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Liquefaction of humins from C6-sugar conversions using heterogeneous catalysts

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1. Introduction

ABSTRACT

Biomass is considered an important resource for the production of carbon based chemicals to be used for important daily life products (plastics, paints, etc). Platform chemicals such as furfural, 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) have been identified as interesting biomass derived chemicals with high application potential. However, conventional processes for these chemicals, e.g. the acid-catalysed dehydration of the biomass source in water, are associated with the formation of large amounts of carbonaceous, insoluble humin byproducts formed by polymerisation reactions of substrates, intermediates and products. The formation of these humins reduces the carbon efficiencies of the processes. As such, there is a strong incentive to either reduce the amount of humins formed or to develop efficient valorisation technologies for these solid materials. In this respect, it is of high importance to have insight in the molecular structure of humins and their formation mechanism. This chapter summarises the findings in literature on platform chemicals from biomass, as well as studies concerned with the structural characterisation and valorisation of humin byproducts.

Keywords: humins, molecular structure, characterisation, hydrogenation, liquefaction

1.1. THE BIOREFINERY CONCEPT

According to the International Energy Agency (IEA), “*Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy*”.^[1] A biorefinery can be a facility, a process, a plant, or even a cluster of facilities. Although the term biorefinery is new, the concept is already used for decades in many traditional biomass processing plants in the sugar, starch, pulp and paper industry.^[2-10] In recent years, economic and environmental pressure such as global warming, energy conservation, security of supply, and agricultural policies have stimulated the development of biorefineries.

The input for a biorefinery is a biomass feed from various sources. Well known sources are primary biomass and residues from forestry and agricultural activities. Products of a biofinery can be intermediates and final products, including food, feed, materials, chemicals, fuels and heat and power. In Figure 1-1, an example of a second generation biorefinery is given using wood chips as input for the production of bioethanol, electricity, heat, and phenols.^[1] The wood chips are transported to the biorefinery, where they are pretreated and hydrolysed to a sugar and lignin fraction. The C₅ and C₆ sugars are fermented to bioethanol and the lignin is used to produce bio-oil via a pyrolysis step. The phenols from the bio-oil are separated and valorised and the residues are combusted to produce electricity and heat.

The biorefinery system provided in Figure 1-1 is (partly) demonstrated already. The production of second generation bioethanol has been developed till semi commercial scale (e.g. by Abengoa,^[11] Poet^[12]), and the proof of concept for the pyrolysis of lignin has been demonstrated on laboratory scale.^[13, 14] Recent R&D findings reveal that the integration of bioethanol production from wood with pulp and paper production offers promising synergies like handling and logistics of wood, water and waste water treatment, electricity and steam infrastructure.^[15-23]

For successful large scale introduction of biorefineries, the environmental, economic, and social sustainability should be assessed for the

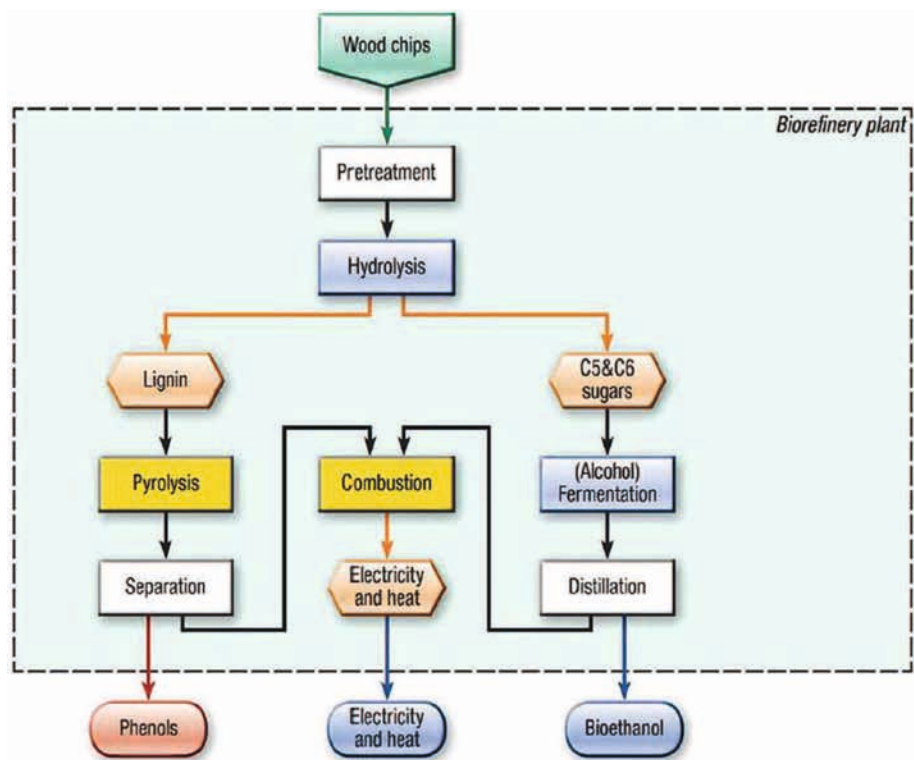


Figure 1-1. An example of a biorefinery using wood chips for bioethanol, electricity, heat, and phenols production^[1].

entire value chain and aspects like competition of the biomass feed with food applications should be carefully considered. An important product group from biorefineries are so called platform chemicals. These are intermediates for the chemical industry that can be converted to a wide range of products with a broad application range.

1.2. PLATFORM CHEMICALS FROM BIOMASS

The Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) presented a highly appreciated report

in 2004 entitled “Top Value Added Chemicals from Biomass: Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas”.^[24] In this report, the 12 most important building block chemicals from biomass were selected. The selection procedure is given in Figure 1-2.

