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HydroThermal Liquefaction of Biomass and Model Compounds

Pedersen, Thomas Helmer

HYDROTHERMAL LIQUEFACTION OF BIOMASS AND MODEL COMPOUNDS

BY
THOMAS HELMER PEDERSEN

DISSERTATION SUBMITTED 2016

AALBORG UNIVERSITY
DENMARK

HydroThermal Liquefaction of Biomass and Model Compounds

Ph.D. Dissertation

Thomas Helmer Pedersen

Aalborg University
Department of Energy Technology

Abstract

Hydrothermal liquefaction (HtL) is an advanced biomass conversion technology that converts biomass into a biocrude by processing in a near or supercritical water environment. The presence of water as a reaction medium makes biomass pre-drying obsolete resulting in a highly biomass-flexible and energy efficient technology. The biocrude from HtL is an energy-dense liquid and a renewable oxygenated equivalent to fossil petroleum. Further processing of the biocrude into transport fuels and commodity chemicals is therefore of tremendous interest. The prospects of the biocrude obtained from HtL are promising and detailed knowledge on how the biocrude is chemically formed is pivotal, but unfortunately scarce, and therefore needs to be expanded.

The centerpoint of this thesis was the chemical conversion of biomass, with lignocellulose as the cornerstone, and biomass model compounds under supercritical water conditions. In order to establish a link between the fundamental structures of lignocellulosic biomass and the compounds obtained in the biocrude, micro-batch experiments of aspen wood and representative model compounds were carried out. Results showed that the majority of compounds was distributed between ketones and oxygenated aromatics having number of carbon atoms mainly in the range of C_6-C_9. Linear relationships were established relating the distribution of ketones and oxygenated aromatics to the fraction of carbohydrates (glucose and xylose) and lignin. An overall reaction mechanism was proposed based on the results.

Co-liquefaction of neat glycerol/aspen wood and crude glycerol/aspen wood was investigated to assess the interaction of lignocellulose and glycerol. It was found that glycerol has a synergetic char-reducing effect when mixed with aspen wood. Char formation could be reduced by more than half (to approximately 7 %) and at the same time increase the biocrude yield when glycerol and aspen wood were mixed in a 1:3 mass ratio. Co-liquefaction of crude glycerol/aspen wood was also investigated. As in the case of glycerol, similar char-reducing effects were observed were co-processing crude glycerol and aspen wood. An added-value of co-processing with crude glycerol is its basic properties, alleviating the needs of adding catalysts, and its residual fatty acids and fatty acid methyl acids, which transfer directly to the biocrude.

Bench-scale continuous experiments of glycerol/aspen wood co-liquefaction were performed in which an aqueous phase recirculation procedure was incorporated. Based on a fixed 30 %

feedstock loading (50/50 glycerol/aspen wood) in the feed slurries, results showed that steady continuous operation could be achieved under the applied conditions. High quality biocrudes were obtained in mass yields ranging from 20-32 %. A slightly increasing trend in the biocrude quality was observed when the aqueous phase was recirculated. However, of concern was the accumulation of water-soluble organics and inorganics in the aqueous phase, which for prolonged operation may pose a technical challenge.

A biocrude obtained from the bench-scale experiments was fractional distilled and upgraded to investigate the compounds within the biocrude and to assess the amenability of the biocrude for further processing. Approximately 50 % of the biocrude was distilled at 350 °C and succesful separation of the different chemical group was observed in the fractions. Upgrading of a biocrude mixture reduced the oxygen content from 14.5 to 4.6 % resulting in a bulk product consisting mostly of hydrocarbons and phenolics.

In the attempt to increase hydrogenation selectivity during HtL, a nickel-based catalyst was prepared and tested in a micro-continuous system. Model compound experiments with glucose and p-cresol were carried out. Using a nickel-based catalyst experiments showed that glucose can be completely gasified at common HtL conditions and can thereby served as an in-situ hydrogen source. However, under the investigated conditions the catalyst proved not to be selective for hydrogenation of p-cresol as attempted.

Resumé

Hydrothermal liquefaction (HtL) er en avanceret termokemisk proces, der omdanner biomasse til en bio-råolie i nær- eller superkritisk vand. Grundet tilstedeværelsen af vand som reaktionsmedie er tørring af biomassen overflødig, hvilket resulterer i en biomasse-fleksibel og energieffektiv teknologi. Bio-råolien fra HtL er en energitæt væske og en vedvarende, iltet ækvivalent til fossilt råolie. Efterbehandling af bio-råolien til transportbrændstoffer og kemikalier har derfor enorm interesse. Potentialet for bio-råolien fra HtL er stort og detaljeret viden om, hvordan bio-råolien kemisk bliver dannet, er altafgørende. Desværre er denne viden endnu knap og skal derfor nødvendigvis undersøges dybdegående.

Omdrejningspunktet for denne afhandling var den kemiske omdannelse af biomasse og modelkomponenter, med lignocellulose som hjørnesten, under superkritiske betingelser. Mikrobatch forsøg med aspetræ og repræsentative modelkomponenter blev udført i forsøget på at etablere en forbindelse mellem de grundlæggende strukturer i lignocellulosen og de opnåede kemiske stoffer i bio-råolien. Forsøgsresultaterne viste, at en overvejende del af de kemiske stoffer i bio-råolien fordelte sig mellem ketoner og aromater med kulstofkæder hovedsageligt i intervallet C_6-C_9. Lineære sammenhænge mellem fordelingen af ketoner og aromater i bioråolien, og sammensætningen af kulhydrater (glukose og xylose) og lignin i biomassen kunne etableres. På baggrund af resultaterne blev der foreslået en reaktionsmekanisme.

Co-HtL af glycerol/aspetræ og rå-glycerol/aspetræ blev udført for at undersøge mulige synergieffekter mellem lignocellulose og glycerol. Det blev konstateret, at glycerol har en koks-reducerende effekt, når det blandes med aspetræ. Koksdannelsen kunne mere end halveres (til ca. 7 %) og samtidig øge udbyttet af bio-råolien, når glycerol og aspetræ blev blandet i et masseforhold på 1:3. Co-HtL af rå glycerol/aspetræ blev også undersøgt. Som i tilfældet med glycerol udviste rå-glycerol en lignende koks-reducerende effekt. Rå-glycerol havde tilmed en merværdi i det dens allerede basiske egenskaber overflødiggjorde tilsætning af katalysator, og samtidig blev resterende fedtsyrer og methylestere i rå-glycerolen tilgængelige i bio-råolien.

Storskala, kontinuerte forsøg med glycerol/aspetræ blev udført, hvori en recirkulationsprocedure af vandfasen var inkorporeret. Baseret på en fødeopskrift med 30 % iblanding af glycerol og aspetræ (50/50 glycerol/aspetræ) kunne stabil kontinuert drift opnås under superkritiske betingelser. Bio-råolie af høj kvalitet blev produceret i udbytter spændende fra 20 til 32 %. En svagt stigende tendens i bio-råoliens kvalitet blev observeret, når vandfasen blev recirkuleret.

Der blev yderligere observeret en ophobning af vandopløselige organiske komponenter og uorganisk materiale i vandfasen som funktion af recirkulationen, som kan udgøre en teknisk udfordring for længere tids drift.

For at opnå en dybere forståelse af den kemiske sammensætning af bio-råolien og dennes egenskaber for viderebehandling, blev den producerede rå-olie fra de kontinuerte eksperimenter fraktioneret ved destillation og senere opgraderet. Ca. 50 % af bio-råolien kunne destilleres ved 350 °C og adskillelse af de forskellige kemiske gruppe viste sig at være succesfuld. Opgradering af en blanding af destillationsfraktioner viste, at iltindholdet kunne reduceres fra 14,5 til 4,6 %, hvoraf det opgraderede produkt bestod hovedsageligt af kulbrinter og phenoler.

I forsøget på at øge selektiviteten af hydrogeneringsreaktioner i HtL blev en nikkel-baseret katalysator fremstillet og testet i et mikro-kontinuerligt system. Eksperimenter med glukose og p-cresol som repræsentative modelkomponenter blev udført. Det blev fundet, at glukose kan fuldstænding forgasses under gængse HtL betingelser ved tilstedeværelsen af katalysatoren, og glukosen kan dermed fungere som en in-situ hydrogenkilde. Desværre viste det sig, at den fremstillede katalysatoren ikke umiddelbart var selektiv med hensyn til hydrogenering af p-cresol under de undersøgte betingelser.

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Thesis Details

Thesis Title: Hydrothermal liquefaction of biomass
Ph.D. Student: Thomas Helmer Pedersen
Supervisor: Prof. Lasse Aistrup Rosendahl, Aalborg University

The main body of this thesis is based on the following papers and book chapters:

[1] Thomas H. Pedersen, Lasse A. Rosendahl, "Production of fuel range oxygenates by supercritical hydrothermal 2 liquefaction of lignocellulosic model systems", *Biomass and Bioenergy*, pp. 206–215, 2015.

[2] Thomas H. Pedersen, Lukas Jasiūnas, Luca Casamassima, Shashank Singh, Thomas Jensen, Lasse A. Rosendahl, "Synergetic hydrothermal co-liquefaction of crude glycerol and aspen wood", *Energy Conversion and Management*, pp. 886–891, 2015.

[3] T.H. Pedersen, I.F. Grigoras, J. Hoffmann, S.S. Toor, I.M. Daraban, C.U. Jensen, S.B. Iversen, R.B. Madsen, M. Glasius, K.R. Arturi, R.P. Nielsen, E.G. Søgaard, L.A. Rosendahl, "Continuous Hydrothermal Co-liquefaction of Aspen Wood and Glycerol with Water Phase Recirculation", *Applied Energy*, pp. 1034–1041, 2015.

[4] T.H. Pedersen, C.U. Jensen, L.A. Rosendahl, "Production of commodity chemicals and drop-in fuels from biomass by biocrude distillation and upgrading", *In submission for publication*, 2016.

[5] S.S. Toor, L.A. Rosendahl, J. Hoffmann, T.H. Pedersen, R.P. Nielsen, E.G. Søgaard, "Hydrothermal liquefaction of biomass", *Application of hydrothermal reactions to biomass conversion. red. / Fangming Jin. Springer Publishing Company, pp. 189-217 (Green Chemistry and Sustainable Technology)*, 2014.

[6] J. Hoffmann, T.H. Pedersen, L.A. Rosendahl, "Hydrothermal Conversion in Near-Critical Water - A Sustainable Way of Producing Renewable Fuels", *Near-critical and Supercritical Water and Their Applications for Biorefineries. red. / Zhen Fang; Chunbao (Charles) Xu. Vol. 2 Springer Science+Business Media B.V., pp. 373-400 (Biofuels and Biorefineries, Vol. 2)*, 2014.

In addition to the main body, the following publications and contributions have also been made:

Publications

- Jacob Becker, Per R. Christiansen, Anders J. Mørup, Thomas Helmer Pedersen, "Fra affald til olie: Kør på gylle flyv på græs", *Aktuel Naturvidenskab (2)*, pp. 14-19, 2013.

- Iulia Daraban, Lasse Aistrup Rosendahl, Thomas Helmer Pedersen, Steen Brummerstedt Iversen, "Pretreatment methods to obtain pumpable high solid loading wood-water slurries for continuous hydrothermal liquefaction systems", *Biomass and Bioenergy (81)*, pp. 437-443, 2015.

- Iulia Daraban, Lasse Aistrup Rosendahl, Thomas Helmer Pedersen, Saqib Sohail Toor, "Alkaline pretreatment of lignocellulosic biomass for continuous HTL process", *In submission to Renewable Energy, Elsevier*, 2015.

Conference contributions

- Thomas H. Pedersen, Lukas Jasiūnas, Luca Casamassima, Shashank Singh, Thomas Jensen, Lasse A. Rosendahl, "Synergetic Wood-glycerol Co-liquefaction in Supercritical Water for High Yield of High Quality Biocrude", *Oral presentation at the 23th European Biomass Conference and Exhibition, Vienna*, June 1-4th 2015.

- Thomas H. Pedersen, Lasse A. Rosendahl, "Oil and Char Formation of Lignocellulose Model Compounds and Derivatives during Hydrothermal Processing in Supercritical Water ", *Poster presentation at the 23rd European Biomass Conference and Exhibition, Vienna*, June 1-4th 2015.

- Iulia M. Daraban, Thomas H. Pedersen, Lasse A. Rosendahl, Anna L. Jensen, Claus U. Jensen, Kristine M. Rasmussen, Simon S. Nielsen, "Modeling Black Liquor Hydrothermal Liquefaction in Aspen Plus®", *Poster presentation at the 22nd European Biomass Conference and Exhibition, Hamburg*, June 23-26th 2014.

- Iulia M. Daraban, Thomas H. Pedersen, Lasse A. Rosendahl, "Particle size and solids concentration impact on rheology and stability of wood-water slurries", *Poster presentation at the 22nd European Biomass Conference and Exhibition, Hamburg*, June 23-26th 2014.

This thesis has been submitted for assessment in partial fulfillment of the PhD degree. The thesis is based on the submitted or published scientific papers which are listed above. Parts of the papers, book chapters and projects I have supervised are used directly or indirectly in the extended summary of the thesis. As part of the assessment, co-author statements have been made available to the assessment committee and are also available at the Faculty. The thesis is not in its present form acceptable for open publication but only in limited and closed circulation as copyright may not be ensured.

Preface

This PhD thesis has been submitted to the Faculty of Engineering and Science, Aalborg University, Denmark, to fulfill the requirements for obtaining the PhD degree. The PhD program was commenced on August 1, 2012 and carried out at the Department of Energy Technology, Aalborg University. The project was funded by the Danish Agency for Science, Technology and Innovation, Grant no. 10-094552. The project was granted through a Sino-Danish collaboration the Zhejiang University, China, under the project title "*FLEXIfuel - Optimizing fuel flexibility through high quality bio-oils*".

- The Danish Agency for Science, Technology and Innovation under the project "*FLEXI-fuel - Optimizing fuel flexibility through high quality bio-oils*" for financial support.

Thomas Helmer Pedersen
Aalborg University, February 1, 2016

Nomenclature

$\bar{M}_n$	Number average molar mass
$\bar{M}_w$	Mass average molar mass
$\dot{m}$	mass flow rate
ρ	density
c	cohesive energy density
C_B	Base Capital cost
C_C	Capital cost
f_M	Material correction factor
f_P	Pressure correction factor
f_T	Temperature correction factor
H	heat of vaporization
Q_B	Base Capital cost
Q_C	Capital cost
R	gas constant
R_0	Process severity
V_m	Molar volume
K_2CO_3	Potassium carbonate
Na_2CO_3	Sodium carbonate
H/C_{eff}	Hydrogen-to-carbon effective ratio

BOM   Bureau of Mines

BtL   Biomass-to-Liquids

C#   Number of carbon atoms

CGE   Carbon Gasification Efficiency

CLU   Continuous Liquefaction unit

FAME   Fatty acid methyl ester

FFA   Free fatty acid

HSP   Hansen Solubility Parameters

HTP   Hydrotreatment product

KOH   Potassium hydroxide

L   reactor lenght

LBL   Lawrence Berkeley Laboratory

M   Capacity scale factor

NaOH   Sodium hydroxide

PDU   Process Development Unit

PERC   Pittsburgh Energy Research Center

PSR   Partial Steam Reforming

r   reactor inner radius

T   Reaction temperature

t   residence time

TOC   Total Organic Carbon

WGS   Water-gas shift

WSO   Water-Soluble Organics

Part I

Introduction

Chapter 1

Introduction

It is evident that in the transition from a fossil to a renewable energy based society, the whole energy sector is facing a paradigm change regarding conversion and distribution of energy. The main reasons for this change are the diminishing finite and economically accessible fossil crude oil reserves followed by increasing extraction costs and the ever increasing demand by emerging economies. Even today, crude oil is the principal energy resource for the World's transportation sector, which for centuries has revolutionized human mobility and living standards. The reason is the valuable products from crude oil refineries; energy carriers mainly in the form of liquid state hydrocarbons. An excerpt of different products obtainable from crude oil refining is illustrated in Fig. 1.1. Worldwide, some 90 millions barrels of crude oil are daily consumed [1], and in a future facing shortage on the principal energy source there is a need for new energy sources and carrier substitutes for the existing transportation.

In the long-term future energy system there is a necessity for energy- and resource-efficient Biomass-to-Liquids (BtL) processes, which is why research attention towards biomass as a supply for liquid energy carriers has been and still is rapidly growing [2]. Although many countries are striving to move beyond fossil fuels, reality is that fossil hydrocarbons will continue their dominance in the energy mix for a long time to come. Future indications are, however, that the ever increasing energy demands will increase future crude oil costs towards a level, at which previous stunted renewable alternatives are becoming economically attractive [1]. Switching to biomass-derived fuels would not only slash current World carbon emissions, but potentially deflect the carbon emissions towards a descending trajectory.

BtL is a major ongoing research focus worldwide due to the renewable aspects and abundance of biomass. Moreover, biomass is an energy carrier consisting of e.g. carbon and hydrogen; the backbone constituents of current hydrocarbon fuels. Breaking down and chemically modifying the biomass structure provides numerous prospective pathways to synthetic renewable bio-fuels and bio-materials that can offer an alternative to the current fossil based hydrocarbon infrastructure.

Since the current energy infrastructure has been established upon the end-use possibilities of refined crude oil, in terms of technology transition flexibility, crude oil-like substitutes are highly attractive [3]. Consequently, there is a strong argumentation for the production of marketable "drop-in" fuels; that is fuels with similar characteristics as crude oil derivatives that can directly substitute petrol, diesel and jet fuel cuts etc. existing in the current infrastructure. This ultimately defines that any feedstock and/or conversion technology development must be done with the end-use needs in mind [4]. The potentially very attractive option for introducing biomass-derived materials into the fuel market via biobased blendstock in a standard petroleum refinery was reviewed by Talmadge et al. [5]. This option would facilitate a renewable and economically advantage by using the already established, multi-trillion dollar infrastructure. Producing bio-blendstock, or ultimately marketable, renewable fuels from biomass is, however, confronting a multitude of challenges. Fuels produced from a fossil origin are still economically favorable over sustainable bio-fuels. More important is that any marketable bio-fuels need to conform to the following:

- Be sustainably produced

- Be based on an abundant non-food feedstock or feedstock mixture to have a high impact factor, locally and globally

- Exhibit drop-in properties in the sense that the hydrocarbon infrastructure remains unaltered

- Obey all current regulations on fuel specifications and standards

A major objective in bio-fuel production is therefore to obtain products, which perform like existing conventional hydrocarbons in terms of e.g. octane and cetane number, energy density, volatility, and hydrophobicity. As observed from Fig. 1.1, current hydrocarbon fuels consist mainly of aliphatic, alicyclic, and aromatic hydrocarbons in a variety of different compounds. Crude oil is often characterized in terms of a boiling point range of the fractions (naphtha, kerosene, diesel, etc.) obtained from the crude oil, which to an extent can be translated to number of carbon atoms (C#) as shown in Fig. 1.1. Each of these fractions has characteristic properties determining their use-end applications.

As already mentioned, biomass consists of hydrogen and carbon, like hydrocarbons, but also of heteroatoms like oxygen, nitrogen, and sulphur, which are inevitable traced in the BtL products. Consequently, in order to conform to a "drop-in" aspect a target in any advanced BtL process is to reduce the great amount of especially oxygen in the biomass to approach the composition of fossil products as illustrated by Eq. 1.1

$$-CH_2O- \rightarrow -CH_2- \tag{1.1}$$

Despite the challenges of introducing bio-based products to a commodity market it is a well-recognized fact that biomass holds a yet untapped key potential as a feedstock for high valuable

	Number of carbons	Boiling point range	Uses
Gases	1–4	0–30°C	Bottled and natural gas
Naphthas	5–10	30–180°C	Gasoline
Kerosenes	10–16	180–260°C	Kerosene for home heaters, jet fuel
Gas oils	16–60	260–350°C	Diesel fuel, feedstock for cracking
Lubricants	>60	350–575°C	Motor oil, feedstock for cracking
Fuel oil	>70	>490°C	Candles, fuel oil for ships and power stations
Asphalt	>80	>580°C	Roofing tar, road tar

Crude oil ~400°C

Petroleum distillation tower   **Petroleum fractions**

Fig. 1.1: General principal of crude oil distillation and obtainable fractions. Adapted from [6].

fuels and chemicals etc. [7, 8]. Moreover, the term *biorefinery* is becoming well-established for the single process or compilation of processes exploring the full valorization potential of biomass.

The objective of biorefineries is to optimize the use of resources, and minimize wastes, thereby maximizing benefits and profitability. The Royal Society, 2008 [4].

The biorefinery vision foresees a processing factory that separates the biomass into component streams and then transforms the component streams into an array of products using appropriate catalytic or biochemical processes, all performed at a scale sufficient to take advantage of processing efficiencies and resulting improved process economics. In essence, this concept is the modern petroleum refinery modified to accept and process a different feedstock and make different products using some of the same unit operations along with some new unit operations. Elliott, 2004 [9].

The technology road map for the future biorefinery is, on the other hand, an ongoing discussion far-reaching from already commercialized processes, such as fermentation and transesterification, through to highly selective catalytic processes [10]. Already in 1998, a *technology road map for plant/crop-based renewable resources* was formulated by the U.S. Department of Energy. The road map stated that at least 10 % of the basic chemical building blocks should be plant-derived renewables by 2020 (a fivefold increase from the 1998 level) and 50 % by 2050 (a subsequent fivefold increase from the 2020 level), depicted in Fig. 1.2 [11]. In the road map
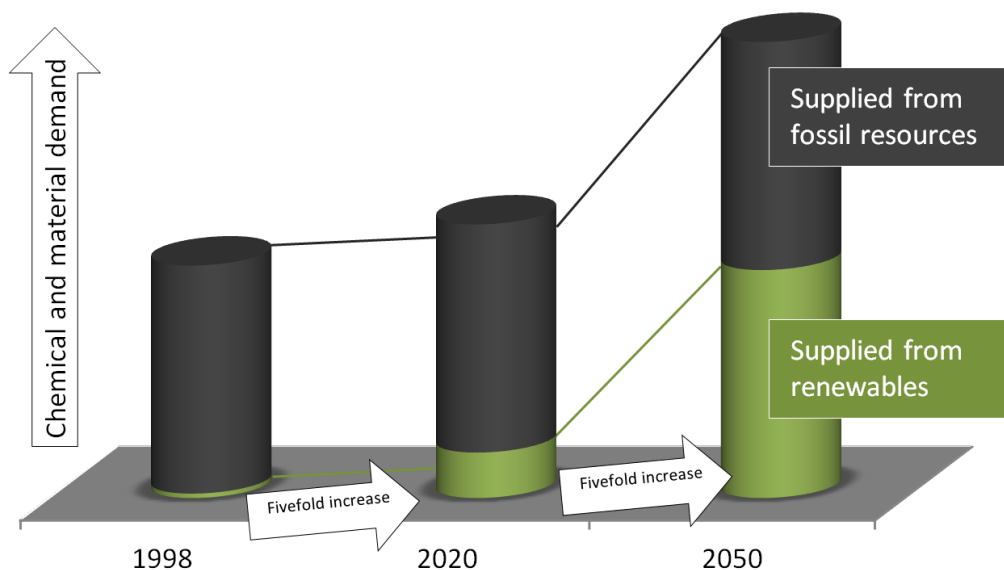
Fig. 1.2: Renewables as basic chemical building blocks targets set by the U.S. Department of Energy. In 2020, at least 10 % of the basic chemical building blocks from plant-derived renewables by 2020 (a subsequent fivefold increase from the 2020 level) and 50 % by 2050 (a subsequent fivefold increase from the 2020 level). Adapted from [11].

it is assumed that the demand for consumable goods increases and that the total resource consumption is therefore increasing rapidly in global terms. Thus, within the 2050 time frame it is not expected that renewable resources will replace hydrocarbon resources, but more that 1) renewables are not competing directly with non-renewables (this is not a competitive replacement strategy), and that 2) both renewable resources and non-renewable resources will be needed to meet demands within the 2050 time frame. The roadmap postulated that key opportunities to increase the use of renewable resources and to achieve set targets can be grouped into four areas representing the whole value chain as shown in Fig. 1.3.

A successful roadmap to increase the volume of renewables in the chemical in fuel production therefore relies on optimization of the whole BtL value chain. As mentioned previously, an imposing barrier for the market entry of biomass-derived materials is the competitive cost situation with fossil-derived materials, but overcoming this barrier does not only include a cost
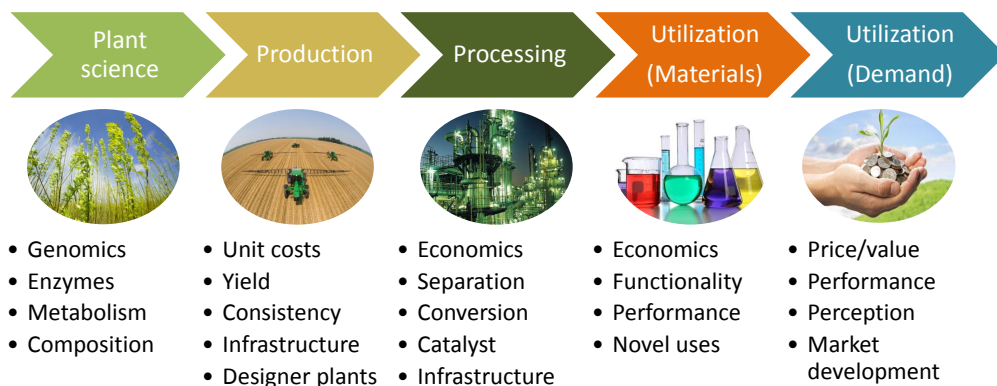
Fig. 1.3: Major barriers, identified for conversion of renewable resources into renewable products, grouped into four main groups [11].

reduction. To obtain high volumes of renewables in the current petroleum-dominated market, highly efficient biomass farming yielding high throughputs of biomass is a necessity. So is resource and energy-efficient, and feedstock-flexible BtL processing technologies to maximize the yield of value-added renewable products to yield a high impact factor on the market.

The many different BtL processing technologies may be categorized based on several measures related to for instance input feedstock (1. generation, 2. generation, 3. generation etc.), process chemistry (biochemical vs. thermochemical), process path (direct vs. indirect) defining e.g. the process sustainability, flexibility, and severity. Another classification method depends on whether or not *fractionation* of the biomass is compulsory prior the core BtL process. Fractionation, in this context, refers to the process step of isolating individual biomass fractions; cellulose, hemicellulose, lignin, lipids and proteins. Fractionation must be distinguished from *pretreatment*; a more overall term which also includes but is not limited to fractionation. Common fractionation methods cover e.g. the Kraft process [12], Organosolv process [13], explosion (using e.g. steam, ammonia, and CO_2) [14], Sulfite process [15], ionic liquids [16] etc.

Since cellulose, hemicellulose, lignin, lipids and protein hold different physical and chemical properties, complete fractionation naturally offers an increased degree of freedom with respect to process flexibility. By complete fractionation, BtL processes can then be tailored to the homogeneous fractional cuts of the biomass [17]. The downside is that multiple highly efficient processes must be developed (one for each product stream) within a biorefinery. Moreover, since each single process is optimized for a single biomass fraction, a constant and high quality throughput is required, which makes the concept vulnerable to seasonal and regional biomass changes. Furthermore, no universal fractional method has yet been identified that completely fractionates biomass into its native cellulose, hemicellulose, lignin, lipids, and protein, concur-

rently. Hence, the common denominator for all the previous mentioned methods is that they are all tailored to efficiently isolate usually one fraction (typically cellulose or lipids) and sacrifice the remaining macrostructures with changes in their physico-chemical properties. Therefore, the resulting subsequent process flexibility is highly dependent on the fractionation efficiency and the accompanying physico-chemical alterations [18].

Less constrained BtL processes cover thermo-chemical processes such as hydrothermal liquefaction (HtL), pyrolysis and gasification etc., which do not require biomass fractionation and are therefore more flexible in terms of the input feedstock. The product of these BtL processes are biocrudes (liquefaction), bio-oils (pyrolysis) or syngas (gasification) with petroleum-like characteristics and therefore represent a potential blendstock for further refining in the existing infrastructure. The main difference between these processes is that HtL and pyrolysis are *direct* processes, whereas gasification is an *indirect* process, when the target is to process liquid products. For indirect processes, the Fischer Tropsch synthesis is often applied as final conversion step for liquid fuel production according to Eq. 1.2.

The main difference between HtL and pyrolysis is the reaction medium. HtL is carried out in an aqueous environment at processing conditions close to the critical point of water (T_c=647 K, P_c=22 MPa) to benefit from the unique properties of hot-compressed water [19]. Pyrolysis is carried out under nearly inert, "dry" conditions typically in a e.g. fluidized bed, ablative or rotating cone reactor [20]. Usually biomass have a relatively high moisture content, and for some "wet" biomass the moisture content may even be as high as 95 %. It is expected, that the direct use of highly moist or even wet biomass is more suitable than initial drying and subsequent treatment by a "dry process", which, in terms of flexibility, advances HtL over pyrolysis [21].

As previously discussed, the HtL and pyrolysis biocrudes contain significant amounts of heteroatoms (oxygen, nitrogen, sulphur), and especially of oxygen originating from the natural biomass composition. Converting these oxygenated biocrudes into alkanes, a hydroprocessing (HPR) step is needed according to Eq. 1.3.

$$-CH_2O- \xrightarrow{\text{Gasification}} xH_2 + yCO \xrightarrow{\text{Fischer Tropsch}} -CH_2- + H_2O \qquad (1.2)$$

$$-CH_2O- \xrightarrow[\text{Pyrolysis}]{\text{Liquefaction}} C_xH_yO_z \xrightarrow[\text{+H}_2]{\text{HPR}} -CH_2- + H_2O \qquad (1.3)$$
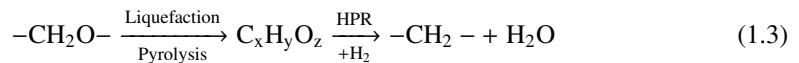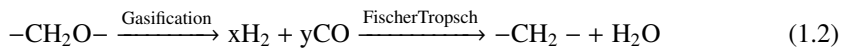
Drawing parallels to conventional hydrotreatment processes carried out at current refineries, it is envisioned that these biocrudes initially can be co-processed along with, but ultimately replace, fossil crude oils and thereby adopt the current fuel infrastructure. In doing so a major challenge associated with this conceptual idea is, however, precisely how to remove residual oxygen in the biocrudes, whilst minimizing the consumption of expensive hydrogen. Generally, the biocrudes obtained from HtL demonstrate lower oxygen content than pyrolysis bio-oils and hence more favorable properties [15, 23, 24]. In terms of subsequent hydrotreatment, biocrudes
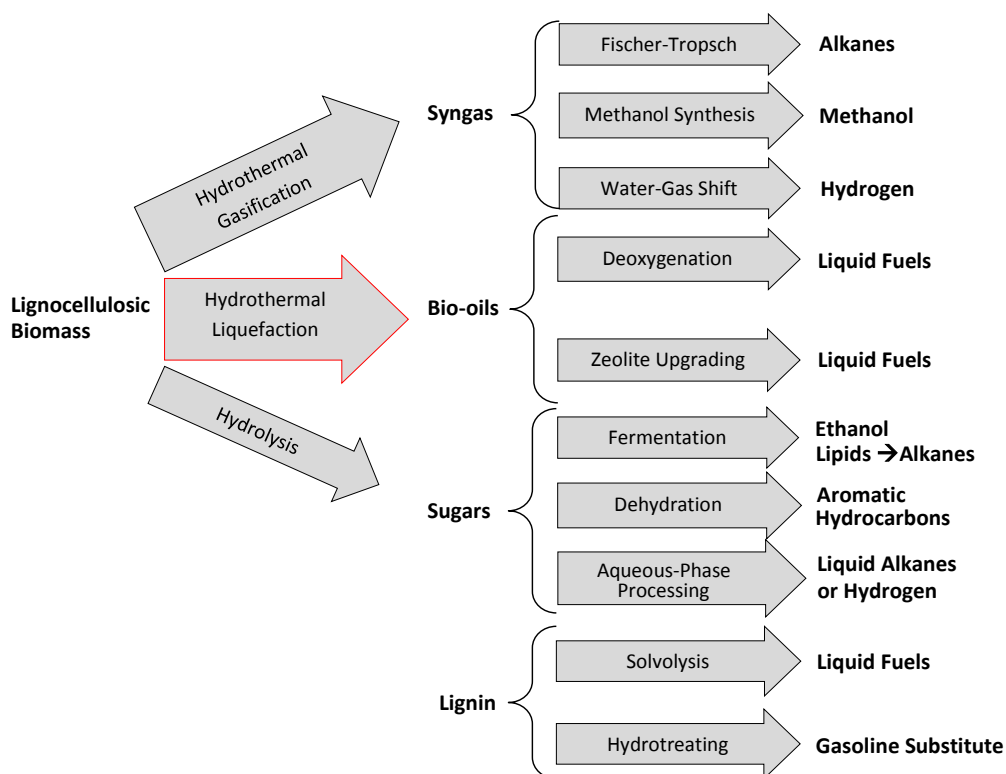
Fig. 1.4: Flow chart of lignocellulosic conversion route using an aqueous medium. Modified from Huber and Dumesic [22].

are thus more attractive since theoretically less hydrogen is needed in turning the biocrude into hydrocarbons.

A second major challenge in BtL, and especially in a HtL context, is the yet poorly established relationship between the input biomass feedstock and the resulting product quality [25–29]. As previously mentioned, any feedstock and conversion technology must be related to the end-use profile. The poorly established link between the biomass feedstock and the resulting product quality therefore blurs the determination of the full potential of these biocrudes as blendstock. Fig. 1.4 displays some of the obtainable, but also very different, products from processing biomass in an aqueous medium. The poorly defined link between feedstock, process conditions and product quality is to a great extent a consequence of the complex nature of biomass combined with the multiple of possible reaction pathways occurring at severe processing conditions [19, 30]. This combination may lead to biocrudes containing several hundreds of compounds with different chemical functionalities, which complicates the biocrude char-

acterization. The mixture of oxygenated compounds contained in the biocrude raises several drawbacks over conventional crudes, which results in technical and economical challenges such as:

- Low thermal stability

- Low chemical stability

- Low heating value

- Low volatility

- pH non-neutrality

- High polarity

- High water content

These properties lead to several challenges such as low solubility with fossil crude oils, which must be addressed. For this reason, the *National Science Foundation* made the following future research priorities in order to address the challenges associated with biocrude production and downstream processing [23]:

1. Improvement of upstream processes (i.e. pyrolysis and liquefaction), to make the resulting biocrudes more amenable to downstream processing.

