CeO₂ catalyst

Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the actual Pt content of the catalyst. The analyses were performed on a Perkin Elmer 4300 DV device. Samples were calcined at 900 $^{\circ}\text{C}$ and subsequently dissolved in an aqueous HNO_3 (2% wt). Transmission electronic microscopy (TEM) images were obtained using a Philips CM12 operated at an acceleration voltage of 120 kV. A small amount of sample was placed in a glass vial and 5 mL ethanol was added. Subsequently, the mixture was ultrasonically dispersed for about 15 min. The resulting suspension was then deposited on a copper grid coated with carbon and subsequently analyzed. The images were taken with a slow scanning CCD camera.

4.3. RESULTS AND DISCUSSION

4.3.1. Synthesis and characterization of the pyrolytic sugar (PS)-derived humins

The PS-derived humins used in this study were obtained by thermal treatment of a technical, non-purified PS (obtained from pine wood) at 130 °C for 22 h. The synthesis was performed without the addition of an acid catalyst, as typically done for humin synthesis, as PS already contain some organic acids (Table 1). Typically, this process gives 73 wt% of solids (referred to as raw PS-humins). The resulting sample was either used as such or extracted with water to remove any entrapped low molecular weight compounds. After water extraction, the final purified humin yield (PS-humins) was about 32 wt%. Surprisingly, the PS-humins are soluble in typical organic solvents like DMSO and THF. This is in contrasts with previously reported humin samples obtained from glucose and fructose upon heating in the presence of an acid [6, 24]. The higher solubility of the PS-humins prepared in this study is likely due to a lower molecular weight and less condensed structure compared to the typical humins from glucose/fructose, supported by analyses (*vide infra*). This solubility in selected organic solvents allowed a more detailed study on the molecular structure of the PS-humins sample by GPC and HSQC-NMR techniques, instead of the typically used solid state analysis techniques for highly insoluble humins.

The PS-humins contain 59 wt% [C], 35 wt% [O] and 5.5 wt% [H], which is in the range with reported values for glucose-derived humins and HMF (see Table 2 for details). A van Krevelen plot with H/C and O/C molar ratios of the humins is given in Figure 3. The results indicate that the PS-humins used in this study is less dehydrated and thus likely less condensed than the typical humins from glucose (*vide infra*).

Table 2. Elemental composition of humins samples from this study and literature data.

Element (wt%)	Raw PS-humins	PS-humins	Glucose-derived humins [23]	Fructose-derived humins [6]	HMF*
C	54	59	65.7	66.4	57.1
H	6	5.5	4.4	4.2	4.8
N	0.07	0.36	n/a	n/a	n/a
S	< 0.01	< 0.01	n/a	n/a	n/a
O	40	35	29.9	32	38.1

*as reference.

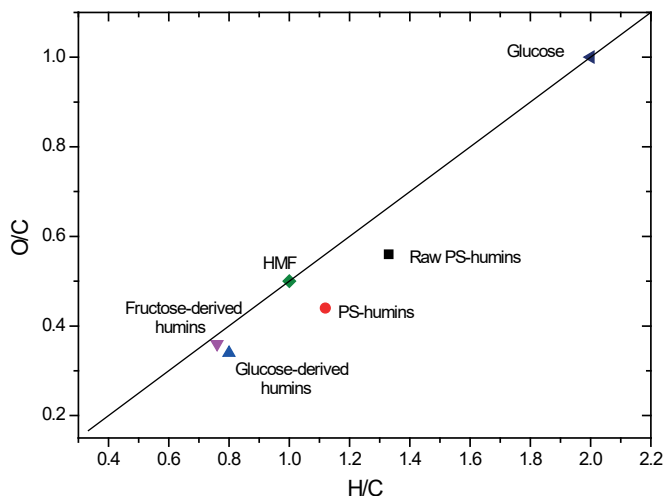


Figure 3. Van Krevelen plot of the different types of humins given in Table 2. Solid line represents the dehydration line.

Molecular weight distribution for both raw PS-humins and PS-humins are given in Figure 4. The average molecular weight (M_w) for the purified humins was about 900 g mol^{-1} , which suggests that on average about 8-10 sugar/furan units are present. When comparing both distributions, it is evident that a large amount of low molecular weight components are removed by the water extraction procedure. Analysis of the liquid extract (by HPLC technique) after water extraction of the raw PS-humins, reveals the presence of low molecular weight sugars like levoglucosan and cellobiosan (see Supporting Information, Figure S3).

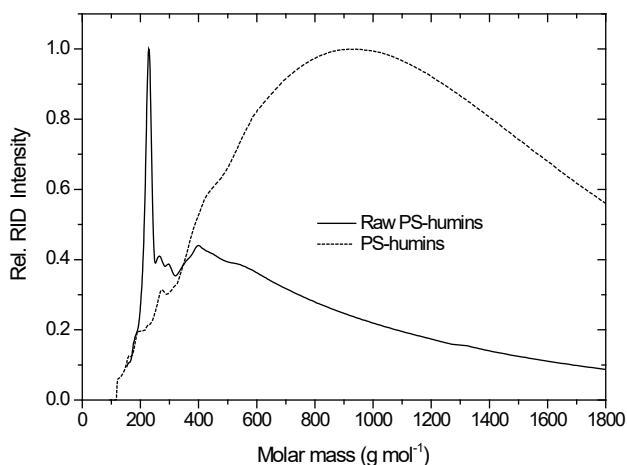


Figure 4. Molecular weight distribution of PS-derived humins as measured by GPC (THF) using polystyrene standards.

FT-IR analyses were performed to investigate the functionalities and chemical linkages in the humin samples before and after water extraction (Figure 5). The spectrum for the PS-humins sample shows strong similarities with those reported for humins derived from glucose and fructose [6, 25]. A broad peak at $3200\text{--}3400\text{ cm}^{-1}$ is present, which originates from the C-O stretch vibration of alcohols and possibly some residual water. Strong broad bands are present in the $1800\text{--}1600\text{ cm}^{-1}$ region corresponding to C=O stretch vibrations of acids, esters, aldehydes and ketones as well as substituted furanic rings (about 1600 cm^{-1}). A comparison of the spectra for the raw PS-humins (before extraction) and PS-humins (after extraction) shows that the peak intensities in the $3400\text{--}3000\text{ cm}^{-1}$, $1800\text{--}1600\text{ cm}^{-1}$ and particularly the $1100\text{--}900\text{ cm}^{-1}$ region is higher for the former. This is due to a reduction of the amount of sugar-based molecules after extraction (glucose and levoglucosan, which show strong bands in the $1100\text{--}900\text{ cm}^{-1}$ region), in accordance with HPLC data for the water phase after extraction (Figure S3).

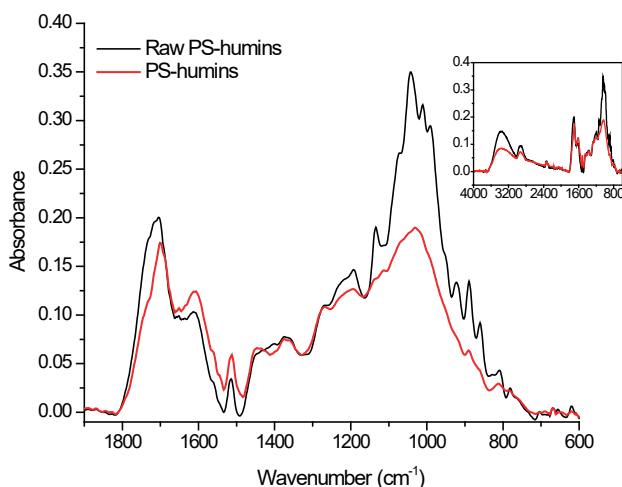


Figure 5. FT-IR spectra of raw PS-humins (black) and PS-humins (red). Inset plot is from $4000\text{--}600\text{ cm}^{-1}$ region.

To further understand the chemical composition of the PS-humins, two-dimensional $^1\text{H}\text{--}^{13}\text{C}$ HSQC-NMR was performed using DMSO-d_6 as the solvent (Figure 6). Major chemical groups can be clearly identified on the basis of the available literatures [6, 17, 24, 26]. In line with the FT-IR analysis, NMR analysis confirms that the PS-humins contains aliphatic C-H bonds, aliphatic (sugar) CH-O(H) motifs and aromatic (furanics) C-H bonds. In addition, a clear OMe signal is present, which is likely due to the presence of some residual guaiacol units in the structure. It is possible that covalent bonds between carbohydrate bonds and lignin fragments either from the biomass feed or formed during pyrolysis end up in the PS fraction and thus ultimately in the humins. Another possibility is the incorporation of monomeric phenolics, which are known to be present in the PS due to incomplete separation from the pyrolytic lignins. Estimations for the amounts of combined phenolics/aromatics in PS have

been reported in the literature and are between 4.5 and 7.5 wt% [27]. We have reported detailed characterization studies for a PS fraction obtained from pine wood using a similar separation technique as used here to isolate the PS [28] and estimated that about 8% of the volatiles detected by GC are phenolics. Considering the fact that the volatile fraction is less than 50% of the PS (GPC) [27], the amounts of low molecular weight phenolics is in the < 4% range, which is considerable and as such it is possible that monomeric phenolics may participate in the condensation reactions leading to humins.

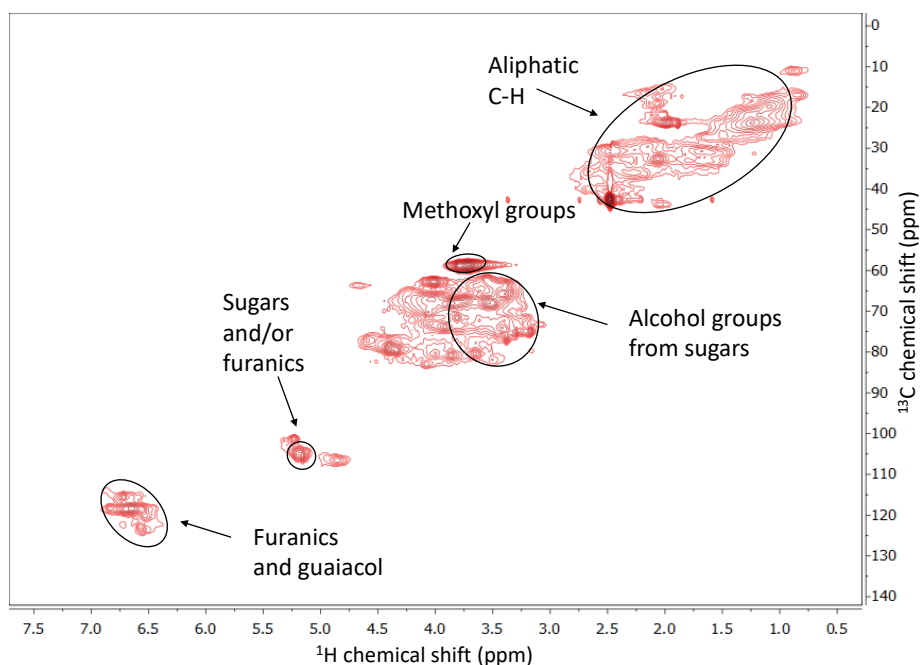


Figure 6. HSQC spectra of PS-humins (400 MHz, DMSO- d_6).

To obtain information on the presence of other carbonyl groups in the humin structure e.g., from ketones/acids/esters, a 1D ^{13}C -NMR spectrum of the PS-humins sample was acquired (Figure S5, Supporting Information). It indeed shows (broad) resonances in the 170-180 range from the carbonyl groups of acids and esters.

On the basis of the NMR results, FT-IR and GPC analyses, a proposal for the structure of the PS-humins is provided in Figure 7. It consists of sugar and furanic fragments linked with among others (substituted) aliphatic and ester units. In addition, a phenolic fragment with a -OMe group is added, in line with the HSQC-NMR data and Py-GC-MS analyses (*vide infra*).

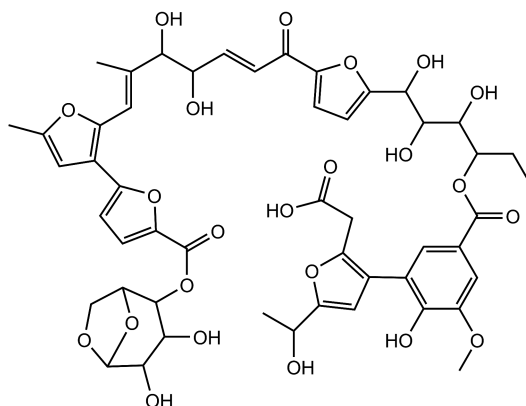


Figure 7. Proposed molecular structure for humins from pyrolytic sugars.

4.3.2. Thermal pyrolysis

4.3.2.1. TGA studies

The thermal behavior of the humins were studied using TGA under N_2 (Figure 8). The total weight loss was about 72 wt% for the raw PS-humins and 62 wt% for the PS-humins. This difference is likely due to the presence of low molecular weight, volatile compounds in the raw PS-humins, supported by HPLC measurements (*vide supra*). For both humin samples, three distinct weight loss stages were observed in the derivative thermo-gravimetric, DTG image (Figure 8, right). The first stage started at around 70 °C and is likely due to evaporation of very small entrapped volatile organics. Subsequently, two major peaks were observed, one at about 265 and another at about 380°C. The ratio of the peak heights differs considerably for both samples. The peak at 265 °C is highest for the raw PS-humins, and considerably lower for PS-humins. As such, this peak is likely due to the decomposition and evaporation of volatile, low molecular weight and sugar-like components (e.g., levoglucosan). TGA data for highly condensed and insoluble humins derived from glucose and fructose were reported by Rasrendra et al. [19]. Here, a maximum mass loss was at 450 °C, which is higher than found for our samples, and suggest indeed that the PS-humins are less condensed than those reported for glucose/fructose. In addition, and in line with this statement, lower overall weight losses (50%) were reported for those glucose/ fructose-derived humins.

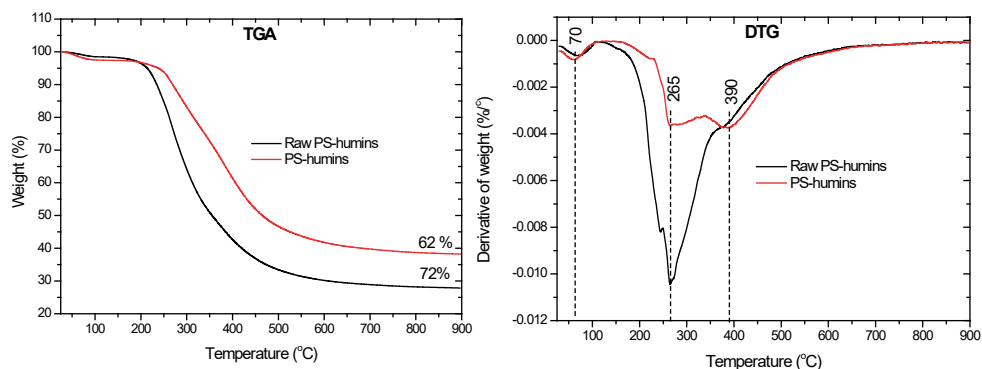


Figure 8. TGA (left) and DTG (right) plots of raw PS-humins (black line) and PS-humins (red line).

4.3.2.2. Pyrolysis experiments

Thermal (non-catalytic) pyrolysis of the PS-humins was performed in a mg scale (PTV-GC-MS) to gain insights in the composition of the vapor phase. The TGA data imply that 400–500 °C is sufficient to volatilize the majority of the feed and thus a pyrolysis temperature of 550 °C was selected for further studies. A typical chromatogram of the volatiles is shown in Figure S6 (Supporting Information) and shows that phenolics are the main products, together with furanics and substituted cyclopentanones. Interestingly, D-glucose-derived humins mainly gave furanics such as 2-methylfuran, 2,5-dimethylfuran and 1,2-furanylethanone upon thermal pyrolysis [23]. This observation confirms that the PS-humins used in this study also contain some phenolic structures besides furan and sugars units. This is also supported by NMR data (*vide supra*), which showed the presence of methoxy groups, in line with the presence of significant amounts of 4-methylguaiacol in the chromatogram (compound 7, Figure S6). However, it should be noted that some phenolics may also be formed by the (thermal) decomposition of sugar derivatives, a well-known example is the formation of 1,2,4-benzenetriol from HMF [29].

4.3.2.3. Catalytic pyrolysis

Catalytic pyrolysis was investigated to determine the possibility to convert the PS-humins into industrially relevant aromatics like BTXNE. Experiments with PS-humins were performed in a PTV-GC-MS unit at 550 °C with a humin to catalyst ratio of 0.05 w/w. Based on previous studies [30], HZSM-5-50 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 50) was selected as the catalyst. Considerable amounts of BTXNE (61.6% on total GC detectable monomers) were formed, corresponding to 5.1 wt% based on the PS-humins feed (Figure 9). Other GC detectable products were CO_2 and higher aromatics such as substituted naphthalenes, indanes and indenenes. The BTXNE yield is considerably higher than for glucose-derived humins (1.5 wt%) obtained at similar pyrolysis conditions, and comparable to the yields obtained for kraft lignin (6 wt%) [23]. The latter is

considered a promising feed for BTXNE [23]. These results indicate that PS-humins have the potential to be converted to biobased aromatics via catalytic pyrolysis.

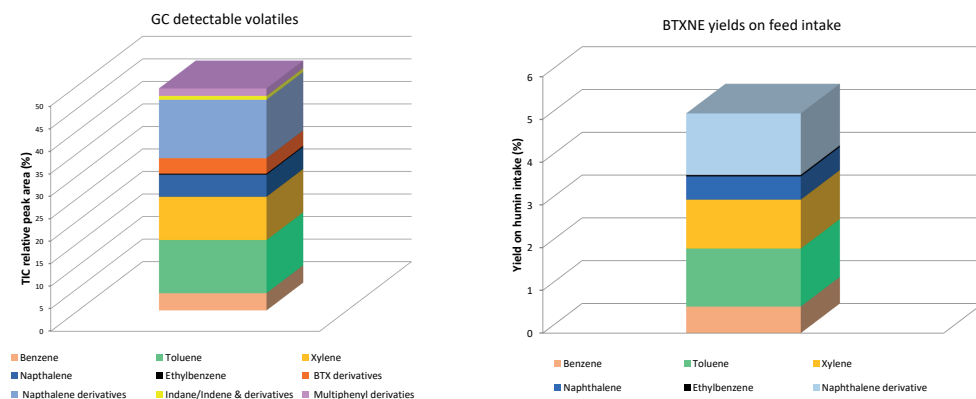


Figure 9. Representative GC detectable monomers for the catalytic pyrolysis of PS-humins with HZSM-5-50 as the catalyst (humin to catalyst ratio of 0.05 w/w) at 550 °C (left) and BTXNE yields based on PS-humins intake (right).

4.3.3. Catalytic liquefaction using Pt/CeO₂ catalyst

PS-humins liquefaction experiments were carried out in a batch setup with IPA as the solvent and H₂ donor using a Pt/CeO₂ catalyst (see Supporting Information for catalyst characterization) at 350 °C for 4 h batch times with the objective to depolymerize the humin structure and obtain low molecular weight aromatics. All experiments were performed in duplicate, showing a very good reproducibility for the experimental procedure (Table 3). Mass balance closures for the PS-humins liquefaction experiments were excellent (> 95 wt %). A liquid product was obtained in about 79 % yield. The PS-humins conversion, calculated based on the amounts of solids isolated after reaction and corrected for catalyst intake, was of about 80%. Hence, these experiments show that humins derived from PS can indeed be liquefied to a large extent using Pt/CeO₂ as the catalyst in combination with IPA.

Table 3. Product yields and compositions for the catalytic liquefaction of PS-humins in IPA*.

	Run 1	Run 2
Humins intake, wt% on total feed	24.4	24.2
Liquid yields, wt % on total feed	79.6	79.2
Solid residue, wt% on total feed	4.8	4.2
Humins conversion, wt% on total humin intake	81.1	83.2
Gas phase, wt% on total feed	14.2	11.7
Mass balance closure	98.6	95.3

*Reaction condition: 350 °C, 4 h, 1300 rpm, with Pt/CeO₂ (12 wt% on humin intake).

The humin oil composition was determined using GC-MS, GCxGC-FID and GPC. GCxGC-FID analyses (Figure 10) show the presence of numerous products belonging to various organic product classes viz. ketones, phenolics, and aromatics as well as aliphatic hydrocarbons. The presence of these components classes was further confirmed by GC-MS analyses (see Supporting Information, Figure S7). IPA is still present in considerable amounts, indicating that its conversion at the prevailing reaction conditions is far from quantitative. Typical reaction products of IPA (e.g., acetone and (hydrogenated) aldol condensation products derived thereof like methylisobutylketone (MIBK), 2-hexanol, and 2,6-dimethyl-4-heptanone) were detected [31]. Phenolics, naphthalenes, and aromatics in the humin oil are most likely formed from humins and not from IPA [32, 33]. The amounts of the individual component classes in the humin oil were determined an average response factor for each group (Table 4). Among the humin-derived products, phenolics (phenol, methoxyphenol and dihydroxybenzene) were present in the largest amounts, with a total yield of about 14.1% based on the GC detectables in the humin oil. Aromatics (mono-aromatics, naphthalenes) were the second main product (10.6%). Interestingly, considerable amount of organic acids – possibly propionic, acetic and formic acid, were detected. These organic acids may be formed from residual sugars present in the PS-humins (Figure 7). A GPC chromatogram of the liquid phase after removal of residual IPA shows the presence of substantial amounts of low molecular weight products along with a higher molecular weight tail (Supporting Information, Figure S8). It shows that the catalytic liquefaction procedure indeed results in significant depolymerization of the PS-humins structure by cleavage of inter unit bonds.

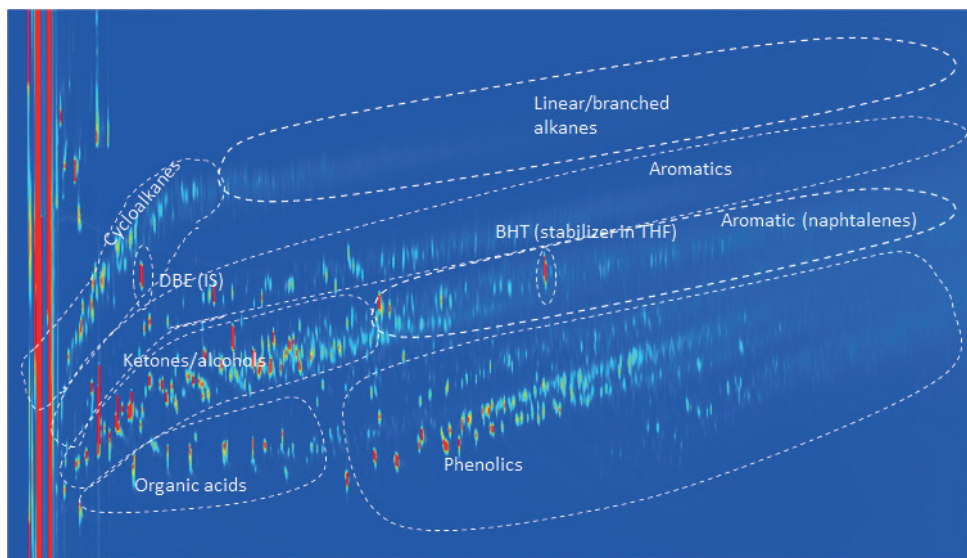


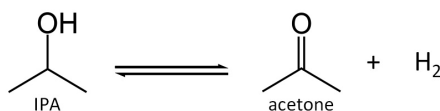
Figure 10. GCxGC-FID of the humin oil from PS-humins reaction with IPA and Pt/CeO₂ catalyst at 350 °C for 4 h (crude reaction mixture before solvent evaporation). DBE: internal standard (IS).

Table 1. Overview of the humin oil composition from catalytic liquefaction of PS-humins (GCxGC-FID).

Component class	Amount (%)*
Phenolics	14.1
Aromatics	10.6
Linear/branched alkanes	0.6
Cycloalkanes	2.6
Organic acids	7.9
Ketones/alcohols	64.2

*based on GC detectables in the humin oil, values are average from duplicate experiments at 350 °C for 4 h.

A substantial amount of a gaseous products were obtained (on average around 12.5 wt% based on feed intake), indicating that part of the solvent (IPA) and the PS-humins are converted to gas components. The composition of the gas phase was determined by GC-TCD (Table S1) and shown to consist of propane (41.5 mol%), carbon dioxide (20.5 mol%), methane (12.1 mol%), and hydrogen (11 mol%). Hydrogen is likely formed from IPA dehydrogenation (Scheme 1), a well-known reaction catalyzed by Pt.


Scheme 1. IPA dehydrogenation to acetone and hydrogen.

Wang et al. proposed a reaction network to explain the formation of various products in the humin oil and gas phase during the catalytic liquefaction of humins using Pt/C and IPA, see Supporting Information (Scheme S1). [33]. Although the starting material and temperature used in this work are different, it is likely also applicable for the results presented here.

4.4. CONCLUSIONS

In this work, we have prepared humins (PS-humins) from the technical, unpurified PS fraction of commercial pyrolysis oil, characterized them in detail and explored the potential to convert them to low molecular weight biobased compounds. Unlike typical sugar (glucose, fructose)-derived humins reported in the literatures, PS-humins obtained from unpurified PS under relatively mild conditions are soluble in common organic solvents. This allows for the characterization of the materials by GPC and NMR. All characterization data showed that these humins have a relatively low molecular weight (Mw about 900 g mol⁻¹) and consist of furanics and sugar-like fragments. Thus, the results suggest the formation of relatively uncondensed (and therefore still relatively soluble) humins that are the result of the relatively mild conditions applied.

The PS-humins can be converted to liquid products (humin oil) using catalytic pyrolysis and a treatment with Pt/CeO₂ in IPA. Catalytic pyrolysis using HZSM-5 (SiO₂/Al₂O₃ = 50) catalyst at 550 °C gave an BTXNE yield of 5.1 wt% based on PS-humins intake, which is close to that obtained for Kraft lignin under similar conditions. Catalytic liquefaction using IPA as solvent and hydrogen donor and Pt/CeO₂ catalyst at 350 °C resulted in significant depolymerization and liquefaction of the PS-humins. Humins oil analysis using GCxGC-FID showed that low molecular weight components, particularly phenolics and aromatics (estimated 24.7% based on GC detectables in the humin oil) are present, together with higher molecular weight fragments (observed by GPC). As such, this study has shown that PS-humins may be (partly) depolymerized to liquid products, containing significant amounts of low molecular components. These findings imply that the techno-economic viability of pyrolysis oil biorefineries can be improved by converting humin type byproducts to high value, low molecular weight biobased chemicals.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the Ministry of Research, Technology and Higher Education, Republic of Indonesia for financing the PhD study of R.M. Abdilla-Santes. The Biomass Technology Group (Enschede, the Netherlands) is acknowledged for providing PS-humins. The authors also acknowledge L. Rohrbach and J. H. Marsman, and J. van der Velde (University of Groningen, The Netherlands) for analytical support, A. Appeldoorn, E. Wilbers, and M. de Vries (University of Groningen, The Netherlands) for technical support and M.B. Figueiredo (University of Groningen, The Netherlands) for assisting in GC-TCD analyses.

REFERENCES

- [1] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr, J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski. The Path Forward for Biofuels and Biomaterials. *Science*, 311 (2006), pp.484-489.
- [2] A. Corma, S. Iborra and A. Velty. Chemical Routes for the Transformation of Biomass into Chemicals. *Chemical Reviews*, 107 (2007), pp.2411-2502.
- [3] J.J. Bozell. Feedstocks for the Future—biorefinery Production of Chemicals from Renewable Carbon. *CLEAN—Soil, Air, Water*, 36 (2008), pp.641-647.
- [4] B. Girisuta, B. Danon, R. Manurung, L. Janssen and H. Heeres. Experimental and Kinetic Modelling Studies on the Acid-Catalysed Hydrolysis of the Water Hyacinth Plant to Levulinic Acid. *Bioresource Technology*, 99 (2008), pp.8367-8375.
- [5] R. van Putten, van der Waal, Jan C, E. De Jong, C.B. Rasrendra, H.J. Heeres and J.G. de Vries. Hydroxymethylfurfural, a Versatile Platform Chemical Made from Renewable Resources. *Chemical Reviews*, 113 (2013), pp.1499-1597.
- [6] I. van Zandvoort, Y. Wang, C.B. Rasrendra, E.R. van Eck, P.C. Bruijninx, H.J. Heeres and B.M. Weckhuysen. Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions. *ChemSusChem*, 6 (2013), pp.1745-1758.
- [7] R. Venderbosch and W. Prins. Fast Pyrolysis Technology Development. *Biofuels, Bioproducts and Biorefining*, 4 (2010), pp.178-208.
- [8] N.M. Bennett, S.S. Helle and S.J. Duff. Extraction and Hydrolysis of Levoglucosan from Pyrolysis Oil. *Bioresource Technology*, 100 (2009), pp.6059-6063.
- [9] K. Sipilä, E. Kuoppala, L. Fagernäs and A. Oasmaa. Characterization of Biomass-Based Flash Pyrolysis Oils. *Biomass and Bioenergy*, 14 (1998), pp.103-113.
- [10] A. Oasmaa and S. Czernik. Fuel Oil Quality of Biomass Pyrolysis Oils State of the Art for the End Users. *Energy & Fuels*, 13 (1999), pp.914-921.
- [11] Bio-materials & chemicals, <http://www.btgworld.com/en/rtd/technologies/bio-materials-chemicals>, 04 May 2016.
- [12] N. Kuzhiyil, D. Dalluge, X. Bai, K.H. Kim and R.C. Brown. Pyrolytic Sugars from Cellulosic Biomass. *ChemSusChem*, 5 (2012), pp.2228-2236.
- [13] S. Helle, N.M. Bennett, K. Lau, J.H. Matsui and S.J. Duff. A Kinetic Model for Production of Glucose by Hydrolysis of Levoglucosan and Cellobiosan from Pyrolysis Oil. *Carbohydrate research*, 342 (2007), pp.2365-2370.
- [14] R. Abdilla, C. Rasrendra and H. Heeres. Kinetic Studies on the Conversion of Levoglucosan to Glucose in Water Using Brønsted Acids as the Catalysts. *Industrial & Engineering Chemistry Research*, 57 (2018), pp.3204-3214.
- [15] Y. Zhang, Y. Wang, H. Cui, P. Zhao, F. Song, X. Sun, Y. Xie, W. Yi and L. Wang. Effects of Hydrolysis and Oxidative Hydrolysis Pretreatments on Upgrading of the Water-soluble Fraction of Bio-Oil via Decarboxylation. *Applied Energy*, 226 (2018), pp.730-742.
- [16] R.M. Abdilla-Santes, H. Heeres and H.J. Heeres. Acid Catalysis Conversion of Pyrolytic Sugars, Manuscript in preparation, (2019).
- [17] Yin Wang. Catalytic Hydrotreatment of Pyrolysis Liquids and Fractions: Catalyst Development and Process Studies. (Doctoral Dissertation), Groningen (2017).
- [18] J. Horvat, B. Klaić, B. Metelko and V. Šunjić. Mechanism of Levulinic Acid formation. *Tetrahedron Letters*, 26 (1985), pp.2111-2114.
- [19] C. Rasrendra, M. Windt, Y. Wang, S. Adisasmito, I. Makertihartha, E. Van Eck, D. Meier and H. Heeres. Experimental Studies on the Pyrolysis of Humins from the Acid-Catalysed Dehydration of C6-Sugars. *Journal of Analytical and Applied Pyrolysis*, 104 (2013), pp.299-307.
- [20] T.M.C. Hoang, L. Lefferts and K. Seshan. Valorization of Humin-Based Byproducts from Biomass Processing—A Route to Sustainable Hydrogen. *ChemSusChem*, 6 (2013), pp.1651-1658.
- [21] J. Pin, N. Guigo, A. Mija, L. Vincent, N. Sbirrazzuoli, van der Waal, Jan C and E. De Jong. Valorization of Biorefinery Side-Stream Products: Combination of Humins With Polyfurfuryl Alcohol for Composite Elaboration. *ACS Sustainable Chemistry & Engineering*, 2 (2014), pp.2182-2190.

- [22] Y. Wang, S. Agarwal, A. Kloekhorst and H.J. Heeres. Catalytic Hydrotreatment of Humins in Mixtures of Formic Acid/2-Propanol with Supported Ruthenium Catalysts. *ChemSusChem*, 9 (2016), pp.951-961.
- [23] S. Agarwal, D. van Es and H.J. Heeres. Catalytic pyrolysis of recalcitrant, insoluble humin byproducts from C6 sugar biorefineries. *Journal of Analytical and Applied Pyrolysis*, 123 (2017), pp.134-143.
- [24] I. van Zandvoort, E.J. Koers, M. Weingarth, P.C. Bruijninx, M. Baldus and B.M. Weckhuysen. Structural Characterization of 13 C-Enriched Humins and Alkali-Treated 13-C Humins by 2D Solid-State NMR. *Green Chemistry*, 17 (2015), pp.4383-4392.
- [25] S. Wang, H. Lin, Y. Zhao, J. Chen and J. Zhou. Structural Characterization and Pyrolysis Behavior of Humin Byproducts from the Acid-Catalyzed Conversion of C6 And C5 Carbohydrates. *Journal of Analytical and Applied Pyrolysis*, 118 (2016), pp.259-266.
- [26] I. van Zandvoort, E.R. van Eck, P. de Peinder, H.J. Heeres, P.C. Bruijninx and B.M. Weckhuysen. Full, Reactive Solubilization of Humin Byproducts by Alkaline Treatment and Characterization of the Alkali-Treated Humins Formed. *ACS Sustainable Chemistry & Engineering*, 3 (2015), pp.533-543.
- [27] X. Li, L.C. Luque-Moreno, S.R.G. Oudenhoven, L. Rehmann, S.R.A. Kersten and B. Schuur. Aromatics Extraction from Pyrolytic Sugars Using Ionic Liquid to Enhance Sugar Fermentability. *Bioresource Technology*, 216 (2016), pp. 12-18.
- [28] W. Yin, R.H. Venderbosch, G. Bottari, K.K. Krawczyk, K. Barta and H.J. Heeres. Catalytic Upgrading of Sugar Fractions from Pyrolysis Oils in Supercritical Mono-Alcohols Over Cu Doped Porous Metal Oxide. *Applied Catalysis B: Environmental*, 166 (2015), pp.56-65.
- [29] A.J. Kumalaputri, C. Randolph, E. Otten, H.J. Heeres and P.J. Deuss. Lewis Acid Catalyzed Conversion of 5-Hydroxymethylfurfural to 1, 2, 4-Benzenetriol, an Overlooked Biobased Compound. *ACS Sustainable Chemistry & Engineering*, 6 (2018), pp.3419-3425.
- [30] J. Jae, G.A. Tompsett, A.J. Foster, K.D. Hammond, S.M. Auerbach, R.F. Lobo and G.W. Huber. Investigation into the Shape Selectivity of Zeolite Catalysts for Biomass Conversion. *Journal of Catalysis*, 279 (2011), pp.257-268.
- [31] M. Sakurai, H. Honda and H. Kameyama. Fundamental Study of A Non-Steady Operation for 2-Propanol De-Hydrogenation. *International Journal of Hydrogen Energy*, 32 (2007), pp.1303-1308.
- [32] Y. Wang, S. Agarwal, Z. Tang and H.J. Heeres. Exploratory Catalyst Screening Studies on the Liquefaction of Model Humins from C6 Sugars. *RSC Advances*, 7 (2017), pp.5136-5147.
- [33] Y. Wang, S. Agarwal and H.J. Heeres. Catalytic Liquefaction of Humin Substances from Sugar Biorefineries with Pt/C in 2-Propanol. *ACS Sustainable Chemistry & Engineering*, 5 (2016), pp.469-480.