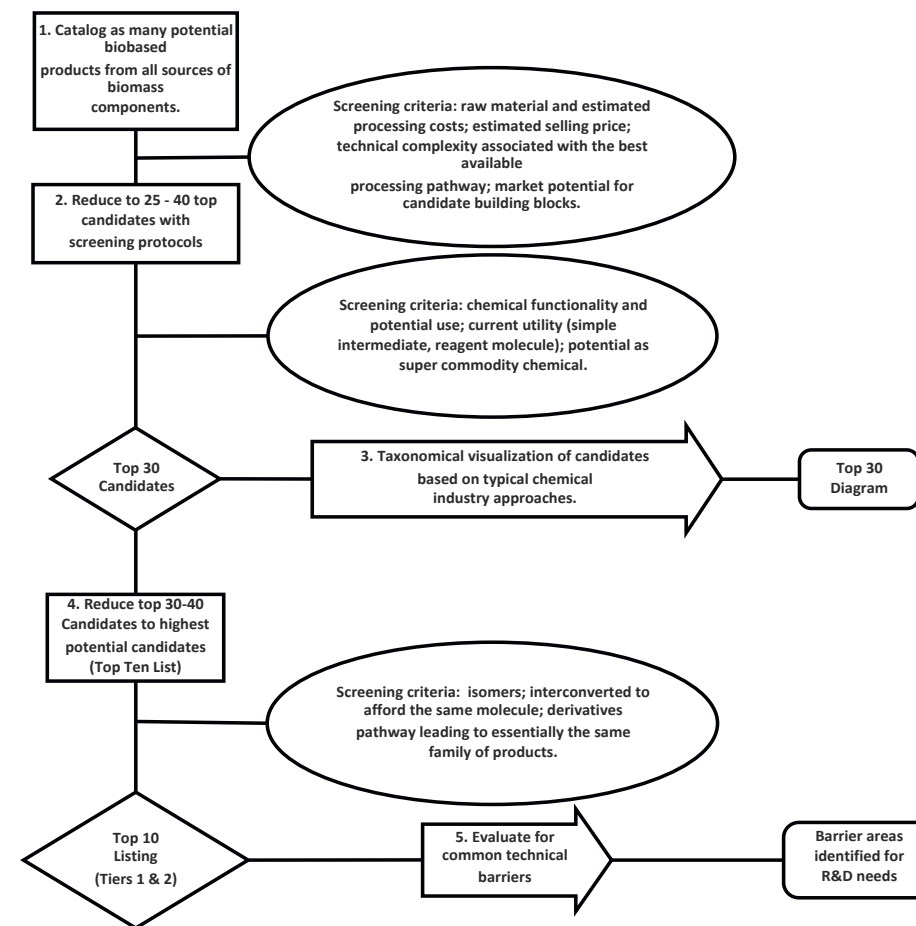


Figure 1-2. Selection strategy for the 12 top value-added chemicals from sugars.

The 12 selected biobased chemicals from sugars were 1,4-succinic acid, 2,5-furan dicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol/arabinitol. The researchers revised their findings in 2010 by paying more attention to the market potential of the biobased chemicals. The 12 top platform chemicals from the cellulose and hemi-cellulose fraction of ligno-cellulosic biomass according to this study are provided in Figure 1-3.^[25]

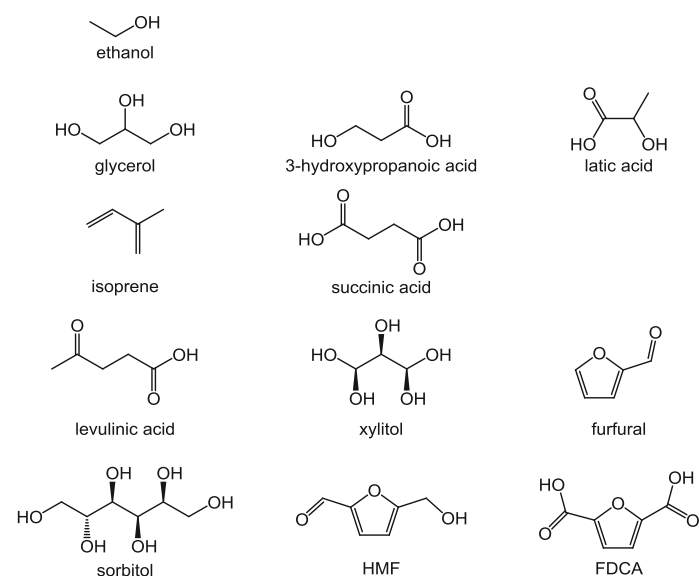


Figure 1-3. Revised top 12 biobased platform chemicals.^[25]

In 2016, a second update was published and the following platform chemicals were selected as being the most economically viable^[26]: butadiene (1,3-), butanediol (1,4-), ethyl lactate, fatty alcohols, furfural, glycerin, isoprene, lactic acid, propanediol (1,3-), propylene glycol, succinic acid and para-xylene. Compared to the previous study, the list contains a number of already existing bulk-chemicals typically derived from crude oil. As such, it can be concluded that these so-called drop-in chemicals are getting more

and more attention. Emerging products were also considered and include adipic acid, acrylic acid, and 2,5-furan dicarboxylic acid. For the latter, 5-hydroxymethylfurfural (HMF) is the feed of choice. In the following paragraph, the synthesis, application potential and commercial status of the production of HMF and levulinic acid (LA) will be presented and discussed in more detail.

