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Master's Thesis

HYDROTHERMAL LIQUEFACTION OF ORGANOSOLV LIGNIN TO BIO-OIL

Written for

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Leoben, 1.8.2014

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Inge Haberle

Abstract

Hydrothermal liquefaction (HTL), a thermochemical conversion process for the production of bio-oil from lignin, is described in this thesis. Bio-oil is considered to be a viable source of aromatic compounds as well as a general energy carrier. Nonetheless degradation of lignin during HTL is currently not fully understood due to the complexity and heterogeneity of lignin.

This study aims to investigate HTL of lignin under subcritical water conditions (270 °C, 290 °C and 310 °C) and three time levels 10 min, 20 min and 30 min to identify the quantitative formation and qualitative composition of bio-oil. The isolated bio-oil fraction contained a mixture of low molar mass lignin degradation products. A general characterization of this fraction was accomplished by applying a set of analytical methods including Gel Permeation Chromatography, Photoacoustic Infrared spectra, the Folin Ciocalteu method, Karl Fischer titration and elemental analysis. The results from Gel Permeation Chromatography measurement indicated the formation of monomers, dimers and trimers (Mw from 260 to 310 g/mol). The carbon content of bio-oil was slightly higher (65.03%) and its oxygen content slightly lower (28.33%) than in the original lignin sample (C content 64.14% and O content 29.88%) as revealed by elemental analysis. Based on its elemental composition a higher heating value (27.98 kJ/g) for bio-oil than for organosolv lignin (26.33 kJ/g) was calculated, emphazing the potential of bio-oil for being a future energy carrier. The Folin Ciocalteu method indicated a coherency between increasing retention times of HTL and increasing phenolic contents in bio-oil (0.157 g GAE/ g bio-oil (10 min), 0.159 g GAE/g bio-oil (20 min) and 0.191 g GAE/ g bio-oil (30 min)), especially at moderate temperatures (290 °C), outlining bio-oil's high potential as aromatic source for chemical industry. These achievements indicated a valorization of lignin occurring during hydrothermal liquefaction.

Zusammenfassung

Die hydrothermale Verflüssigung (HTL), ein thermochemischer Umwandlungsprozess zur Herstellung von Bioöl aus Organosolv-Lignin, wird in dieser Arbeit beschrieben. Bioöl wird derzeit als hochwertiges Ausgangsmaterial für aromatische Stoffe sowie als Energieträger betrachtet. Dennoch werden die Reaktionen des Lignins während der hydrothermalen Verflüssigung, aufgrund der Komplexität und der Heterogenität des Ligins, zur Zeit noch nicht vollständig verstanden. Diese Arbeit untersucht die quantitative Bildung sowie die qualitative Zusammensetzung des Bioöls, welches durch HTL von Lignin bei subkritischen Temperaturen (270°C, 290°C, 310°C) und verschiedenen Verweilzeiten (10, 20, 30 min) erzeugt wird. Die abgetrennte Bioöl-Fraktion enthielt verschiedene Ligninderivate mit niedriger molarer Masse. Die allgemeine Charakterisierung des Bioöl erfolgte mittels Gel-Permeations-Chromatographie, photoakustischem Infrarotspektrum, Folin Ciocalteu Methode, Karl Fischer Titration und Elementaranalyse. Die Resultate der Gel-Permeations-Chromatographie verdeutlichten die Bildung von Monomeren, Dimeren und Trimeren (Mw von 260 zu 310 g/mol). Die Elementaranalyse zeigte, dass der Kohlenstoffgehalt im Bioöl höher (65.03%) und der Sauerstoffgehalt minimal niedriger (28.33%) als im Lignin (C-Gehalt 64.14% und O-Gehalt 29.88%) waren. Basierend auf den Ergebnissen der Elementaranalyse wurden die Heizwerte des Bioöls (27.98 kJ/g) und des Organosolv-Lignins (26.33 kJ/g) berechnet und verdeutlichten hierdurch die Bedeutung des Bioöls als Energieträger. Die Folin Ciocalteu Methode deutete einen Zusammenhang zwischen steigendem Phenolgehalt im Bioöl und steigender Verweilzeit (0.157 g GAE/ g Bioöl (10 min), 0.159 g GAE/g Bioöl (20 min) und 0.191 g GAE/ g Bioöl (30 min)) an, was vor allem bei moderaten Temperaturen (290 °C) ersichtlich war. Diese Ergebnisse unterstrichen die Relevanz des Bioöls für die chemische Industrie. Die Ergebnisse der Arbeit verdeutlichten im Allgemeinen die erfolgreiche Wertsteigerung des Lignins mittels HTL.

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List of abbreviations

Ar	Aryl-group
BET	Brunnauer-Emmett-Teller (surface measurement)
C01	Centrifuge number 1
C content	Carbon content
E01	Evaporator number 1
EA	Elemental analysis
F01	Filter number 1
F02	Filter number 2
F03	Filter number 3
FC	Folin Ciocalteu
FS01	Separatory funnel number 1
FT-IR	Fourier transform infrared spectroscopy
GAE	Gallic acid equivalent
GC-MS	Gas chromatography – mass spectroscopy
GPC	Gel permeation chromatography
HTL	Hydrothermal liquefaction
IR	Infrared
LCA	Life-cycle assessment
M01	Mixer number 1
M02	Mixer number 2
MMD	Molar mass distribution
NDIR	Nondispersive infrared sensor
OC	Organic carbon
O content	Oxygen content
OMe	Methoxylgroup
PA	Photoacoustic

PA-IR	Photoacoustic infrared
PIC	Pressure indicator control
R01	Parr reactor
R	Organic residue
RT	Retention time
T01	Tank number 1 (=storage container)
T02	Tank number 2 (=storage container)
T03	Tank number 3 (=storage container)
T04	Tank number 4 (=storage container)
TC	Total carbon
TOC	Total organic carbon
UV	Ultra violet
V01	Valve number 1
V02	Valve number 2 (=safety valve)
V03	Valve number 3

Nomenclature

A	Absorbance [1]
DF	Dilution factor [1]
Ea	Activation energy [J/mol]
HHV	Higher heating value [kJ/g]
k	Boltzmann constant ($1.38*10^{-23}$ J/K)
M	Mass [g]
Mn	Number average molar weight [g/mol]
Mw	Weight average molar weight [g/mol]
P	Pressure [bar]
PDI	Polydispersity index [1]
R	Ideal gas constant [8.314 J/(mol*K)]
T	Temperature [K]
t	Time [min]

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1 Introduction

To date the world is challenged by global warming, high greenhouse gas emissions, increasing fuel demand and consequently the risk of petroleum depletion. All these environmental influences are mainly of anthropological origin and have tremendously increased since the petroleum boom in the 1970s. [1] Special attention must be paid to the decrease of CO_2 since its rate has reached an enormously high value during the last decades [2]. Based on calculations considering the primary energy consumption it was reported that the annual CO_2 emissions had increased from 25,000 million tons to 30,000 million tones within 6 years (from 2001 to 2007) [3]. As a consequence of these developments research now focuses on a way into a more sustainable future [2].

The previously mentioned fossil fuel depletion is primarily ascribed to the fact that extreme economic developments are currently going on especially in countries such as China or India, which are net importers of fossil fuels. [4] To underline this increasing demand, a closer look at the current situation in India is taken. Power generation in India is still mainly based on the key feedstock of coal. In Indian thermal power plants coal meets 65% of their total installed electrical capacity, which highlights the tremendous demand for fossil fuels, mentioned above. [5] These countries (e.g. China and India) require increasing energy provision and therefore more fossil fuels, since to date fossil fuels are the main suppliers of energy. Furthermore the gas and oil reservoirs become fewer in number and more difficult to access. With regard to a limited availability of fossil fuels based on the imminent fossil fuel depletion in the future, the usage of biofuels is considered to be the sustainable solution to this fuel challenge. Thus with increasing focus on biofuels the importance of biomass as raw material inclines as well. [4]

As a consequence of the energy crisis described in the scenario above the European Union has set the goal, to base 20% of the energy consumption on renewable resources by 2020. Furthermore, until 2020, all member states of the European Union have to achieve a target of 10% of biofuels applied within the transportation sector. [6] This is a reasonable approach since worldwide the transportation sector accounts for the major energy requirement. To highlight the dimension of this requirement, the Indian transportation sector is discussed, which annually expands at 10% and therefore the serious situation in fuel demand is a reasonable consequence [5].

In addition to this general shortage of fossil fuels, there is another rather political fact that claims biomass to be a competitive alternative. It is proven, that biomass can be found in all countries at all times. Therefore, its usage provides higher energy security for countries without oil and natural gas reserves. They do not need to depend on several countries with sufficiently large oil and gas reservoirs anymore, which are mostly politically unstable. Hence, in case of fossil fuels, energy security cannot always be granted, whereas it can be guaranteed in the case of biofuels. [7] The positive side-effect of this new energy independence within the field of fuels is a more extensive diversification and decentralization of energy supplies, which at the same time is related to energy self-sufficiency at a local, regional and even national level. [2]

Nevertheless, biomass being used as alternative fuel and potential source for materials currently gained from fossil fuels is also highly controversial. One of the most critical correlations in the future will be the simultaneous use of biomass as a source for food and energy. The amounts of required food plants and energy plants will increase but the availability of free space for agricultural usage will not change. [8] The consequence is that the more energy is needed, the less food we have. Figure 1 shows, how the growth of the global population is leading to an increasing food demand.

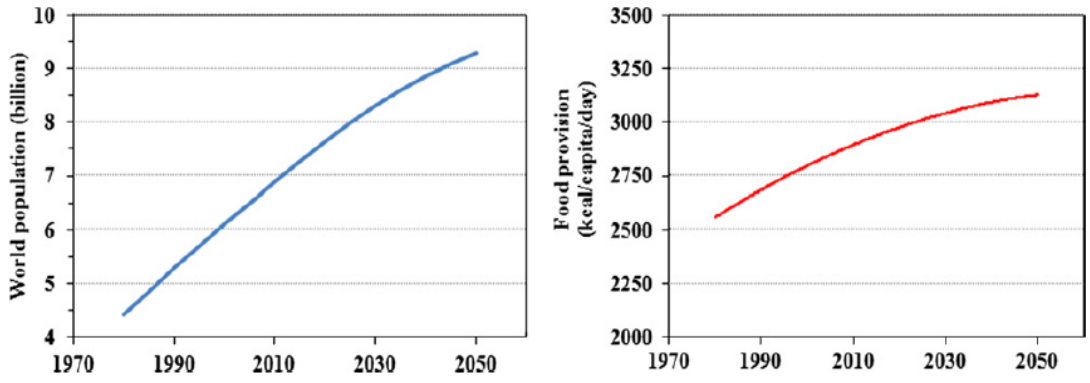

Figure 1: United Nations Population Growth and the needed food supply 2050 [8]

Compared to 2010, where 6.8 billion people were living in the world, the world population will have risen to 9.2 billion by 2050. In 2010 about 2,875 kcal/capita/day were required. In 2050 this value will have increased to 3,125 kcal/capita/day. [8] This increase in food consumption as shown above is explainable since obesity, especially in industrial nations such as the United States of America is highly

increasing [9]. In contrast to this, the global biofuel production was about 18 billion liters per year in 2000. However, in 2007 the amount increased to 62 billion liters/year. Within 7 years, the production of biofuels became 3.5 times higher and it can be assumed that this great leap will not decrease in the future. [10] Therefore, the question arises how biofuels' interference with food supply can be limited in the future.

In order to reduce social impacts of biofuels, biomass feedstock has to fulfil certain criteria. Furthermore, these criteria are extended by criteria meant to minimize the environmental influence of biofuels. The biomass source for biofuels has to have a high-land-use-efficiency, a low water footprint of agricultural activities related to it, a low fertilizer and carbon footprint of biomass itself and eventually a not interfering coexistence with food industry. [8]

Primarily, this is one of the reasons, why biofuels of the 2nd and 3rd generation are of increasing interest. Their precursors in comparison to the 1st generation (e.g. bio-ethanol or biodiesel from rapeseed oil), cannot be digested by human beings. The 2nd generation of biofuels is based on lignocellulosic feedstock, whereas the 3rd generation is based on algae. [11] According to this the coexistence with food industry can be granted. This basic development in biofuels helps decrease the social impacts. This is outlined by a current report performed for the case of the United States. It was suggested that more than 1.3 billion tonnes biomass per year can be sustainably produced from agricultural but above all forestry sources. Coupling advanced biomass-conversion technologies with land-use changes could meet the American demand for liquid transportation fuels without affecting food, feed and fiber production. [12]

In addition, the environmental aspects of biomass combustion are promising, since biomass does not cause high emissions of greenhouse gases, because it only emits what it has chemically stored within its organic structure during growth and the entire chemical process of photosynthesis [13]. During this chemical reaction sunlight, carbon dioxide (CO_2) and water are converted into chemical energy which subsequently leads to the formation of cellulosic biomass components [14]. The chemical reaction occurring during photosynthesis is shown in the equation below [13].

$$6\,CO_2 + 5\,H_2O \xrightarrow{\text{sunlight}} C_6\,H_{10}O_5 + 6O_2 \qquad (1)$$

In case of combustion of biomass, the same amount of CO_2 will be emitted and therefore the overall amount of CO_2 emission of the combustion reaction is assumed to be zero. This generates a high potential of reducing the greenhouse gas emissions and slowing down global warming. [13] The low CO_2 emissions of biomass are outlined by comparing the emitted amount of CO_2 of biomass (17 - 27 g/kWh) to the amount emitted by coal (955 g/kWh), oil (818 g/kWh) or natural gas (446 g/kWh). It is expected, that with improving technologies, the CO_2 emission of biomass can be further decreased to 15 – 18 g/kWh. [13] In addition to the low emission of CO_2, biomass contains only a negligible amount of sulfur and nitrogen and therefore has a lower negative impact on the environment than fossil fuels. [7]

However, a low CO_2 emission rate can also be achieved by wind power, solar power and other sources of renewable energy. Why is biomass then of such an importance for a sustainable future? Biomass is the only renewable resource from which fuels, precursor material for the chemical industry, heat and electricity can be gained with a CO_2 emission close to zero. [6] Within the last years, a field of research dealing with the simultaneous usage of biomass as source of heat, energy, fuel as well as starting material for chemical products manufacturing has been investigated. This field of research, so called biorefineries, focuses on the entire use of all components of biomass. [6]

One component of wooden biomass is lignin. This master's thesis is entirely dedicated to the lignin biopolymer, which builds up lignocellulosic feedstock together with cellulose and hemicellulose. Since cellulose and hemicellulose of this lignocellulosic feedstock are used in pulp and paper plants the previously mentioned concept of biorefineries is now dedicated to identify ways to also use lignin in order to convert the entire biomass. The principle of biorefineries outlines the great potential of lignin for various applications as it will be illustrated in the following chapters of this thesis.

1.1 Background of lignin

Lignin has been intensively studied during the past decade. Its chemical structure is highly complex and heterogeneous, which is considered a drawback for commercial applications. Lignin is the second most abundant natural macromolecule, and its frequency is only exceeded by cellulose. [15] Although its complexity and heterogeneous character are currently making great demands for its utilization, the research focus on this bio-material is steadily increasing. Researchers aim to

identify higher value added sustainable applications of lignin than simple combustion used nowadays. [16]

Lignin, as main by-product of pulp and paper industry, is currently burned in the recovery boiler to generate the process heat for the pulp mill, as already shortly mentioned above [17, 18]. The related availability of lignin gained from pulp and paper industry is enormous since it is estimated to be more than 50 million tons of dry lignin per year, which are produced worldwide [19]. Until now only 2% of the lignin available in pulp and paper industry is commercially used. This percentage comprises of approximately 1,000,000 tons/year lignosulphonates originating from sulphite process as well as about 100,000 tons/ year of kraft lignin. [16] The need for action in case of lignin usage and valorization is outlined by the fact that 60% more lignin are produced than required for meeting the internal energy usage (obtained by combustion) of the plant [12].

In addition to pulp and paper industry, lignin is also produced during bio-ethanol production [20]. In this case, lignin has to be separated from carbohydrates by various pretreatment processes. The cellulose is then hydrolyzed to simple sugars (glucose) and subsequently fermented to ethanol. Consequently it is demonstrated how tremendous the availability of lignin really is.

Currently researchers are working on development of methods for conversion of lignin into bio-oil and consequently production of simple aromatic compounds from lignin. This research is stimulated by the demand for more efficient ways of lignin usage. Hydrothermal liquefaction (HTL) is considered one promising conversion pathway to produce these higher value added products, mentioned above.

This master's thesis will focus on HTL of lignin to bio-oil. Bio-oil itself is a liquid fuel produced from biomass or in case of this thesis from lignin. It is a light brownish yellow to dark brown highly viscous liquid with a rather low pH. Bio-oils are complex mixtures of chemical compounds that are obtained by decomposition of lignocellulose or pure lignin only. [4] The properties of bio-oil entirely depend on its composition. The main components of bio-oil are phenols, aldehydes, ketones, furans, alcohols, acids, esters and a large proportion of lignin derived oligomers. [21] One of the most crucial components of bio-oil, however, is water which influences viscosity, pH, heating value and phase separation. [4] Due to high water content, low pH and high O content bio-oil needs to be further upgraded to eventually be

mixed with e.g. fossil fuels. Therefore, bio-oil formation should be followed by further upgrading steps, which, however, will not be investigated in this master's thesis. [4]

In summary, lignin and consequently bio-oil are of great interest, since they have rather low social and environmental impacts. They do not interfere with human beings' nutrition and their CO_2 balance is very promising. In addition, bio-oil has a high potential for being the future substituent of fossil fuels and becoming a main start material for the production of aromatic products.

1.2 Objectives of the thesis

Despite current expertise on HTL, precise studies on trends of bio-oil formation are still missing, requiring more research. This aim overall creates a research challenge for a more precise understanding on how time and temperature influence the quantity of bio-oil production. As a result, the core part of this thesis is dedicated to the identification of the most superior reaction conditions. Furthermore the objective is to identify the quality of the produced bio-oil, with special attention on total phenolic content in bio-oil and how it changes with adjusted temperature and times.

Finally, this thesis highlights the environmental sustainability of bio-oil production from lignin. The used tool is life-cycle assessment (LCA), which links experimental results to ecological aspects.

2 Theoretical part

Recently, there has been a growing research interest in valorization of lignocellulosic components. This development has led to a focus on lignin as a source for green chemicals and fuels and consequently sustainable substituent for fossil fuels and materials derived from them. The research interest is highly based on lignin's aromatic structure and on the possibility to produce a range of organic compounds from it. [2] Its abundance (50 million tons of dry lignin per year from chemical pulping alone) is enormous and researchers now try to use it most efficiently. [19]

The literature review of the thesis emphasizes that thermochemical conversion of lignin is complex. Common research knowledge on lignin degradation and subsequent conversion to bio-oil, which is considered as lignin valorization, is discussed in the following chapters.

2.1 Organosolv fractionation of lignocellulose

HTL requires lignin, which is fractionated from lignocellulosic feedstock by various fractionation processes, as starting material. The lignin used in this study was fractionated by the organosolv process, described in the following paragraph. Applying organosolv fractionation leads to the conversion of lignocellulose into cellulosic fibres, hemicellulose sugars and low moleculare weight lignin fractions. Alcohols with low boiling points are used for decomposition of lignin's network and solubilisation of hemicellulose, leaving reactive cellulose in solid phase. The process is supported by acid or alkali catalysts. Organosolv lignin is obtained from spent liquor of the pulping process and subsequent precipitation in water. [22]

Organosolv fractionation has numerous advantages compared to other chemical treatments. Primarily, its higher environmental-friendliness compared to Kraft emphasizes its relevance for the production of green solvents and fuels. Minor aggressiveness of the process results from the usage of organic solvents, which can easily be recovered by distillation. Secondly, organosolv liquor, containing degraded hemicellulose and dissolved lignin, is sulfur free and therefore contains a superior precursor material for biofuel applications [23]. Thirdly, the produced lignin is highly suitable for biorefiniery processes because it is of low molecular weight, facilitating subsequent degradation by HTL [22].

Finally, De la Torre et al. even stated that organosolv lignin contained more phenol hydroxyl and carbonyl groups. All these advantages enhance the suitability of organosolv lignin as start material for bio-oil production. [23]

2.2 Chemical structure of lignin

Lignin is the natural amorphous biopolymer that partly (20-30%) builds up wood. [24, 25] It is one of the three components of lignocellulose beside cellulose and hemicellulose [20]. However, lignin content strongly depends on the type of biomass, the wood part, the growing conditions and other aspects (e.g. softwood and hardwood). Expertise has proven that lignin is found in the middle lamella of wooden material, where it is "cementing" the plant to impart strength to wood tissue. [24] The plants structural integrity, water impermeability and the plants resistance against microbial decay are influenced by lignin content. [8]

Lignin consists of three basic phenylpropanoide units, namely p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are also referred to as monolignols [26]. The units differ by their number of methoxyl groups attached to the aromatic ring. Coumaryl alcohol has no methoxyl group, whereas the number of methoxyl groups subsequently increases from one methoxyl group (coniferyl alcohol) to two methoxyl groups (sinapyl alcohol), respectively. [15] Figure 2 presents the three main units building up the lignin structure. If a methoxyl group is present, it occurs in o-position to the oxygen atom, which is situated in the p-position compared to the aliphatic side chain [26].

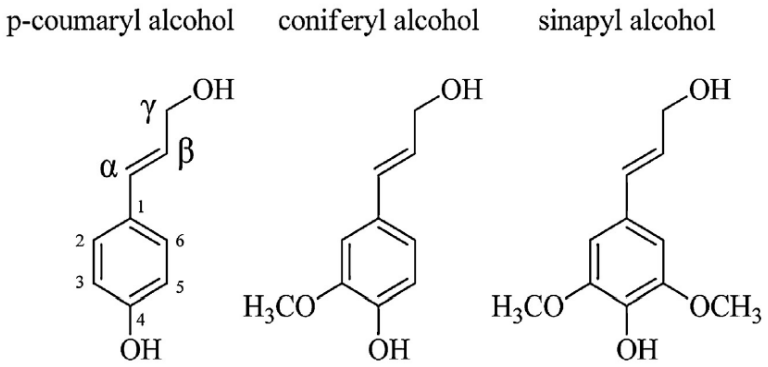

Figure 2: Lignin - structural units [27]

The three units demonstrated in Figure 2 are randomly polymerized by enzyme-initiated dehydrogenation, forming lignin's structure. The most important step of the

polymerization is the initial formation of the mesomorphs of the precursor alcohol. [24] Dimeric and oligomeric lignol radicals subsequently react with monolignol radicals [26]. This entire cross coupling is accompanied by the addition of water, phenolic and aliphatic hydroxyl groups [24]. Thus the emerging question is which bonds crosslink the monolignols during the previously described polymerization.

The three different structural units are bonded together by C-C-bonds and ether-bonds (C-O-C). More than two thirds of the linkages in lignin are ether bonds. The residual one third is C-C-bonds. [27] A more detailed description of the different units and their bonds can be found in Figure 3.

