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Full Characterization of Compounds obtained from Fractional Distillation and Upgrading of a HTL Biocrude

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Abstract

Biocrude from hydrothermal liquefaction of biomass provides a sustainable source from which to produce chemicals and fuels. However, just as for fossil crude, the chemical complexity of the biocrude impedes the characterization and hence identification of market potentials for both biocrude and individual fractions. Here, we reveal how fractional distillation of a biocrude can leverage biocrude characterization beyond state-of-the-art and uncover the full biocrude potential. By distillation combined with detailed individual analysis of the distillate fractions and distillation residue, more than 85 % of the total biocrude composition is determined. It is demonstrated that a total mass fraction of 48.2 % of the biocrude is volatile below 350 °C, comprising mainly value-added marketable ketones, oxygenated aromatics and prospective liquid fuel candidates, which are easily fractionated according to boiling points. Novel, high resolution pyr-GCxGC-MS analysis of the residue indicates a high molecular weight aromatic structure, valuable for bio-materials production or for further processing into fuels. The distillate fractions are mildly hydrotreated to show the fuel and chemical precursor potential of the volatile components. This results in the formation of mainly hydrocarbons and added-value phenolics. This work takes a significant step by going beyond the biocrude as an intermediate bulk energy product and addressing actual applications and pathways to these.

Keywords: Biofuels, Biochemicals, Fractionation, Hydrotreatment, Biorefinery

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1. Introduction

Biomass will become the major sustainable source of carbon for future mass production of commodity chemicals and transport fuels, due to the environmental concerns caused by petroleum consumption. The roadmap for biomass conversion into platform chemicals, able to substitute petroleum-derived equivalents, is complex and ranges from biological to severe catalytic thermochemical processes. Commercial mass production of chemical and energy commodities from biomass relies on scalable, energy and resource efficient, and feedstock flexible processes able to produce renewable bulk platform chemicals sustainably and economically. Hydrothermal liquefaction of biomass is a thermochemical process carried out in a near-critical water environment capable of disintegrating and decomposing biomass macromolecules into lower molecular weight compounds, which are substantially deoxygenated compared to the original macromolecules [1–6]. Compound deoxygenation results in a spontaneous and distinct compound separation; polar compounds (usually termed water-soluble organics (WSO)) are contained in the effluent aqueous phase, whereas non-polar compounds are contained in a nearly water-free liquid bulk fraction termed biocrude. Biocrude is an energy dense, transportable value-added liquid, but also a chemically complex mixture consisting of numerous chemical compounds. The spontaneous phase separation of the process effluent provides an inexpensive means of biocrude recovery, and fractional distillation provides an attractive method of grouping chemically similar compounds based on their volatility. The less complex fractions, compared to the biocrude, may then be further separated or processed into commodity chemicals or fuels resembling existing petroleum operations. Zhang et al. demonstrated the benefits of fractional distillation of a pyrolysis biooil [7]. Using a single stage, atmospheric pressure distillation procedure, they traced 13 major compounds in six different distillate fractions ranging from ambient temperature to 240 °C. A total mass fraction of 52 % was recovered from the biooil of which nearly 60 % was water. Although separation efficiencies of the major compounds were generally high (for some around 90 %), most compounds were still distributed in all distillate fractions. Cheng et al. distilled a biocrude obtained from glycerol-assisted liquefaction of manure [8]. The distillation procedure was carried out at atmospheric pressure from ambient to 500 °C. A volume fraction of only 10 % of the biocrude was distilled at 359 °C, whereas 90 % was distilled at 500 °C.

Thermophysical and chemical properties of the distillate fractions clearly indicated thermal degradation and deoxygenation during distillation. This was evident from the fact that the energy contents of the fractions on a mass basis all were observed greater than that of the crude biooil. Furthermore, alkanes and alkenes having number of carbon atoms in the range of C_5-C_{14} were only identified in the heavier distillate fractions above a distillation temperature of 420 °C. Therefore, atmospheric pressure distillation seems inadequate in obtaining distillate fractions truly presenting the original biocrude. Capunitan et al. fractionated a biooil obtained from pyrolysis of corn stover at atmospheric and slightly reduced pressure (0.5 bar) [9]. A *heavy distillate* mass fraction of 45 % was collected in the 180-250 °C temperature range, a fraction consisting mostly of phenolic compounds. The properties of the fractions were improved in terms of moisture content, TAN number, and heating value as compared to the crude biooil. Hoffmann et al. fractionated a HTL biocrude with 53.4 % mass recovery at 375 °C (atmospheric equivalent), of which the equivalent gasoline, diesel and jet-fuel mass fractions comprised of 12.5, 25.3 and 16.6 %, respectively. An oxygen distribution was established showing that all distillate fractions still contained oxygenates [10]. Only details on the distillation residue included elemental composition and heating value, leaving yet almost 50 % of obtained product uncharacterized. Eboibi et al. investigated vacuum distillation of algae derived biocrude [11]. Due to the high lipid and protein content of the micro algae as compared to a lignocellulosic feedstock, up to 73 % could be distilled at 360 °C. Furthermore, the vacuum distillation greatly improved the quality and metal content of the biocrude.

Hydrotreatment of the biocrude provides another means of reducing the biocrude complexity by chemically altering the many oxygen-containing chemical functionalities mainly via deoxygenation and saturation by hydrogen addition. Hydrotreatment of biocrude has been investigated and reviewed in many aspects and in order to obtain drop-in fuels from biocrude, oxygen removal by hydrotreatment is to some extent regarded as a necessary step [12–18]. In a parametric hydrotreating study, Jensen et al. showed that complete deoxygenation of a HTL biocrude can be achieved [12]. Complete deoxygenation transforms biocrude oxygenates into their corresponding hydrocarbon backbones. Therefore, if a pool of oxygenates of identical hydrocarbon backbones are hydrotreated, a resulting fraction of identical hydrocarbons can be obtained.

The objective of this study is to demonstrate that multistage vacuum fractional distillation of a wood-derived biocrude, obtained from continuous hydrothermal liquefaction, provides a viable route for detailed analysis of a biocrude. Furthermore, characterization of the distillation residue is performed for a full closure on the biocrude chemical characteristics.

2. Materials and Methods

2.1. Biocrude from aspen wood hydrothermal liquefaction

The biocrude used in the present study was obtained from glycerol-assisted aspen wood liquefaction represented in a previous study [19]. In brief, the biocrude was produced under continuous conditions at 400 °C, 300 bar, and a mass flow rate of approximately 14 kg/hr. Wood flour and glycerol was mixed in a 50/50 mass ratio amounting to a mass fraction of 30 % of the total feed slurry. Wood flour and glycerol were slurried in process water together with a potassium carbonate catalyst. The catalyst amounted to 4 % of the total mass of the feed slurries. Based on total organic input (aspen wood + glycerol) yields in the order of 20-30 % were obtained. After processing, the biocrude and aqueous phase were separated gravimetrically. The as-received biocrude was dewatered by distillation according to ASTM D2892 (Appendix X 1) [20]. Light organics distilled during dewatering were reintroduced into the biocrude prior to distillation. Therefore, no moisture is expected to be present in any of the obtained distillate fractions. Table 1 presents the ultimate and proximate analyses of the aspen wood used in the study.

Table 1: Ultimately and proximate analysis of the aspen wood on a dry basis.[a]Oxygen calculated by difference. No sulfur was detected. Data reported from [19].

Elemental analysis	[wt. %][a]	Proximate analysis	[wt. %]
C	50.39	Volatiles	77.04
H	6.19	Fixed Carbon	20.61
O[a]	43.23	Ash	2.35
N	0.19		

2.2. Fractional Distillation

Fractional distillation of the biocrude was carried out in accordance to the ASTM D2892 in a two liter 15:5 distillation column [20]. More information on the distillation equipment was published by Hoffmann et al. [10]. In order to avoid thermal degradation of the biocrude during distillation the vacuum was lowered stepwise to 100 (13332), 15 (2000), and 1 (133) torr (Pa). A similar procedure was used by Lavanya et al. [21]. The distillate was divided into six liquid fractions; first fraction was obtained from an initial boiling point (IBP) of 73 °C to 100 °C, the subsequent 5 distillation fractions were obtained with 50 °C cuts to a maximum atmospheric equivalent temperature (AET) of 350 °C. The initial boiling point was determined based on visual inspection for when the first reflux was observed. The residue represents non-volatile compounds with boiling points above 350 °C. The ash content of the residue is 0.88 wt.%. The AET is based on the formulas that are applied in the ASTM D2892 and derived by Maxwell & Bonnel [22].

2.3. Catalytic Hydrotreatment

A distillate mix of the six obtained distillation fractions, excluding the residue, was catalytically hydrotreated. The distillate fractions were mixed in accordance to their respective ratios obtained from the biocrude distillation. The catalytic hydrotreatment was carried out using a pre-activated and stabilised $NiMo/Al_2O_3$ hydrotreating catalyst in 25 mL micro-batch reactors enabling time resolved pressure logging. A fluidized sand bath at 360 °C facilitated instant heating. Experiments were conducted in duplicates to ensure reproducibility. The catalyst loading equaled 20 % of the biocrude mass, and hydrogen was introduced to 77.5 bar corresponding to 540 NL/L of biocrude. After 1.5 hours of reaction time, reactors were quenched in a water bath prior to gas venting and product separation. The hydrotreated products (HTP) were collected and centrifuged prior to analysis. The liquid recovery and yield of upgraded oil were 85 wt.% and 77wt.%, respectively, which is calculated according to the equations given in [23]. No solid products were observed and the gaseous products were not quantified.