1.3. BIOBASED CHEMICALS: 5-HYDROXYMETHYLFURFURAL (HMF) AND LEVULINIC ACID (LA)

1.3.1. GENERAL

HMF is a six-carbon furan derivative with an aldehyde and alcohol group, whereas LA is a keto acid. HMF and LA are versatile chemicals with a high derivatisation potential to give products with applications in various product sectors (Figure 1-4). The conventional synthetic methodology to prepare HMF and LA involves the mineral acid catalysed hydrolysis of sugars in water. When considering product yield, the best sugar source for HMF is fructose,^[27] whereas for LA, the type of C₆ sugar is of less importance. However, conventional synthesis approaches inevitably lead to solid by-product formation, which are also known as humins. These not only cause operational issues (fouling), but also lower the carbon efficiency of the transformations considerably.^[28-30]

1.3.2. SYNTHESIS AND PRODUCTION OF HMF

1.3.2.1. SYNTHETIC PROCEDURES

HMF is preferably synthesised from fructose and the highest yields of HMF reported so far are for this sugar. A wide range of catalysts and solvents

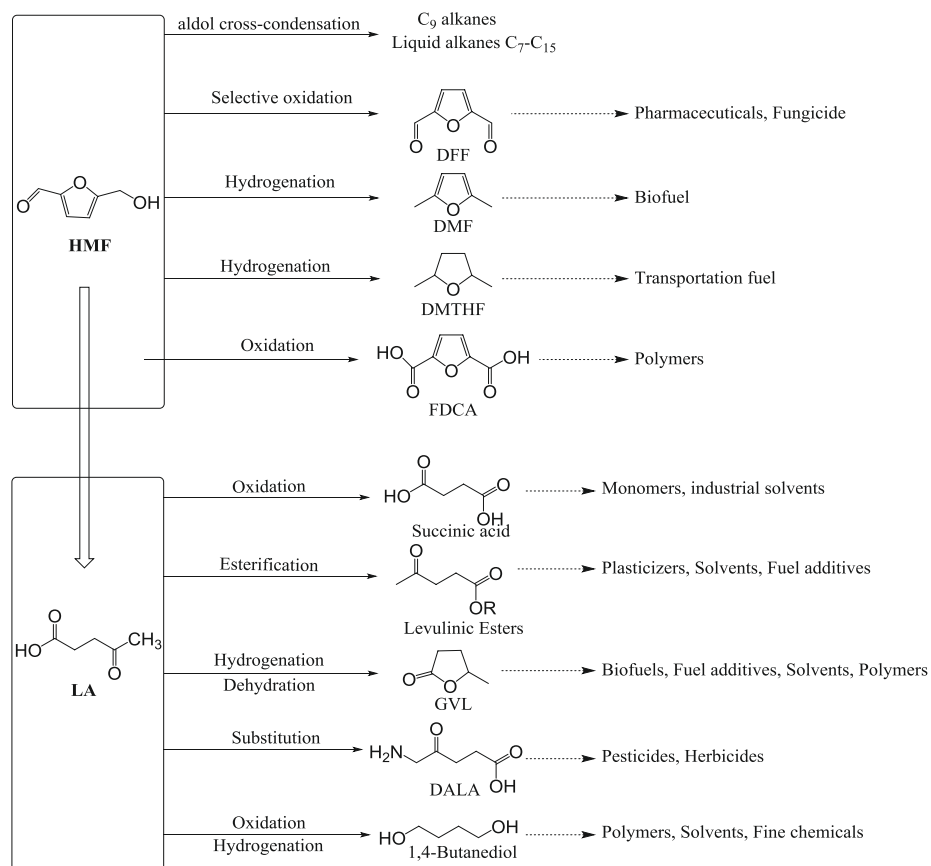


Figure 1-4. Derivatives from HMF and LA.

has been reported. Examples of solvent systems are i) aqueous systems, ii) mixed solvent systems, particularly biphasic systems involving water, and iii) non-aqueous systems including the application of ionic liquids. Solvent effects are not only profound for HMF yields but also play a major role in the design of the product work-up section and solvent/catalyst recovery and recycling. For detailed information regarding the synthetic methodology for HMF, the reader is referred to refs.^[31-42]

A recent development is the use of glucose as the source for HMF synthesis. In this case, glucose is first isomerised to fructose and the fructose is

subsequently converted to HMF. The isomerisation step can either be done separately (e.g. using an enzyme or base) or using an *in-situ* isomerisation catalyst.^[43-50] Recent findings have revealed that certain Sn promoted zeolites can function as dual catalysts which isomerise the glucose to fructose and subsequently convert the fructose to HMF. A landmark paper from Davis *et al.* in 2011 reported that a Sn-beta zeolite isomerises glucose to fructose with high activity in water under both neutral and acidic conditions.^[51] In combination with a biphasic approach, the same group reported that glucose can be directly converted to HMF with over 70 mol% yield with Sn-beta and HCl.^[52]

1.3.2.2. COMMERCIAL STATUS HMF PRODUCTION

A number of companies are actively involved in the commercialisation of HMF and derivatives. Examples are AVA-Biochem and Avantium with their YXY technology platform.^[53, 54] AVA-Biochem produces HMF using a modified hydrothermal carbonisation (HTC) process. Biomass is first hydrolysed, then dehydrated, and HMF is formed as an intermediate. The company currently uses fructose as the feed. The modified process is tuned to stop the reaction at the right moment to extract the maximum amount of HMF. Extraction and purification steps following the HTC reaction allows the synthesis of HMF in up to 99.9% purity. The Biochem-1 plant in Muttenz, Switzerland, started production in the beginning of 2014 and has a production capacity of 20 tonnes of HMF per year.^[55]

Avantium has developed 100% bio-based polyethylene-furanoate (PEF) bottles, fibers and films using plant sugar derived FDCA, of which the latter obtained by oxidation of HMF.