SUPPORTING INFORMATION FOR CHAPTER 4

Figures

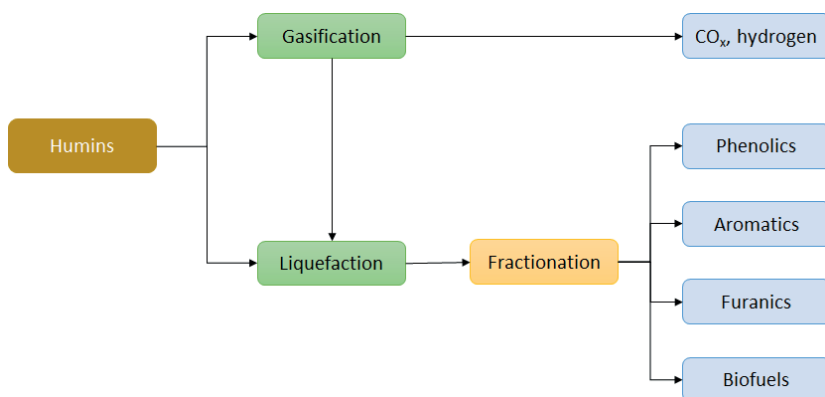


Figure S1. Proposed valorization approach for humins from glucose and fructose (from [1]).

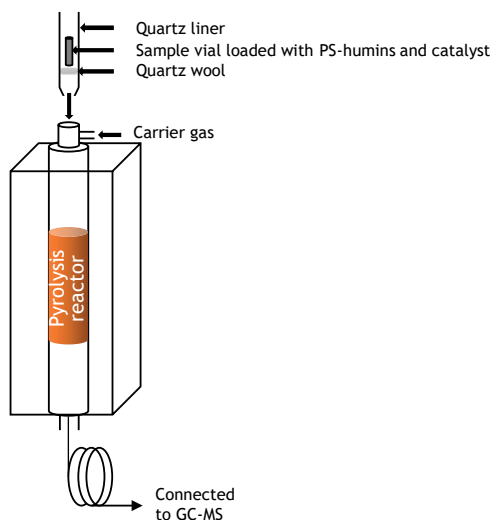


Figure S2. Schematic representation of PTV-GC-MS setup.

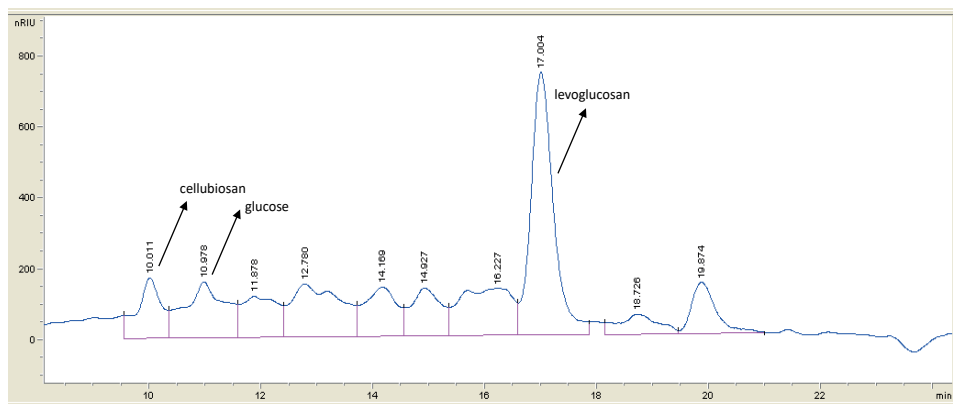


Figure S3. HPLC analysis of the water soluble fraction of PS-humins.

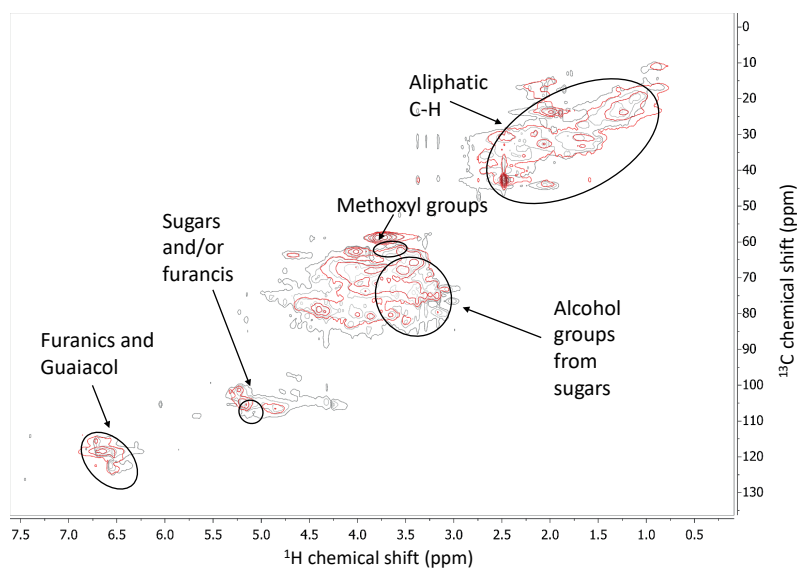


Figure S4. Comparison of HSQC spectra (400 MHz, DMSO- d_6) of raw PS-humins (grey) and PS-humins (red).

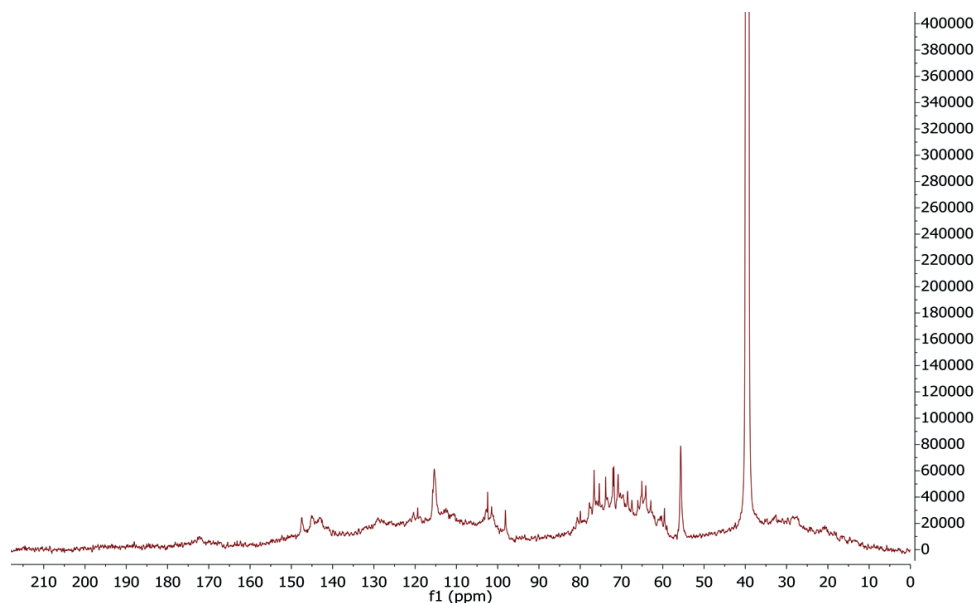


Figure S5. ^{13}C -NMR spectra of PS-humins (400 MHz, $\text{DMSO}-d_6$).

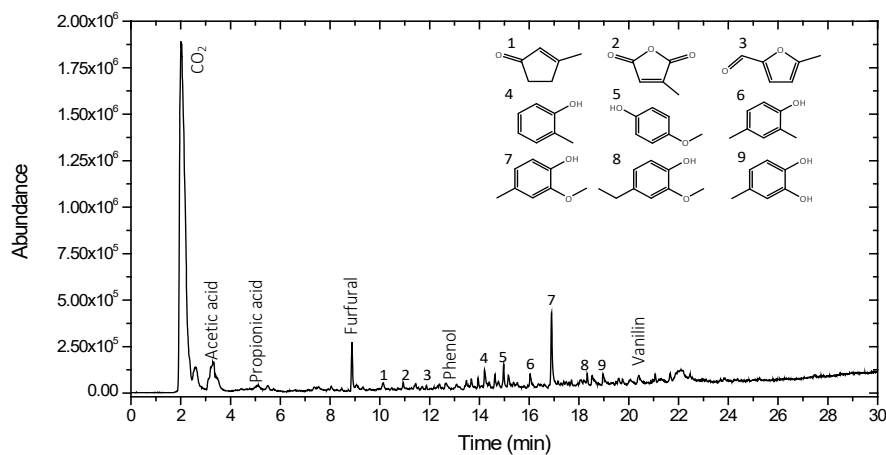


Figure S6. Thermal pyrolysis GC-MS chromatogram PS-humins at 550 °C.

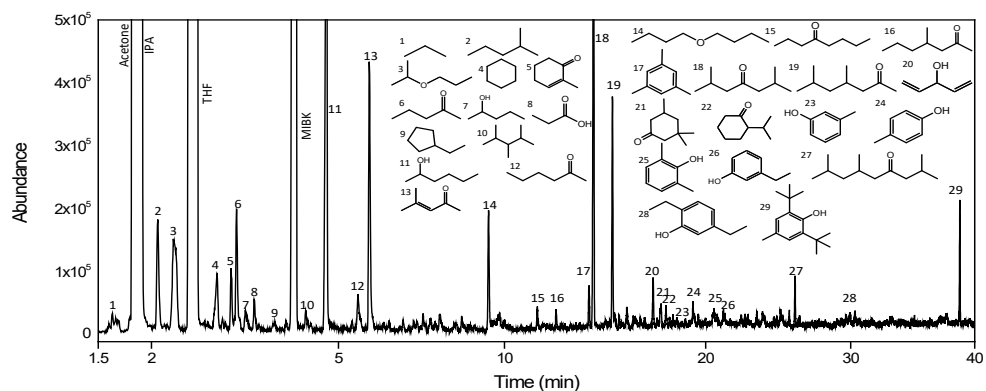


Figure S7. GC-MS spectrum of the humin oil from PS-humins liquefaction with IPA, Pt/CeO₂ catalyst at 350 °C for 4h.

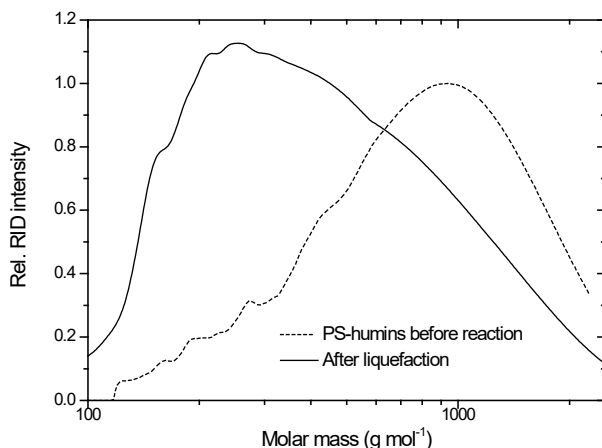


Figure S8. GPC chromatogram of PS-humins before catalytic liquefaction reaction and a representative humin oil obtained from it.

Catalyst characterization data

The catalytic liquefaction of the PS-humins was performed using Pt/CeO₂ (5 wt%) synthesized using a wet impregnation procedure. The actual Pt content of the catalyst was 4.43 wt% (ICP). The average Pt nanoparticle size was 1.8 ± 1.4 nm (TEM images), indicating a good dispersion of the metal on the catalyst support (Figure S9).

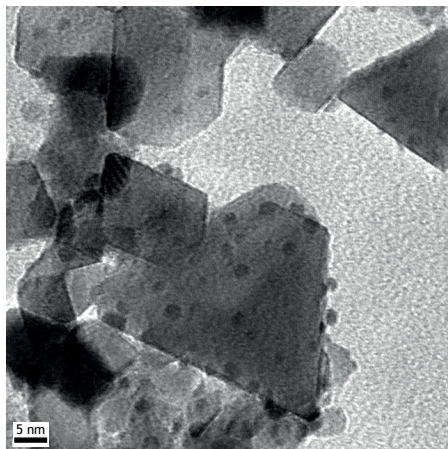


Figure S9. Representative TEM image of the Pt/CeO₂ catalyst.

Gas phase composition from PS-humins liquefaction

The main gas phase components (Table S1) are propane (41.5 mol%), carbon dioxide (20.5 mol%), methane (12.1 mol%), and hydrogen (11 mol%). Hydrogen – which is desirable in the conversion of the PS-humins to lower molecular weight components, is likely formed by the dehydrogenation of IPA to acetone, catalyzed by the supported-Pt catalyst. Substantial amounts of propane in the gas phase were detected. Methane may either be formed by reactions involving the humins, e.g., cleavage of alkyl substituents and/or by subsequent gas-phase hydrogenation reactions of CO_x with hydrogen (eq i). These methanation reactions are known to be catalyzed by supported Pt catalysts [2]. Previously, the formation of considerable amounts of methane (19.7 mol %) arose in the blank reaction (IPA with Pt/C, no humins) [3], confirming that indeed methane formation by gas phase methanation occurs to a significant extent.

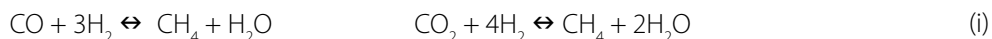


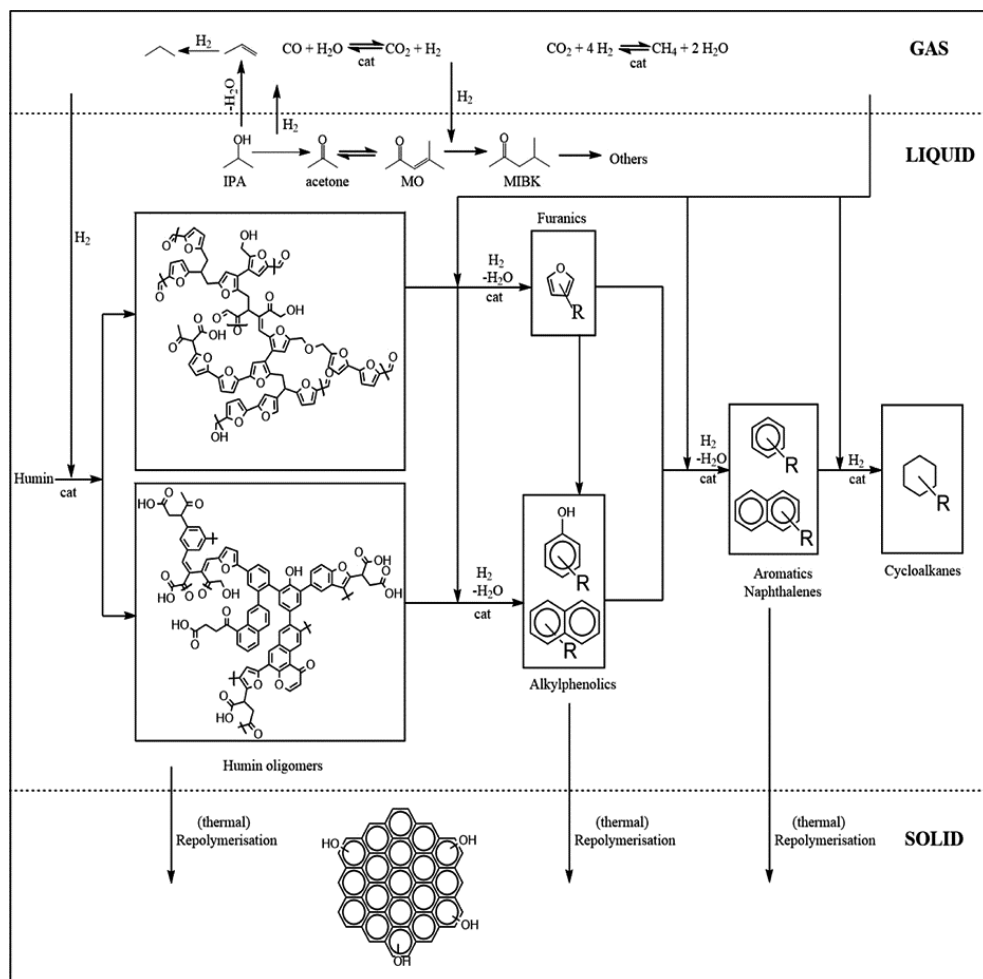
Table S1. Gas phase compositions for the catalytic liquefaction of PS-humins in IPA.

Gas component	% mol detectable*
Carbon dioxide	20.5
Ethylene	0.1
Ethane	4.0
Propylene	3.6
Propane	41.5
Hydrogen	11.0
Methane	12.1
Carbon monoxide	7.2

*average value from duplo experiment.

Reaction condition: 350 °C, 4 h, 1300 rpm, with Pt/CeO₂ catalyst (12 wt% on humin intake).

Reaction network



Scheme S1. Proposed reaction network for humin depolymerization/liquefaction using Pt/C in IPA. Reprinted with permission from [2]. Copyright 2016 American Chemical Society.

In this proposal, the humins (which structure contains significant amounts of substituted furan fragments) are depolymerized, either catalytically or thermally or a combination of the two, to form oligomeric furanics and ultimately lower molecular weight furanics. However, furanics were absent in the reaction products [1]. At elevated temperatures and pressures, it is likely that the furanics are rapidly converted to aromatics and alkylphenolics. Both pathways are feasible according to recent literature [4, 5]. Alternatively, during heating of the reaction mixture, the furanic structure can be dehydrated to a more condensed structure with aromatic and alkylphenolic units [4, 5], which are subsequently depolymerized to alkylphenolics and

aromatics monomers. Both aromatization of the humin structure and depolymerization may also occur in parallel. The majority of the ketones is from subsequent (aldol) condensations of acetone (derived from IPA), which is confirmed by the blank reactions [3]. Furthermore, the presence of alkanes in the mixture is (partly) due to the catalytic hydrogenation of the aromatics formed from the humins with molecular hydrogen formed *in situ* by the dehydrogenation of IPA to acetone.

References for the supporting information

- [1] Y. Wang, S. Agarwal, A. Klokhorst and H.J. Heeres. Catalytic Hydrotreatment of Humins in Mixtures of Formic Acid/2-Propanol with Supported Ruthenium Catalysts. *ChemSusChem*, 9 (2016), pp.951-961.
- [2] J. Gao, Q. Liu, F. Gu, B. Liu, Z. Zhong and F. Su. Recent Advances in Methanation Catalysts for the Production of Synthetic Natural Gas. *RSC Advances*, 5 (2015), pp.22759-22776.
- [3] Y. Wang, S. Agarwal and H.J. Heeres. Catalytic Liquefaction of Humin Substances from Sugar Biorefineries with Pt/C in 2-Propanol. *ACS Sustainable Chemistry & Engineering*, 5 (2016), pp.469-480.
- [4] G. Bottari, A.J. Kumalaputri, K.K. Krawczyk, B.L. Feringa, H.J. Heeres and K. Barta. Copper–Zinc Alloy Nanopowder: A Robust Precious-Metal-Free Catalyst for the Conversion of 5-Hydroxymethylfurfural. *ChemSusChem*, 8 (2015), pp.1323-1327.
- [5] T. Buntara, S. Noel, P.H. Phua, I. Melián-Cabrera, J.G. de Vries and H.J. Heeres. From 5-hydroxymethylfurfural (HMF) to Polymer Precursors: Catalyst Screening Studies on the Conversion of 1, 2, 6-Hexanetriol to 1, 6-Hexanediol. *Topics in Catalysis*, 55 (2012), pp.612-619

5

High-Yield 5-Hydroxymethylfurfural Synthesis from Crude Sugar Beet Juice in a Biphasic Microreactor

This chapter is published as:

High-Yield 5-Hydroxymethylfurfural Synthesis from Crude Sugar Beet Juice in a Biphasic Microreactor

R.M. Abdilla-Santes, W. Guo, P.C.A. Bruijninx, J. Yue, P.J. Deuss and H.J. Heeres
ChemSusChem, 12(18), 2019, 4304-4312.

DOI: 10.1002/cssc.201901115

5-Hydroxymethylfurfural (HMF) is an important biobased platform chemical obtainable in high selectivity by the hydrolysis of fructose (FRC). However, FRC is expensive, making the production of HMF at a competitive market price highly challenging. Here, it is shown that sugar beet thick juice, a crude, sucrose (SUC)-rich intermediate in sugar refining, is an excellent feedstock for HMF synthesis. Unprecedented high selectivities and yields of >90% for HMF were achieved in a biphasic reactor setup at 150°C using salted diluted thick juice with H_2SO_4 as catalyst and 2-methyltetrahydrofuran (MTHF) as a bioderived extraction solvent. The conversion of glucose (GLC), obtained by SUC inversion, could be limited to <10 mol%, allowing its recovery for further use. Interestingly, purified SUC led to significantly lower HMF selectivity and yields, and therefore the use of sugar beet thick juice shows advantages from both an economic and chemical selectivity perspective. This opens new avenues for more cost-effective HMF production.

5.1. INTRODUCTION

As a response to the anticipated decrease in fossil fuel reserves, fluctuating crude oil prices, and environmental issues related to the use of fossil resources, their replacement with renewable alternatives is receiving much attention. Biomass is an important renewable biobased feedstock, particularly for chemicals and materials production. Here, a major role is assigned to platform chemicals that are readily accessible from biomass and can serve as chemical building block for subsequent transformations into final biobased products [1-4]. One identified versatile furanic platform chemical is 5-hydroxymethylfurfural (HMF) [5, 6]. It is attainable from different carbohydrate sources through dehydration by using cheap mineral acids catalysts such as HCl and H_2SO_4 , and can be converted into a wide range of commodity chemicals and products [7, 8]. Different carbohydrate feedstocks have been investigated for HMF synthesis ranging from monomeric carbohydrates, such as glucose (GLC) and fructose (FRC), to polymeric carbohydrates such as starch and cellulose [5, 9-12]. Of the readily accessible monomeric carbohydrates, FRC has been shown to be the most suitable substrate because it offers the highest HMF selectivity, whereas the considerably cheaper GLC leads to low selectivity [5, 13]. When considering the technoeconomic viability of HMF production on a large scale, the feedstock costs are a major contributor to the overall manufacturing costs. As such, the identification of alternative, abundant, and cheap carbohydrate sources, preferably rich in FRC, is of high interest [7, 8].

Sucrose (SUC), a disaccharide of FRC and GLC, has also been explored for HMF synthesis [14, 15]. SUC, widely available as table sugar, is cheaper than pure FRC and is produced in large volumes from sugar beet and sugar cane. In 2017, the global sugar production was estimated to be 179.6 million tonnes, with the EU contributing to 10% of the total amount [16, 17]. Until 2017, the production of sugar in the EU was strictly regulated by the European Commission [18]. From 2017 onwards, restrictions were abandoned, which led to increased production levels in the EU and lower SUC prices in the long term [19]. As such, there is an incentive for sugar beet refiners to explore new markets and possibilities. Meanwhile, the European Commission has targets to replace 30% of fossil-based chemicals and materials with biobased versions and to supply 25% of Europe's transport energy needs by using sustainable advanced biofuels by 2030 [20]. As such, both from a price and legislation perspective, the coproduction of biobased products such as HMF in a sugar beet refinery is highly attractive.

Thick juice is an intermediate product in a typical sugar beet refinery. It is a viscous, clear, yellow liquid rich in SUC (typically 60–70 wt%) with residual water, various salts, organic acids, and minerals (see Table S1 in the Supporting Information for details provided in the literature) [21, 22]. To obtain crystalline SUC, the thick juice is treated in specially designed vacuum pans to remove water and allow crystallization to occur [23]. Thick juice can be stored (for up to 1 year) and used for the production of sugar after the sugar beet processing campaign. For the coproduction of biobased chemicals in a sugar refinery, the use of thick juice instead of crystalline SUC is expected to be beneficial because the costly crystallization step is avoided. The conversion of

thick juice to bioethanol [21, 24, 25] and biohydrogen [26, 27] through fermentation routes has been successfully demonstrated. However, studies on (chemo-) catalytic valorization routes of thick juice to platform molecules such as HMF are limited to only one report from our group [22].

We have recently reported a comprehensive kinetic study on the conversion of pure SUC to HMF and levulinic acid (LA) by using H_2SO_4 as catalyst in water [14]. The initial step involves rapid hydrolysis of the glycosidic bond between the sugar monomers in SUC to give FRC and GLC. Subsequently, FRC is dehydrated to give HMF in a moderate yield. For example, only 22 mol % of HMF yield was obtained from an aqueous solution of SUC at 140 °C with H_2SO_4 as the catalyst [14]. The formation of HMF from GLC was shown to be slow and to occur with a low selectivity [28], and it is thought to require an initial isomerization step of GLC to FRC [29–31]. The main reason for the low HMF yields from carbohydrates in aqueous systems is the formation of byproducts such as the soluble and insoluble oligomers and polymers known as humins. Additionally, HMF itself is not stable under the prevailing reaction conditions and is easily converted to LA and formic acid (FA). For these reasons, alternative dehydration methodologies have been developed, including biphasic concepts with advanced catalyst systems [32–35] and reactor designs [36, 37] as well as combinations of alternative solvent systems using either monophasic or biphasic liquid–liquid systems with catalysts [5, 38–46]. Biphasic systems often involve an aqueous phase with the catalyst and an organic phase with a high affinity for HMF. Methyl isobutyl ketone (MIBK) and *n*-butanol are among the most common organic solvents used and have been shown to lead to reduced byproduct formation by extraction of HMF from the reactive aqueous phase [8, 47–51]. This effect can be enhanced by the addition of salts such as NaCl to the aqueous phase [52]. An overview of selected reports on the conversion of SUC to HMF in biphasic systems is provided in Table S2 (in the Supporting Information).

When using SUC as a source for HMF, two main strategies can be considered. In the first approach, FRC is converted to HMF, and the remaining GLC is in situ isomerized to FRC and subsequently converted to HMF. For this, effective isomerization catalysts are required, and well-known examples are CrCl_3 and SnCl_4 [53, 54]. However, these catalysts are expensive, toxic, and do not always show the desirable compatibility with the dehydration reaction. Additionally, this method typically requires the use of ionic liquids or other alternative, expensive solvents to obtain high HMF yields from GLC. The second approach relies on the conversion of SUC to HMF (from FRC) and GLC. This is possible through careful control of the reaction conditions (Figure 1) by making use of the fact that FRC is significantly more reactive than GLC at temperatures around 140 °C [14, 55]. This then allows for GLC to be separated after the reaction and subsequently processed to other biobased chemicals or isomerized to FRC and then recycled to the reactor.

Here, we present a study on the synthesis of HMF and GLC from thick juice in a biphasic liquid–liquid system by using H_2SO_4 as the catalyst. Initial experiments were performed in a batch reactor, with and without salt addition. In addition to the commonly used MIBK, 2-methyltetrahydrofuran (MTHF) was used as an extraction solvent, which is considered a green, biobased solvent obtained by the hydrogenation of LA or γ -valerolactone (GVL) [56]. This approach showed that unexpectedly high HMF yields and good yields of coproduced GLC

can be achieved from thick juice. Subsequently, the use of a biphasic continuous microreactor operated in the slug-flow regime was shown to be extremely beneficial for further improving HMF selectivity (Figure 2) [57]. The results were compared with those obtained for pure SUC, clearly showing the beneficial effect of the use of crude thick juice for HMF and GLC production.

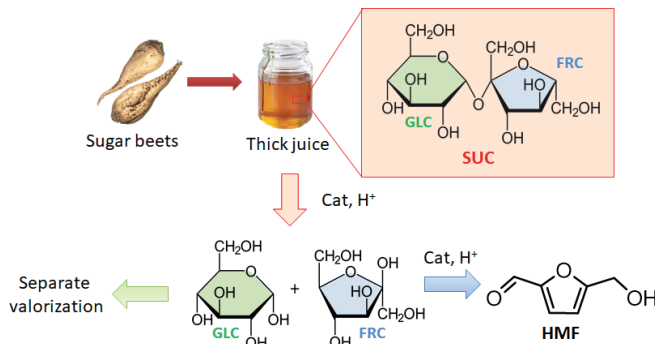


Figure 1. Sugar beet thick juice-based SUC to HMF and GLC separation strategy applied in this work.

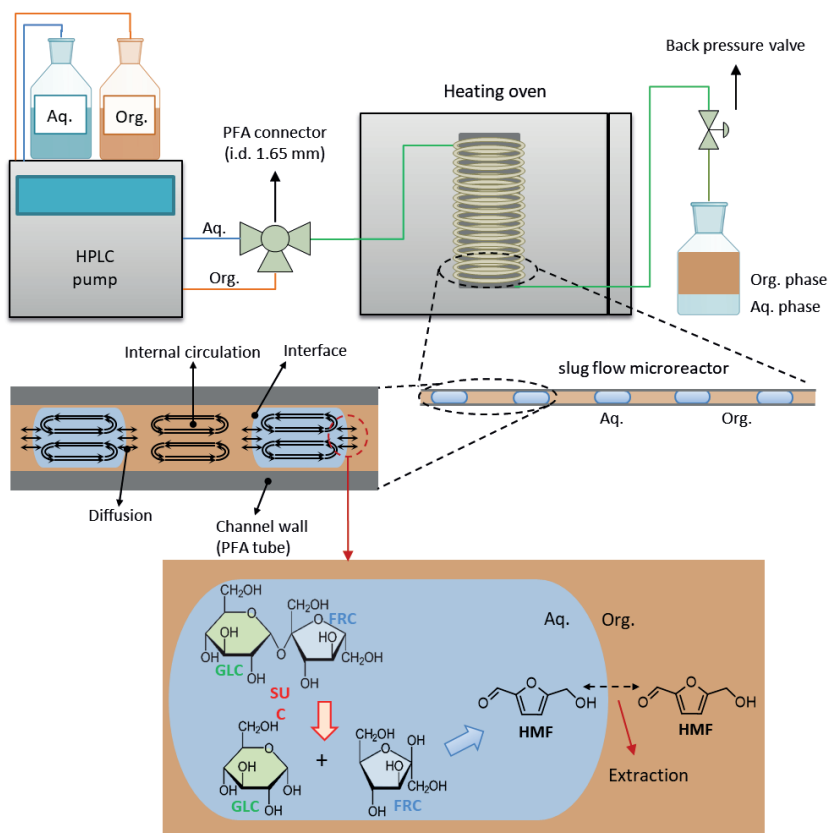


Figure 2. Schematic overview of the continuous slug-flow microreactor setup used in this study to allow for efficient HMF and GLC synthesis from the SUC contained in sugar beet thick juice.

5.2. EXPERIMENTAL SECTION

5.2.1. Chemicals

Thick juice was kindly provided by Suiker Unie-Royal Cosun (62 wt% of SUC determined by polarimeter and mild hydrolysis by using 5 mM H_2SO_4 at 100 °C followed by quantification of FRC and GLC by HPLC). H_2SO_4 (96–98 wt%), SUC (≥ 99 wt%), GLC (≥ 99.5 wt%), FRC (99 wt%), NaCl, Na_2SO_4 , MTHF, HMF and FA were obtained from Sigma–Aldrich (Steinheim, Germany). MIBK was acquired from Merck Millipore (Darmstadt, Germany). LA was purchased from Alfa Aesar. All chemicals were used without further purification. For all experiments, Milli-Q water was used to prepare the solutions.

5.2.2. Experimental procedures

5.2.2.1. HMF formation in batch experiments

Reactions were performed in Ace pressure tubes (bushing type, front seal, and volume ≈ 9 mL) with a length of 10.2 cm and an outer diameter of 19 mm, equipped with a magnetic stir bar. The tubes were filled with a 1:4 v/v ratio of water and an organic solvent (MIBK or MTHF). The water phase contained the appropriate amount of thick juice or SUC and H_2SO_4 (0.5 and 0.05 M, respectively). For some experiments with salt addition (NaCl or Na_2SO_4), 0.3 g salt was added per mL of the aqueous phase (containing thick juice or SUC) prior to mixing with the organic phase. As such, the initial concentration of SUC (0.44 M) and catalyst (0.044 M) in the aqueous phase were slightly different. Otherwise the pH value was set by careful addition of H_2SO_4 to a salty solution of thick juice or SUC. After filling, the tubes were closed and submerged in a temperature-controlled heating bath ($T=150^\circ\text{C}$). During the reaction, the mixture was stirred at 500 rpm. At various reaction times, a tube was taken out and quickly immersed in cold water to stop the reaction. The two-phase reaction mixture was then subjected to centrifugation (HeraeusTM, MegafugeTM 40, 4500 rpm for 10 min), and both phases were separated and collected. Aliquots of the aqueous phase and the organic phase were withdrawn, filtered when necessary (0.45 μm polytetrafluoroethylene (PTFE) filter), and analyzed by HPLC and GC-FID, respectively.

5.2.2.2. HMF formation in continuous microreactor experiments

Reactions were performed in a perfluoroalkoxy alkane (PFA) tube with an internal diameter of 1.651 mm and a total length of 4.5 m. To improve heat transfer, the tube was coiled around a cylindrical shaped aluminum block (50 mm diameter), which was placed inside a temperature-controlled oven ($T=150^\circ\text{C}$). A schematic representation of the setup is depicted in Figure 2. The aqueous and organic solutions were introduced into the reactor by HPLC pumps (Agilent 1100 with flow rate range of 0–5 mL min^{-1}). The aqueous feed contained the appropriate amount of thick juice (0.5 M SUC equiv.) and H_2SO_4 (0.05 M). For experiments with NaCl (0.1 g mL^{-1}), the

initial concentrations of SUC and H_2SO_4 in the aqueous phase were 0.48 and 0.048 M, respectively. An aqueous to organic solvent phase ratio of 1:4 was applied. Prior to entering the heating oven, the two liquid phases were combined in a Y-type connector to create a slug-flow. Owing to the hydrophobic nature of the tubing, the aqueous phase formed droplets separated by a continuous organic phase. A back-pressure valve was placed at the outlet of the reactor to adjust the pressure to 8–10 bar. Residence times were set by adjusting the flow rates of the HPLC pump (see Table S7 in the Supporting Information). The reactor typically reached a steady state after approximately two times of the residence time. Samples were collected from the outlet, and the two-phase mixtures were subjected to centrifugation (HeraeusTM, MegafugeTM 40, 4500 rpm for 10 min). Afterwards, both phases were separated, and aliquots of aqueous phase and organic phase were withdrawn, filtered when necessary (0.45 μm PTFE filter), and then analyzed by HPLC and GC-FID, respectively.