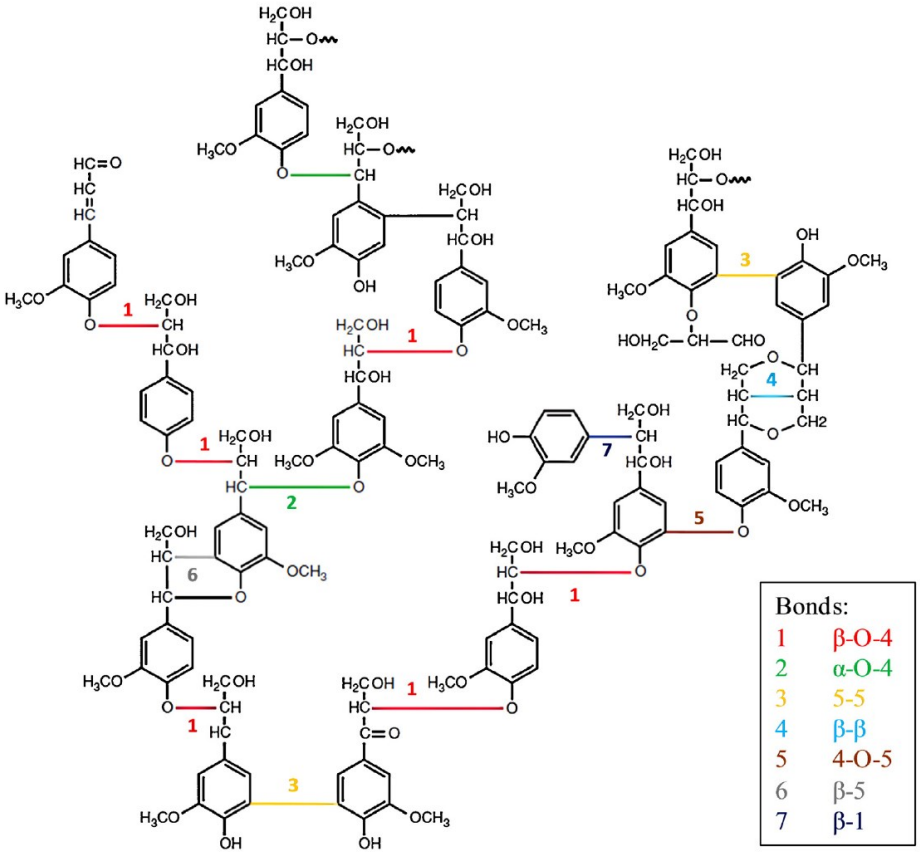

Figure 3: Schematic structure of lignin – softwood [27]

Figure 3 demonstrates the diversity of different bond types in lignin, creating difficulties in the identification of suitable reaction pathways, since various bonds require different conditions for cleavage. The red bonds are the highly abundant β-O-4-ether-bonds, which are the second weakest bonds in lignin structure after α-O-4 bonds both cleaving off fast. In comparison to the weakest bonds in lignin

polymers (the α- and β-aryl-ether-bonds) aryl-aryl-bonds are more stable. [15] High dissociation energies (422 kJ/mol) emphasize the high stability of aryl-aryl-bonds [28].

Temperature, however, positively influences bond cleavages with restriction to certain limits. If temperature becomes too high, secondary reactions occur. In that case, the previously formed carbon-centered radicals start to react with each other and C-C-bonds are consequently formed, leading to the formation of char as undesired by-product of HTL. [29]

Researchers now focus on the optimization of reaction parameters, for improving degradation processes by controlled bond cleavages. Current expertise on HTL is described in the next chapter.

2.3 Current research focus in HTL

HTL is a thermochemical conversion process, imitating the chemical reforming process of wood or organic material, which once formed fossil fuels. However, in contrast to fossil fuel formation, which took thousands of years, HTL produces bio-oil within minutes. HTL is performed by biomass or lignin being heated and pressurized in the presence of water in an autoclave. [30] HTL takes advantage of high temperature and pressure, causing degradation of bonds between lignin units. During HTL, depolymerization of high molecular lignin leads to the formation of lower molecular weight compounds. [27] Long-chained organic polymers break into short-chain hydrocarbons, which mostly are syngas and oil [30]. The products of HTL are bio-oil, undegraded lignin, char, aqueous phase and gases. [27]

In Figure 4 the differentiation between various thermochemical treatments of lignin is demonstrated. The temperature scale reveals that there is a temperature-overlap between flash-slow pyrolysis and liquefaction. Figure 4 further elucidates that HTL is limited to a temperature range of 150 °C to 400 °C.

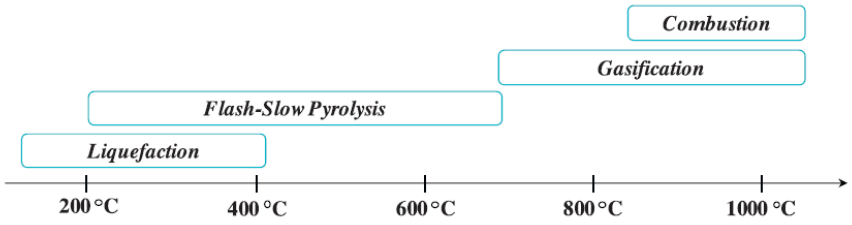

Figure 4: Temperature ranges of thermochemical conversions [27]

In order to guarantee the production of a sufficiently high mass fraction of bio-oil, temperatures are recommended to exceed 200 °C, otherwise the conversion step might not lead to discernable bio-oil yields. In the table below characteristic data of bio-oil is listed.

Table 1: Comparison of pyrolysis oil, liquefaction oil and heavy fuel oil [31]

property	pyrolysis oil	liquefaction oil	heavy fuel oil
moisture content, wt %	15−30	5.1	0.1
pH	2.5		
specific gravity	1.2	1.1	0.94
elemental composition, wt %			
carbon	54−58	73	85
hydrogen	5.5−7.0	8	11
oxygen	35−40	16	1.0
nitrogen	0−0.2		0.3
ash	0−0.2		0.1
higher heating value, MJ/kg	16−19	34	40
viscosity (50°c), cP	40−100	15000 (at 61°C)	180
solids, wt %	0.2−1		1
distillation residue, wt %	up to 50		1

Table 1 demonstrates that the oxygen content in bio-oil is an enormous drawback of liquefaction oil. Biomass-based oils (pyrolysis oil and liquefaction oil showed approximately 40wt% and 16wt% oxygen respectively) highly exceed the oxygen content of heavy fuel oil (1wt% oxygen). Most intercessional for liquefaction oil is the high HHV, which is caused by the lower oxygen content. The heating value of pyrolysis oil (16-19 MJ/kg) is highly inferior to heating values of liquefaction oil (34 MJ/kg) and heavy fuel oil (40 MJ/kg). Nonetheless, liquefaction oil is inferior to heavy fuel oil in case of HHV. Liquefaction oil demonstrates a high carbon content of 73wt%, which is only exceeded by 85wt% carbon content of heavy fuel oil. When comparing liquefaction oil to other fossil fuels, its carbon content even exceeds the carbon content of lignite (56.96wt%) [32]. Nonetheless, in comparison to hard coal having a carbon content ranging from 84.8wt% to 89.3wt% liquefaction oil is inferior [33]. However, in all the relevant categories such as carbon content, heating value and oxygen content liquefaction oil is superior to pyrolysis oil [31]. Therefore, the conclusion is acceptable that liquefaction oil is a more suitable precursor for fuel applications (compared to pyrolysis oil) and a competitive alternative to heavy fuel oil. The resulting question is how liquefaction oil can be produced.

Currently, HTL, mostly influenced by temperature, pressure, solvent, retention time, presence and type of catalyst, is highly discussed in case of bio-oil production. Catalysts are required as a result of lower operating temperatures related to HTL compared to pyrolysis. Lignin depolymerization at such low temperatures does not occur as fast as it does at higher temperatures. Lignin degradation, nonetheless, requires certain temperatures because in contrast to aryl-alkyl bonds, cleaving off in subcritical conditions, aryl-aryl bonds are defined by a higher degree of stability. Their breakage requires higher temperatures and pressure. Hence, it has become a well-established approach to add a catalyst such as NaOH, enhancing lignin bonds cleavage and preventing condensation reactions. NaOH, added in a percentage of 4-5wt%, converts hydroxyl groups of phenolic and catecholic compounds to phenolates. [4] Hydroxyl groups cleave off more easily due to base-catalysts and the reaction sequences lead to the formation of reactive carbenium ions. [29] As a consequence to this conversion, the internal hydrogen bonding between hydroxyl groups is reduced and the solubility of lignin increases. An increase in solubility of lignin results in easier accessible ether bonds and therefore the cleavage of phenolic monomers from lignin molecules is facilitated. [4] Literature review showed that the principle of NaOH addition is well established, as demonstrated by current research reports discussed below.

Toor et al. used subcritical and supercritical water as solvent. The applied pressure varied from 5 MPa to 25 MPa. The reactions were carried out at relatively low retention times (approximately 10 min) and in presence of 1wt% NaOH. The liquid yields at these conditions were between 58% and 79% and the solid residues ranged from 12% to 37%. According to their findings different catalysts were ranked based on their activity, starting from NaOH being the weakest (K_2CO_3>KOH>Na_2CO_3>NaOH). [34]

Lavoie et al. used an aqueous solvent solution, at a pressure range of 9 to 13 MPa and a temperature range of 300 to 330 ^oC. In their experiments 5wt% of NaOH were applied as a catalyst. [35]

However, what is the motivation of current researchers to devote their work to supercritical and subcritical water?

Figure 5 outlines the advantages of supercritical water, which after having exceeded the critical point, reacts as catalyst as well as reagent. Consequently temperature and pressure increase positively enhance the solvent characteristics of water.

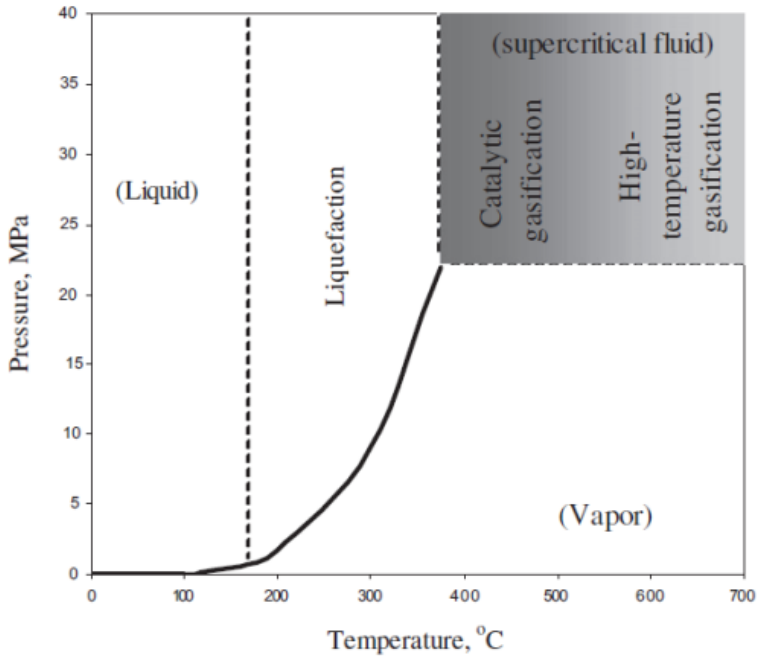

Figure 5: Phase diagram of water as catalyst and reactant [34]

The reactivity of supercritical water encounters degradation difficulties of lignin occurring during pyrolysis, which is a dry process. Consequently, the presence of water is considered the main advantage of HTL compared to pyrolysis. [34] Reactivity of water is improved due to the increase of ionic product of water and the decrease of dielectric constant at higher temperatures and pressures. [36] The influence of temperature on Kw is illustrated in Figure 6.

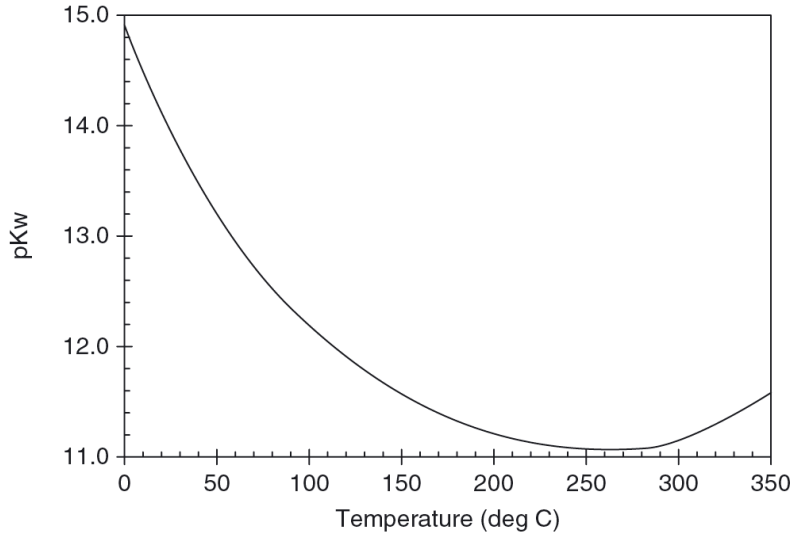

Figure 6: Temperature dependence of water ionization at 25 MPa [30]

Data in Figure 6 was evaluated at constant pressure (25 MPa). The dissociation constant Kw is listed as pK_w. The water dissociation constant (K_{w0}) at room temperature (25 °C) and atmospheric pressure is 10^{-14}. According to the figure above, the water molecules dissociation constant at 300 °C is 500 times higher than that at room temperature. [30] The highest values are identified between 250 °C and 290 °C. Above 290 °C water dissociation constant decreases again. Nonetheless, water is not exclusively used as solvent and consequently literature review revealed other common solvents applied during HTL.

Cheng et al. used pure ethanol as well as water/ethanol mixtures (50/50) for HTL of wood. Al_2O_3 with active carbon and even metals such as Ru, Pt and Ni were used as catalysts and accelerated the process. A series of reaction times was applied starting from 15 min up to 360 min. [17]

Ethanol as solvent was also tested by Xu and Etcheverry. They focused on a temperature range between 200 °C and 350 °C and a correlating pressure of 2 to 10 MPa. Acceleration of degradation was achieved by adding FeS and $FeSO_4$ as catalysts (5wt% based on the wooden sample). [7]

Fang et al. approached the solvent selection differently and used water as solvent in combination with various lignin and phenol ratios. These experiments were carried out at high temperatures of 400 °C to 600 °C and >9 MPa. The retention times varied from 5 to 60 min. [37]

Nevertheless, successful lignin degradation strategies are not only influenced by the selection of catalysts but also by the chosen atmosphere (N_2 or H_2 atmosphere) in which the reactions occur. However, high costs of H_2 weaken commercial feasibility of HTL (in case of H_2 usage). Furthermore H_2 is explosive, whereas N_2 is an inert gas. [4] Therefore, N_2 was used in this current work.

Currently, a maximum of 20wt% of product oil can be formed by HTL. Up-to-date research work focuses on the usage of non-catalyzed system in order to increase oil yields by exclusively optimizing the process parameters. [29] However, in order to increase oil yields the occurring degradation reactions have to be fully understood. The general idea of the chemical reactions occurring during HTL of lignin is illustrated in Figure 7.

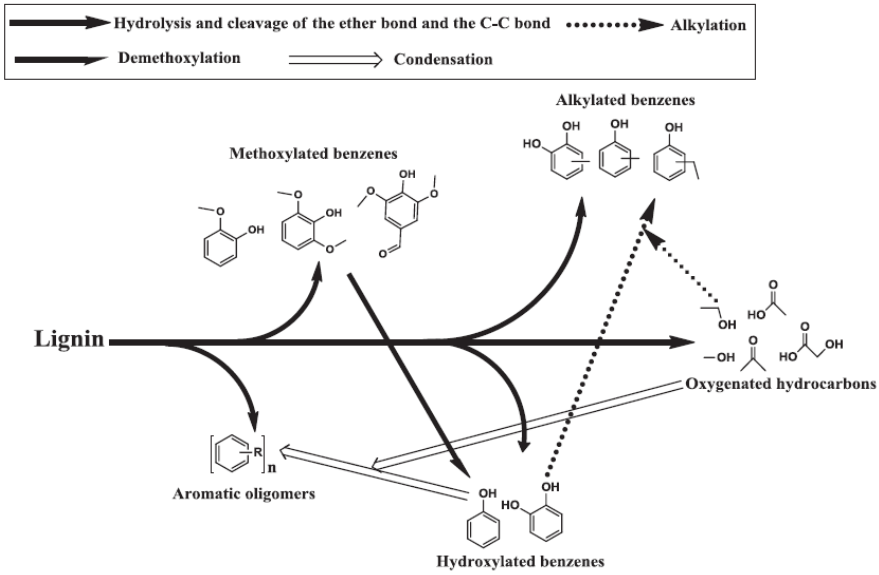

Figure 7: Chemical reactions of lignin during HTL of lignin [20]

Figure 7 demonstrates the reaction scheme of the chemical reactions occurring during HTL. The degradation of lignin is related to cleavages of ether bonds as well as C-C-bonds, which occur due to hydrolysis. This initial reaction chain is followed by demethoxylation and alkylation as well as condensation reactions, which at the same time have to be avoided due to their favor to cause char (polylignols) formation. According to Figure 7 hydroxylated benzenes, which would be desirable phenolic compounds, have only been identified as intermediates which are likely to further react to aromatic oligomers via condensation reactions. [20]

Demethoxylation and alkylation of lignin require high temperatures. Contrastively, phenolic monomers and dimers are formed at moderate temperatures and shorter retention times, emphasizing the challenge of choosing the most suitable reaction temperatures. In order to facilitate the identification of the solution to this challenge a better understanding of lignin degradation has to be enforced. [20]

Based on this current state-of-arts, the experimental design of this thesis was made. The applied parameters in the papers mentioned above such as temperature, retention times and pressure were used as reference points. Nonetheless, for successful bio-oil production subsequent separation steps of product streams of HTL are required, which are therefore presented in the next chapters.

2.4 Theory of applied separation methods

Numerous separation technologies have been applied to bio-oil. Separation is one of the most important steps of bio-oil production, since impurities in bio-oil such as char and water have to be removed. A successful separation is the solid foundation for upgrading of bio-oil. Conventional separation methods for bio-oil separation are column chromatography, solvent extraction and distillation. [38]

2.4.1 Liquid-liquid-extraction

Liquid-liquid-extraction is a well-established chemical separation method, with phase separation based on different solubility. Liquid-liquid extraction requires two immiscible phases, whereof one has to be organic (=bio-oil) and the other one has to be an aqueous phase. Subsequently, the extraction solvent can be recovered by evaporation and reused, increasing the environmental-friendliness of the process. [39] Extraction can include different solvents such as water, ethyl acetate, paraffin, ethers, ketones and alkaline solutions. Already the selection of the solvent is essential for the success of removal of impurities from bio-oil. Diethyl ether and dichloromethane are most commonly used for extraction of water-insoluble fractions from water-soluble fractions. [38]

An established principle of liquid-liquid-extraction was reported by Toledano et al. who separated bio-oil from the aqueous phase by adding ethyl acetate. Ethyl acetate is an organic solvent and therefore suitable for extracting the organic phase from the aqueous phase. Ethyl acetate can easily be recovered by evaporation. The approach was an initial acidification of the liquid product of HTL with HCl until pH of 1-2. This step was required for successful precipitation of undegraded lignin. Remaining bio-oil and aqueous phase were finally separated by extraction. Toledano et al. assumed that this entire liquid phase contained the phenolic compounds, predominantly in the bio-oil fraction. [40]

Not only bio-oil can be extracted by liquid-liquid-extraction but also phenols of the residual bio-oil. Nevertheless, since liquid-liquid extraction is time consuming, the Folin Ciocalteu (FC) method for phenolic OH determination was used in this study.

Researchers have also studied supercritical fluid extraction. Most commonly supercritical CO_2 is used for extraction, since it has a series of promising dissolving abilities it does not have at ambient conditions. [38]

This chapter elucidates that liquid-liquid-extraction is a highly effective and rapid separation method for splitting bio-oil from residual products of HTL.

2.4.2 Molecular distillation

Distillitation separates compounds in bio-oil according to their different volatilities. Atmospheric pressure distillation, vacuum distillation and steam distillation are currently highly discussed in context with bio-oil separation but their application is restricted by bio-oil's instability at higher temperatures. Vacuum distillation is interesting, since in contrast to atmospheric pressure distillation, the boiling points of the compounds in bio-oil are decreased in vacuum which is highly favorable because of bio-oil's thermal sensitivity. Introducing steam into the distilling vessel for heating the bio-oil, decreases bio-oil's viscosity and expels its volatile compounds. Nonetheless, steam distillation consequently requires high temperatures, making it inappropriate for bio-oil separation. In summary, molecular distillation successfully operates despite these temperature limitations in bio-oil separation. The causes of this applicability are low operating temperature, short heating times and high separation efficiency of molecular distillation. [38]

The principle of molecular distillation mostly relies on either repulsive or attractive forces between molecules, which depend on the spacing between molecules. The distances between gas molecules are large, leading to negligible forces between them except when the molecules collide. This distance between collisions is called free path (λ_m) and it is the influencing parameter of molecular distillation (see equation 2).

$$\lambda_m = \left(\frac{k}{(\sqrt{2}} * \frac{1}{\pi}\right) * \left(\frac{T}{d^2 * p}\right) \quad (2)$$

The free path depends on temperature T (°C), the size of the molecule d (m), pressure P (Pa) and Boltzmann constant (k). Therefore at fixed temperature and pressure the free path only depends on the molecule size. When the liquid is heated, the surface molecules will overcome the intermolecular forces and liberate as gas molecules. Subsequently, the amount of gas molecules increases and at some point, some molecules return to the liquid surface. Under certain conditions, molecular motion reaches equilibrium. [38]

There are a heating surface and a cooling surface, whose distance is less than the mean free path of light molecules. Therefore after heating and having sufficient

energy, light molecules will reach the cooling surface and condense there, whereas heavy molecular compounds will not reach the cooling surface due to a shorter free path and return to the liquid phase. Due to continuous condensations, this balance is broken and light molecules are continuously released. Figure 8 visualizes the described theory of molecular distillation. [38]

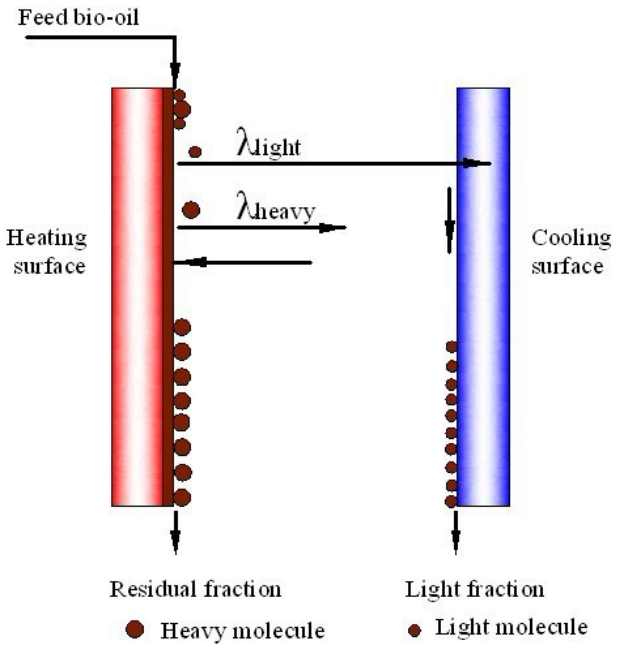

Figure 8: Principle of Molecular distillation [38]

Molecular distillation is most important for further applications of bio-oil as a source of chemicals because the produced bio-oil has to be split into its heavy, middle and light fractions anyhow. [41]

2.4.3 Column chromatography

Liquid chromatography is considered as an effective method for separating high and low molar mass compounds [42]. The samples are separated based on their adsorption capabilities on the stationary phase. High polar molecules are easily adsorbed whereas weak polar compounds are not. The eluent is most critical for the success of separation. Aliphatic compounds can be separated by using paraffin eluents such as hexane. Aromatic compounds, which are also most likely found in bio-oil, are usually eluted with toluene or benzene. [38]

Nevertheless, a drawback of this technology is the high consumption of solvents. In addition the regeneration of silica gel solid phase, which is used as stationary phase, is cost-intensive making this separation method rather uneconomic. [42]

2.5 Theory of upgrading of bio-oil

Current research highly focuses on possible upgrading methods of bio-oil because only upgrading leads to competitive products for the fuel market.

Crude bio-oil cannot be directly used instead of fossil fuels due to several poor chemical and physical properties, such as high corrosiveness, poor volatility, high coking tendency, immiscibility with petroleum fuels as well as relatively low heating values [43]. Upgrading is additionally obligatory due to bio-oil's instability, which provokes storage difficulties due to ongoing reactions in bio-oil even after HTL. [2] However, which upgrading methods are currently applied to solve these limitations of current bio-oil?