1.3.3. LA SYNTHESIS AND PRODUCTION

1.3.3.1 SYNTHETIC PROCEDURE FOR LA

The first study on the preparation of LA was reported in the 1840s by the Dutch scientist G. J. Mulder.^[56] The theoretical yield of LA from C₆-sugars is 64.5 wt% due to the co-production of formic acid.^[57] Commonly, LA yields of about two thirds of the theoretical value are attained. These lower yields are due to the formation of undesired black insoluble-materials known as humins.

Several reviews on the production of LA from various feedstocks under different catalytic conditions have been reported.^[58-65] A recent development is the use of biphasic liquid-liquid systems for LA synthesis. A landmark paper was recently published by Dumesic *et al.* It was reported that high yields of LA and formic acid (up to 70%) can be obtained using a biphasic reaction systems consisting of GVL and an aqueous HCl (0.1–1.25 M) solution and cellulose as the feed. Up to 75% of the LA formed is extracted to the GVL phase.^[66]

1.3.3.2. COMMERCIAL STATUS LA PRODUCTION

The Biofine company has been actively involved in the conversion of lignocellulosic biomass for the continuous production of LA in the last 15 years.^[67] An overview of the process is given in Figure 1-5. The lignocellulosic biomass and sulphuric acid are mixed in water, and the resulting slurry is supplied continuously to a tubular reactor operated at 210–220 °C with a residence time of about 12 s. In this first reactor, the cellulose and hemi-cellulose are converted to soluble monomers (hexoses and pentoses). The reactor content is fed to a continuously stirred tank reactor operated at 190–200 °C with a residence time of 20 min. The reaction conditions are such that formic acid and furfural, the two major low molecular weight products, are vapourised and collected. The liquid phase with the LA and

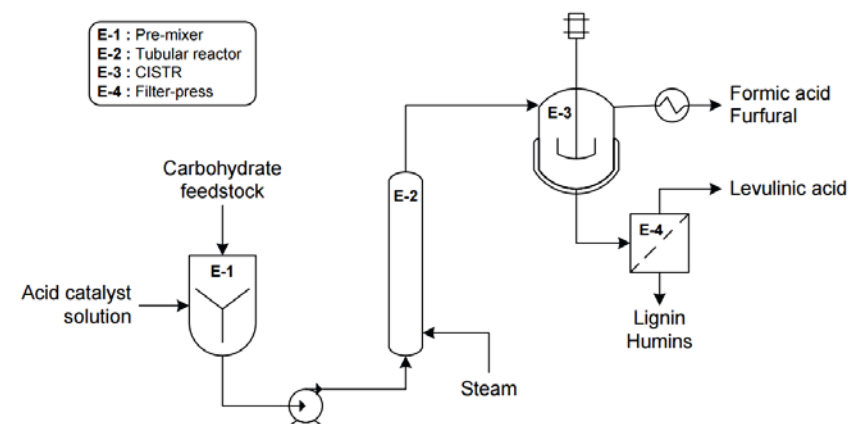


Figure 1-5. Layout of the LA process developed by Biofine. Reproduced with permission.^[68]

solids (humins, lignins) is filtered to obtain an aqueous LA solution, which is neutralised and further purified to collect the LA. Typical yields of LA are between 15 and 41 wt% on feed, the exact value being a function of the reaction conditions and biomass source.

GFBiochemicals recently reported a Biofine derived process to produce LA from a wide range of biomass feeds^[69]. Yield improvements were reported based on further optimisation/modification of the reactor and work-up section, though details are to the best of our knowledge not reported yet. Commercial production in Casserta, Italy started in the summer of 2015. The unit will be scaled up to a full capacity of 10,000 MT/a by 2017. A schematic overview of the process concept is given in Figure 1-6.

1.4. HUMINS: MOLECULAR STRUCTURE

1.4.1. GENERAL FEATURES

As discussed in the previous paragraphs, HMF and LA synthesis are inevitably accompanied with solids formation, particularly when using water as

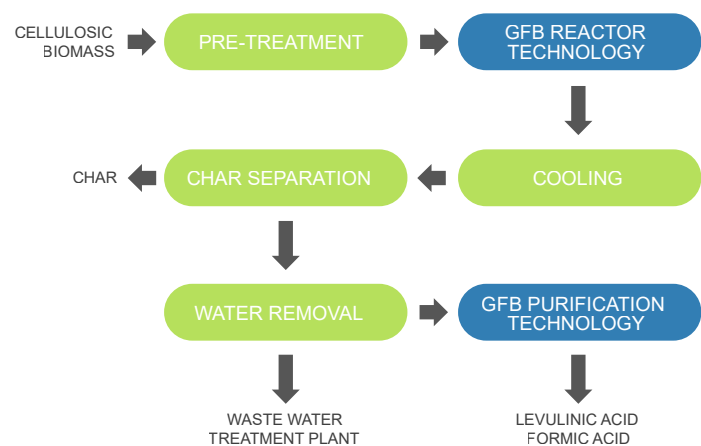


Figure 1-6. Schematic representation of the GFBiochemicals process for LA^[69].

the solvent. Humin formation will block valves and pipes in the plant and decrease the yields of desired products. These humin byproducts are also known as humin-like substances,^[70] humic solids,^[71, 72] or Biofine char.^[73] In the biofine process for LA from sugars, up to 30 wt% of the carbohydrate source can end up in the humin by-product.^[73] The exact amount of humins formed during acid catalysed sugar conversions to platform chemicals is difficult to obtain from literature. The formation of 8-20 mol% humin from HMF,^[74] 16-34 mol% from fructose^[74] and 32 wt% from glucose^[75] using homogeneous mineral acids in water have been reported.

In the next paragraph, proposals regarding the molecular structure of humins will be reviewed. This information is of relevance for the rational design of catalysts for the conversion of humins to value-added chemicals and biofuels.