2. Development of methods to increase the overall efficiency of the process. For example, perhaps process chars can be used for process energy purposes and the water soluble products used for hydrogen production via reforming.

3. Techniques for effective removal of acidity. Decarboxylation would be desirable, but the most efficacious route (e.g. catalysis, reaction chemistry) is currently unclear.

4. Identification of desirable oxygen compounds that improve the fuel properties.

5. Development of technologies that produce fuels compliant with sulfur specifications, while preserving only the desirable oxygen compounds in the biofuels. There may be advantages in leaving certain oxygenated compounds in the fuel for lubricity. There are multiple ways to improve lubricity. The possible benefits of some oxygenates in fuels are increased lubricity and higher cetane number and in some cases the improved reactivity in the soot.

6. With respect to C-O bond cleavage, the bond energy distributions for biocrudes must be determined. The less stable bonds must be identified. Molecular-level detailed composition information will be necessary to determine bond energy.

It is evident that there is a need of a better process understanding including detailed knowledge about reaction mechanisms, which is identified as critical in understanding, designing and controlling processes towards high quality biocrudes amenable to downstream processing.

From previous discussion it has been argued that biomass is a necessity in the future energy mix due to their inherent hydrogen and carbon source holding the possibility to substitute current petroleum-based hydrocarbons. Also, biorefineries for complete valorization of biomass are still yet conceptual but emerging in all aspects due to technological and scientific progress. The roadmap for a biorefinery reality is blurred by the wide range of commercial BtL processes and research processes yet to be proven feasible. The fact is that current commercial BtL processes are not sufficient for a high impact biorefinery reality derived from the intense ongoing research for new BtL processes. The major reason is that current commercial BtL processes do not produce products holding "drop-in" properties or are sufficiently feedstock-flexible to be based on abundant non-food feedstock or feedstock mixture to have a high impact factor.

Thermo-chemical processes such as liquefaction, pyrolysis and gasification hold the ability to produce "drop-in" products with a high impact most likely through two-stage processes according to Eq. 1.2 and 1.3. From a chemical process point of view, HtL is the most flexible process in terms of feedstock input due to the presence of an aqueous reaction medium excluding any prior feedstock drying. From previous discussion it is also clear that the chemical compound distribution and hence the biocrude quality is highly feedstock dependent. Production of desirable hydrocarbons directly from biomass hydrothermal processing has not yet been achieved. Evidently, downstream upgrading (e.g. hydrotreatment) of the biocrudes is required to eliminate especially residual oxygenated functionalities. Since HtL biocrudes exhibit higher quality oil over pyrolysis, it is expected that the effort needed for making HtL biocrudes amenable to downstream processing is less extensive and expensive.

The greatest challenge yet to be addressed is to link the biomass composition to the biocrude quality. Understanding and enabling reaction chemistry selectivity towards product compounds that are feasible as fuel precursors and amenable to upgrading for marketable fuel products is paramount for process commercialization.

The main objective of this dissertation is to expand the current knowledge-base on reaction mechanisms of HtL when processing biomass model compounds and real biomass. The dissertation investigates experimentally the link between biomass composition and biocrude quality from a biomass composition point of view. An objective is to enhances the prediction of biocrude compounds. This aspect is valuable in both a "single" feedstock processing context but more important in a biomass compounding context, where different types of biomass are likely to be processed concurrently.

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Part II

Technical Background of Hydrothermal Liquefaction

Chapter 2

Properties of sub- and supercritical water

HtL is a thermo-chemical process utilizing an aqueous medium both as a biomass vehicle in continuous processing applications and as a reactant mainly for chemically disintegration of the biomass macrostructures. Chemical disintegration of the macrostructures demands the overcoming of the activation energies of the various biomass chemical bonds, which practically involves processing at elevated temperatures. In order to substantially liquefy biomass into a water-insoluble biocrude, processing conditions have to approach near-critical water conditions. At these conditions the water properties change significantly, which in turn may affect the pathways of chemical reactions. In the following chapters, the chemical and technical aspects of HtL will be explained and the current HtL status reviewed.

Hot compressed water possesses interesting properties as a solvent and as a reactant in chemical conversion of biomass that are tunable by varying process conditions. Fig. 2.1 displays the phase diagram of water. Below its critical point (374 °C, 221 bar) water exists in a two-phase vapor/liquid equilibrium.

Above the critical point, water exists in a homogeneous phase where the density of water can vary from gas to liquid-like values and still remain in a homogeneous phase. In the transition from sub- to supercritical conditions water properties change drastically, which opens opportunities for tuning properties according to desirable reactions during biomass conversion.
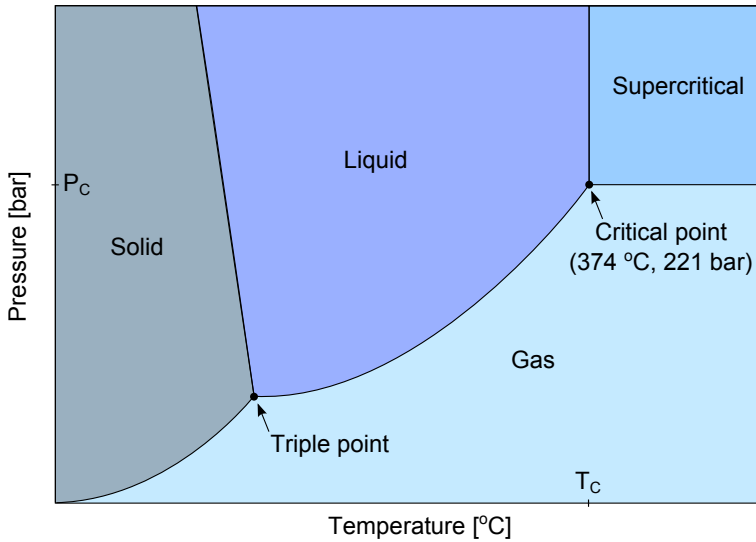
Fig. 2.1: Phase diagram of water. (T_C=Critical temperature (374 °C), P_C=Critical pressure (221 bar)).

1   Density

Water is relatively incompressible in the subcritical region and varies only little with changes in temperature or pressure. On the contrary, density changes drastically at vaporization or as conditions approach the critical point. Fig. 2.2 shows the density changes at various temperatures and pressures. At vaporization, the density changes discontinuously whereas at supercritical conditions the density can be varied continuously. The solvent power and diffusion properties of water are strongly dependent on the water density and hence can be controlled by density variation. From a chemical point of view, high diffusion rates are favorable for high reaction rates, when water as a reactant has to entrain the biomass macrostructures.

From a practical point of view, density is important in determining the volumetric flow in continuous systems. For a fixed reactor volume, a change in density directly corresponds to a changes in residence time according to Eq. 2.1.

$$t = \frac{\rho L \pi r^2}{\dot{m}}$$

(2.1)

where:

t = residence time
ρ = density
L = reactor length
r = reactor inner radius
$\dot{m}$ = mass flow rate
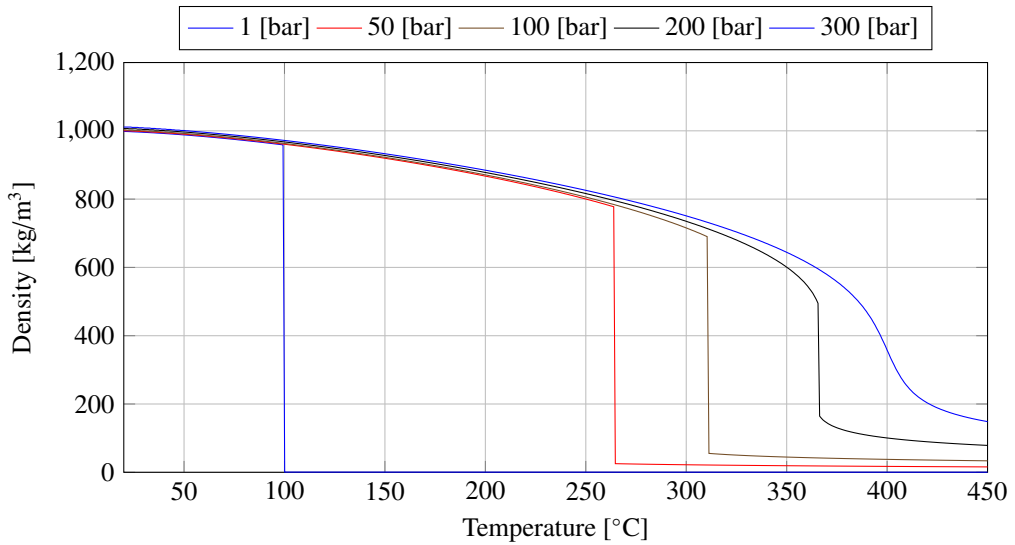
Fig. 2.2: Water density as a function of temperature and pressure.

2   Enthalpy

Enthalpy also changes significantly around the critical point. From an energetic point of view, process pressure should always be kept above the saturation pressure corresponding to the process temperature. In Fig. 2.3 the discontinuities in the isobaric lines correspond to a energetic penalty due to vaporization, which is to be avoided at any time. Since there is no phase transition above the critical pressure, the enthalpy change is also continuous above the critical pressure. Hence, large energy savings can be achieved by maintaining the process pressure above the critical pressure.

The energy-related costs of operating at more severe conditions have been a subject for discussion. Undoubtedly, the single most energy requiring process in the whole HtL process train is heating the feed stream to process conditions, mainly as a result of the high fraction
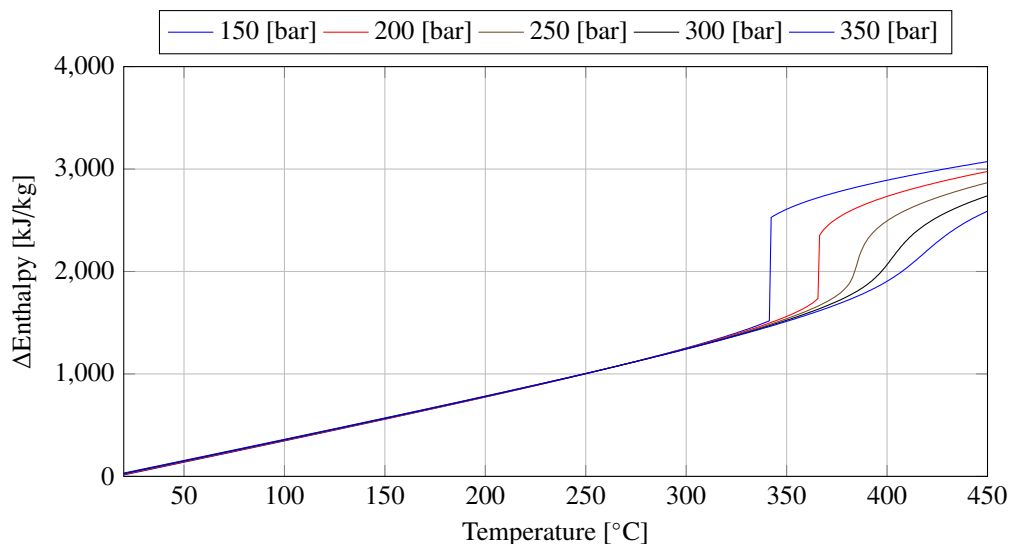
Fig. 2.3: Enthalpy change of water as a function of temperature and pressure.

of water present. Increasing for instance the temperature e.g. from 350 to 400 °C (@250 bar) increases the energy requirements by more than 60 %. Increasing the temperature e.g. from 350 to 400 °C (@300 bar) increases the energy requirements by approximately 35 %. System pressure may therefore also be a controlling parameter for the process energy intensity. The substantial amount of energy required to heat the feedstream to process conditions has to be recovered by heat integration in any case. Therefore, the actual energy penalty of increasing the process severity from e.g. subcritical to supercritical conditions has to be determined by process simulations. This will be discussed in more details in Chapter 5.

3   Static dielectric constant

In chemical synthesis, in which a solvent is used, solubility of reactants in the solvent is an important parameter. At the microscopic level, single water molecules remain polar at super-critical conditions [1]. However, on a macroscopic level the polarity of water as a solvent can be changed be changing process conditions, where the hydrogen bonding network may eventually collapse. It is observed from Fig. 2.4 that at ambient conditions water is a polar solvent, but its static dielectric constant constantly decreases with increasing temperature decrease the polarity significantly. At sub- and critical conditions, the static dielectric constant drops to about 1 meaning that it is miscible with non-polar compounds. For instance, the solubility of saturated medium- and long-chained fatty acids in hot compressed water increases exponen-
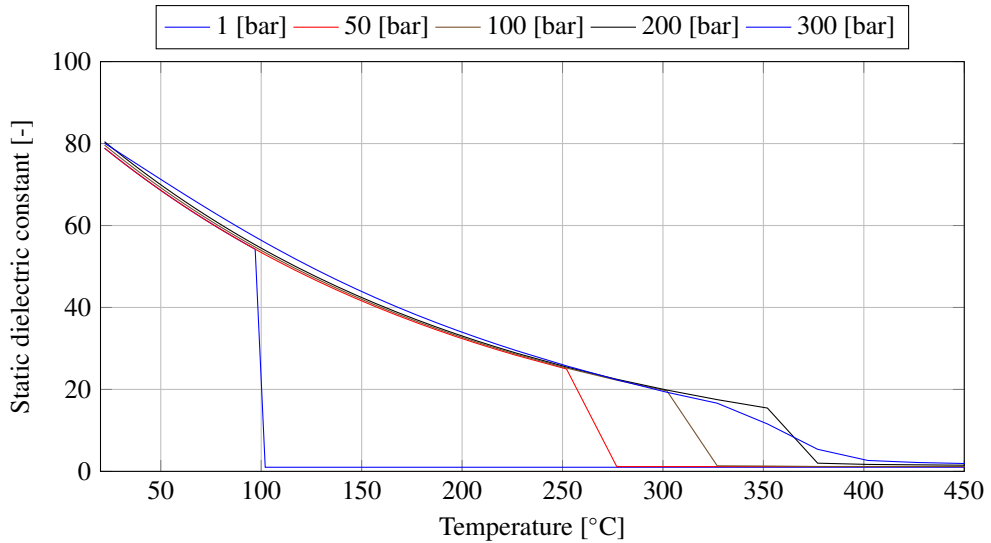
Fig. 2.4: Static dielectric constant of water as a function of temperature and pressure

tially as a function of temperature [2]. This fact is interesting since as the biomass conversion progresses, biomass compounds become increasingly non-polar and hence more soluble in the solvent. Then, when products are later brought to ambient conditions, water reclaims its high polarity, and non-polar compounds are easily obtained from the aqueous phase. The "tunability" in miscibility of different compounds also allows selective precipitation of certain compounds. For instance, salt precipitation at supercritical conditions has been investigated in several supercritical water applications, e.g. supercritical water oxidation (SCWO) [3], and supercritical water gasification (SCWG) of biomass [4].

Chapter 3

Effects of process conditions

Process conditions in HtL can be tuned to obtain desirable properties of the water environment mainly by controlling temperature and pressure as discussed in Chapter 2. From a chemical point of view these properties are of great importance, but experiments have shown that a great number of other factors than water properties play an important role when liquefying biomass. In 1982 Sabri Ergun reviewed biomass liquefaction efforts made in the 1970s in the light of the energy crisis [5]. Already then it was stated that:

"*Selection of a chemical approach, from among the published methods of wood liquefaction, that may have the potential of being technically and economically feasible is by no means easy*" [5].

Furthermore, it was concluded that approaches involving excessive residence times, expensive solvents as a vehicle and expensive catalysts that present recovery problems may be turned down. The complexity of HtL is best illustrated by listing an excerpt of parameters that has or may have an effect on the process (batch and continuous):

- Type of biomass
- The physical condition of the biomass
- Capacity of the autoclave
- Weight of biomass charged
- Carrier vehicle
- Vehicle/biomass weight ratio
- Composition of the gas phase imposed

- Initial pressure
- Catalyst
- Catalyst/biomass ratio
- Stirring or mixing
- Rate of heating
- Final reaction temperature
- Retention time
- Rate of cooling

Biomass in general is any organic matter derived from living and recently living organisms. This is in contrast to fossil organic matter, which is derived from dead organisms over millions of years. Biomass covers a broad range of different compounds that vary in chemical and structural composition that is of great importance when processing it for fuels and chemicals. Biomass is often divided into subgroups based on the chemical type of biomass, e.g. woody or lignocellulosic biomass, herbaceous plants, starch- and triglyceride-producing plants, etc., or based on an application context such as agricultural waste, energy crops, forestry waste, etc. The European Committee for standardization (CEN) has previously made an attempt to standardize land-based biomass into the four following biomass categories:

- Lignocellulosic biomass

- Herbaceous biomass

- Fruit biomass

- Blends and mixtures

Alongside land-based biomass, aquatic biomass like water hyacinth and algae is also of particular interest. Common for all biomass, land-based or aquatic, is that the biomass macro-molecules, or building blocks, are basically identical although they appear in different ratios. Biomass macromolecules include cellulose, starch, hemicellulose, lignin, lipids, and proteins, and then the presence/absence and the quantitative distribution of these six macromolecules de-termines the chemical and structural nature of a particular biomass. Ideally this means that any biomass of blends/mixtures of biomass can be characterized based on the relative distribution of these six macromolecules. Of the macromolecules, the majority of starch is usually concen-trated in the edible part of biomass and is commonly considered controversial in a biomass to fuels and chemicals context due to the conflict with food and feed production. The inedible part of biomass, intended for e.g. fuels and chemicals, therefore contains mainly cellulose, hemicel-lulose, lignin, lipids, and proteins. It can be argued that lipids and proteins are also in a conflict position like starch, but for some abundant types of biomass like algae, lipids and proteins are not easily accessible and may still play a significant role when processing biomass for fuels and chemicals.

1   Effects of reaction temperature

Reaction temperature is a key parameter in thermochemical conversion of biomass and strongly influences both yield and quality of the biocrude. Initially, as the reaction temperature increases, thermal effects activate the fragmentation of the biomass macrostructure into its monomers or more reactive species. The breakdown of the different macrostructures initiates under different temperatures depending on the chemical structure of the particular macromolecule.

Fig. 3.1 displays the common temperature regions of hydrothermal conversion of biomass including hydrothermal carbonization, HtL, and hydrothermal gasification, and in addition the approximate activation temperatures of macrostructures degradation and selected reactions.

Cleavage of the abundant ether bonds present in biomass by hydrolysis is usually the initial pathway for degradation of the macromolecules. Due to the heterogeneous and amorphous structure of hemicellulose, degradation of hemicellulose in neutral hot compressed water is initiated already at approximately 180 °C. Lignin degrades at approximately 200 °C, and cellulose degrades around 240 °C due the more recalcitrant nature caused by its crystalline structure [6].

Hydrothermal carbonization of biomass operates in the temperature range of 180-250 °C. In this temperature range substantial hydrolysis reactions have been initiated, and dehydration reactions of especially carbohydrates are selective. Dehydration reactions followed by polymerization of the obtained chemical compounds significantly carbonizes the biomass [7]. Reaction kinetics are naturally also affected by the reaction temperature, and thus hydrothermal carbonization requires long residence times in the range of 1-74 hours.

The common temperature range of HtL includes both the sub- and the supercritical water region and ranges typically between 280-420 °C. The vast majority of HtL literature is, however, concentrated in the region of subcritical water conditions. As the name implies, the main objective in HtL is to maximize the yield of liquid compounds. Differently from hydrothermal carbonization, a secondary water-insoluble liquid phase (biocrude) is observed when processing biomass under common liquefaction conditions. Hence, the chemistry involved in biocrude formation must be different from that of carbonization.

At more severe conditions, gasification is initiated. Although gas formation is also observed in the carbonization and the liquefaction temperature range, under non-catalyzed conditions high temperatures (>600 °C) are needed to achieved substantial gasification efficiencies.

The temperature effects on the rate of hydrolysis of cellulose in sub- and supercritical was investigated by Sasaki and coworkers [8]. Fig. 3.2 reproduces the results obtained at supercritical conditions. It is observed that even at a short residence time (0.01 s) nearly all cellulose has been converted. At subcritical conditions (350 °C) similar trends have been observed, although a somewhat longer reaction time (1.5 s) was needed for complete cellulose conversion. Moreover, it was found that at both sub- and supercritical water conditions, cellulose is rapidly converted into oligomers of different number of units, and monomers. At supercritical conditions, the rate of hydrolysis is remarkably enhanced and exceeded the rate of subsequent monomer decomposition, resulting in a total yield of oligomers and monomers of almost 80 % at the shortest reaction time. At subcritical conditions, a total yield of oligomers and monomers of approximately 60 % was achieved, due to a slower hydrolysis rate compared to the rate of monomer decompositon. Therefore, it is reasonable to assume that at both sub- and supercritical conditions, polysaccharides (hemicellulose and cellulose) will immediately hydrolyze into carbohydrate monomers before decomposing. Consequently, studying the reaction chemistry of carbohydrates should serve as a reasonably representative baseline for understanding the reaction chemistry of polysaccharides.
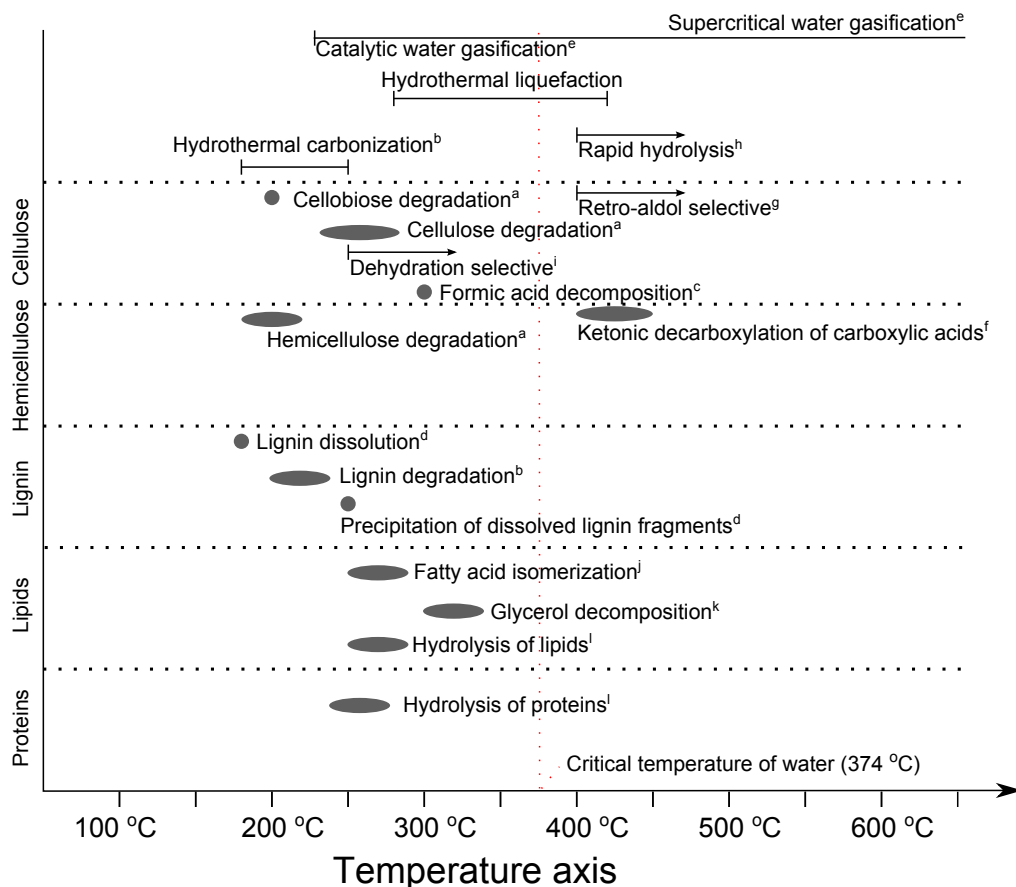
a: Bobleter, 1994, Prog. Polym. Sci. (19), pp. 797-841
b: Funke and Ziegler, 2010, Biofuels, Bioprod. Bioref. (4), pp. 160-177
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h: Sasaki et al., 2000, Ing. Eng. Chem. Res. (37), pp. 2883-2890
i: Lü and Saka, 2012, J. of Supercritical Fluids (61), pp. 146-156
j: Guo et al., 2015, Renew. Sust. Energ. Rev. (48), pp. 776-790
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l: Toor et al., 2011, Energy (36), pp. 2328-2342

Fig. 3.1: Activation of degradation of macromolecules and initiation of selected chemical reactions as a function of temperature.
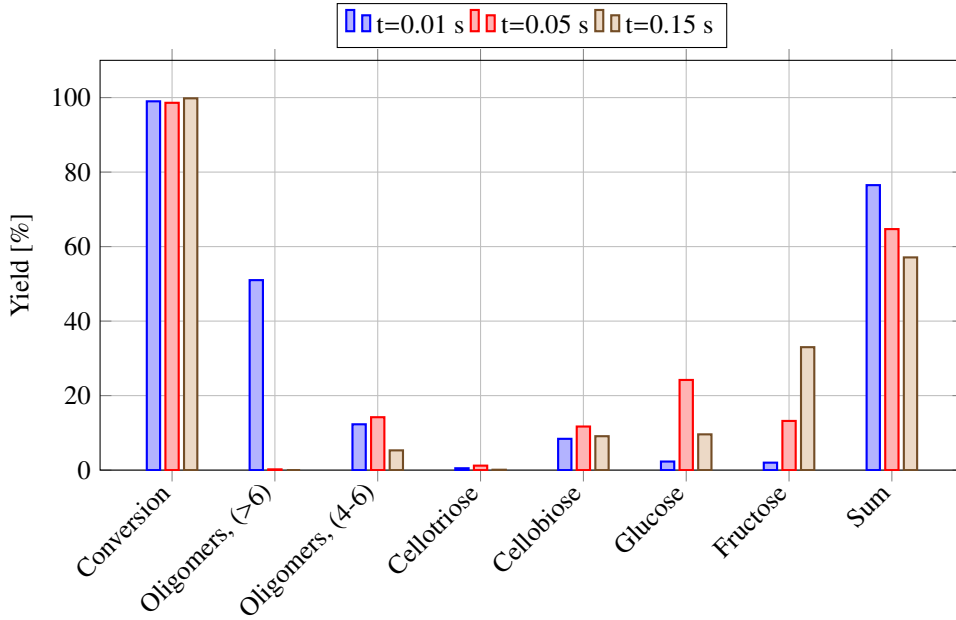
Fig. 3.2: Conversion and product yields from supercritical hydrolysis of cellulose at 400 °C, 25 MPa, a three reaction times: 0.01, 0.05, and 0.15 seconds. *Conversion* = conversion of cellulose *Oligomers, (>6)* = Oligomers of more than 6 units, *Oligomers, (4-6)* = oligomers of 4-6 units, *Sum* = sum of oligomers and monomers. Data obtained from [8].

In the temperature range of HtL, the degradation of biomass is rapid and the obtained fragments rearrange in a complex reaction network involving e.g. further decomposition, condensation, polymerization etc. The initial reaction decomposition chemistry of carbohydrates (at short reaction time) has been studied and reviewed extensively and is believed to be well-understood [2, 9, 10]. On the contrary, the formation of the biocrude is yet not fully understood. The initial degradation of the most abundant carbohydrates, including pentoses and hexoses, in biomass was studied by Lü et al. in the temperature range of 160-250 °C [11]. The carbohydrate degradation was related to the process severity, R_0, derived by Abatzoglou and coworkers according to Eq. 3.1 [12].

$$R_0 = \int_0^t exp\frac{T(t) - 100}{14.75}dt \tag{3.1}$$

where:

R_0 = Process severity
t = Reaction time
T = Reaction temperature
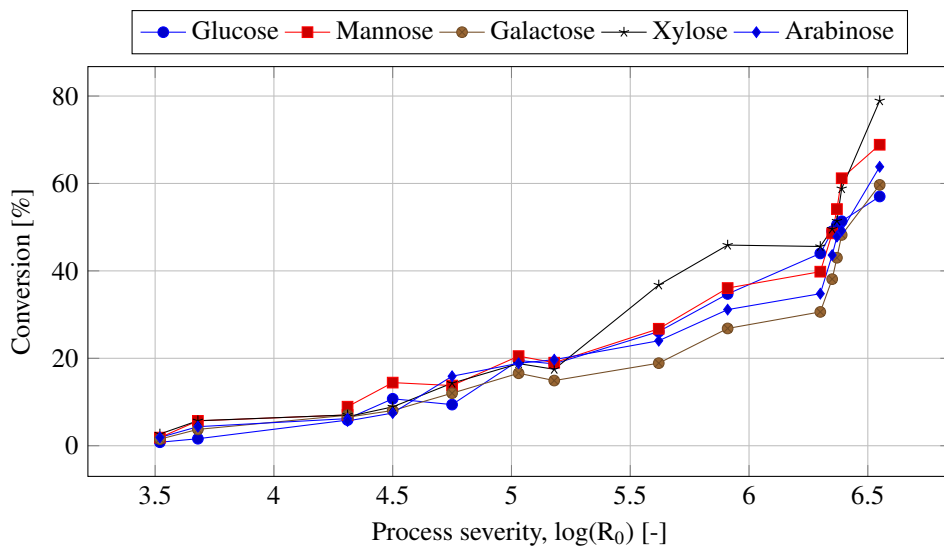
Fig. 3.3: Conversion of pentoses (xylose and arabinose) and hexoses (glucose, mannose, and galactose) as a function of process severity, R_0, in hot-compressed water. Data adopted from [11].

According to Fig. 3.3, the conversion of carbohydrates clearly increases as process severity increases. The carbohydrates investigated represented pentoses and hexoses for which the distributions of degradation products were found dissimilar. For pentoses, furfural was the major degradation product, whereas 5-HMF was the major product from hexoses. The amount of furfural and 5-HMF increases with increases reaction time and temperature. This observation further manifests that the preferred reaction pathway of carbohydrates is dehydration under non-catalytic and low temperature conditions.

The temperature effects on the compound distribution, when hydrothermally processing lignocellulose (fern fronds) under both sub- (300 °C, 25 MPa) and supercritical (400 °C, 25 MPa) conditions was studied by Carrier et al. [13]. The obtained product compounds were lumped into five classes of compounds, namely: *Cyclopentenones, Phenols, Guaiacols, Benzene,* and *Others*. Their results are reproduced in Fig. 3.4.

From their results it is evident that the compound distribution is significantly affected by the process temperature. At subcritical conditions, *Guaiacols* were the most abundant compounds followed by *Cyclopentenones*. *Phenols, Benzene*, and *Others* were almost equally distributed. At supercritical conditions, *Cyclopentenones* were the most abundant compounds followed by almost equal amounts of *Phenols* and *Guaiacols*. Hardly no *Benzene* or *Others* were observed at supercritical conditions.
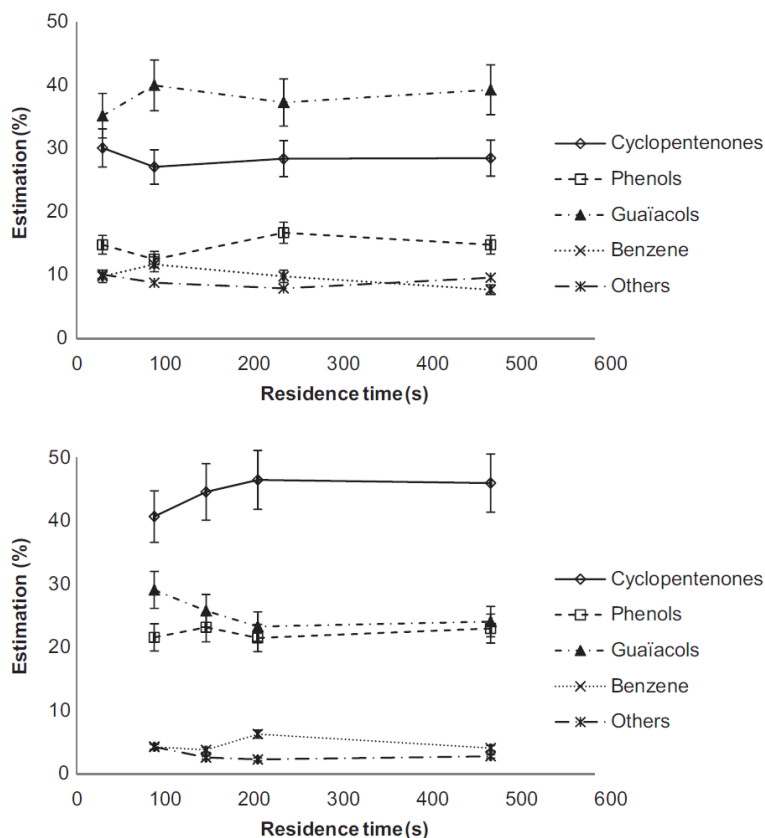
Fig. 3.4: Production distribution then processing fern (top) at 300 °C, 25 MPa, and (bottom) at 400 °C, 25 MPa for different reactions times. Data reprinted with permission from [13].

On a more bulk level the effects of reaction temperature on the biocrude yield has been reviewed by Akhtar and Amin [14]. An *optimum* reaction temperature cannot be prescribed as this will greatly dependent on other process conditions and especially on the nature of the biomass. Akhtar and Amin concluded that, *"the useful temperature range for hydrothermal liquefaction can range from 300 to 350 °C"*, which incorporates sufficient thermal energy for an efficient depolymerization of the biomass whilst minimizing gas formation. However, these reflections are based exclusively on the mass yield of the biocrude and therefore exclude important biocrude quality parameters when the biocrude is intended for e.g. fuel applications.