Primarily, catalytic cracking is applied, which is a conventional petroleum reforming process. In the case of fossil fuels, the heavy fractions are reduced to medium and light distillates. The process requires acidic and hydrophobic catalysts, in order to produce CO_2, CO and H_2O under atmospheric pressure. Due to high temperatures of this process, the bonds in the larger molecules are cleaved off, reducing their molecular weight. At the same time, compounds are deoxygenated and desirable fuel-range hydrocarbons are formed. Nevertheless, a current main drawback of this refining method is the related choking of catalysts, reducing their efficiency. [2]

Combining hydrogenation with catalytic cracking is called hydro-cracking. Hydro-cracking is a thermal process occurring above 350 °C. High pressure from 0.7 MPa to 13.7 MPa is required for successful hydro-cracking. The cracking function is supplied by silica-alumina (or zeolite) catalyst, whereas platinum and tungsten oxides catalyze the reactions. [44]

Secondly, there is hydrotreating, which is used to saturate olefins and aromatic compounds. In addition, contaminants such as nitrogen, metals or sulfur are removed. This upgrading process uses bi-metallic acid catalysts (e.g. CoMo/γ Al_2O_3), that support the removal of sulfur or nitrogen by hydrodesulphurization and hydrodenitrification. Oxygen is removed via hydrodeoxygenation. [2] In comparison to hydro-cracking, hydrotreating requires moderate conditions. However, at the same time the bio-oil yield is lower. Most

disadvantageous are high quantities of char, produced during upgrading, which clog the catalysts and reduce their reactivity. [44]

Thirdly, supercritical fluids have gained increasing research interest because they are favorable to bio-oil formation and high bio-oil quality. They can support gasification or liquefaction reactions. This upgrading process has recently succeeded in producing bio-oil with higher calorific values. Especially water in supercritical conditions has attracted attention in case of HTL. [44]

Fourthly, the addition of solvents to bio-oil, namely esterification, is a promising upgrading method. Especially polar solvents such as methanol or ethanol are suitable for homogenization and reduction of viscosity of bio-oils. The decrease in viscosity is accompanied by an increase in heating value because bio-oil is mixed with a polar solvent that provides a higher heating value than most bio-oils. [44] Stability increases, since highly reactive species such as carboxylic acids and aldehydes stabilize by esterification under mild conditions. In general esterification reduces the number of reactive species and consequently there is less char formed during further hydrotreatment of esterified bio-oil. [45]

Fifthly, emulsification is discussed as upgrading method, where bio-oil is mixed with diesel to specific extents. 5-30% of bio-oil in diesel has already been tested so far. These emulsions are less corrosive and their ignition characteristics are very promising. Therefore, this emulsion is more suitable for car engines than crude bio-oil. Above all, the emulsion is more chemically stable than untreated crude bio-oil. [44]

Nonetheless, the current overall main drawback of upgrading methods is the deactivation of the applied catalysts due to clogging. [2] Therefore a periodical and continual regeneration of the blocked catalyst is inevitable, which causes refining processes to be more complex. [46]

3 Experimental part

The experiments were documented precisely to enable future repeatability and therefore outline the statistically representative character of the experiments.

3.1 Experimental focus based on current-state-of-arts

Currently HTL is still complicated by the dearth of clear information on degradation of lignin and bio-oil formation. Therefore the objective of the experimental part of this thesis was to identify the most suitable conditions for the formation of high bio-oil mass fractions. The quality of bio-oil was determined by subsequent GPC, EA, FC method, PA-IR and Karl Fischer titration. Additionally, mass and energy balances were identified to draw conclusions on how efficiently the educts were transformed into products.

With regard to common research knowledge stating that temperature and retention time highly influence HTL (compare Kang et al. [20]), the experimental series was implemented by adjusting retention time and temperature. Only water in subcritical conditions was used as solvent, due to the solvent's low cost and environmental-friendliness. Finally own results were approved with other researchers' findings.

3.2 Materials

3.2.1 Lignin

Beech organosolv lignin from the Frauenhofer Institute CBP in Leuna was used in this study. Figure 9 presents a sample of organosolv lignin - primarily, in the condition at delivery (left) and secondly after grinding (right picture). The lignin sample was grinded for 0.5 min with a mill manufactured by Janke & Kunkel K.G. (Type A 10, 20.000 rpm).

Figure 9: Organosolv lignin – before and after grinding

The elemental composition of organosolv lignin was analyzed and the data is listed in Table 2. Data for kraft lignin is included for comparison.

Table 2: Elementary analysis of lignin

	C [%]	**H [%]**	**N [%]**	**O [%]**	**S [%]**	**Total**
Organosolv	62.54	5.91	0.25	30.85	0	99.55
Kraft	63.95	5.84	0.56	27.24	1.94	99.53

One of the primary objectives of the thesis was to define how HTL influenced the elemental composition of bio-oil compared to the composition of fed lignin, making elemental analysis of lignin necessary.

In addition to the elemental analysis, the heating values of these two lignin samples were analyzed using bomb calorimeter PARR 6200. The measured temperature increase of the water bath and therefore the generated heat energy were put into correlation with values of benzoic acid whose data was taken from NIST library. Based on this relation higher heating values (HHV) of lignin samples were determined. Organosolv lignin had a heating value of 25.73 kJ/g, whereas kraft lignin had a heating value of 26.23 kJ/g. This difference in heating values resulted from lower oxygen content in kraft lignin (27.24%) than in organosolv lignin (30.85%).

Additionally ash content and moisture content of organosolv lignin were analyzed. Two samples were put into the oven at 105 °C over night. The weight loss occurring due to drying correlated to the water content, which was calculated to be 1.67wt%. Ash content was determined by combustion of the samples in a muffle furnace at

525 °C for 4 hours. Combustion residues were weighed and an ash content of 0.08wt % was determined.

3.2.2 Chemicals

Ethyl acetate (purity of 99.5%), chloroform (purity of >99.8%), gallic acid (purity of 98%), THF (purity of 99.8%) and FC-reagent were purchased from Sigma-Aldrich (Germany). 1 M H_2SO_4 was supplied by the laboratory staff at Aalto University, where it was prepared from non-diluted acid. The anhydrous sodium carbonate (purity of >99.9%) required for this analysis was bought from Merck KGaA. NaOH was purchased from VWR and had a purity of 98%.

3.3 Methods

3.3.1 Experimental design

The experimental plan below (Figure 10) describes the process steps of bio-oil production applied in this study. It was designed with Microsoft Visio.

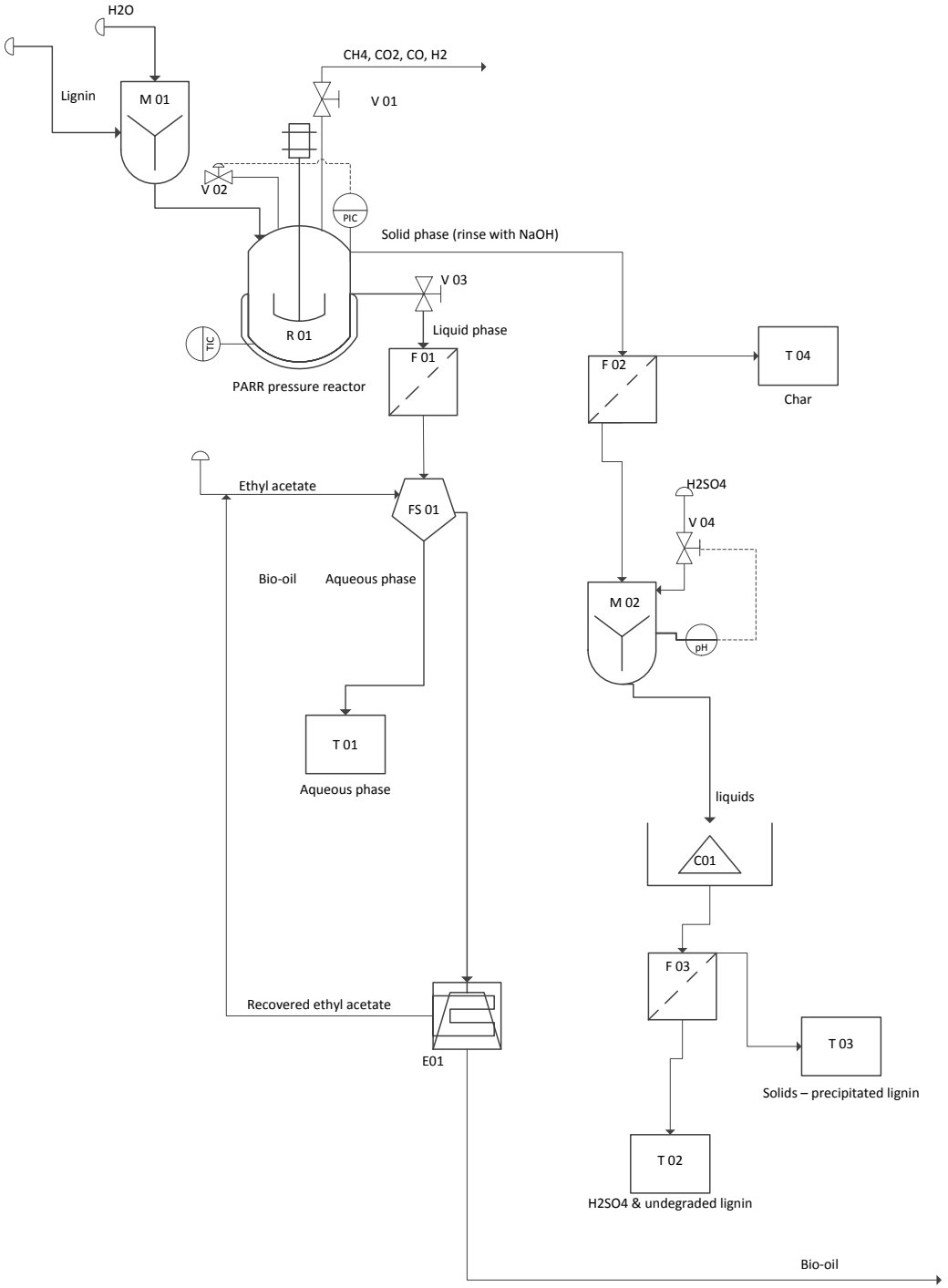

Figure 10: Experimental plan

The relevant abbreviations of the devices mentioned in Figure 10 are explained in *List of abbreviations*. According to Figure 10 lignin was mixed with water before being added to the reactor (R 01). The lignin concentration in water was 25 g/l (lignin: water = 1:40) and 200 ml lignin suspension were used for HTL. The enclosed air in the autoclave was removed by purging the reactor three times with N_2.

Subsequently, 2 MPa were used as starting pressure. Following the heating step, the gas phase was released by opening valve V 01. The liquid-solid phase, which contained water, char, bio-oil and undegraded lignin, was further treated. The aqueous phase, containing the organic compounds, was collected and filtrated through filter paper (F01) (Whatman 41 or Whatman 42).

Subsequently, ethyl acetate was added to the 2-phase-solution and the solution was separated with a separatory funnel (FS01) by liquid-liquid extraction after the ethyl acetate was left in the funnel for 3 min. Longer retention times were also tested, without detection of significant improvement in bio-oil extraction. Ethyl acetate was added in two steps to guarantee the most efficient extraction of bio-oil [47]. In the overall ratio, ethyl acetate was mixed with the liquid product in a ratio of 1:2.2 (ethyl acetate: liquid product). In the first step 70 ml ethyl acetate were added to the aqueous phase followed by supplementary 20 ml added to the aqueous phase obtained after the first liquid-liquid-extraction. This approach resulted in two products, being a bio-oil-ethyl-acetate-solution (dark brown) and an aqueous solution (yellow) (see Figure 11), respectively.

Figure 11: Liquid-liquid extraction of bio-oil

Ethyl acetate was recovered from bio-oil-ethyl-acetate-solution by evaporation in a Buechi rotary evaporator (E01). The residual bio-oil was air-dried at ambient temperature and later analyzed in terms of total phenolic compounds, molar mass distribution, elemental analysis and water content. TOC analysis was performed with aqueous solution for identification of residual dissolved lignin after extraction.

After removal of the liquid phase, the reactor R 01 was rinsed with 0.5 M NaOH. NaOH was heated to 130 °C, thereby dissolving remaining solids in the vessel. The dissolved solids were collected and filtered with filter paper (F02) (MN 640), for char (undissolved) separation from undegraded lignin (dissolved). Acidification of NaOH solution with 1 M H_2SO_4 (until pH of 1-2) caused precipitation of dissolved undegraded lignin. The suspension was subsequently centrifuged (C01) using Thermo scientific SL 40 FR for 30 min at 4,500 rpm and filtered (F03). The separated liquid phase was analyzed by TOC to identify the residual organic carbon content.

This valorization pathway of lignin is also visualized in the figure below. Figure 12, however, only outlines the bio-oil production and separation, not considering the solids in more detail. This was due to the fact, that bio-oil was considered the main valorization product of lignin during HTL in this study.

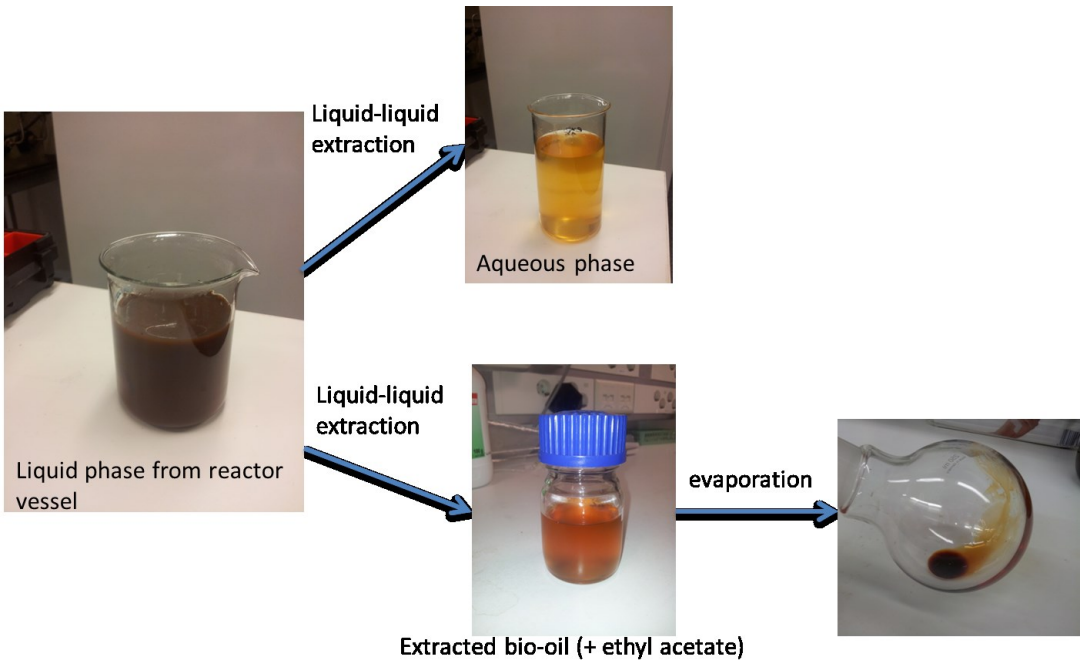

Figure 12: Bio-oil production from lignin and separation process

The first picture on the left presents the liquid product produced after HTL. After filtration, extraction and evaporation the valuable bio-oil (right picture) was obtained.

3.3.2 Implementation of experimental plan

To meet the objective of this thesis, which is the identification of the most promising reaction parameters of HTL, the previously described experimental plan was implemented by adjusting retention time and temperature.

3.3.2.1 Adaption of temperature and retention time

Temperature is the most crucial parameters of HTL, which is mainly based on the occurance of different chemical reactions at different temperatures. [28] Temperature had to be kept in a moderate range, in order to enhance bio-oil formation but hinder enhancement of char formation. The start temperature of the experiments was 270 °C in order to guarantee a sufficiently high bio-oil formation. Subsequently, 290 °C and 310 °C were tested. The applied temperatures are listed in the table below. In order to prove repeatability, each experiment was run at least twice. In case of deviation, one further experiment was performed.

Table 3: List of experiments and applied conditions

Trial	Temperature	Solvent	Lignin	H2O	time	lignin: H2O
	°C	-	g	ml	min	1: x
1	270	subcrit. Water	5	200	10	x = 40
2	270	subcrit. Water	5	200	12.10	x = 40
3	270	subcrit. Water	5	200	20	x = 40
4	270	subcrit. Water	5	200	22.10	x = 40
5	270	subcrit. Water	5	200	30	x = 40
6	270	subcrit. Water	5	200	32.10	x = 40
7	290	subcrit. Water	5	200	10	x = 40
8	290	subcrit. Water	5	200	15.29	x = 40
9	290	subcrit. Water	5	200	20	x = 40
10	290	subcrit. Water	5	200	25.46	x = 40
11	290	subcrit. Water	5	200	30	x = 40
12	290	subcrit. Water	5	200	35.61	x = 40
13	290	subcrit. Water	5	200	40	x = 40
14	310	subcrit. Water	5	200	10	x = 40
15	310	subcrit. Water	5	200	17.03	x = 40
16	310	subcrit. Water	5	200	20	x = 40
17	310	subcrit. Water	5	200	27.14	x = 40
18	310	subcrit. Water	5	200	30	x = 40
19	310	subcrit. Water	5	200	37.40	x = 40

In addition to temperatures, retention times are crucial in case of HTL because a certain reaction time has to be reached for sufficient formation of monomeric

compounds and consequently sufficient degradation and liquefaction of lignin. In contrast, an overshoot of certain reaction times results in increasing formation of char (polylignols) and decreasing bio-oil yields based on ongoing secondary reactions. [36]

A reliable comparison of bio-oil yields obtained at different temperatures required the calculation of isothermal times, whose adjustment is listed in Table 3. The first experimental series was therefore performed at hold times of 10 min, 20 min and 30 min. These times did not consider the heating up process, whose influence on degradation is significant because of ongoing chemical reactions and degradation of lignin already occurring at elevated temperatures. The inclusion of the effect of the heating up process was performed by the calculation of isothermal times according to the equation below.

$$t_{isothermal} = e^{\left(-\frac{Ea}{R}*\left(\frac{1}{Te}-\frac{1}{Ta}\right)\right)} \quad (3)$$

Ea is the activation energy [J/mol] of the reaction. Due to the lack of specific data in case of chemical reactions of lignin Ea was assumed to be 103 J/mol. Nonetheless, it was found that the effect of Ea on isothermal times was insignificant. Ta and Te [K] were the measured temperatures that were documented every 30 seconds. R is the ideal gas constant in J/[mol*K].

3.3.2.2 HTL in PARR pressure reactor

A 4575 PARR high-pressure reactor was used for HTL of organosolv lignin to bio-oil in this study (Figure 13). Its volume was 500 ml, the temperature limitation was 500 °C and the pressure limitation was 34.5 MPa.

Figure 13: 4575 PARR pressure reactor

The entire reactor settings were controlled by Parr 4848 B reactor controller. The sealings of the reactor were grafoil (made out of graphite) gaskets. The sealings showed a good resistance to high pressure and temperature conditions, confirming their suitability for HTL.

3.3.3 Analysis of bio-oil

3.3.3.1 Folin Ciocalteu for determining phenolic content

The Folin Ciocalteu (FC) method was performed for determination of all hydroxyl aromatic compounds and thereby quantification of total phenolic content in bio-oil. Its principle relies on chemical reduction of FC reagent (a mixture of tungsten and molybdenum oxides). The products of the reduction are blue and have a discernible light absorption with a maximum at 765 nm. Subsequently, related absorption data is used for quantification of total phenols. The most critical parameters of the FC method are the presence of alkali conditions (Na_2CO_3 is used) and precise reaction times of FC reagent with the sample. FC-reagent should be added to the reaction media before Na_2CO_3. Otherwise, air-oxidation of phenols may occur, leading to falsification of the analytics. [48]

Light absorption was measured by UV-VIS spectrophotometry (SHIMADZU/ model UV-2550) with 1 cm cuvettes. The settings of the device were based on a wavelength range of 700 to 800 nm.

The calibration procedure of FC was adapted from Rover et al. who performed it with gallic acid. The standard solution had a concentration of 5 g/l gallic acid. By diluting the standard solution to different extends in water, the calibration standards (0, 50, 100, 250, 500 mg/l) were generated. [49] The figure below (Figure 14) presents the identified calibration curve.

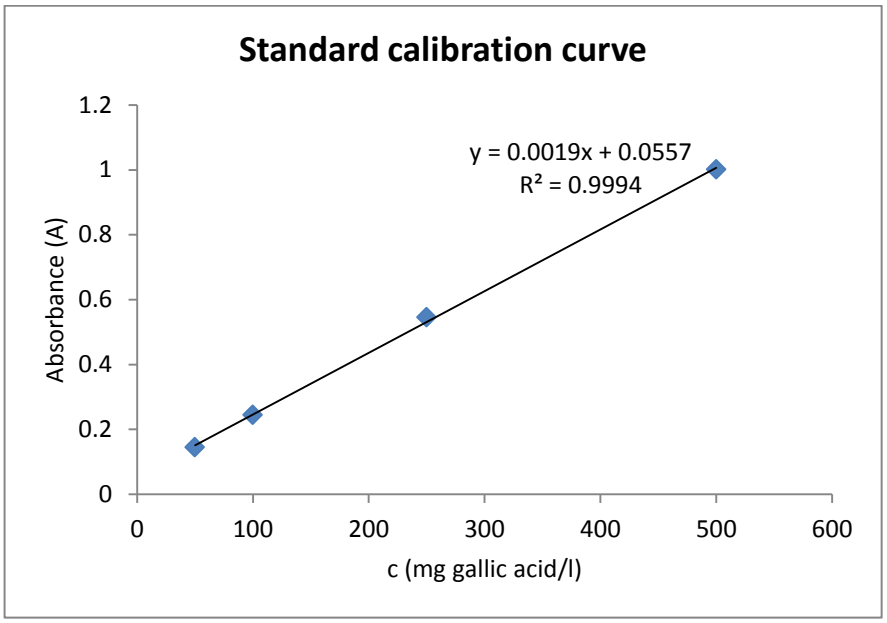

Figure 14: Calibration curve of gallic acid for FC

After successful identification of a calibration curve the samples were analyzed. Primarily bio-oil samples were dissolved in 3 ml ethyl acetate. This dilution was necessary because of the high viscosity of bio-oil. Subsequently, 20µl of this solution were diluted in 3 ml ethanol because non diluted samples exceeded the detection limit of the spectrophotometer. 20 µl of this solution were used as sample for FC. These diluted samples were mixed with 1.58 ml of water and 100 µl of FC reagent and stirred for 5 min. Afterwards sodium carbonate solution (300µl) was added, followed by 2 h of stirring at room temperature. For these samples the light absorbance was measured and the quantity of total phenols in bio-oil was consequently calculated in [g/g] of gallic acid equivalent (GAE). [49] The applied equation was adapted from Abdelhady et al. and is shown below. [50]

$$T = c * DF * \left(\frac{V}{M}\right) = c * DF * \frac{1}{\rho} \quad (4)$$

T is the total phenolic content in g GAE/ g bio-oil, c is the concentration identified according to calibration curve, DF the dilution factor and ρ is the density of bio-oil.