5.2.3. Analytical methods

The SUC content in the thick juice feed was determined by polarimetry (Schmidt and Haensch, Polatronc MH8). A series of SUC solutions of known concentrations were prepared and the observed rotation (α_{obs}) of each solution was determined. Measurements were performed at a wavelength (λ) of 589.44 nm and in a cell with a length of 100 mm. These data were used to calculate the specific rotation of SUC ($[\alpha]$; see the Supporting Information for details). Afterwards, a solution of thick juice with a known dilution factor was measured and used to calculate the SUC concentration in the thick juice feed.

High performance liquid chromatography (HPLC) was used to determine the composition of the aqueous phases after reaction. The instrument consisted of an Agilent 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87H), a refractive index detector, and an ultraviolet detector. The HPLC column was operated at 60 °C, and aqueous H_2SO_4 (5 mM) was used as the mobile phase with a flow rate of 0.55 mL min⁻¹. The injection volume of the sample was set at 5 μL . Concentrations of compounds in the product mixture were determined by using calibration curves obtained by analyzing standard solutions of known compounds with known concentrations.

Gas chromatography, GC (model: Finnigan, Trace GC Ultra equipped with flame ionization detector (FID) and Stabilwax-DA column 30 m $\times$ 0.32 mm inner diameter and film thickness of 1 μm) was used to determine the composition of the organic phases after reaction. The carrier gas was helium with a 2.2 mL min⁻¹ flow rate, and the split ratio was set at 50:1. The injector temperature was set at 260 °C. The oven temperature was kept at 40 °C for 5 min, then increased to 240 °C at a rate of 15 °C min⁻¹, and then held at 240 °C for 10 min.

The pH of the reaction mixtures was measured at room temperature using an InoLab pH 730 pH-meter equipped with a SenTix 81 probe (both probe and meter from WTW, Germany).

5.2.4. Determination of yield and conversion

At the typical reaction conditions used in this study ($T > 100\text{ }^{\circ}\text{C}$), SUC is immediately converted (inverted) into FRC and GLC in the initial stage of the reactions [14]. As such, the initial concentrations of the individual sugars were set equal to the initial concentration of SUC in the aqueous phase. For the biphasic reaction, it is known that the solubility of FRC and GLC in the organic phase is very low and therefore assumed negligible for conversion and yield calculations. However, small amount of organic phase can dissolve into the aqueous phase and vice versa, resulting in the volume changes of both phases ($V_{\text{initial}} \neq V_{\text{final}}$). To compensate for changes in the volumes of the organic phase and aqueous phase after reaction, a factor R was applied, which is defined as the ratio of the final volume to the initial volume. R was estimated by the software package Aspen (see Table S5). This factor R is also used in the conversion and yield calculations. The conversion of FRC and GLC including R are given in eqs 1 and 2, respectively.

$$X_{\text{FRC}} = \frac{N_{\text{FRC},0} - N_{\text{FRC}}}{N_{\text{FRC},0}} = \frac{V_{\text{aq}} C_{\text{FRC},\text{aq},0} - V_{\text{aq}} R_{\text{aq}} C_{\text{FRC},\text{aq}}}{V_{\text{aq}} C_{\text{FRC},\text{aq},0}} \quad (1)$$

$$X_{\text{GLC}} = \frac{N_{\text{GLC},0} - N_{\text{GLC}}}{N_{\text{GLC},0}} = \frac{V_{\text{aq}} C_{\text{GLC},\text{aq},0} - V_{\text{aq}} R_{\text{aq}} C_{\text{GLC},\text{aq}}}{V_{\text{aq}} C_{\text{GLC},\text{aq},0}} \quad (2)$$

Unlike the sugars, HMF is present in both the aqueous and organic phase after reaction. The yield of HMF on SUC basis is given in eq 3.

$$Y_{\text{HMF}(\text{SUC})} = \frac{N_{\text{HMF, tot}}}{2 N_{\text{SUC},0}} = \frac{V_{\text{org}} R_{\text{org}} C_{\text{HMF,org}} + V_{\text{aq}} R_{\text{aq}} C_{\text{HMF,aq}}}{2 V_{\text{aq}} C_{\text{SUC},0}} \quad (3)$$

Since the conversion of GLC is very low (which in this work was intentional), the yield of HMF can also be expressed based on FRC only ($Y_{\text{HMF}(\text{FRC})}$), see eq 4.

$$Y_{\text{HMF}(\text{FRC})} = \frac{N_{\text{HMF, tot}}}{N_{\text{FRC},0}} = \frac{V_{\text{org}} R_{\text{org}} C_{\text{HMF,org}} + V_{\text{aq}} R_{\text{aq}} C_{\text{HMF,aq}}}{V_{\text{aq}} C_{\text{FRC},0}} \quad (4)$$

Similarly, the HMF selectivity can be expressed on SUC basis ($S_{\text{HMF}(\text{SUC})}$, eq 5) or FRC basis ($S_{\text{HMF}(\text{FRC})}$, eq 6):

$$S_{\text{HMF}(\text{SUC})} = \frac{Y_{\text{HMF}(\text{SUC})}}{X_{\text{FRC}} + X_{\text{GLC}}} \quad (5)$$

$$S_{\text{HMF}(\text{FRC})} = \frac{Y_{\text{HMF}(\text{FRC})}}{X_{\text{FRC}}} \quad (6)$$

The carbon balance closure (CBC) is defined as total moles of carbon in HPLC detectable compounds (FRC, GLC, HMF, and in some cases FA and LA) at a certain reaction time or residence time divided by the moles of carbon in the feed (eq 7).

$$\text{CBC} = \frac{\text{mol C in HPLC detectable compounds}}{\text{mol C in the feed}} \times 100\% \quad (7)$$

The partition coefficient (P) is defined as the ratio of the concentration of a component in the organic phase to the concentration of the component in the aqueous phase. As an example, the partition coefficient of HMF is given in eq 8.

$$P_{\text{HMF}} = \frac{C_{\text{HMF, org}}}{C_{\text{HMF, aq}}} \quad (8)$$

5.3. RESULTS AND DISCUSSION

5.3.1. Thick juice and SUC biphasic reactions in a batch setup

Initial reactions were performed in batch with stirred glass pressure tubes. To ensure low GLC conversion and to avoid excessive humin formation, the temperature was set to 150 °C and an extraction solvent was used [14]. The reactions, monitored at different reaction times, were run at equal H₂SO₄ concentrations (0.05 M, pH 1.6) for MTHF (Figure S1 a in the Supporting Information) and MIBK (Figure S2 in the Supporting Information) as well as at a set pH achieved by the careful addition of H₂SO₄ (pH 0.7 at 25 °C, Figure 3a). Because HMF is highly soluble in water, an excess of the organic solvent (1:4, v/v aqueous to organic ratio) was used to ensure high extraction efficiencies [58].

Because SUC is immediately converted to GLC and FRC at an acidic pH, the SUC concentration is not shown in the graphs. At pH 1.6, half of the released FRC was converted after approximately 30 min for both biphasic solvent systems, whereas at pH 0.7 full conversion was achieved within 20 min. A higher HMF selectivity was observed when using MTHF compared with MIBK (82 and 75 %, respectively, after 30 min), which was attributed to the higher partition coefficient of HMF in MTHF/water (P=1.9; determined experimentally) compared with HMF in MIBK/water (P=1.0), demonstrating the beneficial effect of more extensive removal of HMF from the acidic aqueous phase [32-35, 59]. Low GLC conversion (<10%) and an overall excellent carbon balance of >90% was observed at incomplete FRC conversion for both extraction solvents and even for MTHF at pH 0.7. After full FRC conversion was reached, the carbon balance gradually decreased owing to unselective GLC conversion as well as HMF decomposition. This is likely associated with the formation of humin substances, which are not detected by HPLC.

To further improve HMF extraction from the aqueous phase, the effect of NaCl (0.3 g mL⁻¹) on HMF production from thick juice was determined in batch at equal H₂SO₄ concentrations (MTHF, Figure S1 b; MIBK, Figure S3 in the Supporting Information). The addition of salt led to a

nearly two-fold increase for the partition coefficient of HMF (from 1 to 1.8 for MIBK and from 1.9 to 3.7 for MTHF) by the salting-out effect, which is in line with other previous studies [32, 33, 60, 61]. This led to a significantly higher HMF selectivity (>90%) at high FRC conversion (>99%) and low GLC conversion (<10%). Because the addition of salt also led to a significant pH drop and thus increase in reaction rate [62, 63], the reactions with and without salt were also compared at equal pH (MTHF, Figure 3 b). Satisfyingly, this also resulted in a high HMF selectivity (96%) although at the cost of GLC conversion (17%) at similar FRC conversion (>99%, 30 min). A key observation was that the concentrations of HMF did not decrease in these experiments, which is very different compared with previous report using pure SUC [14] as well as from our own comparative experiments (shown below). Indeed, an excellent carbon balance closure (>95%) was found even at such high FRC conversions. Humin formation was observed in the form of black precipitate and some coloration of the extraction liquid, but to a minimal extent. Additionally, only traces of LA and FA were detected by HPLC. In these experiments, the latter two were even excluded from the carbon balance because the concentrations were too low for adequate quantification. In addition to NaCl, experiments were performed with Na₂SO₄ (Figures S4 and S5 in the Supporting Information). Although the salting-out effect for salts with double-charged anions is significantly larger than for salts with single-charged ions (partition coefficient of HMF increased from 1.8 to 3.5 with MIBK and from 3.7 to 4.4 with MTHF) [64, 65], this did not lead to improved HMF yield owing to the anion effects on the different reaction rates [33, 66].

To compare the performance of thick juice to purified SUC, similar biphasic reactions were performed with SUC and MTHF as the extraction solvent (pH 0.7 Figure 3 c, pH 0.3 Figure S1 c in the Supporting Information). In general, the reactions with pure SUC as the starting material show somewhat higher conversion rates for both FRC and GLC compared with the reactions with thick juice even at equal pH. This is accompanied by a lower selectivity of HMF (87–89 mol% at 20–30 min) compared with thick juice (96 mol% at 20–30 min). Some contribution from GLC to the HMF yield can also not be excluded in this case because GLC conversion is significantly higher (>40 mol% after 30 min). LA and FA are formed (up to 0.04 M, see Figure S6 in the Supporting Information) and the carbon balance (including LA and FA) is significantly lower (82%) compared with thick juice. This indicates the formation of substantial amounts of unidentified compounds (e.g., soluble humins) as also evident from the increased formation of black precipitate as well as significantly more coloration of the extraction phase. A possible explanation for the observed difference between pure SUC and thick juice must lie with the difference in composition. Besides SUC, thick juice contains salts, organic acids, and other minor components (Table S1 in the Supporting Information) [21, 22]. However, the presence of the salts alone cannot explain the difference, as demonstrated by an experiment of pure SUC in which NaCl was added to the level of those present in thick juice, which led to an overall 10% lower carbon balance (Figure S7 in the Supporting Information). What (combinations of) components in thick juice cause these improved results for HMF synthesis is the subject of further studies. Here, we focused on optimizing the yields of HMF from thick juice even further.

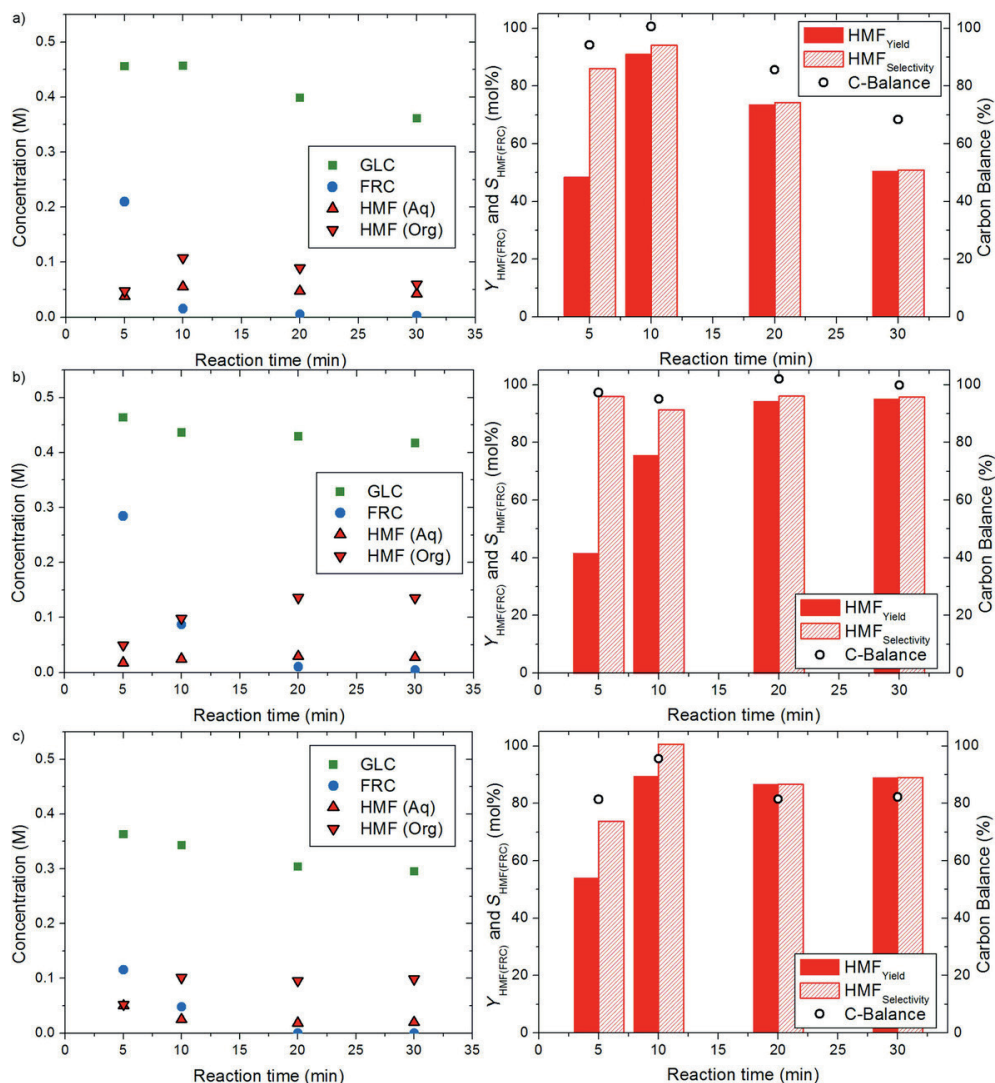


Figure 3. Concentration-time profile (left) and yield, selectivity and carbon balance (right) of H_2SO_4 catalyzed SUC hydrolysis in biphasic system with MTHF as extraction phase and a) thick juice without addition of salt ($C_{\text{SUC(equiv),0}} = 0.5 \text{ M}$, $\text{pH}_{\text{aq}} = 0.65$ at 25°C), b) thick juice with added 0.3 g mL^{-1} NaCl ($C_{\text{SUC(equiv),0}} = 0.5 \text{ M}$, $\text{pH}_{\text{aq}} = 0.65$ at 25°C) and c) pure SUC with added 0.3 g mL^{-1} NaCl ($C_{\text{SUC(equiv),0}} = 0.5 \text{ M}$, $\text{pH}_{\text{aq}} = 0.65$ at 25°C). Reaction conditions: $T = 150^\circ\text{C}$, 1:4 v/v aqueous : organic ratio.

5.3.2. Thick juice and SUC biphasic reactions in a continuous slug-flow microreactor setup

With the obtained excellent results in hand for the conversion of SUC in thick juice to HMF, the reaction was performed in a continuous slug-flow microreactor to further improve performance (Figure 2). The use of this setup leads to improved mass-transfer characteristics and thus a more efficient extraction of HMF from the aqueous phase as well as improved heat transfer [37, 67]. MTHF was selected as the solvent of choice based on the results obtained in batch (*vide supra*). A microreactor made up of a hydrophobic PFA tubing was used, in which the aqueous phase is present as droplets and the MTHF phase forms the slugs (Figure S8 in the Supporting Information). This was done to prevent significant deposition of humins because these are initially formed in the aqueous phase and thus will not come into contact with the reactor wall. The experimental conditions were similar to the batch system except for the pH, which was set to 1.2, and the use of a lower NaCl concentration (0.1 g mL^{-1} aqueous) instead of 0.3 g mL^{-1} to avoid clogging of the tube as a result of salt precipitation at the reactor outlet. Residence time variations between 5 and 20 min (obtained by adjusting the flow rates) were explored (Figure 4a, see the Supporting Information for details on the flow rates and residence time determinations). Excellent performance with respect to HMF selectivity was found in the microreactor, showing stable HMF production over extended run times of up to 10 h (Figure S10 and Table S4 in the Supporting Information). HMF yields as high as 91.6 mol% (93.6 mol% selectivity, 97.7 mol% FRC conversion) were obtained at a residence time of 20 min. In addition, GLC conversion was very limited and at most 11.2 mol% at 20 min residence time. A reaction with thick juice without the addition of salt (NaCl) at higher pH was also performed for reference (Figure S9 in the Supporting Information), showing high selectivity but at lower FRC conversion. The use of higher SUC concentration is beneficial for increasing the space–time yield. In our setup, we could run a thick juice solution diluted to 1 M of $\text{SUC}_{\text{equiv.}}$ concentration. This also led to good HMF selectivity (Table S5 in the Supporting Information) even after 10 h runtimes (Table S4 in the Supporting Information). Operation with less diluted thick juice was not possible owing to operational issues with the feed pump related to the high viscosity of the feed.

Comparison of the results from the batch and continuous slug-flow experiments shows that the conversion of FRC was significantly higher in the microreactor, and particularly the HMF selectivity was improved considerably if no salt was added (Table 1, entries 1–4). High yields could be obtained in both setups although a higher salt concentration was used in batch (Table 1, entries 5–7). Thus, the use of a microreactor can be beneficial for thick juice conversion compared with a batch reactor. It is interesting to compare the performance of the thick juice in the microreactor with that of pure SUC at the same pH (Figure 4b). In the microreactor, thick juice performed significantly better than pure SUC. The selectivity of HMF from the reaction with thick juice was higher at all residence times, giving 93.6 mol% at 97.7 mol% FRC conversion compared with only 84 mol% for the reaction with pure SUC

at the same FRC conversion. In addition, the GLC conversion of 22.7 mol% was far higher in experiments with pure SUC compared with experiments (at 15 min residence time) with thick juice (10.1 mol%), which is not advantageous considering that GLC conversion does not lead to HMF but mostly to humins. Consequently, the carbon balance for SUC is worse than for thick juice, indicating that SUC gives higher amounts of unidentified compounds such as oligomeric and polymeric humin-type products. Also, some precipitation of such humins causes disturbance of the flow patterns and eventually leads to blockage, leading to lower reproducibility of the results from this reaction, as was evident from the larger standard deviations from multiple experiments. These differences between the use of thick juice and pure SUC in the microreactor are in line with the obtained batch data discussed above.

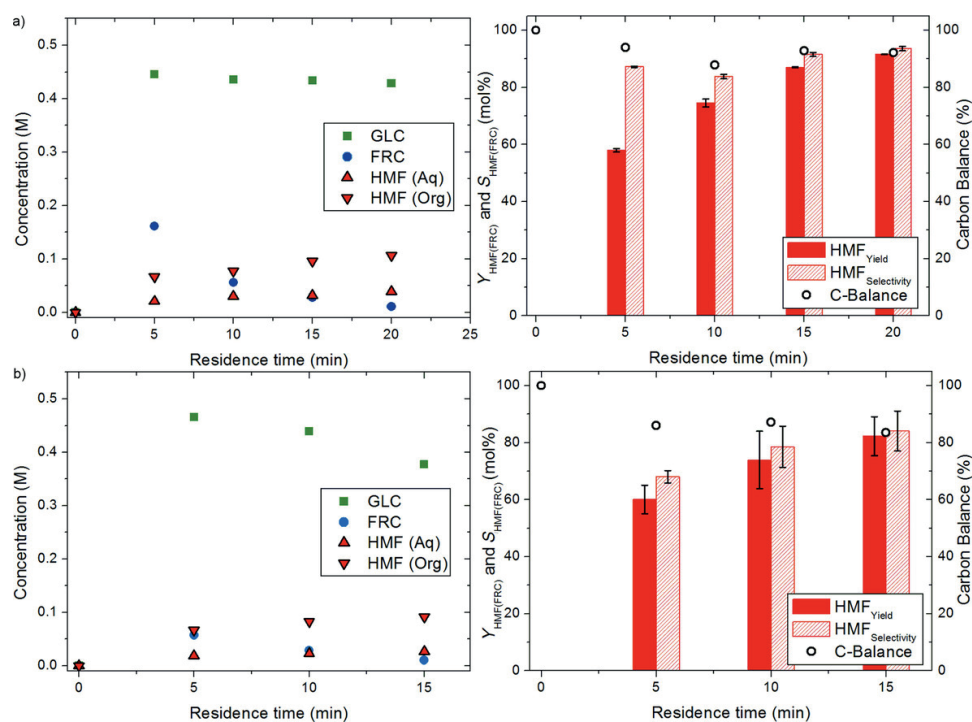


Figure 4. Concentration–time profile (left) and yield, selectivity, and carbon balance (right) of a) thick juice and b) SUC hydrolysis in slug-flow microreactor in a biphasic system with MTHF in the presence of NaCl (0.1 g mL^{-1}) at different residence times obtained by adjusting the flow rate. Solid bar: HMF yield (FRC-based); shaded bar: HMF selectivity (FRC-based); circle: carbon balance. Reaction conditions: $C_{\text{SUC(equiv)0}} = 0.48 \text{ M}$, $T = 150^\circ\text{C}$, aqueous to organic ratio 1:4 v/v, $\text{pH}_{\text{aq}} = 1.2$ (25°C). Error bars represent average values from three separate experiments.

Table 1. Comparison of data for thick juice to HMF reaction in batch and continuous setups ^(a)

Entry	Reaction setup	$t^{(b)}$ (min)	pH	C_{NaCl} (g mL ⁻¹)	$X_{\text{FRC}}^{(c)}$ (mol%) ^[b]	$S_{\text{HMF}}^{(c,d)}$ (mol%)
1	Batch	15	1.6	-	24.1	76.7
2	Cont.	15	1.6	-	43.9	71.5
3	Batch	30	1.6	-	51.2	81.7
4	Cont.	30	1.6	-	65.8	87.4
5	Batch	15	0.7	0.3	99.0	89.4
6	Cont.	15	1.2	0.1	94.4	91.5
7	Cont.	20	1.2	0.1	97.7	93.6

(a) Reactions performed at $T=150^\circ\text{C}$, H_2O to MTHF ratio of 1:4 v/v, H_2SO_4 as acid catalyst. (b) Batch/residence time.

(c) Determined by HPLC. (d) Based on FRC conversion

5.3.3. Comparison with literature data for HMF production from FRC and SUC

An overview of the literature data on the conversion of FRC (and SUC) to HMF in biphasic liquid–liquid systems, as well as comparison with the data obtained in this study using thick juice is given in Table 2. Although direct comparison is somewhat skewed owing to variations in process conditions, HMF yields and selectivities based on converted FRC found in this study (batch and continuous) are significantly higher than those reported for pure carbohydrates. For pure SUC and FRC, previous reports typically show 70–75 % selectivity for HMF at similar conditions, something that was also observed in our batch experiments for pure SUC. When pure SUC is used in the continuous slug-flow microreactor in the presence of an extractive solvent and 0.1 g mL^{-1} NaCl, this could be improved to 84%, which is already a significant increase over previous reports. A further increase in HMF selectivity to over 90 % was reached when thick juice (as a crude and significantly cheaper SUC feedstock) is used. This led to a 15 % higher selectivity compared with previous reports and by far the best achieved thus far in an aqueous solvent system. Better selectivities have previously only been achieved from FRC by using alternative solvent systems such as ionic liquids, which provide significant challenges in the recovery of HMF, solvent, and unconverted carbohydrate.

Table 2. Selected examples of HMF yields and selectivities in biphasic liquid–liquid systems in batch and continuous setups with MIBK and MTHF as extraction solvents ^(a)

Entry	Feed	Setup	Conditions	X_{FRC} (mol%)	S_{HMF} (mol%)	Ref
1	FRC	Batch	Aqueous : MIBK 1:4, 150 °C, 30 min	23	43.5	[68]
2	FRC	Batch	Aqueous : MIBK 1:4, 160 °C, 2 h	96.8	76	[68]
3	FRC : GLC ^(b)	Cont.	Aqueous : MIBK 1:4, 140 °C, 2 h, 0.05 M H ₂ SO ₄	94.4	72	[55]
4	FRC	Batch	Aqueous : MIBK 1:4, 150 °C, 45 min, 100 g L ⁻¹ H ₃ BO ₄ , 50 g L ⁻¹ NaCl	70	65.7	[69]
5	SUC	Batch	Aqueous : MIBK 1:4, 150 °C, 2 h, 100 g L ⁻¹ H ₃ BO ₄ , - 50 g L ⁻¹ NaCl	-	70	[69]
6	FRC	Cont.	Aqueous : MIBK 1:3, 140 °C, 15 min, 0.25 M HCl, -	-	74 ^(c)	[70]
7	Thick Juice	Batch	Aqueous: MTHF 1:4, 150 °C, 30 min, 0.044 M H ₂ SO ₄ , 0.3 g mL ⁻¹ NaCl	99.0	89.4	This work
8	Thick Juice	Cont.	Aqueous : MTHF 1:4, 150 °C, 20 min, 0.048 M H ₂ SO ₄ , 0.1 g mL ⁻¹ NaCl	97.7	93.6	This work

(a) HMF selectivity shown in the table is calculated based on FRC (b) 1:1 mixture (c) Isolated yield

5.4. CONCLUSIONS

Thick juice has significant potential as feedstock for the synthesis of HMF, as shown here by an aqueous biphasic reaction system using MIBK or MTHF as the extraction solvent in batch and continuous setups. When using this crude SUC-rich feedstock, excellent selectivities for HMF were achieved in both setups, which surpass all previous reports in aqueous media. The best results in batch were obtained with MTHF in the presence of NaCl, giving 96 mol % selectivity of HMF at near quantitative FRC conversion after 15 min reaction time with 14 % GLC conversion or 89 % selectivity at higher pH with limited GLC conversion (3.9 mol %) after 30 min reaction time. The use of a continuous microreactor led to a similar HMF selectivity even at lower NaCl concentrations. These high selectivities were achieved with sulfuric acid as a cheap catalyst and sodium chloride as the sole additive to increase the extraction efficiency. To illustrate the improvements from the use of thick juice further, results with thick juice were compared with those for pure SUC, reaching only 84 mol % HMF selectivity in the microreactor setup. It is highly unusual that feedstock impurities have such a dramatic positive effect on reaction performance, but in this case, it seems that the use of the cheaper crude feedstock offers a significant advantage. Nevertheless, the exact nature that underlies this positive effect is difficult to determine because thick juice is a highly complex mixture of many different components. Although certain salts and organic acids could be beneficial and explain the excellent results for thick juice, detailed studies are required to investigate this further. Overall, this study implies that thick juice is a very attractive feedstock for HMF synthesis. It is expected to be significantly cheaper than refined SUC and as such will have a positive effect on the techno-economic viability of HMF production. In addition, the current study showed that low

GLC conversions are possible by proper tuning of the reaction conditions, making use of the fact that FRC is by far more reactive than GLC. This is of high relevance because GLC is known to be far less selective for HMF synthesis than FRC. As such, the unconverted GLC, present in the aqueous phase after reaction, may either be isomerized to FRC and recycled to the reactor or converted separately either by chemo- or biocatalytic conversions to biobased products (e.g., lactic acid, sorbitol, succinic acid, etc.).

ACKNOWLEDGEMENT

The authors kindly thank Suiker Unie, Erik van Hellemond, Olaf van Baal, and Marilia Foukaraki from Suiker Unie R&D for arranging thick juice samples and useful discussions. Maarten Vervoort and Léon Rohrbach are acknowledged for their assistance with creating necessary glass laboratory equipment and support with product analysis. R.M.A.-S. acknowledges the Directorate General of Higher Education, Ministry of Education and Culture, Indonesia for funding. W.G. acknowledges financial support from the China Scholarship Council (grant number 201606740069).

REFERENCES

- [1] J. E. Holladay, J. F. White, J. J. Bozell and D. Johnson. , Top Value-Added Chemicals from Biomass - Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin, PNNL-16983, (2007), Pacific Northwest National Laboratory (PNNL), Richland, WA (US) .
- [2] K. Kohli, R. Prajapati and B.K. Sharma. Bio-based Chemicals from Renewable Biomass for Integrated Biorefineries. *Energies*, 12 (2019), pp.233.
- [3] L. Wu, T. Moteki, A.A. Gokhale, D.W. Flaherty and F.D. Toste. Production of Fuels and Chemicals from Biomass: Condensation Reactions and Beyond. *Chem*, 1 (2016), pp.32-58.
- [4] P.J. Deuss, K. Barta and J.G. de Vries. Homogeneous Catalysis for the Conversion of Biomass and Biomass-derived Platform Chemicals. *Catalysis Science & Technology*, 4 (2014), pp.1174-1196.
- [5] R. van Putten, van der Waal, Jan C, E. De Jong, C.B. Rasrendra, H.J. Heeres and J.G. de Vries. Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources. *Chemical Reviews*, 113 (2013), pp.1499-1597.
- [6] J.J. Bozell and G.R. Petersen. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—The US Department of Energy’s “Top 10” Revisited. *Green Chemistry*, 12 (2010), pp.539-554.
- [7] A.A. Marianou, C.M. Michailof, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidis and A.A. Lappas. Effect of Lewis and Brønsted Acidity on Glucose Conversion to 5-HMF and Lactic Acid in Aqueous and Organic media. *Applied Catalysis A: General* 555 (2018), pp.75-87.
- [8] J.N. Chheda, Y. Román-Leshkov and J.A. Dumesic. Production of 5-hydroxymethylfurfural and Furfural by Dehydration of Biomass-derived Mono-and Poly-saccharides. *Green Chemistry*, 9 (2007), pp.342-350.
- [9] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr, J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski. The Path Forward for Biofuels and Biomaterials. *Science*, 311 (2006), pp.484-489.
- [10] J. Lange, E. van der Heide, J. van Buijtenen and R. Price. Furfural—A promising Platform for Lignocellulosic Biofuels. *ChemSusChem*, 5 (2012), pp.150-166.

- [11] G. Jeong, C.H. Ra, Y. Hong, J.K. Kim, I. Kong, S. Kim and D. Park. Conversion of Red-algae *Gracilaria verrucosa* to Sugars, Levulinic Acid and 5-Hydroxymethylfurfural. *Bioprocess and Biosystems Engineering*, 38 (2015), pp.207-217.
- [12] S.P. Teong, G. Yi and Y. Zhang. Hydroxymethylfurfural Production from Bioresources: Past, Present and Future. *Green Chemistry*, 16 (2014), pp.2015-2026.
- [13] R. van Putten, J.N. Soetedjo, E.A. Pidko, van der Waal, Jan C, E.J. Hensen, E. de Jong and H.J. Heeres. Dehydration of Different Ketoses and Aldoses to 5-Hydroxymethylfurfural. *ChemSusChem*, 6 (2013), pp.1681-1687.
- [14] J.N. Tan-Soetedjo, van de Bovenkamp, Henk H, R.M. Abdilla, C.B. Rasrendra, J. van Ginkel and H.J. Heeres. Experimental and Kinetic Modeling Studies on the Conversion of Sucrose to Levulinic Acid and 5-Hydroxymethylfurfural using Sulfuric Acid in Water. *Industrial & Engineering Chemistry Research*, 56, 45 (2017), pp. 13228-13239
- [15] H.T. Kreissl, K. Nakagawa, Y. Peng, Y. Koito, J. Zheng and S.C.E. Tsang. Niobium Oxides: Correlation of Acidity with Structure and Catalytic Performance in Sucrose Conversion to 5-Hydroxymethylfurfural. *Journal of Catalysis*, 338 (2016), pp.329-339.
- [16] Sugar: World Markets and Trade, <https://apps.fas.usda.gov/psdonline/circulars/sugar.pdf>, 17-01-2018.
- [17] <http://www.fao.org/faostat/en/#data/QD>, 17-01-2018.
- [18] EU sugar quota system comes to an end, http://europa.eu/rapid/press-release_IP-17-3487_en.htm, 18-01-2018.
- [19] EU set for big sugar beet crops as EU drops quotas, <https://uk.reuters.com/article/europe-sugar-crops/eu-set-for-big-sugar-beet-crop-as-eu-drops-quotas-idUKL8N1LO4U8>, 22-01-2018.
- [20] <http://biconsortium.eu/library/bic-documents>, 18-01-2018.
- [21] L. Tan, Z. Sun, S. Okamoto, M. Takaki, Y. Tang, S. Morimura and K. Kida. Production of Ethanol from Raw Juice and Thick Juice of Sugar Beet by Continuous Ethanol Fermentation with Flocculating Yeast Strain KF-7. *Biomass and Bioenergy*, 81 (2015), pp.265-272.
- [22] I. van Zandvoort. Towards the Valorization of Humin By-Products: Characterization, Solubilization and Catalysis (Doctoral Dissertation), Utrecht (2015).
- [23] From Beet Field to Sugar Factory, http://www.comitesucre.org/site/wp-content/uploads/2013/09/Brochure-CIBE-CEFS-Final_05.05.2010_Chapter-From-Beet-Field-to-Sugar-Factory.pdf, 22-01-2018.
- [24] S. Dodić, S. Popov, J. Dodić, J. Ranković, Z. Zavargo and R.J. Mučibabić. Bioethanol Production from Thick Juice as Intermediate of Sugar Beet Processing. *Biomass and Bioenergy*, 33 (2009), pp.822-827.
- [25] R. Razmovski and V. Vučurović. Bioethanol Production from Sugar Beet Molasses and Thick Juice using *Saccharomyces cerevisiae* Immobilized on Maize Stem Ground Tissue. *Fuel*, 92 (2012), pp.1-8.
- [26] E. Boran, E. Özgür, M. Yücel, U. Gündüz and I. Eroglu. Biohydrogen Production by *Rhodobacter capsulatus* in Solar Tubular Photobioreactor on Thick Juice Dark Fermenter Effluent. *Journal of Cleaner Production*, 31 (2012)150-157.
- [27] D. Foglia, W. Wukovits, A. Friedl, M. Ljunggren, G. Zacchi, K. Urbaniec and M. Markowski. Effects of Feedstocks on the Process Integration of Biohydrogen Production. *Clean Technologies and Environmental Policy*, 13 (2011), pp.547-558.
- [28] B. Girisuta, L.P.B.M. Janssen and H.J. Heeres. Green chemicals: A Kinetic Study on the Conversion of Glucose to Levulinic Acid. *Chemical Engineering Research and Design*, 84 (2006), pp.339-349.
- [29] M.S. Feather and J.F. Harris. On The Mechanism of Conversion of Hexoses into 5-(Hydroxymethyl)-2-Furaldehyde and Metasaccharinic Acid. *Carbohydrate Research*, 15 (1970), pp.304-309.
- [30] D.W. Harris and M.S. Feather. Evidence for a C-2→ C-1 Intramolecular Hydrogen-Transfer During the Acid-Catalyzed Isomerization Of D-Glucose to D-Fructose. *Carbohydrate Research*, 30 (1973), pp.359-365.
- [31] D.W. Harris and M.S. Feather. Intramolecular Carbon-2. Far. Carbon-1 Hydrogen Transfer Reactions During the Conversion of Aldoses to 2-Furaldehydes. *The Journal of Organic Chemistry*, 39 (1974), pp.724-725.
- [32] Y. Roman-Leshkov, J.N. Chheda and J.A. Dumesic. Phase Modifiers Promote Efficient Production of Hydroxymethylfurfural from Fructose. *Science*, 312 (2006), pp.1933-1937.
- [33] Y. Román-Leshkov and J.A. Dumesic. Solvent Effects on Fructose Dehydration to 5-Hydroxymethylfurfural in Biphasic Systems Saturated with Inorganic Salts. *Topics in Catalysis*, 52 (2009), pp.297-303.