2.4. Characterization of biocrude and distillate fractions

Elemental composition was measured using a Perkin Elmer 2400 Series II system (ASTM D5291). Sulfur content of the aspen wood was below detection level and is therefore not reported. For the distillate fractions, nitrogen and sulfur were both below detection limits and therefore not reported. Functional group identification was done by IR spectroscopy carried out at room temperature on a Thermo Scientific Nicolet 380. Spectrum resolution was 1 cm^{-1} and recorded in the range of 4000-650 cm^{-1}. GC-MS analyses of all samples were carried out on a Thermo Scientific Trace 1300 ISQ GC-MS system (Length: 30 m., i.d.: 0.25 mm., Film: 0.25 μm, HP-5MS column). Higher boiling fractions (Fraction 5 and 6) were derivatized using a BSTFA reagent prior to analysis. Samples were then diluted in diethyl ether (DEE) and subjected to the following oven temperature profile; ramped from 40 °C to 300 °C at 10 °C/min. Injector and ion source temperatures were 300 °C, split ratio was 1:20, and flow rate of the carrier gas (helium) was 1.0 mL/min. The distillation residue was analyzed by pyrolysis-GCxGC-MS, using a GC-MS QP-2010 Ultra (Shimadzu) equipped with a PY-3030S Single Shot pyrolyzer (Frontier Laboratories) and liquid nitrogen modulation (ZOEX). About 0.2 mg of sample was used and the pyrolysis temperature was set to 600 °C. The column set was an Agilent DB-5 (length: 60 m, i.d.: 0.25 mm, film: 0.1 μm) on the first dimension and an Agilent DB-17 (length: 1 m, i.d.: 0.18 mm, film: 0.18 μm) on the second dimension. The column oven was ramped from 50 °C to 280 °C at 4 °C/min. and the modulation time was six seconds. In pyrolysis-GC the sample is thermally degraded by rapid heating in an inert atmosphere prior to entering the GC column, and this method was chosen due to the high boiling point range of the residue. Thermogravimetric analysis of the residue was performed on a TA Instuments Discovery TGA. The sample was heated to 600 °C with 100 °C/min ramp, and held isothermal for one hour to mimic the pyrolysis-GCxGC-MS temperature profile. Calorific values were measured using a IKA C2000 oxygen combustion calorimeter (ASTM D2015). Total acid number (TAN) was measured by color-indicating titration. A sample of approximately 0.1 g was diluted in a 50 mL 50/50 solution of isopropanol and toluene. Phenolphtalein was used as color indicator and a 0.1M KOH/ethanol solution was used for titration. Measurements were carried out in duplicates to ensure reproducibility.

3. Results and Discussion

3.1. Distillation yields

Table 2 summaries the distillation yields within each distillate cut. Fractional distillation of the biocrude resulted in a distillate mass recovery of 47 % at an AET of 350 °C. The IBP of the biocrude was 73 °C and only a mass fraction of 1.6 % was distilled in the light naptha range below 100 °C. Fraction 2, 3 and 4 are also minor mass fractions accounting for 4.1 %, 6.3 %, and 6.0 %, respectively. Fraction 5 represents the largest fraction representing 15.3 % of the bulk biocrude mass, with Fraction 6 being the second largest fraction accounting for 10.3 %.

The distillation residue boiling above 350 °C accounts for 51.8 % of the total mass. The residue is solid at room temperature, but becomes liquid upon heat-up to approximately 100-150 °C. Based on the high boiling point range, only pyrolysis-GCxGC-MS analysis could be carried out for the residue. Apart from water bound in the biocrude due to compound polarities, which may not have been entirely removed during initial dewatering, additional reaction water may have been formed during distillation. Chemically formed water by thermally induced condensation reactions of reactive compounds at elevated temperatures have previously been observed in other studies [24–26]. At a vacuum of 15 torr and below, such reaction water will not condense in the condenser, but it will condense in the cold trap. By Karl Fischer titration it was determined that 59.7 % of this fraction was water. In addition to the fraction collected in the cold trap, an additional distillation mass loss of 1.2 % is observed from Table 2. This mass loss is above the ASTM D2892 guidelines (0.4 %) but the procedure is considered adequate for the current study [20].

Figure 1 display the distillation curve and Table 2 also summaries elemental composition, higher heating value (HHV) and TAN for both the bulk biocrude, distillate fractions, and the distillation residue. An elemental and HHV balance is included in the table in order to verify the results obtained from fractional distillation. The weighted sum of HHV and the carbon contents of the fractions are within a satisfactory range of the original biocrude. A 3.9 % hydrogen discrepancy indicates that the hydrogen content of the fractions have been slightly underestimated resulting in an equally higher oxygen content that is calculated by difference. Generally, the balances indicate smooth distillation, where thermal degradation

Table 2: Properties of the biocrude, distillation fractions, and distillation residue.

	TBP	Yield		HHV	Elemental analysis [wt.%]					TAN
Sample	[°C]	[wt.%]	[vol.%]	[MJ/kg]	C	H	O[a]	H/C [-]	O/C [-]	[mg KOH/g]
Biocrude	-	-	-	34.3	76.4	8.4	15.2	1.31	0.15	50
F1	<100	1.6 %	2.2 %	33.8	67.7	13.5	18.9	2.37	0.21	7
F2	100-150	4.1 %	5.3 %	36.0	74.2	12.8	13.1	2.05	0.13	29
F3	150-200	6.3 %	7.4 %	35.5	75.7	11.0	13.3	1.74	0.13	16
F4	200-250	6.0 %	6.9 %	37.1	78.8	10.5	10.7	1.59	0.10	14
F5	250-300	15.3 %	16.2 %	34.0	73.6	9.0	17.4	1.46	0.18	33
F6	300-350	10.3 %	10.8 %	35.5	77.8	9.2	13.0	1.41	0.13	71
Res	>350	51.8 %	-	35.2	81.0	6.3	12.8	0.92	0.12	66[b]
Cold trap	-	3.4 %	3.5 %	12.5	14.0	9.9	76.1	8.42	4.08	59
Balance	-	98.8 %	-	0.3 %	-0.3 %	-3.9 %	3.6 %	-	-	-

[a] Oxygen by difference, [b] Estimated based on a weighted average calculation.

of the biocrude has been avoided.

3.2. Properties of distillation fractions

FTIR spectra of the distillate fractions are presented in Figure 2. Major absorptions in the 1700 cm^{-1} and 3300 cm^{-1} range indicate the presence of carbonyl and hydroxy groups throughout the fractions. More specifically, carbonyl absorption at 1715 cm^{-1} and 1745 cm^{-1} reflects six-membered and five-membered cyclic ketones, respectively, which seem to be mostly present in Fraction 1, 2 and 3 [27]. The sharp absorption around 1685 cm^{-1} in Fraction 4, 5 and 6 is likely to be α,β-unsaturated ketones or carbonyl absorption on aromatic structures. By comparing the hydroxy absorption in the range from 3650 cm^{-1} to 3000 cm^{-1}, hydroxy groups seem to be mostly present in Fraction 5 and 6, which is very likely related to the presence of phenolics and glycerol identified by GC-MS. Aromatic structures, identified by absorptions around 1600 cm^{-1} and slight absorptions between 3000-3050 cm^{-1}, are observed in all fractions but most pronounced in Fraction 6.

The elemental composition of the fractions are generally patterned in the way that increasing boiling points are correlated with decreasing H/C ratios, indicating a decreasing saturation of the compounds at higher boiling points. Oxygen is distributed in all distillate fractions and no general pattern in the oxygen content is observed. The HHV of the dewatered biocrude was 34.3 MJ/kg, whereas the fractions ranged from 33.8 MJ/kg for Fraction 1 to 37.1 MJ/kg for Fraction 4. The HHV of the fraction collected in the cold trap was 12.5

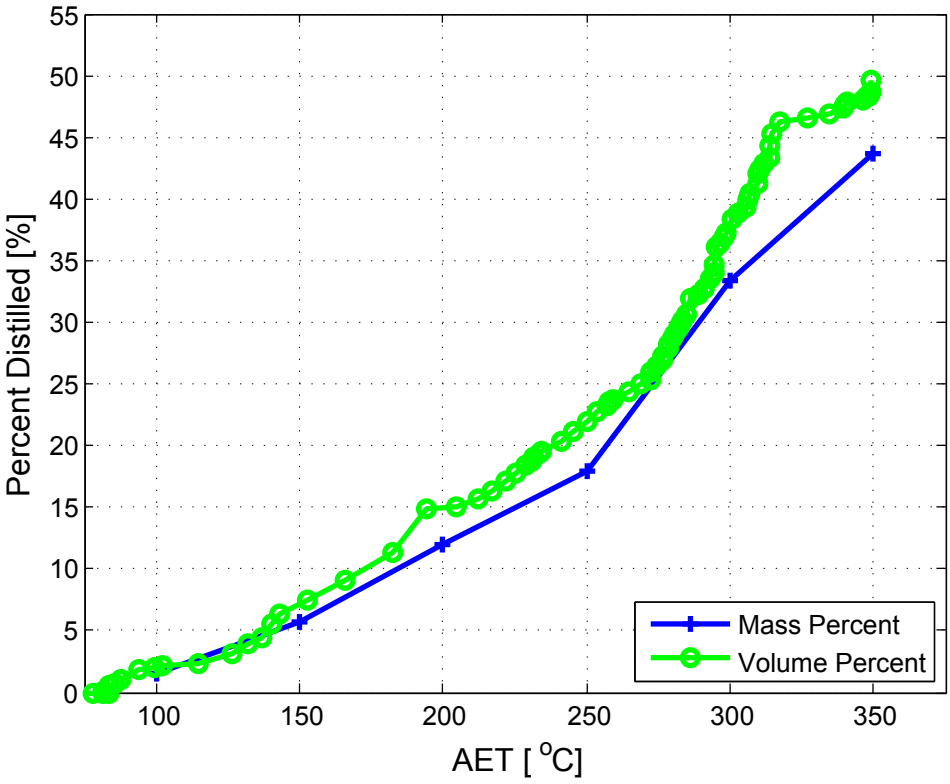

Figure 1: Distillation profile from 15:5 fractional distillation of the biocrude.