The quantity of phenols in bio-oil is tremendously significant, since phenolic compounds are responsible for the reactivity and stability of bio-oil. [49]

3.3.3.2 Molar mass determination of bio-oil by GPC

Gel permeation chromatography (GPC) was used for determination of molar mass distribution of bio-oil. Differentiation occurred based on hydrodynamic volumes of molecules. [51]

In Figure 15 the principle of GPC is explained. The columns contain a porous packing of pore size in the order of the hydrodynamic volumes of the analyzed polymer molecules. The fresh solvent is filtered and degased and subsequently enters the columns. A pump forces the mobile phase through intermediate capillaries into the injector, columns and finally detectors. The task of the injector is to add the sample into the high-pressure carrier stream. [52]

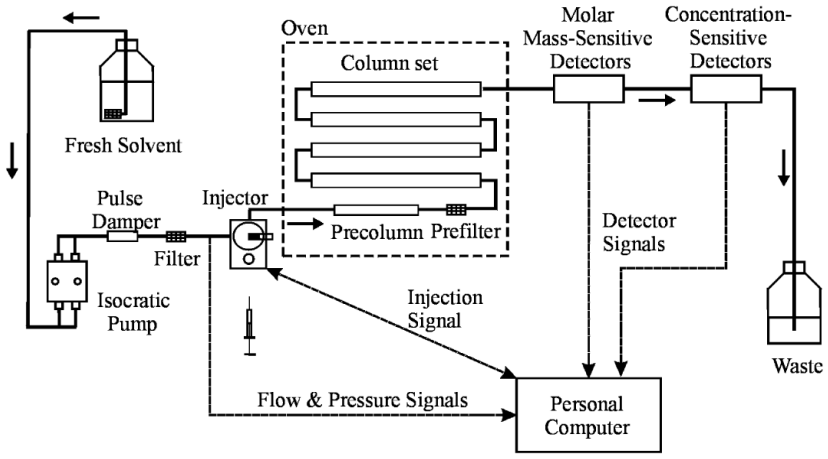

Figure 15: Schematic diagram of GPC [52]

Differently sized compounds elute through the columns with different velocities and emerge at the end of the chromatograph at different times. [51] The difference between low molar weight and high molar weight particles is measured by a detector. [52]

The number average molecular weight distribution (Mn) and the weight average molecular weight distribution (Mw) is calculated as a result of GPC according to the equations below. [53]

$$M_n = \frac{\Sigma M_i * N_i}{\Sigma N_i} \quad (5)$$

$$M_w = \frac{\Sigma M_i^2 * N_i}{\Sigma M_i * N_i} \quad (6)$$

The relation of these both values is presented by the PDI. [53]

$$PDI = \frac{M_w}{M_n} \quad (7)$$

GPC of this thesis was implemented with the device (Agilent/ model 1260 HPLC with a binary pump and diode array detector) situated in the Biochemistry Department at Aalto University. The first column was Phenogel 5u Linear/Mixed, Guard column 50x7.8 mm. Subsequently, the eluent passed through Phenogel 5u 10E3A, 300x7.8 mm. Finally the column Phenogel 5u 50 A, 300x7.8mm was applied. The eluent of the GPC analysis implemented as part of this thesis was THF Merck LiChrosolv® with a purity of >99.9%.

First calibration trials were run with polystyrene and THF. Organosolv lignin was dissolved in THF and MMD of it was measured. Bio-oil samples were also diluted in THF and tested by GPC. The MMD of organosolv lignin was the reference for bio-oils. Mn and Mw were calculated with Matlab.

3.3.3.3 Water content analysis by Karl-Fischer titration

Water content is a highly critical quality characteristic of bio-oil, which is mainly due to its influence on heating value and viscosity. In this study Karl-Fischer titration was performed for determination of water content mainly because of its accuracy, speed and high selectivity, respectively. [54] The principle of the method is a redox-reaction, as demonstrated in the equation below. [55]

$$SO_2 + I_2 + 2H_2O \leftrightarrow H_2SO_4 + 2HI \quad (8)$$

Sulfur dioxide was oxidized by iodine and the reaction consumes water [55]. The required titrant contained I_2, SO_2 and the base imidazole. The solvent was methanol-formamide. The sulfur trioxide formed methylsulfate salt of the base together with methanol. [56] The endpoint of the titration is controlled with a double platinum electrode or so called Karl Fischer electrode. [55] When the reactions had finished,

all water had been removed and the available iodine caused a drop in electrical resistance.

A device manufactured by Mettler Toledo (model DL 53) was used for Karl-Fischer titration of bio-oil produced during this thesis. Limitations of Karl-Fischer titration cannot be excluded in case of bio-oil, because of the variety of compounds (e.g. aldehydes, ketones, etc.) found in bio-oil. Nevertheless, according to Smets et al. the results of Karl-Fischer titration applied to pyrolysis oil were comparable to that of GC/MS-corrected azeotropic distillation. [54] Therefore, interference of bio-oil with Karl-Fischer titration was considered negligible in this study.

Standard calibration of Karl-Fischer was performed with a standard solution (water content 1%). Due to high density and viscosity bio-oil samples could not be injected directly. As a consequence, bio-oil was dissolved in a mixture of chloroform and methanol in a ratio of 3:1 v/v. The solvent mixture can dissolve almost all components of bio-oil, which was necessary to allow full access of the titrant to the bio-oil. This furthermore was required for an accurate reaction and therefore a correct titration and consequently determination of water-content of bio-oil. [1]

3.3.3.4 Total carbon content determination (TOC)

Total organic carbon (TOC) was determined for the solution of undegraded lignin and the aqueous phase. TOC determination is based on destruction of organic matter either by heat or chemical reactions. The carbon in the sample is converted to CO_2 and detected by NDIR. [57]

TOC was performed with the TOC-V CPH device manufactured by Shimadzu. As part of this thesis, TOC was performed for determining the efficiency of liquid-liquid-extraction. Higher TOC values correlated to higher residual quantities of dissolved lignin in the aqueous phase, indicating an incomplete extraction of organic compounds. For completion of the mass balance the residual C content (derived from organosolv lignin and equaling dissolved lignin) in H_2SO_4 and aqueous phase had to be known. The concentration of TOC was ascribed to the concentration of dissolved lignin, by considering the elementary composition of lignin.

3.3.3.5 Dissolved lignin concentration determination by UV

Based on the refraction of UV light of aromatic compounds, the lignin concentration in the aqueous phase was estimated. The light absorbance at 205 nm was indicative

for the aromatic compounds in the solution. The correlation of lignin to light absorbance is demonstrated in the equation below.

$$soluble\ lignin = \frac{A}{\varepsilon} * DF \quad (9)$$

A is the absorbance rate, DF is the dilution factor (300) and ε is the extinction coefficient (110 L/g). According to this equation the residual lignin in aqueous phase was determined and compared to the results of TOC.

3.3.3.6 BET-surface area of char

The surface area and porosity of char were analyzed by the Brunnauer-Emmett-Teller (BET) method. The purpose was to identify potential alternative applications of biochar produced during HTL. This thesis emphasized the current research focus on biochar as activated carbon source.

In advance to proceeding the char samples to the BET-device, they were grinded with a mortar. The samples were put into the oven over night. Subsequently, they were degased (at 150 °C for 1 h) by *micrometrics Flow Prep 060 Sample Degas System*. The sample's weight after degasification was relevant for the surface determination. The surface area, measured with *micrometrics TriStar II* apparatus, was based on the measurement of the monomolecular gas layer on the char particles due to gas adsorption. A density of 0.3 g/cm^3 was estimated for the samples, since the device required an approximate value for the density for calculation of the BET surface in m^2/g.

3.3.3.7 Photoacoustic infrared spectroscopy of bio-oil

Infrared spectroscopy is widely used for characterizing and analyzing the chemical features of synthetic and natural polymers. The fundamentals of this analysis are varying degrees of translation and rotation freedom of molecules. [58] Different bonds start to stretch, swing, bend and react to the absorbed energy at different wavenumbers leading to a differentiation between functional groups. [59]

The complex structure of bio-oil samples was analyzed with photoacoustic infrared spectroscopy (PA-IR). The device used for photoacoustic measurements was FTS 6000 spectrometer produced by BioRad combined with PA 301 photoacoustic detector by Gasera. The interferometer of this device was 896 interferometer. The PA-signals of bio-oil samples were finally normalized by the PA-IR signal at 1600 cm^{1}, indicative for aromatic skeletal vibrations. The clarification of degradation

reactions occurring during HTL required a reference spectrum of organosolv lignin, the bio-oil spectra could subsequently be compared to. Therefore organosolv lignin was also tested with PA-IR as a reference value. Baseline correction was performed with black carbon samples a priori to running bio-oil samples.

3.3.3.8 Elemental analysis of bio-oil

C, H, O, N and S contents in bio-oil, char, undegraded lignin and beech organosolv lignin were determined by elemental analysis (EA). The sample were therefore combusted at high temperature and carbon, present in the sample, was converted to carbon dioxide, hydrogen to water, nitrogen to nitrogen gas/ oxides of nitrogen and sulfur to sulfur dioxide. [60] Subsequently, these combustion products were swept out of the combustion chamber by an inert carrier gas. All gases passed through absorbent traps and only carbon dioxide, water, nitrogen and sulfuric dioxides were left. These products were finally detected and elemental composition was determined. [60]

Elemental analysis of this thesis was performed by the Chemistry Department of Aalto University in co-operation with the Department of Forest Products Technology. The used device was manufactured by Perkin Elmer (Model 2400 Series II CHNS Elemental Analyzer (230 V)). The operating gases were oxygen and helium.

In addition, selected samples were analyzed by the Frauenhofer-Institut fuer Angewandte Polymerforschung, IAP (Germany), who used a Flash EA 1112 Elemental Analyzer Series CHNS/O with Autosampler MAS200R from Thermo Finnigan.

In case of the samples measured at Aalto University no oxygen was measured by the device, but it was calculated back to 100wt%. In case of Frauenhofer-Insitut fuer Angewandte Polymerforschung IAP (Germany) the oxygen content of the samples was explicitly measured. This enabled the comparison of backcalculated oxygen content and measured oxygen content and consequently determine how reliable back calculation of oxygen content was.

3.3.3.9 Monte-Carlo Simulation of bio-oil at 290 °C

As a result of the current dearth of data on potential trends of bio-oil formation a Monte-Carlo Simulation was implemented in order to obtain a prognosis model for bio-oil formation at 290 °C for different retention times ranging from 10 to 35 min.

Primarily, a trend line (derived from the first experimental series) was identified with Excel. Subsequently, this line was used to calculate the bio-oil yields for different times. The times were assumed to be random, since they were mostly influenced by external drivers such as human reaction time etc. In addition it was assumed that times did not deviate more than 0.5 min to the set reaction times. With regard to this assumption the average times for 1492 random samples were determined and a 99%-confidence-interval was calculated. If the sample's time was within this interval, the related bio-oil yield was considered to be reliable and used for calculation of the overall average bio-oil yield.

Prognosis of bio-oil formation was implemented for 10, 20 as well as 30 min retention time. Finally this estimated average was compared to the empirical value and the deviation was analyzed.

4 Results and Discussion

4.1 Effect of reaction conditions on product yields

4.1.1 Calculation of isothermal times

As already mentioned in Chapter 3 reliable comparison of product yields obtained at 270°C, 290°C and 310°C required isothermal times. The first series of experiments (hold times of 10, 20 and 30 min) was performed to identify the heating trend of the reactor. The influence of the heating process on time increased with increasing reaction temperature. Temperature inclination was therefore detected every 30 sec and used for the calculation of isothermal times. The identified relation between isothermal times and hold times is listed in Table 4.

Table 4: Isothermal times

Temperature [°C]	Hold time 1st series [min]	Isothermal time 1st series [min]	Hold time 2nd series [min]	Isothermal time 2nd series [min]
270	10	12.1057	8	10.1057
	20	22.1057	18	20.1057
	30	32.1057	28	30.1057
290	10	15.29825	5	10.3198
	20	25.46279	15	20.27988
	30	35.61523	24.5	30.033
310	10	17.02715	3.5	10.09863
	20	27.13979	14	20.5215
	30	37.39055	23.5	30.14989

In Table 4 two different isothermal times are present. The first series of isothermal times (3rd column) was calculated from the initially applied hold programs (2nd column) and the second series included accurate isothermal times of 10 min, 20 min and 30 min (see 5th column). According to these isothermal times, the hold program of the second experimental series was adjusted (see 4th column).

4.1.2 Temperature influence on bio-oil and char formation

Temperature influence on bio-oil formation was analyzed by comparing bio-oil yields at 270 °C, 290 °C and 310 °C. Figure 16 visualizes the bio-oil yields in wt% obtained at 270 °C.

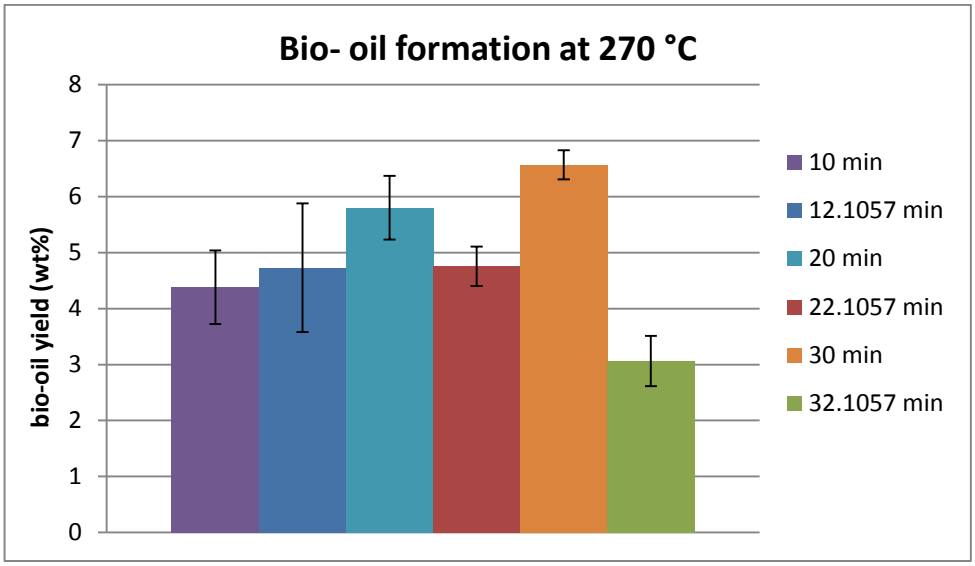

Figure 16: Bio-oil yields at 270 °C

In comparison to 290 °C (Figure 17) and 310 °C (Figure 18), the deviation of bio-oil yields indicated by the error bars in Figure 16 was higher at 270 °C. Especially experiments performed at shorter retention times differed in bio-oil yields, emphasizing the higher influence of reactor controlling at lower temperatures. The heating process, cooling process and the temperature fluctuation during the hold times were assumed to have a higher influence on bio-oil yields at lower temperatures. At 20 min and 30 min higher bio-oil yields were identified. Similar maxima were detected at 290 °C and 310 °C. Initial increase in bio-oil yields, successive decrease and final increase led to the assumption that condensation reactions were partially occurring to a higher degree than depolymerization reactions between 20 and 30 min. Ongoing degradation reactions caused the bio-oil yield to increase again at 30 min. The last reduction in bio-oil yield might be due to predominating condensation reactions compared to depolymerization reaction rates. The overall yields at 270 °C were lower than at 290 °C and 310 °C, never exceeding 7wt%. Figure 17 contrastively demonstrates the bio-oil yields obtained at 290 °C, emphasizing the inferiority of bio-oil yields of experiments at 270 °C.

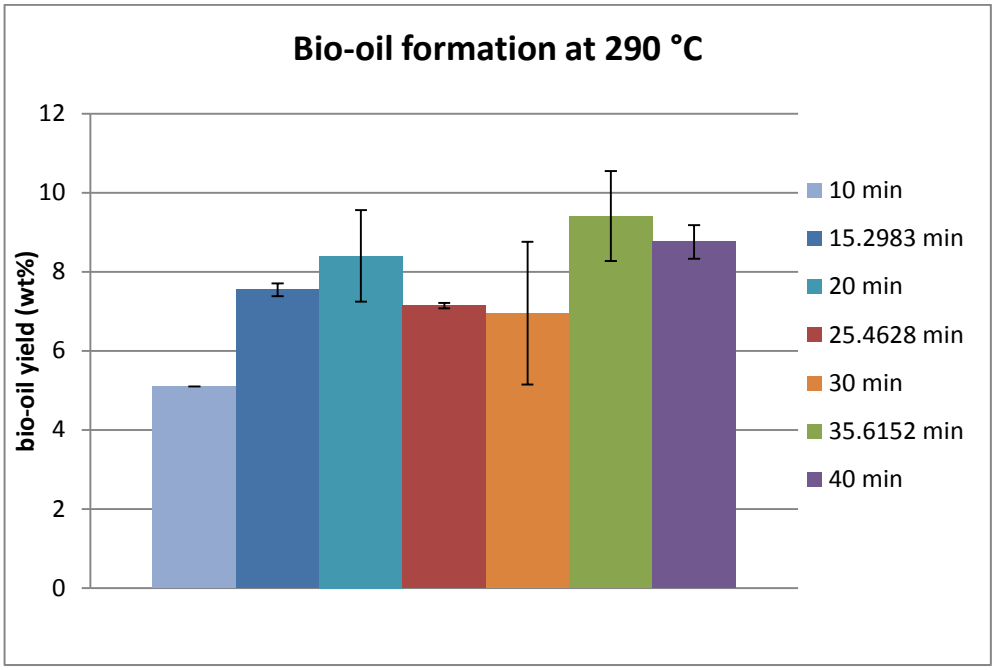

Figure 17: Bio-oil yields at 290 °C

Bio-oil formation trends at 290 °C were similar to results obtained at 270 °C. Nonetheless, due to higher reaction temperature the deviation in bio-oil formation decreased (except at 35 min). Two quantitative maxima (at 20 min and 35.62 min) were identified. At 35.62 min bio-oil yields even exceeded 10wt%. 290 °C was therefore considered superior for bio-oil formation, among the three temperatures tested.

Reliability of the data was proven by the high agreement of the results of this study with previous findings of Karagöz et al., who produced 8.6wt% of bio-oil out of lignin (alkaline). Their temperature was 280 °C and the retention time was 15 min, which were similar to 290 °C and 20 min of this thesis. [61]

Completion of the experimental series of this study required HTL at 310 °C (Figure 18).

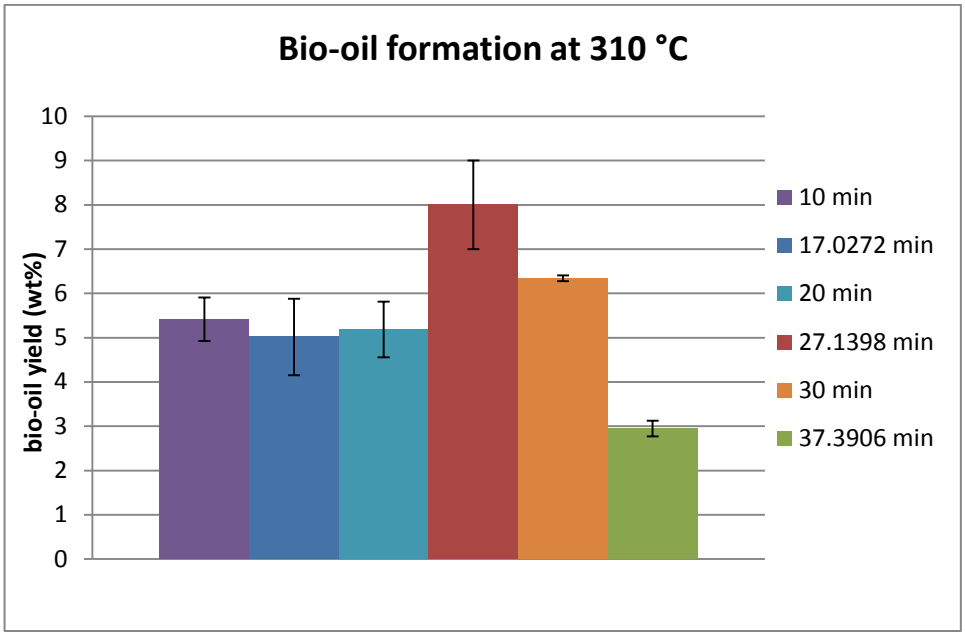

Figure 18: Bio-oil yields at 310 °C

In comparison to 270 °C and 290 °C, the bio-oil formation trend at 310 °C (Figure 18) was accelerated, meaning that the formation maxima at 310 °C were reached at earlier times. The first maximum was assumed to have occurred before detection had even started (earlier than 10 min). Potential acceleration was emphasized by the second formation maximum (at 27.14 min) which was 3 to 9 min earlier than in case of 270 and 290 °C, respectively.

In agreement to the assumption were findings by Kang et al. who stated that higher reaction pressure also increased the amount of H^+ or OH^- and consequently accelerated the hydrolysis leading to a faster formation of bio-oil. However, high pressure had also been reported to decrease the overall decomposition rate and be adverse to free-radical reactions, indicated by the identified decreases in bio-oil yields at 310 °C, after having reached a maximum at 290 °C. [20]

Figure 19 is summing up bio-oil formation trends at different temperatures, which have been previously discussed. It clearly emphasizes the maximum in bio-oil formation at 290°C. To elucidate the temperature influence on bio-oil formation, isothermal times at different temperatures were compared. Short retention times (10 min) were related to higher bio-oil yields at higher temperatures. At higher retention times (30 min) lower temperatures (e.g. 270 °C) favored bio-oil formation, which was outlined by the increase in bio-oil formation from 10 to 30 min (from 4.38wt% to 6.57wt%).

In case of 270 and 310 °C, results indicated an increasing bio-oil production with increasing retention times. In contrast the coherency between bio-oil-formation and time in case of 290 °C showed slight inconsistency, since a decrease in bio-oil formation at 30 min (6.96wt%) following a maximal value at 20 min (8.40wt%) was detected. The discrepancy was explainable, since one experiment at 290 °C and 30 min resulted in very low bio-oil yields, decreasing the overall average value. The second experiment succeeded in producing 8.77wt% bio-oil, indicating an increase in bio-oil formation with increasing time from 8.40wt% (20 min) to 8.77wt% (30 min) at 290 °C. The accuracy of the second experiment at 290 °C and 30 min (8.77wt%) was emphasized by the bio-oil yield obtained at 35 min (8.76wt%), which consequently confirmed the hypothesis, that bio-oil yields increased with increasing retention times at all three temperatures tested (see Figure 19).

However, the overall yields (<10wt%) were comparably low since catalytic liquefaction of organosolv lignin results in bio-oil yields of 12.95wt% to 18.5wt%. [62]

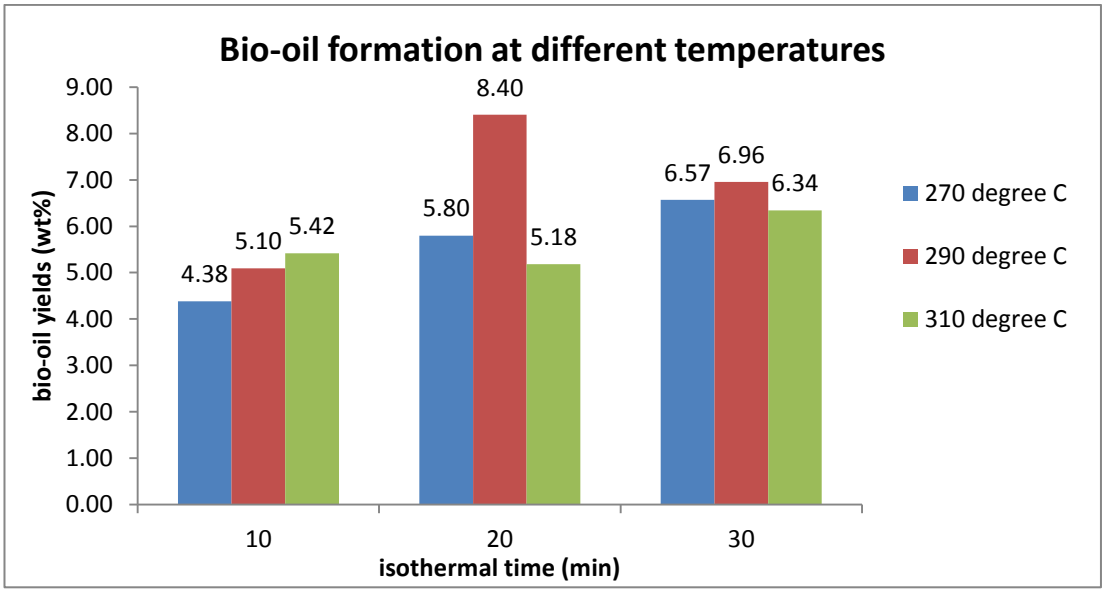

Figure 19: Comparison of bio-oil trends at different temperatures

In addition to degradation reactions and solubilizing of lignin to bio-oil, condensation reactions occurred during HTL resulting in char formation. At lower temperatures char formation was constant with increasing retention times. Contrastively, char yields tremendously increased with higher retention times at 310 °C. The minimal decrease of char in case of 270 °C (20 min) and 290 °C (20 min) was due to losses occurring during separation, since filtration only roughly separated the products (Figure 20).