For energy applications it is reasonable to relate the biocrude quality to its calorific value. Fig. 3.5 shows the higher heating value (HHV) of biocrudes from various feedstock as a function of the reaction temperature. It is observed that the calorific value of the biocrude is gen-
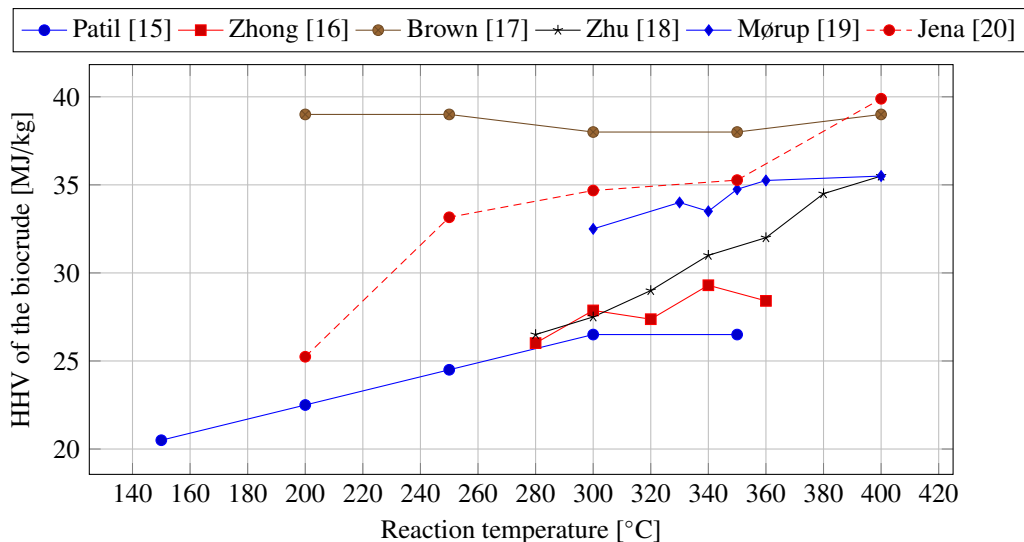
Fig. 3.5: Effect of reaction temperature on the biocrude quality expressed as higher heating value (HHV). • Wheat straw, ♦ Wood, • Algae (Nannochloropsis sp.), ⋆ Barley straw, ♦ DDGS (dried distillers grains with solubles), • Algae (Spirulina platensis)

erally positively correlated with the reaction temperature and thus higher process severities are generally beneficial for a better biocrude quality - although at the expense of a lower mass yield according to [14]. Since the objective of this thesis is to investigated the potential of the biocrude in energy applications, the temperature region investigated in this thesis is reserved to supercritical water conditions.

2 Reaction pressure

As explained in Chapter 2, the main purpose of the reaction pressure is to maintain water in a liquid or a supercritical phase and hence avoiding water vaporization and energy penalties. In continuous systems this means that the pressure should always be kept above the saturation pressure corresponding to the reaction temperature, which also avoids large enthalpy changes. In batch systems the pressure is autogenous and corresponds to the phase equilibrium pressure at the given reaction temperature. In the subcritical region, water properties are only slightly affected by the reaction temperature, whereas its properties such as ionization product, density, dielectric constant and hence solubility, enthalpy etc. can be tuned in the supercritical region by varying the pressure as mentioned in Chapter 2. On the conversion chemistry of biomass, reaction pressure has only been scarcely investigated, which may in turn indicate that reaction pressure has only marginal effects on the chemistry involved. At near-critical conditions,

Goudriaan and Naber found that pressure has no significant effect, provided that the water is in a liquid state [21]. Akhtar and Amin conclude that a high-density (high pressure) medium efficiently penetrates the biomass macrostructures resulting in enhanced decomposition. However, once supercritical conditions are achieved, pressure imparts little or negligible influence on yield of biocrude and/or gas yield [14].

3   Reaction time

Reaction time is an important parameter especially from an economical perspective, since e.g. reaction sizing directly corresponds to the reaction time according to Eq. 2.1 on page 18. The reaction time must be sufficient to break down the biomass macrostructures and long enough to facilitate reaction synthesis that enhances the biocrude formation and its quality. Under supercritical conditions the biomass break down is expected to occur at relatively high rates. Z. Fang and C. Fang investigated complete dissolution of willow under sub- and supercritical conditions, and with and without an alkaline catalyst (Na_2CO_3) [22]. As illustrated in Fig. 3.6, willow can be completely dissolved under alkaline conditions in about 30 seconds. As a result it is expected that the yield of liquid products (including water-soluble and water-insoluble compounds) reaches maximum at relatively short retention times, which is supported by other studies, e.g. [23, 24]. The recombination reactions depend on the type biomass, e.g. carbohydrates, lipids, etc. hence the recombinations reactions forming the biocrude should be in focus when optimizing the reaction time of the process.

29.6 s, T_h=330 °C   32.9 s, 347 °C   34.4s,355°C,33MPa   48.0s, T_{max}=400°C   Room Temp.
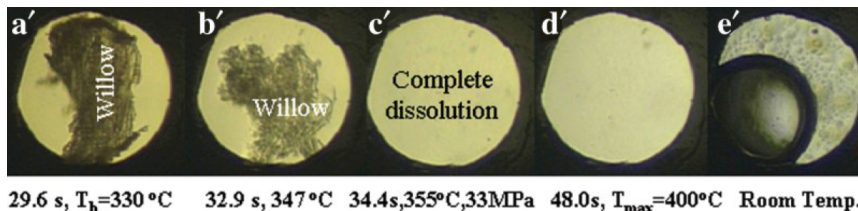
Fig. 3.6: Complete dissolution of willow under alkaline conditions and rapid heating (8 °C/s). Willow volume concentration is 35 % (approximately a 17.5 % mass loading[1]). Reprinted with permission from [22].

Carrier et al. investigated the sub- and supercritical liquefaction of *Pteris vittata* fronds [13]. In the residence time range from 30-480 seconds (excluding the heating period, 12 °C/min), the chemical composition of the biocrude varied only marginally, concluding that the reaction time has only significant impact at short reaction times when processing the given feedstock. A similar observation was done by Xu and Savage on processing algae (*Nannochloropsis* sp.) [25]. Increasing the reaction time from 10 to 60 minutes slightly increased the biocrude mass yield from 38.2 to 40.5 %. In this study the quality of the biocrude was insensitive to the reaction

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[1]Assuming a willow density of 0.5 kg/m^3

time. The optimal reaction time also has to be related to the type of biomass. For instance, the lipid content of the biomass contributes almost directly to the biocrude and the reaction time for high lipid containing feedstock should only be long enough to facilitate sufficient hydrolysis. For proteins, polysaccharides, and lignin this may not the case, since recombination reactions have to take place for the biocrude formation.

4   Catalysts

As already mentioned in Chapter 2, the properties of water change dramatically as it approaches sub- and supercritical conditions, which may open opportunities for chemical reactions. In the context of catalysis, the increasing ionic product as conditions approach supercritical may play a role in acid-base catalyzed reactions [26]. In HtL hydrolysis reactions are naturally of great interest, due to 1) the abundance of ether bonds in the biomass macrostructure, which are strongly susceptible to hydrolysis [27], and 2) the benign sustainability aspect of using water of a reactant for breaking down the macrostructures.

Another important subset of chemical reactions are reduction reactions. Since one of the main purposes of liquefaction is removal of hetero-atoms especially oxygen, reduction reactions bring the biocrude closer to more chemically desirable properties. Unfortunately, these reactions have not been shown very selective under non-catalytic conditions, which is most likely why the majority of experimental HtL is carried out in the presence of a catalyst. The use of homogeneous and heterogeneous catalysts in HtL of biomass has been widely studied for their promoting effects on both yield and quality of the biocrude. Catalysts serve various purposes in the conversion such as enhancement of initial degradation rate of the biomass, enhancement of reducing reactions in the presence of a reducing agent, and suppression of char formation etc.

Both acidic and basic conditions are well-known for their enhancement on the rate of hydrolysis [6]. Acidic conditions generally exhibit the higher rate of hydrolysis, but also promote charring reactions through dehydration reactions. For this reason, acidic conditions are generally preferable for hydrothermal carbonization but avoided in HtL. Under basic conditions, char formation is suppressed most probably due to a shift in the reaction mechanism.

For homogeneous catalysts, water-soluble basic compounds such as hydroxides, carbonates, bicarbonates, and formates of an alkali or alkaline earth metal have all proven effective catalysts. Strictly speaking, since these homogeneous compounds will likely undergo conversion upon reaction with other present compounds, they are unlikely to be reclaimed from the process effluent in their original form. Therefore, such compounds should rather be termed additives or promoters rather than catalysts due their destructive fate. However, as catalyst is normally used to describe them, so will it be in the following.

The role of these catalysts on the reaction chemistry has been studied in great details and many reaction mechanisms have been proposed, but their impact is still not fully understood. Ogi et al. investigated the effects of various alkali salts during direct liquefaction of wood at 300 °C [28]. The results are reproduced in Fig. 3.7. Compared to the case without any catalysts, it
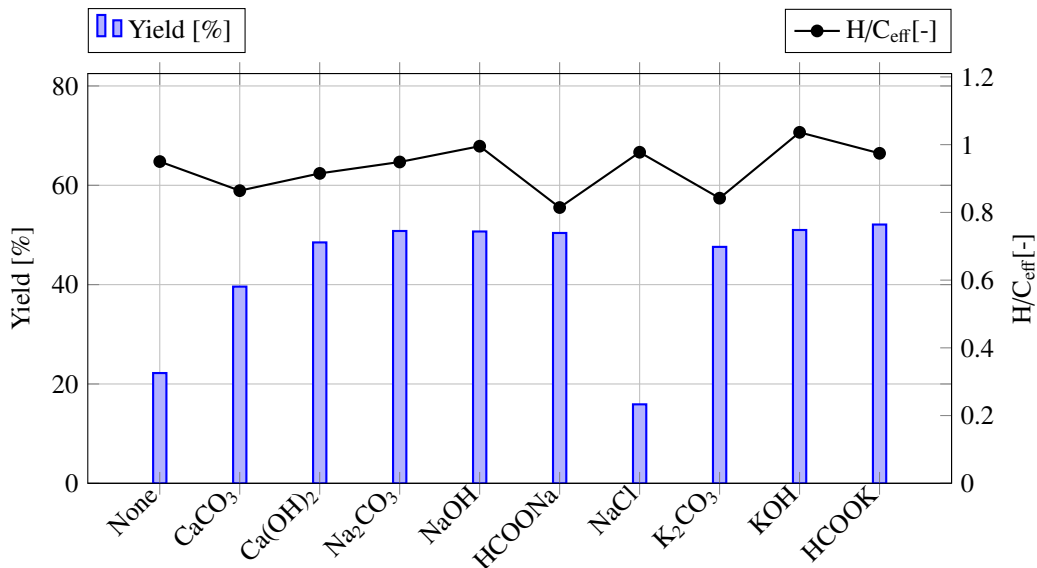
Fig. 3.7: Biocrude mass yield and quality in terms of the H/C$_{\text{eff}}$. Data reproduced from [28]

appears that alkali salts strongly enhance the biocrude yield. Furthermore, the addition of NaCl seems to have none or even negative impact on the biocrude yield. From the results no distinct differences between hydroxides, carbonates, bicarbonates, and formates are observed despite from the slightly lower yield obtained with CaCO$_3$. This may in turn be explained by the much lower solubility in water of alkaline earth metals than alkali metals. Moreover, no distinct differences are observed between the presence of an alkali metal (sodium and potassium) or an alkaline earth metal (calcium). Looking at the biocrude quality, no clear trends appear in the performance of the salts. Similar trends were observed by Karagöz et al., although the different alkali salts showed great variations on the amount of solid residue [29]. The lower amount of solid residue resulted in a slightly higher yield of biocrude. The catalytic performance was ranked according to the following sequence:

$$K_2CO_3 > KOH > Na_2CO_3 > NaOH.$$
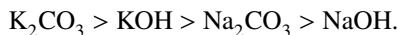
Some proposed purposes of the basic salts have been given by Appell et al. [30]:

I In the presence of carbon monoxide, they are converted to formates which are reducing agents and transfer hydrogen to the oxygenated or unsaturated compounds, and then are regenerated in situ. In other words, they serve as homogeneous catalysts for converting solid wastes to oil.

II Alkali carbonates are catalysts for the water-gas shift reaction.

III Alkaline materials are catalysts for many known organic rearrangements and dispropor-
tionations that yield materials containing less oxygen than the original carbohydrates.

IV Alkaline salts may neutralize organic acids formed in the system. Without neutralization,
these acids could promote charring. Much more work is required before the mechanism of
catalytic action by alkali salts is clear. But the postulation that formates are intermediates
is consistent with these facts.

V Formates have been identified in the aqueous solution obtained from cellulose treatment.

VI Formates are intermediates in water-gas shift reactions catalyzed by a number of salts.

VII Formates may be synthesized in good yield by treating alkali carbon ates with carbon
monoxide and water under conditions of the waste conversion reaction.

VIII Cellulose can be converted to oil in the absence of carbon monoxide, by heating with
large amounts of sodium formate and water.

According to [I] and [II] is has been proposed that carbonates convert to formates via the
following sequence [9]:

$$K_2CO_3 + H_2O \rightleftharpoons KHCO_3 + KOH \tag{3.2}$$
$$KOH + CO \rightleftharpoons HCOOK \tag{3.3}$$
$$HCOOK + H_2O \rightleftharpoons KHCO_3 + H_2 \tag{3.4}$$
$$2\,KHCO_3 \rightleftharpoons H_2O + K_2CO_3 + CO_2 \tag{3.5}$$
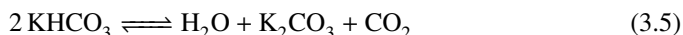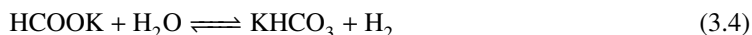
Furthermore, this has also been proposed as the promoting mechanism of the WGS reaction
forming hydrogen in-situ. However, this mechanism will imply the co-existence of OH^- and
HCO_3^- ions, which is not a stable system. OH^- and HCO_3^- ions will instantaneously react to
CO_3^{2-} ions according to Eq. 3.6.

$$OH^-(aq) + HCO_3^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l) \tag{3.6}$$
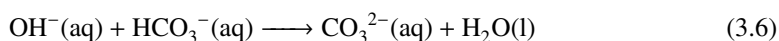
Moreover, when CO_2 is formed in the presence of an alkali carbonate, for example K_2CO_3,
a series of reactions can take place according to Eq. 3.7-3.10. These reactions are actively
utilized in e.g. the Benfield process for CO_2 absorption.

$$K_2CO_3(aq) \rightleftharpoons 2\,K^+(aq) + CO_3^{2-}(aq) \tag{3.7}$$
$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{3.8}$$
$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \tag{3.9}$$
$$CO_3^{2-}(aq) + H_2CO_3(aq) \rightleftharpoons 2\,HCO_3^-(aq) \tag{3.10}$$
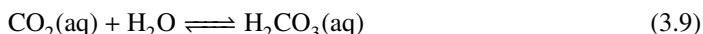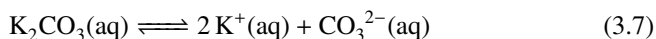
When CO_2 is absorbed in the aqueous phase, carbonate ions accept protons from carbonic acid to form bicarbonate ions. In fact, any formed acids during liquefaction will be neutralized via a similar mechanism and thus consume carbonates, bicarbonates, and hydroxides as implied by [IV], and summarized in Eq. 3.11-3.13.

$$2\,H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons H_2O(l) + CO_2(aq) \qquad \text{(Carbonates)} \qquad (3.11)$$

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2O(l) + CO_2(aq) \qquad \text{(Bicarbonates)} \qquad (3.12)$$

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + CO_2(aq) \qquad \text{(Hydroxides)} \qquad (3.13)$$
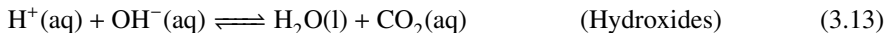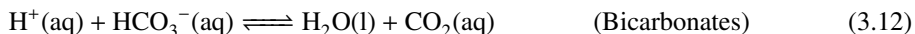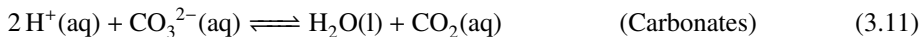
When applying hydroxide as a catalytic promoter, another destructive fate may be carbonation according to Eq. 3.14, which is chemically irreversible. Therefore, when hydroxides react with CO_2 into carbonates, Eq. 3.7-3.10 also apply.

$$2\,M^+OH^- + CO_2 \longrightarrow M_2CO_3 + H_2O \qquad\qquad (3.14)$$
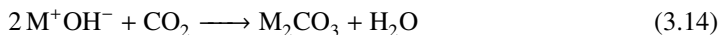
where:

  M = alkali metal

The amount of alkalinity in the aqueous phase is also pH related. The concentrations of different ions are presented in Fig. 3.8. At a pH above approximately 10.2, hydroxides and carbonates may co-exist. If the pH is lowered below 10.2, no hydroxides are present but only carbonates and bicarbonates. At around a pH of 8.3 all carbonate ions will be consumed. At lower pH, bicarbonate ions are protonated to form carbonic acid, which may decompose to water and carbon dioxide according to the reversible reaction in Eq. 3.9, depending on process conditions. As a result, when alkalis are added as a catalytic promoter, a significant amount of carbon dioxide can be formed if a sufficient amount of acids is produced during liquefaction.

A supporting work to this statement was carried out by Akgül et al., who investigated the effect of bicarbonate alkali salts on the subcritical water-gas shift reaction [31]. It was found that by increasing the amount of bicarbonate salt, the hydrogen content in the gas phase was nearly unaffected whereas the CO_2 content increased with increasing bicarbonate concentration.

Conversion of carbohydrates at sub- and supercritical conditions in the presence of an alkaline catalyst is known for the formation of different organic acids. Therefore, when processing for example glucose in K_2CO_3 the pH of the aqueous phase is expected to decrease as glucose is decomposed. Table 3.1 shows the time dependent total organic carbon content (TOC) and the pH of the water phase when processing glucose in the presence of K_2CO_3. This manifests that acidic compounds are initially formed. The pH is observed to decrease drastically from an initially strong basic solution to acidic conditions. The pH then slightly increases, indicating consumption of acidic compounds probably through condensation reactions. The final pH in the
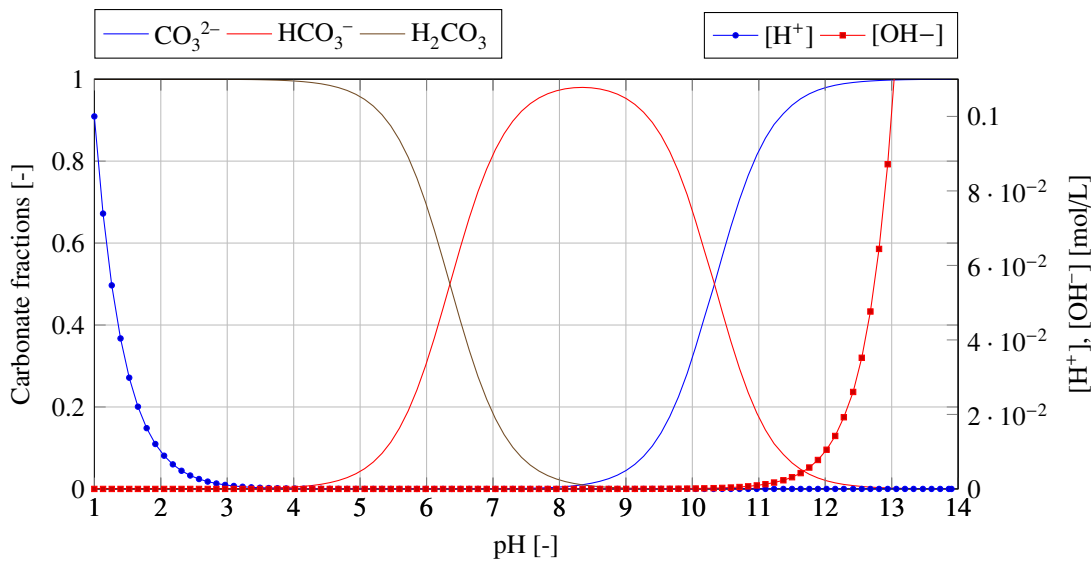
Fig. 3.8: Fractions of carbonates, and $[H^+]$ and $[OH-]$ concentrations as a function of pH.

Table 3.1: Time course of pH and total organic carbon (TOC) of the water phase during supercritical processing of glucose. Data reproduced from [32]

	Initial	1 min.	3 min.	5 min.
pH	11.5	4.01	5.05	5.25
TOC [mg/L]	100	53.3	35.3	37.9

region of pH 5 states that nearly all carbonates and bicarbonates have been consumed according to Fig. 3.8.

The presence of the alkali or alkaline earth metal has been proposed as the promoting factor. However, other basic compounds such as ammonium hydroxide (NH_4OH) and isoquinoline (C_9H_7N) have also shown great effects on the conversion, although they do not contain any metals [30]. A disadvantage of using nitrogen-containing additives is the higher nitrogen content observed in the obtained biocrude, and these types of catalysts will therefore not be discussed in further details [33, 34]. Another option is the use of heterogeneous catalysts. In coal liquefaction iron-based catalysts have been widely used. The chemistry utilized in the case of an iron catalyst relies on iron oxidation, similar to the steam-iron process. In this process, iron ore is oxidized by the water vapor yielding an hydrogen rich gas. Using an iron ore catalyst can therefore produce hydrogen in-situ for reducing reactions. Other examples of heterogeneous catalysts include transition and precious metal containing catalysts typically for promoting hydrogenation reactions. The utilization of heterogeneous catalysts will be discussed in greater details in Chapter 6.

Chapter 4

Historical development of hydrothermal liquefaction

1 Pioneering research at the Pittsburgh Energy Research Center

Efforts for direct liquefaction of biomass into liquid fuels dates back to World war II prompted by the gasoline shortage. Later in the 1960s direct liquefaction of biomass was also investigated as a means for overcoming the scarcity for urban waste landfills by converting the organic waste into energy carriers [35]. Under the U.S. Bureau of Mines Solid Waste Program, cellulosic wastes and sewage sludge were converted in batch reactors under both sub- and supercritical water conditions [30, 35]. Impelled by the oil crisis, intensive investigation of biomass conversion was undertaken in the mid-1970s, where the pioneering research was conducted at the U.S. Bureau of Mines' Pittsburgh Energy Research Center (PERC). Initially, the process was termed *carboxylolysis* and based on biomass liquefaction in an alkaline water slurry in the presence of carbon monoxide as a reducing gas; an outgrowth procedure of earlier studies of low rank coal liquefaction [5].

$$Na_2CO_3 + H_2O + 2\,CO \longrightarrow 2\,HCOONa + CO_2 \tag{4.1}$$

$$\underbrace{C_6H_{10}O_5}_{\text{Wood}} + HCOONa \longrightarrow \underbrace{C_6H_{10}O_4}_{\text{Oil}} + NaHCO_3 \tag{4.2}$$

$$NaHCO_3 + CO \longrightarrow HCOONa + CO_2 \tag{4.3}$$

$$HCOONa + H_2O \longrightarrow NaHCO_3 + {}''H_2{}'' \tag{4.4}$$

$${}''H_2{}'' + \underbrace{C_6H_{10}O_5}_{\text{Wood}} \longrightarrow \underbrace{C_6H_{10}O_4}_{\text{Oil}} + H_2O \tag{4.5}$$
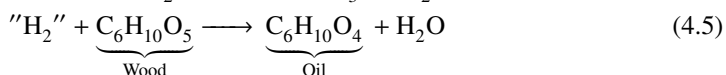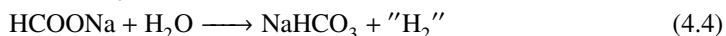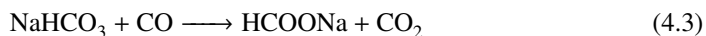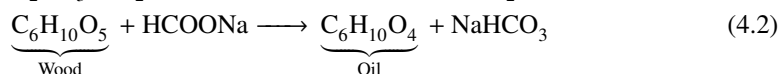
It was believed that carbon monoxide reacted with an alkaline catalyst in the presence of water to form formate intermediates that reacted with the biomass. The primary purpose of the water was to interact in the formate formation and not to directly react with the biomass. Ultimately, the alkali salts acted as a promoter for the water-gas shift (WGS) reaction producing hydrogen in situ, which then participated in hydrogenation reactions reducing the oxygenated nature of biomass. The reaction stoichiometric in a woody context was proposed according to Eq. 4.1-4.5.
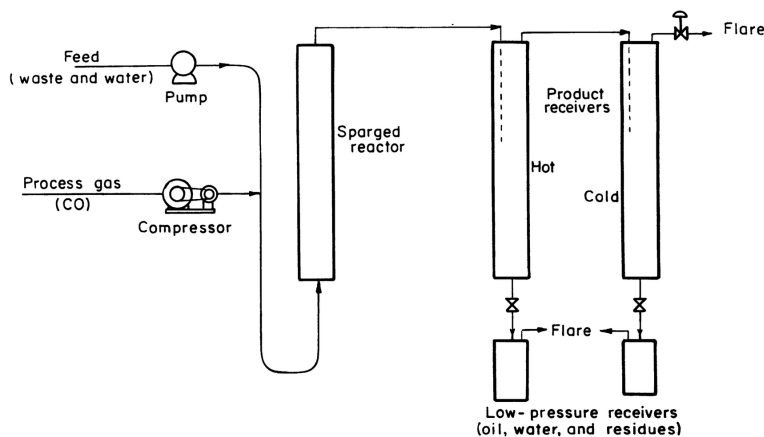
Fig. 4.1: Schematic diagram of the PERC's continuous liquefaction unit. Adapted from [30]

Under the lead of Herbert R. Appell, batch experiments were carried out in a 500 mL autoclave to investigate processing conditions. It was found that yields of 40 % of biocrude were achievable and that high process temperatures (380 °C) led to liquid products compared to solid products at low process temperatures (250 °C). Based on the positive outcome of the batch experiments, a continuous reactor facility was constructed with a capacity of 500 g/hr, and a working pressure and temperature of 5,000 psi (344 bar) and 500 °C, respectively [30]. The process scheme is illustrated in Fig. 4.1. Using the continuous system, e.g. cellulose-to-water mass ratio was tested from a 1:1 ratio to a 1:4 ratio. Within these conditions it was observed that the biocrude yield increased for more diluted feed slurries. Generally for continuous operation it was concluded that:

"*A liquid phase is helpful as a vehicle for feeding substrates and for keeping reactive, unsaturated organic intermediates apart so that they do not condense to a char. Water may be the best vehicle, since it dissolves the catalyst and some organic intermediates; it is the least expensive; and in any case, it must be present to some extent. Urban refuse, sewage sludge, and other substrates may contain sufficient water so that no more need be added.*" [30].

Nevertheless, it was found reasonable to try replacing the water with other vehicles or solvents. The main reasons were: 1) Excess of water undesirably enhances conversion of introduced gaseous carbon monoxide directly through the WGS reaction without formate formation, and 2) the vapor pressure of water is relatively high at high temperature operating conditions leading to high system pressures. Anthracene oil and isoquinoline were investigated as alternative solvents, and it was found that biocrude yields were significantly increased compared to the case were only water was present as solvent. Compared to the 30-40 % yields obtained using an aqueous medium, yields of 51-57 % were obtained with anthracene oil. Extensive experimental work was carried out on the anthracene oil configuration to examine process parameters [5, 30]. The alkali catalyst was fed to the system by a secondary aqueous stream in order to dissolve the salts. This process was later termed the BOM-process and/or the PERC-process referring to the U.S. **B**ureau **o**f **M**ines' **P**ittsburgh **E**nergy **R**esearch **C**enter. The greatest operational difficulty encountered in the small bench-scale continuous unit was the pumping of the feed slurry.

2   The Albany, Oregon Biomass Liquefaction Facility

Fostered by the continuing oil crisis, a fast track decision was made to speed up the construction of a 3 tons/day process development unit (PDU) in Albany, Oregon, based on the PERC process. The design was completed in 1974 and construction completed in 1977. The process scheme is illustrated in Fig. 4.2.

The PERC process, for which the PDU was built, called for injection of a feed slurry containing 30 % wood flour in 70 % recycle oil on a mass basis, in order for the process to be economic feasible. As for the batch experiments carried out at PERC, wood flour was initially slurried in anthracene oil and then eventually in process recycle oil as it became available. The following three aspects of the process were identified as critical: 1) the energy intensive predrying and grinding step required for wood flour preparation, 2) wood-recycle oil-water slurries could not be fed at concentrations greater than 10 % without causing system plugging, 3) high recycle ratios of biocrude (up to 19:1) required excessive heat [37]. Although biocrude yields around 40-50 % were achievable, the low mass loading of wood resulting in a low productivity per cycle of 5 % or less biocrude yield based on the total feed.

The need for a higher productivity per cycle led to the development of an alternative water-based process at the Lawrence Berkeley Laboratory (LBL). In this process wood chips were chemically pretreated in a dilute acid medium followed by mechanical refining to make wood-water slurries pumpable at wood concentrations above 30 %. After pretreatment, the slurry was neutralized by adding alkali. The LBL-process was later implemented at the Albany PDU. The process scheme for this setup is illustrated in Fig. 4.3.

The first test with the LBL-process produced the first wood-derived biocrude at the Albany unit. The shortcoming of this test run was a low biocrude yield of 11.1 %. Several tests in the LBL-configuration were conducted successfully with wood concentrations as high as 23
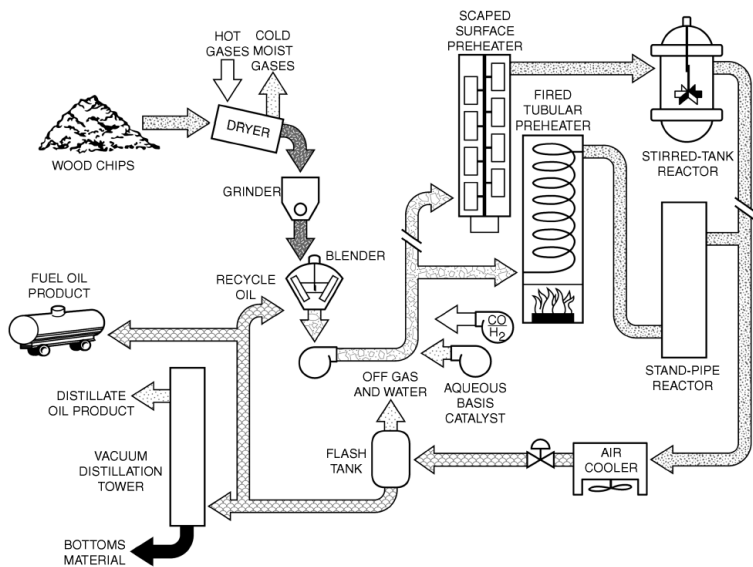
Fig. 4.2: Schematic diagram of the Albany PDU configured to the PERC process. Reprinted from [36].
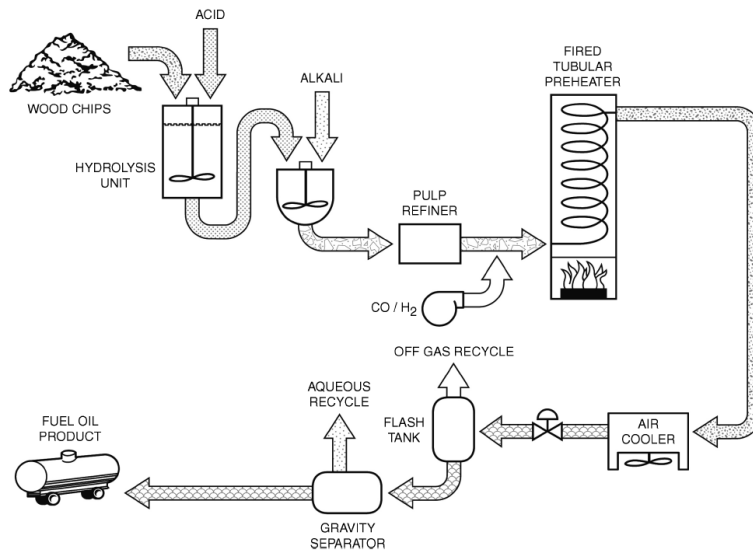
Fig. 4.3: Schematic diagram of the Albany PDU configured to the LBL process. Reprinted from [36]

% based on further experimental investigation at the Lawrence Berkeley Laboratory. These tests, led to a wide range of biocrude yields (8.5-34.4 %) but still consistently lower compared to the PERC-process, mainly due to the loss of carbon to the aqueous phase in the form of water-soluble organics (WSO).

3   Research at the Lawrence Berkeley Laboratory

Due to the shortcoming of the low yield (11.1 %) obtained by the LBL-process in the first test run at the Albany PDU, a downsized bench-scale, continuous liquefaction unit (CLU) of the Albany facility (1:400 scale) was designed and built at the LBL to further investigate and develop a water-based process. The reactor setup is illustrated in Fig. 4.4. The system was fitted with a feed slurry recirculation loop, in which a colloid mill was incorporated, for further mechanical refinement and re-homogenization of the pre-hydrolyzed wood. Like for all previous system configurations, the CLU at LBL also utilizing a reducing atmosphere.

Several experimental runs were carried out based on a wood concentration of 20 %. Biocrude mass yields were observed in the range of 27-33 %, and char mass yield in the range of 1-10 %. Although these yields were still lower than those demonstrated by the PERC-process, they were still substantially higher than the 11.1 % initially obtained at the Albany unit and comparable to later runs in Albany. Some interesting experiments were conducted to investigate the effects of the temperature level and the impact the reducing gas. The results are presented in Table 4.1.

Table 4.1: Experimental runs carried out at the Lawrence Berkeley Laboratory [37].