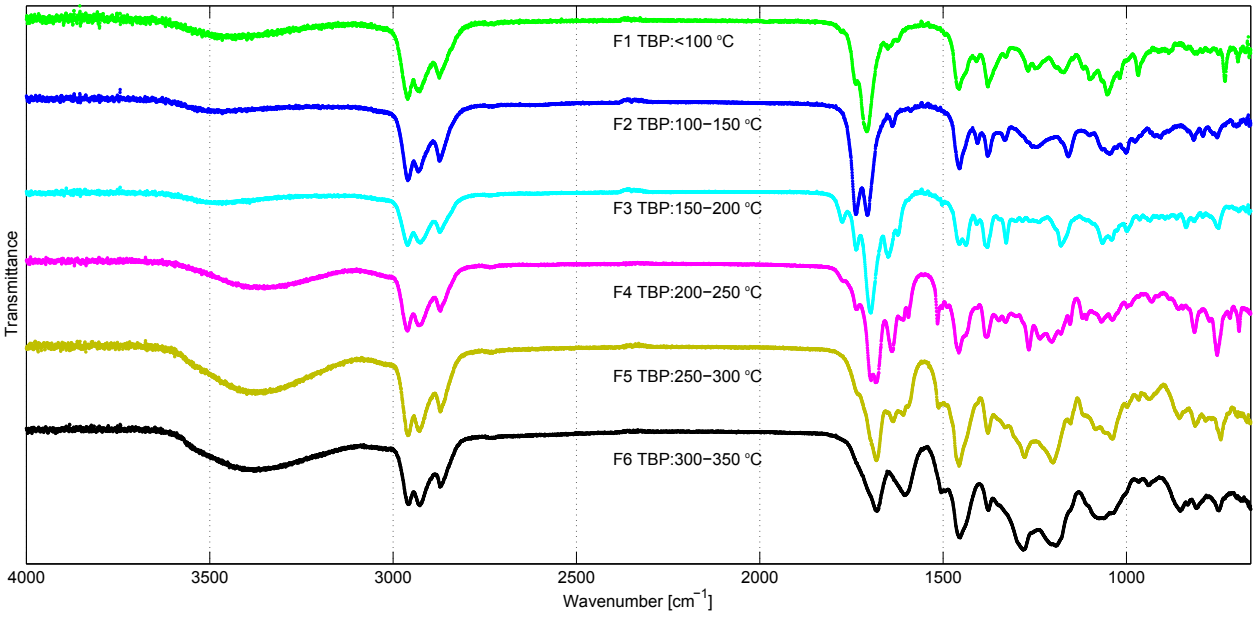

Figure 2: Infrared spectra of the distillate fractions obtained from the fractional distillation.

MJ/kg, which supports the significant share of water measured by Karl Fisher titration. The oxygen weight percent above 18 % combined with a H/C atomic ratio of 2.37 indicates that the chemical compounds obtained in Fraction 1 are mainly volatile oxygenated compounds having low number of carbon atoms. Based on elemental composition, Fraction 2 and 3 are chemically similar with Fraction 3 being slightly more oxygenated, which is also emphasized by HHV and FTIR observations. Of all the fractions, Fraction 4 exhibits the lowest oxygen content and so the highest HHV. In terms of elemental composition, Fraction 5 is chemically different from the other fractions. The boiling point range of Fraction 5 includes the boiling point of glycerol (290 °C), which was a major constituent in the feedstock used for the biocrude production. Hence, the high oxygen content observed is likely related to the recovery of unconverted glycerol in this fraction. GC-MS analysis showed that glycerol is in fact present in Fraction 5. The H/C atomic ratio of Fraction 6 indicates that aromatic structures are dominating. The residue displays a HHV close to that of Fraction 6, but with a H/C ratio below unity. This fact points in the direction of high molecular weight and unsaturated oxygenates probably of multi-ring structures.

The elemental composition of the distillate fractions can be summarized by plotting the H/C and O/C atomic ratios in a Van Krevelen chart as shown in Figure 3. All fractions but the residue show H/C ratios higher than that of the biocrude. Furthermore, all fractions but Fraction 1 and 5 show O/C ratios lower than that of the biocrude. For transport fuel production the ideal position in the Van Krevelen chart is at the H/C axis, resulting in pure hydrocarbon structures. However, in terms of HHV and elemental composition it appears that none of the fractions obtained from distillation have chemical properties significantly improved from those of the biocrude. If the ultimate objective is to produce transport fuels further chemical processing of all distillate fractions is necessary.

3.3. Compound identification in distillation fractions

Fractionation of the biocrude by fractional distillation allows for the separation of the many chemical compounds present in the biocrude due to differences in volatilities. The fractions obtained contain fewer chemical species, as compared to the biocrude, and are therefore chemically less complex, which in turn facilitates the identification of the chemical compounds. The compound identification is valuable and important in order to understand

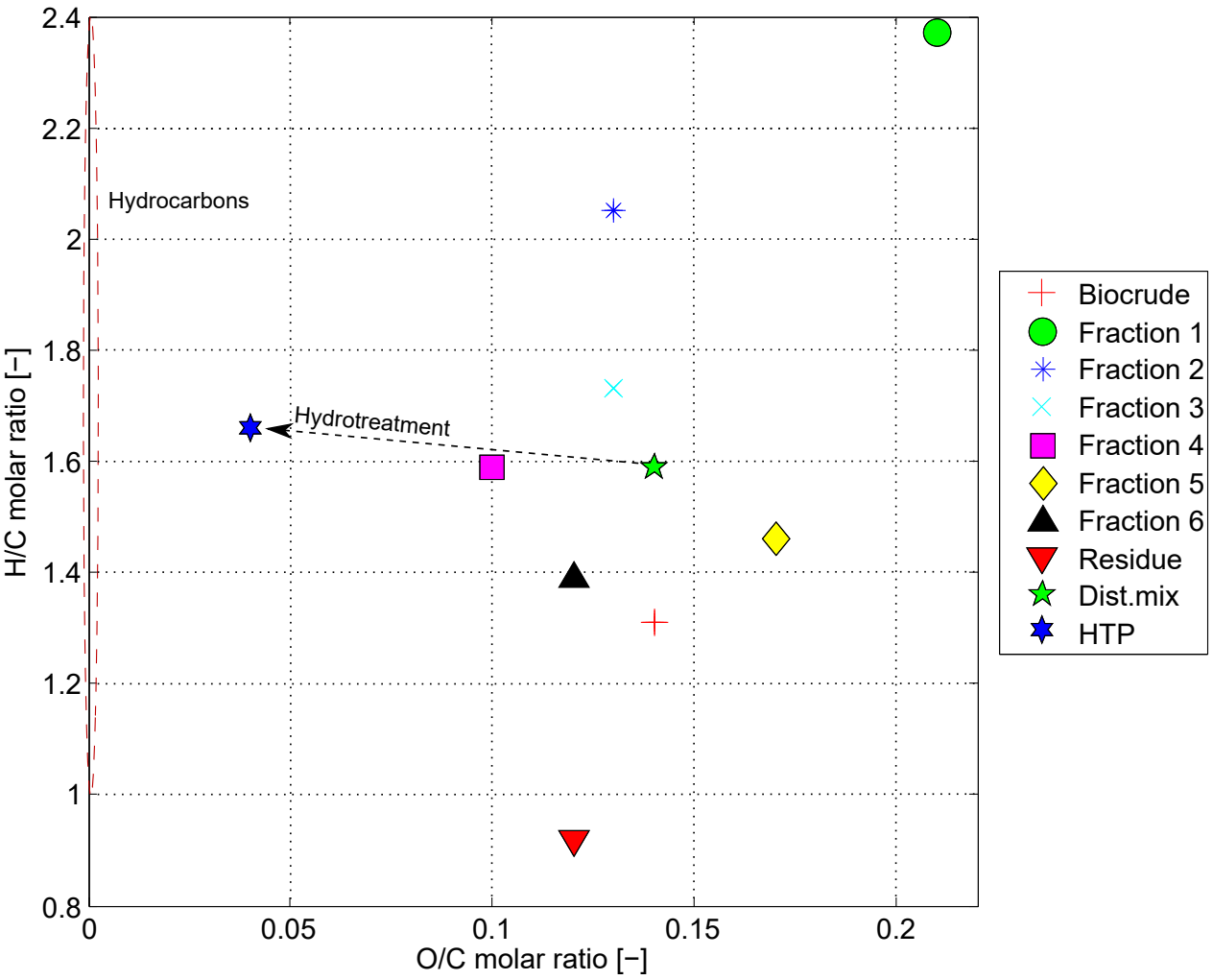

Figure 3: Van Krevelen diagram of the biocrude, distillation fractions, distillation mix and HTP.

the underlying chemical pathways responsible for the formation of specific chemicals. Understanding such reactions permits one to direct the composition of the biocrude by controlling the feedstock composition and process conditions for favorable chemical reactions.