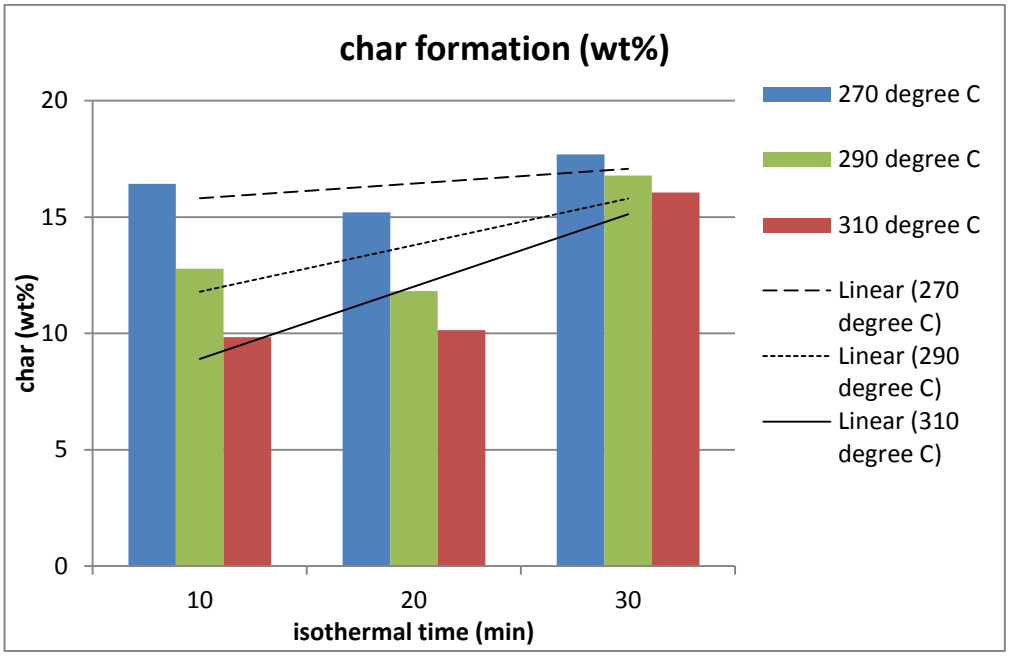

Figure 20: Char formation

Based on trend line formation, increasing retention times at high temperatures were successfully linked to highly increasing char formation. Temperature influence on char production was previously explained by Sarkanen et al. who stated that condensation reactions occurred during acidolysis treatment. The reactions involved benzyl cations and as temperature raised condensation reactions likely led to linkages between these benzylic carbon atoms and aromatic nuclei. Due to the condensation reactions polylignols formed to an increasing extend. [63]

The contradicting high char values at 270 °C and 290 °C were due to inefficient separation methods in case of low-temperature products. The discrepancy was explained by the presence of undegraded lignin in char, perhaps misleadingly identified as such.

4.2 Characterization of bio-oil

4.2.1 Water content determination

Water content was measured for three selected samples. The measured values were below 3.5wt%, which correlated to previous findings by Huber et al. who reported a water content of 5wt% [31]. It was found that the water content decreased with increasing retention time and was reduced from 3.5wt% at 20 min retention time (at 310 °C) to 3.3wt% at 30 min (at 310 °C).

According to Sarkanen and Schuech the water loss occurred due to condensation reactions of C-α with C-5 and C-6. It is common research knowledge that condensation reactions accumulate with increasing temperature and retention time, explaining the measured decrease in water content from 20 min to 30 min of this study. [63]

4.2.2 Molar mass distribution by GPC

A key tenet for bio-oil characterization was its molar mass distribution (MMD), identifying how effectively lignin degraded into low molar mass compounds during HTL. Figure 21 demonstrates MMD of bio-oils obtained at 270 °C.

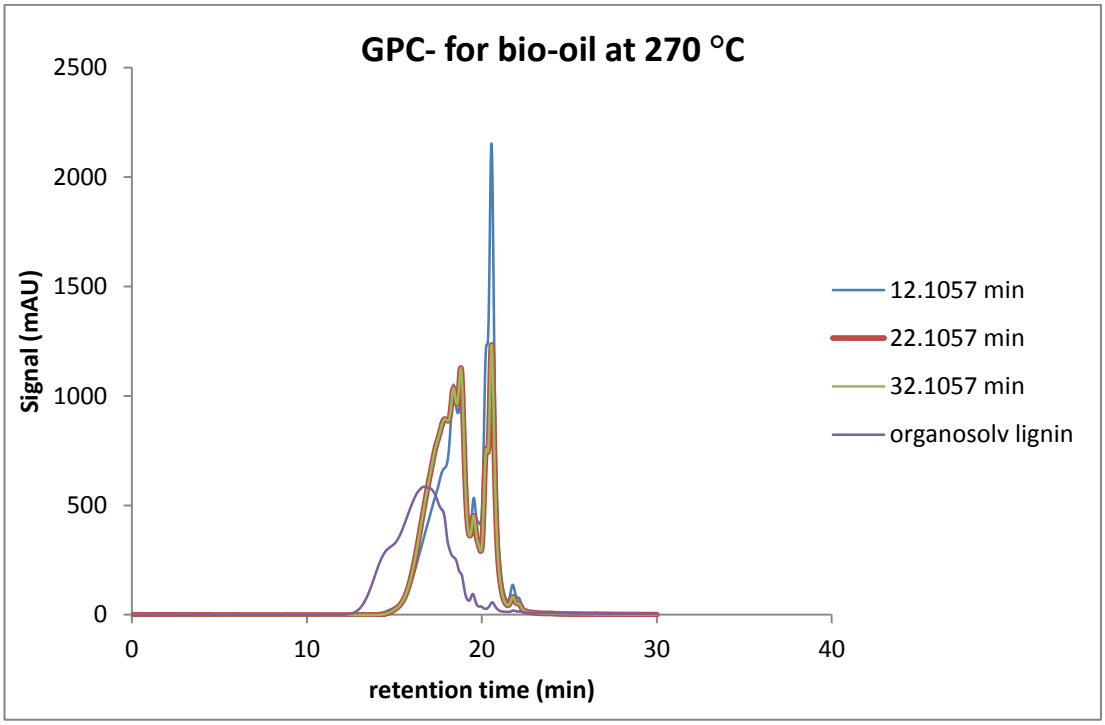

Figure 21: GPC results at 270 °C

The violet chromatogram of organosolv lignin in Figure 21 is included as a reference (Mw 3,433 g/mol; Mn 1,191 g/mol). The table below (Table 5) demonstrates the MMD of bio-oils at 270 °C.

Table 5: Mw and Mn values for 270 °C

	isothermal time [min]					
[min]	10	12	20	22	30	32
Mw [g/mol]	328	362	280	289	311	263
Mn [g/mol]	232	236	218	218	224	212
PDI	1.41	1.53	1.28	1.32	1.38	1.24
bio-oil yield [wt%]	4.38	4.73	5.80	4.17	6.58	3.06

Mw of all bio-oil samples was relatively low compared to organosolv lignin, leading to the conclusion that mostly monomers and dimers were present in bio-oil. Successful lignin degradation in absence of a high degree of repolymerization reactions was a reasonable interpretation of the discernible decrease in Mw at such low temperatures. This finding correlated to the results of numerous other works which reported the presence of low-molecular weight material in the hydrolysis liquor of lignin [63]. The coherency between the decrease in Mw with increasing retention time and bio-oil yields (wt%) is demonstrated in Figure 22.

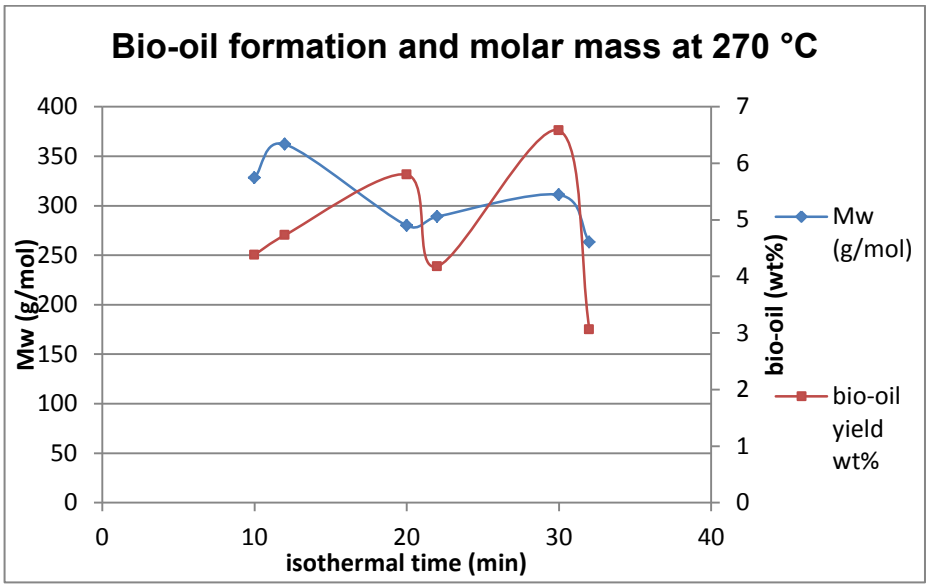

Figure 22: Relation of bio-oil yield and molar mass distribution at 270 °C

At 10 and 12 min molar masses above 328 g/mol were observed, indicating a lower degree of degradation at short retention times (compared to >20 min). The first maximum in bio-oil formation at 20 min (Figure 22) correlated to low Mw, indicative for a high degree of decomposition of lignin. This ongoing decomposition was explained by reports of Sarkanen et al. claiming that degradation of lignin even occurred by action of water at elevated temperatures. These conditions liberated compounds in lignin, which dissolved in the aqueous solution and consequently rendered the solution acidic. Due to these mild acidic conditions lignin degradation was further catalyzed. [63]

With respect to this explanation, Lundquist et al. reported a more detailed reaction route in weak acidic conditions than Sarkanen et al. According to Lundquist et al., homolysis reactions degraded lignin in weak acidic conditions. Homolysis of C-β-O-bonds occurred, resulting in the formation of quinonmethide structured

intermediates. Lundquist et al. found that the transitional state of quinonmethide formation was followed by radical-exchange reactions or radical coupling, as demonstrated in the figure below. [64]

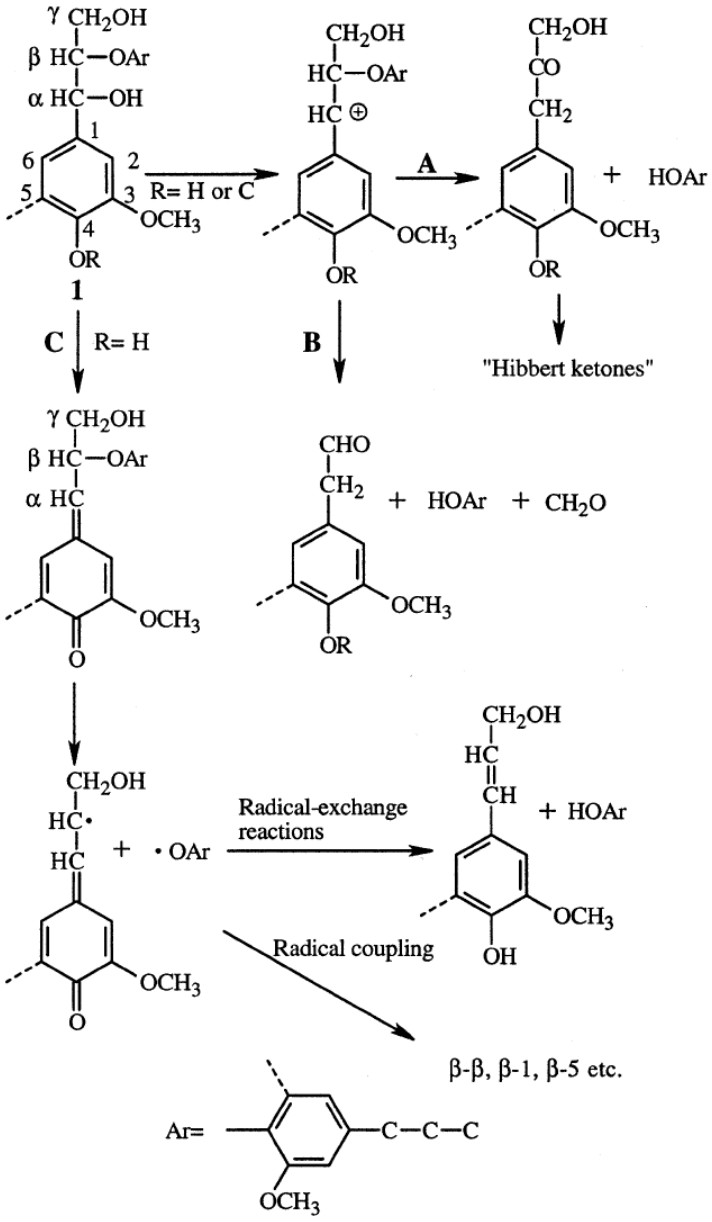

Figure 23: Acid catalyzed lignin degradation [64]

Reaction pathway A and B in Figure 23 indicate cleavages of β-ethers, which occur in slightly to strongly acidic conditions. Benzylic carbocations form subsequently to β-ethers cleavage. [64] These reaction routes (A, B) were not relevant for HTL of this thesis because of the weak acidity that was measured (pH 3-5).

In addition to MMD of bio-oils obtained at 270 °C, the molar masses at 290 °C were determined as well and compared to results of the 270 °C experimental series. Figure 24 demonstrates the GPC results for 290 °C.

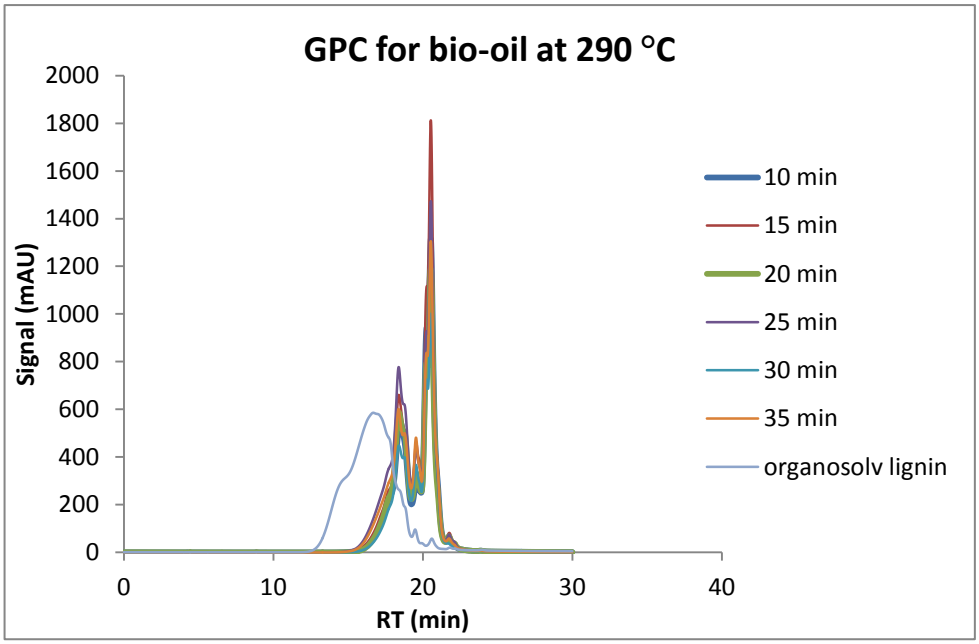

Figure 24: GPC results 290 °C

Figure 24 presents the chromatogram at 290 °C, which detected mainly monomers, dimers and trimers (also see Table 6). MMD at 290 °C was similar to MMD at 270 °C. The data of this study was in agreement with findings by Kang et al., who stated that phenolic monomers and dimers were obtained at moderate temperatures and short retention times [20].

At 20 min, where the first maximum in bio-oil formation at 290 °C was reached, the Mw was low (see Figure 25 and Table 6). Mw subsequently increased again indicating the start of condensation reactions.

Table 6: Mw and Mn values for 290 °C

	isothermal time [min]					
[min]	10	15	20	25	30	35
Mw [g/mol]	271	274	278	317	266	329
Mn [g/mol]	215	213	220	232	213	238
PDI	1.26	1.28	1.26	1.36	1.25	1.38
bio-oil yield [wt%]	5.09	7.54	8.40	7.14	6.95	8.76

The experiments at 290 °C revealed a relatively constant degree in degradation (no significant Mw change from 10 to 20 min), contradicting the initially high decrease found at 270 °C. This indicated that at 290 °C decomposition of lignin had reached

its maximum already before 10 min, suggesting an acceleration of degradation with increasing temperature.

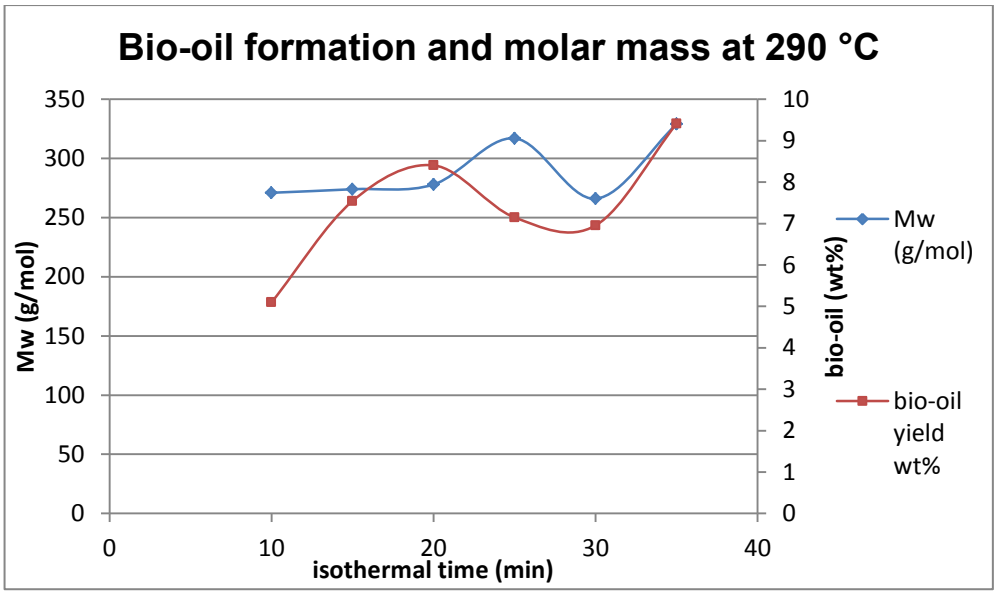

Figure 25: Relation of bio-oil yield and molar mass distribution

The last inclination in Mw in Figure 25 was related to ongoing condensation reactions, forming products with higher Mw. Finally, MMD determined at 270 °C and 290 °C were compared to results of molar masses at 310 °C (Figure 26).

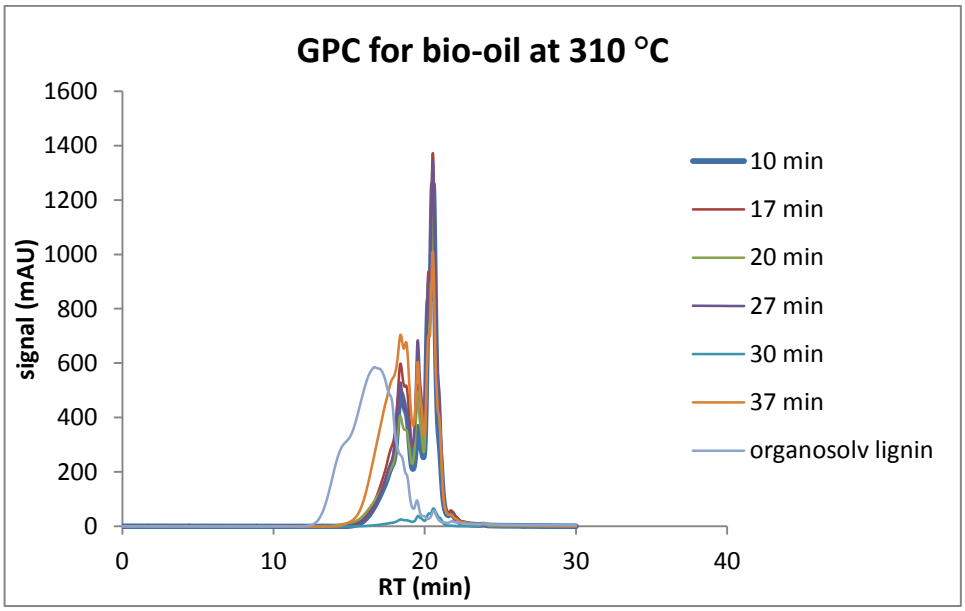

Figure 26: GPC results for 310 °C

The signals in Figure 26 were indicative for monomers, dimers and trimers. MMD analyzed at 310 °C (see Table 7) was comparable to previous findings obtained at 270 °C and 290 °C.

Table 7: Mw and Mn values for 310 °C

	isothermal time [min]					
[min]	10	17	20	27	30	37
Mw [g/mol]	297	309	309	292	267	280
Mn [g/mol]	221	224	219	223	180	225
PDI	1.34	1.37	1.41	1.31	1.48	1.24
bio-oil yield [wt%]	5.41	4.96	5.18	8	6.34	2.94

The increase of Mw from 30 min onwards was related to an increasing degree of ongoing condensation reactions. Figure 27 outlines a slight decrease in Mw after having reached the maximum in bio-oil formation at 27 min. The slight increase of Mw detected after 30 min (310 °C) was comparable to findings at 290 °C but deviated from results obtained at 270 °C. Based on this data the conclusion was reasonable that condensation reactions did not dominate over depolymerisation reactions at low temperatures (270°C).

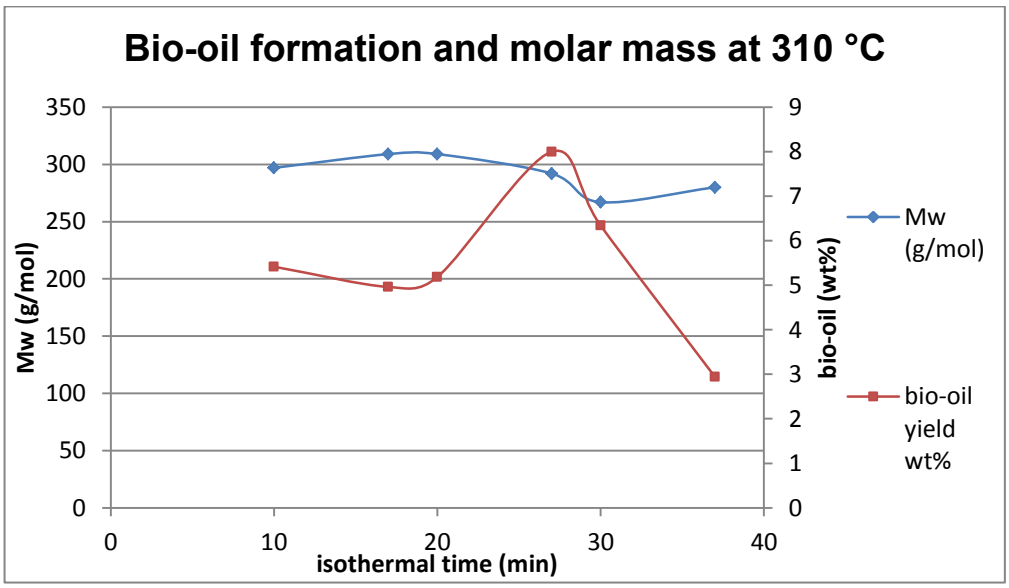

Figure 27: Relation of bio-oil yield and molar mass distribution at 310 °C

Building from the knowledge that depolymerization and condensation reactions were occurring simultaneously during HTL, the reaction rate of depolymerization in case of 270 °C and >30 min still overweighed the reaction rate of condensation reactions. In case of 290 °C and 310 °C the reaction rates of condensation reactions already predominated the reactions rates of depolymerization. This was highlighted by the

final decrease in Mw in case of 270 °C (see 32 min in Figure 22) compared to the starting increase of Mw in case of 290 °C (see 35 min in Figure 25) and 310 °C (see 37 min in Figure 27).

Nevertheless, with regard to the degree of decomposition all three temperatures demonstrated comparable results, with their lowest Mw ranging from 267 g/mol (310 °C) to 266 g/mol (290 °C) and 263 g/mol (270 °C).