- [34] H. Zhao, J.E. Holladay, H. Brown and Z.C. Zhang. Metal Chlorides in Ionic Liquid Solvents Convert Sugars to 5-Hydroxymethylfurfural. *Science*, 316 (2007), pp.1597-1600.
- [35] X. Qi, M. Watanabe, T.M. Aida and R.L. Smith Jr. Efficient Process for Conversion of Fructose to 5-Hydroxymethylfurfural with Ionic Liquids. *Green Chemistry*, 11 (2009), pp.1327-1331.
- [36] T.Tuercke, S.Panic and S.Loebbecke. Microreactor Process for the Optimized Synthesis of 5-Hydroxymethylfurfural: A Promising Building Block Obtained by Catalytic Dehydration of Fructose. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 32 (2009), pp.1815-1822.
- [37] T. Shimanouchi, Y. Kataoka, T. Tanifuji, Y. Kimura, S. Fujioka and K. Terasaka. Chemical Conversion and Liquid-Liquid Extraction of 5-Hydroxymethylfurfural from Fructose by Slug Flow Microreactor. *AIChE Journal*, 62 (2016), pp.2135-2143.
- [38] B.F.M. Kuster. 5-Hydroxymethylfurfural (HMF), A Review Focussing on its Manufacture. *Starch - Stärke*, 42 (1990), pp.314-321.
- [39] C. Moreau, A. Finiels and L. Vanoye. Dehydration of Fructose and Sucrose into 5-Hydroxymethylfurfural in the Presence of 1-H-3-Methyl Imidazolium Chloride Acting Both as Solvent and Catalyst. *Journal of Molecular Catalysis A: Chemical*, 253 (2006), pp.165-169.
- [40] S. Hu, Z. Zhang, J. Song, Y. Zhou and B. Han. Efficient Conversion of Glucose into 5-Hydroxymethylfurfural Catalyzed by A Common Lewis Acid SnCl_4 in An Ionic Liquid. *Green Chemistry*, 11 (2009), pp.1746-1749.
- [41] F. Ilgen, D. Ott, D. Kralisch, C. Reil, A. Palmberger and B. König. Conversion of Carbohydrates into 5-Hydroxymethylfurfural in Highly Concentrated Low Melting Mixtures. *Green Chemistry*, 11 (2009), pp.1948-1954.
- [42] X. Qi, M. Watanabe, T.M. Aida and R.L. Smith. Fast Transformation of Glucose and Di-/Polysaccharides into 5-Hydroxymethylfurfural by Microwave Heating in an Ionic Liquid/Catalyst System. *ChemSusChem*, 3 (2010), pp.1071-1077.
- [43] Z.Zhang, Q.Wang, H.Xie, W.Liu and Z.K.Zhao. Catalytic Conversion of Carbohydrates into 5-Hydroxymethylfurfural by Germanium (IV) Chloride in Ionic Liquids. *ChemSusChem*, 4 (2011), pp.131-138.
- [44] T. Ståhlberg, S. Rodriguez-Rodriguez, P. Fristrup and A. Riisager. Metal-Free Dehydration of Glucose to 5-(Hydroxymethyl)furfural in Ionic Liquids with Boric Acid as a Promoter. *Chemistry-A European Journal*, 17 (2011), pp.1456-1464.
- [45] Z. Wei, Y. Li, D. Thushara, Y. Liu and Q. Ren. Novel Dehydration of Carbohydrates to 5-Hydroxymethylfurfural Catalyzed by Ir And Au Chlorides In Ionic Liquids. *Journal of the Taiwan Institute of Chemical Engineers*, 42 (2011), pp.363-370.
- [46] L.Hu, Z.Wu, J.Xu, Y.Sun, L.Lin and S.Liu. Zeolite-Promoted Transformation of Glucose into 5-Hydroxymethylfurfural in Ionic Liquid. *Chemical Engineering Journal*, 244 (2014), pp.137-144.
- [47] C. Moreau, R. Durand, C. Pourcheron and S. Razigade. Preparation of 5-Hydroxymethylfurfural from Fructose and Precursors over H-Form Zeolites. *Industrial Crops and Products*, 3 (1994), pp.85-90.
- [48] Q.P. Peniston (Ed.), *Manufacture of 5-hydroxymethyl 2-furfural*. US Patent (1956).
- [49] L. Rigal and A. Gaset. Direct Preparation of 5-Hydroxymethyl-2-Furancarboxaldehyde from Polyholosides: A Chemical Valorisation of the Jerusalem Artichoke (*Helianthus tuberosus* L.). *Biomass*, 3 (1983), pp.151-163.
- [50] C.V. McNeff, D.T. Nowlan, L.C. McNeff, B. Yan and R.L. Fedie. Continuous Production of 5-Hydroxymethylfurfural from Simple and Complex Carbohydrates. *Applied Catalysis A: General*, 384 (2010), pp.65-69.
- [51] B. Saha and M.M. Abu-Omar. Advances in 5-Hydroxymethylfurfural Production from Biomass in Biphasic Solvents. *Green Chemistry*, 16 (2014), pp.24-38.
- [52] Z. Xu, X. Wang, M. Shen and C. Du. Synthesis of 5-Hydroxymethylfurfural from Glucose in A Biphasic Medium with AlCl_3 and Boric Acid as the Catalyst. *Chemical Papers*, 70 (2016), pp.1649-1657.
- [53] S. Lima, P. Neves, M.M. Antunes, M. Pillinger, N. Ignatyev and A.A. Valente. Conversion of Mono/Di-/Polysaccharides into Furan Compounds Using 1-Alkyl-3-Methylimidazolium Ionic Liquids. *Applied Catalysis A: General*, 363 (2009), pp.93-99.
- [54] Q. Hou, W. Li, M. Zhen, L. Liu, Y. Chen, Q. Yang, F. Huang, S. Zhang and M. Ju. An Ionic Liquid-Organic Solvent Biphasic System for Efficient Production of 5-Hydroxymethylfurfural from Carbohydrates at High Concentrations. *RSC Advances*, 7 (2017), pp.47288-47296.

- [55] B.E. Lubach. HMF Synthesis from Glucose/Fructose Mixtures in A Slug-Flow Microreactor. (Master Thesis). Groningen (2016).
- [56] M.J. Climent, A. Corma and S. Iborra. Conversion of Biomass Platform Molecules into Fuel Additives and Liquid Hydrocarbon Fuels. *Green Chemistry*, 16 (2014), pp.516-547.
- [57] Y. Muranaka, H. Nakagawa, R. Masaki, T. Maki and K. Mae. Continuous 5-Hydroxymethylfurfural Production from Monosaccharides in a Microreactor. *Industrial & Engineering Chemistry Research*, 56 (2017), pp.10998-11005.
- [58] S. Mohammad, C. Held, E. Altuntepe, T. Köse and G. Sadowski. Influence of Salts on the Partitioning of 5-Hydroxymethylfurfural in Water/MIBK. *The Journal of Physical Chemistry B*, 120 (2016), pp.3797-3808.
- [59] L.C. Blumenthal, C.M. Jens, J. Ulbrich, F. Schwering, V. Langrehr, T. Turek, U. Kunz, K. Leonhard and R. Palkovits. Systematic Identification of Solvents Optimal for the Extraction of 5-Hydroxymethylfurfural from Aqueous Reactive Solutions. *ACS Sustainable Chemistry & Engineering*, 4 (2015), pp.228-235.
- [60] L. Yang, X. Yan, S. Xu, H. Chen, H. Xia and S. Zuo. One-Pot Synthesis of 5-Hydroxymethylfurfural from Carbohydrates using An Inexpensive Fe₃O₄ Catalyst. *RSC Advances*, 5 (2015), pp.19900-19906.
- [61] E. Nikolla, Y. Román-Leshkov, M. Moliner and M.E. Davis. "One-Pot" Synthesis of 5-(Hydroxymethyl)Furfural from Carbohydrates using Tin-Beta Zeolite. *ACS Catalysis*, 1 (2011), pp.408-410.
- [62] T. Kobayashi, P. Khuwijitjaru and S. Adachi. Decomposition Kinetics of Glucose and Fructose in Subcritical Water Containing Sodium Chloride. *Journal of Applied Glycoscience*, 63 (2016), pp.99-104.
- [63] J. Liu, Y. Tang, K. Wu, C. Bi and Q. Cui. Conversion of Fructose Into 5-Hydroxymethylfurfural (HMF) and Its Derivatives Promoted by Inorganic Salt in Alcohol. *Carbohydrate Research*, 350 (2012), pp.20-24.
- [64] L.A. Reber, W.W. McNabb and W.W. Lucasse. The Effect of Salts on the Mutual Miscibility of Normal Butyl Alcohol and Water. *The Journal of Physical Chemistry*, 46 (1942), pp.500-515.
- [65] M. Görgényi, J. Dewulf, H. Van Langenhove and K. Héberger. Aqueous Salting-Out Effect of Inorganic Cations and Anions on Non-Electrolytes. *Chemosphere*, 65 (2006), pp.802-810.
- [66] M. Li, W. Li, Y. Lu, H. Jameel, H. Chang and L. Ma. High Conversion of Glucose to 5-Hydroxymethylfurfural using Hydrochloric Acid as A Catalyst and Sodium Chloride as A Promoter in A Water/ γ -Valerolactone System. *RSC Advances*, 7 (2017), pp.14330-14336.
- [67] J. Yue. Multiphase Flow Processing in Microreactors Combined with Heterogeneous Catalysis for Efficient and Sustainable Chemical Synthesis. *Catalysis Today*, 308 (2018), pp.3-19.
- [68] H. Ma, F. Wang, Y. Yu, L. Wang and X. Li. Autocatalytic Production of 5-Hydroxymethylfurfural from Fructose-Based Carbohydrates in A Biphasic System and Its Purification. *Industrial & Engineering Chemistry Research*, 54 (2015), pp.2657-2666.
- [69] T.S. Hansen, J. Mielby and A. Riisager. Synergy of Boric Acid and Added Salts in the Catalytic Dehydration of Hexoses to 5-Hydroxymethylfurfural in Water. *Green Chemistry*, 13 (2011), pp.109-114.
- [70] M. Brasholz, K. Von Kaenel, C.H. Hornung, S. Saubern and J. Tsanaksidis. Highly Efficient Dehydration of Carbohydrates To 5-(Chloromethyl) Furfural (CMF), 5-(Hydroxymethyl)Furfural (HMF) and Levulinic Acid by Biphasic Continuous Flow Processing. *Green Chemistry*, 13 (2011), pp.1114-1117.

SUPPORTING INFORMATION FOR CHAPTER 5

Tables

Table S1. Thick juice compositions as reported in literature.

	Tan et al. [1]		van Zandvoort [2]
Lactic acid (mg L ⁻¹)	13586 ± 545.9	Zn (wt%)	< 0.0002
Acetic acid (mg L ⁻¹)	2176 ± 117.4	Al (wt%)	< 0.0002
SUC (mg L ⁻¹)	640.3 ± 23.8	Mn (wt%)	< 0.0002
GLC (mg L ⁻¹)	87.9 ± 6.4	Fe (wt%)	< 0.0002
FRC (mg L ⁻¹)	-	K (wt%)	0.6 – 0.8
NH ₄ ⁺ (mg L ⁻¹)	104.6 ± 3.8	Na (wt%)	0.1
Ca ²⁺ (mg L ⁻¹)	1568 ± 73.5	Malic acid (wt%)	0.02 – 0.1
Mg ²⁺ (mg L ⁻¹)	110.6 ± 7.4	Lactic acid (wt%)	0.2 – 0.5
K ⁺ (mg L ⁻¹)	5432 ± 63.6	Acetic acid (wt%)	0.1
		Pyrrolidone carboxylic acid (wt%)	0.2
		Citric acid (wt%)	0.02 – 0.1
		SUC (wt%)	60 – 70

Table S2. Selected examples of HMF synthesis from SUC in biphasic systems.

No.	SUC amount	Cat.	Cat. amount	Time	Solvent(s)	T (°C)	HMF yield* (mol%)	Ref.
1	30 mg	Al-TUD-1	20 mg	2-6 h	H ₂ O:Toluene 0.3:0.7 (v/v)	170	17	[3]
2	10 wt%	HCl	pH 1	5 min	H ₂ O:DMSO 4:6 (w/w) and MIBK:2-BuOH 7:3 (w/w) with aq:org of 1:2 (w/w)	170	50	[4]
3	10 wt%	none	-	4.5 h	H ₂ O:DMSO 3:7 (w/w) and DCM with aq:org of 1:1 (w/w)	170	51	[4]
4	3.5 g	H-mordenite Si/Al = 11)	1 g	1 h	H ₂ O:MIBK 1:5 (v/v)	165	28	[5]
5	10 wt%	H ₂ SO ₄	0.1 N	10 min	H ₂ O:n-BuOH 1:1 (w/w)	150	30	[6]
6	n.a.	SPC-108	In fixed bed	12 h	H ₂ O:MIBK 1:3 (v/v)	78	41	[7]
7	23 wt%	TiO ₂	In fixed bed	3 min	H ₂ O:n-BuOH 1:3 (w/w)	180	16	[8]
8	120 g L ⁻¹ ILs	CrCl ₃	0.04 M	4 h	[BMIM]Cl:MIBK 3:7 (v/v)	100	100	[9]
9	5 wt%	Zr(O)Cl ₂	10 mol%	5 min	H ₂ O:MIBK 1:1 (v/v)	120	39	[10]
	100 mg	ZrP	50 mg	2 h	NaCl-H ₂ O:Diglyme 1:3 v/v	180	53	[11]
10	2.5 mmol	InCl ₃	50mM	2h	NaCl-H ₂ O:THF 1:3 v/v	200	52	[12]
11	0.75 mmol	ZnCl ₂ /HCl	0.2 mmol (27 mol%)	1 h	NaCl-H ₂ O:THF 1:10 v/v	180	65.6	[13]
12	200 mg	SnCl ₄	10 mol%	4h	EMIMBr:glycol dimethyl ether 250 mg:2 mL	100	65.7	[14]

*Yields are based on monosaccharide concentration.

Specific rotation of SUC

The specific rotation of SUC ($[\alpha]$) was determined using the following equation:

$$[\alpha]_D^{25} = \frac{\alpha_{\text{obs}}}{c \times l} \quad (\text{S1})$$

Where:

$[\alpha]_D^{25}$ = specific rotation of the compound at 25 °C using the D-line of the sodium lamp ($\lambda = 589.3 \text{ nm}$)

α_{obs} = observed optical rotation

c = the concentration of the solution in grams per mL

l = the length of the cell tube in decimeters

Volume changes in the biphasic system

Over the course of reaction, small amounts of organic solvent will dissolve in the aqueous phase (and *vice versa*) and consequently change the volume of both phases. This will affect the yield calculations and therefore corrections need to be made regarding the solvents. The changes in volume can be modeled using the Aspen software (Aspen V7.3 NRTL-RK) and the results are presented in Table S3. As samples are both taken and analyzed at room temperature, the volume change simulation is done at 20 °C.

Table S3. Modeled volume changes of aqueous: organic mixtures at 20° C as estimated by Aspen.

Water – MIBK mixture						
Ratio (Aq:Org)	V_{aq} (L)		R_{aq}	V_{org} (L)		R_{org}
	Initial	Final		Initial	Final	
1:4	100	99.22	0.9922	400	400.78	1.0020
1:2	100	99.48	0.9948	200	199.13	0.9957
1:1	100	100.99	1.0099	100	98.30	0.9830
2:1	200	203.49	1.0175	100	95.77	0.9577
4:1	400	408.48	1.0212	100	90.70	0.9070

For Water – MTHF mixture						
Ratio (Aq:Org)	V_{aq} (L)		R_{aq}	V_{org} (L)		R_{org}
	Initial	Final		Initial	Final	
1:4	100	98.246	0.98246	400	401.754	1.004385
1:2	100	99.123	0.99123	200	200.877	1.004385
1:1	100	99.561	0.99561	100	100.439	1.004385
2:1	200	199.562	0.99781	100	100.439	1.004385
4:1	400	399.562	0.99890	100	100.439	1.004385

$$R_{(\text{aq or org})} = \frac{\text{Final volume}}{\text{Initial volume}} \quad (\text{S2})$$

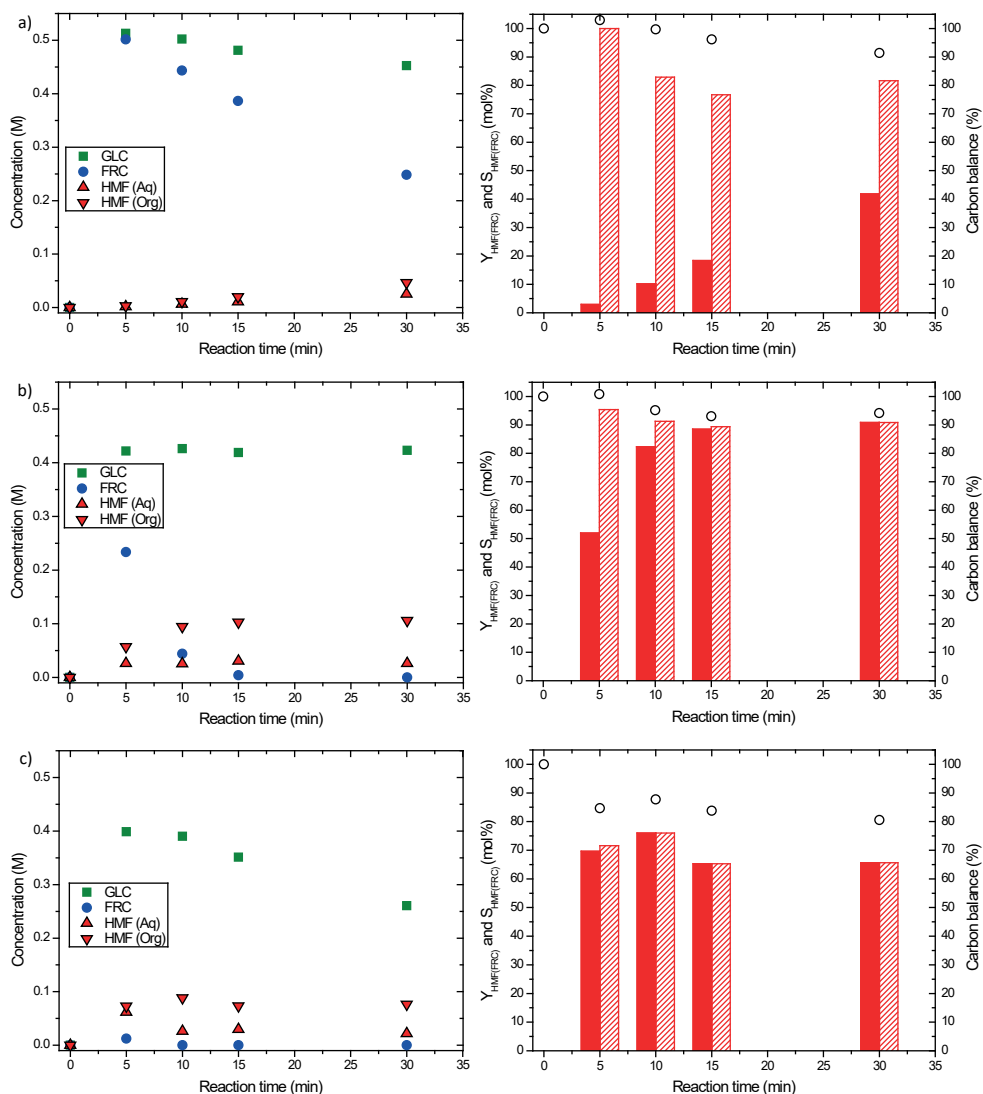
Thick juice reactions in biphasic system with MTHF (equal H_2SO_4 concentration)

Figure S1. Concentration-time profile (left) and yield, selectivity and carbon balance (right) of SUC hydrolysis in biphasic system with MTHF as extraction phase and a) thick juice without addition of salt ($C_{\text{SUC(equiv),0}} = 0.5 \text{ M}$, $C_{\text{H}_2\text{SO}_4} = 0.05 \text{ M}$, $\text{pH}_{\text{aq}} = 1.62$ at 25°C), b) thick juice with added 0.3 g mL^{-1} NaCl ($C_{\text{SUC(equiv),0}} = 0.44 \text{ M}$, $C_{\text{H}_2\text{SO}_4} = 0.044 \text{ M}$, $\text{pH}_{\text{aq}} = 0.73$ at 25°C) and c) SUC with added 0.3 g mL^{-1} NaCl ($C_{\text{SUC,0}} = 0.44 \text{ M}$, $C_{\text{H}_2\text{SO}_4} = 0.044 \text{ M}$, $\text{pH}_{\text{aq}} = 0.33$ at 25°C). Solid bar: HMF yield (FRC based), shaded bar: HMF selectivity (FRC based), circle: carbon balance. Reaction conditions; $T = 150^\circ\text{C}$, 1:4 v/v aqueous : organic ratio.

Thick juice reactions in biphasic system with MIBK

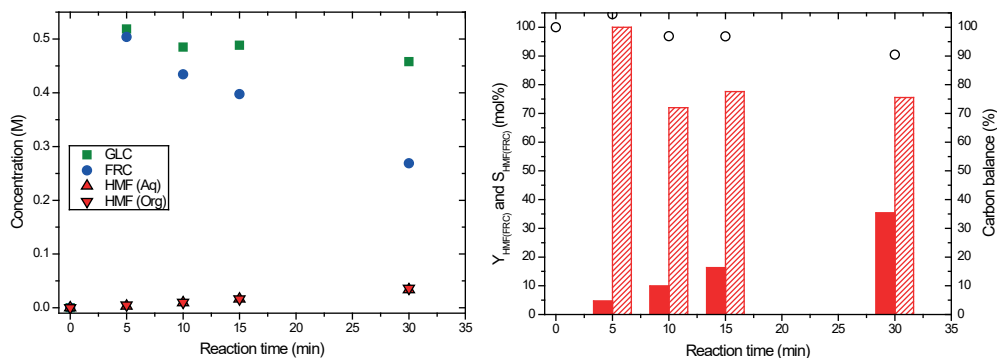


Figure S2. Concentration-time profile (left) and yield, selectivity and carbon balance (right) of thick juice hydrolysis in biphasic system MIBK as extraction solvent. Solid bar: HMF yield (FRC based), shaded bar: HMF selectivity (FRC based), circle: carbon balance. Reaction conditions: $C_{\text{SUC(equiv),0}} = 0.5 \text{ M}$, $T = 150 \text{ }^{\circ}\text{C}$, $C_{\text{H}_2\text{SO}_4} = 0.05 \text{ M}$, 1 : 4 v/v aqueous : organic ratio, $\text{pH}_{\text{aq}} = 1.62$ (at $25 \text{ }^{\circ}\text{C}$).

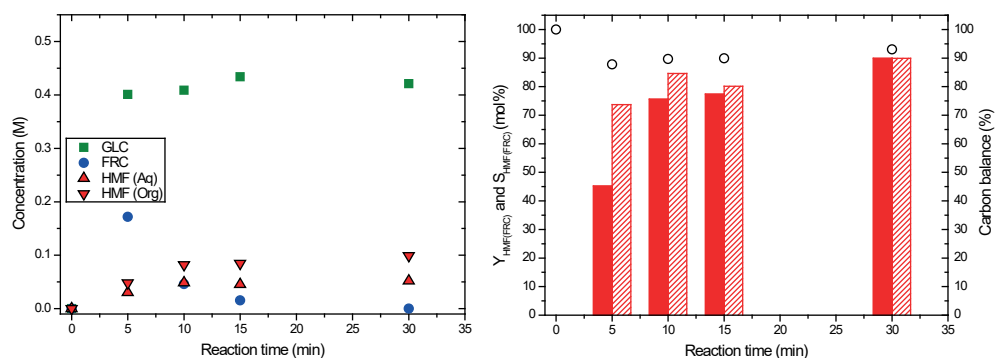


Figure S3. Concentration-time profile (left) and yield, selectivity and carbon balance (right) of thick juice hydrolysis in biphasic system MIBK as extraction solvent and NaCl (0.3 g mL^{-1}). Solid bar: HMF yield (FRC based), shaded bar: HMF selectivity (FRC based), circle: carbon balance. Reaction conditions: $C_{\text{SUC(equiv),0}} = 0.44 \text{ M}$, $T = 150 \text{ }^{\circ}\text{C}$, $C_{\text{H}_2\text{SO}_4} = 0.044 \text{ M}$, 1 : 4 v/v aqueous : organic ratio, $\text{pH}_{\text{aq}} = 0.73$ (at $25 \text{ }^{\circ}\text{C}$).

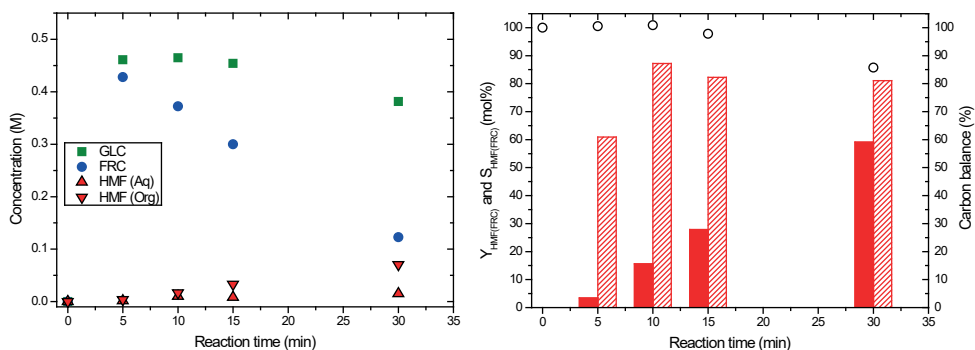
Thick juice reactions in biphasic system with addition of Na_2SO_4 

Figure S4. Concentration-time profile (left) and yield, selectivity and carbon balance (right) of thick juice hydrolysis in biphasic system with MIBK as extraction solvent and Na_2SO_4 (0.3 g mL^{-1}). Solid bar: HMF yield (FRC based), shaded bar: HMF selectivity (FRC based) only, circle: carbon balance. Reaction conditions: $C_{\text{SUC(equiv),0}} = 0.45 \text{ M}$, $T = 150^\circ\text{C}$, 500 rpm, $C_{\text{H}_2\text{SO}_4} = 0.045 \text{ M}$ and 1 : 4 v/v aqueous : organic ratio. $\text{pH}_{\text{aq}} = 2.26$ (at 25°C).

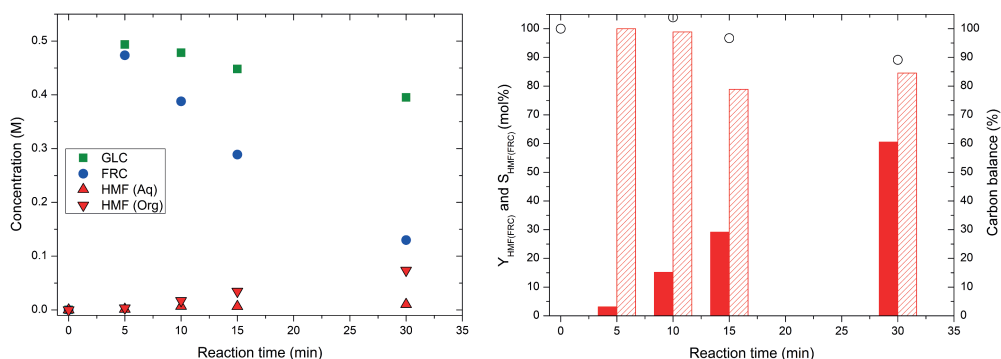


Figure S5. Concentration-time profile (left) and yield, selectivity and carbon balance (right) of thick juice hydrolysis in biphasic system with MTHF as extraction solvent and Na_2SO_4 (0.3 g mL^{-1}). Solid bar: HMF yield (FRC based), shaded bar: HMF selectivity (FRC based) only, circle: carbon balance. Reaction conditions: $C_{\text{SUC(equiv),0}} = 0.45 \text{ M}$, $T = 150^\circ\text{C}$, 500 rpm, $C_{\text{H}_2\text{SO}_4} = 0.045 \text{ M}$ and 1 : 4 v/v aqueous : organic ratio. $\text{pH}_{\text{aq}} = 2.26$ (at 25°C).

FA and LA formation in SUC reaction in biphasic system with addition of NaCl

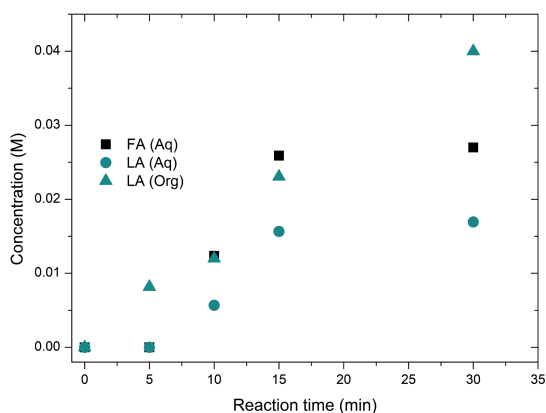


Figure S6. Concentration-time profile for FA and LA obtained from SUC hydrolysis in biphasic system with MTHF extraction solvents and addition of NaCl (0.3 g mL^{-1}). Reaction condition: $C_{\text{SUC},0} = 0.44 \text{ M}$, $T = 150 \text{ }^{\circ}\text{C}$, 500 rpm , $C_{\text{H}_2\text{SO}_4} = 0.044 \text{ M}$ and $1 : 4 \text{ v/v}$ aqueous : organic ratio. $\text{pH}_{\text{aqueous}} = 0.33$ ($25 \text{ }^{\circ}\text{C}$).

FA was only detectable in the aqueous phase. For the purpose of carbon balance calculation, the concentration of FA in the organic phase (in this case MTHF) was estimated using the partition/distribution coefficient value of FA in MTHF-water system found in the literature – which is ranging from 1.41 – 1.71 at room temperature [15, 16]. A partition coefficient value of 1.56 (an average value from literature data) is then used to estimate the FA concentration in this reaction.

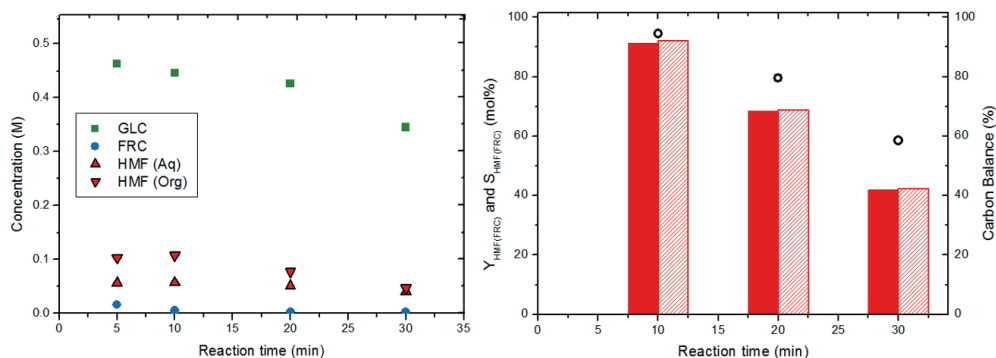


Figure S7. Concentration-time profile (left) and yield, selectivity and carbon balance (right) of SUC hydrolysis in biphasic system with MTHF as extraction solvent and NaCl (0.003 g mL^{-1}). Solid bar: HMF yield (FRC based), shaded bar: HMF selectivity (FRC based), circle: carbon balance. Reaction conditions: $C_{\text{SUC},0} = 0.5 \text{ M}$, $T = 150 \text{ }^{\circ}\text{C}$, $1 : 4 \text{ v/v}$ aqueous : organic ratio. $\text{pH}_{\text{aq}} = 0.65$ (at $25 \text{ }^{\circ}\text{C}$).

Slug-flow microreactor



Figure S8. Photograph of the obtained slug-flow of the aqueous phase (small bubbles) and the MTHF organic phase (larger slugs).

Thick juice reaction in continuous slug-flow microreactor without the addition of salt

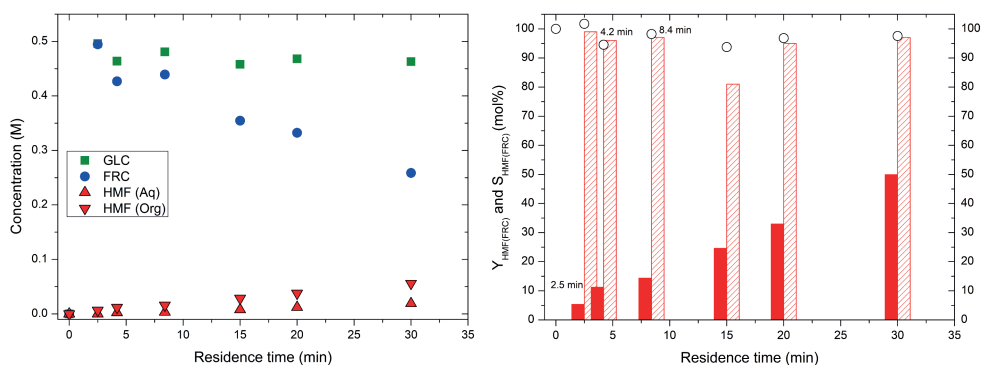


Figure S9. Concentration-time profile (left) and yield, selectivity and carbon balance (right) of thick juice hydrolysis in slug-flow microreactor in biphasic system with MTHF extraction solvents, without addition of NaCl over various residence times. Solid bar: HMF yield (FRC based), shaded bar: HMF selectivity (FRC based), circle: carbon balance. Reaction condition: $C_{\text{SUC(equiv),0}} = 0.48 \text{ M}$, $T = 150^\circ\text{C}$, $C_{\text{H}_2\text{SO}_4} = 0.048 \text{ M}$, 1:4 v/v aqueous:organic ratio, $\text{pH}_{\text{aq}} = 1.62$ (25°C).