GC-MS analysis of the distillate fractions enables a visual inspection of the compound separation efficiency and furthermore indicates the chemical complexity of the fractions compared to the biocrude. Figure 4 shows the normalized chromatograms of the six distillate fractions analyzed. It is clear that compound overlapping is a fact between preceding and proceeding distillate fractions as a result of imperfect distillation. However, an overlap must

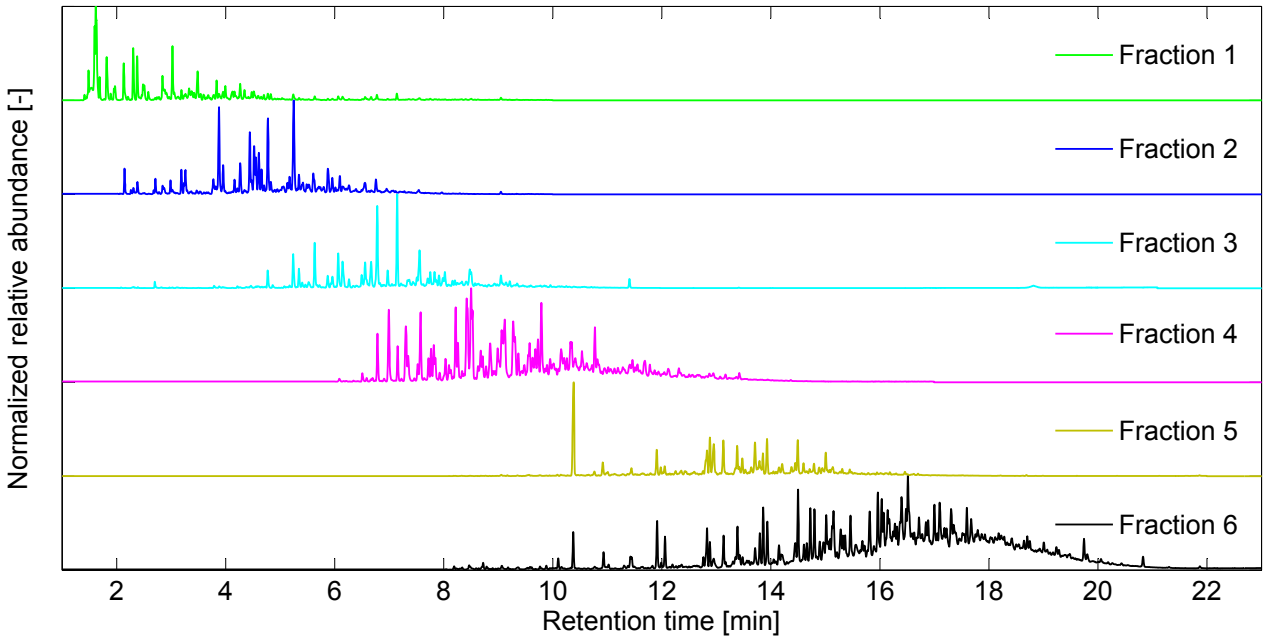

Figure 4: GC-MS chromatograms of the distillate fractions. Chromatograms have been normalized to highest peak.

be expected; according to the ASTM D2892, the overlap is 15-20 °C when running a 15:5 vacuum distillation. In addition, it must be kept in mind that for the derivatized samples (Fraction 5 and 6) some bias is inevitably introduced due to shifts in volatility for certain compounds obscuring the separation efficiency interpretation. In Table 3 the 15 most abundant (by GC-MS peak area interpretation) chemical compounds identified in each distillate fraction are presented. From the table it appears that in Fraction 1 mainly short chained commodity chemicals are collected such as acetaldehyde, ethanol, and propanol alongside various ketones and hydrocarbons like toluene ranging from C_2-C_8 in number of carbon atoms [28]. Except from a few alcohols, Fraction 2 contains almost exclusively saturated ketones ranging from C_4-C_7 in number of carbon atoms, mainly in the form of cyclopentanones. This observation is consistent with the elemental composition and the FTIR interpretation. A less pronounced overlap is observed between Fraction 2 and Fraction 3. From Table 3 it follows that substituted saturated and unsaturated cycloketones are dominating Fraction 3, such as mono- and dimethylated cyclopentenones and cyclohexanones. Here a rather successful separation is observed from the fact that only a few of the major compounds are identified

in both distillate fractions. Ketones of C_5- and C_6-membered napthenic ring backbones are potential hydrocarbon precursors. The ease of hydrotreating these ketones is demonstrated later. Like in Fraction 3, Fraction 4 is also dominated by cycloketones. Different from Fraction 3, the cycloketones in Fraction 4 are heavilier substituted in the form of ethylation and trimethylation. Nevertheless, the potential of these heavier substituted ketones as hydrocarbon fuel is equivalent to those in Fraction 2 and 3, and thus Fraction 2-4 are dominated by chemical candidates for fuel production. Oxygenated aromatics in the form of substituted phenolics are also present in Fraction 4. The separation of compounds between Fraction 4 and 5 is concluded successful. The major peak in Fraction 5, interfering the compound range of Fraction 4, is identified as glycerol. As mentioned, the chemical derivatization of for instance glycerol decreases the boiling point causing interpretation bias. Except from a significant share of glycerol, Fraction 5 consists predominately of phenolic derivatives. The identification of compounds in Fraction 5 and 6 by NIST library search was poor compared to the lighter fractions, resulting in the identification of many identical or isomeric compounds. The presence of hydroxy, alcoholic, and carboxylic functionalities were evident from mass spectra interpretation by the observation of trimethylsilylation (m/z=73) as a result of derivatization. The chemical potential of oxygenated aromatics is ranging widely [29]. In a lignin context, which is the most abundant source of aromatics, it has previously been concluded that high volume production of low molecular weight aromatic molecules is an attractive and very desirable goal, but perhaps also the most challenging and complex barrier for turning lignin into high valuable chemicals [29]. Due to the presence of the different monomeric aromatics, Fraction 4-6 are evidently sources of such high valuable aromatics with a summed distillate mass fraction over 30 %, which are likely to originate mainly from the lignin fraction.

The findings of the compound identification by GC-MS is summarized by lumping the compounds into four major classifications; *hydrocarbons*, *ketones*, *other non-aromatic oxygenates*, and *aromatic oxygenates* and presented in Figure 5. Figure 5 also indicates the average number of carbon atoms of the compounds of each fractions. The average is based on the identified compounds and the relative peak area obtained from GC-MS analysis. The trend increases almost linearly with increasing boiling point. Fraction 5 diverges from the

trend, which is most likely due to the presence of glycerol.

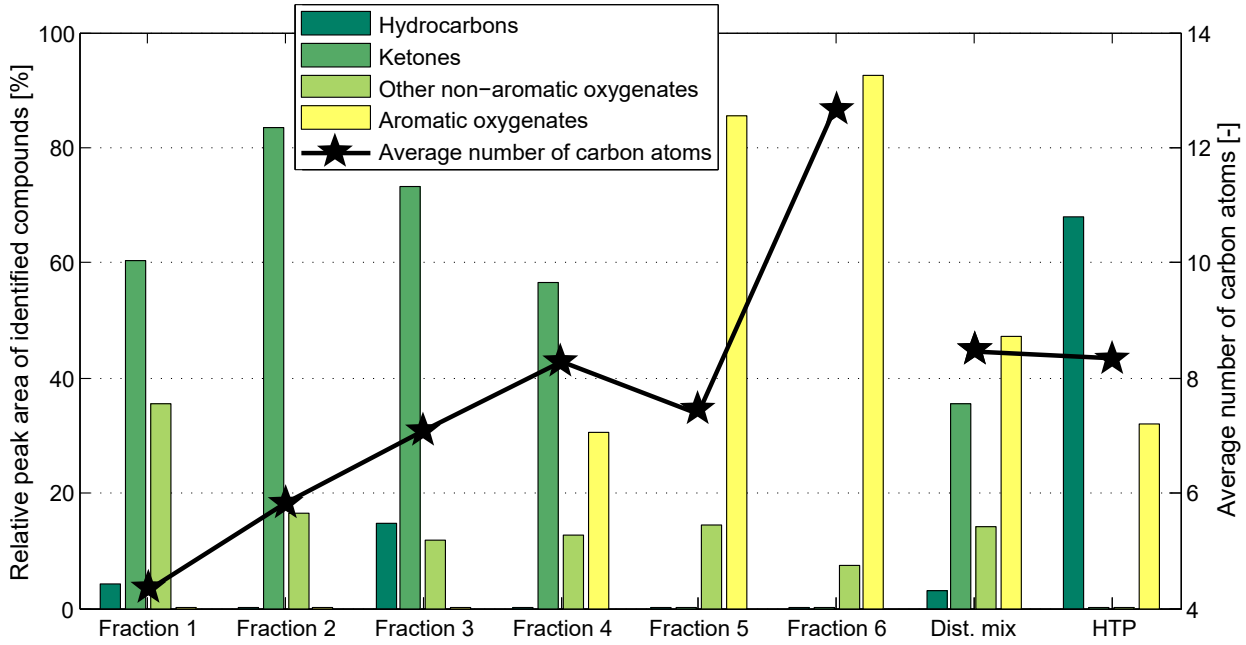

Figure 5: Relative distribution of hydrocarbons, ketones, other non-aromatic oxygenates and aromatic oxygenates in the distillation fractions and the HTP.

Table 3: List of major compounds identified in the distillate fractions including their relative abundance.