4.2.3 Results of elemental analysis

The elemental composition of bio-oil was primarily required for identification of temperature and time influence on C, H, N and O contents. Secondly, EA was required for HHV calculations. Table 8 presents the results of elemental analysis performed at Aalto University (O was back calculated) and the Frauenhofer-Institut fuer Angewandte Polymerforschung IAP (O explicitly measured). The results measured by the IAP are written in bold (20 min of all temperatures). With respect to this data, back calculation of O content proved to be an accurate alternative to explicit measurement of O content.

Table 8: Elemental analysis of bio-oil measured

Temperature [°C]	Time [min]	C [%]	H [%]	N [%]	S [%]	O [%]
270	10	62.54	6.52	0.20	0.00	30.74
270	**20**	**62.64**	**6.36**	**0.16**	**0.00**	**31.12**
270	30	63.07	6.90	0.26	0.00	29.77
290	10	63.17	6.53	0.28	0.00	30.02
290	**20**	**62.53**	**6.44**	**0.14**	**0.00**	**30.83**
290	30	62.92	6.50	0.25	0.00	30.33
310	10	62.48	6.63	0.16	0.00	30.73
310	**20**	**62.88**	**6.39**	**0.13**	**0.00**	**30.38**
310	30	62.85	6.69	0.18	0.00	30.28
lignin		62.54	5.91	0.25	0.00	30.85

Table 8 demonstrates that 10 min retention time at 270 °C (C content of 62.54wt%) and 310 °C (C content of 62.48wt%) were clearly too short for discernible changes in elemental composition of lignin (C content 62.54wt%). Contrastively, EA led to the

conclusion that the entire lignin structure was preserved although significant depolymerization had occurred according to MMD. This depolymerization might be due to the scission of α- and β-O-4 bonds, which were attacked most likely under acidic solvolysis [63]. If water content in bio-oil was considered, EA slightly changed as shown in Table 9. An average water content of 3.0.wt% in case of bio-oil and 1.67wt% of water content in case of organosolv lignin were taken into account. The calculation is shown in the Annex.

Table 9: Elemental composition in water free condition

Temperature [°C]	Time [min]	C [%]	H [%]	N [%]	S [%]	O [%]	total [%]
270	10	64.44	6.19	0.21	0.00	29.17	100
270	**20**	64.32	6.03	0.16	0.00	29.49	100
270	30	64.83	6.57	0.27	0.00	28.33	100
290	10	65.03	6.20	0.29	0.00	28.49	100
290	**20**	64.51	6.11	0.14	0.00	29.23	100
290	30	64.80	6.17	0.26	0.00	28.77	100
310	10	64.35	6.30	0.16	0.00	29.19	100
310	**20**	65.01	6.06	0.13	0.00	28.80	100
310	30	64.69	6.36	0.19	0.00	28.77	100
lignin		64.14	5.72	0.26	0.00	29.88	100

Table 9 reveals an increasing carbon content with increasing retention times (compare 10 min and 30 min). The inconsistency at 290 °C was related to the overall low change in composition. With respect to the data of this thesis it was concluded that dramatically higher temperatures were required for significant changes of EA as reported by literature.

Ngyuen et al. used kraft lignin for the production of bio-oil by thermochemical conversion of lignin in near-critical water conditions (350 °C and 25 MPa). Their bio-oil contained 74.2wt% C, 16wt% O and 6.9wt% H. [65]

Barbier et al. found 73wt% of C and 20wt% of O, respectively, after 5 min retention time at 370 °C [66]. Despite the superior data reported by literature, HTL of this study was still considered successful since it already indicated the trend suggested by literature (increase in C content etc.).

Subsequently to EA, HHV was calculated in [kJ/g] according to equations proposed by Mahler, Boie and Gumz [67]. The C, N, H, S and O contents were included in the equation as mass fraction and considered in water free conditions. The applied equations are listed below.

Mahler: $\Delta H = 34.07 * C + 144.4 * H - 12.56 * (O + N)$ (10)

Boie: $\Delta H = 35.160 * C + 116.22 * H - 11.090 * O + 6.28 * N + 10.465 * S$ (11)

Gumz: $\Delta H = 34.03 * C + 124.31 * H - 9.836 * O + 6.278 * N + 19.09 * S$ (12)

Table 10: HHV of bio-oil samples in water free conditions

Temperature [°C]	Time [min]	Mahler [kJ/g]	Gumz [kJ/g]	Boie [kJ/g]
270	10	27.46	26.63	26.76
270	20	26.89	26.36	26.49
270	30	27.98	27.30	27.46
290	10	27.49	26.92	27.05
290	20	27.11	26.55	26.68
290	30	27.34	26.78	26.90
310	10	27.33	26.72	26.87
310	20	27.26	26.71	26.83
310	30	27.58	26.95	27.10
lignin		26.33	25.91	26.02

The energetically most valuable bio-oil (with respect to its HHV) was obtained at 270 °C and 30 min (27.98 kJ/g calculated by Mahler). In addition, 310 °C and 30 min (27.58 kJ/g calculated by Mahler) was also superior to other experimental settings. The most remarkable evidence for successful lignin valorization via HTL was that HHV of all bio-oils exceeded the initial HHV of organosolv lignin (26.33 kJ/g according to Mahler) (Figure 28).

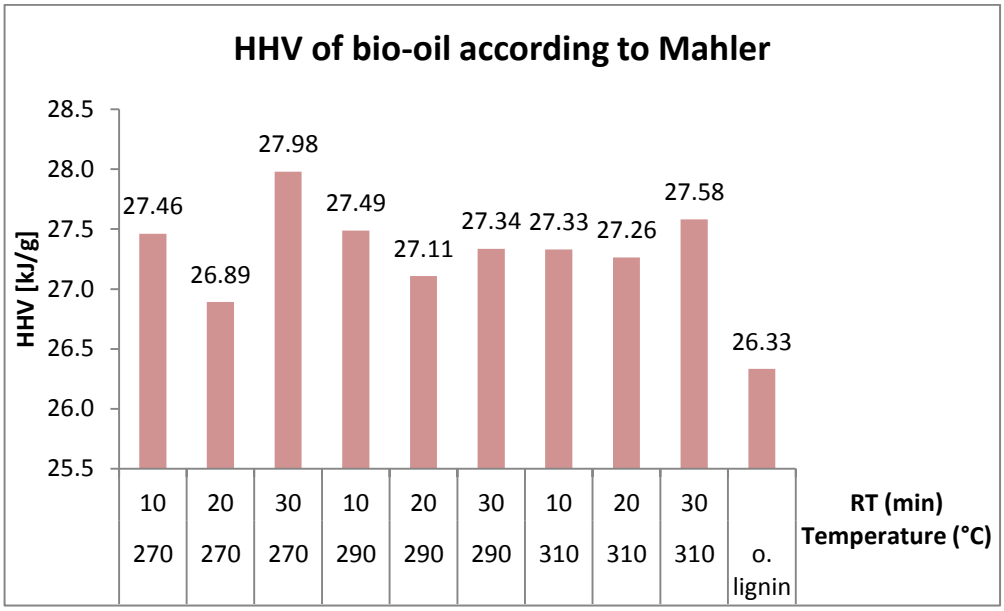

Figure 28: HHV of bio-oil calculated according to Mahler

Most compelling, however, was the decreasing HHV at 20 min of all temperatures tested. This degree of deviation decreased with increasing temperature. Future research therefore has to determine the validity of this decrease by evaluating HHV of bio-oil samples with bomb calorimeter. With respect to the current knowledge, it could not be excluded that the inconsistency in HHV was a result of the calculation of HHV from EA based on average water contents.

4.2.4 Phenolic content of bio-oil

The FC method was applied for the identification of the influence of pressure, temperature and retention time on the total phenolic content in bio-oil.

Figure 29 demonstrates how temperature and time influenced the quantity of total phenols in bio-oil. Phenolic content in bio-oil increased with increasing retention time. This finding was in high agreement with previous research implemented by Pinkowska, reporting that the highest phenolic contents were measured at the longest retention time [68].

Overall lower temperatures (270 °C) led to low quantities of phenolic content, with a dicernible increase in the quantity of total phenols from 10 to 20 min (from 0.068 to 0.11 g GAE/g bio-oil). At higher temperatures (310 °C) the overall change with increasing retention time was limited. Total phenolic content ranged from 0.113 to 0.12 g GAE/g bio-oil.

The highest phenolic contents of all three temperatures tested were found at moderate temperatures (290 °C), with values even exceeding 0.157 g GAE/g bio-oil and finally reaching 0.191 g GAE /g bio-oil (see Figure 29).

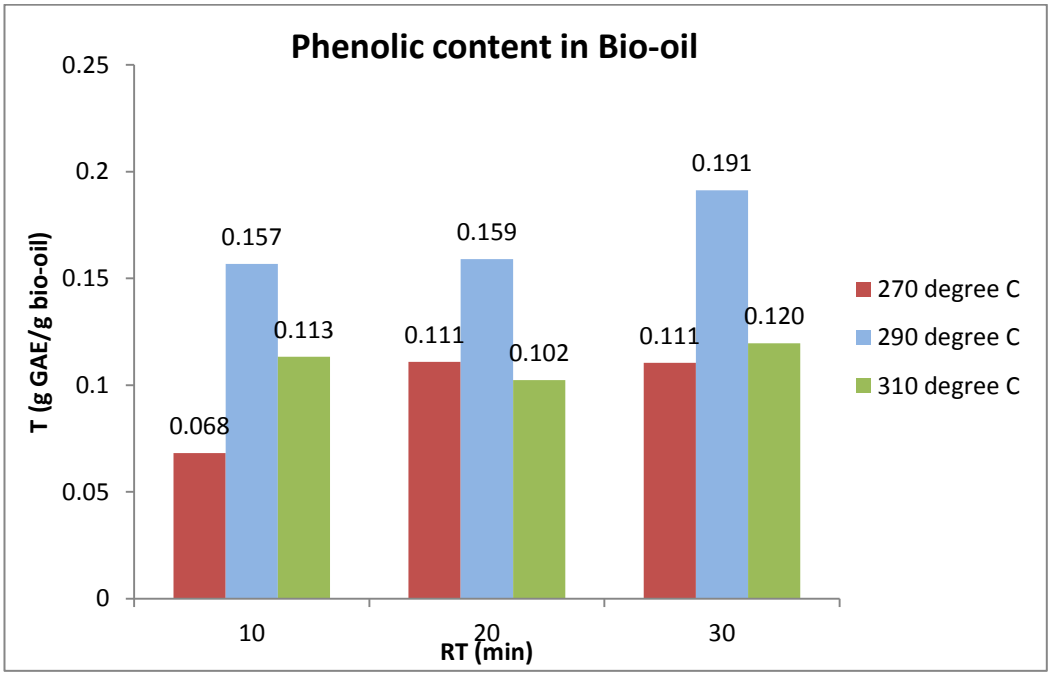

Figure 29: Phenolic content in bio-oil

The quantity of total phenolic content is very likely also expressed as wt% GAE, as it is suggested by Rover et al [49]. The table below demonstrates the relation between g GAE/ g bio-oil and wt% GAE.

Table 11: Temperature and time dependence of phenolic content in bio-oil

Temperature [°C]	time [min]	g GAE/ g bio-oil	wt% GAE
270.00	10.00	0.068	6.82
	20.00	0.111	11.09
	30.00	0.111	11.05
290.00	10.00	0.157	15.67
	20.00	0.159	15.90
	30.00	0.191	19.12
310.00	10.00	0.113	11.33
	20.00	0.136	13.64
	30.00	0.120	11.96

These results were in agreement with findings by Rover et al, who reported a total phenolic content of 25.8wt% GAE to 29.5wt% GAE (pyrolysis oil was tested) [49].

With regard to the quantification of hydroxyl aromatic compounds in bio-oil the total phenolic content was related to Mw of bio-oil. Figure 30 demonstrates the relation between change in total phenolic content (wt% GAE) and molar weight.

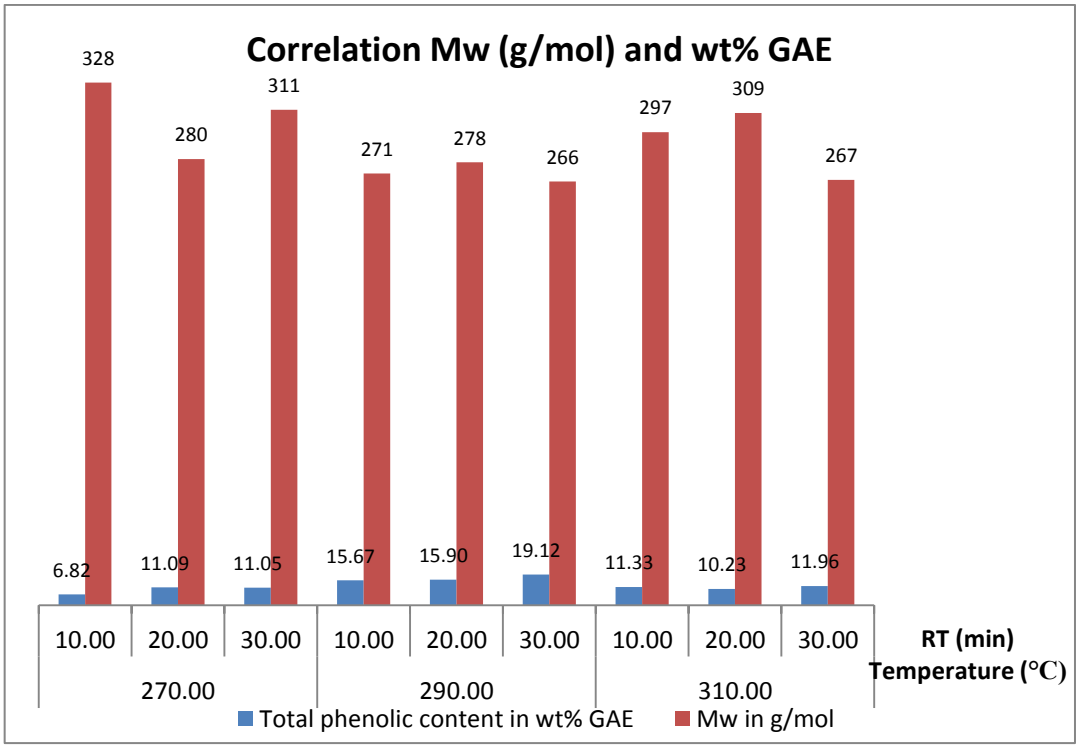

Figure 30: Relation Mw and total phenolic content

The identification of a reasonable relation between total phenolic content and Mw was compelling. Several explanations were possible, of which one was a linkage between increasing phenolic contents and decreasing Mw (compare 310 °C 20 to 30 min; 290 °C 20 to 30 min and 270 °C 10 to 20 min). Contrastively, an increase in Mw was related to a decrease in phenolic content. However, there was a certain inconsistency in this trend (see 290 °C 10 to 20 min), making a finer-grained approach to the relation between Mw and phenolic content necessary.

4.2.5 Degradation of lignin in aqueous phase

Assumptions on how lignin degraded at elevated temperatures and pressures in aqueous phase were performed with regard to the results of TOC and UV analysis. The structure of original lignin was broken during HTL and lignin content in water was therefore named “lignin equivalent” in the figure below. Deviations between UV

and TOC measurements were related to the calculation of dissolved lignin from TOC because Mw of lignin was taken from literature. Figure 31 demonstrates the lignin equivalent content in aqueous phase.

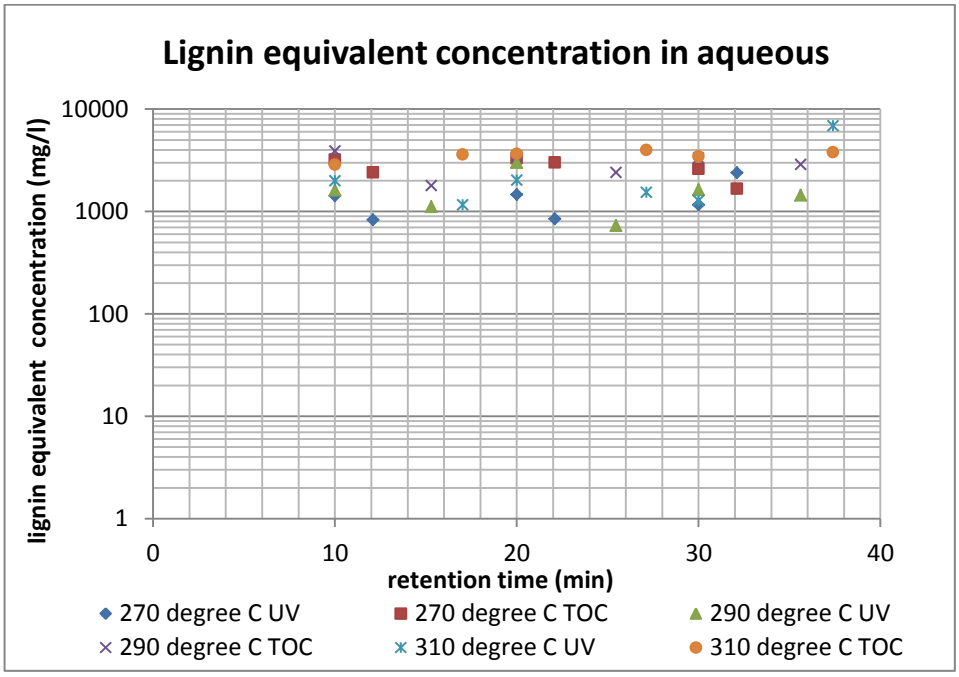

Figure 31: Lignin equivalent concentration in aqueous phase

Sarkanen et al. described the hydrolysis of lignin in water as shown in the equation below. Their precursor was wood, but it was assumed that lignin behaved comparably. [63]

$$wood \xrightarrow{hydrolysis} solubilized\ lignin\ fragments \xrightarrow{hydrolysis\ and\ hydrogenolysis} stabilized\ lignin\ fragements$$

The partial breakdown of lignin by reactions with H^+ and OH^- (hydrolysis) produced larger fragments. These fragments were soluble in water and consequently diffused into the aqueous phase, explaining why TOC was detected after all. Acidity of the solution reinforced further degradation. The solubilized lignin fragments were degraded to monomers, dimers and trimers, as previously described by GPC results of this study. These compounds were later found in bio-oil and were consequently extracted from the aqueous phase. The described stabilization of lignin fragments referred to condensation reactions. [63]

Nevertheless, the relatively high lignin equivalent contents in aqueous phase of this study (see Figure 31), led to the conclusion that the chosen extraction method can

be improved since there was still soluble lignin in the water phase although it should have been extracted as bio-oil with ethyl acetate. Ethyl acetate was not fully extracting the organic compounds and future research has to test the efficiency of other extraction solvents (e.g. diethyl ether).

4.2.6 Results of PA- IR for identification of functional groups

The PA-IR spectra of all bio-oil samples showed absorption bands at similar wavenumbers but with deviating intensities. The figure below demonstrates the PA-IR spectra of bio-oils obtained from the series at 310 °C (Figure 32). Organosolv lignin was always listed as a reference value to identify the influence of HTL.

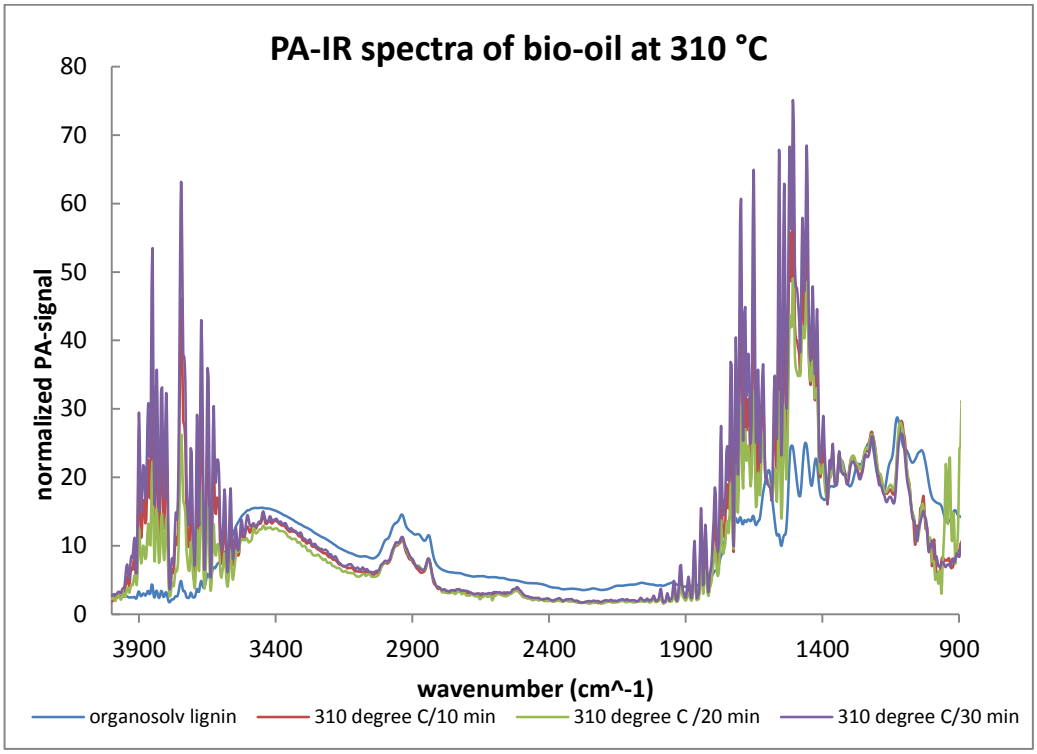

Figure 32: Normalized PA-IR spectra of bio-oil for 310 °C

Figure 32 emphasizes that HTL caused changes in the aromatic structure of organosolv lignin, because significant differences in band intensities were revealed from 3400 cm^{-1} to 4000 cm^{-1} as well as from 1720 cm^{-1} to 1100 cm^{-1}. Within these ranges the band intensities of bio-oils had highly increased and even exceeded the absorption rates of organosolv lignin. This was also highlighted by Figure 33, showing the peak ratios of bio-oils (obtained from various retention times) to organosolv lignin. According to their band intensities bio-oils obtained from shorter retention times (10 min and 20 min) at higher temperature (310°C) had already undergone significant changes in chemical features. However, band intensities

revealed negligible changes occurring from 10 min to 20 min. The most pivotal change in the aromatic structure of initial organosolv lignin occurred at 310 °C and 30 min, as already demonstrated in Figure 32.

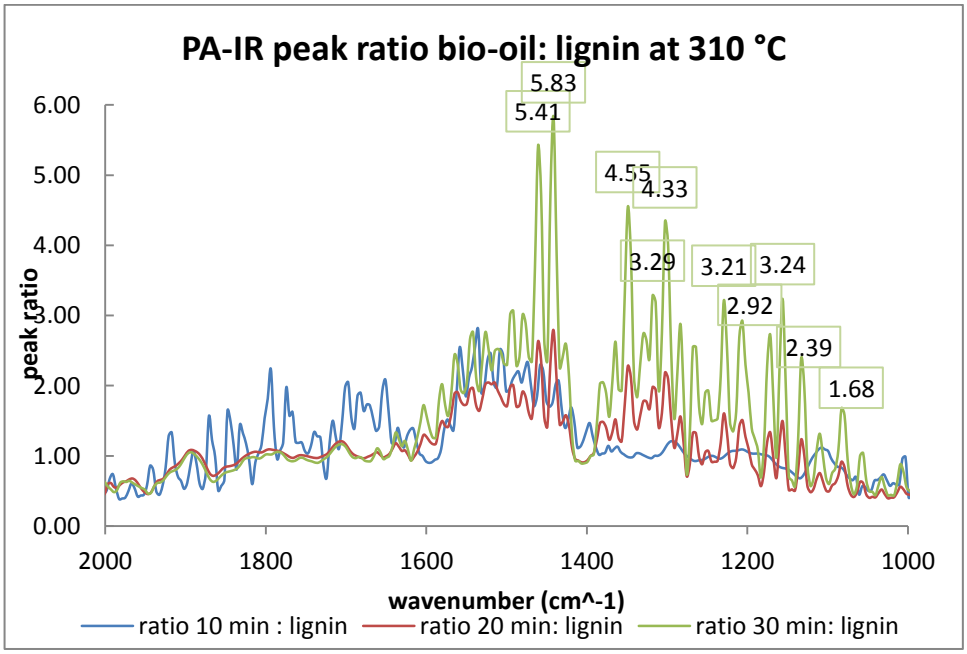

Figure 33: PA-signal ratios at 310 °C

Subsequently, the focus was set on band intensities from 1720 cm^{-1} to 1100 cm^{-1} and the related identification of band origins (more detailed bands are shown in Figure 34).