Run ID	11 (A)	11 (B)	12 (A)	12 (B)
Temperature [°C]	340	360	340	360
$CO:H_2$ ratio [mol:mol]	1:0	1:0	0:1	0:1
Biocrude yield [%]	33	33	27	27
Char yield [%]	4	4	5	5
C [%]	76	77	76	77
H [%]	7.2	7.3	7	7.3
O [%]	17	16	17.5	16
H/C_{eff}[-]	0.80	0.83	0.76	0.83
$\bar{M}_n$	323	254	271	246
$\bar{M}_w$	400	336	349	336

It was found that higher process temperatures resulted not only in a more feasible H/C_{eff} ratio of the biocrude, the molecular weight of biocrude was also reduced at higher temperatures. Interestingly it was also found that hardly no differences were observed in the product characteristics when changing the CO gas to H_2. Moreover, based on calculations of the CO consumption (excluding the consumption by the WGS reaction) it was found that the replace-

ment of CO with H_2 or any reducing gas had negligible effect in the LBL process. A similar observation was later done at the Albany facility operating in the PERC-configuration:

"One interesting facet of Test Run no. 9 was the experiment near the end of the run wherein the feed syngas was reduced by first 20 percent for 13 hours then 50 percent for 7.5 hours. No noticeable change in operating conditions or product characteristics was observed. Syngas was replaced with nitrogen finally with a rise in product viscosity and solid content." [38].

The report does not give any other remarks on the product quality, but the observation that the effect of CO is only marginal is interesting. If the presence of syngas is not compulsory for a successful process, this can significantly simplify the process scheme and reduce production cost.

The carbon balance across the LBL process was estimated, which yielded approximately 59 % of carbon in the biocrude and char, 14 % carbon in the gas phase (mainly in the form of CO_2), and 27 % carbon in the aqueous phase. It was found that after pretreatment carboxylic acids were formed of which the major were glycolic, acetic, and formic acid. After the HtL step, the amounts of glycolic and acetic acid were observed to further increase whereas the concentrations of formic acid decreased probably due to thermal decomposition. The total amount of WSO was roughly 25 % of the organic input, of which about half was carboxylic acids.
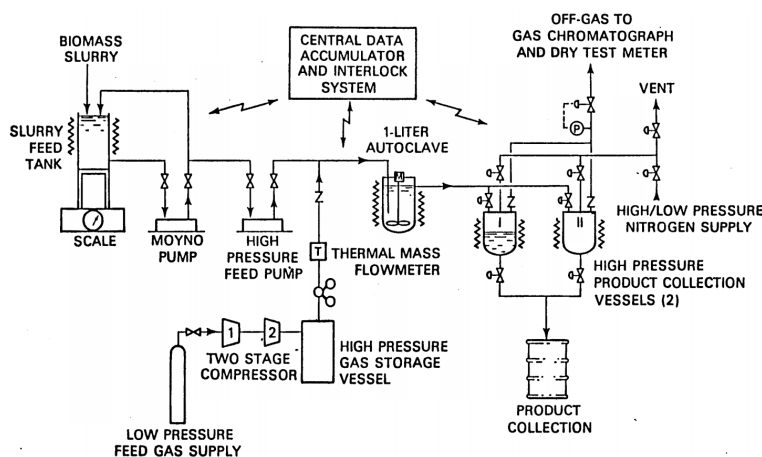
Fig. 4.4: Schematic diagram of the Lawrence Berkeley Laboratory's continuous liquefaction unit. Adapted from [37].

4   Other hydrothermal liquefaction processes and the CBS1-unit

Several other hydrothermal processes have been developed closely related to the LBL. Some of the most interesting processes are listed in Table 4.2. More details about these processes can be found in [39, 40]. Different from the rest of the processes, the Thermal Conversion Process is a two stage process. Firstly, the biomass is pre-liquefying by pulping at 200-300 °C. Secondly, the pulp is flashed to remove water and finally pyrolyzed into liquid fuels. Of the "pure" hydrothermal processes, the CAT-HTR technology is probably currently on the highest technology readiness level having a production capacity of approximately 20 tonnes/day in a pilot scale unit [1]. From the list it also appears that most processes are catalytic but do not operate with a reducing gas. In a recent work by the National Advanced Biofuels Consortium (NABC[2]), the transition towards a more scalable design was investigated by further examination of processing conditions [41]. It was found that:

- The only feed preparation required was grinding for slurry preparation.

- Liquefaction did not require a reducing gas environment.

- Water recycle led to improvement in biocrude quality, carbon yields, and reduced water consumption/wastewater disposal.

- Reduced reaction severity led to lower quality biocrude.

Table 4.2: List of hydrothermal liquefaction processes and processing conditions. The list also indicates if hydrogen as an reducing and catalysts are used in the process.

Process name	Developer	T [°C]	P [bar]	H_2	Cat.
PERC-Process	Pittsburg Energy Research Center (USA)	330-370	200	Yes	Yes
LBL-Process	Lawrence Berkeley Laboratory (USA)	330-360	170-240	Yes	Yes
HTU-Process	Shell Research Institute (NL)	265-350	180	No	No
STORS process	Environmental Protection Agency (USA)	300	110-150	No	Yes
STORS process	Organo Corp. (JP)	300	110-150	No	Yes
CatLiq-Process	SCF Technologies (DK)	280-350	22.5-25	No	Yes
BFH-process	BFH (GER)	380	100	Yes	Yes
B/M-process Mueborit	Müller & Bothur(GER)	< 220	6	No	No
Thermal Conversion Process	Changing World Technologies Inc. (USA)	200-300, 500 (2 stages)	N.A.	No	Yes
CAT-HTR technology	Licella/Ignite Energy Resources (AU)	300	300	No	Yes
Hydrofaction	Steeper Energy (CAN/DK)	> 374	> 220	No	Yes

During the project period, the Department of Energy Technology at Aalborg University, Denmark, established a biomass conversion platform in the form of a semi-continuous bench-scale (CBS1) liquefaction unit. The unit was designed, built, and commissioned by Steeper

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[1]http://www.igniteer.com/technology
[2]http://www.nabcprojects.org

Energy[3] and officially inaugurated at the Department of Energy Technology on May the 24th, 2013. The process diagram is illustrated in Fig. 4.5. With a maximum operating pressure and temperature of approximately 350 bar and 450 °C, respectively, the system is designed for operating at both sub- and supercritical conditions.

The semi-continuous process is operated by preparing the feed slurry batch wise in barrels containing approximately 100 kg. Pretreatment and feed slurry preparation is performed in a stand-alone mixer. Steady state conditions of the CBS1 at the preset operating conditions (pressure and temperature) are reached by circulating hot-compressed water through the unit. Once reached, the recirculated water is replaced by a batch of prepared feed and continuous biomass processing commences. After each batch of approximately 100 kg, hot-compressed water is again recirculated to maintain process conditions. The feed barrel is reloaded with another batch of premixed feed and processed continuously, and so on.
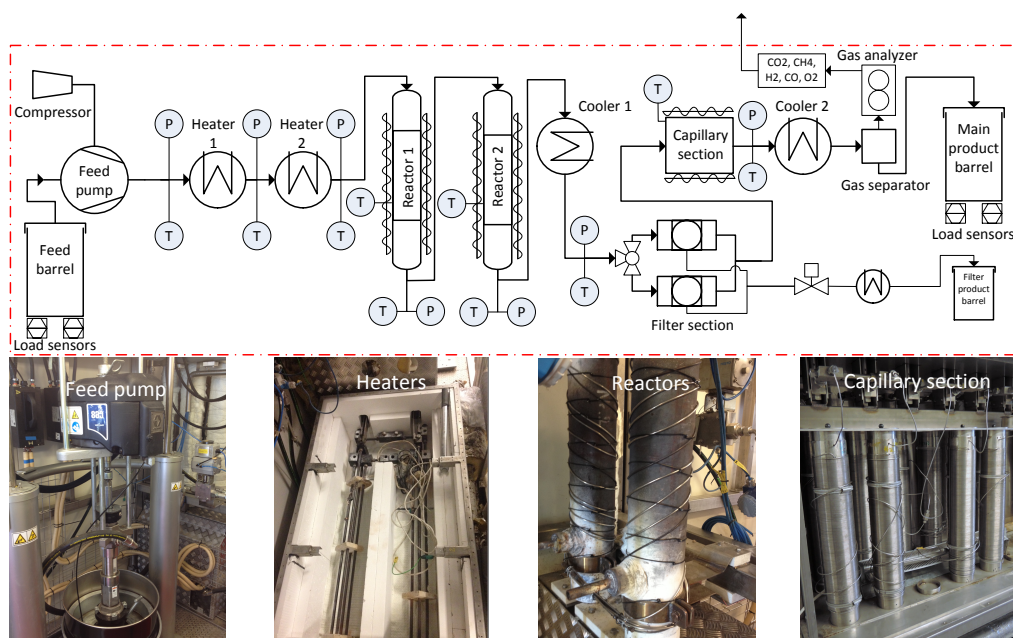
Fig. 4.5: Schematic diagram and pictures of the core process of the CBS1 unit.

In the core process the feed slurry is heated to process conditions in two serial, induction heated heaters. The outlet temperature of the two heaters can be controlled independently. After the second heater the slurry enters the first out of two serial, heat-traced reactors. The reactors

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[3]http://steeperenergy.com

are basically high pressure vessels of approximately 5 L each, providing retention time for the chemical synthesis. After the second reactor, the slurry is cooled in a primary cooler to terminate chemical reactions. The product stream is not cooled to ambient in the primary cooler but kept at slightly elevated temperatures to maintain low viscosity. The pressure let down system consists of several coils of capillary tubes of different inner diameters and lengths. The coils are then engaged or disengaged individually to comprise a single set a serial tubes, which entirely by friction provides the back pressure of the entire system. Hence, controlling the system pressure by the feed pump, the capillary coil configuration acts as a means of controlling the system flow rate. Existing the capillary section at close to ambient pressure the production stream is cooled to ambient in a secondary cooler before collected in the product barrel.

Chapter 5

Process energy and costs

Hydrothermal liquefaction as a biomass conversion technology has been developed and investigated extensively decades ago. Several pilot and demonstration plants have been constructed and the core process proven technically feasible. Nevertheless, the technical readiness of hydrothermal liquefaction is still on a research level, where long term tests on development scale need to be accomplished accounting for all recycle and waste streams. Therefore, the overall technical feasibility of hydrothermal liquefaction has not fully been established and yet not transparent due to the fact that the complete pathway from biomass to finished fuels and/or chemicals still has to be demonstrated. Moreover, the quality and hence the potential of the obtained biocrude, the utilization of gas, aqueous, and solid phases is not fully understood, which blurs the determination of its market value. In addition, only few techno-economic assessments of the HtL process are available contributing to a deeper understanding of the process economy.

Fig. 5.1 shows a conceptual layout of a biomass to fuels and chemicals process based on a HtL core process followed by upgrading and/or fractionation of the biocrude into commodities. As mentioned in the Introduction, the potential of blending biocrude into the existing petroleum infrastructure seems very attractive and from that perspective, downstream units for further product processing are not considered mandatory units in a biocrude production facility. The layout in Fig. 5.1 also illustrates a simplified representation of the HtL core process.

As it reviewed in Chapter 4, the HtL process basically consists of a high pressure feeding system, heaters, reactors, coolers, and a pressure let down system. Although the effect of a reducing gas cannot be fully disregarded, it is believed that the increased degree of system complexity by such incorporation is not vindicated by a more feasible product. Therefore, the use of externally supplied reducing will not be considered in further details. In addition to the core process, several process units are mandatory such as pretreatment and waste handling. Furthermore, process stream loops may be a reality for e.g. aqueous phase recirculation.
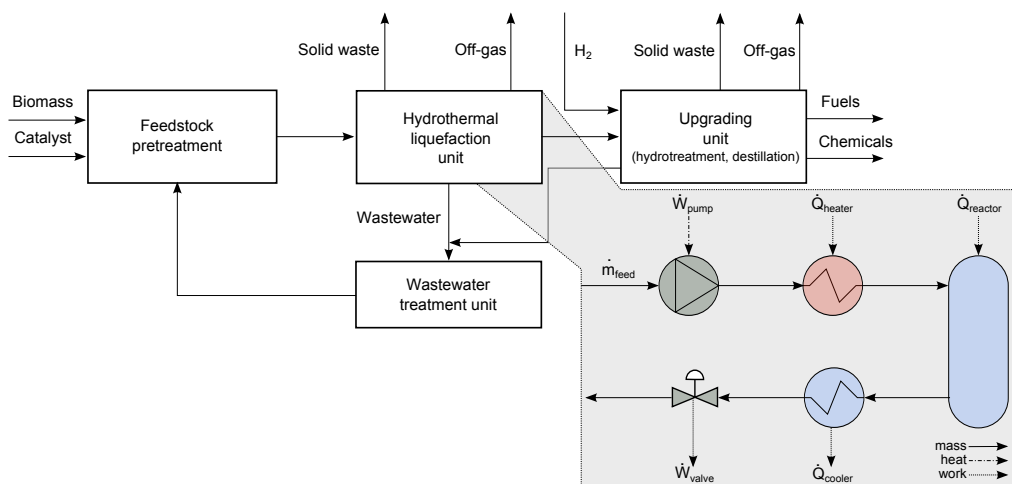
Fig. 5.1: Simplified conceptual process diagram of a HtL plant including feedstock pretreatment, wastewater treatment, and upgrading unit.

A techno-economic assessment of a system configuration identical to Fig. 5.1 was carried out by the Pacific Northwest National Laboratory[1] (PNNL) [42]. The system framework was centered around wood liquefaction (8 % mass loading of wood) at subcritical conditions (350 °C, 205 bar) at a plant capacity of 2000 metric tons dry biomass per day. The cost disbtribution in the assessment was divided into a "HtL" part and an "Upgrading" part, which were further subdivided into *Fixed operating expenditures (OPEX)*, *Variable OPEX*, and *Capital expenditures (CAPEX)*. The costs distribution is illustrated in Fig. 5.2 yielding a total cost estimate of approximately 114 million US$/year. From the figure it appears that the biocrude production is far more expensive than upgrading in all aspects under the given conditions. Assuming that the already exsisting refinery infrastructure could be utilized for upgrading, either as blendstock or as primary refinery feedstock, it is expected that the cost associated to upgrading may even be even further reduced.

1   OPEX distribution

Breaking down the Variable OPEX, it appears from Fig. 5.3 that the price of feedstock (wood) is contributing more than 75 % of the total Variabel OPEX, or approximately 25 % of the total cost. In the current study a feedstock price of 60 US$/dry tonne of forest residue (wood) is used (12.9 US$/MWh). In Table 5.1 the costs of wood, biocrude, refined biocrude, and common market

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[1]http://www.pnnl.gov/

Fig. 5.2: Cost distribution of biocrude production and upgrading of from wood liquefaction at a 2000 metric dry tons per day facility. [42]

commodities are presented on an energy basis. From this it is very clear that the price of the feedstock must be kept low and that the energy recovery in the biocrude must be high in order to obtain a feasible process. It also appears that neither the biocrude nor the refined biocrude are price competitive to fossil commodites in the current market and under the given processing conditions and assumptions in the economic assessment. However, it must be kept in mind that fossil crude oil prices are currently record low[2], outcompeting all renewable technologies. In a future scenario, it is expected that prices of crude oil will increase, which will then increase the cost competiveness of biocrudes. And moreover, the current HtL assessment assumes a 8 % wood loading in the feedstock. Although an increase in solid loading will not affect the unit price of feedstock, the unit price of produced biocrude will decrease by increasing the solid loading due to a higher throughput per installed plant capacity.

Table 5.1: Costs of fossil commodities, wood, biocrude production (HtL), refined biocrude production (HtL + Upgrading)

Type	Brent[a]	WTI[a]	Gasoline (reg)[a]	Diesel (Low sulfur)[a]	Wood[b]	HtL[b]	HtL + Upgrading[b]
US$/MWh	29.28	27.52	43.30	47.36	12.90	53.70	62.59

[a] Obtained from http://www.eia.gov/ (2016-1-18).
[b] Obtained from [43].

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[2]$28.55/bbl. (Brent), Bloomberg, Januar 2016

From Fig. 5.3 it is also shown that solid disposal and wastewater treatment are negligible in comparison. An assessment assumption is, however, that no inorganics are left in the biocrude or in the aqueous byproduct, but are all removed by a solids separator. Contrary to the assumption, the authors also comment:

"*the separation is not perfect and there is certainly some mineral content left in both the aqueous and biocrude products. The effects of long-term operation could be significant without sufficient flushing of mineral content from the water via the wastewater stream..*".

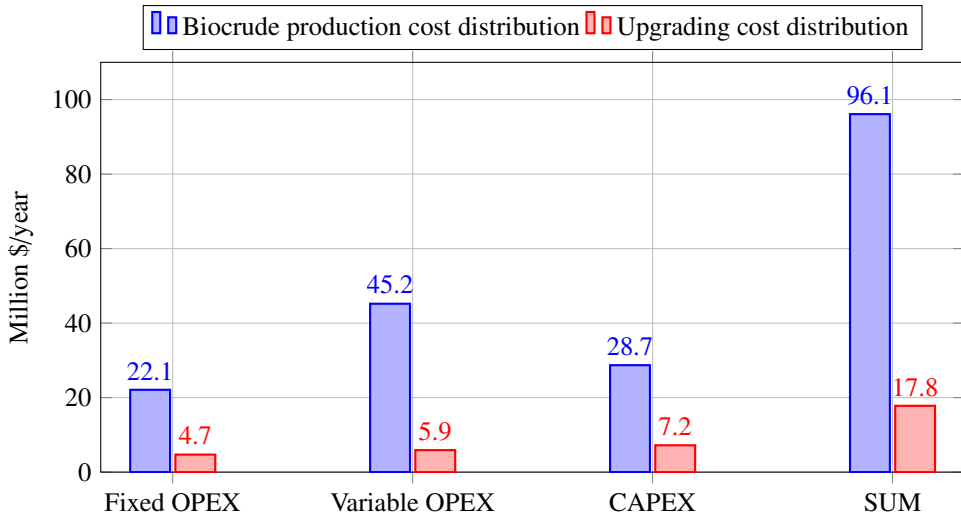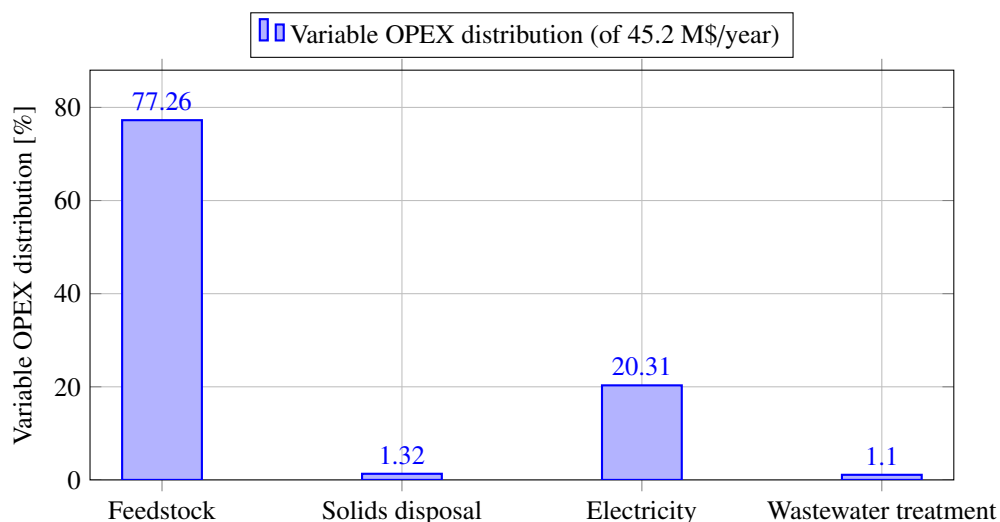**Fig. 5.3:** OPEX distribution of biocrude production and upgrading of from wood liquefaction at a 2000 metric dry tons per day facility [42].

In addition, in the baseline assessment process scheme approximately 85 % of the effluent aqueous phase is direct recycled to the HtL unit - the remaining 15 % is treated in a wastewater unit. In this case, the WSO in the wastewater are removed by anaerobic digestion forming methane at the cost of 0.73 US$/m^3 of wastewater. The methane is later used for hydrogen production.

Recycling 85 % of the aqueous phase without further treatment may introduce several processing drawbacks. In a recent study on the CBS1-unit, the effects of direct recirculation of the aqueous phase were tested during continuous co-liquefaction of aspen wood and glycerol [44]. The feed slurry for first batch (Batch #1) was prepared using demineralized water, the feed slurry for Batch #2 was then prepared by using the aqueous effluent from Batch #1 and so forth. Aqueous phase parameters monitored from such direct recirculation procedure are presented

in Table 5.3. Results showed that inorganics mainly accumulated in the aqueous phase and to some extent in the biocrude and hence is not removed in the form of solids. Therefore, removal of inorganics is expected to be more extensive (and expensive) than assumed in the techno-economic assessment by PNNL. Typical desalination technologies are presented in Table 5.2, which may serve as a cost indicator for the removal of inorganics in the aqueous phase. In this case, typically desalination costs per cubic meter of wastewater are comparable to the cost of WSO removal from the aqueous phase, as assumed by PNNL. It is also observed that WSO accumulate almost linearly in the aqueous phase with the number of aqueous phase recirculations. By recirculating 85 % of the aqueous phase directly to the HtL process, the water content of the aqueous phase will then gradually decrease and the organic content gradually increase. Eventually this will lead to a *thermal organic solvolysis* process rather than a hydrothermal process. The consequences hereof still have to be investigated.

Table 5.2: Technologies and costs of water desalination [45].

Technology	RO^a	MED^b	MSF^c	VC^d
Cost US\$/m^3	0.30-0.61	0.48-2.22	0.48-1.99	1.83-2.43

^{a}Reverse osmosis, ^{b}Multi-effect distillation,
^{c} Multistage flash, ^{d}Vapor compression

In the same study it was found that the biocrude quality (based on a H/C_{eff} ratio) increased with aqueous phase recirculation, which is supported by similar findings in [41]. For these reasons it is recommended that further analysis is conducted in order to understand the extent of aqueous phase recirculation in terms of general technical processibility and feasibility, reaction chemistry, and economy.

Table 5.3: Effluent aqueous phase analyses from four subsequent batches: Mass fraction of ash, total organic carbon (TOC), pH and potassium (K) content of four different batches. Initial potassium concentration of Batch #1 is approximately 30 g/L.

	Batch #1	Batch #2	Batch #3	Batch #4
Ash [%]	6.20	9.41	10.7	12.6
TOC [g/L]	54.1	96.9	106.3	136.2
pH	5.28	5.91	6.02	5.35
K [g/L]	27.2	50	56.4	61.7

2 CAPEX distribution and reactor cost

Breaking down the CAPEX distribution it appears from Fig. 5.4 that the HtL unit is by far the most expensive unit in the process diagram accounting for more than 60 % of the CAPEX. The unit includes subunits like pumps, heaters, heat exchangers, reactors, etc. A further subunit cost distribution of the HtL unit could not be obtained. Other units in the process scheme are within parity to each other.
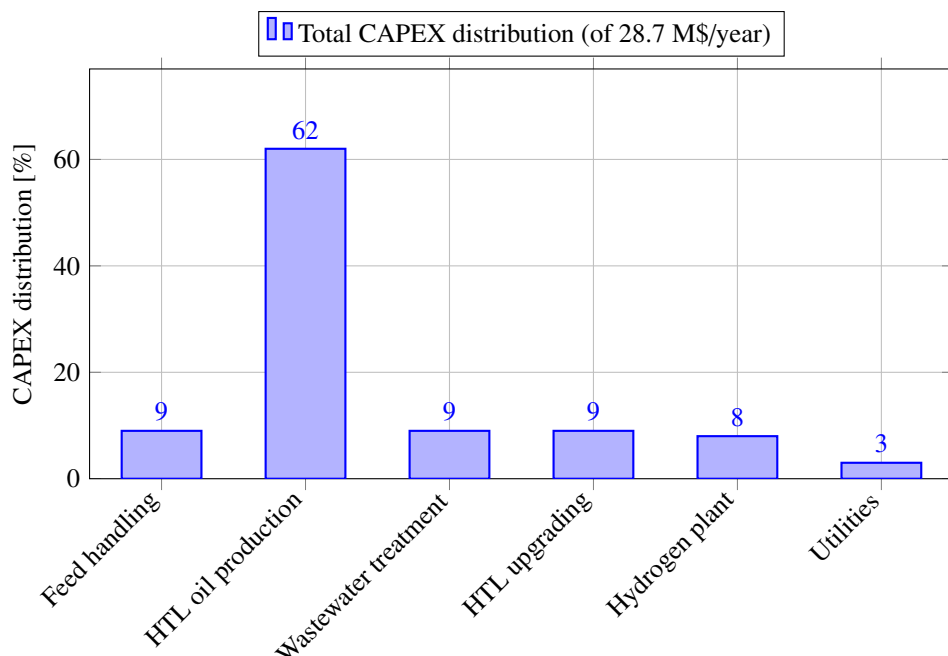
Fig. 5.4: CAPEX distribution of biocrude production and upgrading of from wood liquefaction at a 2000 metric dry tons per day facility. [42]

Effects of process conditions on water properties and reaction chemistry were previous discussed in Chapter 2 and 3. In relation to process economy, process conditions are naturally also of great importance. When estimating process unit costs, baseline cost trends can be estimated using Eq. 5.1. This equation estimates the unit cost (C_C) by extrapolation from a fixed known baseline unit of known cost (C_B) and capacity (Q_B). Additional cost factors can be adding accounting for different working pressure and temperature, material of construction etc. from the baseline unit.

$$C_C = C_B \cdot \left(\frac{Q_C}{Q_B}\right)^M f_M f_P f_T \qquad (5.1)$$

where:

C_C = Capital cost
C_B = Base Capital cost
Q_C = Capacity
Q_B = Base Capacity
M = Capacity scale factor
f_M = Material correction factor
f_P = Pressure correction factor
f_T = Temperature correction factor

Table 5.4: Typical equipment temperature, pressure, material, and scale cost factors, according to [46].

Material	Correction factor fM	Design pressure (bar absolute)	Correction factor fP	Design temperature (°C)	Correction factor fT
Carbon steel	1	0.01	2	0-100	1
Aluminum	1.3	0.1	1.3	300	1.6
Stainless steel (low grades)	2.4	0.5 to 7	1	500	2.1
Stainless steel (high grades)	3.4	50	1.5		
Hastelloy C	3.6	100	1.9		
Monel	4.1				
Nickel and Inconel	4.4				
Titanium	5.8				

Applying Eq. 5.1, the relative change in e.g. reactor cost can be estimated as a function process conditions. In following the reactor cost as a fuction of reactor temperature is estimated relatively according to the assumption that $Q_C = Q_B$. Below the critical point, the design pressure is assumed equal to the saturation pressure corresponding to the reactor temperature. Above the critical point, design pressure is set to the critical pressure of water. Fig. 5.5 shows the general cost trend by increasing the reactor temperature. Since the saturation pressure of water exhibits a cubic growth to temperature, the relative cost increases rapidly as temperature increases. The these cases the reactor cost increases by approximately 30 % by increasing the reactor design temperature from 350 to 400 °C. In addition, if high grade alloys are needed due to higher a design temperature and/or pressure or due to corrosion resistivity, corrections for the construction material may substantially increase the reactor cost, any other process unit. Therefore, properties of the reaction phases need to be known such e.g. pH in order to address metallurgy challenges like caustic embrittlement (stress corrosion) or acidic corrosion.

Another factor that greatly affects the reactor cost is reaction time. Since the reactor capacity is directly proportional to the reaction time, it is obviously preferable to find the minimum reaction time that yields high biocrude yield and quality, in order to minimize the size and cost of the reactor.
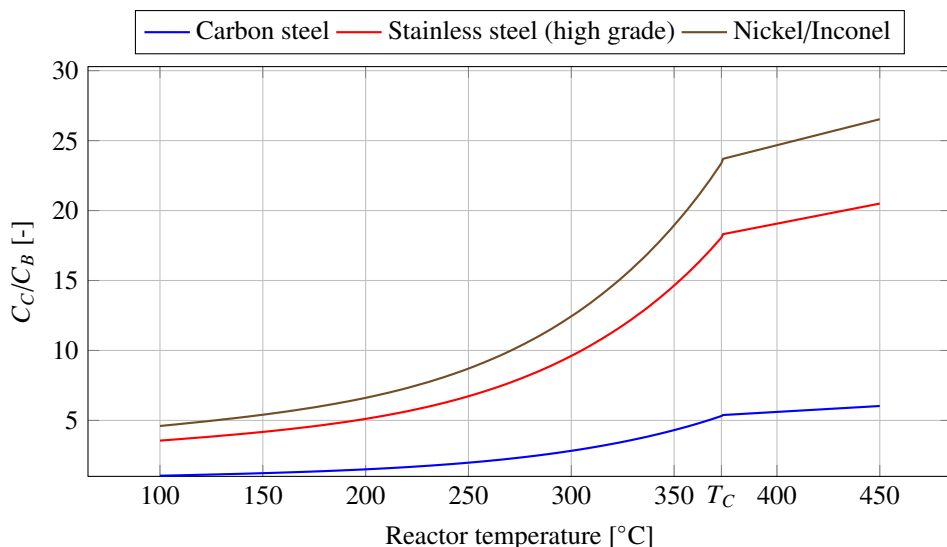
Fig. 5.5: Estimated relative increase in HtL reactor cost as function of reactor temperature, pressure, and construction material based on Eq. 5.1. The operating pressure is defined as the saturation pressure at the corresponding reactor temperature. $Q_C = Q_B$.

3   Process energy balance

When assessing a process the process energy balance is of vital importance. For HtL, only few published energy studies are available. One of the challenges in establishing an energy balance of the HtL process is the lack knowledge on the process chemistry, challenging the determination of heat duty of the reactor. An approach for overcoming the lack of chemical insight is to estimate the change in reaction enthalpy by modeling the input and out streams as mixtures of model compounds based in experimental results. The change in enthalpy between reaction reactants and products then defines the reactor duty, according to Eq. 5.2.

$$\Delta h_{rxn} = \sum h_{(products)} - \sum h_{(reactants)} \tag{5.2}$$

This approach involves certain pitfalls, such as the accuracy of modeling the process streams. For instance, "wood" or "algae" etc. are not standardized compounds, nor are many of the biomass macromolecules constituting biomass. Therefore, appropriate model compounds must be selected carefully simulating the physical properties of biomass. The same it true for modeling the product streams. Since the products streams consists of hundreds of compounds, of which many have not even been identified, the challenge is to select a suitable number of compounds representing the properties of the bulk phases. Next to selecting appropriate model compound, selecting properties methods for estimating model compound properties seems as

important [47]. In Fig. 5.6 the heat and work duties for three different HtL case studies are presented. It clearly appears from all three cases studies that the work duty associated with feedstock pumping is only marginal compared to feedstock heating to process conditions. Interestingly, all case studies predict overall endothermic reaction mechanisms.
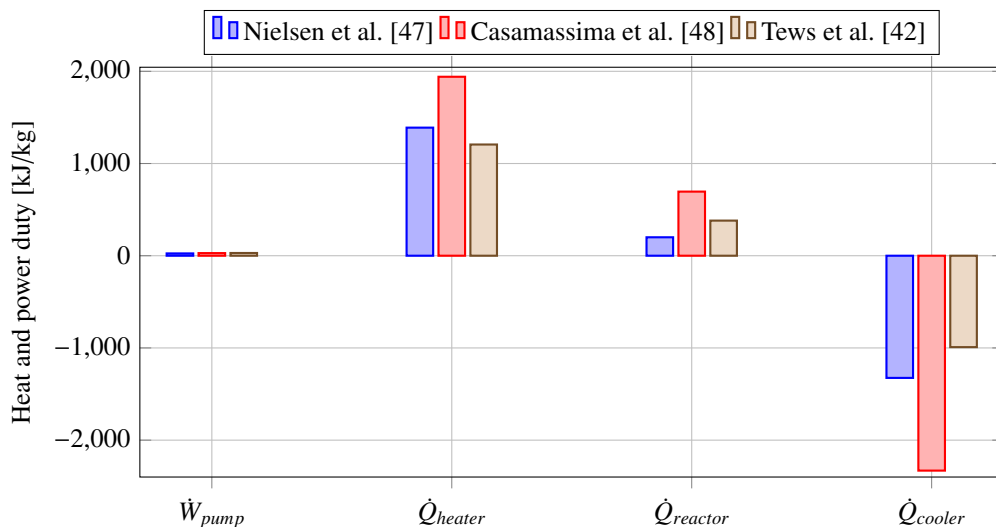
Fig. 5.6: Heat duties and pump work for three different HtL case studies based on three different feedstock; Black liquor (16.5 %, 350 °C, 260 bar) [47], wood-crude glycerol (20 %, 400 °C, 300 bar) [48], and wood (8 %, 350 °C, 206 bar) [42]. Heat and work duties are presented based on the total feedstock. The parentheses indicate organic mass loading of the feedstock, reactor temperature, and reactor pressure.

The heat duties of the feedstock heaters are mainly dictated by the amount of water present in the feed slurry that has to be heating to process conditions. Therefore, increasing the dry matter content of the feed slurry does not only decrease the unit price of produced biocrude per installed capacity, the heat duty of the heaters also decreases at the same time.

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Part III

Hydrothermal liquefaction of biomass and model compounds

4 Chemical and structural composition of biomass

In Chapter 3 it was briefly stated that biomass macromolecules include cellulose, starch, hemicellulose, lignin, lipids, and proteins. The concept of characterizing biomass based on macromolecules distribution is illustrated in Fig. 5.7. Although the relative distribution of macromolecules can differ greatly between and within each type of biomass, lignocellulose for instance consists mainly of cellulose, hemicellulose, and lignin, and algae consists of lipids, proteins, and carbohydrates (sugars, starch, cellulose).

The potential or suitability of the individual macromolecules as a starting point for fuel production can be indirectly assessed by inspecting the inherent macromolecule "quality" in terms of elemental composition. Such suitability measure is frequently expressed as an effective hydrogen-to-carbon ratio according to Eq. 5.3. Here, the hydrogen (H), carbon (C), and oxygen (O) is expressed as number of atoms of each element.

$$H/C_{eff} = \frac{H - 2O}{C} \tag{5.3}$$
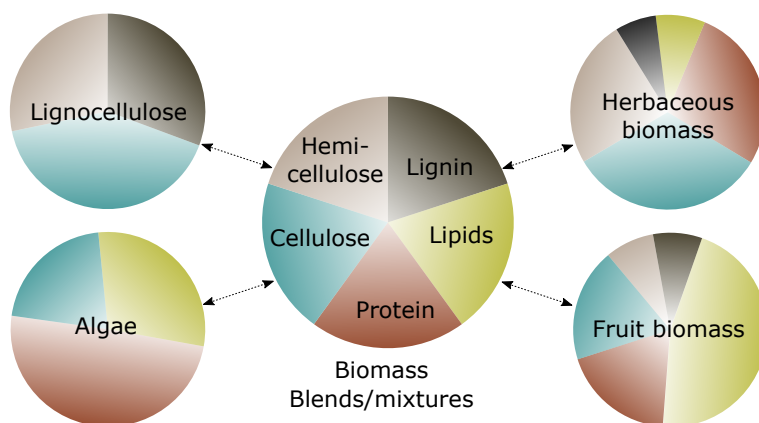
Fig. 5.7: Characterization of biomass based on the distribution of biomass macromolecules.