		Peak area (%)						
RT (min)	Identified compound	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6	C#
1.41	Acetaldehyde	0.9%						2
1.49	Ethanol	10.6%						2
1.69	1-Propanol	2.8%						3
1.82	2-Butanone	11.4%	9.0%					4
1.89	Ethyl Acetate	1.2%						4
1.96	1-Propanol, 2-methyl-	3.9%	3.9%					4
2.14	2-Butanone, 3-methyl-	9.2%						5
2.15	1-Butanol		4.0%					4
2.31	2-Pentanone	11.10%						5
2.38	3-Pentanone	1.60%						5
2.51	n-Propyl acetate	2.70%						5
2.58	Butanoic acid, methyl ester	0.90%						5
2.7	1,2-propanediol			9.00%				3
2.71	1-Butanol, 2-methyl-		2.40%					5
2.85	3-Pentanone, 2-methyl-	4.70%						6
2.99	1-Pentanol		2.10%					5
3.03	Toluene	1.70%						7
3.19	3-Hexanone	1.00%	2.90%					6
3.26	Cyclopentanone		3.70%					5
3.49	Cyclopentene, 1,2,3-trimethyl-	1.00%						8

Table 3 – continued from previous page

		Peak area (%)						
RT (min)	Identified compound	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6	C#
3.88	Cyclopentanone, 2-methyl-		11.80%					6
3.96	Cyclopentanone, 3-methyl-		3.10%					7
4.45	Cyclopentanone, 2,5-dimethyl-		8.10%					7
4.53	Cyclopentanone, 2,5-dimethyl-		9.20%					7
4.61	Cyclopentanone, 2,3-dimethyl-		1.90%					7
4.66	Cyclohexanone, 3-methyl-		2.20%					
4.78	2-Cyclopenten-1-one, 2-methyl-		4.50%	3.90%				6
5.25	2-Cyclopenten-1-one, 3,4-dimethyl-		6.50%	4.00%				7
5.35	2-Cyclopenten-1-one, 3,4-dimethyl-			2.40%				7
5.41	Cyclopentanone, 2,3-dimethyl-			2.10%				7
5.64	2-Cyclopenten-1-one, 3-methyl-			2.90%				6
5.85	Phenol				3.60%			6
5.87	Cyclohexanone, 2,6-dimethyl-			3.70%				8
5.96	Cyclohexanone, 2-ethyl-			11.80%				8
6.07	2-Cyclopenten-1-one, 3,4-dimethyl-			3.10%				7
6.15	2-Cyclopenten-1-one, 2,3-dimethyl-			8.10%				7
6.56	1-Isopropylcyclohex-1-ene			9.20%				9
6.67	1-Methylcyclooctene			1.90%				9
6.78	2-Cyclopenten-1-one, 2,3-dimethyl-			2.20%	3.50%			7
6.99	Phenol, 2-methyl-				3.20%			7
7.15	2-Cyclopenten-1-one, 2,3,4-trimethyl-			4.50%	2.10%			8
7.31	Phenol, 3-methyl-				4.30%			7
7.56	2-Cyclopenten-1-one, 3,3,4-trimethyl-			6.50%				8
7.57	2-Cyclopenten-1-one, 2,3,4-trimethyl-				6.20%			8
7.77	2-Cyclopenten-1-one, 3-(1-methylethyl)-				1.80%			8
8.22	2-Cyclopenten-1-one, 3-(1-methylethyl)-				5.20%			8
8.43	Phenol, 3,5-dimethyl-				4.20%			8
8.5	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-				8.60%			9
8.85	Phenol, 2,3-dimethyl-				2.10%			8
8.99	Phenol, 2-ethyl-5-methyl-				2.00%			9
9.12	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-				8.40%			9
9.3	1-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-				5.00%			10
9.79	3-Cyclohexene-1-carboxaldehyde, 1,3,4-trimethyl-				3.10%			10
10.39	Glycerol					9.57%		3
11.43	Nonanoic acid						1.43%	11
11.45	3,5-Dimethylphenol					0.80%		8
11.91	4-Methylcatechol					3.99%	1.11%	7
12.83	4-Hydroxyphenethyl alcohol					5.57%	1.21%	8
12.89	2-Hydroxyphenethyl alcohol					5.20%		8
12.96	4-Isopropylphenol					6.03%		9
13.14	2-Hydroxyphenethyl alcohol					5.31%		8
13.39	3-Hydroxyphenethyl alcohol					5.39%	1.40%	8
13.49	3-Hydroxy-benzeneacetic acid					2.38%		8
13.72	3-methyl-4-Hydroxy-benzeneacetic acid					4.11%		9
13.8	2-Hydroxy-2-phenylacetic acid					2.44%		8
13.86	3-Hydroxy-benzeneacetic acid					2.44%	1.04%	8
13.94	2-Hydroxy-4-methylbenzoic acid					4.35%	0.92%	8
14.5	3-Hydroxy-benzeneacetic acid					5.55%		8
14.73	1-Hydroxypentene, 1,3-diphenyl						0.92%	19
14.8	5-Isopropyl-2-methylphenoxy						0.96%	10
15.02	3-Hydroxy-benzeneacetic acid					3.05%	1.53%	8
15.15	tert-Butylhydroquinone						1.80%	14
15.29	1,3-Benzenedicarboxylic acid						1.34%	12
16.15	3-Hydroxyphenylpropionic acid, ethyl ester						0.94%	11
16.4	3,5-di-tert-Butyl-4-hydroxyacetophenone						1.10%	16
16.52	3-Hydroxyphenylpropionic acid, ethyl ester						2.32%	11
17.31	Phenol, 2,4,6-tris(1,1-dimethylethyl)-						1.26%	18
Total		64.41 %	75.29 %	75.29 %	63.41 %	66.18 %	19.28	

3.4. Compound identification in the distillation residue

The distillation residue was analyzed by pyrolysis-GCxGC-MS. The most abundant (by peak area interpretation) identified chemical compounds are shown in Table 4. Note that these compounds are pyrolysis products of the residue fraction. The use of GCxGC-MS generally improves both the peak separation and the sensitivity compared to 1D GC-MS. As a result, the number of detected components can be very large for complex samples, which is also the present case. Thermogravimetric analysis of the residue has shown that approximately 70 % of the residue is volatilized at 600 °C. Hence, the pyrolysis-GCxGC-MS results serve as an almost complete indication of the residue chemical structure. The identified components of the residue fraction are mainly aromatics, as also indicated by the low H/C ratio in Table 1 as discussed earlier. Many of the components are oxygenated (several phenols and benzenediols are for instance detected), but some are not. This differs from the analyses of the six distillate fractions, where almost all identified compounds were oxygenated. The presence of non-oxygenated compounds in the chromatogram of the distillation residue can at least partly be explained by the formation of oxygen containing pyrolysis products such as carbon dioxide and water. Overall, the great similarity between the compounds obtained from the residue pyrolysis and the compounds obtained from distillation illustrates that by cracking of the residue this can contribute to increase the yield of the volatile fractions on a chemically similar basis. Ultimately, as will be explained later, the obtained cracking products can likewise be hydrotreated to yields drop-in fuels.

3.5. Proposed reaction mechanisms

In the following, a reduced reaction mechanism is proposed based on the general observations in the compound structures with each distillate fraction, and the fact that the biocrude was obtained by co-liquefaction of aspen wood and glycerol. Such a reduced reaction mechanism will not be conclusive but will serve as explanatory indicators of the formation of the specific compounds observed.

The formation of short chained compounds primarily observed in Fraction 1, but to some extent also in Fraction 2, indicates the occurrence of C-C bond cleavage reactions. Glycerol

Table 4: List of major compounds identified in the distillate residue including their relative abundance.

RT (min)	Identified compound	Peak area (%)	C#
3.43	1-Butanol	3	4
3.62	Butanal, 3-methyl-	4.75	5
3.82	1-Hexene	1.8	6
4.42	(Z)-2-Heptene	0.94	7
4.83	1,3,5-Heptatriene, (E,E)-	1.01	7
5.03	Toluene	1.74	7
5.32	1-Octene	0.59	8
9.63	Pentanoic acid	0.48	5
9.63	3-Hexenoic acid (E)-	0.73	6
9.64	Phenol	0.67	6
11.15	2-Cyclopenten-1-one, 2,3-dimethyl-	0.51	7
11.74	Phenol, 2-methyl-	0.94	7
11.94	2-Cyclopenten-1-one, 3,4,4-trimethyl-	0.49	8
12.34	Phenol, 3-methyl-	1.27	7
14.84	Phenol, 2,3-dimethyl-	1.73	8
15.44	Phenol, 3,4-dimethyl-	1.17	8
16.35	Phenol, 3,5-dimethyl-	0.51	8
18.55	Phenol, 2-ethyl-4-methyl-	0.51	9
18.65	1,2-Benzenediol, 3-methyl-	0.84	7
18.95	Phenol, 2,3,6-trimethyl-	0.68	9
19.55	1,2-Benzenediol, 4-methyl-	1.1	7
21.65	1,4-Benzenediol, 2,6-dimethyl-	0.98	8
22.55	1,3-Benzenediol, 4,5-dimethyl-	1.8	8
23.35	1,3-Benzenediol, 2,5-dimethyl-	0.53	8
24.15	1,4-Benzenediol, 2,3,5-trimethyl-	1.06	9
24.45	Benzene, 1,4-dimethoxy-2-methyl-	0.68	9
25.45	1,3-Benzenediol, 4-propyl-	0.56	9
25.95	Phenol, 4-ethyl-2-methoxy-	0.69	9
26.45	Phenol, 5-methoxy-2,3-dimethyl-	0.84	9
28.55	1,4-benzenediol, 2-(1-methylpropyl)-	0.53	10
29.75	Naphtalene, 1,2,3,4-tetrahydro-1,5,7-trimethyl-	0.7	13
30.55	Benzene, 1,2,3,4-tetramethyl-4-(1-methylethenyl)-	1.35	13
31.85	Benzene, 1,3-diethyl-2,4,5,6-tetramethyl-	0.54	14
33.66	Benzene, 1,2,3-trimethoxy-5-(1-propenyl)-, (E)-	0.67	12
35.56	1-Naphthol, 2,5,8-trimethyl-	0.53	13
38.44	n-Hexadecanoic acid	1.93	16
38.56	5-Isopropyl-3,8-dimethyl-1,2-dihydronaphtalene	0.88	15
40.46	Phenanthrene, 2,5-dimethyl-	1.55	16
42.54	Octadecanoic acid	1.78	18
43.04	Eicosanoic acid	0.68	20
44.26	Retene	2.21	18
45.47	Benzene, 1,3-dimethoxy-5-[(1E)-2-phenylethenyl]-	0.74	16
50.67	Anthraquinone, 1,2,4-trimethyl-	0.99	17
Total		47.68 %	