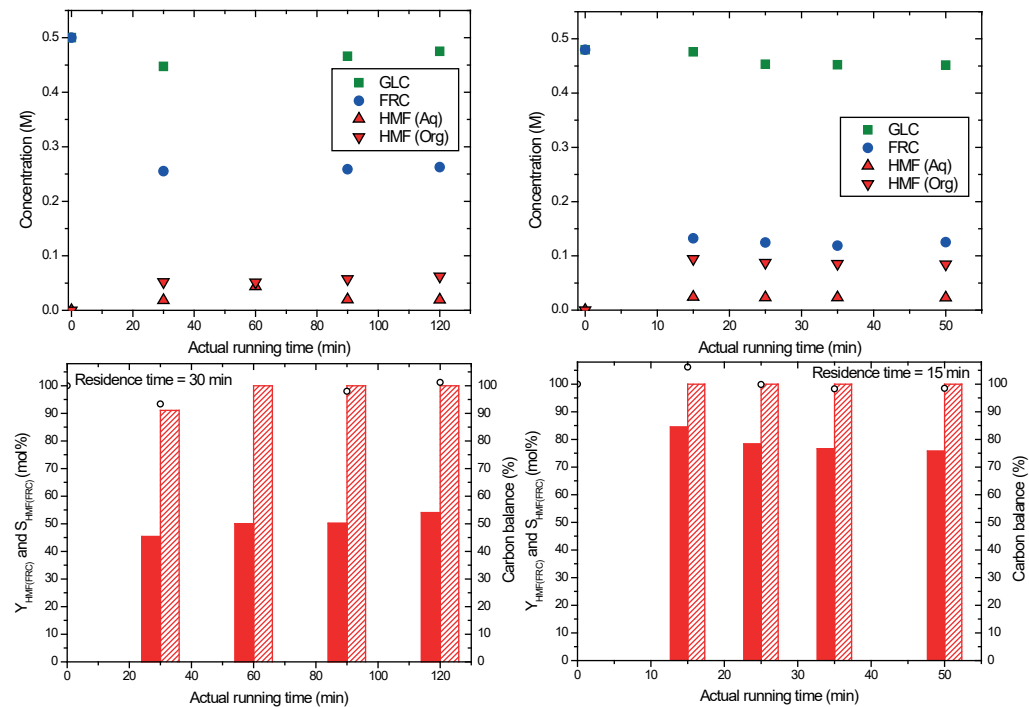


Figure S10. Concentration-time profile (above) and yield, selectivity and carbon balance (below) of thick juice hydrolysis in a slug-flow microreactor in biphasic system with MTHF as extraction solvent, without addition of NaCl (left, 30 min residence time) and with addition of NaCl, 0.1 g mL⁻¹ (right, 15 minutes residence time). Solid bar: HMF yield from FRC only, shaded bar: HMF selectivity based on FRC only, circle: carbon balance. Reaction condition: $C_{SUC(equiv),0} = 0.5$ M, $T = 150$ °C, 1:4 v/v aqueous:organic ratio, $pH_{aq} = 1.2$ (25 °C).

Table S4. Conversion of thick juice in a microreactor. Reaction conditions: $C_{SUC(equiv),0} = 1$ M, residence time 5 min, 150 °C, pH 1.2 (25 °C), 0.1 g mL⁻¹ NaCl.

Running time	Y_{HMF} mol%	S_{HMF} mol%
5 min	14.79	37.96
10 min	23.25	53.32
15 min	53.82	89.26
10 h	55.10	92.49

Residence time and flowrate calculations for the microreactor

In the microreactor, the residence time and flowrate of the reaction mixture can be calculated as follows:

$$u_s = \frac{Q}{A_{\text{tube}}} \quad (\text{S3})$$

$$\tau = \frac{L}{u_s} = \frac{L A_{\text{tube}}}{Q} \quad (\text{S4})$$

where:

u_s = superficial velocity of a given phase, m min^{-1}

Q = volume flow rate of the phase, $\text{m}^3 \text{min}^{-1}$

A_{tube} = cross sectional area of the tube, m^2

τ = residence time, min

L = length of the reactor tube, m

The reaction in the microreactor was performed at 150 °C with MTHF acting as the extracting solvent. At this temperature, the volume of both aqueous and organic phases change due to the solubility of the two liquids and changes in the liquid density due to temperature effects. To compensate for this, the volume change of the different solvent ratios for water-MTHF system were also modeled in Aspen at 150°C (see Table S5) and the R value (for total volume change) was incorporated into equation S3, resulting in:

$$u_s = \frac{Q R_{\text{tot}}}{A_{\text{tube}}} \quad (\text{S5})$$

Table S5. Modeled volume changes of aqueous:organic mixtures at 1:4 v/v ratio at various temperature as estimated by Aspen.

T (°C)	V _{aq} (L)		R _{aq}	V _{org} (L)		R _{org}	V _{tot} (L)		R _{tot}
	Initial	Final		Initial	Final		Initial	Final	
140	100	48.50	0.4850	400	533.11	1.3328	500	581.61	1.1632
150	100	46.47	0.4647	400	545.18	1.3630	500	591.65	1.1833
160	100	43.55	0.4355	400	561.24	1.4031	500	604.79	1.2096

Example of microreactor flowrate calculation for a reaction run at 150 °C is as follows:

Reaction condition:

Reactor length = 4.5 m

Reactor i.d. = 1.651 mm

Desired residence time (τ) = 20 min

The superficial velocity of the mixture and residence time at 150 °C are calculated from:

$$u_s = \frac{L}{\tau} = \frac{4.5}{20} = 0.225 \text{ ml min}^{-1} \quad (\text{S6})$$

With correction on volume changes during reaction, the flowrate can be calculated as follow:

$$u_s = \frac{Q R_{\text{tot}}}{A_{\text{tube}}} = 0.225 \left(\frac{\text{m}}{\text{min}} \right) = \frac{Q * 1.1833}{\pi * \frac{0.001651^2}{4}} \left(\frac{1}{\text{m}^2} \right) \quad (\text{S7})$$

$$Q = 4.07 \times 10^{-7} \left(\frac{\text{m}^3}{\text{min}} \right) = 0.407 \text{ ml min}^{-1} \quad (\text{S8})$$

To obtain a residence time of 20 min, the HPLC pump was set at 0.407 mL min⁻¹ flowrate. The HPLC pump used in this study has two inlets – one for the organic and one for the aqueous phase. Therefore, 0.407 mL min⁻¹ was the total flowrate of both phases. The pump inlet setting was set to 20% for aqueous and 80% for organic to obtain the 1:4 v/v ratio of aqueous to organic phase. The complete residence times and flowrates used in this study are given in Table S6.

Table S6. Residence time and flowrate setting used in the continuous reaction with the slug-flow microreactor with MTHF as extracting solvent.

Residence time (min)	(Total) Flowrate (mL min ⁻¹)
5	1.628
10	0.814
15	0.523
20	0.407

References for the supporting information

- [1] [L. Tan, Z. Sun, S. Okamoto, M. Takaki, Y. Tang, S. Morimura and K. Kida. Production of Ethanol from Raw Juice and Thick Juice of Sugar Beet by Continuous Ethanol Fermentation with Flocculating Yeast Strain KF-7. *Biomass and Bioenergy*, 81 (2015), pp.265-272.
- [2] I. van Zandvoort. *Towards the Valorization of Humin By-Products: Characterization, Solubilization and Catalysis* (Doctoral Dissertation), Utrecht (2015).
- [3] S. Lima, M.M. Antunes, A. Fernandes, M. Pillinger, M.F. Ribeiro and A.A. Valente. Acid-Catalysed Conversion of Saccharides Into Furanic Aldehydes in the Presence of Three-Dimensional Mesoporous Al-TUD-1. *Molecules*, 15 (2010), pp.3863-3877.
- [4] J.N. Chheda, Y. Román-Leshkov and J.A. Dumesic. Production of 5-Hydroxymethylfurfural and Furfural by Dehydration of Biomass-Derived Mono-and Poly-Saccharides. *Green Chemistry*, 9 (2007), pp.342-350.
- [5] C. Moreau, R. Durand, C. Pourcheron and S. Razigade. Preparation of 5-Hydroxymethylfurfural from Fructose and Precursors Over H-form Zeolites. *Industrial Crops and Products*, 3 (1994), pp.85-90.
- [6] Q.P. Peniston (Ed.), *Manufacture of 5-Hydroxymethyl 2-Furfural*. US Patent (1956).

- [7] L. Rigal and A. Gaset. Direct Preparation of 5-Hydroxymethyl-2-Furancarboxaldehyde from Polyholosides: A Chemical Valorisation of the Jerusalem Artichoke (*Helianthus tuberosus* L.). *Biomass*, 3 (1983), pp.151-163.
- [8] C.V. McNeff, D.T. Nowlan, L.C. McNeff, B. Yan and R.L. Fedie. Continuous Production of 5-Hydroxymethylfurfural from Simple and Complex Carbohydrates. *Applied Catalysis A: General*, 384 (2010), pp.65-69.
- [9] S. Lima, P. Neves, M.M. Antunes, M. Pillinger, N. Ignatyev and A.A. Valente. Conversion of Mono/Di/Polysaccharides into Furan Compounds using 1-Alkyl-3-Methylimidazolium Ionic Liquids. *Applied Catalysis A: General*, 363 (2009), pp.93-99.
- [10] B. Saha, S. De and M. Fan. $\text{Zr}(\text{O})\text{Cl}_2$ Catalyst for Selective Conversion of Bbiorenewable Carbohydrates and Biopolymers to Biofuel Precursor 5-Hydroxymethylfurfural in Aqueous Medium. *Fuel*, 111 (2013), pp. 598-605.
- [11] A. Jain, A.M. Shore, S.C. Jonnalagadda, K.V. Ramanujachary and A. Mugweru. Conversion of Fructose, Glucose and Sucrose to 5-Hydroxymethyl-2-Furfural Over Mesoporous Zirconium Phosphate Catalyst. *Applied Catalysis A: General*, 489 (2015), pp. 72-76.
- [12] Y. Shen, J. Sun, Y. Yi, M. Li, B. Wang, F. Xu and R. Sun. InCl_3 -Catalyzed Conversion of Carbohydrates into 5-Hydroxymethylfurfural in Biphasic System. *Bioresource Technology*, 172 (2014), pp. 457-460.
- [13] G.R. Gomes, D.S. Rampon and L.P. Ramos. Production of 5-(Hydroxymethyl)-furfural from Water-Soluble Carbohydrates and Sugarcane Molasses. *Applied Catalysis A: General*, 545 (2017), pp. 127-133.
- [14] Q. Hou, W. Li, M. Zhen, L. Liu, Y. Chen, Q. Yang, F. Huang, S. Zhang and M. Ju. An Ionic Liquid–Organic Solvent Biphasic System for Efficient Production of 5-Hydroxymethylfurfural from Carbohydrates at High Concentrations, *RSC Advances*, 7 (2017), pp.47288-47296.
- [15] A.G. Demesa, A. Laari, E. Tirronen and I. Turunen. Comparison of Solvents for the Recovery of Low-Molecular Carboxylic Acids and Furfural from Aqueous Solutions. *Chemical Engineering Research and Design*, 93 (2015), pp. 531-540.
- [16] H.D. Hoving, D.A. Rijke, G.M.C. Wagemans, R.F.M.J. Parton and K. Babic (Eds.). Process for the Separation of Levulinic Acid from Biomass. Patent, 2014.

6

5-Hydroxymethylfurfural Synthesis from Sugar Beet Thick Juice: Kinetic and Modeling Studies

Manuscript in preparation, titled as:

5-Hydroxymethylfurfural synthesis from sugar beet thick juice: kinetic and modeling studies

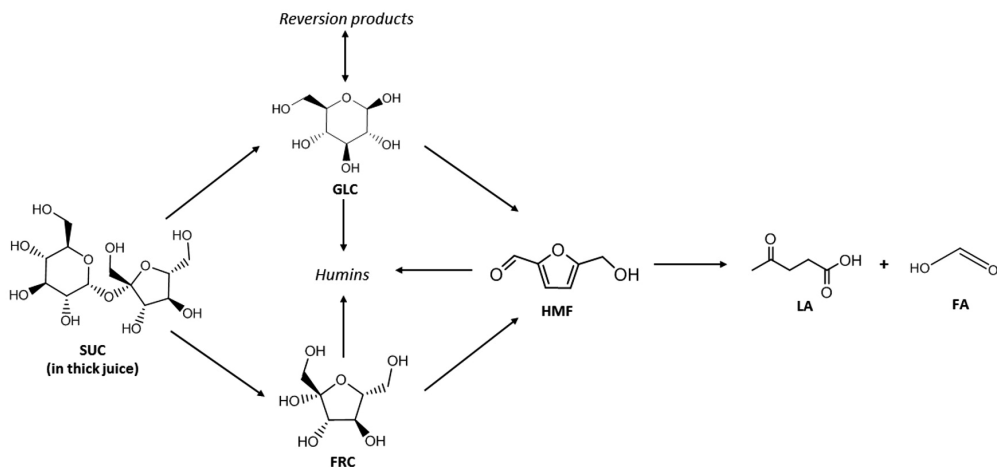
R.M. Abdilla-Santes, J.G.M. Winkelman, I. van Zandvoort, B.M. Weckhuysen, P.C.A. Bruijninx,
P.J. Deuss and H.J. Heeres

5-Hydroxymethylfurfural (HMF) is a promising biobased platform chemical with a high derivatization potential. It is accessible by the acid-catalyzed hydrolysis of various carbohydrate containing feeds, preferably with a high content of fructose. We here report a detailed study on the use of sucrose (SUC) and thick juice, an intermediate stream in a sugar factory, for the synthesis of HMF in a batch reactor setup (water, sulfuric acid (0.01 M), 180°C). Distinct differences in reactivity were found for both feeds, related to the presence of impurities (organic acids, salts) in the feed. Detailed model studies were performed involving the use of SUC in combination with one of the impurities (organic acids like maleic acid, and a range of salts with potassium, sodium, calcium and magnesium as the cations and carbonates, chlorides and sulfates as the anions). The data were successfully modeled using a kinetic model for the main reactions in the network. It revealed that sulfate anions have a major effect on the HMF yield and the batchtime required to reach optimum HMF yield. In addition, the sulfate anions are the likely cause for the differences in reactivity between pure SUC and thick juice.

6.1. INTRODUCTION

Environmental issues related to the use of fossil resources have led to extensive efforts to identify alternative feedstocks for the production of chemical products. Of all options, biomass is considered an attractive feed for biofuels and biobased chemicals [1-4]. Among the many chemicals that may be derived from biomass, 5-hydroxymethylfurfural (HMF) is considered very attractive. It is accessible by an acid-catalyzed hydrolysis reaction of saccharides, both monomeric and polymeric in nature. Among the saccharides investigated [2, 5-8], fructose (FRC) is known to be the most suitable one in terms of HMF yields and, in aqueous acidic conditions, HMF yields of up to 50% have been reported. In contrast, when using abundantly available glucose (GLC) in water, HMF yields are typically below 10% [9]. Major byproducts during HMF synthesis from these carbohydrates are insoluble polymers known as humins, levulinic acid (LA) and formic acid (FA).

Sucrose (SUC), produced globally in large volumes from either sugar beets or sugar cane, is a disaccharide consisting of FRC and GLC. It has been tested as a feed for HMF synthesis [6, 10] and an overview on the acid-catalyzed conversion of SUC to HMF in water using Brønsted acid catalysts is provided in Table S1 (Supporting Information). Recently, we reported a comprehensive study on the conversion of SUC to HMF and LA using sulfuric acid in water in the temperature range of 80 – 180 °C [9]. A reaction network was proposed involving rapid hydrolysis of SUC to give FRC and GLC, followed by FRC dehydration to HMF. Byproducts are LA, FA and (solid) humins [11-13].



Scheme 1. Proposed reaction scheme of SUC in thick juice conversion to HMF and LA [9].

We have also recently demonstrated the use of thick juice for the synthesis of HMF in a biphasic reaction system [14] and showed that HMF yields > 90% (calculated on FRC basis) are possible in a microreactor setup at 150°C (H_2SO_4 as catalyst and 2-methyltetrahydrofuran as a bioderived extraction solvent). Thick juice is a SUC rich intermediate product stream produced in sugar factories (see Supporting Information, Figure S1) and contains, besides water and SUC (about 65 wt%), impurities like organic acids and salts (Table 1).

Table 1. Composition of thick juice.

	Tan et al. [15]		van Zandvoort [16]
Lactic acid (mg L^{-1})	13586 ± 545.9	Zn (wt%)	< 0.0002
Acetic acid (mg L^{-1})	2176 ± 117.4	Al (wt%)	< 0.0002
SUC (g L^{-1})	640.3 ± 23.8	Mn (wt%)	< 0.0002
GLC (g L^{-1})	87.9 ± 6.4	Fe (wt%)	< 0.0002
FRC (g L^{-1})	-	K (wt%)	0.6 – 0.8
NH_4^+ (mg L^{-1})	104.6 ± 3.8	Na (wt%)	0.1
Ca^{2+} (mg L^{-1})	1568 ± 73.5	Malic acid (wt%)	0.02 – 0.1
Mg^{2+} (mg L^{-1})	110.6 ± 7.4	Lactic acid (wt%)	0.2 – 0.5
K^+ (mg L^{-1})	5432 ± 63.6	Acetic acid (wt%)	0.1
		Pyrrolidone carboxylic acid, PCA (wt%)	0.2
		Citric acid (wt%)	0.02 – 0.1
		SUC (wt%)	60 – 70

The use of thick juice in the biphasic system instead of pure SUC led to significantly higher HMF yields [14], and it was proposed that the impurities present in the thick juice have a positive effect, though the exact cause remained unclear. In this manuscript, we present a model study in a batch reactor setup using water as the solvent and sulfuric acid as the catalyst and SUC, either pure or in the presence of impurities known to be present in the thick juice (organic acids, salts). The performance was compared in terms of FRC reactivity and HMF yield with that of thick juice to get further insight into what impurities cause the positive effect. The experimental data were modeled using a reaction network earlier proposed by us for pure SUC [9] and this allowed quantification of the kinetic rate constants for the relevant reactions. With this information, it was shown that particularly the presence of salts with sulfate anions have a major effect and are the likely cause for the differences observed between pure SUC and thick juice.

6.2. EXPERIMENTAL SECTION

6.2.1. Chemicals

Thick juice was kindly provided by Suiker Unie-Royal Cosun. Sulfuric acid (96–98 wt%), SUC (≥ 99 wt%), GLC (≥ 99.5 wt%), FRC (99 wt%), Na_2SO_4 , K_2SO_4 , PCA, HMF, citric acid, malic acid, lactic acid, NaCl, CaCO_3 , MgCl_2 and FA were obtained from Sigma-Aldrich (Steinheim, Germany). KCO_3 , NaCO_3 , MgCO_3 , CaCl and KCl were acquired from Merk Millipore (Darmstadt, Germany). LA and oxalic acid were purchased from Alfa Aesar. Maleic acid was obtained from Acros Organic. All chemicals were used without further purification. For all experiments, Milli-Q water was used to prepare the solutions.

6.2.2. Sugar content in thick juice

The SUC content of thick juice solution was determined by polarimetry (see section 2.4). This method is a suitable alternative for HPLC, for which accurate SUC analyses is difficult due to SUC hydrolysis to GLC and FRC when using a typical acidic mobile phase. According to polarimetry, the thick juice used in this study consist of 62 wt% SUC (± 2 M). To test the validity of this method, we also hydrolyzed the thick juice under a very mild condition (5 mM H_2SO_4 , 100 °C, and 0.5 g thick juice in 10 mL) and analyzed the changes in GLC and FRC concentrations over time. After 60 min of hydrolysis reaction, no increase in GLC and FRC concentrations was observed and both of them were found in an equimolar ratio and the concentrations remained steady till 75 min. Therefore, we concluded that at 60 min of reaction under this condition, SUC in thick juice was fully inverted to GLC and FRC. From the GLC and FRC concentration we obtained, SUC concentration in the original thick juice could be calculated, and according to this hydrolysis method, the SUC content is 62 ± 1 wt%. Therefore, the validity of our measurement with by polarimetry is verified.

6.2.3. Batch experiment in water

The experimental methods for the aqueous experiments are based on published work by Girisuta et al. [17]. The reactions were carried out in glass ampoules with an internal diameter of 3 mm, a wall thickness of 1.5 mm and a length of 15 cm. A total of 8 ampoules were used for one series of experiments. The ampoules were loaded with approximately 0.3 mL reaction mixture consisting of a pre-determined amount of thick juice (circa 0.5 M of SUC equivalent) or SUC (0.5 M) and catalyst (0–0.1 M sulfuric acid). The ampoules were then sealed with a torch and arranged in an aluminium rack and subsequently placed in a temperature-controlled oven (GC oven, Hewlett Packard 5890A) at $T = 180$ °C. At different reaction times, an ampoule was removed and immediately submerged in cold water to stop the reaction. After the solution reached room temperature, the ampoules were opened and the reaction mixture

was withdrawn. The mixture was filtered with 0.45 μm PTFE filter to remove any insoluble matter. Subsequently, an aliquot of the clear solution was taken (28 μL) and diluted with Milli-Q water (1672 μL). The obtained sample was subjected to analysis by high performance liquid chromatography (HPLC).

6.2.4. Analytical methods

Polarimetry. The SUC content in thick juice was determined using a polarimeter. A series of known concentration of SUC solutions were prepared and the observed rotation (α_{obs}) of each solution was obtained by a polarimeter (Schmidt + Haensch, Polatronic MH8). The wavelength (λ) and cell length used are 589.44 nm and 100 mm respectively. This data is then used to calculate the specific rotation of SUC ($[\alpha]$) (see Supporting Information for details). Afterwards, a solution of thick juice with a known dilution factor is measured for its observed optical rotation and the SUC concentration in the original thick juice is determined.

pH measurements. The pH of the reaction mixtures was measured at room temperature using an InoLab pH 730 pH-meter equipped with a SenTix 81 probe (both probe and meter from WTW, Germany).

High Performance Liquid Chromatography (HPLC). The composition of aqueous reaction phases were determined by HPLC. The instrument consists of an Agilent 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87H), a refractive index detector and a ultraviolet detector. The HPLC column was operated at 60 $^{\circ}\text{C}$ and aqueous sulfuric acid (5 mM) was used as the mobile phase with a flow rate of 0.55 mL min^{-1} . The injection volume of the tested sample was set at 5 μL . Concentration of compounds in the product mixture were determined using calibration curves obtained by analyzing standard solutions of known compounds with known concentrations.

6.2.5. Definitions

The concentrations of the relevant compounds involved in the reaction were determined by HPLC. These concentrations were used to calculate the conversion of SUC (X_{SUC}) and the yield of HMF (Y_{HMF}) according to the definitions given in eqs 1 and 2.

$$X_{\text{SUC}} = \frac{(C_{\text{SUC},0} - C_{\text{SUC}})}{C_{\text{SUC},0}} \quad (1)$$

$$Y_{\text{HMF}} = \frac{C_{\text{HMF}}}{2C_{\text{SUC},0}} \quad (2)$$

Here, $C_{\text{SUC},0}$ is the initial concentration of SUC. All definitions are on a molar basis. The carbon balance closure is defined as total moles of carbon in HPLC detectable compounds (FRC, GLC, HMF, FA and LA) at certain reaction time or residence time divided by the moles of carbon in the feed (eq 3).

$$\text{Carbon balance closure} = \frac{\text{mol C in HPLC detectable compounds}}{\text{mol C in the feed}} \times 100\% \quad (3)$$

6.2.6. Kinetic modeling approach

A kinetic model for the reaction of SUC/thick juice in water with sulfuric acid catalyst was developed based on the reaction mechanism provided in Scheme 1. This reaction scheme was also featured in the previous kinetic study performed in our group [9]. The kinetic parameters were determined using a nonlinear least squares approach using the MATLAB function *lsqnonlin*, which is based on a trust region reflective algorithm, and involves minimization of the errors between the experimental data and the kinetic model.

6.3. RESULTS AND DISCUSSION

6.3.1. Benchmark experiments in water with thick juice and pure SUC

The hydrolysis reaction of thick juice (62% SUC) was carried out in a batch reactor at small scale (0.3 mL liquid intake) at 180 °C, with 0.01 M H₂SO₄ catalyst and an initial thick juice loading corresponding with 0.5 M SUC. The pH of the solution was about 3.8 at room temperature. The product distribution versus reaction time for a 6 h run is shown in Figure 1 (left side). SUC is rapidly converted to FRC and GLC and actually SUC could not be detected in the first product sample (15 min). Both FRC and GLC are converted in the course of the reaction, though it is clear that FRC is by far more reactive, in line with literature data [9, 14]. The maximum HMF yield was 24.6 mol% at 90 min batchtime. At longer reaction times, the HMF concentration gradually decreases and levulinic acid (LA) and formic acid (not shown) are formed. The carbon balance based on HPLC detectables at the end of the reaction is far from quantitative (Figure 1), indicating that substantial amounts on non-HPLC detectables, likely humins, are formed. In line with this statement is the observation that the carbon balance closure is time dependent, with better closures at the start of the reaction. Humin formation is also clear from the visual appearance of the reaction mixture during reaction, changing from clear/transparent yellow to brown and the formation of small brown/black solids (see Figure S2 in the Supporting Information for more details).

An experiment with pure SUC was performed as comparison initially at the same H₂SO₄ concentration (0.01 M). However, the pH of this mixture (pH 1.8) is lower compare to the one from thick juice. As such, to allow a fair comparison, we reduced the amount of H₂SO₄ added and set the pH to the similar value of the thick juice reaction instead (pH 3.7). The results of this experiment are given in Figure 1 (right side). Distinct differences in the concentration-time profiles between thick juice and pure SUC were observed. In both cases, FRC is converted at

essentially the same rates, whereas GLC is less reactive in the case of SUC. The highest yield of HMF (26 mol %) was similar to that for thick juice and was achieved at about 75 min of reaction. However, the HMF concentration profile shows a sharper maximum for pure SUC reaction, in contrast to the shallower one found for thick juice. This implies that the rate of conversion of HMF to LA and humins is much higher for SUC than for thick juice. In line with this observation is a higher amount of LA at the end of the reaction. The carbon balance for the SUC reaction is, as for thick juice, far from quantitative, though slightly better than for thick juice.

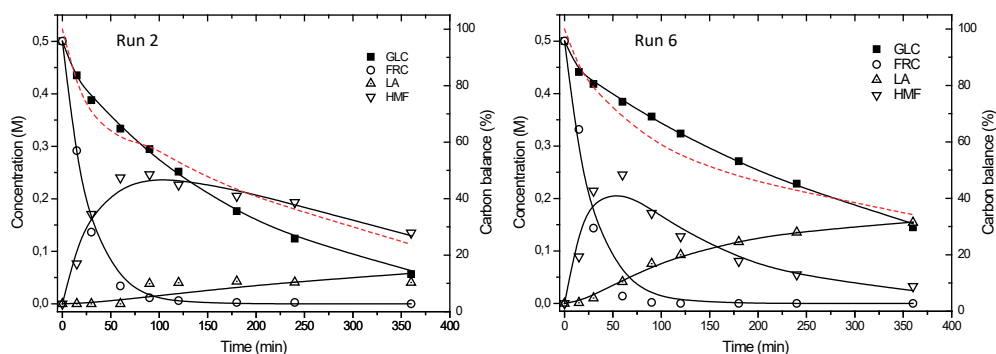
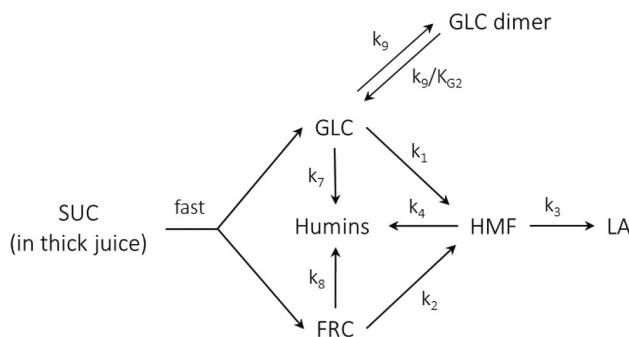


Figure 1. Concentration-time profiles for thick juice (left, run 2) and pure SUC (right, run 6). Reaction conditions: $C_{\text{SUC}(\text{equiv.}),0} = 0.5 \text{ M}$, $T = 180^\circ\text{C}$. Initial pH 3.8 for thick juice and 3.72 for pure SUC. Red dashed lines represent carbon balances. Solid lines represent model values. Run numbers refer to data in Table 3 and Figure S4.

6.3.2. Kinetic modeling

The concentration-time profiles for the individual components for the benchmark experiments with thick juice and SUC (section 3.1) were modeled to obtain the kinetic constants of the individual reactions in the network. All data were obtained at 180°C , and as such only rate constants at this temperature (k values) were derived, without a Temperature dependency. This approach provides quantitative information, which will be used to determine the difference in performance of thick juice and SUC regarding HMF synthesis. The kinetic model used for this purpose is given in Scheme 2 and is based on kinetic model developed earlier in our group for pure SUC reactions in water (Scheme 1) [9]. The reaction rates of each component are given in Table 2.



Scheme 2. Reaction network used for kinetic modeling.

Table 2. Reaction rate equations used in the kinetic model based on Scheme 2.

Reaction	Reaction rate
GLC → HMF	$r_1 = k_1 C_{\text{GLC}}$
FRC → HMF	$r_2 = k_2 C_{\text{FRC}}$
HMF → LA	$r_3 = k_3 C_{\text{HMF}}$
HMF → Humins	$r_4 = k_4 C_{\text{HMF}}$
GLC → Humins	$r_7 = k_7 C_{\text{GLC}}$
FRC → Humins	$r_8 = k_8 C_{\text{FRC}}$
2GLC → GLC dimer	$r_9 = k_9 C_{\text{GLC}}^2 - \frac{k_9}{K_{G2}} C_{G2}$
Component	Component production rate
GLC	$R_{\text{GLC}} = -r_1 - r_7 - 2r_9$
FRC	$R_{\text{FRC}} = -r_2 - r_8$
HMF	$R_{\text{HMF}} = r_1 + r_2 - r_3 - r_4$
LA	$R_{\text{LA}} = r_3$
GLC dimer	$R_{G2} = r_9$

As SUC almost instantaneously inverted to GLC and FRC in a 1 to 1 molar ratio at 180°C [9], the rate of this reaction is not included in the model. In addition, all reactions are considered to be first order in substrate, the only exception being the conversion of GLC to reversion products like GLC oligomers and anhydrosugars. At high sugar loadings ($> 200 \text{ mg mL}^{-1}$), up to 12 wt% of GLC is converted to reversion products which are mainly disaccharides [18]. As such, reversion chemistry is simplified by assuming that GLC is dimerized to a GLC dimer and has a second order dependency in GLC. Additionally, this reaction is also known to be a reversible reaction [18] and reversibility was also considered in the model. The value of the equilibrium constant (K_{G2}) for the reaction was taken from the literature [9].

It is also assumed that both FRC and GLC react independently to HMF which is based on literature evidence for kinetic studies on SUC in our group [9], studies using GLC only [17] and for a FRC-GLC mixture in water-acetone system [19]. As such, the existence of an equilibrium reaction between FRC and GLC was not included in the model. Finally, it is assumed that GLC, FRC as well as HMF form soluble and insoluble humins, whereas cross condensation reactions between the sugars and sugars/HMF do not occur to a significant extent [9].

Using these assumptions, an excellent fit between data and model was obtained (see Figure 1 for details), confirmed by a parity plot showing the experimental and modeled concentrations of the main products (Figure 2).

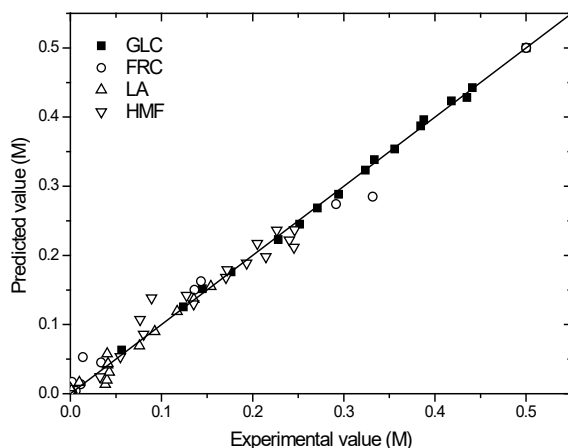


Figure 2. Parity plot for experimental and modeled data for the benchmark experiments.

The individual k values for the benchmark experiments with thick juice and SUC are given in Figure 3, showing remarkable differences between the two feeds.

When considering the relevant kinetic constants associated with HMF formation/disappearance (k_1 , k_2 , k_3 and k_4), these are higher for SUC than for thick juice, with the only exception is k_1 which is lower for SUC than for thick juice. The finding on k_2 , k_3 and k_4 values imply that FRC and its product HMF react much faster when using pure SUC compared to thick juice, as observed experimentally. The kinetic constant k_1 is related to reaction involving GLC to HMF, and the obtained value suggest that GLC is less rapidly converted to HMF when using pure SUC which in line with the experimental observation (Figure 1). Kinetic constant k_7 and k_8 are related to the formation of humins from GLC and FRC respectively. For the k_7 , the obtained value suggested that GLC converted to humins slightly faster when using pure SUC than thick juice. As for the k_8 , it is apparent that FRC conversion to humin is lower for SUC than for thick juice. The k value for GLC inversion to dimers (k_9) was considerably higher than the other kinetic constants in the reaction network for both feeds (see Supporting Information, Table S2 for details) and not included in Figure 3.

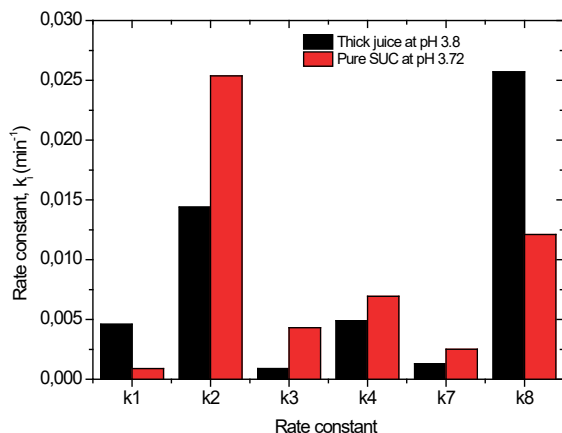


Figure 3. Kinetic constants for thick juice and pure SUC for the benchmark experiments (Reaction conditions: $C_{\text{SUC(equiv),0}} = 0.5 \text{ M}$, $T = 180 \text{ }^{\circ}\text{C}$, sulfuric acid as the catalyst)

6.3.3. Model studies on the effects of minor components in the thick juice

The differences in the reaction rate constants of the individual reactions in the reaction network must originate from the difference in composition between thick juice and SUC. Thick juice contains (besides SUC) considerable amounts of salts, organic acids and other minor components (see Table 1). All these compounds may affect the rate of the individual reactions in the network. In addition, thick juice is slightly basic and as such the pH of the reaction mixture may also play a role. To systematically investigate the effect of pH as well as other components like organic acids and salts on the individual reaction rates in the network, a number of experiments were performed with SUC as the starting material. For this purpose, various acids and salts (similar to the ones found in thick juice) were added to the SUC (see Table 3 for details). Some of the experiments were performed in duplicate and show good reproducibility (Supporting Information, Figures S3).