The suitability of the macromolecules and of typical biomass is illustrated in Fig. 5.8. Here it is observed that carbohydrates (cellulose, starch, and hemicellulose) yield the lowest quality, whereas lipids yields the highest quality. The objective of any BtL process is to reduce the great amount of especially oxygen, increasing the H/C_{eff} ratio and thereby climbing the staircase, in order to conform to the "drop-in" aspects outline on page 4. As it as been mentioned previously, production of "drop-in" fuels with a high market impact through hydrothermal conversion of biomass is likely a two-stage process approach, 1) biocrude production through HtL followed by 2) hydrotreatment to achieve "drop-in" properties.
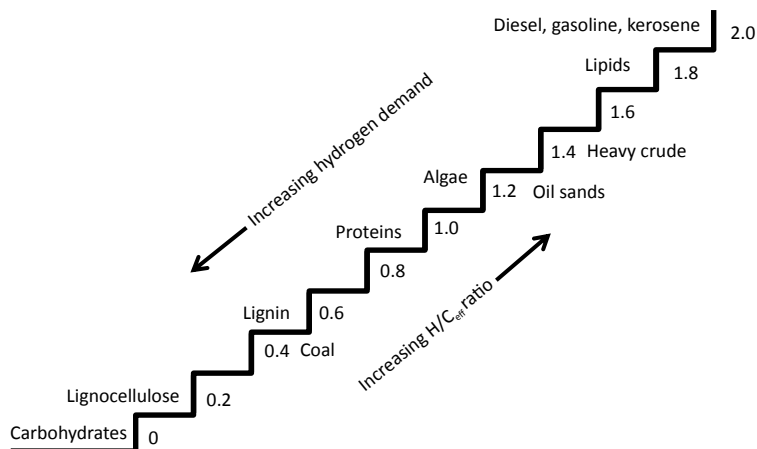
Fig. 5.8: The H/C$_{eff}$-staircase of biomass, biomass macromolecules, and market fuels. Modified from [1].

In relation to the H/C$_{eff}$ ratio, the purpose of HtL is thus to chemically alter the macro-molecules in a way that moves the products as high as possible on the H/C$_{eff}$-staircase. The further up the staircase, the less amount of hydrogen is required to turn the biocrude into mar-ketable fuels. Clearly from Fig. 5.8, biocrudes from high lipid containing biomass are therefore expected to be of higher quality H/C$_{eff}$-wise than biocrudes obtainied from e.g. carbohydrates. Since the biocrude obtained from hydrothermal conversion of biomass is directly affected by the biomass composition, knowing how the macromolecules are distributed in the biomass al-lows for tailoring the biomass composition by intentional mixing. In addition, by knowing the direct chemical coupling between the individual macrostructures and the biocrude composition, biomass composition can be tailored according to preferable properties of the biocrude.

5 Hydrothermal conversion of lignocellulosic biomass

As the most abundant form of biomass, lignocellulosic biomass holds a BtL potential, which must be addressed if biorefineries are to become a reality. The mass distribution of cellulose, hemicellulose, and lignin may vary substantially, but ranges generally by the following: 35-50 % cellulose, 20-35 % hemicellulose, and 10-25 % lignin. A range of examples of lignocellulosic biomass is shown in Table 5.5.

Physically, the structure of lignocellulose is highly complex and consists of a rigid crys-talline cellulose fraction embedded in a matrix of hemicellulose and lignin defining the woody architecture [3]. The structure is depicted in Fig. 5.9. The rigid structure of lignocellulose represents a challenge in continuous processing systems since the solid structure is almost in-soluble in any common solvents - and especially in water [4]. This means that the liquid phase

Table 5.5: Cellulose, hemicellulose and lignin distribution of several lignocellulosic materials. Data obtained from Demirbas [2].

	Cellulose	Hemicellulose	Lignin
Tobacco leaf	41.54	43.45	15.01
Corn cob	32.32	52.49	15.19
Corn straw	30.88	51.53	17.59
Wheat straw	45.2	33.82	20.98
Beech wood	31.86	46.27	21.87
Hard wood	32.26	45.85	21.89
Ailanthus wood	26.73	47.52	25.75
Tobacco stalk	28.89	44.32	26.79
Soft wood	24.82	42.68	32.5
Spruce wood	21.31	47.11	31.58
Hazelnut shell	30.29	26.7	43.01
Wood bark	30.28	25.59	44.13
Olive cake	21.63	23.08	55.29

of a lignocellulosic-based slurry (mainly water) acts more as a slurrying vehicle for suspended biomass particles than as an actually solvent. When pumping water and lignocellulosic biomass slurries, the slurries have a tendency to dewater thereby separating the liquid and the solid phases. This separation effect limits the mass loading of lignocellulosic biomass in an aqueous slurry and consequently penalizes process economy. Several initiatives can and have been performed to increase the mass loading of lignocellulose such as, grinding the biomass to fine powder, adding a slurry stabilizer like heavy oil and recycle biocrude [5], or carboxymethyl cellulose (CMC) [6], or by chemically altering the rigid structure to enhance the solubility in water (e.g. the LBL-process).

Although lignocellulose is an inherent hydrogen and carbon source it yet positions at the bottom of the H/C_{eff}-staircase due to a substantial amount of oxygen. The ultimate analysis of a broad excerpt of different lignocellulosic biomass was examined by Friedl et al. and represented in Table 5.6 [7]. It is evident from the table that for lignocellulosic biomass oxygen is in any case a well-represented element. Conversely, sulfur and nitrogen are minor constituents, if not absent. How these different elements are distributed within the lignocellulosic macromolecules along with the redistribution into biocrude compounds is vital knowledge.

5.1 Hemicellulose

Hemicellulose is a heteropolymer consisting of both pentoses and hexoses branched together into polymers with an amorphous structure. The pentoses and hexoses distribution of hemicellulose is greatly dependent on the biomass [8]. Hardwood consists mostly of xylans (polymers of xylose units) and softwood consists mostly of mannans (polymers of mannose units). It is
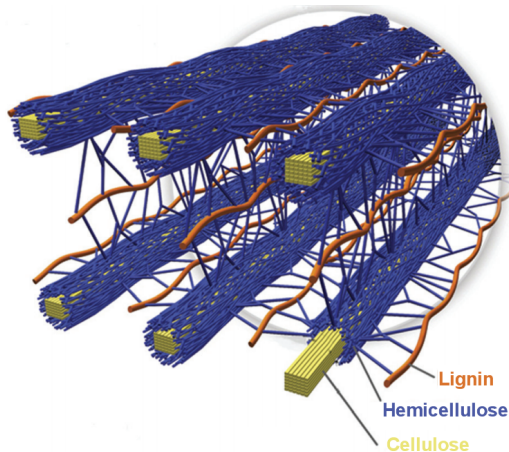
68

Fig. 5.9: Structure of lignocellulose including cellulose, hemicellulose and lignin. Adapted from [3].

generally known, that due to the branched structure of hemicellulose, which inhibit inter- and intramolecular hydrogen bonds, hemicellulose is less resistant to hydrolysis than cellulose and therefore is the first macromolecule to disintegrate [8]. Lü and Saka investigated the degradation of the several monosaccharides present in lignocellulose for which the distributions of degradation products were found dissimilar. For pentoses, furfural was the major degradation product, whereas 5-HMF was mainly found in the products of hexose. The amount of 5-HMF and furfural increases with increased reaction time and temperature [9].

Degradation pathways of xylose during hydrothermal treatment

Next to arabinan, galactan and mannan, xylan is commonly a major component of hemicellulose. Xylose degradation in hot-compressed water has been studied extensively and it generally accepted that degradation occurs through two main pathways: Retro-Aldol condensation and dehydration [10–12]. A proposed degradation mechanism is illustrated in Fig. 5.10.

Retro-Aldol condensation leads to the formation of lighter oxygenated compounds through C-C bond cleavage, whereas dehydration leads to the formation of furfural. All these compounds are believed to be intermediate compounds and are formed at short residence times, where after inter- and intra-molecular reactions rapidly occur leading to the formation of a broad range of different chemical compounds. Most of these compounds holds carbonyl functional groups in the form of aldehydes, ketones, and carboxylic acids. Although it is generally accepted how carbohydrates degrade in hot-compressed water, the formation of biocrude compounds from these intermediates is only speculative. Under alkaline supercritical water conditions (400 °C, 15 min.) it was found that xylose forms a mass fraction of approximately 30 % of ether-soluble (diethyl ether) compounds. The biocrude consisted of substainally deoxygenated

Table 5.6: Ultimate analyses of a range of lignocellulosic biomass. Data obtained from Friedl et al. [7].

Feedstock:	C	H	O	N	S	H/C_{eff}
Willow wood	49.9	5.9	41.8	0.6	0.1	0.16
Pine chips	49.7	5.7	38.1	0.5	0.1	0.23
Oak wood	48.6	6.5	42.3	2.6	0	0.3
Bamboo wood	48.8	6.3	42.8	0.2	0	0.23
Wheat straw	43	5.4	47	0	0	0
Corn straw	44.7	5.9	40.4	0.6	0.1	0.23
Rice straw	38.2	5.2	36.3	0.9	0.2	0.21
Sugarcane straw	43.5	6.1	41.1	0	0	0.27
Rice husk	38.5	5.2	34.6	0.5	0	0.27
Corn stover	45.5	5.5	41.5	0.7	0	0.08
Cotton stalk	47.1	4.6	42.1	1.2	0	0
Switchgrass	46.7	5.8	37.4	0.8	0.2	0.29
Sugarcane bagasse	43.8	6	43.4	1.7	0	0.16
Almond shell	48.8	5.9	43.7	0.5	0	0.11
Sunflower seed shell	51.7	6.2	41.1	1	0	0.25
Peanut shell	47.4	6.1	44.4	2.1	0	0.14
Hazelnut shell	50.9	5.9	42.8	0.4	0	0.13
Pistachio shell	45.5	5.6	47.2	1.7	0	0

$>C_6$ compounds [13]. Fig. 5.11 shows a typical chromatogram of the volatile ether-soluble fraction obtained when processing xylose. First of all, it is observed that the biocrude consists of many different chemical compounds that likely co-elute obscuring the compounds identification. Despite the fact that many different compounds are obtained, it has been found that the majority of volatile compounds group into, 1) ketones, mainly of a C_5 or C_6 backbone, and 2) single ring oxygenated aromatics [13]. The formation of compounds having a higher number of carbon atoms than 5 (C_5 for xylose), and an oxygen content substantially lower than that of the origin pentose unveil the occurrence of reductive C-C bond forming condensation reactions. Proposed reaction mechanisms for the formation of biocrude compounds are further discussed in Section 8.

5.2 Cellulose

Cellulose is a well-defined polymer of anhydro-D-glucopyranose units linked by glycosidic β(1-4) linkages in a crystalline structure. When processing cellulose hydrothermally, the first degradation mechanism of cellulose polymers is scission of the glycosidic bonds for depolymerization. Two scission pathways have been suggested; thermal cleavage via dehydration at reducing-end units and hydrolysis of the glycosidic bonds by which glucose units are obtained. Thermal cleavage takes place at intermediate temperatures and low pressures, while hydrolysis
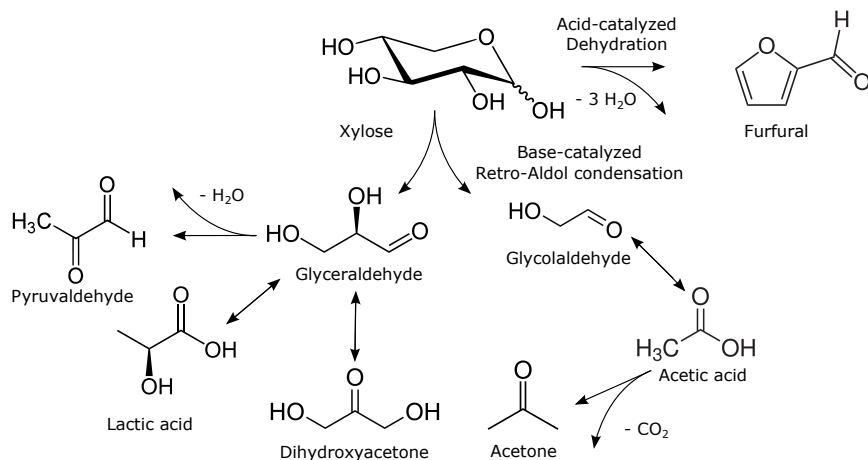
Fig. 5.10: Proposed degradation mechanism of xylose.

becomes predominant in the near and supercritical region. Similarly, it has been found that the degradation of cellobiose, the dimeric model of cellulose, occurs through two pathways; Retro-Aldol condensation and hydrolysis, similar to xylose degradation. In the subcritical region the rate constants of the two pathways were found almost invariant with pressure, but showed great variation in the supercritical region. This can partly be explained by the variance in density in the two regions. As for cellulose degradation, the hydrolysis rate was enhanced by increasing pressure [14]. Hence, reaction pathways are tunable by manipulating reaction conditions. The degradation rates are naturally also affected by catalysts present. The depolymerization of cellulose is both acidic and alkaline aided, where the latter demonstrates the highest rates. However, acidic conditions exhibit the highest rate for further degradation reactions of fragmented cellulose [8].

Degradation pathways of glucose during hydrothermal treatment

As for cellulose and cellobiose, the degradation of glucose units obtained from hydrolysis has also shown to follow two pathways; Retro-Aldol condensation and dehydration.

At low temperatures in the subcritical region, glucose conversion is mainly dominated by dehydration reactions. Shifting to higher temperatures in the supercritical region, Retro-Aldol condensation reactions are predominant followed eventually by gasification reactions as temperature increases further. As for cellobiose, the conversion rates of glucose degradation pathways show hardly any response to pressure in the subcritical region [15]. However, when entering the supercritical region, pressure effects can be quite significant, hence selectivity in the supercritical region can be controlled by changing reaction conditions [14]. At high temperatures, glucose tends to epimerize into fructose, before transforming into a broad product slate similar
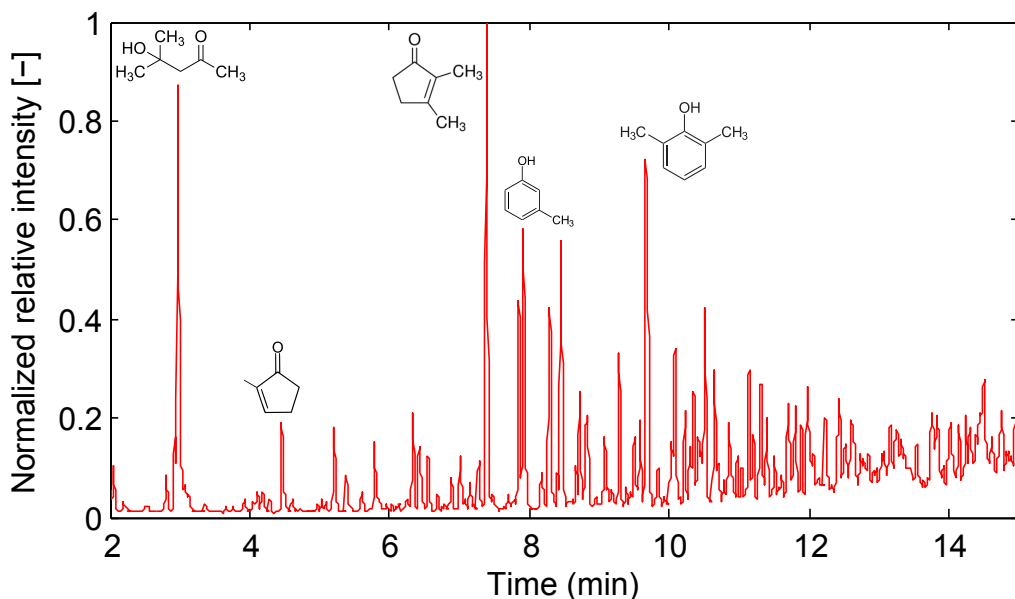
Fig. 5.11: Typical normalized chromatogram of the ether-soluble biocrude from processing xylose.

to the one obtained from glucose [16].

The rate of glucose degradation displays an Arrhenius relation through both the subcritical and supercritical region. However, at subcritical conditions the degradation rate of glucose is much faster than its formation from cellulose scission, why nearly only glucose degradation products are formed from cellulose degradation at subcritical conditions. However, close to the critical point of water the degradation rate of cellulose discontinuously increases by approximately an order of magnitude, thereby the glucose formation rate exceeds its degradation rate. Hence, by applying short reaction times, thereby avoiding further degradation, high selectivity towards glucose units can be obtained in the supercritical region.

As for hydrolysis scission, the selectivity of the different glucose degradation components is also highly affected by whether alkaline or acidic conditions are applied. At alkaline conditions dehydration reactions are suppressed, why mainly short chained carboxylic acids together with various ketones and aldehydes are predominately formed, of which almost all are showing carbon number below the original C_6 of glucose.

When processing glucose at alkaline supercritical water conditions (400 °C, 15 min.), a biocrude (ether-solubles) mass fraction approximately 30 %. A striking similarity has been found between the yield of biocrude and char, but also in the compounds obtained from xylose and glucose, respectively. This is further illustrated in Fig. 5.13, where the individual chromatograms of the volatile ether-soluble fractions are compared. This observation indicates that
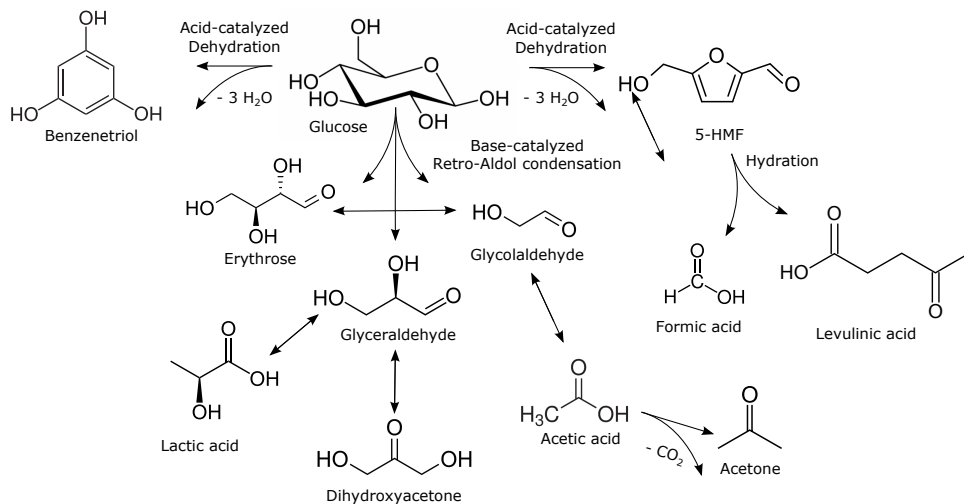
Fig. 5.12: Degradation pathways and product of glucose.

not only do xylose and glucose decompose along the same chemical pathways, forming similar intermediates, the chemical pathways for biocrude formation are also similar leading to almost identical biocrudes. More about chemical mechanism in Section 8.

5.3 Lignin

Lignin is a natural amorphous phenolic biopolymer of high molecular weights. The backbone units are coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. Schematic appearances of the three units are shown in Figure 5.14. The distribution of the individual units is biomass depended but normally softwood comprises mainly of coniferyl alcohol units, hardwood of coniferyl alcohol and sinapyl alcohol units and grasses of p-coumaryl alcohol units.

As it is observed from Fig. 5.14, the backbones of lignin are C_9-C_{11} units with different oxygen-containing functional groups.

Although lignin is a random polymer in the sense that the backbone unit distribution and unit linkages are randomized, general trends still exist. Table 5.7 presents common lignin linkages and distribution in softwood and hardwood.

Depolymerization of lignin

It has been suggested that degradation of lignin in an aqueous medium proceeds along two pathways; an ionic pathway through hydrolysis of ether bonds leading to the formation of phenols and a radical pathway, along which ether and C-C bonds are thermolytically cleaved. In non-catalyzed water the general trend is that the most abundant β-O-4 linkage is readily cleaved

Fig. 5.13: Normalized chromatograms of the ether-soluble biocrudes from processing glucose and xylose.
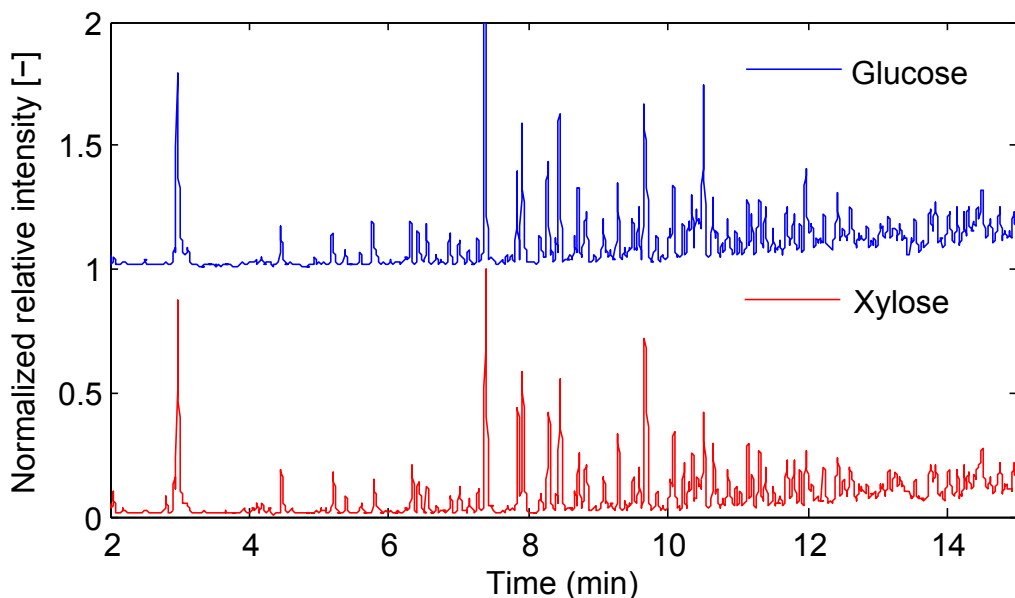
whereas the 4-O-5 bonds together with C-C bonds are stable under common hydrothermal liquefaction conditions. As an example, diphenyl ether (DPE) has been studied as a 4-O-5 ether bond lignin model compound in supercritical water. Penninger et al. investigated the degradation of DPE in supercritical water with and without the presence of NaCl. It was found that the salt promoted degradation, but at a reaction temperature of 430 °Cand after 5 hours the conversion of DPE was only around 3 % [18, 19]. However, Roberts et al. found that the 4-O-5 bond is far less stable when adding an alkaline catalyst (Li_2CO_3, Na_2CO_3, K_2CO_3). At 400 °C and in the presence of K_2CO_3 conversion of more than 50 % was obtained after one hour [20]. It was found that the conversion of diphenyl ether decreased at increased densities but that the hydrolysis reaction pathway was found favored at high water densities. It is noteworthy that the hydrolysis selectivity was found 100 % for all catalysts at low temperature (320-370 °C) but decreased at 400 °C for all but K_2CO_3. The observation is explained by the decreased catalyst solubility at supercritical conditions. The observed hydrolysis pathway selectivity may also partly explain why oil formation and char reduction is enhanced in liquefaction by adding an alkaline catalyst.

Radicals formed from the radical pathway are responsible for the formation of high molecular weight compounds by re-polymerization, oligomerization, condensation etc. and undesirable char formation comprised mainly of condensed C-C bonds. Pedersen et al. processed alkali lignin, as a model lignin, under supercritical alkaline conditions. Roughly 15 % of ether-soluble
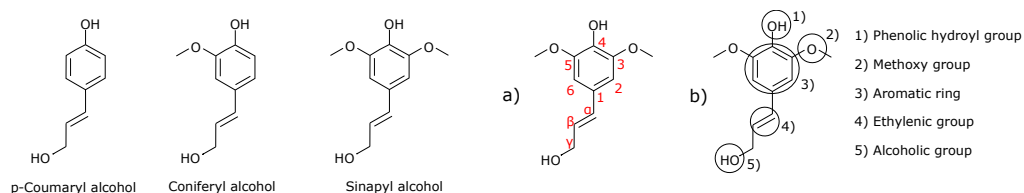
Fig. 5.14: Backbone polymeric units of lignin.

| | Percentage of total linkages | |
Linkage type	Softwood	Hardwood
β-O-4	45-50	$\approx$60
5-5	19-27	3-9
β-5	9-12	3-11
Spiro-dienone	2	3-5
4-O-5	4-7	7-9
β-1	1-9	1-2
Dibenzodioxocin	5-7	0-2
β-β	2-6	3-12
α-O-4	2-8	7

Table 5.7: Common lignin linkages and distribution in softwood and hardwood [17].

compounds were obtained, of which the majority were comprised of oxygenated aromatics. A comparison of GC chromatograms of biocrudes obtained from lignin, glucose, and xylose is shown in Fig. 5.15. Whereas the chemical composition of xylose and glucose-derived biocrude are almost identical, the lignin-derived biocrude comprised to a greater extent of oxygenated aromatics, although many compounds were found identical in all three biocrudes. Remarkably was that nearly 50 % of the lignin remained as a solid phase. Hence, the radical pathway is an undesirable reaction pathway of lignin if radicals cannot be stabilized. Another side effect of this reaction is observed when processing whole lignocellulosic biomass. Hashaikeh et al. visually observed that during hydrothermal treatment of willow lignin and hemicellulose dissolute around 200 °C [21]. As temperature increased to 250 °C lignin precipitated and formed capping fragments preventing cellulose dissolution. As a consequence, when temperature was further increased to 350 °C cellulose underwent pyrolysis rather than hydrolysis.

In the attempt to alleviate or prevent char formation, radical scavengers like phenols and alcohols have been used to cap reactive fragments. Miller et al. studied base catalyzed alcoholysis of Kraft and Organosolv derived lignin and lignin model compounds in methanol and ethanol at 290 °C [22]. Ether insoluble fraction levels as low as 5 % were achievable with an ethanol solvent. From the model compound study it is clear that at these conditions alkylation and dealkylation of benzene rings occur due to interaction with ethanol. In addition it
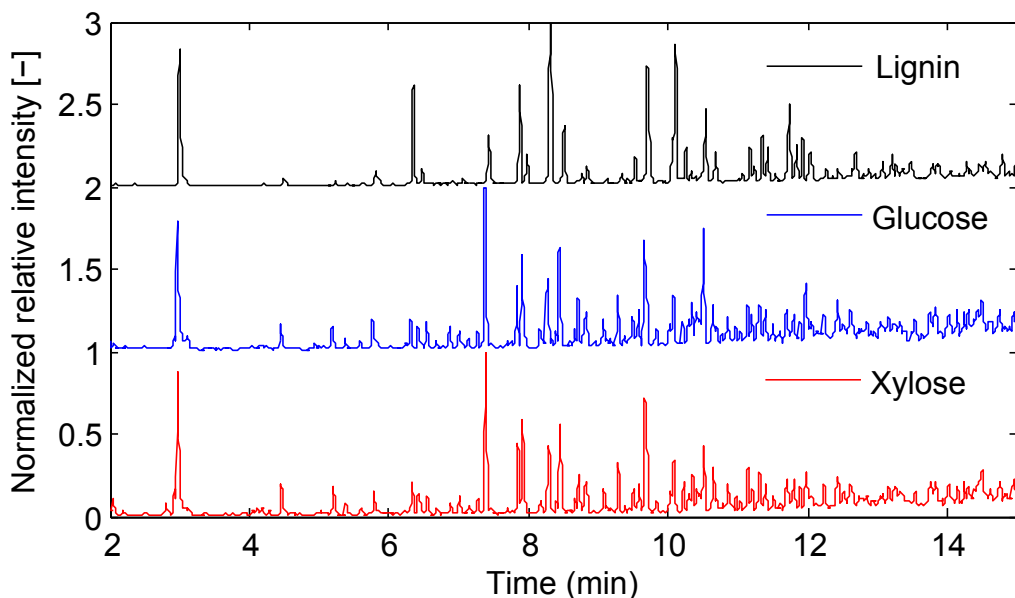
Fig. 5.15: Comparison of normalized chromatograms of the ether-soluble biocrudes obtained from lignin, glucose, and xylose.

was found that C-C bonds are not cleaved at these conditions, hence compounds like biphenyl, diphenyl methane and bibenzyl are unreactive. A similar fact has been confirmed in a aqueous environment. Here it was concluded that aryl-aryl and methylene bonds can only be cleaved below 400 °C with the addition of a proper base catalyst. The alcoholysis is somewhat different from hydrolysis. In hydrothermal medium phenols are stable compounds, whereas in alcoholic solvents they undergo alkylation. The ability of liquefying alkali lignin in a ethanol, water, and ethanol:water co-solutions was investigated by Cheng et al. [23]. It was found that the amount of liquefied compounds followed the following sequence: ethanol:water co-solution > water > ethanol.

The highest yield of liquefied compounds was accompanied by the lowest yield of residues. Char formation can almost be neglected in a 1:1 water:ethanol co-solution.

Although the depolymerization/repolymerization mechanisms have been widely studied, previous work dedicated for turning isolated lignin into a biocrude is scarce. Roberts et al. reports the yield of a dark-brown product, formed by the utilization of base-catalyzed depolymerization and boric acid as a repolymerization inhibition agent [20]. A maximum yield of 52 % was obtained at a NaOH/boric acid weight ratio of 0.75. It was found that a multitude of process parameters influenced the yield like temperature, pressure, residence time and weight ratios between lignin, base and boric acid.

Valuable aromatic compounds can be derived from lignin, mainly in the form of oxygenated

aromatics, if chemical bonds are substantially cleavage and fragments subsequently stabilized to prevent repolymerization and char formation. Based on the preceding discussion, a stabilizing agent has to be present when liquefying lignin in order to obtained sufficient liquid yield and to suppress char formation. In Section 7 it is discussed how synergies in mixing of different types of biomass can be obtained, specifically on how radical scavengers can be naturally produced from biomass.

6   Conversion of other model compounds

From the results obtained from processing xylose, glucose, lignin at supercritical conditions, some conclusions can be drawn:

- Xylose and glucose form equal amounts of biocrude and char. This is evident from Fig. 5.16.

- The composition of biocrudes obtained from xylose and glucose is almost identical.

- Biocrude from carbohydrates consist mainly of ketones and oxygenated aromatics.

- Lignin forms mainly oxygenated aromatic through a direct cleavage and stabilizing mechanism.
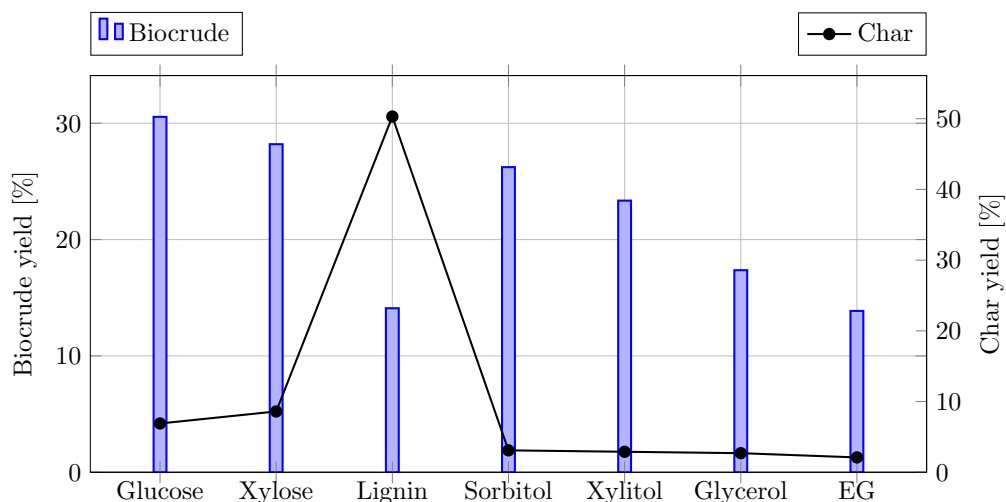

Fig. 5.16: Biocrude and char yield for different model compounds.

The aromatic composition of the lignin-derived biocrude is expected based on the aromatic nature of lignin. Cleavage of chemical bonds in between lignin monomers and subsequent

stabilization of reactive fragments directly derived aromatic compounds. Ketone and aromatic formation from carbohydrates is not as straight forward as the liquefaction of lignin. It has briefly been indicated that the occurrence of reductive C-C bond forming condensation reactions may be responsible for ketones formation from carbohydrate intermediates.

To investigate the chemical mechanisms, other model compounds have been processed under identical conditions. The model compounds include sorbitol (C_6) and xylitol (C_5), the reduced derivatives of glucose and xylose, respectively, glycerol (C_3), ethylene glycol (C_2), and acetone (C_3). It was found that all model compounds formed an ether-soluble fraction and a char fraction, see Fig. 5.16. It was found that sorbitol and xylitol performed similar to glucose and xylose. Although slightly less biocrude and char were formed, the biocrude compositions were almost identical. Both glycerol (C_3) and ethylene glycol (C_2) formed ketones of in the C_5-C_8 and to a less extent oxygenated aromatics. These results indicate that the same intermediates for ketones formation are formed from all investigated model compounds. The resulting H/C_{eff} ratios ranged from 0.96-1.14 for the model compounds investigated. Acetone clearly showed C-C bond forming Aldol condensation under the given conditions. Fig. 5.17 shows the chromatogram for the ether-solubles obtained from processing acetone.