conversion under near- and supercritical water conditions has been proposed to undergo C-C splitting through an ionic and a radical pathway forming acetaldehyde, formaldehyde, formic acid, ethanol and others [30, 31]. Under alkaline hydrothermal conditions, high selectivity towards lactic acid formation has been observed when processing glycerol. 1,2-propandiol has been detected as a minor reaction compound [32]. 1,2-propandiol, which is detected in Fraction 3, is proposed to be derived from hydrogen-abstraction of glycerol to a glyceraldehyde intermediate, followed by dehydration and hydrogenation with in-situ generated hydrogen [32–34]. The occurrence of hydrogenation reactions may then also explain the formation of propanol, ethanol, and pentanol probably from the reduction of carbonyl functionalities.

Ketones observed throughout Fraction 1-4 range from butanone observed in the light fractions to heavily substituted pentanones and hexanones observed at higher boiling points. The abundance of ketones suggests a more global pathway for ketonization of intermediates of similar chemical characteristics. Under supercritical, alkaline water conditions, carbohydrates are known to form carboxylic acids such as formic, acetic, propionic, and lactic acid etc. through Retro-Aldol reactions. These may then undergo homogeneous and heterogeneous ketonic decarboxylation forming a variety of different ketones. Zhang et al. claim that the observation of these ketones in the distillate of a pyrolysis biooil is the result of *reactive* distillation, since no carboxylic acids were detected in the biooil [7]. However, ketonic decarboxylation of carboxylic acids proceeds at temperatures well above the boiling points of the precursor acids and in the presence of a base catalyst [35, 36]. In the present study ketones were in fact observed in the biocrude but no carboxylic acids were detected, leading to the conclusion that ketones are more likely formed a priori distillation and hence not as a result of reactive distillation. The observation of a variety of different substituted ketones indicates that formed ketones further react with other compounds present. Ketonic decarboxylation of carboxylic acid like acetic and propionic acid with lactic acid can also explain the observation of ethyl and propyl acetate. Another potential pathway to ketone formation is base-catalyzed dimerization of acetone yielding diacetone alcohol. Acetone is the product of ketonic decarboxylation of acetic acid. Self-condensation of diacetone alcohol yields a cyclohexanone or methyl-cyclopentanone. More complex ketones, such as methyl- and ethyl-substituted pentanones and hexanones, cannot be explained simply as products of

ketonic carboxylation reaction but involves further substitution and condensation reactions. Hu et al. investigated polymerization reactions of a model biooil and found that pentanone reacts with carboxylic acids, such as formic and acetic acid, upon heating [24]. As an example, ethylated hydroxy-pentenone was found as a condensation product, which points in the direction of a condensation reaction between cyclopentanone and acetic acid. Furthermore, Hu et al. also found that cyclopentanone in the model biooil was stable when the model biooil was blended in methanol and hence does not react with alcohols when heated. For more reduced compounds such as dimethyl-hexanone and ethyl-hexanone, condensation reactions must have been necessitated by hydrogen-transfer reactions.

In the higher boiling fractions a dominance of aromatics is observed. The formation of oxygenated aromatics from lignocellulose processing is well-known. The three monolignols of lignin are the precursors of many aromatic compounds [37], alongside dehydration reactions of carbohydrates [38]. In contrast to the mono-functional ketones, the oxygenated aromatics generally show multiple functionalities resulting in far more complex compounds derived from the complex and heterogeneous structure of lignin. Formation of monomers proceeds mainly through thermal degradation and hydrolysis of ether bonds. The proposed reactions are summarized in Figure 6.

3.6. Hydrotreating

Hydrotreating is tested as a way to decrease the chemical complexity of the biocrude. The distillate fractions are previously found to contain hydrocarbon derived compounds with various oxygen functional groups and various aromatic substitutions. For the biocrude or fractions to be used as drop-in biofuels or bio-chemicals, deoxygenation and purification is required. Due to a high degree of similarity in the hydrocarbon backbones of the compounds, observed from GC-MS analysis, deoxygenation may also result in a product mixture consisting of highly similar compounds.

Table 5 lists and compares the elemental analysis, TAN and HHV of the distillate mix before and after hydrotreating. The HHV is increased by 22 % during hydrotreating, which is favorable in a biofuel context. The improved HHV is mainly the result of a 68 % reduction in oxygen content from 14.5 to 4.6 %. Likewise, the H/C ratio has increased slightly from 1.59 to 1.66 indicating some saturation of double bonds. The TAN value is decreased from 36

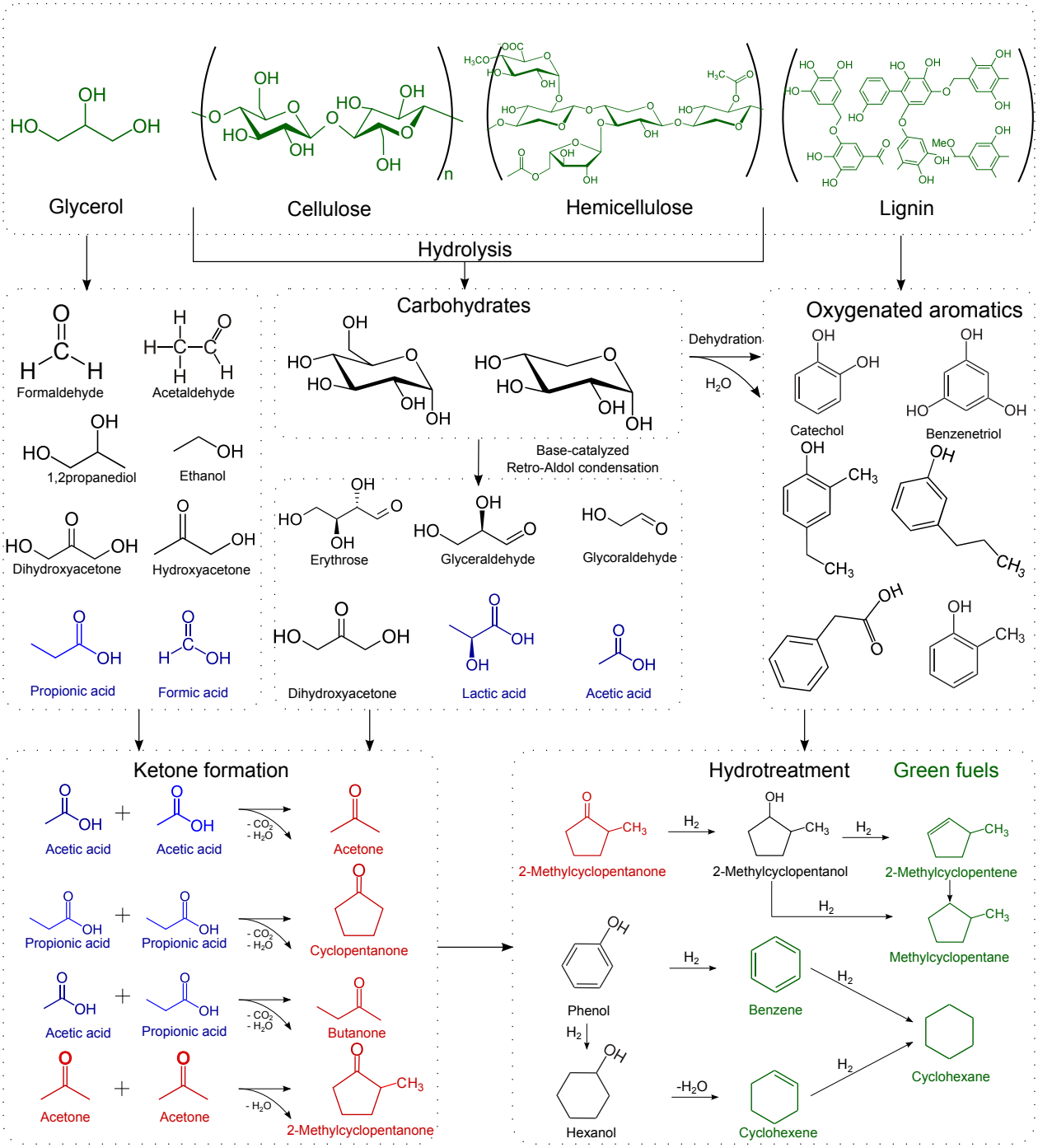

Figure 6: Proposed reaction pathways for the formation of chemicals and fuels.

to 7 mg KOH/g. Although these parameters reveal a significant quality improvement from a fuel perspective, the oxygen content and acid number indicate incomplete deoxygenation under the given processing conditions. This is also emphasized by the FTIR spectra in Figure 7, where slight hydroxy and carbonyl absorptions still appear. Without being conclusive on a quantitative basis, the HTP spectra suggests that carbonyl absorption has been reduced to a greater extent than the hydroxy absorption. This is not surprising considering the relatively higher deoxygenation reactivity expected for ketones compared to e.g. phenols [13, 14]. Furthermore, the conditions applied, (residence time and catalyst:feedstock mass ratio) corresponding to an equivalent WHSV of 3.3, are considered as rather mild conditions, where more severe conditions would likely be beneficial for complete deoxygenation [12, 23].