Table 3. Experimental details on thick juice and SUC reactions^(a)

Run	Starting material	Initial pH	H ₂ SO ₄	Additives	Y _{HMF} max ^(e) (mol%)	t at Y _{HMF} max ^(e) (min)
1	Thick Juice	8.5	-	-	22.6	161
2 ^(b)	Thick Juice	3.8	0.01 M	-	27.2	106
3	Thick Juice	1.88	pH adjusted with H ₂ SO ₄	-	28.5	45
4	SUC	5.7	-	-	25.5	58
5	SUC	1.8	0.01 M	-	30.2	12
6 ^(b)	SUC	3.72	pH adjusted with H ₂ SO ₄	-	26.2	58
7	SUC	11.17	pH adjusted with KOH	-	13.7	228
8 ^(c)	SUC	1.75	0.01 M	Citric, malic, oxalic, lactic, acetic acid and PCA	29.2	12
9 ^(c)	SUC	2.7	-	Citric, malic, oxalic, lactic, acetic acid and PCA	26.6	50
19	SUC	3.75	0.01 M	CaCO ₃ (1 mg mL ⁻¹) ^(d)	30.2	85
20	SUC	3.7	0.01 M	Na ₂ CO ₃ (1 mg mL ⁻¹) ^(d)	33.6	108
21	SUC	3.76	0.01 M	K ₂ CO ₃ (1 mg mL ⁻¹) ^(d)	34.0	112
22	SUC	3.72	0.01 M	MgCO ₃ (1 mg mL ⁻¹) ^(d)	32.8	92
23	SUC	1.95	0.01 M	CaCl ₂ (1 mg mL ⁻¹) ^(d)	30.2	11
24	SUC	1.93	0.01 M	NaCl (1 mg mL ⁻¹)	31.0	11
25	SUC	1.98	0.01 M	KCl (1 mg mL ⁻¹)	29.5	19
26	SUC	1.96	0.01 M	MgCl ₂ (1 mg mL ⁻¹) ^(d)	30.5	10
27	SUC	2.2	-	0.01 M Maleic acid	29.0	26
29	SUC	1.742	0.01 M	0.006 M KNO ₃	29.5	13
30	SUC	1.804	0.01 M	0.01 M Na ₂ SO ₄	26.2	37
31	SUC	2.178	0.01 M	0.05 M Na ₂ SO ₄	34.4	85
32	SUC	2.285	0.01 M	0.1 M Na ₂ SO ₄	33.4	81
33	SUC	1.975	0.01 M	0.01 M K ₂ SO ₄	26.2	43

(a) All runs were done at T = 180 °C with initial feed concentration, C_{SUC(equiv),0} = 0.5 M.

(b) Benchmark experiment (Figure 1).

(c) Amounts based on the values reported in the literature (Table 1) for thick juice.

(d) Concentration is about 0.01 M.

(e) Simulated values based on the kinetic model, calculation procedures are given in the Supporting Information.

6.3.3.1. pH effects

To investigate pH effects on the rates of the individual reactions in the network, 7 experiments at different initial pH values (1.9 - 11.2) and constant temperature (180 °C) were performed. Three experiments were conducted with thick juice (Table 3, run 1 – 3) and four with pure SUC (Table 3, run 4 – 7). The concentration versus time profiles of these experiments including the model lines are presented in Figure 4.

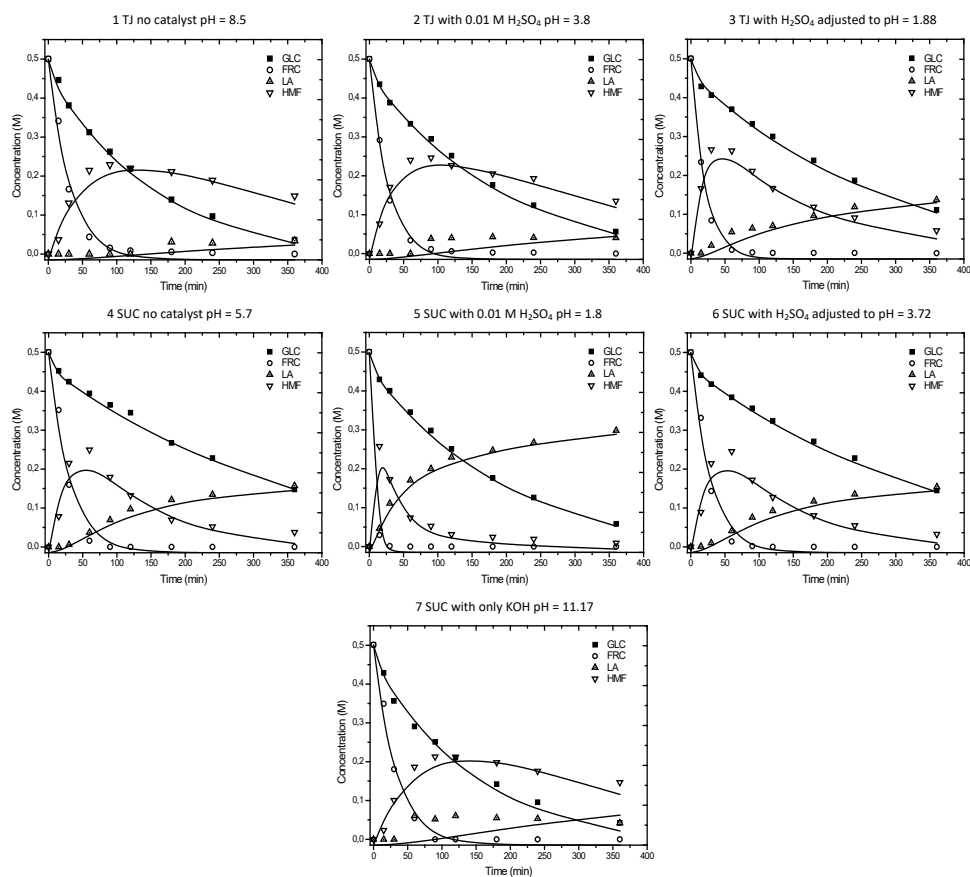


Figure 4. Concentration-time profiles for thick juice and pure SUC at different pH values. Reaction conditions: $C_{\text{SUC(equiv.)},0} = 0.5 \text{ M}$, $T = 180 \text{ }^{\circ}\text{C}$. Solid lines represent model values. Numbers above the graphs correspond to run numbers in Table 3.

Qualitatively, the curves for both feeds differ considerably, both in terms of the rate of reactions (i.e., conversion of FRC and GLC) and the shape of the HMF concentration profile. To obtain quantitative information, the kinetic constants for the individual reactions were determined using the kinetic model and the results for main reactions involving the formation and disappearance of HMF (reaction 1, 2, 3, and 4, see Scheme 1) are given in Figure 5 and the Supporting Information (Table S2).

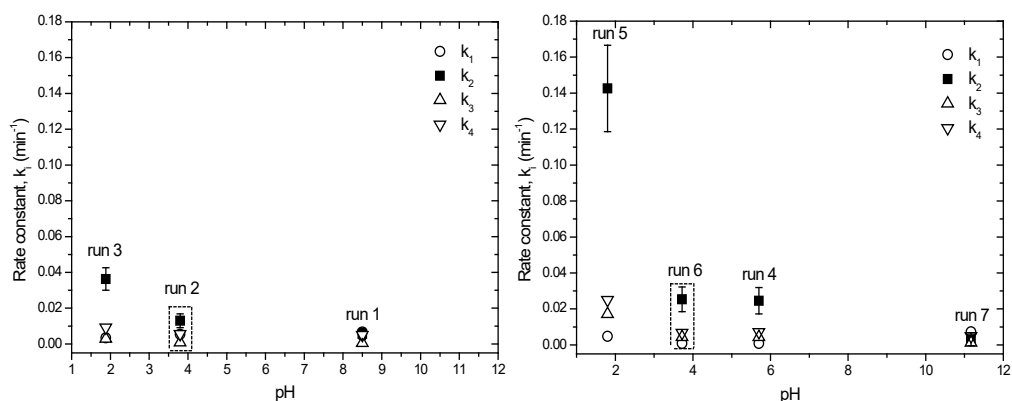


Figure 5. Rate constants for main reactions associated with HMF versus pH. Left side: thick juice experiments 1 – 3; right side: pure SUC (4 – 7). Data in the box (pH 3.7–3.8) are for the benchmark experiments.

For both thick juice and SUC, the pH has as a relatively small effect on the values of the kinetic constants in the range 3.8 – 8.5. For an experiment at pH 1.8 (run 3), the value for k_2 (FRC to HMF) is higher than for the experiments at higher pH values. For SUC, a similar trend is observed and the pH has a small effect in the pH range 4–6, whereas it is considerably increased at the low pH value of 1.8. This increase, particularly for k_2 is by far higher for SUC than for thick juice. A similar pH trend was found by Kusters et al. [20] in a study on the conversion of FRC to HMF in water at 175 °C in a stirred tank reactor. Here, the kinetic constant of the rate of the reaction of FRC to HMF (k_2) also showed a significant increase in value when the pH was below 2. This suggests the existence of two pH regimes, one at low pH values where Brønsted acidity plays a major role and a thermal regime, where the Brønsted acidity plays a minor role (pH > 1.8). Of interest is also the observation that at pH 11.2, so in a basic regime, SUC is still converted to the same products as found in acidic conditions, indicating that the chemo-selectivity of the thermal conversion of FRC to HMF is not significantly changed when switching from acidic to slightly basic conditions. Furthermore, the value of k_1 for thick juice reactions are all similar, while a very slight changes observed for the pure SUC reactions. This results indicate that GLC conversion to HMF is not influence by pH and the HMF produced in the reaction mixtures originated mostly from FRC. It has also been proven in the literature that in aqueous system GLC gives a very poor HMF yield (< 10 mol%) [9] which is in line with this work.

On the basis of these experiments, we can conclude that the pH within the ranges studied (1.9-11.2) has a major effect on the values of the kinetic constants for the relevant reactions and as such affect the concentration-time profiles of the products.

6.3.3.2. Effects of organic acids

Thick juice contains various organic acids (see Table 1 for detail) which may affect the rates of the individual reactions in the reaction network. To investigate the effect of organic acids on reaction rates, several SUC experiments (180 °C, 0.5 M SUC) were conducted in the presence of organic acids (Table 3 run 8, 9 and 27). Experiments were conducted with a mixture of organic acids (citric, malic, oxalic, lactic, acetic acid and PCA) with similar amounts as found in thick juice (Table 1) to mimic the thick juice composition (Runs 8 & 9). Run 8 was conducted in the presence of 0.01 M sulfuric acid, whereas no sulfuric acid was added for run 9. One experiment was performed using maleic acid (run 27, no sulfuric acid added), as it is known to have a positive effect on the selectivity of the hexose dehydration reaction to HMF [21].

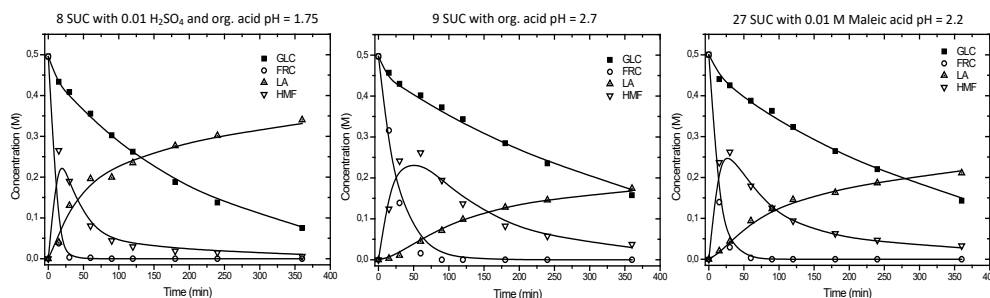


Figure 6. Concentration-time profiles for SUC hydrolysis in the presence of various organic acids. Reaction conditions: $C_{\text{SUC},0} = 0.5 \text{ M}$, $T = 180 \text{ }^{\circ}\text{C}$. Solid lines are model values. Numbers above the graphs correspond to run numbers in Table 3.

The concentration-time profiles and the kinetic constants of these experiments are given in Figure 6 and 7, respectively. The modeled kinetic constants for run 8 (organic acids in the presence of 0.01 M sulfuric acid, pH 1.75) are essentially similar to those observed for an experiment with SUC with the same amount of sulfuric acid but without the addition of organic acids (run 5, Table 3, pH 1.8), thus showing no significant influence of the organic acids. This is most likely because sulfuric acid ($\text{p}K_{\text{a},1} = -3$) is a by far stronger acid than the organic ones (lactic acid, 3.85, malic acid, 3.40, acetic acid, 4.8), and as such the latter are likely fully protonated in solution and have a minor catalytic effect. As such, an experiment with the organic acids without sulfuric acid addition was performed (pH 2.7, run 9). Indeed, this resulted in lower rates for the relevant reactions to HMF compared to an experiment in the presence of sulfuric acid. However, the kinetic constants are about similar to those found for the benchmark SUC experiment at pH 3.72, and higher than found for thick juice at pH 3.8. Thus, it appears that the presence of organic acids does not have a major effect on the

reaction rate constants, and as such these acids are not the major cause for the observed differences in performance between thick juice and SUC.

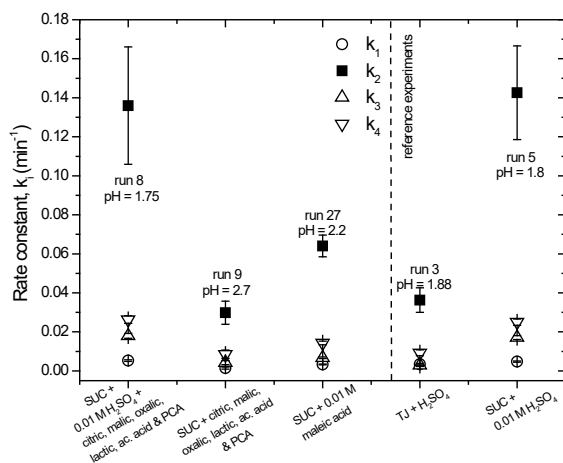


Figure 7. Relevant rate constants for SUC hydrolysis in the presence of organic acids.

6.3.3.3. Effects of salts

Thick juice contains significant amounts of salts (Table 1). Both cations and anions are known to affect the reaction rates of GLC and FRC conversions to HMF and LA [22, 23]. A systematic study was performed to investigate the influence of the salts on the product profiles using salts with potassium, sodium, calcium and magnesium as the cations and carbonates, chlorides and sulfates as the anions. All experiments were performed at 180°C, 0.5 M SUC initial loading, and with sulfuric acid (0.01 M) as catalyst. Due to the differences in the basicity of the anions, the pH of the solutions was not similar and pH effects were taken into account in the discussion. An overview of these experiments is given in Table 3 (runs 19 – 22 (carbonates), 23 – 26 (chlorides) and 30–33 (sulfates)).

6.3.3.3.1 Effects of carbonate salts

The initial pH of the four experiments with carbonate salts (pH 3.7–3.8, run 19–22) is higher than for experiments with SUC and sulfuric acid only (pH 1.8) and actually similar to that for a thick juice reaction with 0.01 M H₂SO₄ (pH around 3.7–3.8). The concentration-time profiles and the kinetic constants of these experiments are given in Figure 8 and 9, respectively. The concentration time profiles are all remarkable similar, indicating that the effect of the cations on the rates of reactions within the reaction network are not very pronounced. This was also confirmed by comparing the relevant kinetic constants for HMF (Figure 9), which are similar within the experimental error for these 4 experiments.

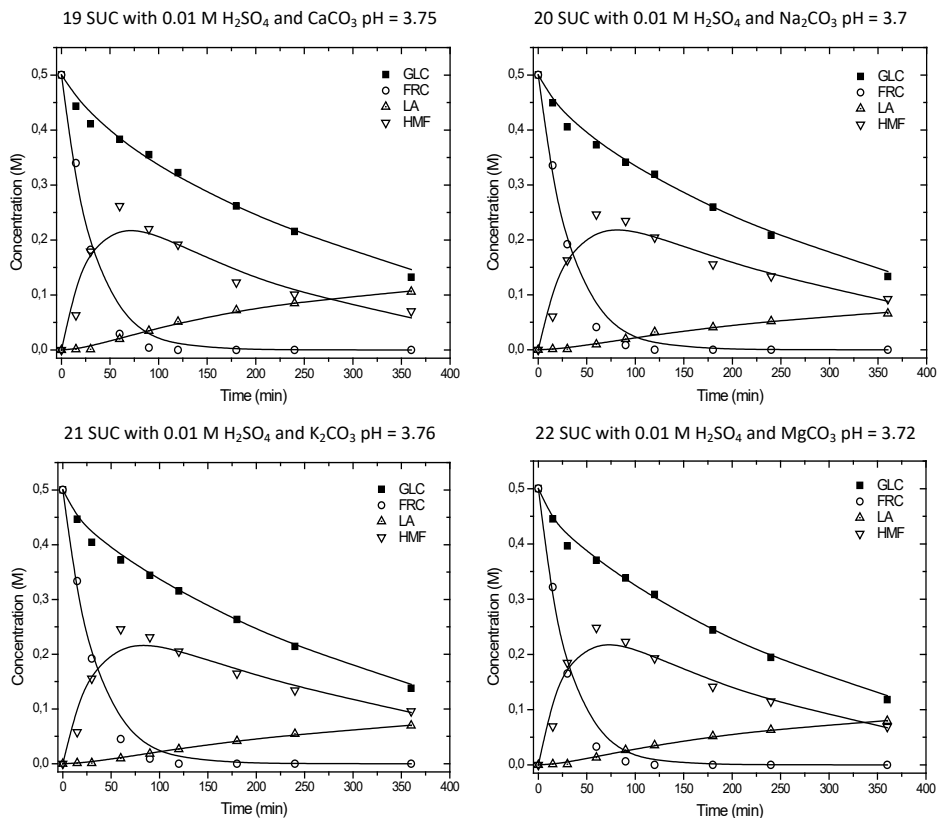


Figure 8. Concentration-time profiles for SUC hydrolysis in the presence of carbonate salts. Reaction conditions: $C_{\text{SUC}(\text{equiv},0)} = 0.5 \text{ M}$, $0.01 \text{ M H}_2\text{SO}_4$, $T = 180^\circ\text{C}$. Solid lines represent model values. Numbers above the graphs correspond to run numbers in Table 3.

It is of interest to compare the experimental data with the benchmark experiments of SUC and thick juice, which were performed at the same pH value as for the reactions with the carbonate salts. As shown in Figure 9, the values of k_1 are similar for all the experiments. When compared to the benchmark, these k_1 values are in the same range as the one from SUC but lower compared with the one from thick juice. Moreover, k_2 values for the carbonate experiments are slightly more in line with the one from SUC, whereas k_3 and k_4 are quite similar to the one from thick juice. The molar intakes of the salts in the SUC experiments (0.008 – 0.011 M) are in the range of sulfuric acid (0.01 M). Thus the carbonate anions are close to quantitatively converted to CO_2 and water, and as such only the cations and sulfate anions are present in solution. The data imply that these sulfate anions have an impact on the reaction rates in the network (*vide infra*), and particularly lower the rate of reactions 3 and 4 (from HMF to LA (k_3) and to humins (k_4)).

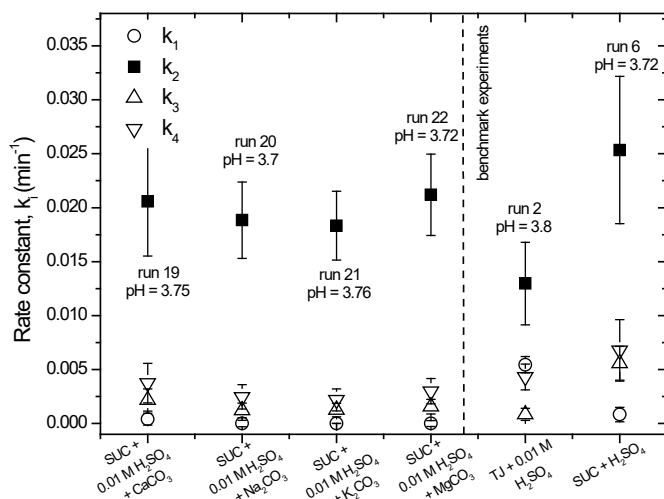


Figure 9. Rate constants for relevant reactions during SUC hydrolysis in the presence of carbonate salts.

6.3.3.3.2 Effects of chloride salts

Four experiments (Table 3, runs 23 – 26) were performed with calcium, sodium, potassium and magnesium chlorides in the presence of sulfuric acid (0.01 M). The initial pH of solutions were between 1.93 and 1.98. The concentration-time profiles of these experiments are given in Figure 10, while the main kinetic constants are shown in Figure 11. As the pH is shown to affect the rates considerably when the pH is below 2, the experimental data are compared with SUC and thick juice experiments at the same pH (1.8–1.9) instead of the benchmark experiments (pH 3.8).

The concentration-time profiles shown in Figure 10 are very similar to those of the pure SUC hydrolysis reaction (0.01 M H_2SO_4 catalyst at initial pH of 1.8), implying only a minor effect of the addition of chloride salts. This is confirmed by comparing the relevant kinetic constants (Figure 11) which shows that the kinetic constants are similar to those for pure SUC. The only exception is KCl, which shows lower values for particularly k_2 and k_4 . This finding implies that this cation in particular may have an effect of the rate of these reactions, though later we will show that the effect of specifically sulfate anions is by far more pronounced (*vide infra*).

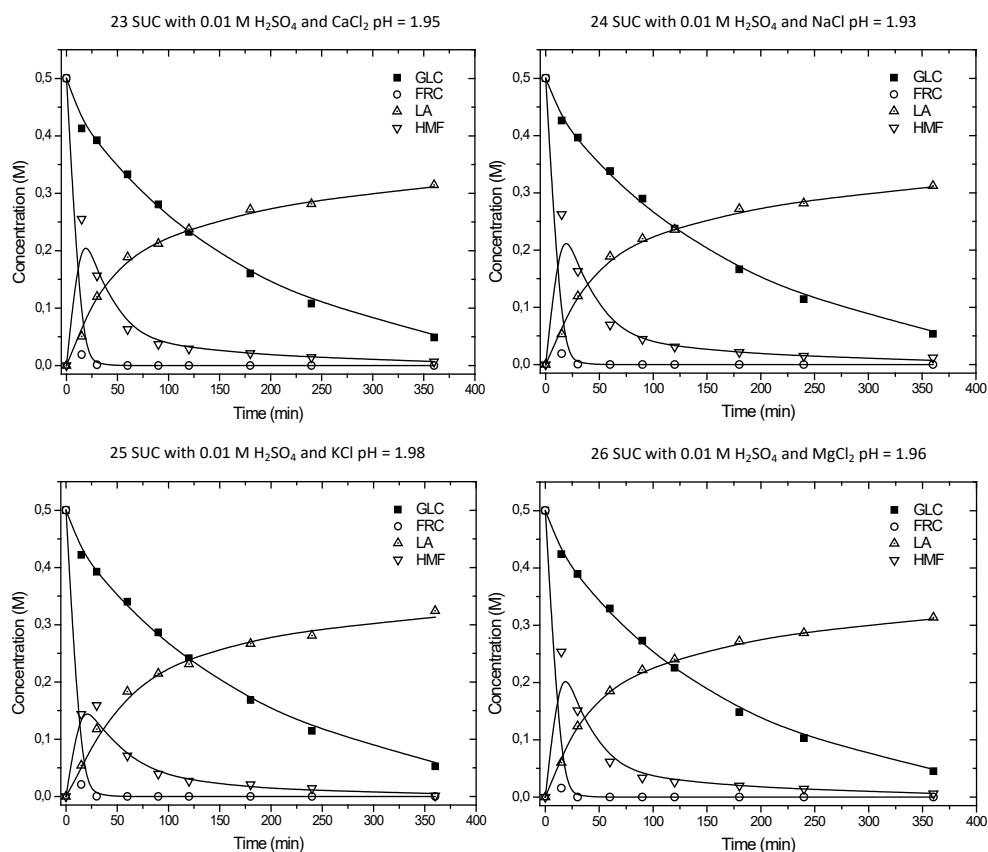


Figure 10. Concentration-time profiles for SUC hydrolysis in the presence of chloride salts. Reaction condition: $C_{\text{SUC},0} = 0.5 \text{ M}$, $0.01 \text{ M H}_2\text{SO}_4$, $T = 180^\circ \text{C}$. Solid lines represent model values. Numbers above the graphs correspond to run numbers in Table 3.

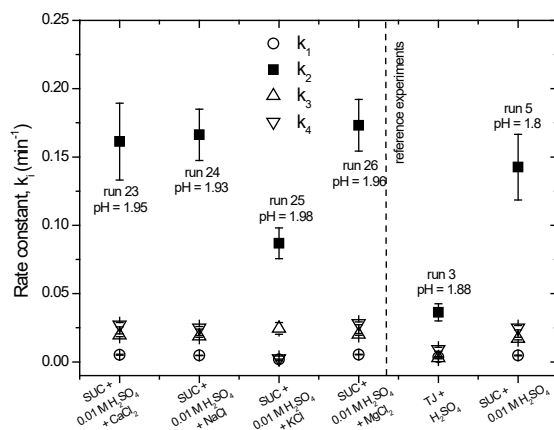


Figure 11. Rate constants for of relevant reactions during SUC hydrolysis in the presence of chloride salts.

6.3.3.3.3 Effects of sulfate salts

The experiments with carbonate and chloride salts did not reveal any effect of the cations on the rates of the reaction. As such, the full range of cations was not explored and only Na and K sulfate were tested. Experiments were performed at 180°C, with 0.01 M salt and 0.01 M sulfuric acid concentrations, leading to initial pH values of 1.8 and 1.98 (Table 3, experiments 30 and 33). The concentration-time profiles of these experiments are given in Figure 12, while the main kinetic constants are given in Figure 13. In the latter figure, the kinetic constants for experiments with thick juice and SUC at pH 1.8 (instead of the benchmark) are provided to avoid interference with pH effects.

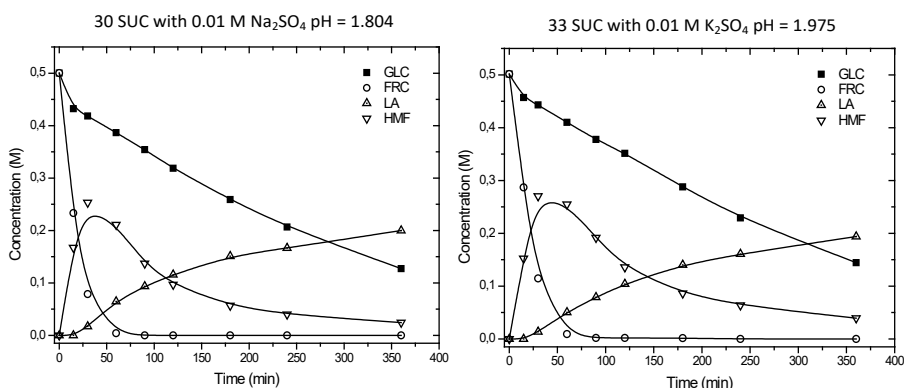


Figure 12. Concentration-time profiles of SUC hydrolysis in the presence of sulfate salts. Reaction conditions: $C_{\text{SUC},0} = 0.5 \text{ M}$, $0.01 \text{ M H}_2\text{SO}_4$, $T = 180^\circ\text{C}$. Solid lines represent model values. Numbers above the graphs correspond to run numbers in Table 3.

The experimental data in Figure 13 reveal that the sulfate anions indeed have a major effect on the rate of the major reactions involving HMF. While the rate constant k_1 remained similar, and a noticeable decrease was observed for k_3 and k_4 , and particularly k_2 . The rate constant k_2 has reduced four-fold when comparing the experiments with pure SUC with those in the presence of sulfate anions. Of relevance is also the observation that the actual rate constants are now very close to those found for thick juice, a very good indication that particularly the presence of sulfate ions in the thick juice causes the major difference in performance for HMF synthesis compared to pure SUC. In addition, and in line with the chloride and carbonate experiments, is the observation that cation effects are absent, except for a small effect of K^+ (*vide supra*). As such, cation effects are much smaller than sulfate effects and do not play a major role in the reaction rates for the individual reactions.

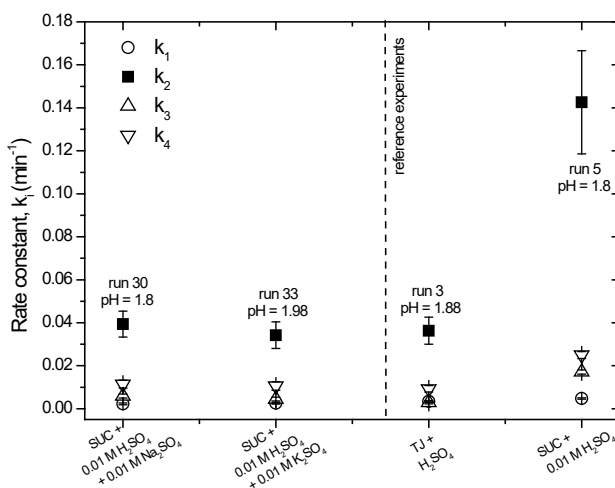


Figure 13. Rate constants for relevant reactions during SUC hydrolysis in the presence of sulfate salts.

To probe the effects of the concentration of the sulfate salts, additional experiments were performed with other Na_2SO_4 concentrations. As such, three Na_2SO_4 concentrations were tested (0.01, 0.05 and 0.1 M, 0.5 M SUC, 0.01 M sulfuric acid, Table 3 run 30 – 32). The initial pH values for these experiments were depending on the sulfate concentration and were at 1.8, 2.18 and 2.29 respectively. The concentration-time profiles obtained from these experiments are presented in Figure 14, and relevant kinetic constants are given in Figure 15. The data in the latter figure show that the values of the kinetic constants are depending on the sulfate concentrations, with higher sulfate concentrations leading to lower values of $k_2 - k_4$. However, this statement is not necessary true as also the pH of the solutions is a function of the sulfate concentrations, with higher concentrations leading to higher pH values (from 1.8 at 0.01 M Na_2SO_4 to 2.3 at 0.01 M Na_2SO_4). Though this trends, caused by buffering effects, seems relatively small, the rate constants in this pH regime are a function of the pH, see Figure 5 for details.

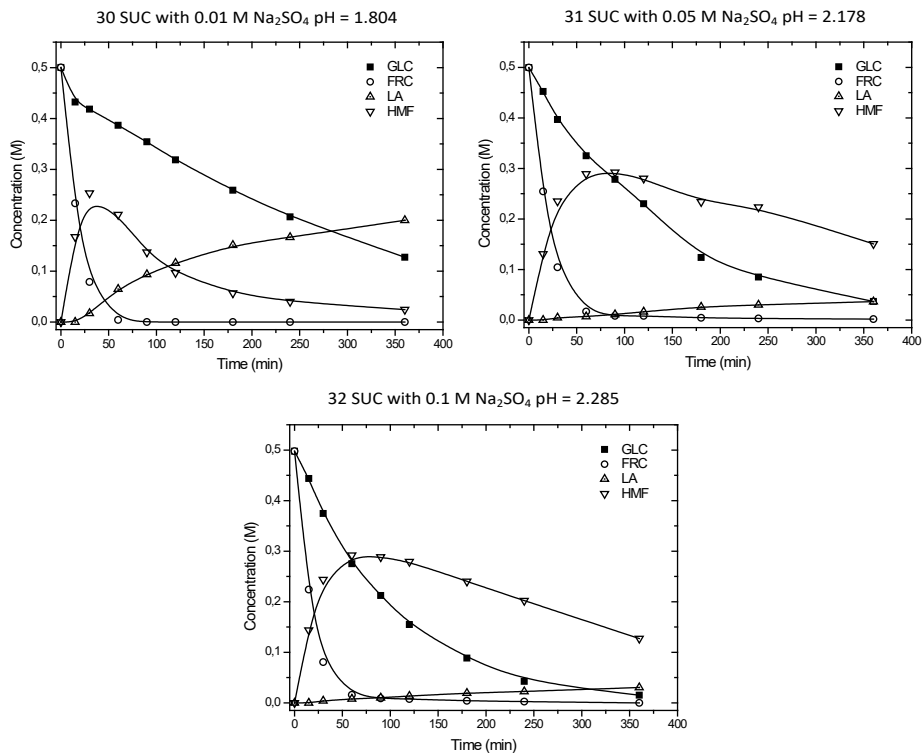


Figure 14. Concentration-time profiles of SUC hydrolysis in the presence of sulfate salts at different concentration. Reaction conditions: $C_{\text{SUC},0} = 0.5 \text{ M}$, $0.01 \text{ M H}_2\text{SO}_4$, $T = 180^\circ\text{C}$. Solid lines represent model values. Numbers above the graphs correspond to run numbers in Table 3.

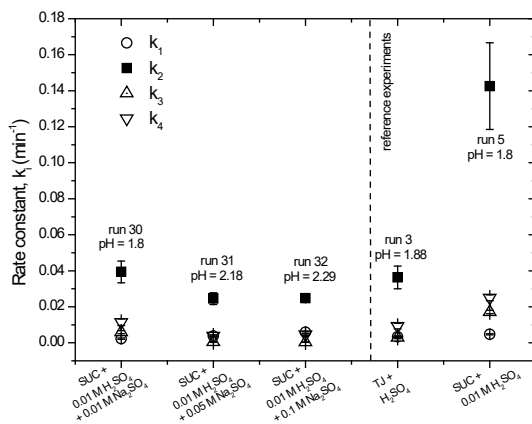


Figure15. Rate constants for relevant reactions during SUC hydrolysis at different concentrations of Na_2SO_4 .

6.3.4. Discussion

The study reported in this manuscript indicates that the main rate constants for HMF reactions in the reaction network ($k_2 - k_4$ with the exception of k_1) are a function of the pH of the solution, whereas the presence of salts (< 0.01 M) in the form of anions like carbonates, chlorides and cations like Na^+ , K^+ , Ca^{2+} , Mg^{2+} , have no or a small (K^+) effect. The only exception are sulfate ions, which lead to a considerable reduction in the relevant kinetic constants. This remarkable observation may be due to a number of effects. It is possible that it is related to the $\text{H}_2\text{SO}_4/\text{SO}_4^{2-}$ couple, which is a known buffer and will affect the pH development during a batch reaction. In the case of reactions with sulfuric acid only, significant amounts of LA and formic acid are formed (Figure 1), which will have an effect on the pH of the reaction mixture. In the presence of SO_4^{2-} , buffering effects will occur and a more constant pH during reaction is expected, which likely affects the reaction rates.