1.4.2. SOIL HUMINS

Soil contains certain organic fractions, collectively known as humus.^[76] The organic constituents of humus are known to be (partly) derived from

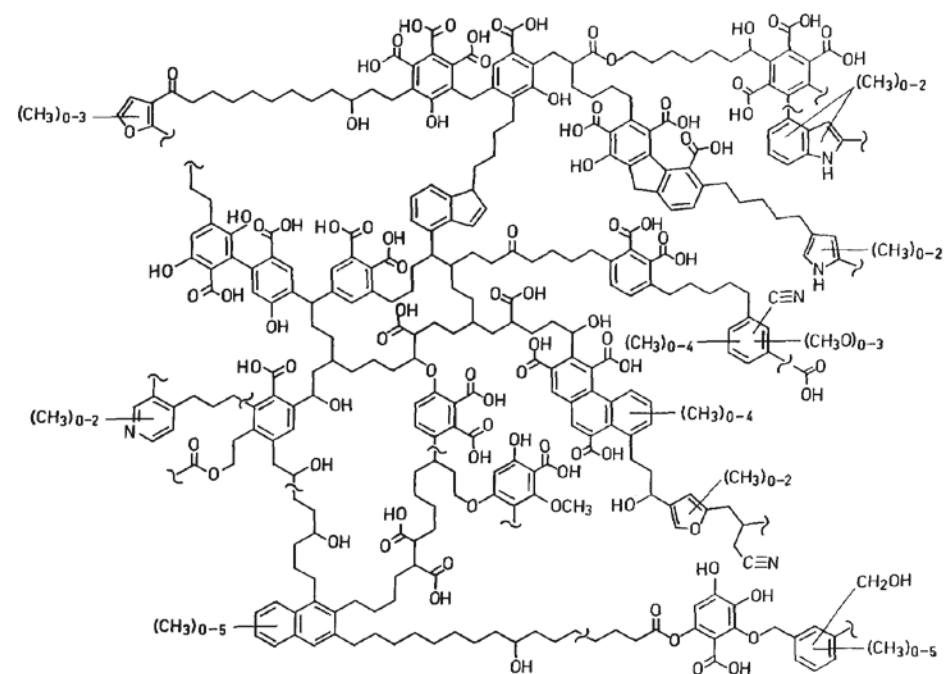


Figure 1-7. Schematic representation of the molecular structure of the humic acid fraction. Reproduced from Schnitzer *et al.* with permission.^[77]

the decay of carbohydrates. As such, there may be a relation between the structures of such humic substances and those obtained by the accelerated breakdown of carbohydrates. Humus consists of three main components: fulvic acids, which are soluble in water at any pH, alkali-soluble humic acids and insoluble soil humins.^[76] Structural models have been proposed for the various fractions, and an example of the humic acid fraction is given in Figure 1-7.^[77] It shows a complex structure with aromatic, phenolic and pyridine units with a wide variety of linkers.^[78] This structural diversity is due to the introduction of non-sugar components such as fatty acids, amino acids, lignin, and inorganics in the structure. As such, there is likely not a one to one relation between the structure of humus and the humins obtained from low molecular weight sugars.

1.4.3. STRUCTURAL FEATURES OF HUMINS FROM SUGAR CONVERSIONS.

The elucidation of the molecular structure of humins is seriously hampered by the poor solubility of the humins in most organic solvents. In this respect, there is a strong resemblance with lignins.^[79-82] For instance, liquid phase NMR, a very powerful technique to unravel the molecular structure of complex (macro-) molecules cannot be used.^[83-85] In addition, it is also not possible to determine average molecular weights of the humins using GPC. However, a combination of various (analytical) techniques such as IR, elemental analysis, Py-GC-MS and advanced solid state NMR has been applied and shown to give considerable insights in the molecular structure of humins.^[86] In addition, analytical protocols applied for lignins for the quantification of certain organic component groups (alcohols, acids, etc.), may also be used for humin characterisation.^[87, 88]

Structural studies on humins derived from sugar conversions to platform chemicals are scarce. Most of the information is obtained from studies on hydrothermal carbons (HTCs).^[89, 90] These are typically prepared by a hydrothermal treatment of sugars in the absence of acids. As such,

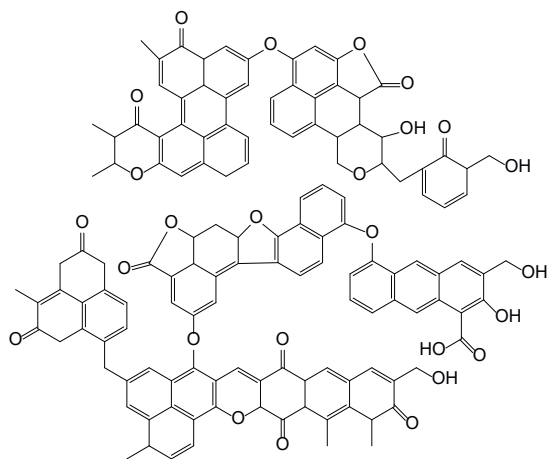


Figure 1-8. Structural model for HTCs by Sevilla *et al.* Reproduced with permission.^[86]

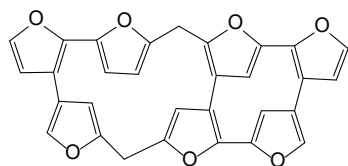
structural similarities are likely to be present between HTCs and humins from sugars. However, the chemical pathways for humin formation may be affected by the presence of the acid catalysts used when preparing humins. Additionally, the acid may also be incorporated (partly) in the structure. For instance, when using sulphuric acid, sulphur was detected in the samples by elemental analysis, indicating the presence of organic sulphur groups (e.g. sulphonates) in the humin structure. In the following paragraphs, structural models for HTCs will be presented and discussed followed by a discussion on the structure of humins derived from acid catalysed low molecular weight sugar conversion.