Table 5: Properties of the distillate mix and HTP.

	HHV	Elemental analysis [wt.%]					TAN
Sample	[MJ/kg]	C	H	O[a]	H/C [-]	O/C [-]	[mg KOH/g]
Dist. mix	35.2	75.4	10.1	14.5	1.59	0.14	35.58
HTP	42.9	83.7	11.7	4.6	1.66	0.04	7.00

[a] Oxygen by difference

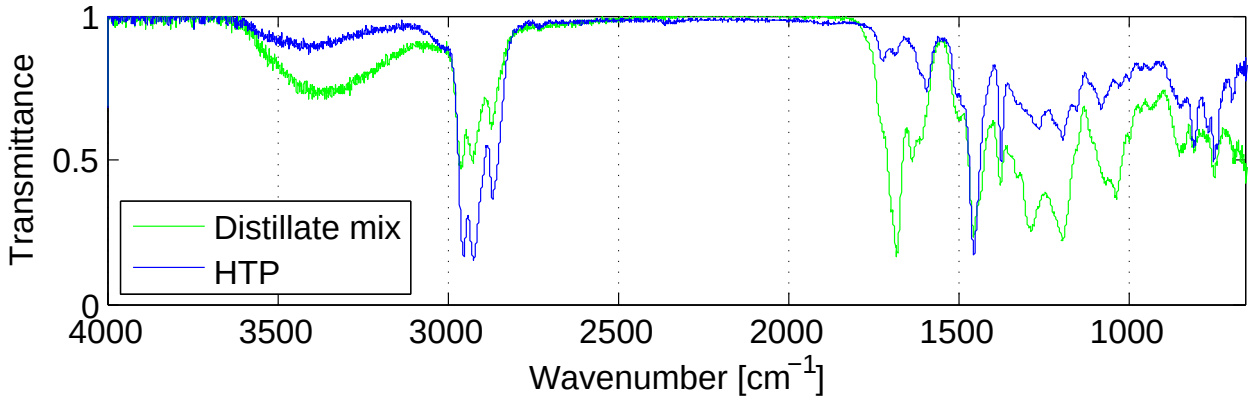

Figure 7: FTIR spectra of the distillate mix before and after hydrotreating.

3.7. Compound identification of HTP

Figure 5 shows the relative distribution of compound classes within the distillate mix and the HTP. It appears that after hydrotreatment the rather complex distillate mix has

been converted into HTP containing solely hydrocarbons and aromatic oxygenates. Table 6 lists the most abundant (by GC-MS peak area interpretation) compounds found in the HTP. Approximately two thirds of the identified compounds are hydrocarbons of which the majority are five- and six-membered napthenic rings with different substitutions. It is expected that these hydrocarbons are mainly the counterparts to the broad range of ketones identified in the Fraction 2, 3, and 4, but also to a minor extent derivatives of the oxygenated aromatics. Compounds like propyl-phenol, 2-methyl-phenol, and 4-hydroxyphenethyl alcohol observed in Fraction 5 and 6, could potentially be the oxygenated phenolic counterparts of propyl-cyclohexane, 2-ethyl-5-methyl-hexane, ethyl-cyclohexane, respectively, observed in the HTP. Generally, the hydrocarbons in this table are chemically very similar, indicating that the chemical complexity of the distillate mix has been significantly reduced. From a biofuel perspective, such deoxygenated compounds will serve as a high quality bio drop-in e.g. in a gasoline pool due to high octane numbers or in jet-fuel due to good cold flow properties.

Table 6 also indicates that the high share of oxygenated aromatics in the distillate mix is still present in the HTP. These are expected to originate from the compounds found in Fraction 5 and 6. Whereas the oxygenated aromatics in Fraction 5 and 6 demonstrated many different oxygenated functional groups, such as phenolics, carboxylic acids, esters e.g., the only oxygenated functional group identified in the HTP is phenolics. Therefore, it is expected that the oxygenated aromatics in Fraction 5 and 6 will undergo incomplete deoxygenation and end up as phenolics with different degrees of hydrocarbon substitution under the given processing conditions. I.e. the oxygenated functional groups such as e.g. acetic acids, and ethyl alcohols will be deoxygenated to an ethyl substitution on a stable phenol. Phenols are known to be relatively resistant to deoxygenation due to aromatic stabilization [14].

Hydrotreating has deoxygenated and chemically simplified the distillate mix to mostly substituted cyclopentanes and cyclohexanes as well as substituted phenols. The present experiment demonstrated the easiness of hydrotreating ketones. This was also demonstrated by Kong et al., who investigated deoxygenation of various aliphatic ketones over nickel-based catalysts [16]. Even at low temperatures (160 °C) they found that all the ketones investigated were easily reduced to corresponding alkanes. For cyclohexanone they proposed that the catalytic hydrogenation proceeds effectively to cyclohexanol, which then may undergo de-

Table 6: List of major chemical compounds identified in the hydrotreated sample including their relative abundance.

RT (min)	Identified compound	Chemical Formula	Peak area (%)	C#
2.17	Cyclohexane	C_6H_{12}	1.70%	6
2.31	Cyclopentane, 1,3-dimethyl-	C_7H_{14}	4.30%	7
2.4	Hexane, 3-methyl-	C_7H_{16}	1.37%	7
2.62	Cyclohexane, methyl-	C_7H_{14}	2.94%	7
2.72	Cyclopentane, ethyl-	C_7H_{15}	1.56%	7
2.76	Cyclopentane, 1,2,4-trimethyl-	C_8H_{16}	1.29%	8
3.1	Cyclopentane, 1,2,4-trimethyl-	C_8H_{17}	1.93%	8
3.26	Cyclopentane, 1-ethyl-3-methyl-	C_8H_{16}	4.84%	8
3.81	Cyclohexane, ethyl-	C_8H_{16}	3.10%	8
3.9	1,3-Diethylcyclopentane	C_9H_{18}	3.36%	9
4.49	Cyclopentane, 1-methyl-2-propyl-	C_9H_{18}	2.21%	9
4.81	Cyclohexane, 1-ethyl-2-methyl-	C_9H_{18}	1.95%	9
5.15	Cyclohexane, propyl-	C_9H_{18}	2.98%	9
5.27	Cyclopentane, 1,2-dipropyl-	$C_{11}H_{22}$	1.42%	11
5.83	1,2-Dihydrocatechol	$C_6H_8O_2$	1.91%	6
9.37	Phenol, 3,4-dimethyl-	$C_8H_{10}O$	1.61%	8
10.02	Phenol, 2,3-dimethyl-	$C_8H_{10}O$	0.95%	8
10.92	2-Methyl-1-phenyl-1-butanol	$C_{11}H_{16}O$	0.95%	11
12.48	Phenol, 4-ethyl-3-methyl-	$C_9H_{12}O$	0.85%	9
13.1	Phenol, 3-ethyl-5-methyl-	$C_9H_{12}O$	0.95%	9
13.3	Phenol, 2,4,6-trimethyl-	$C_9H_{12}O$	1.23%	9
13.42	Phenol, 2,3,6-trimethyl-	$C_9H_{12}O$	1.17%	9
13.61	2,5-Diethylphenol	$C_{10}H_{14}O$	0.71%	10
14.16	Phenol, 2,4,6-trimethyl-	$C_9H_{12}O$	0.55%	9
15.14	Phenol, 2,3,5,6-tetramethyl-	$C_{10}H_{14}O$	0.89%	10
15.38	Phenol, 2,3,5,6-tetramethyl-	$C_{10}H_{14}O$	0.69%	10
15.49	Phenol, 2,3,5,6-tetramethyl-	$C_{10}H_{14}O$	3.16%	10
16.74	Phenol, 2,3,5,6-tetramethyl-	$C_{10}H_{14}O$	0.78%	10
30.63	Retene	$C_{18}H_{18}$	0.06%	18
Total area			51.43%	

hydration to cyclohexene that is then quickly reduced to cyclohexane. Considering the HTP product distribution in Table 6, this reaction mechanism seems very likely for deoxygenation of the cyclic ketones together with similar mechanisms for the substituted equivalents.
The effects of hydrogenation on the various methyl-substitutions of phenolics were investigated by Massoth et al. [39]. Generally they found high resistance towards hydrogenation resulting in conversion efficiencies less than 50 % for both phenol and all mono-, di-, and trimethyl-substituted phenols investigated. Moreover, they suggested that the dependency on the conversion rates of the various substituted phenols was an adsorption phenomenon due electrostatic potentials rather than a matter of steric effects. They proposed two reaction pathways; one involving ring saturation followed by dehydration to cyclohexenes, and one leading to the formation of aromatics. They found that when the number of methyl-substitutions were increased, the pathway for aromatics formation became more favorable. This may explain why hardly any phenolics are saturated in the present results. Although oxygenated aromatics are still present in the HTP, it is expected that the degree of deoxygenation and saturation can easily be tuned with catalyst development and in particular optimisation of the hydrotreating conditions such as residence time [12]. In order to chemically simplify the products even more, separate hydrotreating of Fraction 1-4, 5-6 and the residue may also prove as a successful method to produce deoxygenated napthenes and substituted phenols, respectively.