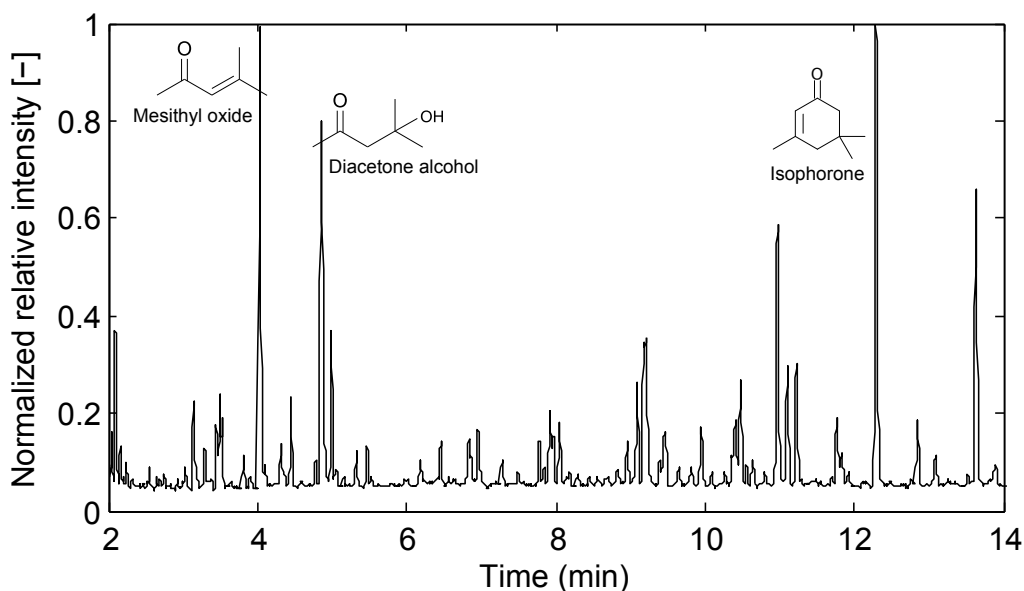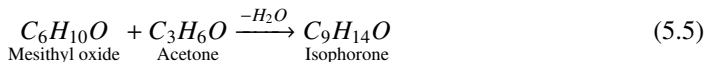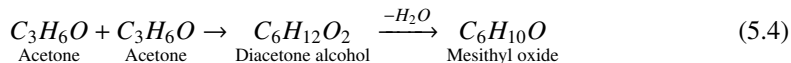**Fig. 5.17:** Normalized gas chromatogram of compounds identified from acetone processing at alkaline, supercritical conditions.

The compounds identified reveal that acetone self-condensates to diacetone alcohol C_6 followed by dehydration yielding mesithyl oxide C_6. Mesithyl oxide then further condensates with acetone, yielding isophorone C_9 upon dehydration. The reactions are summarized in Eq. 5.4

and 5.5

$$C_3H_6O + C_3H_6O \rightarrow \underset{\text{Diacetone alcohol}}{C_6H_{12}O_2} \xrightarrow{-H_2O} \underset{\text{Mesithyl oxide}}{C_6H_{10}O} \qquad (5.4)$$

$$\underset{\text{Acetone}}{C_3H_6O} \quad \underset{\text{Acetone}}{C_3H_6O}$$

$$\underset{\text{Mesithyl oxide}}{C_6H_{10}O} + \underset{\text{Acetone}}{C_3H_6O} \xrightarrow{-H_2O} \underset{\text{Isophorone}}{C_9H_{14}O} \qquad (5.5)$$

7   Processing model compounds and biomass mixtures

7.1   Carbohydrates and lignin

It is generally known that during pyrolysis and liquefaction of lignocellulose, the yield of liquid products decreases and the yield of char increases proportionally to the lignin content [24, 25]. Meier et al. performed liquefaction experiment on different lignocellulosic biomass, cellulose, and holocellulose and lignin samples at 375 °C in the presence of a palladium catalyst and hydrogen atmosphere. Results showed that the H/C_{eff} ratio of all samples ranged from 0.47-0.85, lowest for lignins (0.47-0.51), cellulose, holecellulose and lignocellulosic samples were comparable (0.67-0.85). In order to investigate how the distribution of carbohydrates and lignin in lignocellulosic biomass affects the biocrude composition, mixtures of glucose, xylose, and alkali lignin have been processed at supercritical, alkaline conditions. Fig. 5.18 presents the relative distribution of ketone and aromatic formation together with the elemental composition as a function of the carbohydrate and lignin content. From Fig. 5.18 it is concluded that:

- Ketones and oxygenated aromatics vary linearly to the carbohydrate and lignin content.

- The elemental composition of the biocrudes is almost invariant to the distribution of carbohydrates and lignin.

- H/C_{eff} ratios range from 0.87-0.98, placing the biocrudes nearly midway on the H/C_{eff}-staircase.

From the HC ratios obtained it appears that processing model compounds and model mixtures yield biocrudes of higher quality than the biocrudes obtained by Meier et al. at 375 °C. The conclusions are interesting since the biocrude composition can then be predicted based on the distribution of model compounds. Similar predictability in microalgae composition has been observed by Leow et al. [26]. Contrary, the predictability of biocrude derived from aspen wood of known carbohydrate and lignin composition turned out poor. The aromaticity of the aspen wood-derived biocrude was higher than predicted. Further tests have to be done to find if the predictability from lignocellulosic model compounds to real biomass can be improved.
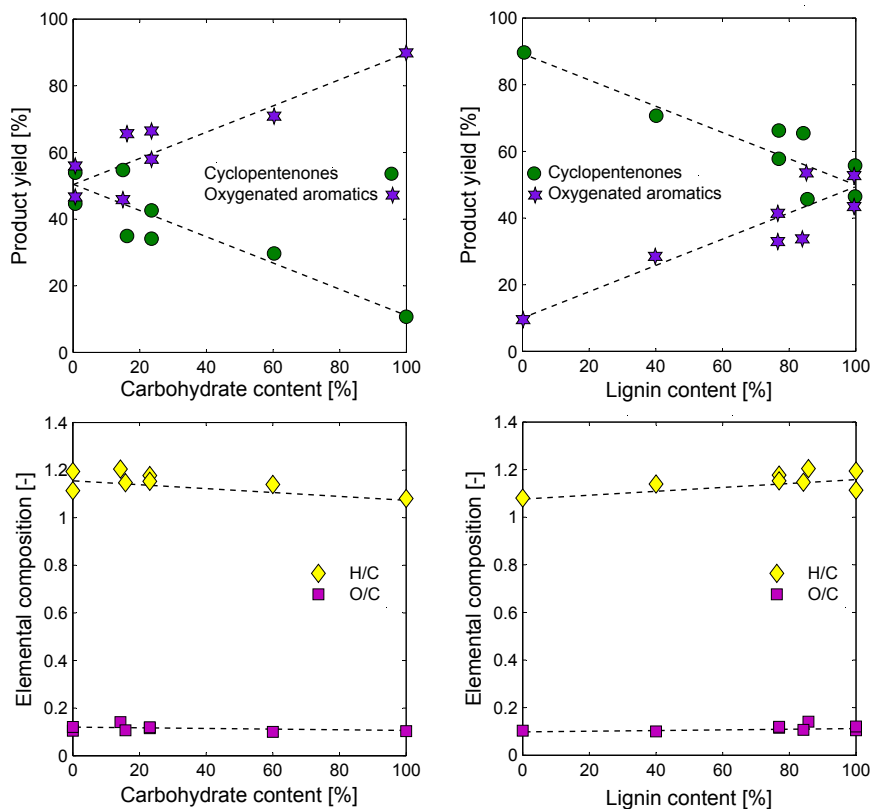
Fig. 5.18: Normalized relative distributions of cyclopentenones (CPs) and oxygenated aromatics (OAs) in the biocrudes, and atomic H/C and O/C ratios as functions of the carbohydrate and lignin content in the model mixtures.

7.2   Wood and glycerol mixtures

Glycerol is a derivative compound alongside fatty acids derived from hydrolysis of glycerides. It has been found that glycerol form ether-soluble compounds when processed at supercritical water conditions. Glycerol has also been observed as a radical scavenger for liquefying lignocellulose and lignin. In the presence of a base catalyst, glycerol undergoes hydrogen-abstraction and can thereby act as a hydrogen-donor. In the context of liquefying lignocellulosic it was therefore hypothesized that by adding glycerol, or glycerides forming glycerol through hydrolysis, char formation was expected to be alleviated. Fig. 5.19 shows how biocrude and char yield vary with the glycerol content of aspen wood-glycerol mixtures. From the figure it is evident that char yield substantially decreases as glycerol is added to the mixture. Moreover, the biocrude yield may even increase as synegetic effect probably due to the fact more lignin

is liquefied rather than solidified. The fact that the biocrude and char yields do not follow a linear trends indicates that chemical interactions occur between glycerol and the lignocellulosic constituents. It was further found that the H/C_{eff} ratio was nearly unaffected by the mixing ratio, which is in agreement with previous findings for processing model compounds.

Fig. 5.19: Biocrude and char yields as a function of glycerol to aspen wood mass ratio in the feedstock. Data reproduced from Pedersen et al. [27].

7.3 Wood and crude glycerol mixtures

Today glycerol is produced mainly as a byproduct from the biodiesel industry. The unrefined byproduct is termed crude glycerol and is a bulk emulsion of mainly glycerol, but also residual base catalyst, free fatty acids (FFA) and fatty acid methyl esters (FAME). Due to the positive effects of basic conditions and the addition of glycerol when processing lignocellulosic, crude glycerol is a prospective industrial byproduct that could possess synergetic properties in co-processing effects in wood liquefaction. The conceptual idea is depicted in Fig. 5.20.

Experiments have been conducted by co-processing aspen wood and crude glycerol. Due to the high alkalinity of the crude glycerol no further catalysts were added to the experiments. Some of the main results are presented in Fig. 5.21. From the results it was concluded that:

- Equal amounts of char is produced from processing aspen wood with glycerol or crude glycerol.

- The H/C_{eff} ratio varied linearly to the mixing ratio of crude glycerol and aspen wood (from 0.96 to 1.63).
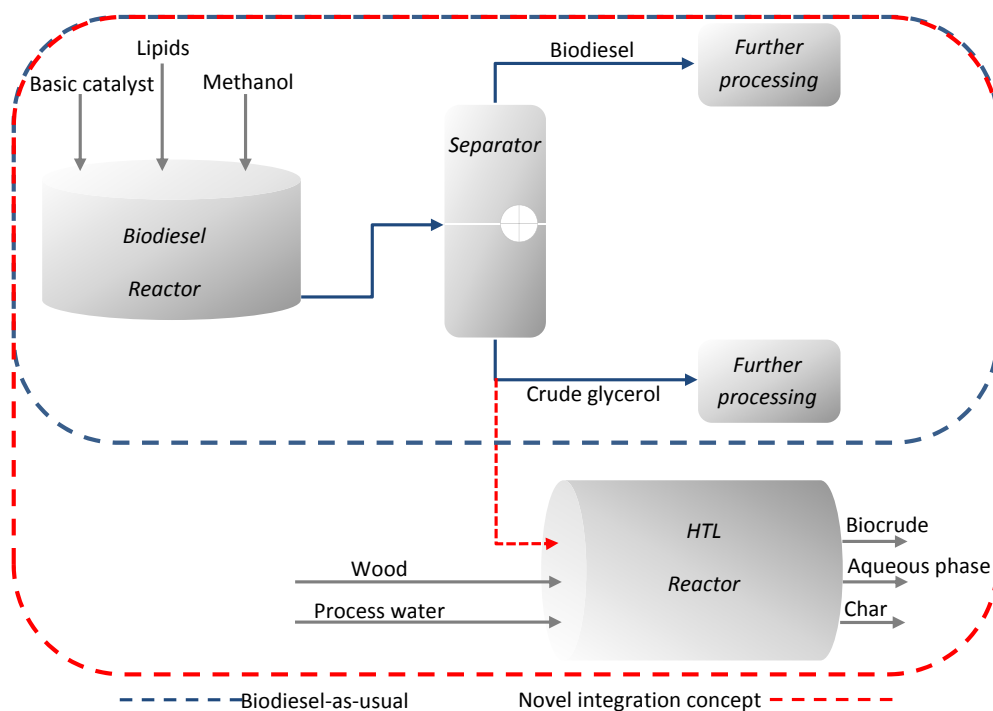
Fig. 5.20: Conceptual integration of biodiesel production and HtL by alternative utilization of crude glycerol.

- FFAs and FAMEs passed almost unaltered through the process.

- Biocrude composition prediction based on mixing ratio was straightforward.

- The alkalinity of crude glycerol is sufficient to achieved successful liquefaction results.

Besides the chemical synergies obtainable when co-processing crude glycerol and aspen wood, energetic synergies can furthermore be obtained by process integration of the biodiesel production and a HtL facility [28]. Process simulations have shown that in total a 17.1 % and a 20.18 % reduction in heating and cooling requirements, respectively, can be achieved by process integration.

8 Identification of reaction mechanisms

In-depth knowledge of the interaction reactions between water and biomass, and between biomass constituents and intermediates has not yet been established. The complex role of water in super-
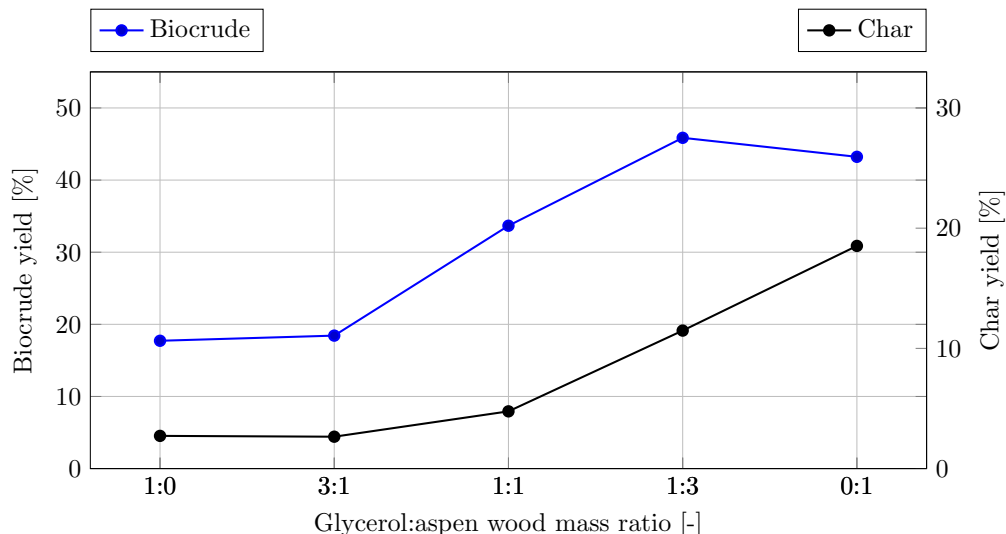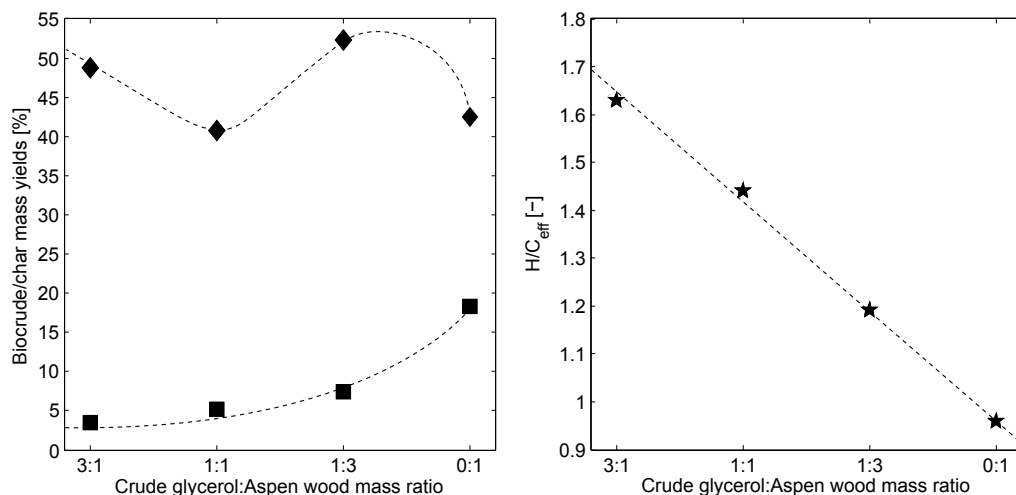
Fig. 5.21: Biocrude and char yields as a function of crude glycerol to aspen wood mass ratio in the feedstock. Data reproduced from Pedersen et al. [27].

critical water synthesis applications have been discussed by e.g. Kruse and Dinjus, and Akiya and Savage [29, 30]. A summary of effects of water was given by Akiya and Savage and is reproduced in Table 5.8. It is clear that the complexity of chemical synthesis in hot-compressed water is high and that several effects may be affected the chemical mechanism.

When processing biomass at severe HtL conditions cascades of chemical reactions are initiated resulting in the formation of numerous chemical compounds. Parallel hydrolysis and thermolysis reactions of abundant ether-bonds fragment macromolecules producing intermediates and radicals according to Eq. 5.7-5.8.

$$R{-}O{-}R' + H_2O \rightarrow 2\,R{-}OH \tag{5.6}$$

$$R{-}O{-}R' \xrightarrow{\text{heat}} R{-}O + R'\bullet \tag{5.7}$$

$$R{-}R' \xrightarrow{\text{heat}} R\bullet + R'\bullet \tag{5.8}$$

Subsequent reductive C-C bond forming condensation reactions may then be responsible for ketones formation from carbohydrate intermediates. H-transfer reactions may stabilize the radicals hydrogen donation according to Eq. 5.9. Hydrogen donation may even cause hydrogenolysis reactions, removing undesirable oxygen or saturate double bonds according Eq. 5.10-5.11, respectively.

Table 5.8: Summary of effects of water for organic chemical reactions in high temperature water. Table obtained from [30].

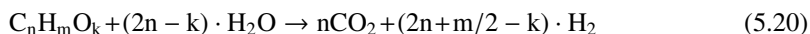| role of water	applicable conditions	affected reactions
reactant/product	any, but importance increases at higher water densities	reaction in which water is a reactant (e.g., hydrolysis, hydration, hydrogen abstration)
catalyst	any	proton-transfer reactions in which water interacts with reactant(s), typically via hydrogen bonding
acid/base catalyst precursor	more important at higher temperatures and liquid-like densities	acid/base-catalyzed reactions
preferential solvation/ desolvation of transition state	any, but probably less important at gas-like densities	reactions with change in solute-solvent interactions between reactants and transition state; examples include reactions with a change in polarity along the reaction coordinate
hydrophobic effect	more important at near-ambient conditions than in HTW	condensation reactions with immiscible organic reactants
solvent dynamics	more important at liquid-like densities	very fast reactions (faster than solvent reorganization)
density inhomogeneities	supercritical conditions	any reaction can be affected by the local composition differing from the bulk composition
energy transfer	more important at gas-like densities; at liquid-like densities, energy transfer is not likely to be rate limiting	nominally unimolecular elementary reactions
cage effects	more important at liquid-like densities	bimolecular reactions (in forward or reverse direction)

$$R\bullet + R'\bullet \xrightarrow{2H^{\bullet}} RH + R'H \qquad (5.9)$$

$$R-OH + H_2 \rightarrow 2\,R-H + H_2O \qquad (5.10)$$

$$R=R' + H_2 \rightarrow R-R' \qquad (5.11)$$

In addition to the important effects of water in breaking down the macromolecules and acting as a feedstock vehicle, Furimsky argues that water also takes part in hydroprocessing reactions such as a free radical scavenger and as a hydrogen donor [31]. This argument is supported by the observation of hydrogen exchange in deuterium oxide (D_2O) doped thermal steam-cracking of bitumen [32] by tracing the deuterium. However, it was found that the amount of deuterium to the total amount of hydrogen totaled less than 1 % in all cases. The following reactions are examples of possible direct and indirect hydroprocessing reactions involving water:

$$R\bullet + H_2O \rightarrow RH + OH\bullet \tag{5.12}$$

$$R\bullet + HO\bullet \rightarrow ROH \tag{5.13}$$

$$R\bullet + H_2O \rightarrow ROH + H\bullet \tag{5.14}$$

$$R\bullet + H\bullet \rightarrow RH \tag{5.15}$$

$$R\bullet + R\bullet \rightarrow RR \tag{5.16}$$

$$ROH \rightarrow R'' + H_2O \tag{5.17}$$

$$R'' + H_2 \rightarrow RH \tag{5.18}$$

$$R\bullet + H_2 \rightarrow RH + H\bullet \tag{5.19}$$

$$C_nH_mO_k + (2n-k)\cdot H_2O \rightarrow nCO_2 + (2n+m/2-k)\cdot H_2 \tag{5.20}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{5.21}$$

Based on previous findings from processing lignocellulosic biomass and model compounds under alkaline, supercritical conditions, it is evident that ketones and oxygenated aromatics are major compounds in the biocrudes. It is reasonable to conclude that oxygenated aromatics and fatty acids are "biomarkers" of lignin and lipids, respectively, and that ketones and other non-aromatic compounds are mainly derived from carbohydrates, glycerol etc. An overall reaction mechanism summarizing these findings is illustrated in Fig. 5.22.

The chemistry must involve a redistribution of elements forming a "hydrogen-richer" fraction, the biocrude, and "hydrogen-leaner" fractions, e.g. WSO and gas (mainly CO_2). Due to element conservation, when the H/C_{eff} ratio of a fraction of the biomass (the biocrude) increases, the H/C_{eff} ratio of some other fractions have to decrease. For lignin and fatty acids, the aromatic and aliphatic backbones are almost preserved, although hydrolysis and thermolysis result in monomeric compounds. This also results in the fact that the H/C_{eff} ratios of the biocrudes obtained from ligning and lipids are only slightly higher than that of the initial macromolecules. This fact also indicates that the major H/C_{eff} improvement is probably caused by carbohydrate synthesis. There is a key distinction between carbohydrates, and lignin and lipids. Lignin and lipids have their hydrogen atoms bonded mainly to carbon atoms. Therefore, any loss of oxygen is often accompanied by a loss of carbon. For carbohydrates the hydrogen atoms are equally bonded to carbon and oxygen atoms, and any loss of oxygen is therefore accompanied by a loss of carbon but also to a great extent loss of hydrogen. Liberation of oxygen through dehydration reactions do not change the H/C_{eff} ratio of the dehydrated compounds and therefore cannot explain neither the H/C_{eff} improvement nor the increase in carbon chain observed for biocrude formation. Liberation of oxygen through decarboxylation is a viable route for increasing the H/C_{eff} ratio, which can also explain the observation of CO_2 being the most abundant species in the gas phase. Decarboxylation on the other hand decreases the carbon chain of the decarboxylated compounds, which is contradicting the observation of compounds of longer carbon chains than the original starting compound. Hydrogenation or transfer hydrogenation reactions will
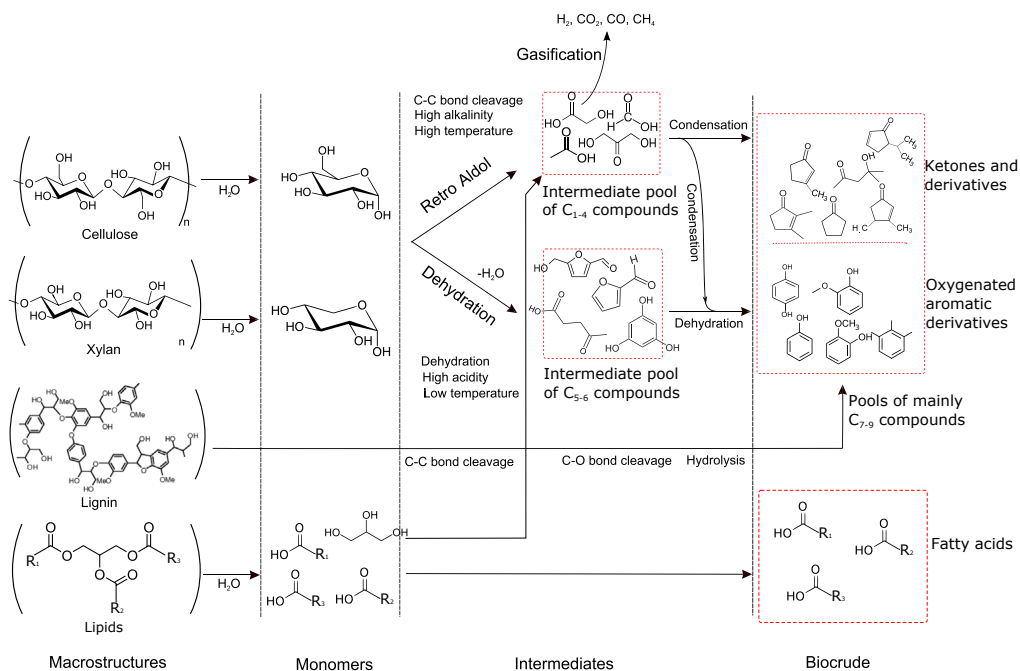
Fig. 5.22: Proposed overall reaction scheme for the formation of biocrude from lignocellulose macromolecules.

result in a hydrogen-richer and a hydrogen-leaner fraction. A prerequisite for hydrogenation reactions is the formation of gaseous hydrogen. Steam reforming (Eq. 5.20) is the preferred reaction for hydrogen generation. However, the reaction is strongly favored thermodynamically, and in the absence of a transition or noble metal catalyst high temperatures are needed. Furthermore, hydrogenation does not increase the carbon chain. Therefore, although hydrogenation is a possible pathway for biocrude formation, it is not a plausible governing reaction pathway. Table 5.9 presents characteristics of common reactions observed in carbohydrate synthesis. Interestingly, of the mentioned reactions, ketonic decarboxylation is the only reaction that simultaneously increases the H/C_{eff} ratio and the carbon chain. Ketonic decarboxylation is the condensation of carboxylic acids followed by the expulsion of a water and a CO_2 molecule to form a ketone group. The formation of C_5-C_8 compounds then requires condensation of C_1-C_8 carboxylic compounds, but more likely C_1-C_6 intermediates obtained from C-C bond cleavage reactions.

Table 5.9: Effects of chemical reactions on the H/C$_{eff}$ ratio and carbon chain. (+) indicates an increase, (-) indicates a decrease, (0) unaffected.

	H/C$_{eff}$	c-chain
Hydrolysis	+/-	-
Aldol reaction	0	+
Aldol condensation	0	+
Retro Aldol reaction	0	-
Dehydration	0	0
Hydrogenation	+	0
Hydrogenolysis	+	-
Oxidation	-	0
Esterification	0	+
Decarboxylation	+	-
Decarbonylation	+	-
Claisen condensation	-	+
Michael reaction	0	+
Diels-Adler reaction	0	+
Cannizzaro reaction	+/-	0
Ketonic decarboxylation	+	+
Rearrangement	0	0

8.1 Water phase extraction

To further investigate the formation pathways of biocrude compounds an analysis of the biocrude and aqueous phase compounds has been carried out. For carbohydrates it is expected that pools of intermediates exist that will then further react to form biocrude compounds. Compounds identified by extraction of the aqueous phase obtained from aspen wood-glycerol co-liquefaction is presented in Table 5.10. The list includes carboxylic acids, alcohols, ketones, esters, furans, diols, etc., in the range of C$_2$-C$_8$. Furthermore, it is observed that several isomers exist having different functional groups. This fact complicates the identification of reaction pathways, since multiple pathways can lead to the formation of the same compounds. For instance, acetic acid is commonly produced from hydrothermal conversion of carbohydrates, as observed in Fig. 5.10 and 5.12. However, acetic acid can also be produced from glycerol by C-C cleavage of glycerol, which forms acetic acid and methanol; two compounds which can then be responsible for the ester formation. A third pathway is the base-induced Cannizzaro reaction of acetaldehyde yielding acetic acid and ethanol, both compounds identified from the aqueous phase and the biocrude. These reactions are summarized in Eq. 5.22-5.24.

$$C_6H_{12}O_6 \longrightarrow 3CH_3COOH \longleftrightarrow 3CH_2CHO \tag{5.22}$$

$$2CH_2CHO \xrightarrow{OH-} CH_3COOH + C_2H_5OH \tag{5.23}$$

$$C_3H_8O_3 \longrightarrow CH_3COOH + CH_3OH \tag{5.24}$$
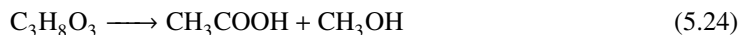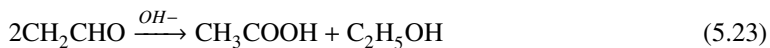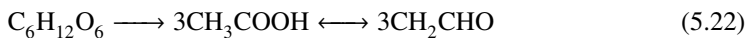
Dehydration of glycerol also produces propionic acid, an isomer of acetic acid methyl ester. This means that the formation of acetic acid methyl ester could potentially be the product of e.g. C-C bond cleavage, esterification, dehydration, and rearrangement reactions. This is summarized by Eq. 5.25-5.27.

$$C_3H_8O_3 \longrightarrow CH_3CH_2COOH + H_2O \tag{5.25}$$

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O \tag{5.26}$$

$$CH_3CH_2COOH \longrightarrow CH_3COOCH_3 \tag{5.27}$$

The presence of alcohols, which are highly reduced compared to the original compounds, indicates disproportionation reactions, such as the Cannizzaro reaction (Eq. 5.23) or hydrogen transfer reactions, which are both base-induced. Glycerol, for instance, has been observed to undergo hydrogen-abstraction under basic conditions [33, 34]. This hydrogen-abstraction is hypothesized to be partially responsible for the reduced char formation in alkaline wood-glycerol co-liquefaction as a result of radical scavenging, but the hydrogen may also participate in hydrogenation reactions forming e.g. alcohols. Hydrogen-abstraction of glycerol leads to the formation of lactic acid or dihydroxyacetone, intermediates from decomposition of carbohydrates, which illustrates the convergence of common intermediate compounds from different source compounds (e.g. carbohydrates and glycerol). Ketone formation is of particular interesting since these are observed as a major compound class. Aldol reactions of aldehydes, e.g. acetaldehyde, is a C-C bond forming reaction leading to the formation of hydroxy-aldehydes or hydroxy-ketones. These adducts may then dehydrate to unsaturated compounds. Further condensation can then eventually lead to the formation of cyclic ketones. Eq. 5.28 and 5.29 shows the Aldol condensation of acetaldehyde into a methyl-cyclopentenone, which are observed in the aqueous phase and in the biocrude. In this case the carbon chain lenght is increased but the H/C_{eff} ratio kept constant ($H/C_{eff}=1$).

$$CH_3CHO + CH_3CHO \longrightarrow C_4H_8O + H_2O \tag{5.28}$$

$$C_4H_6O + CH_3CHO \longrightarrow C_6H_8O + H_2O \tag{5.29}$$
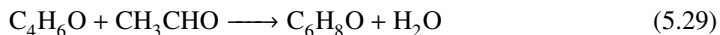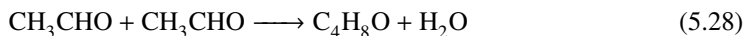
Another reaction pathway for ketone formation is ketonic decarboxylation. This pathway simultaneously increases the H/C_{eff} ratio and the carbon chain length by the expulsion of a water and a CO_2 molecule upon condensation of two carboxyl groups to form a ketone group. As it

Table 5.10: Compounds identified in the aqueous phase from aspen wood-glycerol co-liquefaction by solvent extraction using pentanol, ethyl acetate, and diethyl ether.

Identified compound	Formula	C$_\#$
Acetic acid	$C_2H_4O_2$	2
Acetic acid, methyl ester	$C_3H_6O_2$	3
1-Propanol	C_3H_8O	3
Propionic acid	$C_3H_6O_2$	3
1,3-Propanediol	$C_3H_8O_2$	3
2-Propanone, 1-methoxy-	$C_4H_8O_2$	4
2-Butanone	C_4H_8O	4
Butanol	$C_4H_{10}O$	4
Acetoin	$C_4H_8O_2$	4
Butanoic acid	$C_4H_8O_2$	4
1,2-Propanediol, 3-methoxy-	$C_4H_{10}O_3$	4
Butanal, 3-methyl-	$C_5H_{10}O$	5
Propanoic acid, ethyl ester	$C_5H_{10}O_2$	5
n-Propyl acetate	$C_5H_{10}O_2$	5
1-Pentanol	$C_5H_{12}O$	5
Cyclopentanone	C_5H_8O	5
2-Cyclopenten-1-one	C_5H_6O	5
2-Furanol, tetrahydro-2-methyl-	$C_5H_{10}O_2$	5
1-Pentanol, 4-methyl-	$C_6H_{14}O$	6
2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	6
2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	6
Phenol	C_6H_6O	6
Hexanoic acid, 2-methyl-	$C_7H_{14}O_2$	7
4,4-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	7
2-Cyclopenten-1-one, 2,3-dimethyl-	$C_7H_{10}O$	7
1,2-Benzenediol, 4-methyl-	$C_7H_8O_2$	7
2,5-Cyclohexadiene-1,4-dione, 2,6-dimethyl-	$C_8H_8O_2$	8
4-Ethylcatechol	$C_8H_{10}O_2$	8
1,3-Benzenediol, 4,5-dimethyl-	$C_8H_{10}O_2$	8

was observed for acetone in Fig. 5.17, ketones can condensate to hydroxy-ketones. Condensation of ketones of higher carbon chain number than e.g. acetone (such as propanone, butanone, etc.), followed by dehydration and cyclization is a plausible pathway for the formation of hepta- (C_7) and octa- (C_8) ketones. This reaction pathway is desirable, since it removes oxygen by both dehydration but also by decarboxylation. Furthermore, if the formation of intermediates can be targeted selectively and if the subsequent condensation pathway can be controlled simultaneously, this could open a selective way of producing bulk C_{6+} oxygenates amenable for hydrotreatment and thus generating high-value fuels.