Another explanation could be a specific involvement of the sulfate anion on certain reactions within the network. As the rates for the relevant reactions involving HMF are reduced in the presence of sulfate anions, it is well possible that intermediate products in the reactions are stabilized by the formation of sulfates [24], due to reactions of the sulfate anion with mono-alcohol (hydroxyl) groups present in the reactants and intermediates. Further studies with, for instance, other strong acids (HCl, sulfonic acids) in combination with sulfate anions, outside the scope of the current study, will be required to draw conclusions.

The kinetic modeling activities also allow for the determination of those conditions where the yield of HMF is at its maximum and at which batch time this maximum occurs. Details regarding the calculations are given in the Supporting Information, and the results of the calculations are given in Table 3 and Table S2 (Supporting Information). The highest modeled yield was 34%, obtained for SUC using sulfuric acid (0.01 M) in combination with Na_2SO_4 (0.05 M), which is considerably higher than for an experiment with SUC and sulfuric acid only (0.01 M, 30%). However, the higher yield is obtained at longer batch times (85 min versus 12 min) due to the negative effect of sulfates on the relevant reaction rates (*vide supra*).

This study also has clearly proven that major differences in reactivity for HMF synthesis exist between thick juice and pure SUC. As speculated already earlier, this is mainly due to the presence of impurities present in the thick juice. It is now evident that neither the organic acids, nor the cations in the thick juice are the major cause of these differences, but that it is particularly related to the presence of sulfate anions. The results in this study are also in agreement with our previous research, revealing that thick juice showed better HMF selectivity compared to pure SUC at low pH albeit at lower reaction temperature (150 °C). Here, it was also shown that the addition of sulfate ions to the solutions has a positive effect. However, the use of higher sulfate concentrations (up to 0.3 mg mL⁻¹) did not lead to improved HMF selectivities, likely due to rate enhancement of undesired side reactions [14].

6.4. CONCLUSIONS

A model study using SUC, either pure or in the presence of impurities (organic acids, salts) known to be present in thick juice, was performed using water as the solvent and sulfuric acid as the catalyst. The experimental data, supported by kinetic modeling, show that the rates of the individual reactions in the network are strongly affected by the pH of the solutions. Two regimes were observed, one at a pH below 2, in which Brønsted acidity likely plays a major role, and one in the range between 2 and 11.2, where the rates of the main reactions were considerably lower. By carefully taking into account these pH effects, the effects of organic acids and a range of salts with potassium, sodium, calcium and magnesium as the cations and carbonates, chlorides and sulfates as the anions, on the individual reaction rates in the network could be assessed. It was shown that particularly the presence of salts with sulfate anions at the level present in thick juice have a major positive effect on HMF yields as these seem to stabilize the product in solution and are thus responsible for differences observed between this feedstock and pure SUC. The results confirm that the impurities in the thick juice have a positive impact on its conversion to HMF. It also supports our previous suggestion [14] that it is a very attractive feedstock for HMF synthesis as it is expected to be a significantly cheaper feed than refined SUC.

ACKNOWLEDGEMENT

The authors kindly thank Erik van Hellemond, Olaf van Baal and Marilia Foukaraki from Suiker Unie R&D for providing the thick juice sample and useful discussions. Maarten Vervoort is acknowledged for providing the glass laboratory equipment. Léon Rohrbach is acknowledged for support with product analysis. R.M. Abdilla-Santes also kindly thanks the Directorate General of Higher Education, Ministry of Education and Culture, Indonesia for funding of her PhD program.

REFERENCES

- [1] A. Mukherjee, M. Dumont and V. Raghavan. Sustainable Production of Hydroxymethylfurfural and Levulinic Acid: Challenges and Opportunities. *Biomass and Bioenergy*, 72 (2015), pp.143-183.
- [2] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr, J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski. The Path Forward for Biofuels and Biomaterials. *Science*, 311 (2006), pp.484-489.
- [3] Y. Román-Leshkov, C.J. Barrett, Z.Y. Liu and J.A. Dumesic. Production of Dimethylfuran for Liquid Fuels from Biomass-Derived Carbohydrates. *Nature*, 447 (2007), pp.982.
- [4] H.T. Kreissl, K. Nakagawa, Y. Peng, Y. Koito, J. Zheng and S.C.E. Tsang. Niobium Oxides: Correlation of Acidity with Structure and Catalytic Performance in Sucrose Conversion to 5-hydroxymethylfurfural. *Journal of Catalysis*, 338 (2016), pp.329-339.

- [5] J. Lange, E. van der Heide, J. van Buijtenen and R. Price. Furfural—A Promising Platform for Lignocellulosic Biofuels. *ChemSusChem*, 5 (2012), pp.150-166.
- [6] R. van Putten, van der Waal, Jan C, E. De Jong, C.B. Rasrendra, H.J. Heeres and J.G. de Vries. Hydroxymethylfurfural, A versatile Platform Chemical Made from Renewable Resources. *Chemical Reviews*, 113 (2013), pp.1499-1597.
- [7] G. Jeong, C.H. Ra, Y. Hong, J.K. Kim, I. Kong, S. Kim and D. Park. Conversion of Red-Algae *Gracilaria verrucosa* to Sugars, Levulinic Acid and 5-Hydroxymethylfurfural. *Bioprocess and Biosystems Engineering*, 38 (2015), pp.207-217.
- [8] S.P. Teong, G. Yi and Y. Zhang. Hydroxymethylfurfural Production from Bioresources: Past, Present and Future. *Green Chemistry*, 16 (2014), pp.2015-2026.
- [9] J.N. Tan-Soetedjo, van de Bovenkamp, Henk H, R.M. Abdilla, C.B. Rasrendra, J. van Ginkel and H.J. Heeres. Experimental and Kinetic Modeling Studies on the Conversion of Sucrose to Levulinic Acid and 5-Hydroxymethylfurfural using Sulfuric Acid in Water. *Industrial & Engineering Chemistry Research*, 56, 45 (2017), pp. 13228-13239.
- [10] T. Wang, M.W. Nolte and B.H. Shanks. Catalytic Dehydration of C6 Carbohydrates for the Production of Hydroxymethylfurfural (HMF) As a Versatile Platform Chemical. *Green Chemistry*, 16 (2014), pp.548-572.
- [11] M.S. Feather and J.F. Harris. On the Mechanism of Conversion of Hexoses into 5-(hydroxymethyl)-2-Furaldehyde and Metasaccharinic Acid. *Carbohydrate Research*, 15 (1970), pp.304-309.
- [12] D.W. Harris and M.S. Feather. Evidence for A C-2→ C-1 Intramolecular Hydrogen-Transfer During the Acid-Catalyzed Isomerization of D-Glucose to D-Fructose. *Carbohydrate Research*, 30 (1973), pp.359-365.
- [13] D.W. Harris and M.S. Feather. Intramolecular Carbon-2. Far. Carbon-1 Hydrogen Transfer Reactions During the Conversion of Aldoses to 2-Furaldehydes. *The Journal of Organic Chemistry*, 39 (1974), pp.724-725.
- [14] R.M. Abdilla-Santes, W. Guo, P.C. Bruijninx, J. Yue, P.J. Deuss and H.J. Heeres. High yield 5-hydroxymethylfurfural Synthesis from Crude Sugar Beet Juice in a Biphasic Microreactor. *ChemSusChem*, 12, 18 (2019), pp. 4304-4312.
- [15] L. Tan, Z. Sun, S. Okamoto, M. Takaki, Y. Tang, S. Morimura and K. Kida. Production of Ethanol from Raw Juice and Thick Juice of Sugar Beet by Continuous Ethanol Fermentation with Flocculating Yeast Strain KF-7. *Biomass and Bioenergy*, 81 (2015), pp.265-272.
- [16] I. van Zandvoort. Towards the Valorization of Humin By-Products: Characterization, Solubilization and Catalysis (Doctoral Dissertation), Utrecht (2015).
- [17] B. Girisuta, L.P.B.M. Janssen and H.J. Heeres. Green chemicals: A kinetic study on the Conversion of Glucose to Levulinic Acid. *Chemical Engineering Research and Design*, 84 (2006), pp.339-349.
- [18] H.M. Pilath, M.R. Nimlos, A. Mittal, M.E. Himmel and D.K. Johnson. Glucose Reversion Reaction Kinetics. *Journal of Agricultural and Food Chemistry*, 58 (2010), pp.6131-6140.
- [19] A.T. Pedersen, R. Ringborg, T. Grotkjær, S. Pedersen and J.M. Woodley. Synthesis of 5-Hydroxymethylfurfural (HMF) by Acid Catalyzed Dehydration of Glucose–Fructose Mixtures. *Chemical Engineering Journal*, 273 (2015), pp.455-464.
- [20] B.F. Kuster and van der Baan, Hessel S. The Influence of the Initial and Catalyst Concentrations on the Dehydration of D-Fructose. *Carbohydrate Research*, 54 (1977), pp.165-176.
- [21] X. Zhang, B.B. Hewetson and N.S. Mosier. Kinetics of Maleic Acid and Aluminum Chloride Catalyzed Dehydration and Degradation of Glucose. *Energy & Fuels*, 29 (2015), pp.2387-2393.
- [22] X. Wu, J. Fu and X. Lu. Hydrothermal Decomposition of Glucose and Fructose with Inorganic and Organic Potassium Salts. *Bioresource Technology*, 119 (2012), pp. 48-54.
- [23] C. García-Sancho, I. Fúnez-Núñez, R. Moreno-Tost, J. Santamaría-González, E. Pérez-Inestrosa, J.L.G. Fierro and P. Maireles-Torres. Beneficial Effects of Calcium Chloride on Glucose Dehydration to 5-Hydroxymethylfurfural in the Presence of Alumina As Catalyst. *Applied Catalysis B: Environmental*, 206 (2017), pp. 617-625.
- [24] R.A. Al-Horani and U.R. Desai. Chemical Sulfation of Small Molecules - Advances and Challenges. *Tetrahedron*, 66 (2010), pp.2907-2918.

SUPPORTING INFORMATION FOR CHAPTER 6

Determination of SUC concentration in thick juice

The specific rotation of SUC ($[\alpha]$) is determined using the following equation:

$$[\alpha]_D^{25} = \frac{\alpha_{\text{obs}}}{c \times l} \quad (\text{S1})$$

Where:

$[\alpha]_D^{25}$ = specific rotation of the compound at 25 °C using the D-line of the sodium lamp ($\lambda=589.3$ nm)

α_{obs} = observed optical rotation

c = the concentration of the solution in grams per milliliter

l = the length of the cell tube in decimeters

Figures

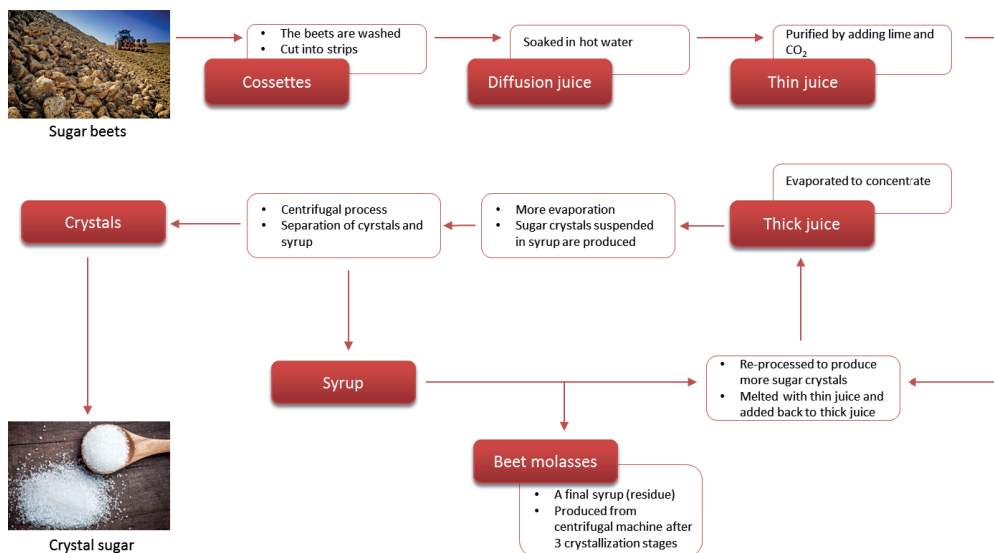


Figure S1. Typical flow scheme of a sugar beet processing unit.

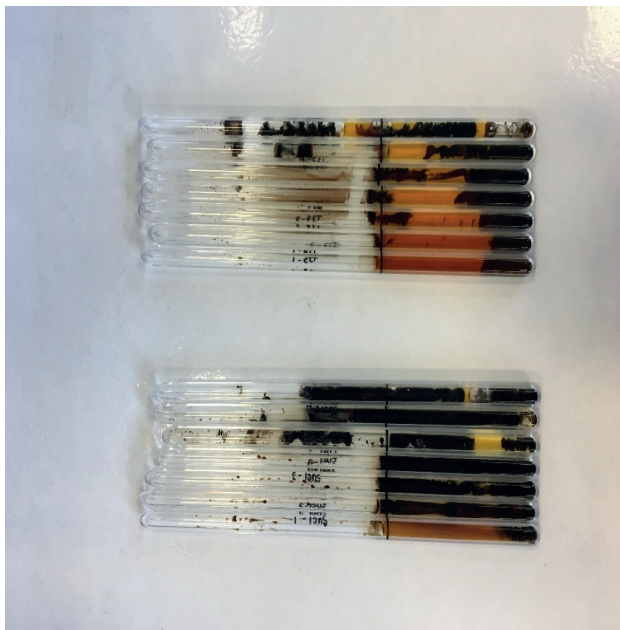


Figure S2. Visual appearance of thick juice (left) and pure SUC reactions at $C_{\text{SUC}(\text{equiv}),0} = 0.5 \text{ M}$, $C_{\text{H}_2\text{SO}_4} = 0.01 \text{ M}$, $T = 180^\circ\text{C}$. Initial pH = 3.8 and 1.8 for thick juice and pure SUC, respectively.

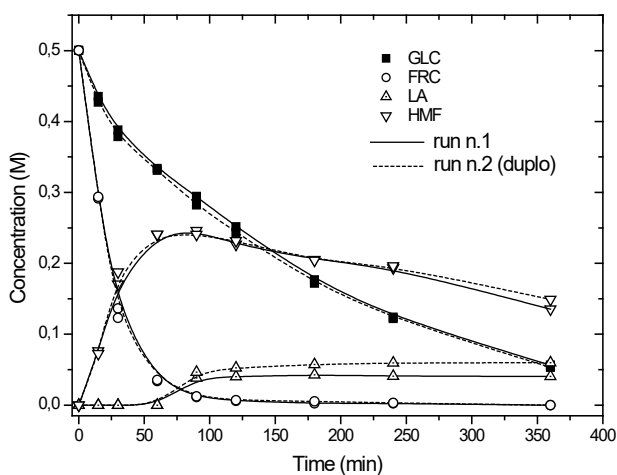


Figure S3. Reproducibility test for a representative thick juice experiment. Reaction condition : $C_{\text{SUC}(\text{equiv}),0} = 0.5 \text{ M}$, $C_{\text{H}_2\text{SO}_4} = 0.01 \text{ M}$, $T = 180^\circ\text{C}$. Lines are for illustrative purposes only.

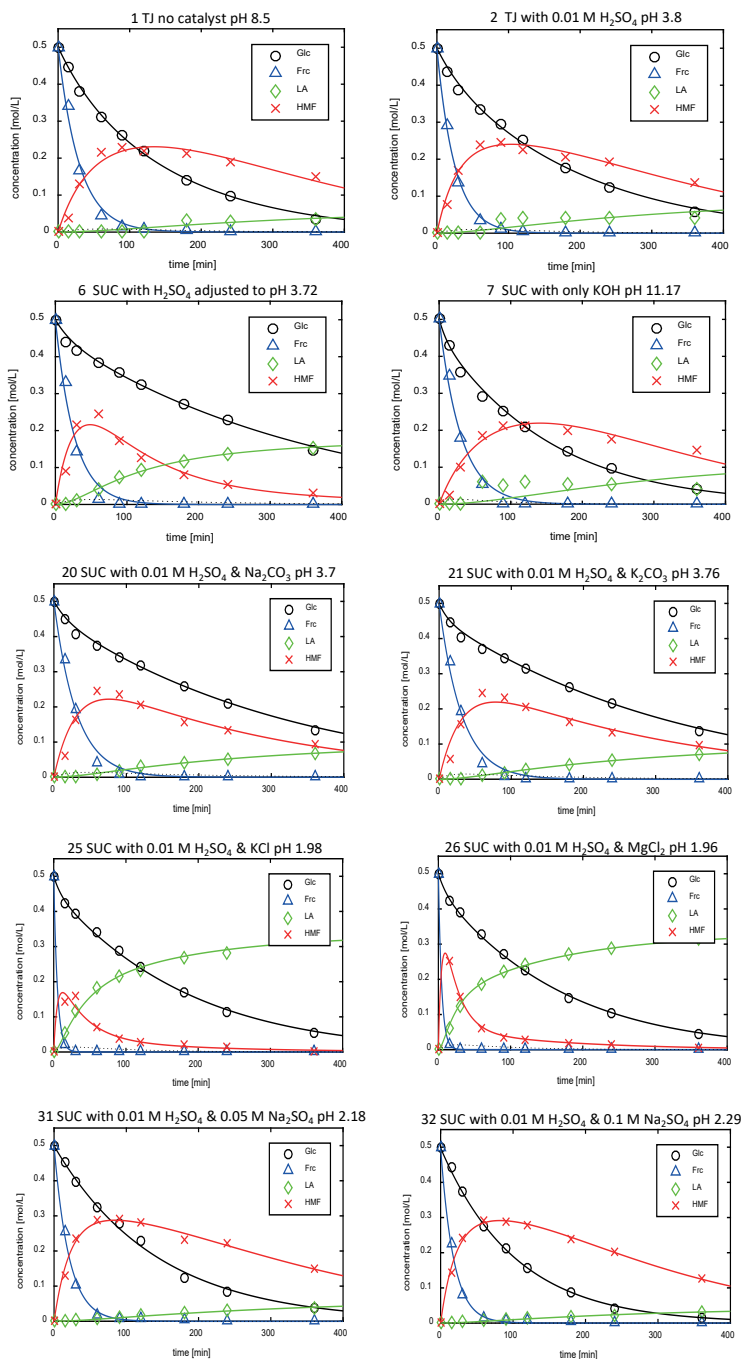
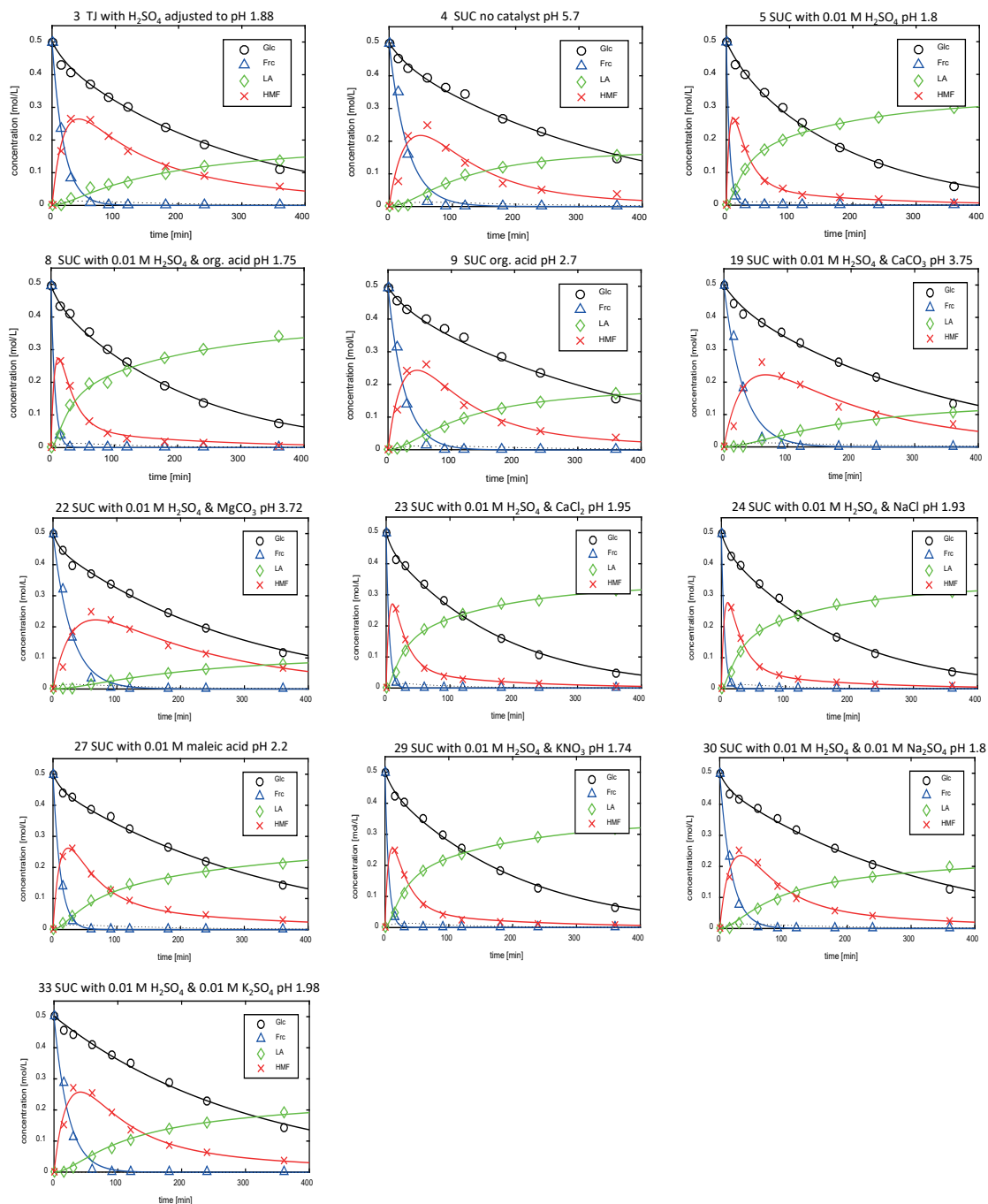


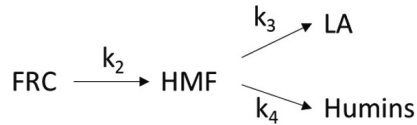
Figure S4. Concentration-time profiles for all experiment described in Table 4. Solid lines represent the model values. Numbers above the graphs correspond to run numbers in Table 3.

HMF from Sugar Beet Juice: kinetic and modeling studies



Modeling of maximum HMF yields and associated batchtimes

The maximum HMF yields and the associated batch times can be predicted from the obtained rate constants (k_i) acquired from the kinetic modeling, following the simplified reactions scheme below (Levenspiel, 1999, p. 55) [1]:



Scheme S1. Simplified reaction scheme for FRC conversion to HMF, LA and humins.

$$\frac{C_{\text{HMF,max}}}{C_{A,0}} = \left(\frac{k_2}{k_3 + k_4} \right)^{\frac{k_3 + k_4}{k_3 + k_4 - k_2}} \quad (\text{S1})$$

$$t_{[\text{HMF}]_{\text{max}}} = \frac{1}{k_{\log \text{ mean}}} = \frac{\ln \left(\frac{k_3 + k_4}{k_2} \right)}{k_3 + k_4 - k_2} \quad (\text{S2})$$

The modeled maximum HMF yield and associated batch times for all experiments are given in Table S2.

Tables

Table S1. Selected examples of HMF and/or LA synthesis from SUC in aqueous systems.

No.	SUC conc.	Cat.	Cat. Conc.	Time	Solvent(s)	T (°C)	HMF yield ^(a) (mol%)	LA yield ^(a) (mol%)	Ref.
1	1.17 M	HCl	2 M	24 h	Water	100	n.a.	21-22	[2]
2	0.86 M	HCl	2 M	1 h	Water	162	n.a.	42-43	[3]
3	0.18 M	HCl	3 M	16 h	Water	125	n.a.	60 ^(b)	[4]
4	0.29 M	HCl	6 M	5 h	Water	108	n.a.	62	[5]
5	0.33 M	HCl	3.84 M	1 h	Water	98	n.a.	50 ^(b)	[6]
6	0.05 M	H ₂ SO ₄	0.05 M		Water	140	22	n.a.	[7]
7	0.66 M	H ₂ SO ₄	1.80 M	8 h	Water	140	n.a.	40-50 ^(b)	[8]
8	0.05 M	H ₂ SO ₄	0.001 M	32 s	Water	250 (345 bar)	25	n.a.	[9]
9	0.18 M	H ₂ SO ₄	1 M	16 h	Water	125	n.a.	42 ^(b)	[4]
10	0.18 M	HBr	1 M	16 h	Water	125	n.a.	70 ^(b)	[4]
11	0.2 M	Acetic acid	0.6 M	n.a. ^(c)	Water	250-260	40 ^(b)	n.a.	[10]
12	25 wt%	Oxalic acid	0.03 M	2.5 h	Water	145, 15 min then 125	27	n.a.	[11]
13	23 wt%	Oxalic acid	0.23 wt%	3 h	Water	200	25	n.a.	[12]
14	18 wt%	Nafion NR50	44 wt%	40 h	Water	140	n.a.	35 ^(b)	[8]
15	12.7 wt%	Niobium phosphate	53% w/w	4 h	Water	100	14	n.a.	[13]
16	19 wt%	Pyridine: H ₃ PO ₄ 5:3 n/n	5%:3% n/n	30 min ^(d)	Water:dioxane 1:1 v/v	220-229	44	n.a.	[14]

(a) Yields are based on monosaccharide concentration; (b) Not clear whether yields are based on SUC or monosaccharide concentration or in mol% or wt%; (c) residence time in continuous reactor is not specified; (d) reaction time excluding 32 min pre-heating.

Table S2. Overview of experimental and kinetic modeling data ^(a).

Run	Starting material	Initial pH	Concentration H_2SO_4	Additives
1	Thick Juice	8.5	-	-
2 ^(b)	Thick Juice	3.8	0.01 M	-
3	Thick Juice	1.88	pH adjusted with H_2SO_4	-
4	SUC	5.7	-	-
5	SUC	1.8	0.01 M	-
6 ^(b)	SUC	3.72	pH adjusted with H_2SO_4	-
7	SUC	11.17	pH adjusted with KOH	-
8 ^(c)	SUC	1.75	0.01 M	Citric, malic, oxalic, lactic, acetic acid and PCA
9 ^(c)	SUC	2.7	-	
19	SUC	3.75	0.01 M	1 mg mL ⁻¹ CaCO ₃ ^(d)
20	SUC	3.7	0.01 M	1 mg mL ⁻¹ Na ₂ CO ₃ ^(d)
21	SUC	3.76	0.01 M	1 mg mL ⁻¹ K ₂ CO ₃ ^(d)
22	SUC	3.72	0.01 M	1 mg mL ⁻¹ MgCO ₃ ^(d)
23	SUC	1.95	0.01 M	1 mg mL ⁻¹ CaCl ₂ ^(d)
24	SUC	1.93	0.01 M	1 mg mL ⁻¹ NaCl
25	SUC	1.98	0.01 M	1 mg mL ⁻¹ KCl
26	SUC	1.96	0.01 M	1 mg mL ⁻¹ MgCl ₂ ^(d)
27	SUC	2.2	-	0.01 M Maleic acid
29	SUC	1.742	0.01 M	0.006 M KNO ₃
30	SUC	1.804	0.01 M	0.01 M Na ₂ SO ₄
31	SUC	2.178	0.01 M	0.05 M Na ₂ SO ₄
32	SUC	2.285	0.01 M	0.1 M Na ₂ SO ₄
33	SUC	1.975	0.01 M	0.01 M K ₂ SO ₄

(a) All of the experiment runs were done at $T = 180^\circ\text{C}$ with initial feed concentration, $C_{\text{SUC}(\text{equiv})_0} = 0.5 \text{ M}$. (b) Benchmark experiment as described in Figure 1. (c) The added amount based on the value reported on the literature (Table 1) for thick juice. (d) Concentration is about 0.01 M. (e) in $\text{M}^{-1} \text{ min}^{-1}$. (f) Simulated based on the kinetic model and calculated based on FRC only.

k_1	k_2	rate constant, k_i (min^{-1})					$Y_{\text{HMF}} \text{ max}^{(f)}$ (mol%)	$t \text{ at } C_{\text{HMF}} \text{ max}^{(f)}$ (min)
		k_3	k_4	k_7	k_8	$k_9^{(e)}$		
0.0055	0.0077	0.0006	0.0044	0.0016	0.0260	1.2440	22.6	161
0.0046	0.0144	0.0009	0.0049	0.0013	0.0257	1.7317	27.2	106
0.0036	0.0364	0.0029	0.0097	0.0006	0.0175	0.7265	28.5	45
0.0009	0.0246	0.0043	0.0073	0.0024	0.0103	1.2503	25.5	58
0.0045	0.1427	0.0171	0.0241	0.0013	0.0448	0.1828	30.2	12
0.0009	0.0254	0.0043	0.0069	0.0025	0.0121	0.8061	26.2	58
0.0069	0.0033	0.0012	0.0045	0.0007	0.0292	2.6373	13.7	228
0.0053	0.1365	0.0180	0.0262	4.1E-05	0.0284	0.6941	29.2	12
0.0014	0.0300	0.0042	0.0084	0.0016	0.0087	0.6682	26.6	50
0.0004	0.0206	0.0022	0.0038	0.0031	0.0126	0.0024	30.2	85
1.8E-06	0.0188	0.0012	0.0025	0.0036	0.0133	0.0037	33.6	108
3.5E-10	0.0183	0.0012	0.0022	0.0035	0.0136	0.0057	34.0	112
1.6E-07	0.0212	0.0016	0.0030	0.0040	0.0140	0.0074	32.8	92
0.0052	0.1613	0.0195	0.0273	0.0011	0.0464	0.0084	30.2	11
0.0048	0.1662	0.0187	0.0250	0.0014	0.0459	0.0071	31.0	11
0.0018	0.0869	0.0245	0.0025	0.0043	0.1108	0.0072	29.5	19
0.0054	0.1732	0.0201	0.0283	0.0013	0.0484	0.0063	30.5	10
0.0033	0.0641	0.0068	0.0143	0.0001	0.0225	0.0058	29.0	26
0.0041	0.1297	0.0189	0.0215	0.0015	0.0469	0.0054	29.5	13
0.0023	0.0394	0.0059	0.0115	0.0014	0.0158	0.0055	26.2	37
0.0038	0.0246	0.0005	0.0039	0.0032	0.0236	1.5E-06	34.4	85
0.0059	0.0248	0.0004	0.0046	0.0038	0.0309	2.3E-14	33.4	81
0.0026	0.0342	0.0045	0.0106	0.0007	0.0100	5.3E-09	26.2	43

References for the supporting information

- [1] O. Levenspiel. *Chemical Reaction Engineering*. ACS Publications, 1999.
- [2] B. McKenzie. Levulinic Acid. *Organic Syntheses*, (1929), pp.50-50.
- [3] R.W. Thomas and H. Schuette. Studies on Levulinic Acid. I. Its Preparation from Carbohydrates by Digestion with Hydrochloric Acid Under Pressure. *Journal of the American Chemical Society*, 53 (1931), pp.2324-2328.
- [4] L.F. Wiggins. The Utilization of Sucrose. *Advances in Carbohydrate Chemistry*, 4 (1949), pp.293-336.
- [5] J. Dahlmann. Preparation of Levulinic Acid. *Chemische Berichte-Recueil*, 101 (1968), pp.4251-&.
- [6] V. Tarabanko, M.Y. Chernyak, S. Aralova and B. Kuznetsov. Kinetics of Levulinic Acid Formation from Carbohydrates at Moderate Temperatures. *Reaction Kinetics and Catalysis Letters*, 75 (2002), pp.117-126.
- [7] J.N. Tan-Soetedjo, van de Bovenkamp, Henk H, R.M. Abdilla, C.B. Rasrendra, J. van Ginkel and H.J. Heeres. Experimental and Kinetic Modeling Studies on the Conversion of Sucrose to Levulinic Acid and 5-Hydroxymethylfurfural using Sulfuric Acid in Water. *Industrial & Engineering Chemistry Research*, 56, 45 (2017), pp. 13228-13239.
- [8] H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L.T. Mika and I.T. Horváth. Integration of Homogeneous and Heterogeneous Catalytic Processes for A Multi-Step Conversion of Biomass: from Sucrose to Levulinic Acid, γ -Valerolactone, 1, 4-Pentanediol, 2-Methyl-Tetrahydrofuran, and Alkanes. *Topics in Catalysis*, 48 (2008), pp.49-54.
- [9] M.J. Antal, W.S. Mok and G.N. Richards. Mechanism of Formation of 5-(Hydroxymethyl)-2-Furaldehyde from D-Fructose and Sucrose. *Carbohydrate Research*, 199 (1990), pp.91-109.
- [10] V. Tarabanko, M.Y. Chernyak, I. Nepomnyashchii and M. Smirnova. High Temperature 5-Hydroxymethylfurfural Synthesis in A Flow Reactor. *Chem Sustain Dev*, 14 (2006), pp.49-53.
- [11] W. Haworth and W. Jones. 183. The Conversion of Sucrose into Furan Compounds. Part I. 5-Hydroxymethylfurfuraldehyde and Some Derivatives. *Journal of the Chemical Society (Resumed)*, (1944), pp.667-670.
- [12] J.A. Middendorp. Sur L'oxyméthylfurfuro. *Recueil des Travaux Chimiques des Pays-Bas et de la Belgique*, 38 (1919), pp.1-71.
- [13] C. Carlini, M. Giuttari, A.M.R. Galletti, G. Sbrana, T. Armaroli and G. Busca. Selective Saccharides Dehydration to 5-Hydroxymethyl-2-Furaldehyde by Heterogeneous Niobium Catalysts. *Applied Catalysis A: General*, 183 (1999), pp.295-302.
- [14] M. Mednick. The Acid-Base-Catalyzed Conversion of Aldohexose into 5-(Hydroxymethyl)-2-Furfural. *The Journal of Organic Chemistry*, 27 (1962), pp.398-403.

A

Summary
Samenvatting
Acknowledgement
List of publications

Summary

The ever increasing global consumption of fossil resources, environmental concerns related to high CO₂ emissions and diminishing petroleum reserves, have boosted research on renewable feedstocks. In the last two decades, the “biobased economy” concept has been proposed as an alternative to the current fossil based economy. It involves the production of heat, power, transportation fuels and chemicals from renewable resources like biomass with a minimum of waste, resource optimization and low greenhouse gas (GHG) emissions. With an estimated annual global production of 170x10⁹ ton, biomass is considered as the only green carbon resource available in high enough quantities to (partly) substitute fossil resources. One of the important elements in a biobased economy is the “biorefinery concept”. It involves separation of the biomass into fractions that are converted using dedicated biological, (bio)-chemical, physical and/or thermal processing. It aims to convert low-value biomass into high value (industrial) intermediates and final products (e.g. fuels, chemicals, material, energy) using sustainable and integrated processes. There are strong analogies between a biorefinery and conventional crude oil refinery regarding operation (not in feeds) and nowadays, biorefineries are strongly advocated.