4. Conclusion

Fractional distillation of a biocrude obtained from hydrothermal liquefaction was performed, resulting in six distillate fractions and a distillate residue. It was found that fractional distillation is a viable means for separating the complex biocrude mixture into fractions containing compounds of similar chemical structures. Light oxygenates holding the potential of fine chemical production were identified in the lighter distillate fractions. A significant share of different ketones were obtained, which proved to be prospective precursors for liquid transport fuels. In the heavier distillate fractions, phenolics were found the most abundant group of compounds. Reaction pathways for the formation of compounds observed in the distillate fractions were proposed. The pool of monomeric and low molecular weight oxygenated

aromatics of various functionalities holds particular potential as precursors for a variety of commodity bio-products. The distillation residue comprised a mass fraction of 51.8 % of the biocrude. Pyrolysis-GCxGC-MS analysis revealed that this residue is mainly of aromatic character. Hydrotreatment of the distillate mixture displayed the amenability of removing certain oxygen functionalities. Ketones were completely converted into saturated hydrocarbons, whereas the various oxygenated aromatics were mainly converted into high-valuable substituted phenolics. In conclusion, hydrothermal liquefaction of biomass coupled with fractional distillation and hydrotreatment could potentially represent a bio-refinery concept for renewable fuel and chemical production.

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References

[1] Biller P, Ross A. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. Bioresource Technology 2011;102:215 –25.

[2] Leow S, Witter JR, Vardon DR, Sharma BK, Guest JS, Strathmann TJ. Prediction of microalgae hydrothermal liquefaction products from feedstock biochemical composition. Green Chem 2015;17:3584–99.

[3] Pedersen TH, Rosendahl LA. Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems. Biomass and Bioenergy 2015;83:206 –15.

[4] Elliott DC, Biller P, Ross AB, Schmidt AJ, Jones SB. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. Bioresource Technology 2015;178:147 –56.

[5] Jensen CU, Rodriguez Guerrero JK, Karatzos S, Olofsson G, Iversen SB. Fundamentals of hydrofaction^{TM}: Renewable crude oil from woody biomass. Biomass Conversion and Biorefinery 2017;:1–15.doi:10.1007/s13399-017-0248-8.

[6] Sintamarean IM, Grigoras IF, Jensen CU, Toor SS, Pedersen TH, Rosendahl LA. Two-stage alkaline hydrothermal liquefaction of wood to biocrude in a continuous bench-scale system. Biomass Conversion and Biorefinery 2017;:1–11.

[7] Zhang XS, Yang GX, Jiang H, Liu WJ, Ding HS. Mass production of chemicals from biomass-derived oil by directly atmospheric distillation coupled with co-pyrolysis. Scientific Reports 2013;3:1–7.

[8] Cheng D, Wang L, Shahbazi A, Xiu S, Zhang B. Characterization of the physical and chemical properties of the distillate fractions of crude bio-oil produced by the glycerol-assisted liquefaction of swine manure. Fuel 2014;130:251–6.

[9] Capunitan JA, Capareda SC. Characterization and separation of corn stover bio-oil by fractional distillation. Fuel 2013;112:60 – 73.

[10] Hoffmann J, Jensen CU, Rosendahl LA. Co-processing potential of htl bio-crude at petroleum refineries - part 1: Fractional distillation and characterization. Fuel 2016;165:526 –35.

[11] Eboibi BEO, Lewis DM, Ashman PJ, Chinnasamy S. Hydrothermal liquefaction of microalgae for biocrude production: Improving the biocrude properties with vacuum distillation. Bioresource Technology 2014;174:212 –21.

[12] Jensen CU, Hoffmann J, Rosendahl LA. Co-processing potential of htl bio-crude at petroleum refineries - part 2: A parametric hydrotreating study. Fuel 2016;165:536 –43.

[13] Hoffmann J, Pedersen T, Rosendahl L. Near-critical and supercritical water and their applications for biorefineries; chap. Hydrothermal Conversion in Near-Critical Water - A Sustainable Way of Producing Renewable Fuels. Springer Netherlands. ISBN 978-94-017-8922-6; 2008, p. 373–400.

[14] Furimsky E. Catalytic hydrodeoxygenation. Applied Catalysis A: General 2000;199:147 –90.

[15] Mortensen P, Grunwaldt JD, Jensen P, Knudsen K, Jensen A. A review of catalytic upgrading of bio-oil to engine fuels. Applied Catalysis A: General 2011;407:1 – 19.

[16] Kong X, Lai W, Tian J, Li Y, Yan X, Chen L. Efficient hydrodeoxygenation of aliphatic ketones over an alkali-treated ni/hzsm-5 catalyst. ChemCatChem 2013;5:2009–14.

[17] Furimsky E. Hydroprocessing challenges in biofuels production. Catalysis Today 2013;217:13–56.

[18] Tews I, Zhu Y, Drennan C, Elliott D, Snowden-Swan L, Onarheim K, et al. Biomass direct liquefaction options: Technoeconomic and life cycle assessment. Tech. Rep.; Prepared for U.S. Department of Energy; 2014.

[19] Pedersen T, Grigoras I, Hoffmann J, Toor S, Daraban I, Jensen C, et al. Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation. Applied Energy 2016;162:1034 –41.

[20] ASTM D2892 . Standard test method for distillation of crude petroleum (15-theoretical plate column). Tech. Rep.; ASTM International; 2005.

[21] Lavanya M, Meenakshisundaram A, Renganathan S, Chinnasamy S, Lewis DM, Nallasivam J, et al. Hydrothermal liquefaction of freshwater and marine algal biomass: A novel approach to produce distillate fuel fractions through blending and of biocrude with petrocrude. Bioresource Technology 2016;203:228 –35.

[22] Maxwell JB, Bonnell LS. Industrial Engineering Chemistry; 1957. Vol. 49, pp. 1187-1196.

[23] Jensen CU, Rosendahl LA, Olofsson G. Impact of nitrogenous alkaline agent on continuous htl of lignocellulosic biomass and biocrude upgrading. Fuel Processing Technology 2017;159:376 –85.

[24] Hu X, Wang Y, Mourant D, Gunawan R, Lievens C, Chaiwat W, et al. Polymerization on heating up of bio-oil: A model compound study. AIChE Journal 2013;59:888–900.

[25] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Conversion and Management 2007;48:87 – 92.

[26] Diebold JP. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. Tech. Rep.; National Renewable Energy Laboratory; Golden, Colorado; 2000.

[27] Nakanishi K. Infrared absorption spectroscopy, practical. Holden-Day, San Francisco; 1962.

[28] Werpy T, Petersen G. Top value added chemicals from biomass. volume i: Results of screening for potential candidates from sugars and synthesis gas (pnnl-14804). Tech. Rep.; Pacific Northwest National Laboratory and the National Renewable Energy Laboratory; 2004.

[29] Bozell JJ, Holladay JE, Johnson D, White JF. Top value added chemicals from biomass. volume ii: Results of screening for potential candidates from biorefinery lignin (pnnl-

16983). Tech. Rep.; Pacific Northwest National Laboratory and the National Renewable Energy Laboratory; 2007.

[30] Bühler W, Dinjus E, Ederer H, Kruse A, Mas C. Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water. The Journal of Supercritical Fluids 2002;22:37 – 53.

[31] Müller JB, Vogel F. Tar and coke formation during hydrothermal processing of glycerol and glucose. influence of temperature, residence time and feed concentration. The Journal of Supercritical Fluids 2012;70:126 –36.

[32] Chen L, Ren S, Ye XP. Lactic acid production from glycerol using cao as solid base catalyst. Fuel Processing Technology 2014;120:40 –7.

[33] Martin A, Armbruster U, Gandarias I, Arias PL. Glycerol hydrogenolysis into propanediols using in situ generated hydrogen a critical review. European Journal of Lipid Science and Technology 2013;115:9–27.

[34] Pedersen TH, Jasinas L, Casamassima L, Singh S, Jensen T, Rosendahl LA. Synergetic hydrothermal co-liquefaction of crude glycerol and aspen wood. Energy Conversion and Management 2015;106:886 –91.

[35] Renz M. Ketonization of carboxylic acids by decarboxylation: Mechanism and scope. European Journal of Organic Chemistry 2005;2005:979–88.

[36] Deng L, Fu Y, Guo QX. Upgraded acidic components of bio-oil through catalytic ketonic condensation. Energy & Fuels 2009;23:564–8.

[37] Patwardhan PR, Brown RC, Shanks BH. Understanding the fast pyrolysis of lignin. ChemSusChem 2011;4:1629–36.

[38] Tompsett GA, Li N, Huber GW. Catalytic Conversion of Sugars to Fuels. John Wiley & Sons, Ltd. ISBN 9781119990840; 2011, p. 232–79.

[39] Massoth FE, Politzer P, Concha MC, Murray JS, Jakowski J, Simons J. Catalytic hydrodeoxygenation of methyl-substituted phenols: correlations of kinetic parameters with molecular properties. The Journal of Physical Chemistry B 2006;110:14283–91.