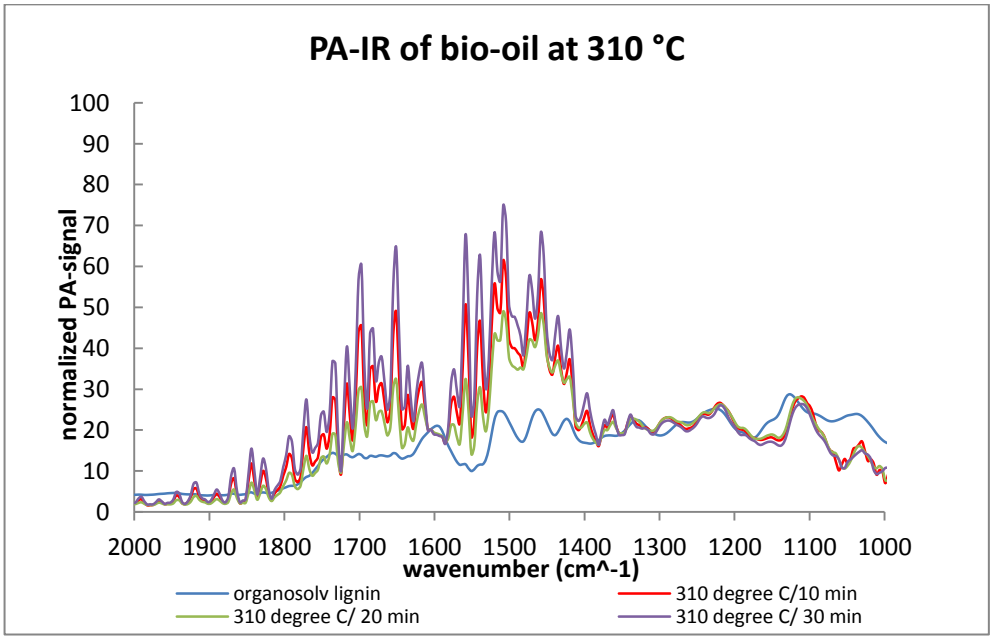

Figure 34: PA-IR spectra of bio-oil - Zoom in at 1000 - 2000 cm^{-1}

Figure 34 reveals higher band intensities of bio oil at 1420 and 1508 cm^{-1}, indicating aromatic skeletal vibrations. Bio-oil obtained after 10 min at 310 °C demonstrated more intense peaks than after 20 min. However, their deviation was low (compare 1420 cm^{-1}), leading to the assumption that after 10 and 20 min changes in the aromatic structure were comparable. Nonetheless, after 30 min, the most discernible band was detected, elucidating the conclusion that with increasing retention time more significant changes in the aromatic structure occurred. The band intensities at 1520 and 1540 cm^{-1}, indicative for C=C bonds of aromatic compounds, led to the assumption that their presence increased in bio-oil. The increasing presence of C=C bonds of aromatic compounds in bio-oil is in agreement with the proposed reaction pathway and intermediates by Lundquist et al. described above [64]. The peaks at 1620, 1651, 1675 and 1680 cm^{-1} were related to C=C stretching of alkenes [69]. The increasing presence of ketones and aldehydes was emphasized by the high band intensities from 1697 to 1700 cm^{-1}, indicating C=O stretching of ketones and aldehydes [69]. At the same time, the increasing presence of unconjugated ketone and carbonyl groups in bio-oil compared to organosolv lignin with increasing retention time was indicated by the band at 1716 cm^{-1}, originating from carbonyl stretching [63]. The increasing band intensities ranging from 3100 to 3700 cm^{-1} were related to OH-stretching, which was primarily, assumed to be related to OH-groups being hydrogen bonded to water molecules. Secondly, this OH-stretching indicated the presence of phenols and alcohols in bio-oil. [70]

However, identification of functional groups according to IR spectra was limited to a certain extent, since lignin and bio-oil contained a high number of different organic compounds, whose absorbance bands interfered with each another, hindering interpretation. [63]

4.3 Analysis of char

The surface area of char was analyzed to identify the influence of temperature and retention time on the quality of char produced. The aim was to determine, if biochar can be used as activated carbon source. The BET-surface area of bio-char obtained from HTL is shown in Figure 35.

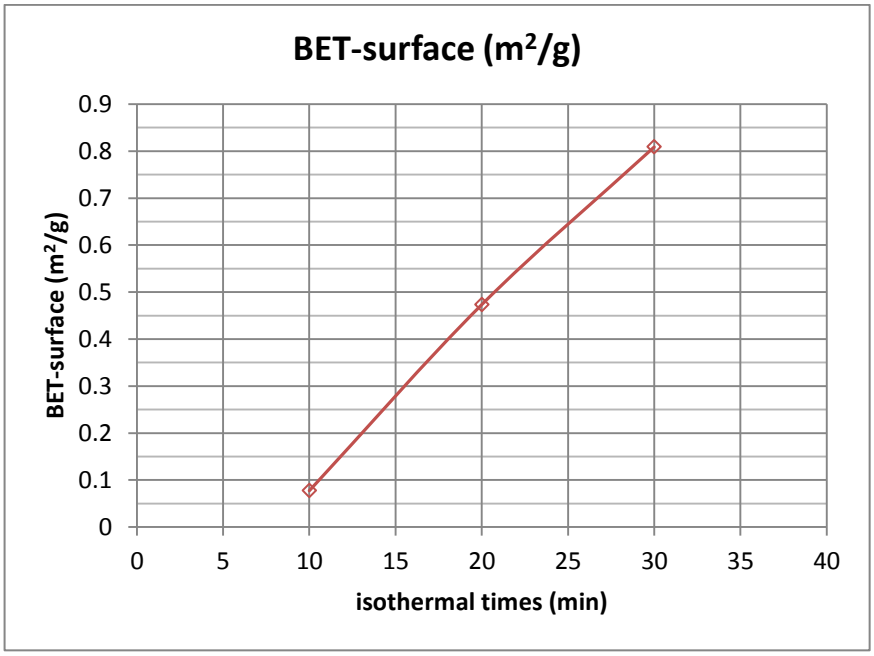

Figure 35: BET-surface of char at 290 °C

Figure 35 demonstrates the almost linear inclination of BET-surface with increasing retention time. The highest value was 0.8 m^2/g obtained at 30 min isothermal time. However, this value was almost 2500 times lower than the required value for activated carbon. However, low BET-surface areas were reasonable because HTL experiments of this thesis were performed at low temperatures (270 to 310 °C) and in presence of water. Furthermore, retention times with a maximum of 0.5 h were too short, for granting an appropriate carbonization and activation process. Even hydrothermal carbonization required retention times of 12 h [3]. In addition to the BET-surface area, the elemental composition of char was also important for an application as activated carbon source. Therefore an elemental analysis was run with the char sample of 30 min at 290 °C. The results of this elemental analysis are demonstrated in Table 12. Contrary to initial expectation the carbon content was very low (41.23wt%).

Table 12: Elemental analysis of char from HTL

	C	H	N	S
Char	41.23 %	5.21 %	0.26 %	0 %

Even though the application of biochar for activated carbon seemed to be restricted, alternative applications of the produced char should be further investigated since biochar was also expected to decay slowly and therefore have a high potential to decelerate the CO_2 emissions to the atmosphere [3].

4.4 Mass balance of bio-oils of HTL

The efficiency of thermochemical conversion of organosolv lignin to bio-oil by HTL was emphasized by the mass balance of the process. The different fractions obtained from HTL are demonstrated in the figure below.

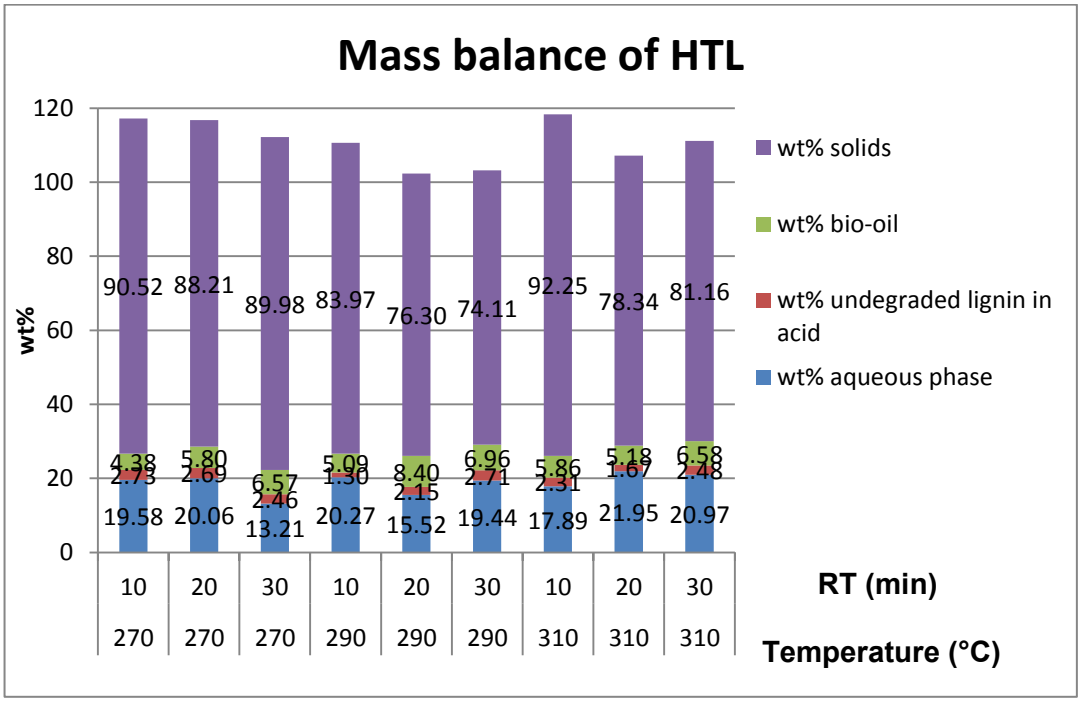

Figure 36: Mass balance of HTL

The overall mass balance (Figure 36) exceeded 100wt%, probably due to errors occurring during char and undegraded lignin separation. The number within the green part of the column indicates the wt% of bio-oil, whereas the number directly below the green part indicates the wt% of undegraded lignin in acid (percentage to small for explicit illustration). The solids were the main product (under studied conditions) of HTL and contained almost always approximately ¾ of the originally fed lignin. These solids were considered as polylignols formed after condensation reactions as well as undegraded lignin. In any case both of these solids were highly polymerized in contrast to the low-molar weight compounds in bio-oil (see GPC results).

Therefore their high quantity entirely correlates to previous findings by Sarkanen et al. who reported that at least half of the material obtained from lignin and water reactions was highly polymerized [63].

4.5 Energy balance of HTL of bio-oil

In order to evaluate if valorization of lignin to bio-oil was feasible a more detailed analysis of the energy balance of HTL was performed. The applied specific enthalpies for educts and products were taken from NIST database and are listed in Table 13.

Table 13: Enthalpy of water - relevant data [71]

Temperature [°C]	Pressure [bar]	h [J/g]
20	0.0233	83.914
85	0.57867	356.01

This data was included in Table 14 where the energy balance was calculated and data taken from literature was marked with (*). Data which had been obtained from the current study (masses) and which was calculated from elemental analysis (HHV) was not explicitly marked in the table below. The input and output state referred to depressurized conditions before and after HTL. Table 14 emphasizes that bio-oil only contributed to a small percentage of 4.65% to the total energy value of the products.

Table 14: Energy balance of HTL at 290 °C

		m [g]	HHV [kJ/g]	h [kJ/g]	H kJ	Sum [kJ]
	organosolv lignin	5.01	25.7		128.7	
Input	water	197.1		0.083914(*)	16.53	145.3
	bio-oil	0.2577	26.62		6.85	
	char	1.0039	14.756		14.81	
	undegraded lignin	2.7479	20.72		56.93	
Output	aqueous phase	193.2		0.35601(*)	68.78	147.4

The aqueous phase taken out from the reactor had a temperature of 85 °C, explaining its higher energy level. The lower HHV of undegraded lignin presented in Table 14 compared to initial organosolv lignin was due to higher moister content in the sample before performing EA. Therefore higher O contents were assumed in the sample. The water contents of undegraded lignin and char were not determined explicitly.

Future research therefore has to focus on determining water contents in undegraded lignin and char to exclude the influence of additional O in the sample, which was slightly manipulating the calculation of HHV.

4.6 Results of Monte-Carlo simulation

In case of 290 °C the calculated deviation of Monte-Carlo Simulation was only +0.011 in case of 10 min retention time, + 0.00156 in case of 20 min retention time and -0.0826 in case of 30 min. It therefore was concluded that this prognosis model for bio-oil formation was highly accurate and the bio-oil yields can be predicted most exactly by applying the equation below (t indicating retention times in min).

$$\text{Bio-oil yield (wt\%)} = -0.00001388*t^5+0.0016*t^4-0.0728*t^3+1.4835*t^2-13.579*t+50.266$$

However, it needs to be considered that this equation had only been tested within a range of 10 to 35 min retention time for 290°C. High deviations are expected for shorter times than 10 min. It is the focus of future research to test other times.

5 Feasibility of bio-oil produced by HTL

The feasibility of bio-oil production by HTL depends on economic viability of the thermochemical conversion and environmental and social compatibility of the process and the product. This thesis takes a finer-grained approach to bio-oil production and the objective of this feasibility study was to establish a CO_2-balance of bio-oil and define environmental compatibility of liquefaction oil.

5.1 Short life-Cycle Assessment of bio-oil

HTL, an energy-intensive process, is assumed to be economically competitive as a result of the termination of the era of cheap fossil fuels. The increasing prices of fossil fuels, the increasing demand for low CO_2-emission and more sustainable fuels have yielded in an increasing interest in research focused on bio-oil. [72]

To obtain a reliable review on sustainability of bio-oil, a life-cycle-assessment (LCA) is highly suitable. LCA is a tool, enabling detailed consideration of the entire emissions and energy consumption of a product throughout its lifetime (from manufacturing to usage). LCA is performed according to ISO 14040. ISO 14040 is followed by ISO 14041 to ISO 14044, where primarily an inventory analysis is performed followed by an impact assessment. The impact assessment includes the CO_2–balance of the production process in order to investigate the environmental compatibility of bio-oil.

In advance to performing the LCA the required agricultural space per liter bio-oil was calculated as shown below. By assuming a lignin presence in wood of 25%, the conclusion was drawn that 1 kg of organosolv beech lignin required 4 kg of wood. [36] These 25% could not be fully recovered due to losses occurring during delignification and subsequent lignin recovery, leading to the assumption that only 20%, instead of 25%, were effectively recuperated. In addition it was estimated that only 30% of the available lignin in pulp and paper plants could be used for bio-oil production, since the residual 70% were required for generating the heat of the pulp and paper plant.

$$kg\ Lignin = kg\ wood * 0.2 * 0.3 \quad (13)$$

The density of beech wood is 0.667 t-atro/m^3 (t-atro refers to dry wood), its potential yield is 5.74 t-atro/a*ha. When considering the average age of beech wood (150 years) this leads to 861 t-atro/ha. [73] The average yield of bio-oil from lignin is 20wt% [62]. Including these factors resulted in the equation below.

$$\frac{l\ bio{-}oil}{ha\ forest} = \frac{51660\ kg\ lignin}{ha\ forest} * \frac{0.2}{1.13\frac{kg}{l}} = \frac{9143.36\ l\ bio{-}oil}{ha\ forest} \quad (14)$$

861 t-atro/ha of wood correlated to 51.66 t lignin/ha and 10.332 t bio-oil/ha (9143.36 l bio-oil/ha). This equals 1.09 m^2 of forest per l bio-oil. The overall LCA of bio-oil produced by HTL was based on 1 l of bio-oil (1.09 m^2 land space). Figure 37 demonstrates the different process steps of bio-oil production. The overall frame of the process considered in the LCA is indicated by the blue box. The small red boxes are the sub-steps of bio-oil production.

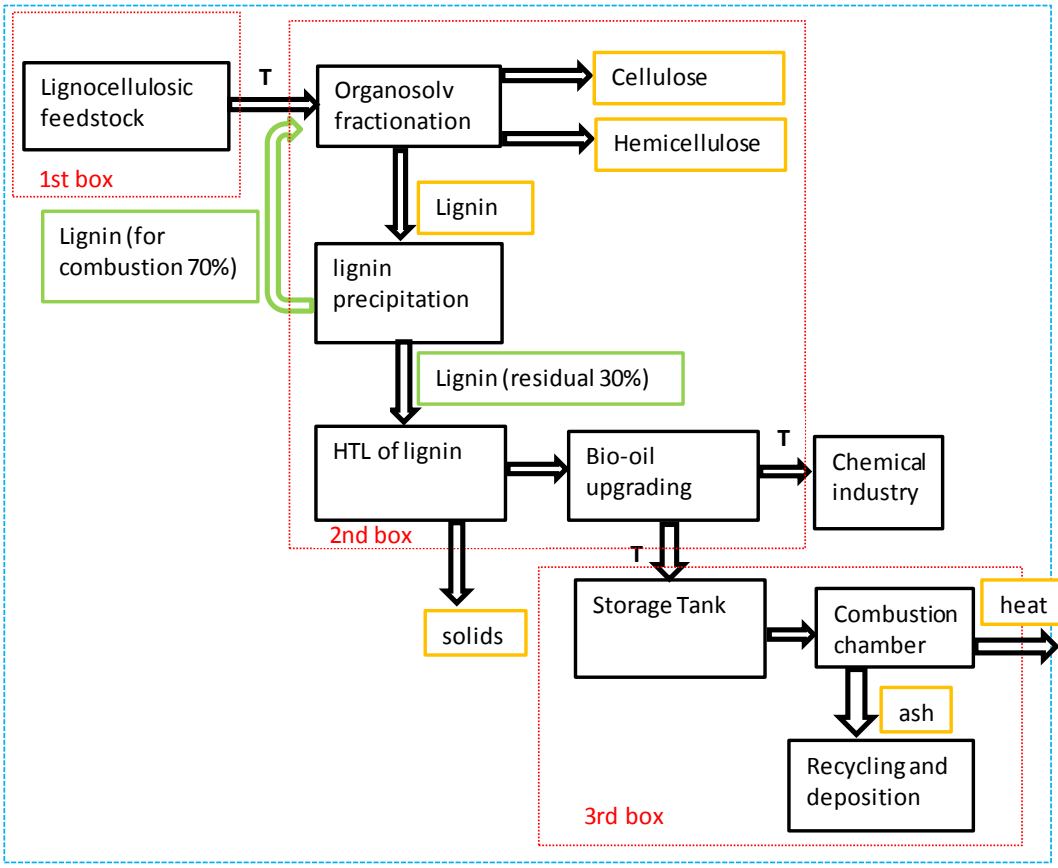

Figure 37: Black box diagram of LCA

In Figure 37, the first box includes harvesting and cultivation of feedstock. The second red box describes the transformation step of lignocellulosic feedstock to upgraded bio-oil. The third box is demonstrating the usage of bio-oil as heating fuel. All these different sub-steps are connected via transportation (T) which itself can cause a lot of greenhouse gas emission if performed by truck. Table 15 reveals the theoretical emissions of the sub-steps of bio-oil production. (+) indicates CO_2 emissions and (-) demonstrates CO_2 storage.

Table 15: Inventory analysis of LCA of bio-oil

Frames	**Stage**	**Sub-step**	**Energy/ material/ equipment**	**Emissions**
1st box	Feedstock	Cultivation +planting	Diesel fuels	+ (CO_2, NOx, CO, particles, SO_2) / - CO_2
		Road construction	Diesel fuels, concrete	+ (CO_2, NOx, CO, particles, SO_2)
		fertilizer	Magnesium chalk	+ CO_2
		Harvesting, clearing	fuel	+ (CO_2, NOx, CO, particles, SO_2)
		Transportation	1) Truck (fuels) OR 2) TRAIN	1) + CO_2, + CO; Particles, NOx, SO_2 2) -
2nd box	Pulp a. Paper	Pulping process	Heat, fuels	+ CO_2, +CO, +NOx,+ SO_2
		Drying of lignin	Heat, fuels	+ CO_2, +CO, +NOx, +SO_2
		Chemicals for lignin precipitation	e.g. alcohols with low boiling points	
		Transportation	Conveyor belt	-
	HTL	HTL - reactor	Heat (elect., fuel)	
		upgrading	Heat (elect. or fuel)	+ H_2O
		Transportation	1) Truck (fuels) OR 2) TRAIN	1) + CO_2, + CO; Particles, NOx, SO_2 2) -
3rd box	Tank	Polymer tank	Petroleum	+ CO_2
		Transportation	1) Truck (fuels) OR 2) TRAIN	1) + CO_2, + CO; Particles, NOx, SO_2 2) -
		Heating	heat	+ Ash, + CO_2, +CO
		Deposition of ash		+particles

Emissions throughout the entire production process discovered by inventory analysis (Table 15), clearly demonstrate that bio-oil's supply chain is CO_2-intensive since all sub-steps are emitting greenhouse gases. According to these theoretical overall emissions emitted during bio-oil's lifetime the CO_2-balance is calculated.

The CO_2-balance (Table 16) was partly implemented with the support of Umweltbundesamt GmbH Austria who calculated specific CO_2 equivalent emissions for harvesting by using the computer program GEMIS. GEMIS is a program applied for eco-balances in general. The CO_2-equivalent value includes all greenhouse gas emissions, which are then related to CO_2 according to their global warming potential. [74]

Table 16: CO_2-balance of bio-oil production based on LCA

Process step	**Substep**	**CO2 kg / 1l bio-oil**
lignocellulosic feedstock	water	0
	lease for land usage	0
	planting + cultivation + clearance	0.976531
Transportation	diesel (average distance 165 km)	0
Production process	paper and pulp	0
	transportation (b.l.)	0
	precipitation lignin/ delignification	0
	drying lignin	0
	transportation lignin	0
	HTL reactor	8
Transportation	diesel (average distance 165 km)	0
Usage	Tank	0.23085
	heating	0
total		9.207381

According to data provided by GEMIS the CO_2-equivalent emission for harvesting is 8,959 kg/ha (= 0.895 kg/m^2 (1 ha = 10.000 m^2)) [74] . This led to the result that 1 l of bio-oil, claiming 1.09 m^2 of forest, was related to 0.976 kg CO_2-equivalent emission. Fertilizers were included in this consideration and were part of the care-taking step. Magnesium chalk was consumed as fertilizer and it was related to an emission rate of 60% CO_2. [74]

Subsequent to cultivation transportation to the pulp and paper plant was performed. The transportation radius of wood and therefore lignin was based on information provided by *austropapier – Vereinigung der Österreichischen Papierindustrie*. According to their data the regional radius for purchasing wooden resources was between 30 and 300 km. Imports from other countries were not taken into account,

since it was assumed that every country was using its own capacities. [75] The arithmetic average (165 km) was considered in LCA. The transportation was assumed to be performed by train because trucks would have been related to high emission rates (2.6 kg CO_2 / L diesel [76]), whereas train transportation was related to 0 kg CO_2 emission (railway construction etc. was not considered).

Lignin production in pulp and paper plants, including precipitation and drying steps, were considered to emit no additional extra CO_2 because lignin production occurred as a side-effect to pulp and paper industry and the emissions related to the process could not be directly ascribed to lignin production. Transportation within the plant was considered to be CO_2 neutral, because the HTL plant was assumed to be constructed next to the pulp and paper plant (according to biorefinery's concept) and infrastructure as well as logistics could therefore be shared. Within the plant area, transportation was assumed to be performed by conveyor belts.