Although the main driver for the transition from fossil based refineries to biorefineries is the need for sustainable heat, power and transportation fuels, the production of biobased chemicals is also of high interest. Biobased chemicals with a high derivatization potential due to the presence of multiple functional groups are often addressed as platform chemicals. In the last two decades, the conversion of lignocellulosic (woody) biomass has received major interest. Lignocellulosic biomass contains about 30-60% cellulose and 20-40% hemicellulose, which are biopolymers containing C6 and C5 sugar units. A wide variety of platform chemicals can be obtained from sugars and among them, 5-hydroxymethylfurfural (HMF) is of our particular interest.

HMF has been identified as one of the top platform chemicals due to its high versatility. HMF contains both an aldehyde and an alcohol group and is typically obtained by the acid-catalyzed conversion of C6 sugars in water. Unfortunately, selectivity is an issue and significant amounts of byproducts such as levulinic acid (LA), formic acid and insolubles known as humins are formed. The commercial scale production of HMF is still in a stage of infancy, due to the high cost of production, associated with low yields, and difficulties with product separation. In water, D-fructose is the C6 sugar feed of choice as it gives a maximum HMF yield of around 55 mol%, whereas for D-glucose, the yield under similar conditions is less than 10 mol%. However, D-glucose is preferred in terms of feedstock price. Oligo- and polysaccharides, as well as lignocellulosic biomass, are potentially interesting feedstocks for HMF and could offer substantial economic and environmental benefits. As such, the identification of alternative cost-efficient feeds for HMF synthesis is of high interest. An ideal feed should be inexpensive, relatively abundant and require minimum or even no pre-treatment before conversion. In this

thesis, experimental studies on the use of two alternative sugar sources namely **pyrolytic sugars** and **thick juice**, for the synthesis of platform chemicals via chemo-catalytic routes are described.

Pyrolytic sugar is the commonly used name for the water soluble fraction of pyrolysis liquids, which are produced from biomass by a thermal conversion route known as fast pyrolysis (450–600 °C, 1–2s, in the absence of oxygen). Fast pyrolysis is as a promising and versatile technology to depolymerize and concentrate sugars from lignocellulosic biomass. Pyrolysis liquids contain low molecular weight sugars like 1,6-anhydro- β -D-glucopyranose (commonly known as levoglucosan), 1,6-anhydro- β -D-glucose (cellobiosan) and sugar oligomers. Levoglucosan (LG) in particular, is an interesting source for glucose (GLC). Thick juice is an intermediate sugar stream in a conventional sugar beet plant and contains approximately 60–70% of sucrose (SUC), a dimeric sugar of fructose (FRC) and GLC.

The main objective of the research described in this thesis is the development of synthetic methodologies to convert both alternative feeds to biobased platform chemicals, with an emphasis on HMF. Experimental and kinetic modeling studies were performed, and the effects of process conditions and catalysts on HMF yield were investigated in detail. In some cases, the studies were performed on model components to reduce complexity. Chapter 2 to 4 report studies using pyrolytic sugars as the feed while Chapter 5 and 6 report studies using thick juice.

In **Chapter 2**, experimental and kinetic modeling studies on the conversion of LG, the major sugar in pyrolytic sugars, to GLC are described. As before mentioned, GLC is an important building block sugar which can be further converted to biobased chemicals, among others LA and HMF. Experiments were conducted in an aqueous-acidic medium using two Brønsted acids (sulfuric acid and acetic acid) as the catalysts under a wide range of conditions in a batch reactor (glass ampoule). The effects of the initial LG loading (0.1–1 M), sulfuric and acetic acid concentrations (0.05–0.5 M and 0.5–1 M, respectively), and reaction temperature (80–200°C) were determined. The highest GLC yields were obtained using sulfuric acid (98 mol%), whereas the yields were considerably lower for acetic acid (maximum 90 mol%) due to the formation of byproducts such as insoluble polymers (humins). Kinetic parameters were determined using a MATLAB optimization routine. A good agreement between experimental and model was obtained when assuming that the reaction is first order with respect to LG. The activation energies were 123.4 kJ mol⁻¹ and 120.9 kJ mol⁻¹ for sulfuric and acetic acid, respectively. The obtained kinetic parameters were then used to determine the optimum hydrolysis conditions for to convert LG into GLC.

The research described in Chapter 2 was extended to the use of a solid catalyst (Amberlyst 16) instead of sulfuric and acetic acid. Systematic studies in batch and in a continuous fixed bed reactor were performed, and the results are given in **Chapter 3**. Mass transfer limitations in this heterogenous catalytic system were carefully examined and accounted for in the kinetic modeling. In the batch setup, the effects of the reaction temperature (352–388 K), initial LG

intake ($100\text{--}1000\text{ mol m}^{-3}$), catalyst loading ($1\text{--}5\text{ wt\%}$), and stirring rate ($250\text{--}1000\text{ rpm}$) on GLC yield were determined. The highest GLC yield was $98.5\text{ mol\%}$ (at 388 K , $5\text{ wt\%}$ Amberlyst 16, $C_{\text{LG},0} = 500\text{ mol m}^{-3}$ at 500 rpm stirring rate and 60 min). From the batch data, relevant kinetic parameters were determined using a first order approach including diffusion limitations of LG inside the Amberlyst 16 particles. The activation energy was found to be $132.3 \pm 10.1\text{ kJ mol}^{-1}$. A good agreement between experiments and kinetic model was obtained, and the kinetic model was successfully applied to model the performance of the continuous setup. At a steady state in the continuous experiments, LG conversion ($73\text{ mol\%}$) and GLC selectivity were in line with the kinetic model obtained in the batch reactor. Catalyst stability appears to be good, as shown by the experiments in the continuous packed bed reactor for up to 30 h times on stream.

During the processing of pyrolytic sugars (e.g., hydrolysis and subsequent conversion processes), solid formation occurs to a significant extent. These insoluble polymer byproducts are known as humins or biochar. **Chapter 4** provides an experimental study on the (catalytic) pyrolysis and hydrotreatment of such humins with the aim to improve the techno-economic feasibility of pyrolytic sugar valorizations. For simplification, a model humin was made from a representative pyrolytic sugar by heating a sample under atmospheric pressure at $130\text{ }^{\circ}\text{C}$, for 22 h in the absence of an acid catalyst followed by water extraction at $100\text{ }^{\circ}\text{C}$ for 5 h . The insoluble residue obtained after water extraction was used as the model humin for further studies (termed as PS-humin). PS-humin was characterized by elemental analysis, GPC, TGA, HPLC, GC-MS, FT-IR, and NMR. In contrast to typical humins obtained from GLC and FRC conversions, PS-humin is soluble in typical organic solvents (DMSO, THF, IPA), allowing characterization by NMR and GPC. From the analyses, it appears that the humin is oligomeric in nature (M_w of about 900 g mol^{-1}), consisting of sugar and furanic fragments linked with among others (substituted) aliphatic, ester units and, in addition, phenolic fragments with methoxyl groups. PS-humin was used as a feed for catalytic pyrolysis and catalytic liquefaction experiments. Pyrolysis of the humin was carried out in an mg scale PTV-GC-MS unit at $550\text{ }^{\circ}\text{C}$ in the absence and presence of a H-ZSM-5-50 catalyst. Analyses show that low molecular weight aromatics (benzene-toluene-xylene-naphtalene-ethylbenzene, BTXNE) were formed in $4.5\text{ wt\%}$ yield on feed intake. The catalytic liquefaction reaction was studied in a batch autoclave reactor at $350\text{ }^{\circ}\text{C}$, for 4 h using isopropanol as both the solvent and hydrogen donor and a Pt/CeO₂ ($4.43\text{ wt\% Pt}$) catalyst. At optimized conditions, $80\text{ wt\%}$ conversion of the humin feed to a product oil was achieved. The product oil from the reaction was characterized in detail using advanced analytical techniques (e.g., GCxGC-FID) and showed that the product oil contains high amounts of phenolics and aromatics (ca. $22\text{ \%}$ based on GC detectables in product oil). These findings will have implications for the techno-economic viability of pyrolysis oil biorefineries, and show that potentially high value products can be obtained from humin type byproducts.

In **Chapter 5**, an experimental study on the conversion of thick juice (a crude SUC-rich intermediate in sugar refining) to HMF using sulfuric acid as the catalyst in a liquid-liquid system is described. The reactions were carried out in a batch reactor and in a continuous slug flow microreactor. Water was used as the reaction medium while methyl isobutyl ketone (MIBK) and 2-methyltetrahydrofuran (MTHF) were used as the organic extraction solvent. Addition of salts to the system to improve the partitioning of HMF was also considered. High selectivity and yields of > 90% (FRC based) for HMF were achieved in a biphasic reactor setup at 150°C using thick juice as the feed with H_2SO_4 as catalyst and MTHF as the bioderived extraction solvent. At these conditions, the conversion of GLC obtained by SUC inversion was limited to < 10 mol%, allowing its recovery for further use. Interestingly, comparative experiments with purified SUC led to only 84 mol% HMF selectivity at > 95 mol% FRC conversion, showing that the use of the crude feedstock is of high interest and opens a new avenue for more cost-effective HMF production.

In the last chapter (**Chapter 6**), a comprehensive study on the conversion of thick juice to HMF is provided. The objective of this study was to identify the origin of the better performance of thick juice compared to (pure) SUC for HMF synthesis. The experiments were carried out in a batch reactor using aqueous SUC solutions with added contaminants typically present in thick juice such as salts and organic acids. The experimental concentration-time profiles were modeled using kinetic expressions for the individual reactions to quantify the observations and to conclude which of the contaminants in the thick juice are responsible for the better performance of this feed for HMF synthesis. It was found that the higher HMF selectivity obtained when using thick juice as the feed compared to pure SUC is mainly due to the presence of sulfate ions, which in combination with sulfuric acid result in a reduction of among others the rate of subsequent reactions of HMF to LA and humins.

Samenvatting

De groeiende consumptie en afnemende reserves van fossiele bronnen in combinatie met toenemende zorgen over hoge CO₂ emissies hebben geleid tot een sterke groei in onderzoek en ontwikkeling naar hernieuwbare grondstoffen. In de afgelopen 2 decennia is de "biobased economie" geopperd als alternatief voor de huidige, op fossiel gebaseerde economie. In toekomstige biobased economieën zullen warmte, stroom, transportbrandstoffen en chemicaliën uit hernieuwbare bronnen zoals biomassa gemaakt worden. Dit moet zo efficiënt mogelijk gebeuren, dus met minimale afval productie en lage emissies van broeikasgassen. Met een geschatte jaarlijkse productie van 170×10^9 ton wordt biomassa beschouwd als de enige groene koolstofbron die voldoende beschikbaar is om fossiele bronnen (deels) te vervangen. Eén van de belangrijkste elementen in een biobased economie is een bioraffinaderij, waar biomassa wordt gescheiden in fracties die vervolgens worden omgezet met behulp van specifieke biologische, (bio)chemische, fysische en/of thermische processen. Het doel is om middels duurzame en geïntegreerde processen laagwaardige biomassa om te zetten in hoogwaardige (industriële) tussen- en eindproducten (zoals brandstoffen, chemicaliën, materialen en energie). Bioraffinaderijen hebben, behalve de voeding, veel overeenkomsten met conventionele olieraffinaderijen en worden alom gezien als veelbelovende opvolgers daarvan.

Hoewel de belangrijkste drijfveer voor de transitie van olieraffinaderijen naar bioraffinaderijen de behoefte aan duurzame warmte, stroom en transportbrandstoffen is, is de productie van biobased chemicaliën ook zeer interessant. Biobased chemicaliën met een hoog derivatiserings potentieel door de aanwezigheid van meerdere functionele groepen worden platform chemicaliën genoemd. In de afgelopen twee decennia heeft de conversie van lignocellulose (hout-achtige) biomassa veel aandacht gekregen. Lignocellulose biomassa bevat ongeveer 30-60% cellulose en 20-40% hemicellulose, biopolymeren met C6 en C5 suikers. Een brede range aan platform-chemicaliën kan verkregen worden uit suikers, waarbij onze specifieke aandacht uitgaat naar 5-hydroxymethylfurfural (HMF).

HMF is geïdentificeerd als één van de top platform chemicaliën vanwege de brede toepasbaarheid. HMF heeft zowel een aldehyde als een alcoholgroep en wordt typisch verkregen door zuur gekatalyseerde conversie van C6 suikers in water. De selectiviteit is echter een probleem en significante hoeveelheden aan bijproducten zoals levulinezuur (LA), mierzuur en een niet oplosbare fractie die bekend staat als "humines" worden gevormd. De productie van HMF op commerciële schaal bevindt zich nog in de kinderschoenen vanwege de hoge productiekosten als gevolg van hoge grondstofprijzen, lage opbrengsten en problemen met productscheiding. In water is D-fructose de optimale C6 voeding met een HMF opbrengst van circa 55 mol%, en dat is significant hoger dan bij gebruik van D-glucose (minder dan 10 mol% bij vergelijkbare condities). Echter, qua kostprijs geniet D-glucose de voorkeur. Oligo- en polysachariden en lignocellulose biomassa zijn tevens interessante HMF

voedingen en bieden mogelijk substantiële economische en milieu voordelen. Identificatie van alternatieve kostenefficiënte voedingen voor HMF-synthese is daarom van groot belang. Een ideale grondstof moet goedkoop zijn, in grote hoeveelheden beschikbaar zijn en een minimale of zelfs geen voorbehandeling vereisen. In dit proefschrift worden experimentele studies beschreven naar het gebruik van twee alternatieve suikerbronnen, namelijk **pyrolytische suikers** en **diksap** voor de synthese van platformchemicaliën via chemokatalytische routes.

Pyrolytische suiker is een veelgebruikte term voor de in water oplosbare fractie van pyrolyseoliën. Deze oliën worden geproduceerd uit biomassa via een thermische conversieroute die bekend staat als pyrolyse (450-600 °C, 1-2 s, in afwezigheid van zuurstof). Pyrolyse is een veelbelovende en veelzijdige technologie om de aanwezige suikerhoudende biopolymeren in lignocellulose biomassa te depolymeriseren en te concentreren. Pyrolyse-oliën bevatten suikers met een laag molecuulgewicht zoals 1,6-anhydro- β -D-glucopyranose (bekend als levoglucosan), 1,6-anhydro- β -D-glucose (cellobiosan) en suiker oligomeren. Vooral levoglucosan (LG) is een interessante bron voor glucose (GLC). Diksap is een suikerstroom in een (conventionele) suikerbieten fabriek en bevat ongeveer 60-70% sucrose (SUC), een dimere suiker bestaande uit fructose (FRC) en GLC.

De belangrijkste doelstelling van het in dit proefschrift beschreven onderzoek is de ontwikkeling van methodologie om beide alternatieve voedingen efficiënt om te zetten in biobased platformchemicaliën, met de nadruk op HMF. Experimentele en kinetische studies zijn uitgevoerd en de effecten van proces-condities en katalysatoren op de HMF-opbrengst zijn in detail onderzocht. In sommige gevallen zijn de onderzoeken uitgevoerd op modelcomponenten om de complexiteit te verminderen. Hoofdstuk 2 tot en met 4 richten zich op studies met pyrolytische suikers als grondstof, terwijl in hoofdstuk 5 en 6 experimenten met diksap beschreven worden.

In **Hoofdstuk 2** wordt een experimentele en kinetische studie beschreven van de omzetting van LG, de belangrijkste suiker in pyrolytische suikers, naar GLC. Zoals eerder vermeld, GLC is een belangrijke suiker die verder kan worden omgezet naar biobased chemicaliën, waaronder LA en HMF. Experimenten zijn uitgevoerd in water met twee Brønsted-zuren (zwavelzuur en azijnzuur) als katalysator in een brede range van condities in een batchreactor (glazen ampullen). De effecten van de initiële LG-concentraties (0.1–1 M), zwavel- en azijnzuurconcentraties (respectievelijk 0.05–0.5 M en 0.5–1 M) en reactietemperatuur (80–200°C) zijn bepaald. De hoogste GLC opbrengsten zijn verkregen met zwavelzuur (98 mol%), terwijl de opbrengsten met azijnzuur als katalysator aanzienlijk lager waren (maximaal 90 mol%) door de vorming van bijproducten zoals onoplosbare polymeren (humines). Kinetische parameters zijn bepaald met behulp van een MATLAB-optimalisatie. Er werd een goede fit gevonden tussen experimentele data en het kinetische model onder de aanname dat de reactie eerste orde in LG is. De activeringsenergieën waren respectievelijk 123.4 kJ mol⁻¹ en 120.9 kJ mol⁻¹ voor zwavelzuur en azijnzuur. De verkregen kinetische parameters zijn vervolgens gebruikt om de optimale reactiecondities voor LG hydrolyse naar GLC te bepalen.

Het in hoofdstuk 2 beschreven onderzoek is uitgebreid met het gebruik van een vaste katalysator (Amberlyst 16) in plaats van zwavelzuur en azijnzuur. Systematische studies in batch en met een continue reactor zijn uitgevoerd en de resultaten zijn in **hoofdstuk 3** beschreven. Massa transport limitaties in dit heterogene katalytische systeem zijn zorgvuldig onderzocht en verdisconteert in de kinetische modellering. In de batchopstelling zijn de effecten van de reactietemperatuur (352–388 K), de initiële LG-concentratie (100–1000 mol m⁻³), de katalysatorlading (1–5 gew.%) en de roersnelheid (250–1000 rpm) op GLC opbrengst bepaald. De hoogste GLC-opbrengst was 98.5 mol% (388 K, 5 gew.% Amberlyst 16, $C_{LG,0} = 500$ mol m⁻³ bij een roersnelheid van 500 rpm en 60 min). Uit de batch-data zijn relevante kinetische parameters bepaald met behulp van een eerste-orde benadering met diffusie-limitatie van LG in de Amberlyst-deeltjes. De activeringsenergie bleek 132.3 ± 10.1 kJ mol⁻¹ te zijn. Er was een goede fit tussen de experimentele data en het kinetische model, welke vervolgens ook met succes is toegepast voor het modelleren van de experimentele data verkregen in de continue opstelling. Experimenten in de continue opstelling bij lange runtijden (30 uur) laten zien dat de katalysatorstabiliteit goed is.

Tijdens de verwerking van pyrolytische suikers (hydrolyse gevolgd door conversieprocessen) ontstaan significante hoeveelheden vaste stof. Deze onoplosbare vaste bijproducten staan bekend als humines of biochar. In **Hoofdstuk 4** wordt een experimenteel onderzoek beschreven naar de (katalytische) pyrolyse en waterstof behandeling van dergelijke humines met als doel de technisch-economische haalbaarheid van pyrolytische suikerconversies te verbeteren. Ter vereenvoudiging is een “model humine” gemaakt van een representatieve pyrolytische suiker door een pyrolytisch suikermmonster gedurende 22 uur bij 130 °C onder atmosferische druk te verwarmen, gevolgd door een waterextractie bij 100 °C. Het onoplosbare residu na waterextractie is gebruikt als “model humine” voor verder onderzoek. Het is gekarakteriseerd met behulp van element analyse, GPC, TGA, HPLC, GC-MS, FT-IR en NMR. Het product is oplosbaar in typische organische oplosmiddelen (DMSO, THF, IPA), in tegenstelling tot typische humines verkregen uit GLC- en FRC-conversies, waardoor karakterisering met NMR en GPC mogelijk was. Uit de analyses blijkt dat de humines een oligomere structuur hebben (M_w is ongeveer 900 g mol⁻¹), bestaande uit suiker- en furaanfragmenten gekoppeld aan onder meer (gesubstitueerde) alifatische estereenheden en daarnaast fenolische fragmenten met methoxygroepen. Het model humine is gebruikt als voeding voor katalytische pyrolyse en katalytische waterstof behandelingen. Pyrolyse van de humines is uitgevoerd in een mg-schaal PTV-GC-MS-eenheid bij 550 °C in de aan- en afwezigheid van een H-ZSM-5 (50) katalysator. Analyses tonen aan dat aromaten met een laag molecuulgewicht (benzeen-tolueen-xyleen-naftaleen-ethylbenzeen, BTXNE) worden gevormd in een opbrengst van 4.5 gew.% gebaseerd op humine voeding bij gebruik van de zeoliet. De katalytische waterstof behandeling is bestudeerd in een batch autoclaaf bij 350 °C gedurende 4 uur met isopropanol als oplosmiddel en waterstofdonor en met Pt/CeO₂ (4.43 gew.% Pt) als katalysator. Bij geoptimaliseerde condities werd 80% van de humine

voeding omgezet naar een vloeibaar product. Deze vloeistof is in detail gekarakteriseerd met behulp van geavanceerde analytische technieken (b.v. GCxGC-FID) en hieruit bleek dat het aanzienlijke hoeveelheden fenolen en aromaten bevat (ongeveer 22% op basis van GC-detecteerbare stoffen in productolie). Deze bevindingen hebben implicaties voor de techno-economische levensvatbaarheid van pyrolyse olie bioraffinaderijen en laten zien dat potentieel hoogwaardige producten kunnen worden verkregen uit humine-achtige bijproducten.

In **hoofdstuk 5** wordt een experimenteel onderzoek naar de conversie van diksap (een ruw SUC-rijk tussenproduct bij het raffineren van suiker) naar HMF met zwavelzuur als katalysator in een vloeistof-vloeistofsysteem beschreven. De reacties zijn uitgevoerd in batch en een continue microreactor. Als reactiemedium is water gebruikt, terwijl methylisobutylketon (MIBK) en 2-methyltetrahydrofuran (MTHF) zijn gebruikt als organisch oplosmiddel. Het toevoegen van zouten aan het systeem om de verdeling coëfficiënt van HMF te verbeteren is tevens onderzocht. Hoge selectiviteit en opbrengsten van > 90% (op basis van FRC) voor HMF zijn bereikt in een twee fase vloeistof systeem bij 150 °C met diksap als voeding, H₂SO₄ als katalysator en MTHF als het biologische verkregen extractie-oplosmiddel. Bij deze condities kan de conversie van GLC, naast FRC verkregen door SUC-inversie, beperkt worden tot < 10 mol%, wat terugwinning en verder gebruik van GLC mogelijk maakt. Vergelijkende experimenten met pure SUC resulteren in lagere HMF-selectiviteit (84 mol%) bij een conversie van > 95 mol% FRC, wat aantoont dat het gebruik van de diksap een interessante optie is voor HMF-productie.

In het laatste hoofdstuk (**hoofdstuk 6**) wordt een uitgebreide studie beschreven naar de conversie van diksap naar HMF. Het doel van deze studie was om vast te stellen waarom diksap in vergelijking met (pure) SUC betere prestaties geeft voor HMF-synthese. De experimenten zijn uitgevoerd in water in een batchreactor met SUC-oplossingen waaraan opzettelijk verontreinigingen zijn toegevoegd die typisch aanwezig zijn in diksap, zoals zouten en organische zuren. De experimentele concentratie-tijd profielen zijn gemodelleerd met behulp van kinetische expressies voor de individuele reacties om de waarnemingen te kwantificeren en om te concluderen welke van de verontreinigingen in het dik sap verantwoordelijk zijn voor de goede prestaties van deze voeding voor de HMF-synthese. Gevonden is dat de hogere HMF-selectiviteit bij het gebruik van diksap voornamelijk het gevolg is van een de aanwezigheid van sulfaationen in diksap wat in combinatie met zwavelzuur resulteert in onder andere onderdrukking van de afbraaksnelheid van HMF naar LA en humines.

Acknowledgements

The time has finally come for me to write the last piece that will complete my thesis. My journey was long, full of ups and downs, and filled with unexpected yet joyful events. Obviously I could not have completed this thesis alone without the help and support of many extraordinary people which I happened to meet along the journey. In this arguably, most read part of this book, I would like to take the opportunity to thank the people who have contributed on the completion of my PhD journey.

First and foremost, I would like to express my sincere gratitude to my supervisor, Prof. H.J. Heeres. Dear Erik, I am truly grateful and honored for the opportunity you gave me to join your research group. Words cannot express how thankful I am for your kind guidance, continuous motivation, support and immense knowledge. During my difficult times, you listened to me with patience and empathy, offer good help and beyond, motivated me to move forwards. I thank you again for your share of knowledge and encouragements, and hopefully I can collaborate with you again in the future in one way or another.

I would like to thank the assessment committee; Prof. F. Picchioni, Prof. P. Pescarmona, and Prof. J.H. Bitter for their valuable time to evaluate my thesis and also for their insightful comments to improve the thesis. My great appreciation also for Dr. P.J. Deuss, Dr. J.G. Winkelman and Prof. J. Yue for research collaborations, support and many fruitful discussions.

I would have not met my supervisor without the help of Dr. C.B. Rasrendra. Dear C.B., you introduced me to Erik and with your recommendation I got admitted to the group. You were my mentor for my master study and also during the first year of my PhD trajectory. You are full of brilliant ideas, very supportive, enthusiastic and taught me various things. Thank you very much for all your support.

My deep gratitude is also addressed to DIKTI (Directorate General of Higher Education) for the financial support. I also thank the University of Brawijaya, Malang for their recommendation to DIKTI. To Ir. Bambang Poerwadi, MS., thank you very much for your kind gesture. Not to forget my previous teacher, mentor and colleagues at ITN Malang and the University of Lambung Mangkurat. Dr. Jimmy, M. Istnaeny Hudha, M.T., Prof. Tri Poespowati (†), Soeparno Djiwo, M.T., Prof. Iryanti Fatyasari Nata, Dr. Chairul Irawan, Dr. Isna Syauqiah, Dr. Muthia Elma, Dr. Hesti Wijayanti, Dr. Primata Mardina, Dr. Meilana Dharma Putra, Dr. Agus Wiryawan, Dr. Abubakar Tuhulaula, Dr. Doni Wicaksono, Prof. Rusdi H.A, mba Titin and the very caring mba Nooryati. Thank you all very much for your motivation and knowledge.

My deep appreciation also for my wonderful paraymphs; Henk van de Bovenkamp and Monique Bernardes Figueirêdo. Thank you for saying yes to my request and reserving your valuable time to help and support me through the graduation process. Henk, you are one of the kindest person I know and always very helpful with everything. Some of our research activities are closely related and I am very grateful for your support. I admire your vast knowledge and I have no doubt that you will excel in your future career. Monique, you are

a very positive, cheerful person with high spirits. I was very lucky to share office with you as you always spread positivity and joy to the room. I am sure your future career will also be as bright as you are.

During my PhD period, I received academic, administrative and technical help, countless knowledge and information from the professors, technicians, secretaries and fellow colleagues of the Chemical Engineering Department of University of Groningen. Erwin Wilbers, Anne Appeldoorn, Marcel de Vries, thank you very much for your help in technical matters, designing - also fixing my experimental setup (also improving my Dutch and organizing the always surprising *labuitje*). Jan Henk Marsman and Léon Rohrbach, thank you for your countless support with analytical matters. I always enjoyed our in between talks. I would also like to thank our department past and present secretaries, Marya de Jonge, Kim Winters and Geraldine Gambier for administrative support within the department. A special thanks to Tim Zwaagstra and Alphons Navest for support in faculty administrative and finance related subjects. I am very thankful to Maarten Vervoort and his coworkers for their support in preparing glass ampoules and other glass reactors. My gratitude goes also for Hans van der Velde for performing elemental analysis.

I want to thank my fellow colleagues and labmates (past and present) of the Chemical Engineering Department; Qingqing Yuan, Arne Hommes, Wenze Guo, Shilpa Agarwal, Yuhue Wang, Rajeesh K.P. Purushothaman, Ramesh Chowdari, Homer Genuino, Patricio Raffa, Bhawan Signh, Anna Piskun, Valeriya Zarubina, Zheng Zhang, Arjan Kloekhorst, Diego Wever, Laurens Polgar, Tim Meinds, María Jesús Ortiz Iniesta, Martijn Beljaars, Jessie Osorio, Idoia Hita, Ionela Gavrila, Douwe Zijlstra, Arjen Kamphuis, Zhiewen Wang, Patrick Figaroa, Inge-Willem Noordergraaf, Frank van Mastriht, Rodrigo Araya. Esteban Araya, Yifei Fan, Zhenchen Tang, Pablo Druetta, Nicola Migliore, Li He and Xiaoying Xi for the enjoyable days, kind support and help during my period at the department. Wenze, Shilpa and Xiaoying, thank you very much for the collaborations. To my office mate, Wang Yin, Monique Bernardes Figueirêdo, Zhenlei Zhang and Shun Fang, thank you all very much for all the discussions and sharing good memories with me. Yin, when I needed to stay late to finish long-run reactions you had no hesitation to keep me company, and always ready to lend me your muscle to open my reactor or check whether my reactor was tightened enough.

Working at the department felt very “homey” thanks to the presents of my fellow Indonesian colleagues. Yusuf Abduh, Erna Soebroto, Louis Daniel, Laura Junistia Wirawan, Jenny Tan-Soetedjo, Teddy, Agnes Ardiyanti, M. Iqbal, Dian Santosa, Frita Yuliati, Miftahul Ilmi, Angela Justina Kumalaputri, Susanti, Henky Muljana, Anastasia Prima Kristijarti, and Boy Arief Fachri. Thank you all very much for cheering up my days, constructive discussions and great share of Indonesian food. Yusuf and Louis, you two are the closest to me and like brothers. I am greatly thankful for your sincere friendship, great memories and all the support during our time in Groningen.

Acknowledgement

My sincere appreciation also for people from the Biomass Technology Group (BTG), Enschede, especially Robbie Venderbosch, and Hans Heeres. When I lived in Enschede, BTG allowed me to use their office space to facilitate my writing process. Thank you very much for this kind gesture.

During my stay in the Netherlands I also met many remarkable people from outside the university (chemical engineering department) who made my days here more colorful. I would like to thank my girlfriends, the (*non*)*dara* squad; Cyndy Soemadiredja, Rani Amelia and Aulia Tirtamarina. I am very happy we found each other. Pandji Triadyaksa & Faizah Mulyani, Illi Fuad, Zakiah & Jelle Vos, Inge Suhita & Henk, Raymond Roepers, Yu & Pauline Chou, Ridwan Maulana, Tony Scheerboom, Ysbrand Galama, Soraya & Maarten Weijer, Tjitske & Frank Panneman, the Galiro team and the big family of PPI Groningen, thank you all for your sincere friendship and support.

I am deeply thankful to my father and mother in law, Henk & Gea Santes for their continuous support, love and other things they did on my behalf. Thank you very much, especially for taking care of my children when I needed to work. I also thank the rest of my Dutch family for their warm heart and kindness; Oom Henk & Tante Bertha, Oom Henk & Tante Gonnie, Oom Henk & Tante Clara, Oom Tieme & Tante Aleida, Oom Jan & Anneke, Tante Luchien Santes, Arjen & Jeanet and also Albert-Jan.

I would not be here today without the love and support from my family in Indonesia. My father and mother, Abdurrachman and Noorlaila. Your love and support are beyond words, I could not write anything good enough to express how important your constant support and prayer are for me. My brother Cholil, thank you for always taking care of me, you have a big heart. My sister in law, Novia, I am glad you came to our family, we are lucky to have you. I thank the rest of my family as well for their love and support, especially to Tante Reni & Om Izzue, Om Bie, and my grandmother Norlatifah.

I want to thank my beloved husband, Martijn Santes for his continuous love and support. I could not have done this without you. We had difficult times especially during the past two years. However you always tirelessly helped me through. Your patience is immense. To my children Liyanna and Alwin, I had to leave you many times to complete my dream which I already had before you came. You know nothing about it yet at this point, but hopefully when you grow up, you will be proud of me.

Lastly I would like to say *Alhamdulillah*. I am finally able to present this thesis to all of you, the reader. I hope the content of this thesis is informative and useful for you in one way or another.

Thank you very much.

Yours truly,

Ria Abdilla-Santes

List of publications

1. Ria M. Abdilla-Santes, J.G.M. Winkelman, I. van Zandvoort, B.M. Weckhuysen, P.C.A. Bruijninx, P.J. Deuss and H.J. Heeres. 5-Hydroxymethylfurfural Synthesis from Sugar Beet Thick Juice: Kinetic and Modeling Studies. Manuscript in preparation.
2. R.M. Abdilla-Santes, S. Agarwal, X. Xi, H. Heeres, P.J. Deuss and H.J. Heeres. Synthesis, Characterization and Conversion of Humin Byproducts from Pyrolytic Sugars. Submitted to Journal of Analytical and Applied Pyrolysis.
3. Ria M. Abdilla-Santes, Wenze Guo, Pieter CA Bruijninx, Jun Yue, Peter J. Deuss, and Hero J. Heeres. High-Yield 5-Hydroxymethylfurfural Synthesis from Crude Sugar Beet Juice in a Biphasic Microreactor. *ChemSusChem* 12, 18 (2019), pp. 4304-4312.
4. Ria M. Abdilla-Santes, C. B. Rasrendra, J. G. M. Winkelman, and H. J. Heeres. Conversion of Levoglucosan to Glucose using An Acidic Heterogeneous Amberlyst 16 Catalyst: Kinetics and Packed Bed Measurements. *Chemical Engineering Research and Design* 152 (2019), pp. 193-200.
5. Ria M. Abdilla, C. B. Rasrendra, and H. J. Heeres. Kinetic Studies on The conversion of Levoglucosan to Glucose in Water using Brønsted Acids as the Catalysts. *Industrial & Engineering Chemistry Research* 57, 9 (2018), pp. 3204-3214.
6. Jenny N.M. Tan-Soetedjo, Henk H. van de Bovenkamp, Ria M. Abdilla, Carolus B. Rasrendra, Jacob van Ginkel, and Hero J. Heeres. Experimental and Kinetic Modeling Studies on the Conversion of Sucrose to Levulinic Acid and 5-Hydroxymethylfurfural Using Sulfuric Acid in Water. *Industrial & Engineering Chemistry Research* 56, 45 (2017), pp. 13228-13239.
7. Boy A. Fachri, R. M. Abdilla, C. B. Rasrendra, and H. J. Heeres. Experimental and Modeling Studies on the Acid-Catalyzed Conversion of Inulin to 5-Hydroxymethylfurfural in Water. *Chemical Engineering Research and Design* 109 (2016), pp. 65-75.
8. Boy A. Fachri, Ria M. Abdilla, Henk van de Bovenkamp, Carolus B. Rasrendra, and Hero J. Heeres. Experimental and Kinetic Modeling Studies on the Sulfuric Acid Catalyzed Conversion of D-Fructose to 5-Hydroxymethylfurfural and Levulinic Acid in Water. *ACS Sustainable Chemistry & Engineering* 3, 12 (2015), pp. 3024-3034.
9. Boy A. Fachri, R. M. Abdilla, C. B. Rasrendra, and H. J. Heeres. Experimental and Modelling Studies on the Uncatalysed Thermal Conversion of Inulin to 5-Hydroxymethylfurfural and Levulinic Acid. *Sustainable Chemical Processes* 3, 1 (2015), pp. 3-8.