1.4.4. STRUCTURAL MODELS FOR HTCS

Sevilla *et al.* proposed a structural model for HTCs derived from various sugar feeds based on elemental analysis, IR and TEM. The TEM images of HTC particles showed a slight difference in contrast between the core and the shell of the particles, suggesting a difference in chemical composition between shell and core. As such, the HTCs were proposed to consist of a poly-aromatic structure with hydrophilic groups on the surface and less reactive (hydrophobic) groups in the core (Figure 1-8).^[86]

A similar structural proposal was reported by Shin and co-workers for HTCs derived from fructose based on Raman spectroscopy and supported by TEM images.^[91]

However, an alternative structure was suggested for various hexose- and pentose-derived HTCs by Titirici and Baccile.^[92] Based on advanced solid state ¹³C NMR of ¹³C-labeled HTCs it was concluded that the HTCs consist of a furan-rich structure which aliphatic linkages on the α - or β -position (Figure 1-9).

Figure 1-9. Structural model for HTCs by Titirici and Baccile. Reproduced with permission.^[92]

1.4.5. STRUCTURAL MODELS FOR HUMINS FROM ACID CATALYSED SUGAR CONVERSIONS

In 1840, Mulder was the first to isolate humin byproducts from the acid-catalysed dehydration of sucrose with HCl. The elemental composition of the material was determined and was shown to consist of 64-65 wt% of C, 5 wt% of H and 31-32 wt% of O.^[56] Schweitzer was the first to propose a structural model for humins, see Figure 1-10 for details.^[93, 94] It was suggested that humins contain pyranose units, formed by dehydration reactions.

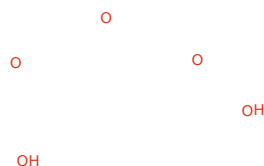
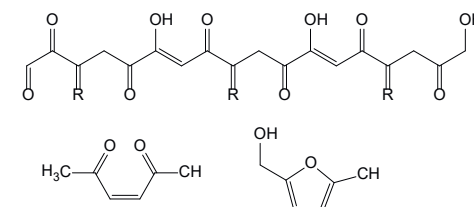
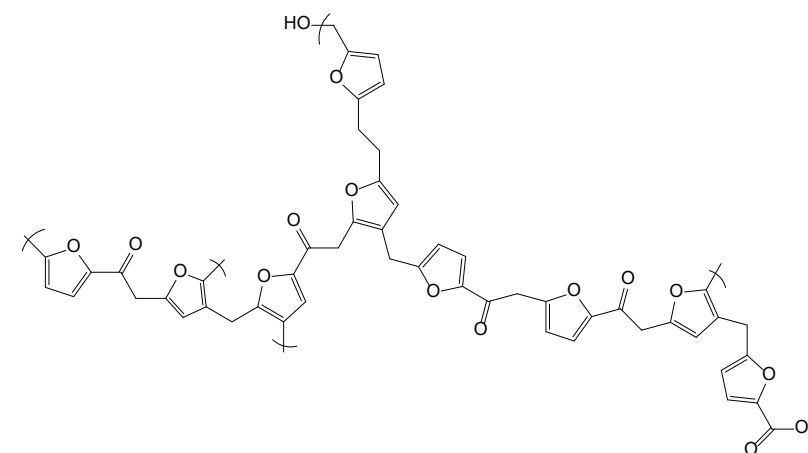


Figure 1-10. Proposed molecular structure of a humin fragment by Schweizer.

The last decade, several structural models have been proposed for humins derived from the acid catalysed dehydration of sugars. Lund *et al.* reported structural studies on HTCs and humins derived from HMF, glucose, fructose and cellobiose (Figure 1-11).^[95]

Zarubin *et al.*, performed studies on humins obtained from various carbohydrates and HMF.^[70] Based on analysis of the solids by IR and ¹³C solid-state NMR, it was proposed that the humins consist of furan rings with aliphatic linkages (Figure 1-12).

Figure 1-11. Proposed molecular structure of a humin fragment by Lund.^[95]Figure 1-12. Proposed molecular structure of a humin fragment by Zarubin *et al.*^[70]Figure 1-13. Proposed molecular structure of a humin fragment by Seshan *et al.*^[96]

Recently, Seshan *et al.* proposed a molecular structure of humins derived from the acid catalysed dehydration of glucose based on ¹³C solid-state NMR, IR and pyrolysis data. It shows a molecular structure where furan rings are connected via ethylene and methyl linkers with ketone functionalities (Figure 1-13).^[96]

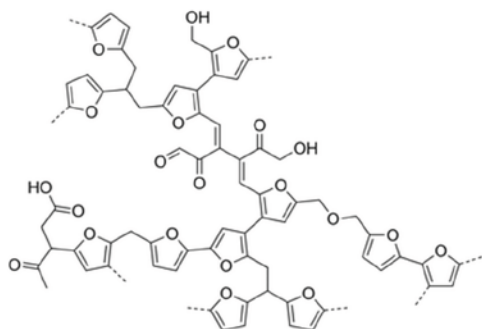


Figure 1-14. Proposed molecular structure of humins from glucose derived humins. Reproduced with permission.^[87]