HTL required wet lignin, making drying processes dispensable and therefore not emitting any CO_2. The energy consumption of HTL was based on the energy flows of the process scheme in Figure 38, which was partly derived from the HTU pilot plant in the Netherlands. Plant size (25,000 t dry biomass/a) and the temperature level of preheating (80 °C) were adapted from HTU pilot plant. [77]

Two heat exchangers, with an estimated efficiency of η= 90%, were included in the production principle for energy recovery from the hot lignin-water-slurry. Recuperated energy was partly used for initial preheating of the lignin-water-slurry before it entered the reactor vessel. The residual recuperated energy was used for power generation in a steam turbine (estimated η = 40%). This energy can be used for pumps and other electrical devices in the plant. In the case of this study, however, it was used for heating the reactor vessel (Figure 38). Nonetheless, due to the small quantities of circulating cooling water assumed in this study, the integration of a steam turbine in this explicit case is meaningless. Nonetheless, it was included in Figure 38 to emphasize the potential of overall energy recuperation. If higher energy could be removed from the lignin-water-slurry by the cooling water, the usage of a steam turbine would be recommendable, since according to HTU preheating is limited to 80 °C.

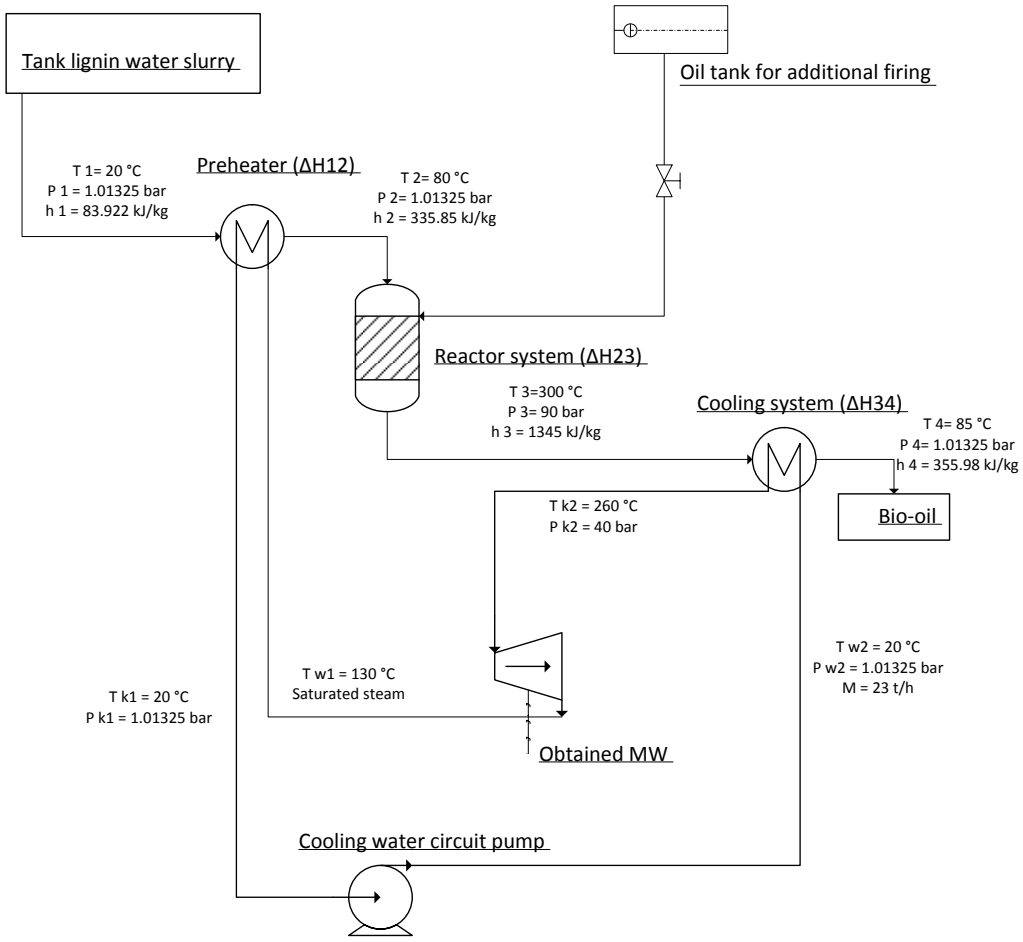

Figure 38: Bio-oil production

Recuperated energy only insignificantly contributed to the energy required for heating the lignin-water-slurry in the reactor. Additional energy was obtained from heavy fuel oil firing, emitting CO_2. The required energies for preheating and the reactor vessel as well as energy removed from the system by cooling water, were based on enthalpies of water and HHV of lignin. To date there is a dearth of technical data for HTL plants, because they have not reached industrial scale yet. Consequently, the assumptions in Figure 38 are exclusively suitable for rough estimations.

The production scheme in Figure 38 emphasized an emission of 8.0 kg CO_2/ L bio-oil, which is relatively high. However, the great potential is based on an increasing bio-oil yield. By raising the mass fraction of bio-oil obtained of HTL (e.g. 50wt%) only 3.25 kg CO_2/ L bio-oil are emitted.

Subsequently, to HTL bio-oil upgrading occurs, which was not taken into account in this study. Finally storage in tanks was related to 2.7g CO_2 equivalent emission per 1 g PE (material the tanks were assumed to be made of). [78]

The combustion of bio-oil produces ash, CO_2 and CO. CO_2 emitted during combustion, was stored by the plant in advance, causing bio-oil firing to be CO_2 neutral.

The CO_2-balance emphasized that bio-oil was not CO_2 neutral (9.22 kg CO_2/ L bio-oil) and that its main drawback hindering a production of commercial scale by HTL were low bio-oil yields. The overall CO_2 emissions per liter bio-oil were relatively high but with a tremendous potential to decrease, if bio-oil yields could be raised. In summary, bio-oil was identified to be related to a high energy- und emission-saving potential if research succeeded in identifying parameters to increase bio-oil mass fractions obtained by HTL.

6 Conclusion

The objective of the thesis was to analyze the importance of bio-oil as biofuel and aromatic source for green chemicals with a high potential to substitute for fossil fuels. In the experimental part of this thesis bio-oil production from organosolv lignin by hydrothermal liquefaction in an autoclave at 270°C, 290°C and 310°C with various retention times of 10, 20 and 30 min was analyzed. The lignin to water ratio (1:40) was maintained. With regard to these experimental settings, the following central research questions were addressed.

1. How do temperature and time quantitatively influence bio-oil formation?
2. Is the produced bio-oil of high quality?
3. Does total phenolic content in bio-oil depend on temperature and time?

The first research question was successfully answered by identifying an increasing bio-oil mass fraction formed with increasing retention times. Moderate temperatures (290°C) were highly enhancing bio-oil formation and a maximal average bio-oil yield of 8.77wt% was obtained at 35 min at 290 °C. In contrast, lower temperature levels (270°C) and exceedingly high temperatures (310°C) resulted in lower bio-oil yields.

The second research question led to ambivalent findings. Bio-oils obtained in this study were characterized by higher carbon contents (65.03wt%) and lower oxygen contents (28.33wt%) than organosolv lignin (C of 64.14wt% and O of 29.88wt% respectively). Nonetheless, their elemental analysis demonstrated lower carbon contents and higher oxygen contents than findings reported in literature (C of 73wt% and O of 16wt% [31]). Consequently, the heating values of bio-oils (27.98 kJ/g) were exceeding initial HHV of organosolv lignin (26.33 kJ/g), but undercutting findings in literature (35 kJ/g [31]). The reason for the inferiority of this study's data compared to literature was not completely clarified. Nonetheless, it was assumed to be based on lower temperature levels applied during this study compared to supercritical temperatures tested in previous research work.

Bio-oil was additionally characterized by molar mass distribution, which indicated the formation of monomers, dimer and trimers, confirming previous research findings and indicating successful lignin degradation, comparable to findings by Sarkanen et al. [63]. With regard to molar mass distribution and elemental analysis, lignin degradation seemed to have occurred to limited extends. Minimal changes in elemental composition indicated a preservation of lignin's structure, but low Mw indicated successful scission of α- and β-O-4 bonds, which was previously reported

by Lundquist et al. [64]. In summary, the second research question had to be negated due to the inferiority of the data of this thesis compared to reported data by literature.

The third research question was approved, since according to the results of the Folin Ciocalteu method, increasing retention time was successfully linked to increasing total phenolic content. Moderate temperatures (290°C) were most successfully enhancing increasing presence of total phenolic content in bio-oil (ranging from 0.157 g GAE/ g bio-oil (10 min) to 0.191 g GAE/ g bio-oil (30 min)). In contrast, lower and higher temperatures than 290 °C resulted in decreasing formation of hydroxyl aromatic compounds in bio-oil.

With regard to these key questions, the hypothesis was confirmed that hydrothermal liquefaction of organosolv lignin to bio-oil resulted in valorization of organosolv lignin.

7 Recommendations

With regard to the qualitative inferiority of bio-oils produced in this study a few recommendations for future research are presented.

Near-critical or even supercritical conditions are recommended, because it is assumed that higher temperature levels enhance the increase of carbon content and the decrease of oxygen content in bio-oil and consequently result in higher HHV of bio-oil.

As a result of low bio-oil fractions obtained in this thesis, the presence of catalysts in HTL is recommended. It is assumed that this adjustment leads to higher bio-oil mass fractions.

Finally a different extraction solvent (e.g. diethyl ether) for liquid-liquid-extraction of bio-oil from aqueous phase has to be applied. Ethyl acetate was considered insufficient, since high lignin equivalent contents and consequently organic compounds were detected in aqueous phase after extraction. Therefore it has to be tested if these losses of valuable bio-oil in aqueous phase can hereby be decreased.

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Annex

sample	empty bowl [g]	sample wet [g]	full bowl dry [g]	sample dry [g]	**water [wt%]**
1	5.011	0.9141	5.9098	0.8988	**1.6738**
2	5.9214	1.0128	6.9172	0.9958	**1.6785**

sample	bowl full [g]	bowl burnt [g]	cup empty [g]	**ash wt%**
1	5.9098	5.0117	5.011	**0.07788162**
2	6.9172	5.9222	5.9214	**0.08033742**

Annex 1: Ash and water content determination

$$\frac{\mathbf{861\ t\ atro}}{\mathbf{ha\ forest}} * \mathbf{0.2} * \mathbf{0.3} = \frac{\mathbf{51.66\ t\ lignin}}{\mathbf{ha\ forest}}$$

$$\frac{51660\ kg\ lignin}{ha\ forest} * \frac{\frac{20\ \%\ bio-oil}{100\ \%}}{\frac{1.13\ kg\ bio-oil}{l}} = \frac{9143.36\ l\ bio-oil}{ha\ forest}$$

$$1\ l\ bio-oil\ \rightarrow 1.09\ m^2 forest$$

Annex 2: Equations for calculation of required land space

	C	H	N	O	total
wt% wet	62.54	6.52	0.2	30.74	100
m wet [g] (1.)	62.54	6.52	0.2	30.74	100
N wet [mol]	5.211 (1)	6.52	0.0142	1.9212	
n relation	364.77	456.4	1	134.48	
N dry [mol]	5.36	6.18	0.0142	1.82 (5.)	
m dry [g]	64.43 (6. – 8.)	6.18 (2.-4.)	0.20 (6.-8.)	29.13 (1.)	100
wt% dry	64.43	6.18	0.20	29.13	100

Numbers in brackets indicate the applied equations for calculation of data.

1. $n = \frac{m}{M}\ [g/(\frac{g}{mol})]$
2. $m\,wet\ (H) = \frac{2 * m\,wet(H2O) * M(H)}{M(H2O)}$
3. $m\,dry\ (H2O) = m\,wet\ (H2O) - \frac{water\ content\ (wt\%)}{100} * 100\ g$
4. $m\,dry\ (H) = \frac{2 * m\,dry(H2O) * M(H)}{M(H2O)}$
5. $n\,wet\ \ (H) : n\,wt\ (O) = n\,dry\ (H) : n\,dry\ (O)$
6. $100 - m\,dry\ (H) - m\,dry\ (O) = m\,dry\ (C) + m\,dry\ (N)$
7. $x = \frac{n\,wet\ (C)}{m\,wet\ (N)}$
8. $m\,dry\ (N) * x + m\,dry\ (N) = 100 - m\,dry\ (H) - m\,dry\ (O)$

Annex 3: Calculation of water free EA

Haberle Inge

From: Pölz Werner <werner.poelz@umweltbundesamt.at>
Sent: 4. maaliskuuta 2014 10:29
Subject: AW: AW: AW: Emission von Kohlenstoffdioxid, bei der Rodung von 1 ha Wald

Sehr geehrte Frau Haberle!

Danke für Ihre Nachricht, die mein Kollege Peter Weiss an mich weitergeleitet hat.

Wir nutzen das Computermodell GEMIS, eine Datenbank für Ökobilanzierungen. Hier finden sich für die Holzernte aus einem durchschnittlichen Wald folgende Angaben, die ich Ihnen hier zusammengestellt habe. Die Daten setzen sich aus folgenden Teilschritten zusammen:

- Hintergrunddaten
- Pflanzung
- Pflege
- Ernte

Ich sende Ihnen die Informationen aus GEMIS zu. Das Ergebnis laut Datenbank ist, dass pro t atro rund 16 kg CO_2-Äquivalent-Emissionen durch die beschriebenen Teilschritte bis zur Ernte entstehen. Ein einem Ertrag von 546 t atro pro Hektar Wald bedeutet das **8.959 kg CO_2-Äqui pro Hektar**.

Hintergrunddaten

	Fichte	Einheit
Rohdichte	430	kg/m3
Heizwert, tr.	19271	MJ/t atro
Faktor	2,33	Efm m.R./t atro
Umtriebszeit	120	a
Industrieholz	140	% Feuchte
Stammholz	70	% Feuchte
Ernte, gesamt	**546,09**	**t atro/ ha**
Ernte, jährlich	4,55	t atro/ha*a

Es wird die **Pflanzung** (Setzen der Schösslinge), Kulturpflege, Jungwuchspflege und die schematische (I) wie selektive (II) Läuterung bilanziert. Bis zu diesem Zeitpunkt fällt kein nutzbares Holz an. Bilanzierungsdaten in MJ pro t atro erzeugtes Stamm und Industrieholz.

	Buche	Eiche	Fichte	Kiefer	
Pflanzung	6,43	8,36	2,74	11,5	Diesel-Schlepper
Kulturpflege	1,93	2,01	2,19	3,45	Zweitakter-Freischneider
Jungwuchspflege	2,07	2,15	0	3,7	Zweitakter-Freischneider
Läuterung I	1,03	1,08	1,18	1,85	Diesel-Schlepper
Läuteruung II	2,07	2,15	2,35	3,7	Zweitakter-Freischneider
Summe	6,06	6,31	4,54	10,84	Zweitakter-Freischneider
Summe	7,46	9,44	3,92	13,34	Diesel-Schlepper

1

Pflege

	Buche	Eiche	Fichte	Kiefer	
Kalkung	4,83	5,03	5,49	8,64	Magnesiumkalk kg/t atro
Wegebau	0,076	0,079	0,086	0,135	Schlepper, Grader MJ/t atro

Magnesiumkalk wird als Kalksteinmehl bilanziert mit einer Emissionsrate von 60% CO2.

Ernte

Dieser Bilanzschritt beschreibt die Aufwände zur **Durchforstung und Endnutzung** des Waldbestandes zur **Erzeugung von Stamm- und Industrieholz** (Schneiden, Fällen, Rücken bis Strasse, ohne Transport).

	Buche	Eiche	Fichte	Kiefer	
Industrie	161,6	189,3	277,5	264,3	MJ Diesel
	25,5	30,4	99,6	56,8	MJ ZTG
	187,1	219,8	377	321,1	MJ Summe

	Buche	Eiche	Fichte	Kiefer	
Stamm	81,7	60,7	123,8	113,8	MJ Diesel
	11,9	21,3	21,8	10,4	MJ ZTG
	93,6	81,9	145,6	124,2	MJ Summe

Ich hoffe, die Daten helfen Ihnen weiter. Falls Sie Fragen stehe ich sehr gerne zur Verfügung.

Mit freundlichen Grüßen

Werner Pölz

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1090 Wien
Österreich/Austria
http://www.umweltbundesamt.at

Annex 4: Email conversation with Umweltbundesamt GmbH (German)

Dear Mrs, Haberle,

Thank you for your email, that my colleague Peter Weiss has forwarded to me.

We are using the computer program GEMIS which is a data bank for life cycle assessments. There, we can find the following data for wood harvesting/ clarification of an average forest. I arranged them for you as illustrated below. The data is based on the following sub-steps:

- Background data
- Planting
- Cultivation
- Clearification/harvesting

I send you the information produced by GEMIS. The result of the data bank is that per t-atro 16 kg CO_2- equivalents emit. This includes all sub-steps until reaching the clearification of the wood. Based on a yield of 546 t-atro/ ha forest, 8 959 kg CO_2 – equiv. are emitted per ha forest.

Background data	**Spruce tree**	**dimension**
Green density	430	kg/m^3
Heating value, dry	19271	MJ/t-atro
Factor	2.33	Efm.m. R./ t-atro
Rotation period	120	A
Pulpwood	140	% moisture
Stemwood	70	% moisture
Harvesting, total	546.09	t-atro/ha
Harvesting, per year	4.55	t-atro/(ha*a)

We balanced planting (planting young trees), cultivation, cultivation of young stands and the schematic clearification (I) as well as the selective clearification (II). At this stage there is no usable wood. Balance data is listed in MJ/ t-atro produced pulpwood or stemwood.

Planting

	Beech	Oak	Spruce	Pine	
Planting	6.43	8.36	2.74	11.2	Diesel-hauler
Cultivation	1.93	2.01	2.19	3.45	Twin-stroke engine
Cultivation young stands	2.07	2.15	0	3.7	Twin-stroke engine

Clearification (I)	1.03	1.08	1.18	1.85	Diesel-hauler
Clearification (II)	2.07	2.15	2.35	3.7	Twin-stroke engine
Sum	6.06	6.31	4.54	10.84	Twin-stroke engine
Sum	7.46	9.44	3.92	13.34	Diesel-hauler

Cultivation

	Beech	Oak	Spruce	Pine	
Liming	4.83	5.03	5.49	8.64	Magnesium chalk
Road	0.076	0.079	0.086	0.135	Hauler, MJ/t-atro

Magnesium chalk was balanced as pulverized limestone with an emission rate of 60 % of CO_2.

Harvesting

This step of LCA describes the effort for thinning and usage of forest stand until the production of pulp wood and stem wood (cutting, chopping, moving to roads – but no transportation).

Pulpwood (industry)	**beech**	**oak**	**spruce**	**pine**	
	161.6	189.3	277.5	264.3	MJ diesel
	25.5	30.4	99.6	56.8	MJ saw
	187.1	219.8	377	321.1	MJ sum

Stem wood	**beech**	**oak**	**spruce**	**pine**	
	81.7	60.7	123.8	113.8	MJ diesel
	11.9	21.3	21.8	10.4	MJ saw
	93.6	81.9	145.6	124.2	MJ sum

I hope the data will help you. In case of any further questions, contact me.

Yours sincerely

Werner Pölz

Annex 5: Translation of email conversation with Werner Pölz (English)

Gmail by Google [redacted]

Anfrage: Bezüge und Lieferungend der Papierindustrie

Mader Patrick <Patrick.Mader@austropapier.at> 17. Februar 2014 13:37
An [redacted]
Cc: Zettl Claus <Claus.Zettl@austropapier.at>, Grieshofer Hans <Hans.Grieshofer@austropapier.at>

Sg Fr Haberle,

wenn Sie uns ihre Post-Adresse geben, dann senden wir ihnen gerne einen Jahresbericht zu in dem Sie einiges zu Ihren Fragen finden.

1. Holz (Durchforstungsholz und Sägenebenprodukte) werden überwiegend regional mit einem Radius von 30 bis 300 Kilometern bezogen. Durch die aktuellen Engpässe im Holzbezug, ausgelöst durch die strak zunehmende Holzverbrennung, musste der Importanteil allerdings immer weiter ausgedehnt werden. Zuletzt betrug der Anteil der Importe rund 40 Prozent, mit einem steigenden Anteil an Fernimporten (> 1000km). Für weitere Details zum Holzbezug darf ich sie an unseren DI Hans Grieshofer verweisen (eMail s.o.)

2. Beim Papierabsatz ist das europäische Geschäft vorherrschend, aber die Branche ist global. Finden sie im Jahresbericht auf Seite 59 eine Liste aller Exportländer.

Vor ein paar Tagen habe ich noch einen Kommentar zur Methode der LCA bekommen, vielleicht interessiert sie das auch

mfG

P.Mader

Mag. Patrick Mader
Kommunikation & Wirtschaft

austropapier
Vereinigung der Österreichischen Papierindustrie
Gumpendorfer Straße 6, A-1061 Wien
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Annex 6: Email conversation with Umweltbundesamt GmbH (German)
Personal data e.g. e-mail addresses have been blacked in this replication of the e-mail conversation.

Rough estimation of energy consumption of HTL (based on HTU)

data from HTU process			***Data source***
mass flow (dry basis)	25000.0	t/a	[77]
hours of operation	7000.0	h/a	assumption
data lignin			
mass flow (dry lignin)	3.6	t/h	=25000/7000
lignin: water ratio	1:20		assumption
mass flow water	71.4	t/h	= 3.57*20
mass flow slurry	75.0	t/h	= 71.43+3.57
bio-oil from lignin	20.0	wt%	with catalyst (see literature [62])
bio-oil	0.7	t/h	= 20/100*3.57
HHV lignin	25700.0	kJ/kg	own research (see elemental analysis and bomb calorimeter)
NIST database - spec. Enthalpies:			
h 1 (20 C, 1.01325 bar)	83.9	kJ/kg	
h 2 (80 C, 1.01325 bar)	335.9	kJ/kg	
h 3 (300 C, 90 bar)	1345.0	kJ/kg	
h 4 (85 C, 1.01325 bar)	356.0	kJ/kg	Nist database [71]
Enthalpies:			
H 1	97780142.9	kJ/h	= h1*m water*1000+HHV lignin*m lignin*1000
H 2	115775000.0	kJ/h	= h2*m water*1000+HHV lignin*m lignin*1000
H 3	187857142.9	kJ/h	= h3*m water*1000+HHV lignin*m lignin*1000
H 4	117212857.1	kJ/h	= h4*m water*1000+HHV lignin*m lignin*1000
Preheating			
η	0.9		assumption (normale 0.9)
Δ H12 (ideal)	17994857.1	kJ/h	= H2 - H1
Δ H12 (real needed for preheating)	19994285.7	kJ/h	= (H2 -H1)+ 10/100*(H2- H1)
Cooling			
η	0.9		
Δ H34 (ideal)	-70644285.7	kJ/h	=H4-H3
Δ H34 (really transferred)	-63579857.1	kJ/h	=(H4-H3)*0.9
Calculation of mw1, Tw1, pw1, hw1			
m k2 = mw2 = m			
assumption : m	23.0	t/h	
hw2 = hw1	2848.3	kJ/kg	=((-1)*(H4-H3)/(m*1000))-h1
m w1 = m k1	23.0	t/h	
m w1 = mk1	23.0	t/h	
m 5 = m 6	23.0	t/h	
H 5	65510063.1	kJ/h	= m5*hw2
Δ H56	-2241663.1	kJ/h	=H6-H5
steam turbine 1			
Δ H56	2241663.1	kJ/h	
η	0.4		
elektrical power	0.2	MW	=0.4*(*-1(H6-H5))*2.77*10^(-7)
Reactor			
Δ H23	72082142.9	kJ/h	=H3-H2
using electrical power	2241663.1	kJ/h	
additional energy needed	69840479.7	kJ/h	= (H3-H2) - electrical power
Source additional energy			
HHV heavy fuel oil	36.0	MJ/L	[76]
m heavy fuel oil	1940.0	L/h	= additional energy needed/ HHV heavy fuel oil
CO2 kg/ L heavy fuel oil	2.6	kg CO2 /L	[76]
CO 2 emission	5044.0	kg CO2 /h	=(m heavy fuel oil)*(CO2 emission in kg/ L heavy fuel oil)
bio-oil	714.3	kg/h	
bio-oil (L)	632.1	L/h	=(bio-oil kg/h)/density
CO 2 emission/ l bio-oil	**8.0**	**kg CO2 / L**	= CO2 emission/Liter bio-oil

Annex 7: Energy calculation for HTL