8.2 Distillation of biocrude

Fractional distillation of the biocrude obtained in Paper C (aspen wood-glycerol derived) was performed in order to identify if chemically similar compounds can be isolated from the com-

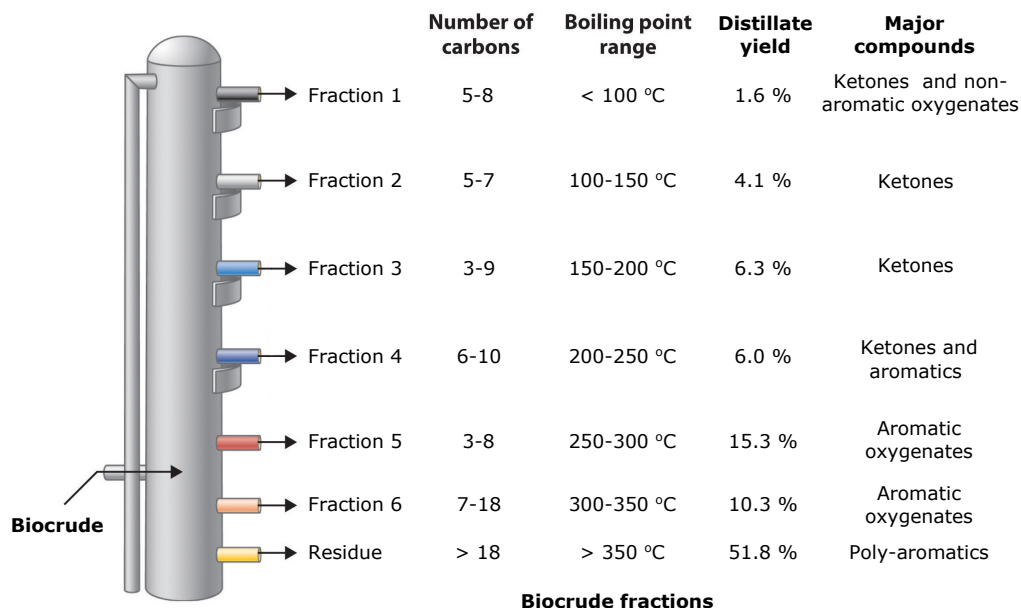plex biocrude. Some of the main findings are illustrated in Fig. 5.23.

	Number of carbons	Boiling point range	Distillate yield	Major compounds
Fraction 1	5-8	< 100 ºC	1.6 %	Ketones and non-aromatic oxygenates
Fraction 2	5-7	100-150 ºC	4.1 %	Ketones
Fraction 3	3-9	150-200 ºC	6.3 %	Ketones
Fraction 4	6-10	200-250 ºC	6.0 %	Ketones and aromatics
Fraction 5	3-8	250-300 ºC	15.3 %	Aromatic oxygenates
Fraction 6	7-18	300-350 ºC	10.3 %	Aromatic oxygenates
Residue	> 18	> 350 ºC	51.8 %	Poly-aromatics

Biocrude fractions

Fig. 5.23: Fractional distillation of a glycerol-aspen wood derived biocrude. Data obtained from [35]. Illustration adapted from [36].

It has been found that:

- A small fraction of light oxygenates is obtained. These compounds are similar to those found in the aqueous phase.

- A significant share of different ketones was obtained in the middle distillate range.

- Oxygenated aromatics were predominant at higher distillation temperatures.

- Relatively "clean" distillation cuts of ketones and oxygenated aromatics are achievable.

- The H/C_{eff} ratio varies between 0.69-1.95, lowest for the residue, highest for Fraction 1.

- All distillate fraction are oxygenated. Oxygen contents varies from 10.7-18.7 %.

- A residue (bp. > 350 °C) is obtained, which has yet not been analyzed.

Based on the findings it is concluded that fractional distillation is a viable means of tuning a complex biocrude into bulk fractions of similar chemical functionalities. However, none of

the fractions have "drop-in" properties and therefore may need further processing depending on the intended application. Furthermore, the realization that around 50 % of the biocrude consists of a non-volatile fraction opens for further investigation in order to fully determine the market potential of the biocrude.

9   Applications of the biocrude compounds

Processing biomass in near-critical water can produce liquid products with a significantly lower oxygen content that the original biomass. Due to the molecular composition of e.g. cellulose and hemicellulose, comprising more than 50 % oxygen on a mass basis, oxygen rejection from these compounds especially are of high priority. The two main reactions involved in oxygen rejection are 1) dehydration, yielding mainly oxygenated aromatics as biocrude compounds and 2) decarboxylation, mainly from partial reforming of light compounds (gasification) and/or derived from condensation of e.g. carboxylic acids forming ketones.

It has been found that product compounds obtained from glucose, xylose, and other (non-aromatic) model compounds mainly consist of short chained aldehydes, ketones, carboxylic acids, and other unsaturated oxygenates; most of which have carbon chain lengths of $>C_6$. Lignin forms oxygenated aromatics dictated by its original chemically structure, and fatty acids are almost inactive chemically and pass through the process unaltered.

Despite the fact that potential compounds are obtainable, obtaining highly desirable hydrocarbons has not yet been successful. Hence, the preceded review and results obtained can be summed by the following statement:

*A near-critical water environment without any admixtures does not support a one-pot process transforming raw biomass, or model compounds, into chemical compounds having "drop-in" properties - but it is a viable medium for producing a variety of fuel **precursors***.

9.1   Biocrude solubility

Although the oxygen content for some biomass compounds can be substantially lowered, the residual oxygen still has to be removed in order to obtain "drop-in" products. Despite the fact that the biocrude fraction is immiscible in water, the biocrude does not blend in hydrocarbon-based fuels such as gasoline and diesel.

In general, for two liquids to be mutually soluble their individual cohesive energy density, given in Eq. 5.30, must be alike [37].

$$\delta = \sqrt{c} = \left[\frac{\Delta H - RT}{V_m} \right]^{1/2} \tag{5.30}$$

where:

c = cohesive energy density
H = heat of vaporization
R = gas constant
T = Temperature
V_M = Molar volume

It was proposed by Charles Hansen to relate the cohesive energy density to three individual force contributions; dispersion (D), polarity (P), and hydrogen bonding (H), according to Eq. 5.31 [38], known as the Hansen Solubility Parameters (HSP).

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{5.31}$$

Calculating fractional HSP, according to Eq. 5.32, one can estimate the solubility of solvents by plotting their fractional HSP in a ternary chart known as the Teas chart, see Fig. 5.24. Simply stated, the closer the solvents are in the Teas chart the more mutually soluble they are.

$$f_D = \frac{\delta_D}{\delta_D + \delta_P + \delta_H} \qquad f_P = \frac{\delta_P}{\delta_D + \delta_P + \delta_H} \qquad f_H = \frac{\delta_H}{\delta_D + \delta_P + \delta_H} \tag{5.32}$$

Fig. 5.24 plots of the compounds identified by fractional distillation of the biocrude obtained from aspen wood/glycerol co-liquefaction [27, 35]. HSP have been estimated using the Yamamoto-Molecular Break (Y-MB) method using the commercial software HSPiP[3]. It is observed that the compounds scatter over a wide range but mainly cluster in two regions comprising mainly oxygenated aromatics and ketones. The preferable region is indicated in the right lower corner, dominated by dispersion forces, characteristic for hydrocarbons. Oxygenated aromatics are characterized by a relatively high contribution from hydrogen bonding caused by predominating phenolic functional groups, whereas ketones are dominated by polarity and dispersion forces. Based on the HSP estimations, it is unlikely that the biocrude, or any substantial part of it, is soluble in hydrocarbons, which has been confirmed by actual blending tests. Therefore, in order to enhance the solubility of the biocrude in hydrocarbons a enhancing co-solvent is therefore needed. For blending in gasoline such co-solvent could be ethanol and for blending in diesel, mixing in fatty acids may enhance the solubility.

The solubility of the bulk biocrude obtained from aspen-wood/glycerol co-liquefaction in common solvents was tested by solubility tests (see Table 5.11) and the HSP were estimated [38]. Briefly, biocrude and solvent were mixed in a 1:10 volume ratio, then swirled by a vortex mixer for several minutes, and finally let to mix/settle for one week. In short, if the biocrude was found soluble in a given solvent, that solvent obtained a score of *1*. If the biocrude was found insoluble in a given solvent, that solvent obtained a score of *0*. For some solvents the biocrude

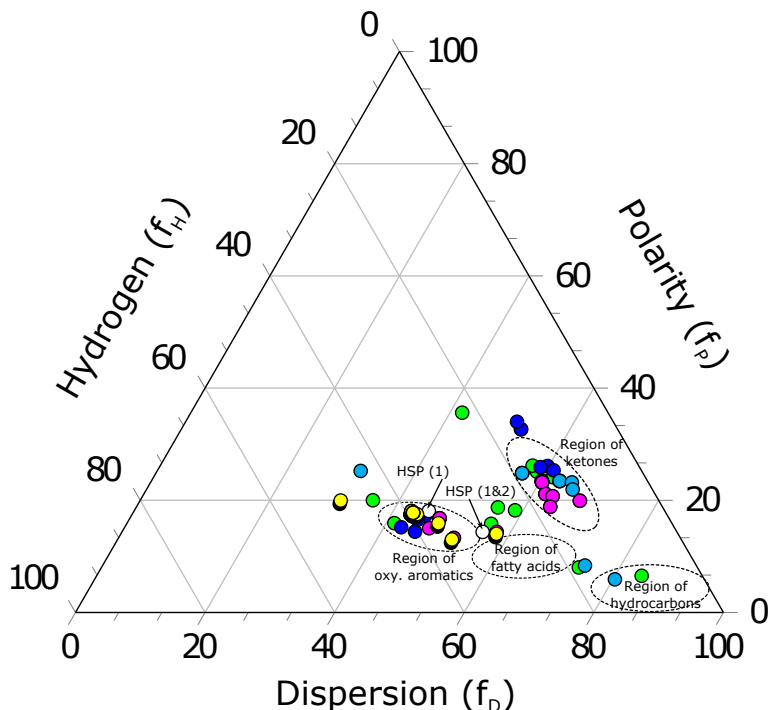---

[3]http://hansen-solubility.com/

Fig. 5.24: Teas chart of the compounds identified from in the biocrude obtained from aspen wood/glycerol co-liquefaction. Compounds identified in distillate fraction: • Fraction 1, • Fraction 2, • Fraction 3, • Fraction 4, • Fraction 5, • Fraction 6.

was found slightly soluble and in that case the solvent obtained a score of *2*. Table 5.11 shows the scores for the tested solvents and the resulting HSP for the two scenarios depending on if solvents scoring (2) are excluded (HSP (1)) or included HSP (1&2)). The fractional HSP are also plotted in Fig. 5.24. It is observed that the calculated HSP based on the solubility tests position close to or within the region of oxygenated aromatics. It must be kept in mind that the solubility tests where based on the bulk biocrude, whereas the compounds plotted only included those identified in the volatile fractions (bp. <350 °C). This fact likely influences the calculated HSP since the biocrude residue is expected to consist of high molecular oxygenated aromatics [35].

9.2 Hydrotreatment

As previously mentioned, the biocrude compounds do not hold "drop-in" properties mainly due to oxygen-functional groups causing undesirable properties. On the other hand, the biocrude may be used directly in "low quality" applications such as a boiler fuel or a heavy fuel for

Table 5.11: Solvent and HSP calculated from solubility tests.

Solvent	Score		(1)	(1 and 2)
Water	0	δ_D	14.98	17.98
DEE	1	δ_P	5.82	4.45
Hexane	0	δ_H	12.06	9.94
MEK	1	δ	12.06	9.94
DCM	1	20.09	21.09	
1-Octanol	1			
Toluene	2			
Acetone	1			
Carbon disulfide	2			
Ethanol	1			
Ethylene glycol	0			
Glycerol	0			
Water	0			

e.g. maritime transport. For other transport applications it is expected that downstream upgrading of the biocrude will be requisite to obey regulations on fuel specifications and standards. Essentially, upgrading of biocrudes is performed like conventional refining of fossil crudes, although the main objective for biocrudes is removal of oxygen-functionalities. In during so, catalytic hydroprocessing of biocrudes has been widely investigated to remove oxygen and thus obtaining the hydrocarbon backbones. Whereas conventional refining of fossil crudes has been commercial on mega-scale for decades, refining of biocrudes is still in a research phase despite that studies in biocrude upgrading have been reported for over 30 years [39]. Challenges in upgrading biocrudes include e.g. [39]:

- Inhomogeneity and chemical complexity of the biocrudes, which makes the understanding of catalysis reactions, mechanisms, and interactions difficult.

- Deterioration of catalysts. Significant amounts of water may be introduced with the biocrude and produced from hydro-deoxygenation, which challenges the design of catalysts.

- Biocrude acidity causing leaching of catalyst and inorganics deposition leading to catalyst deactivation.

- Instability of biocrude compounds results in condensation, polymerization, and ultimately system plugging.

To test the amenability of the aspen wood/glycerol-derived biocrude, a preliminary upgrading study was carried out. Due to incomplete analysis of the biocrude heavy fraction, hydrotreatment was performed on a mixture of distillation fractions in order to enable the tracing

of biocrude compounds converted in the hydrotreatment product (HTP). The concept is illustrated in Fig. 5.25 and further explained in [35].
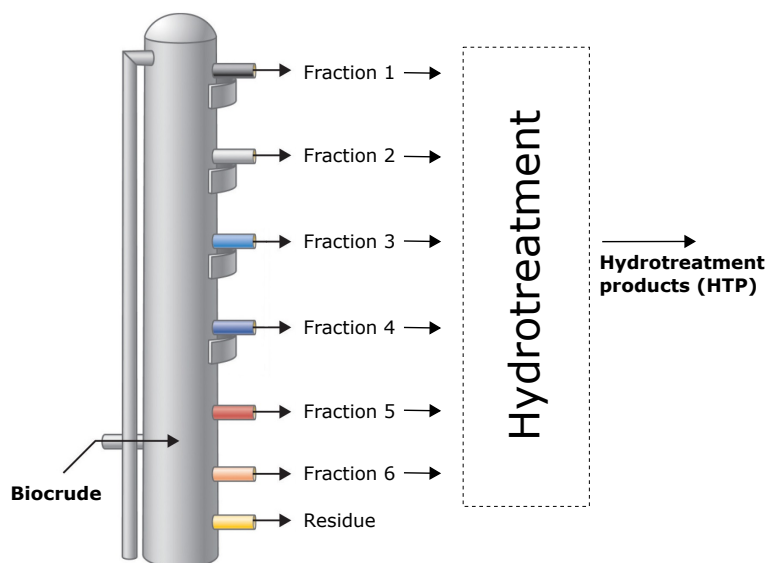

Fig. 5.25: Hydrotreatment of a mixture of distillation fractions. The mixture was obtained from fractional distillation of a aspen wood/glycerol-derived biocrude. Data obtained from [35]. Illustration adapted from [36].

The preliminary hydrotreatment experimental study revealed that:

- The oxygen level could be substantially reduced from 14.5 to 4.6 % (a 68 % reduction).

- The calorific value the HTP was substantially improved (to 42.9 MJ/kg) and the acid number was substantially decreased (to 7 mg KOH/g).

- Ketones are more amenable to hydrotreatment than phenols and were fully converted into their analogue hydrocarbons under the given processing conditions. Phenolic compounds still remained in the HTP.

In addition to the preliminary experimental study, HSP estimations of the compounds identified in the HTP have also been performed. The results are shown in Fig. 5.26. Here, it is clear that the compounds cluster in two distinct groups; hydrocarbons and oxygenates. The part that has been converted into hydrocarbons in the C_6-C_{11} range will perfectly blend in conventional hydrocarbon fuels and will especially be suitable for gasoline blending. The distinct partitioning of compounds into two main clusters also will likely enable the separation of two compound groups be e.g. solvent extraction. Although phenolics may be used as blending compounds in

fuels or further upgraded to benzenes or hydrocarbons [40, 41], aromatic oxygenates may play a more important role as a renewable raw material in the chemical industry [42]. Further investigations will reveal if the more economic strategy for downstream processing of such biocrude is complete hydro-deoxygenation for producing a bulk fraction of hydrocarbons, or a partial/selective de-oxygenation for obtaining both hydrocarbons or oxygenates for other purposes than fuel.
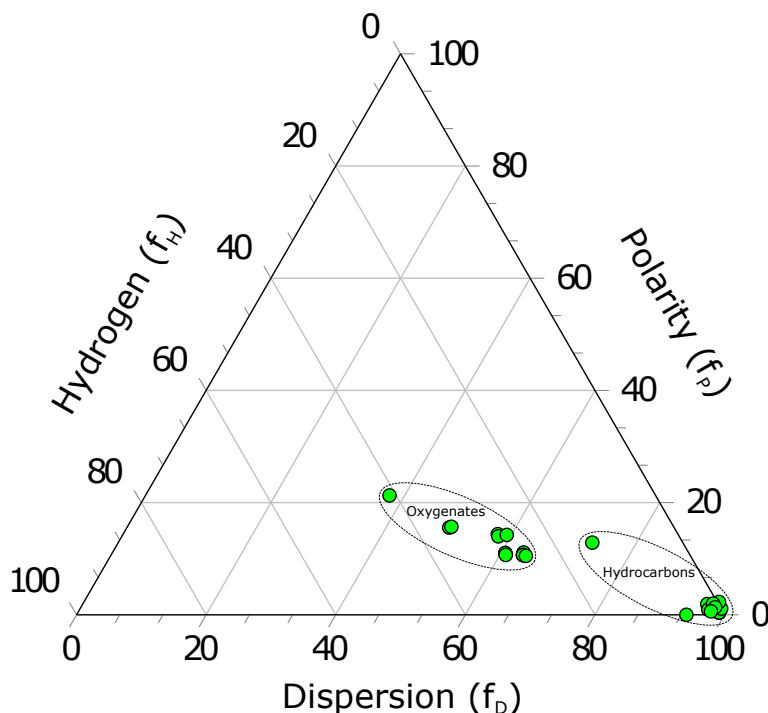

Fig. 5.26: Teas chart of the compounds identified from in the HTP biocrude obtained from aspen wood/glycerol co-liquefaction.

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Chapter 6

Partial gasification/hydrogenation of model compounds

The concept of performing HtL in a reducing atmosphere such as hydrogen (hydro-liquefaction) or carbon monoxide to enhance the process is well-studied and dates back to the PERC process as described in Chapter 4 [43–45]. So is the process scenario of hydrogen donating admixtures such as boric acid [46], formic acid [47, 48], various alcohols [43, 49–51], tetralin [50], and glycerol as studied by Pedersen et al. [27], etc. The primary role of any reducing gases and/or hydrogen donors is to stabilize and reduce the reactive fragmented products by hydrogen transfer reactions.

Processing of biomass in near-critical water can produce liquid products with a significant reduction in oxygen content as compared to the original biomass mainly due to dehydration, decarboxylation, and decarbonylation reactions (Pedersen et al. [6, 13, 27, 35]). Nevertheless, obtaining highly desirable hydrocarbons has not yet been obtained when processing biomass in the absence of a hydrogen source, e.g. a gaseous hydrogen atmosphere or a hydrogen donor combined with the addition of a hydrogenation catalyst, or by a dedicated downstream hydroprocessing step [35, 45, 47, 52]. Consequently, excess hydrogen must be supplied either 1) during the liquefaction process 2) or in a subsequent hydroprocessing step to achieve high quality products affecting the process economy.

Hydroprocessing of oxygenated liquefaction compounds in the already existing aqueous phase holds multiple advantages. The oxygenated products are usually polar and the separation from the aqueous phase is inefficient [52]. Upgrading of these components into nonpolar, hydrophobic compounds on the other hand will ease the separation greatly.

A compound commonly obtained from lignin is guaiacol, which contains an aromatic ring

and two aryl alcohol functional groups. Under standard conditions, guaiacol is highly soluble in water and is therefore usually detected in both the aqueous and the biocrude phase. Guaiacol properties such as solubility in water (decreasing) and heating value (increasing) can by greatly improved by deoxygenation and dearomatization as shown in Fig. 6.1.
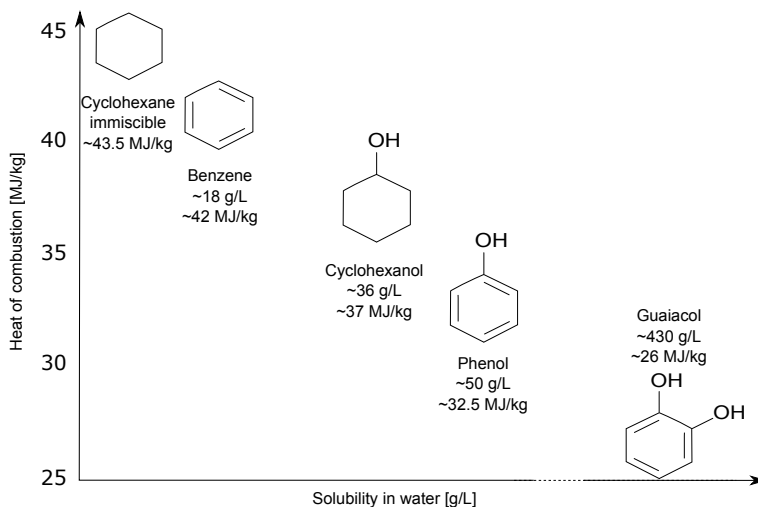

Fig. 6.1: Effects on the solubility in water and heat of combustion when reducing guaiacol to cyclohexane.

Furthermore, during biomass processing in near-critical water in-situ generation of hydrogen, primarily from light compounds, has been stated as a synergetic side reaction [6, 53, 54]. In-situ produced hydrogen may participate in scavenging and/or reducing reactions. As an example, during the investigation of gasification of mixtures of lignocellulosic model compound (cellulose, xylan, and lignin), Yoshida and Matsumura surmised that hydrogen produced from cellulose and xylan may actually function as a hydrogen donor for the present lignin fraction [55]. In another study, Fisk et al. investigated catalytic processing of a mixture of common bio-oil compounds at 350 °C in the presence of various platinum catalysts [56]. Without any externally supplied hydrogen, the oxygen mass fraction of the resulting bio-oil was reduced from 41.4 to 2.8 %. Whereas the model bio-oil consisted of light compounds (e.g. methanol, acetaldehyde, acetic acid) and oxygenated aromatics (guaiacol and vanillin), the product slate was dominated by benzenes and cycloalkanes derived from the oxygenated aromatics. In another study, Yin et al. reported the formation of gasoline compounds from cellulose in an aqueous-phase dehydration/hydrogenation (APD/H) process, where hydrogen was supplied by in-situ steam reforming [57].

Partial steam reforming (PSR) of selected compounds during HtL could be a delicate compromise between, 1) attaining in-situ hydrogen generation and 2) sacrificing the carbon content
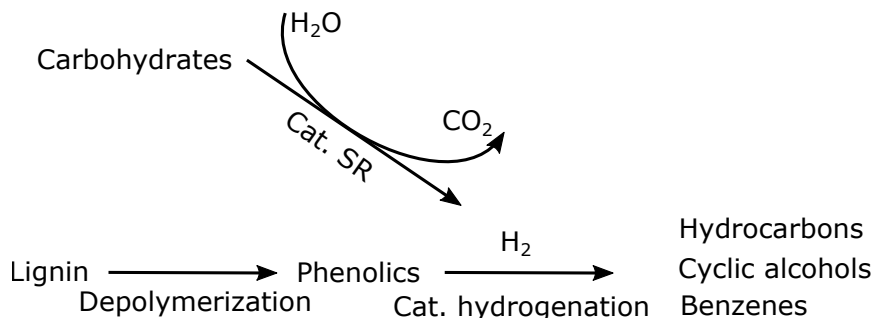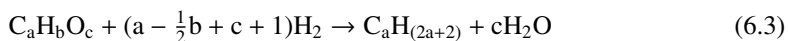
Fig. 6.2: Simplistic scheme of overall reaction mechanism.

in the liquid product as carbon liberated into the gaseous phase (mainly as CO and CO_2). According to Eq. 6.1 and 6.2, during steam reforming of carbohydrates (glucose, xylose, etc.) for instance, water donates an equivalent amount of hydrogen as the inherent hydrogen content of the carbohydrates. If such in-situ generated hydrogen can be "donated" to the remaining oxygenates by reducing reactions (Eq. 6.3), PSR could be a prospective chemical pathway to obtain high quality liquid products without externally supplied hydrogen. Conceptually, such chemical scheme could be represented simplistically as in Fig. 6.2.

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2 \tag{6.1}$$

$$C_5H_{10}O_5 + 5H_2O \rightarrow 10H_2 + 5CO_2 \tag{6.2}$$

$$C_aH_bO_c + (a - \tfrac{1}{2}b + c + 1)H_2 \rightarrow C_aH_{(2a+2)} + cH_2O \tag{6.3}$$

In the context of lignocellulose, lignin is an interesting precursor for liquid fuels due to its three main monolignols; p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The low-oxygen containing C_9-C_{11} aromatic backbones are promising fuel candidates in the gasoline range [40]. Mild hydroprocessing of the lignin fraction may yield reformulated gasoline or alkanes by complete hydro-deoxygenation and/or hydro-dearomatization. Consequently, it is desirable to obtain and preserve the monolignol structures from lignin as fuel precursors.

1   Theoretical rationale of in-situ reforming and hydroprocessing

In the following the rationale behind the PSR/hydroprocessing concept will be outlined. According to Fig. 6.2 the concept proposes selective steam reforming of the carbohydrate fraction (cellulose and hemicellulose) of lignocellulosic matter, thereby in-situ generating hydrogen for 1) stabilizing lignin fragments and 2) mild hydroprocessing of stabilized fragments.

In Section 5.2 it was explained that under supercritical water conditions, cellulose and hemicellulose rapidly undergo hydrolysis yielding monomeric hexose and pentose units, and oligomers. Steam reforming of glucose and xylose was given by Eq. 6.1 and 6.2. Here it is observed that for each mole of glucose (or any hexose) and xylose (or any pentose), potentially, 12 or 10 moles of molecular hydrogen can be produced, respectively, under the assumption that cellulose and hemicellulose are approximated as glucose and xylose.
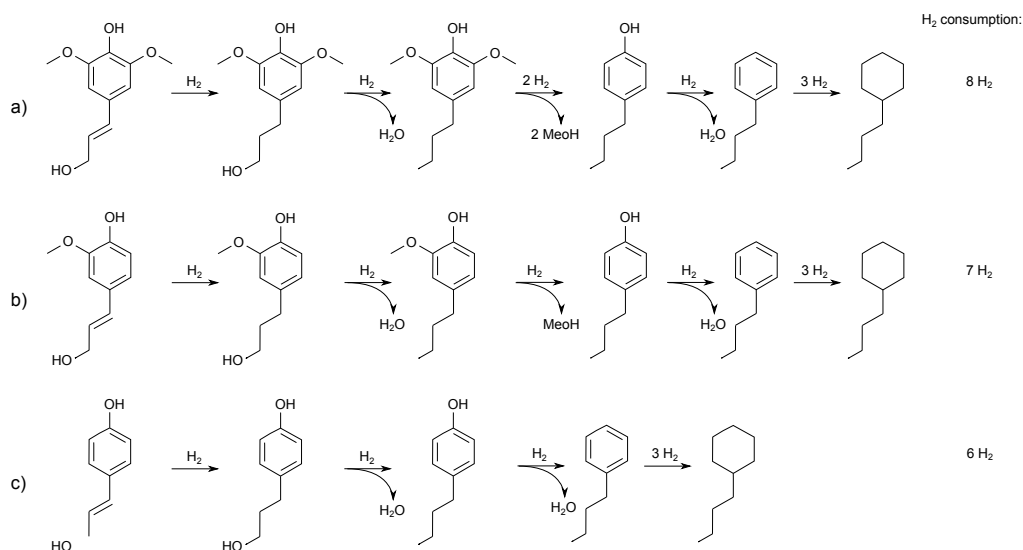

Fig. 6.3: Simplistic scheme of a) sinapyl alcohol, b) coniferyl alcohol, and c) coumaryl alcohol hydrotreatment.

Correspondingly, the molecular hydrogen consumption by the lignin fraction can be approximated by assuming that the lignin fraction consists of the three monomers given in Fig. 5.14. Complete hydro-deoxygenation and saturation of each monomer is presented in Fig. 6.3 together with the respective hydrogen consumption. For each mole of sinapyl alcohol, coniferyl alcohol, and coumaryl alcohol, 8, 7, or 6 moles of hydrogen molecules are consumed, respec-
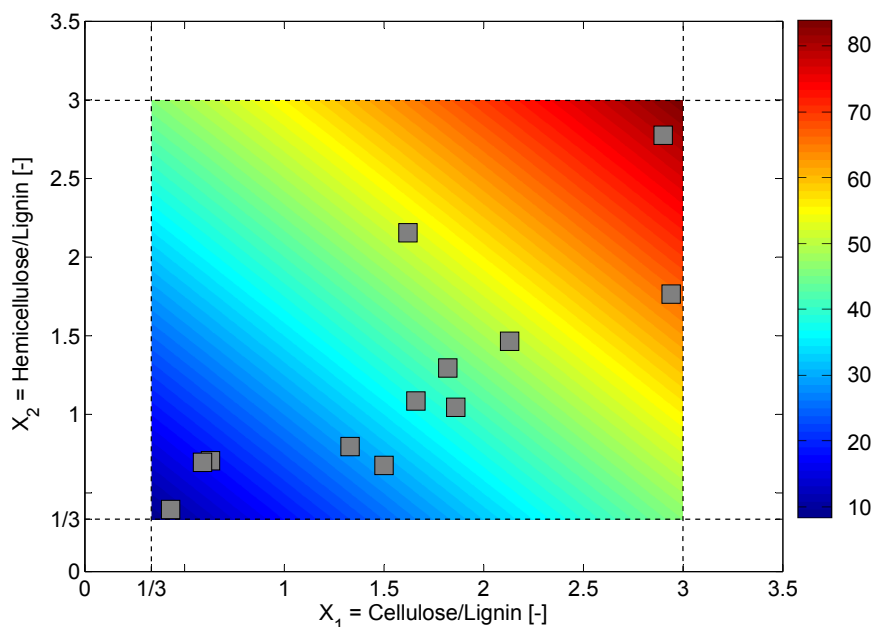
tively.

Fig. 6.4: HDP as a function of cellulose-to-lignin mass ratio (X_1) and hemicellulose-to-lignin mass ratio (X_2).

Evidently, by assuming that Eq. 6.1 and 6.2 proceed stoichiometrically and that lignin consists of monolignol units, the combination effect of in-situ reforming and hydroprocessing can be calculated based on a H-donation potential (HDP):

$$\text{HDP} = \frac{\text{Moles of molecular hydrogen produced from carbohydrates}}{\text{Moles of aromatic monomers}} \qquad (6.4)$$

The HDP is naturally a function of the biomass distribution of cellulose, hemicellulose and lignin, the inherent distribution of pentoses/hexoses, and the distribution of monolignols, since the hydrogen production and consumption varies correspondingly. In Fig. 6.4 several different lignocellulose species are plotted against their respective cellulose-to-lignin (X_1) and hemicellulose-to-lignin (X_2) mass ratios covering the general ranges of lignocellulosic matter [2]. Assuming that cellulose is represented by glucose, hemicellulose by xylose, and lignin by sinapyl alcohol units, the HDP can be calculated as a function of X_1 and X_2. The result is depicted in Fig. 6.4. It is observed that even in the low range of HDP (low X_1 and X_2), HDP values of 10 are still achievable and extends to approximately 80 in the high range. Hence, under the given assumptions, excess hydrogen for complete deoxygenation and ring saturation

of lignin can be obtainable in the entire range of X_1 and X_2 given in Fig. 6.4 and that the values are naturally increasing with increasing X_1 and X_2 values. As mentioned previously, when processing lignin, selective removal of the oxygen-containing functional groups and saturation (partially or fully) of the aromatic ring are main objectives, where the latter is the most hydrogen consuming according to Fig. 6.3. Assuming that only deoxygenation is the main objective, substantially less hydrogen is needed as compared to full saturation. Thereby, under the assumptions given, the rationale presents a chemical scheme that, at least stoichiometrically, balances hydrogen production and consumption simultaneously in order to produce hydrocarbons from lignin precursors.

2   Partial liquefaction of model compounds over heterogeneous nickel catalyst

It is commonly known that in order to obtain high chemical selectivities when processing biomass in near-critical water, the use of catalysts is a necessity. In this regard, unlike commonly used homogeneous catalysts as described in Section 4, heterogeneous catalysts are of specific interest since they are recyclable. However, heterogeneous catalytic processes in near-critical water are subject to several technical challenges regarding maintaining catalyst stability. Commercially used catalysts exposed to sub- and supercritical water usually suffer from severe degradation due to e.g. oxidation of the active metal, hydration or hydrolysis of the supporting material, phase transformation or extensive coke formation [58–61] that leads to inactivation of the catalyst. For instance, the commonly used γ-Al_2O_3 support has been shown to undergo complete formation (into a hydrated boehmite) within the time course of 10 hours in hot-compressed water at 200 °C [62]. Furthermore, tests of several SiO_2/Al_2O_3 supports have shown that only the ZSM-5 zeolite form appears stable in hot-compressed water at 200 °C [63]. In a pioneering work by Elliot et al. searched for stable catalysts in for gasification in subcritical water at 350 °C, where guidelines for metals and supports were given [58]. Of all the supports examined, only α-Al_2O_3, carbon and ZrO_2 (monoclinic) showed high stability. Recently, Zöhrer et al. conducted several stability experiments of ruthenium based catalysts in hot-compressed water and found that rutile (TiO_2) is also a stable support [64]. A second recent research also added yttria-stabilized zirconia (YSZ) to the list of stable supports [65]. Elliot et al. found that suitable useful metals included Ru, Rh, Ni, Pt, Pd and Cu. All other metal investigated were oxidized under the given conditions [58]. Table 6.1 summarizes the findings.