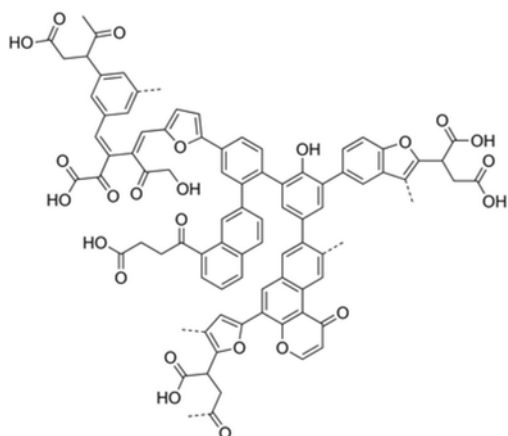


Figure 1-15. Proposed molecular structure for alkali treated humins from glucose. Reproduced with permission.^[87]

While performing this investigation, the Weckhuijsen group in Utrecht published a paper on the structure of humins using advanced solid state NMR studies on ^{13}C -enriched humins.^[87] 1D cross polarization (CP) and direct excitation (DE) ^{13}C solid-state NMR spectra, 2D ^{13}C -detected double-quantum single-quantum (DQSQ) as well as 2D ^1H -detected heteronuclear correlation (HETCOR) were recorded and showed that the humins have a furan-rich structure with aliphatic linkers (Figure 1-14).

Another point of interest is the observation that the humin structure changes upon an alkaline treatment at elevated temperatures. Solid-state NMR data of these alkali-treated ^{13}C -labeled humins reveal that these contain arene-rich structures at the expense of the furanic network (Figure 1-15). This finding has a major implication on the catalytic conversions of humins at elevated temperatures and will have to be considered in reaction networks.

1.5. VALORISATION OF HUMINS

HTCs have shown to have a wide application potential. Examples are the use as active carbon for the adsorption of metal ions and organic contaminants (e.g. phenol).^[97-100] In addition, the solids have been used as soil improver and for CO_2 sequestration.^[73, 101, 102] The humins from acid catalysed sugar conversions may also be applicable in such applications. Recent findings have shown that sulphonated pyrolysed sugars may be used as solid acid catalysts for the esterification of fatty acids to produce biofuels and for the hydrolysis of polysaccharides.^[103-105]

However, catalytic conversions and valorisation of humins have so far not been investigated in detail. In commercial processes, such as the Biofine process, humins are currently burnt to generate heat and/or electricity.^[104] Within the Dutch Catchbio program,^[107] an integrated approach has been proposed for the catalytic conversion of humins using the biorefinery concept, aiming to produce high value chemicals and biofuels. An overview of the concept is given in Figure 1-16.

It involves the initial catalytic conversion of the humins to a liquid that is rich in biobased chemicals, followed by separation into fractions or individual chemicals. The residues are hydrotreated to biofuels and the solid residue is gasified to provide the hydrogen required for the various catalytic conversions. Upon execution of the program, the concept was slightly modified and this version is given in Figure 1-17.

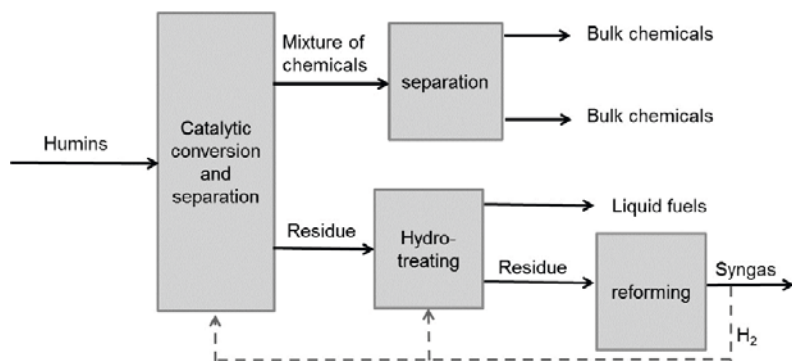


Figure 1-16. Proposed scheme for humin valorization within the CatchBio consortium.

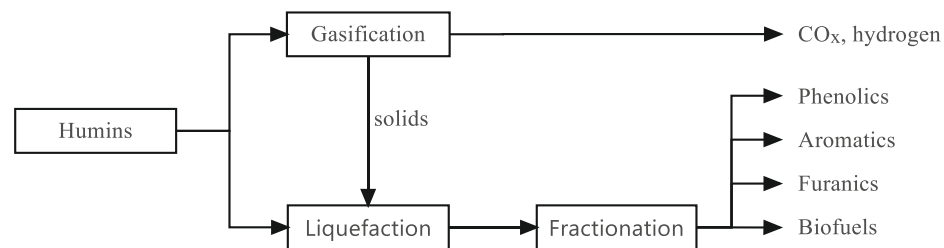


Figure 1-17. Valorization of humins using the biorefinery concept: modified version.

This concept involves two primary conversions i) gasification of the humins to syngas and ii) liquefaction/fractionation to biobased chemicals and biofuels. Within the consortium gasification and particularly steam reforming of humins (900-1200 °C) with the objective to obtain syngas (mixture of CO_x and hydrogen) was studied by Hoang *et al.*^[108] It was shown that the presence of sodium carbonate is essential, which acts as a catalyst and enhances the rate of the gasification reactions. The H₂ to CO ratio of the produced syngas was about 2. However, substantial loss of carbon was observed during the heating up stage (up to 45 wt% on intake). To improve carbon yields, a second catalytic reactor was proposed to gasify the volatiles formed during the heating phase to increase the solid to gas carbon efficiency.

Liquefaction of humins using pyrolysis technology was investigated by Rasrendra *et al.*^[109] Pyrolysis GC-MS showed the presence of furanics and organic acids in the vapour phase, though the individual components were present in only minor amounts (< 1 wt%). Micro-pyrolysis yielded 30 wt% of gaseous and liquid products, the remainder being a solid char. Gas-liquid yields were lower than obtained for a typical lignin sample (Kraft lignin) under similar conditions. As such, pyrolysis seems to be cumbersome and gives relatively low liquid yields.

Other humin liquefaction approaches have been studied within the Catchbio program, examples are catalytic hydrotreatments (the topic of this thesis) and aqueous phase reforming. Catalytic hydrotreatment involves contacting the humins with a hydrogen donor in an appropriate solvent in the presence of a catalyst. The hydrogen donor can be either molecular hydrogen or a donor solvent like formic acid (FA). This synthetic methodology has been explored in detail for the depolymerisation of lignin to low molecular weight chemicals.^[110] Typical catalysts for lignin conversions are metal supported catalysts like NiMo and CoMo on various supports.^[111, 112] Relatively harsh conditions (temperatures up to 450 °C, pressures up to 200 bar) are required for substantial depolymerisation activity. The use of hydrogen donor solvents in both the presence or absence of metal catalysts has been reported. A well known hydrogen donor is FA, which is *in-situ*, either thermally or catalytically, converted to hydrogen and CO/CO₂. Other solvents, either for dilution or to act as a hydrogen donor, are alcohols (ethanol, methanol, IPA), and water. Temperatures between 300 and 380 °C have been explored for lignin, with reaction times ranging from 2-17 h. Kleinert *et al.* were able to convert alkaline extracted lignin from spruce, pine, birch, and aspen wood to a liquid product in 93 wt% on lignin intake yield at 390 °C with a reaction time of 17 h using FA in isopropanol.^[110, 113] Recent research by Liguori *et al.* showed that the reaction times and temperature for lignin can be reduced dramatically when using a catalytic version (Pd/C) in water.^[114] Major products were guaiacols (4.6 wt% on lignin intake) and catechols (4.7 wt% on lignin intake). It was hypothesised that

the heterogeneous catalyst enhances the FA decomposition rate at lower temperature and as such has a positive effect on lignin depolymerisation rates and the rate of the subsequent deoxygenation of the lower molecular weight fragments.^[115] Recently, Xu *et al.* reported the use of Pt/C with ethanol and formic acid for the conversion of switchgrass lignin, and the combination of both formic acid and Pt/C was shown to lead to higher amounts of lower molecular weight compounds in the liquid phase.^[116]

Trautmann *et al.* reported studies on the catalytic treatment of HTC materials to produce biofuels.^[117, 118] Various HTC materials were tested using Ni on titania as the catalyst at temperatures between 200 and 250 °C, and reaction times between 3 and 20 h. Here, hydrogen is formed *in situ* which then serves as the reactant for hydrocracking reactions and the formation of liquid products. Although HTC materials are likely more complex in nature than humins and might contain lignins and minerals (which may be catalytically active), these findings suggest that catalytic hydrotreatment reactions for humins to liquid products may also be feasible.

Within the context of the Catchbio program, van Zandvoort *et al.* recently reported the aqueous phase reforming (APR) of solubilised glucose humin byproducts (by an alkali treatment) to produce aromatic monomers and hydrogen using different Pt-based heterogeneous catalysts (225-250 °C, pH 9-11, 20 h, batch).^[119] Best results were obtained using Pt-Re on a ZrO₂ support. Up to 8 wt% of a humin-oil was obtained which was shown to mainly contain phenolics and aromatic ketones (GC-MS). As such, this study shows that (solubilised) humins can be liquefied using a catalytic approach.

1.6. SCOPE AND OUTLINE OF THIS THESIS

This aims of the research described in this thesis were i) to gain insights in the molecular structure of humin by-products and ii) to provide the proof of concept for the catalytic valorisation of humins using a catalytic hydrotreatment strategy. Experiments were carried out using synthetic humins

prepared by the acid catalysed conversion of low molecular weight sugars, with an emphasis on glucose.

In **Chapter 2**, a multi-parameter and multi-technique approach is described to get insight in the formation, morphology and chemical properties of the humin byproducts from different sugars. Process parameter variation by Design of Experiment (DoE) gave insight in the reaction parameters leading to humin formation. Based on the characterisation data (including elemental analysis, IR, ¹³C solid-state NMR and pyrolysis-GC-MS) a representative model for the molecular structure of humins is proposed.

In **Chapter 3**, a catalyst screening study is reported on the solvent assisted liquefaction of humins. Experiments were carried out in a batch reactor using an artificial model humin derived from glucose with isopropanol as the solvent at 400 °C for a 3 h batchtime. Initial studies were performed using noble metal catalysts (Rh, Pt, Pd, Ru) on a carbon support followed by support screening studies for Pt (TiO₂, ZrO₂, CeO₂). Detailed liquid product analyses (GPC, GC-MS, GC×GC) were performed.

In **Chapter 4**, the results for an experimental study on the catalytic liquefaction of humins using a supported Pt/C catalyst in isopropanol (IPA) as the solvent are described (400°C, 7 h). The product oil was analysed in detail (GC-MS, GC×GC-FID, GPC). A systematic study according to a central composite design (19 experiments) was performed to optimise the reaction conditions (T, humin intake, catalyst intake and batch time) obtaining the highest humin conversion and alkylphenolics yield. A reaction network is proposed based on structural proposals for humins and the main reaction products.

In **Chapter 5**, the results of an experimental study on the catalytic hydrotreatment of humins using supported Ru catalysts (carbon and alumina) is described. Reactions were carried out in a batch set-up at elevated temperatures (400 °C) using a hydrogen donor (formic acid in IPA) with humins obtained from D-glucose. Catalyst performance was compared and the role of FA was assessed. The humin oils were characterised using a range of analytical techniques (GC, GC-MS, GC×GC, GPC) to gain insights in the various reactions taking place during the hydrotreatment process.

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