For the PSR/hydroprocessing concept outlined, a suitable catalyst should show multi-functionality; high selectivity towards hydrogen production from the carbohydrates, low lignin gasification efficiency, and selective towards hydrogenation of oxygenated aromatics. The rank of several metals for reforming sugars and alcohols into hydrogen has been summarized by Davda et al. and supported by similar trends by Zhang et al. [66, 67]. Based on these results, platinum, nickel, and ruthenium could be candidates due to their gasification effectiveness.

useful catalytic metals	inactive metals	metals oxidized at conditions	stable supports	unstable supports	hydrolyzable supports
Ru	Pt	Co	$\alpha - Al_2O_3$	TiO_2(Anatase)	$\gamma - Al_2O_3$
Rh	Pd	Fe	ZrO_2	SiO_2	$\beta - Al_2O_3$
Ni	Cu	Cr	TiO_2(Rutile)	Ca/aluminate	$\eta - Al_2O_3$
		Mo	Carbon	Kieselguhr	SiO_2/Al_2O_3
		W	YSZ	MgO	
		Zn		Y_2O_3	
				CeO_2	
				Hydrotalcite	

Table 6.1: Summary of metals and supports suitable for aqueous phase gasification of p-cresol at 350°C, 20 MPa [58].

$$Pt \approx Ni > Ru > Rh \approx Pd > Ir$$

Additionally, with respect to the ranking of metal supports towards glucose steam reforming, the following conclusions have been drawn based and copper and nickel supported catalysts [68, 69]. In the case where corundum (Al_2O_3) was used as nickel support a higher hydrogen yield was obtained.

$$YSZ > La_2O_3 \approx ZrO2 > \alpha\text{-}Al_2O_3 \quad \text{(Supported Co)} \quad [68]$$
$$\alpha\text{-}Al_2O_3 > YSZ, TiO_2 \quad \text{(Supported Ni)} \quad [69]$$
$$ZrO_2 > Carbon \quad \text{(Supported Ni)} \quad [67]$$

Regarding the ranking of metal activities towards lignin gasification, the following sequence was established by Osada et al. and Elliott et al. [58, 70, 71]:

$$Ru \approx Raney\ Ni > Rh > Pt > Pd \approx Ni$$

Hence, by comparing the two metal rankings with respect to glucose steam reforming and lignin gasification, Ni supported on α-Al_2O_3 catalysts seem to be interesting due to the high and low gasification efficiencies reported for carbohydrates and lignin, respectively, and the documented stability of α-Al_2O_3 in supercritical water. In addition, nickel based catalysts have been widely studies as a suitable for hydroprocessing.

3   Experimental testing of the PSR/hydroprocessing concept

In order to test the PSR/hydroprocessing concept, experimental tests have been performed. Based on previous literature study a Ni/α-Al_2O_3 (10 % loading) catalyst was prepared and its

applicatility in the PSR/hydroprocessing concept tested. Details about the experimental setup, details on the continuous flow reactor, and catalyst preparation can be found in Appendix B.

Preliminary steam reforming experiments were performed to screen process parameter effects on the extent of gasification and the selectivity of H_2 when processing glucose, as cellulose model compound, at supercritical conditions. The extent of gasification was based on a **c**arbon **g**asification **e**fficiency (CGE) according to Eq. 6.5

$$CGE = \frac{\text{moles of carbon in the gas product}}{\text{moles of carbon in the feed}} \quad (6.5)$$

Fig. 6.5 shows the effect of temperature on the CGE when processing glucose at supercritical water conditions. It is observed that the CGE increases almost linearly with increasing temperature. Even at 380 °C the CGE reaches nearly 70 % and close to 100 % at 420 °C. The results clearly illustrates the ability of the prepared nickel catalyst to gasify glucose even at conditions in the range of supercritical HtL.
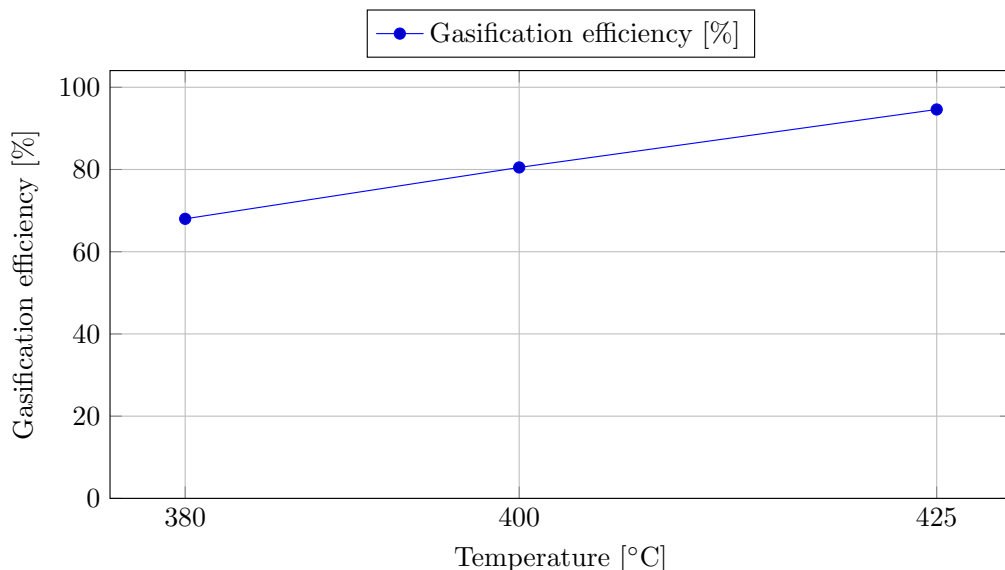

Fig. 6.5: CGE as a function of reactor temperature. WHSV = 3 [h^{-1}]

The gas compositions of the corresponding experiments are shown in Fig. 6.6. From the results it is evident that not only can high CGEs be achieved, so can high hydrogen selectivities. It is observed that the hydrogen yield slightly increases with increasing temperature mainly due to a lower formation of methane. Thereby it can be concluded that the nickel catalyst is suitable

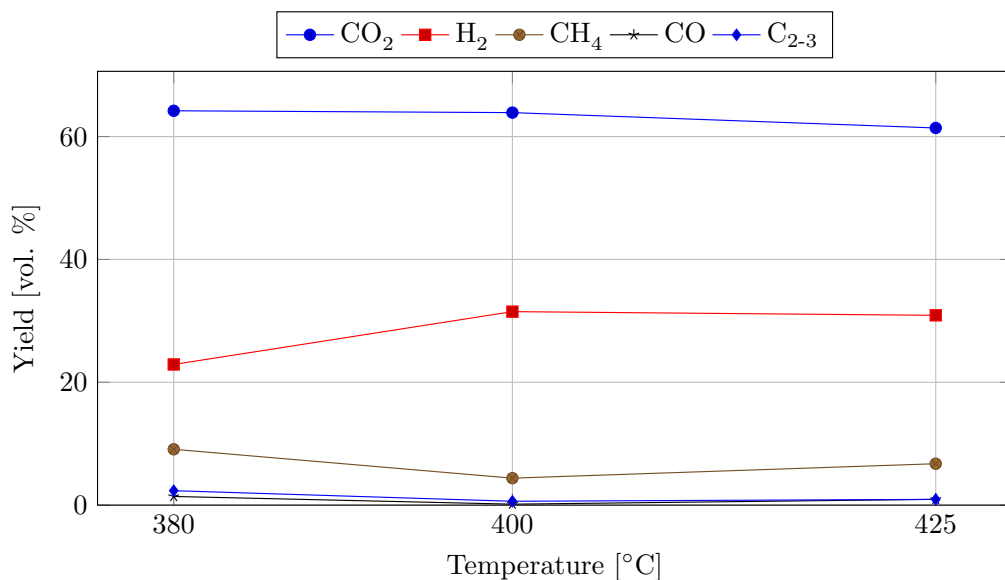for glucose gasification for in-situ hydrogen production.

Fig. 6.6: Gas composition obtained from glucose gasification. WHSV = 3 [h^{-1}]

In order to further test the applicability of the nickel catalyst in the PSR/hydroprocessing concept, a mixture of glucose and p-cresol (3:1 mass ratio) was processed under similar conditions as the glucose experiments. The resulting gas compositions from the mixture experiments can be observed in Fig. 6.7. At 380 °C the gas composition is almost similar to that obtained when processing only glucose under identical conditions. This is an indication that the CGE of lignin at this point is only minimal and therefore a positive outcome. On the other hand, the observation is also an indication that no interaction effects occur, e.g. hydrogenation reactions. As the reaction temperature increases no clear trends are observed. At 400 °C, the volume fraction of hydrogen and methane are reduced and increased, respectively, as compared to the case of 380 °C. The decreased fraction of hydrogen could indicate a parallel hydrogen consumption pathway or simply a dilution effect due to lignin gasification. The increased fraction of methane (approximately 25 %) indicates that gasification of p-cresol is initiated at this point. This indication can be supported when increasing the temperature. An increase in temperature to 425 °C lead to an increasing fraction of hydrogen probably due to a more complete CGE as it was observed from Fig. 6.6. At 425 °C, the methane concentration is also at a level higher than that obtained when processing only glucose under identical conditions indicating gasificatin of p-cresol. A non-catalytic reference point at 400 °C was investigated too. At non-catalytic conditions formation of carbon monoxide is substantial compared to the catalytic runs and therefore
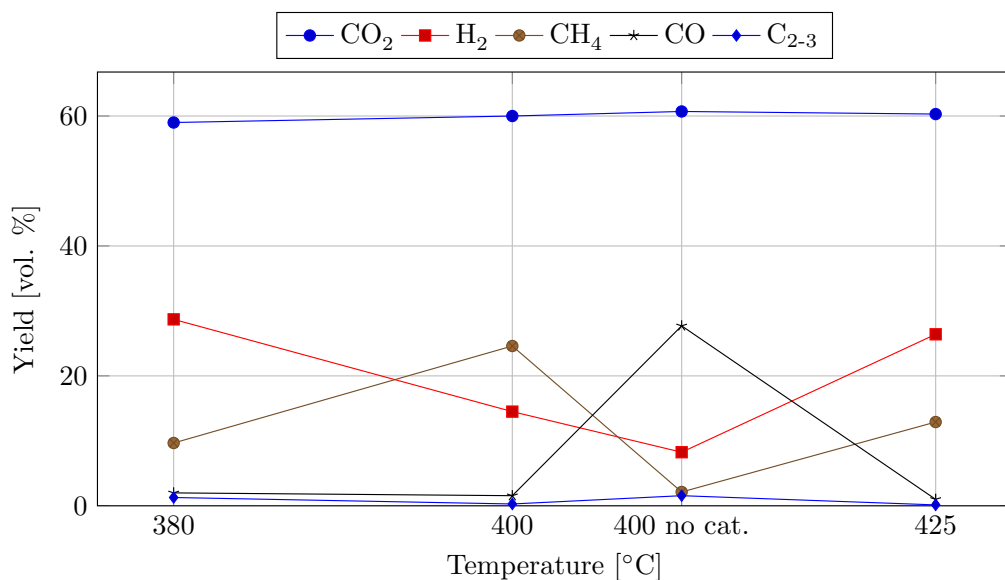
not suitble for in-situ hydrogen formation.

Fig. 6.7: Gas composition obtained from glucose/p-cresol mixture (3:1). WHSV = 3 [h^{-1}].

GC-MS analysis of the liquid products was performed to identify if any reduced compounds were obtained due to hydrogenation reactions. Fig. 6.8 shows the individual chromatograms. At 380 °C and 400 °C the chromatograms clearly show that the main compound is still p-cresol and that some condensation/polymerization has been initiated at this stage. Unfortunately, the chromatograms also reveal that no reduced compounds were detected and hence hydrogenation reactions have not been activated successfully. At 425 °C the observations are similar, despite from the fact that no p-cresol was detected most probably due to severe condensation/polymerization. Several facts may have affected the unsuccessful hydrogenation of p-cresol:

- The nickel-catalyst was simply not suitable for hydrogenation. The specific surface area of the α-Al$_2$O$_3$ support was measured to 8.4 m^2/g by BET analysis, which is significantly lower compared to the commercially used γ-Al$_2$O$_3$ (200-220 m^2/g).

- In the given experiments the mass loading of glucose (or glucose/p-cresol mixture) was 5 %. Although the CGE and hydrogen selectivity of glucose was satisfactory in the temperature range investigated, the partial pressure of hydrogenation may simply be too low for hydrogenation purposes.

- The residence time was too short. The reaction time of HtL is commonly in the range of

minutes, whereas hydrogenation is often performed in the range of hours. This fact may lead to a mismatch in reaction rates.

In conclusion, the study showed that glucose can be gasified with high efficiencies, with almost complete gasification at 425 °C, and that high hydrogen selectivities can be obtained under common HtL conditions by applying a nickel/α-Al$_2$O$_3$ catalyst. Unfortunately, the study also revealed that hydrogenation reactions are not pronounced under the given conditions even with the presence of a nickel-based heterogeneous catalyst.

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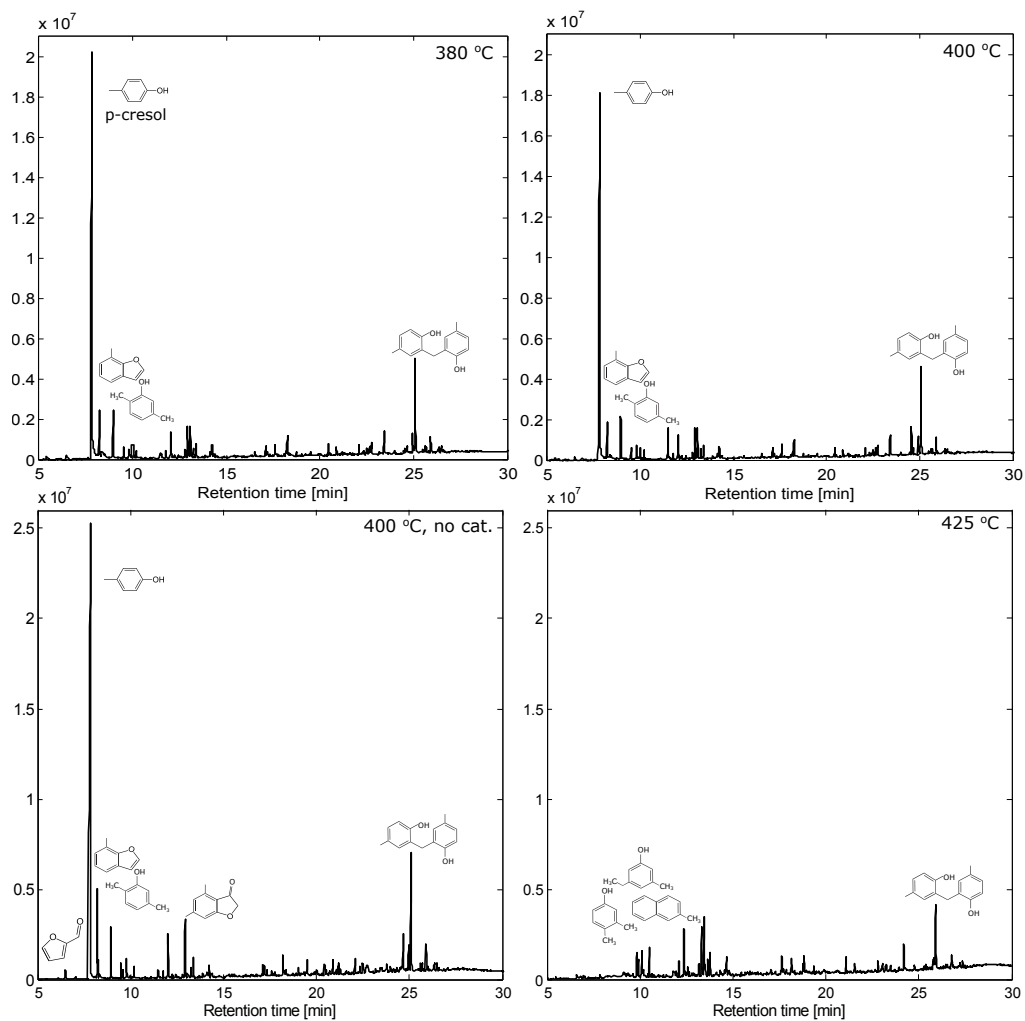
Fig. 6.8: Compounds identified by GC-MS from a glucose - p-cresol mixture.

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Part IV

Conclusion

Conclusion

This dissertation has focused on expanding the understanding of hydrothermal liquefaction with particular focus on the chemical conversion of biomass and biomass model compounds. With lignocellulosic biomass as the cornerstone, this thesis has investigated supercritical conversion of aspen wood including its fundamental chemical building blocks represented as model compounds in the form of carbohydrates (glucose and xylose) and lignin. In addition, several other model compounds and mixtures of these have been prepared and investigated under similar conditions to expand the knowledge base on how biomass and model compounds chemically convert and interact when mixed.

Initially, aspen wood and a range of model compounds were converted at alkaline conditions (400 °C) in order to identify common biocrude compounds and to establish a link between basic biomass compounds and obtained biocrude compounds. Based on the underlying assumption that the chemical conversion of cellulose and hemicellulose can be approximated by the conversion of glucose and xylose, respectively, based on yields and biocrude characteristics, it was concluded that glucose and xylose underwent identical reaction mechanisms. Based on the volatile fractions of the biocrudes that were analyzed it was found that the majority of compounds from aspen wood was distributed between ketones and oxygenated aromatics having number of carbon atoms mainly in the range of C_6-C_9. Based on model mixtures of glucose, xylose, and lignin, linear relationships were established relating the distribution of ketones and oxygenated aromatics to the fraction of carbohydrates (glucose and xylose) and lignin; i.e. the fractions of ketones and oxygenated aromatics were increasing and decreasing, respectively, with an increasing fraction of carbohydrates.

Whereas lignin in general chemically converts by breaking down the macromolecular structure whilst preserving the aromatic backbone, carbohydrates and other non-aromatic model compounds are hypothesized to undergo a more complex synthesis in a hydrothermal medium. Based on the conversion of different model compounds having number of carbon atoms in the range of C_3-C_6 it was found that the chemical composition of the individual biocrudes was highly similar indicating that a pool of intermediate common denominator compounds exists in the reaction mechanism that further leads to the formation of similar compounds. Due to the

fact that similar biocrude compounds are obtained from precursors of different number of carbon atoms, it is hypothesized that for model compounds of C_4-C_6 the formation of the pool of intermediates is governed by cleavage of carbon-carbon bonds. The identification of biocrude compounds in the range of C_6-C_9 then indicates that subsequent carbon-carbon bond forming reactions are governing for the formation of the biocrude.

To further investigate the interaction effects between biomass constituents, glycerol was studied as a co-substrate in aspen wood liquefaction. Interestingly, it was found that substantial interaction effects occur in that the char and biocrude yields decrease and increase, respectively, beyond simple mixing effect and therefore synergetic benefits can be achieved by adding glycerol to wood liquefaction. When processing only aspen wood under alkaline conditions (400 °C, 15 min.) char yield is approximately 18 %. Mixing glycerol and aspen wood in a 1:3 mass ratio, char yield can almost be reduced by half and at the same time increase the biocrude yield. It has been hypothesized that the interaction effect is due to a chemical synergy, where glycerol acts as a hydrogen donor partly acting mainly as a stabilizing agent for scavenging radical forming reactions.

Due to the synergetic effects observed in glycerol/aspen wood co-liquefaction, it was found reasonable to investigate crude glycerol, the unrefined by-product of biodiesel production, as a potential substrate in HtL. As in the case of neat glycerol, similar interaction effects were observed when co-processing crude glycerol and aspen wood under identical conditions. Of value-adding benefits no catalyst needed to be added due to the basicity of crude glycerol and that left-over fatty acids and fatty acid methyl esters contained in the crude glycerol were readily obtained in the resulting biocrude.

As a result of the positive outcome from the glycerol/aspen wood co-liquefaction micro-batch experiments, continuous bench-scale tests were carried out to demonstrate the concept and to further investigate critical processing parameters. During the experimental campaign an aqueous phase recirculation procedure was implemented to test the technical feasibility of such and to assess recirculation effects on the biocrude yield and quality. Overall it was concluded that steady continuous operation can be achieved without any system failure within the campaign testing period. Based on only gravimetric separation between the biocrude and the aqueous phase, biocrude mass yields in the range of 20-32 %. In consequence of poor reproducebility in biocrude mass yield no clear trend between biocrude yield and cycle of aqueous phase recirculation could be established. In terms of biocrude quality a slightly increasing trend was as a function of reciculation cyle. Generally, the biocrude was of high quality showing a higher heating value of 34.2 MJ/kg and a low amount of bound water (3.8 %). On the other hand it was realized that inorganics accumulated mainly in the aqueous phase, and as a result of re-added catalyst in the recycled water for cycle the concentration of inorganics increased almost linearly in the aqueous phase. As a consequence, the fraction of inorganics in the biocrude amounted to nearly 0.5 %, a destructive biocrude property for subsequent processes whether it

be direct use in e.g. combustion engines or in catalytic refinery applications etc.

In the search for a deeper understanding of the biocrude composition and to identify plausible reaction mechanism explained the formation of certain chemical compounds, the biocrude from glycerol/aspen co-liquefaction was fractionally distilled. Six fractional cuts in the temperature range from ambient to 350 °C were obtained, which represented nearly 50 % of the total biocrude. Analysis of the invidual fractions revealed that compounds of similar chemical charateristica can in fact be separated succesfully by distillation, but common for all fractions was that they still contained substantial amounts of oxygen (10.7-18.9 %). The lighter fraction (< 100 °C) was governed by light oxygenates similar to those identified in the aqueous phase. The following cuts (< 250 °C) were governed by ketones representing a C_5-C_8 range of number of carbon atoms. Higher boiling fractions were dominated by oxygenated aromatics in the C_7-C_{18} range. Due to the abundance of ketones observed in the biocrude ranging from C_5-C_8 it is concluded that a dominating reaction pathway for ketonization of intermediate exists. In this respect, ketonic decarboxylation of carboxylic acids is proposed, such as acetic, propionic, and lactic acid etc. This may also explain the formation of substainally deoxygenated compounds having a higher number of carbon atoms compared to the original feed compounds (like in the model compound study). As a screening test, a mixture of distillation fractions was upgraded to test the amenability of the biocrude to hydrotreatment. The oxygen content of the biocrude mix was considerably reduced (from 14.5 to 4.6 %) leading to a higher heating value of 42.9 MJ/kg. Based on analysis of the resulting compounds it was discovered that ketones fully converted into their respective hydrocarbons and that residual oxygen was a result of unconverted phenolic compounds.

A conceptual idea was tested based on a selective partial gasification (of glucose) and hydrogenation (of p-cresol) by incorporating a nickel-based heterogeneous catalyst in the HtL environment. Screening results showed that glucose can be successfully gasified with high hydrogen selectivities under common HtL conditions and nearly full conversion is achieved at 425 °C. Unfortunately, it was realized that selective hydrogenation of p-cresol did not occur under the given conditions.

In conclusion, the work presented in this thesis is considered to expand the knowledge about HtL in many aspects but especially a contribution to a better understanding of how biomass chemically converts. Model compound studies have found that, although the biocrude in general is chemically complex in that hundreds of difference compounds can be formed, only few groups of chemical compounds occur, which can even be linked to specific macrostructures in the biomass. Based on these observations overall reaction mechanisms are proposed, expanding the knowledge of the HtL chemistry. This fact also enables predictability of the biocrude properties based on the input biomass and may even allow for tailoring biocrude properties based on a biomass "recipe". In addition, it is concluded that synergies can be obtained by mixing different types biomass, which needs to be explore in greater details. In parallel to the results presented

in the thesis, research in HtL in all of it aspects has been ongoing including exploration of alternative resources, pretreatment of the feedstock (e.g. pulping), catalytic effects, upgrading of the biocrudes, and modeling of the HtL process. Holistically, this has not only contributed to the fundamental knowledge of HtL chemistry, but expanded the overall knowledge base of HtL.

Part V

Appendices

Appendix A

Micro-batch experimental setup

Micro-scale experiments were carried out in 10 mL stainless steel batch reactors. In a typical experiment a total 5 g of pre-mixed slurry (water, biomass, and catalyst) was loaded into the reactor. The reactor was purged with nitrogen before heating, and then heated to 400 °C in a pre-heated fluidized sand bath (Techne SBL-2D) for 15 min (including the heating period) and finally quenched in water. A schematic layout of the experimental setup is viewed in Fig. A.1.
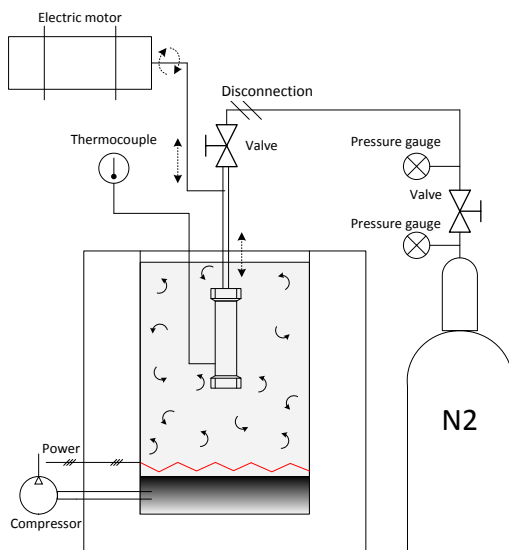
Fig. A.1: Schematic setup of the micro-batch experiments.

It is generally known that heating and cooling effects are important in thermal processes

including HtL. The micro-reactors and the sand bath setup are designed to minimized these effects. Fig. A.2 displays a typical temperature profile for a micro-batch experiment. As observed, heating and cooling rates for the micro-reactors are 250-450 K/min and >1000 K/min., respectively, conclusively eliminating any heating and cooling rate effects compared to the time spent at final reaction conditions. Due to the batch setup, the autogenous reaction pressure typically reaches 260 to 300 bar at 400 °C.
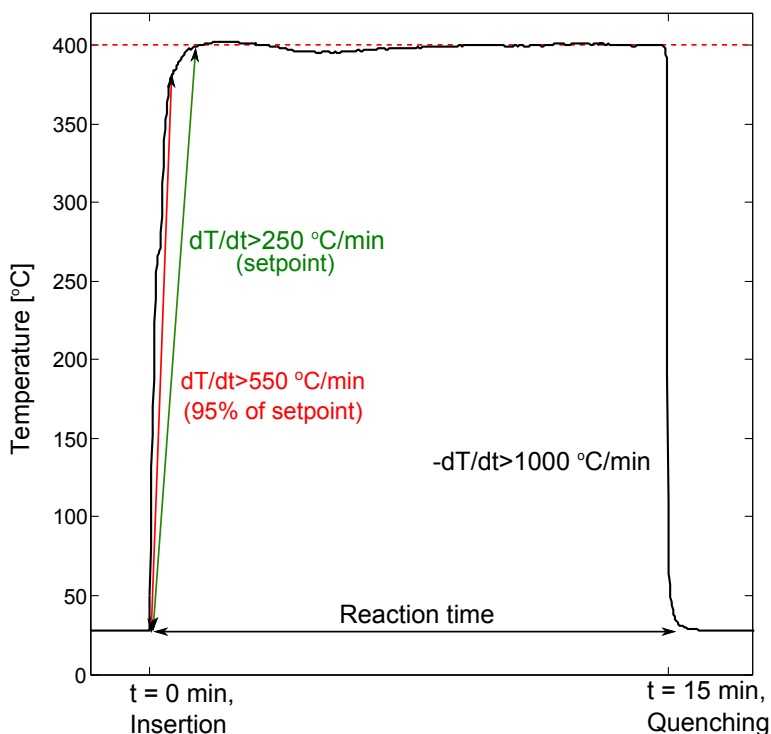

Fig. A.2: Temperature profile of a typical micro-batch experiment.

Appendix B

Experimental micro-continuous reactor system

A schematic diagram of the micro-continuous reactor system located at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) is presented in Fig. B.1. The feedstock, glucose or glucose/p-cresol mixture, was mixed and contained in container. An Eldex (Optos Model 1) HPLC pump was used to feed the feedstock to the reactor. Prior the reactor tube holding the catalyst, a preheater was prepared based on a helix type capillary tube to increase the heating rate of the feedstock. It has been calculated that the feedstock was heated from ambient to the given reactor temperature in approximately 1 minute, resembling the heating rates of the micro-batch reactors. Prepared catalyst was loading into a reactor tube (Inconel 625, 9.55 mm OD, 6.34 mm ID, lenght 20 mm). A filter was mounted into the reactor tube to hold the catalytic bed. The reactor effluent was cooled to ambient by a cooling jacket. Back pressure and pressure relief was controlled by a SWAGELOK valve. A liquid-gas separator allowed for the collection of gas samples and to obtain the liquid effluent for TOC analysis.

1 Catalyst preparation

This section describes the preparation of the nickel-based catalyst supported on α-Al_2O_3. γ-Al_2O_3 (Sasol Alumina Spheres 1.8/210, Germany) was used as a precursor for obtaining the α-Al_2O_3 support. The γ-Al_2O_3 was calcinated in nitrogen at 1200$\pm$1 °C in order to transform the γ-Al_2O_3 into α-Al_2O_3. The transformation was confirmed by X-ray diffraction (XRD) and observed in Fig. B.2.

The catalyst was prepared by incipient wetness impregnation using an aqueous nickel salt solution of $Ni(NO_3)_2 \cdot 6H_2O$. The metal loading for the Ni catalyst was fixed at 10 wt. %. The
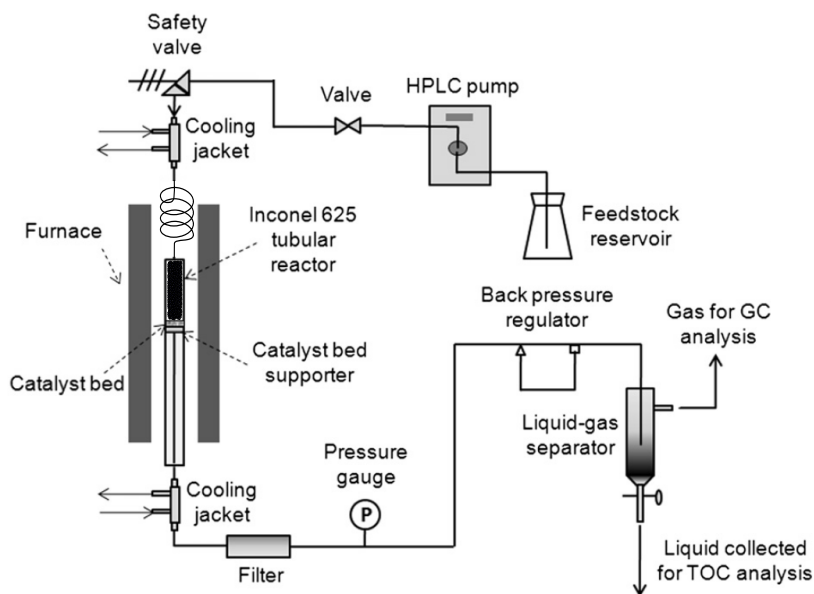
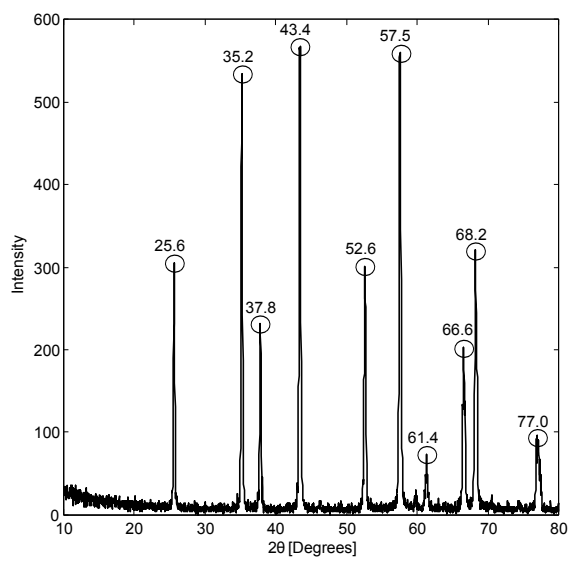**Fig. B.1:** Schematic diagram of the micro-continuous reactor system.
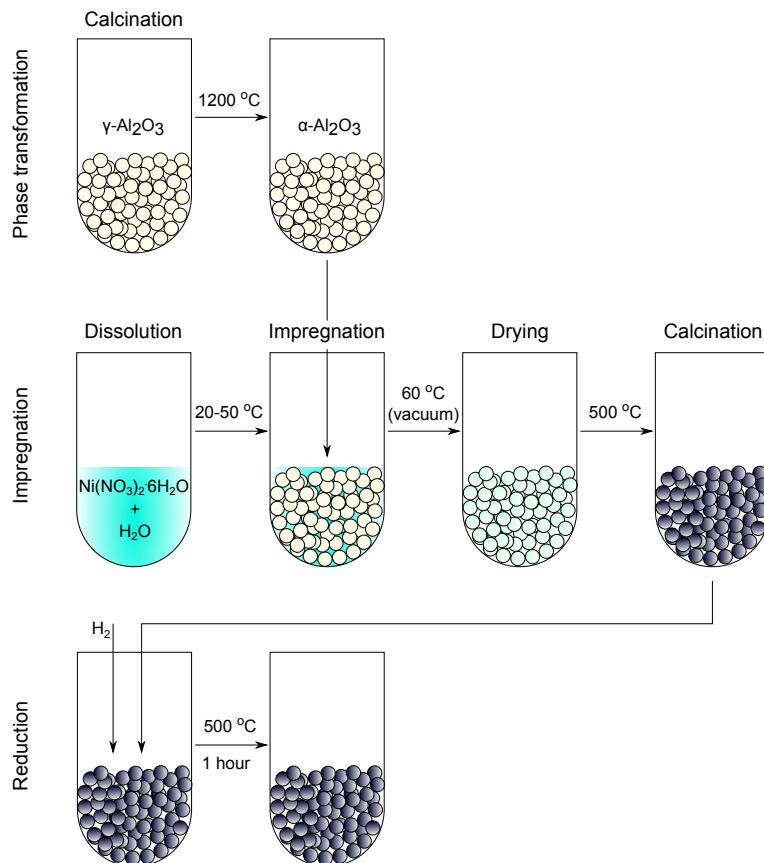

Fig. B.2: XRD measurement of the α-Al$_2$O$_3$ support

Fig. B.3: Preparation procedure for the nickel-based catalyst on α-alumina.

supported catalysts were calcinated in air at 500 °C for 3 h. In situ catalyst reduction was per-
formed at 500 °C for 1 h in a contionuous hydrogen stream. The procedure is summarized in
Fig. B.3.

Catalyst characterization; surface area, total pore volume and average pore diameter of the
catalyst were examined by isothermal adsorption of nitrogen using a Quantachrome Nova 2200e
Surface Area & Pore Size Analyzer (at -196 °C). The specific surface area was found to 8.38
m^2/g.