



Aalborg Universitet

AALBORG UNIVERSITY
DENMARK

Continuous Hydrothermal Co-liquefaction of Aspen Wood and Glycerol with Water Phase Recirculation

Pedersen, Thomas Helmer; Grigoras, Ionela; Hoffmann, Jessica; Toor, Saqib Sohail; Daraban, Iulia Maria; Jensen, Claus Uhrenholt; Iversen, Steen; Madsen, René; Glacius, Marianne; Arturi, Katarzyna Ratajczyk; Nielsen, Rudi Pankratz; Søgaaard, Erik Gydesen; Rosendahl, Lasse Aistrup

Published in:
Applied Energy

DOI (link to publication from Publisher):
[10.1016/j.apenergy.2015.10.165](https://doi.org/10.1016/j.apenergy.2015.10.165)

Creative Commons License
CC BY-NC-ND 4.0

Publication date:
2016

Document Version
Accepted author manuscript, peer reviewed version

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Pedersen, T. H., Grigoras, I., Hoffmann, J., Toor, S. S., Daraban, I. M., Jensen, C. U., Iversen, S., Madsen, R., Glacius, M., Arturi, K. R., Nielsen, R. P., Søgaaard, E. G., & Rosendahl, L. A. (2016). Continuous Hydrothermal Co-liquefaction of Aspen Wood and Glycerol with Water Phase Recirculation. *Applied Energy*, 162, 1034–1041. <https://doi.org/10.1016/j.apenergy.2015.10.165>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- ? Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- ? You may not further distribute the material or use it for any profit-making activity or commercial gain
- ? You may freely distribute the URL identifying the publication in the public portal ?

Continuous Hydrothermal Co-liquefaction of Aspen Wood and Glycerol with Water Phase Recirculation

T.H. Pedersen^a, I.F. Grigoras^a, J. Hoffmann^a, S.S. Toor^a, I.M. Daraban^a, C.U. Jensen^b, S.B. Iversen^b, R.B. Madsen^c, M. Glasius^c, K.R. Arturi^d, R.P. Nielsen^d, E.G. Søggaard^d, L.A. Rosendahl^{a,*}

^a*Department of Energy Technology, Aalborg University, Pontoppidanstræde 101, 9220 Aalborg Øst, Denmark*

^b*Steeper Energy Aps, Sandbjergvej 11, 2970 Hørsholm, Denmark*

^c*Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark*

^d*Department of Chemistry and Bioscience, Aalborg University, Niels Bohrs Vej 8, 6700 Esbjerg, Denmark*

Abstract

Hydrothermal liquefaction is a promising technology for the conversion of a wide range of bio-feedstock into a biocrude; a mixture of chemical compounds that holds the potential for a renewable production of chemicals and fuels. Most research in hydrothermal liquefaction is performed in batch type reactors, although a continuous and energy-efficient operation is paramount for such process to be feasible. In this work an experimental campaign in a continuous bench scale unit is presented. The campaign is based on glycerol-assisted hydrothermal liquefaction of aspen wood carried out with the presence of a homogeneous catalyst at supercritical water conditions, 400 °C and 300 bar. Furthermore, in the experimental campaign a water phase recirculation step is incorporated to evaluate the technical feasibility of such procedure. In total, four batches of approximately 100 kg of feed each were processed successfully at steady state conditions without any observation of system malfunctioning. The biocrude obtained was characterized using several analytical methods to evaluate the feasibility of the process and the quality of the product. Results showed that a high quality biocrude was obtained having a higher heating value of 34.3 MJ/kg. The volatile fraction of the biocrude consisted mostly of compounds having number of carbon atoms in the C₆-C₁₂ range similar to gasoline. In terms of process feasibility, it was revealed that total organic carbon (TOC) and ash significantly accumulated in the water phase when such is recirculated for the proceeding batch. After four batches the TOC and the ash mass fraction of the water phase were 136.2 [g/L] and 12.6 [%], respectively. Water phase recirculation showed a slight increase in the biocrude quality in terms on an effective hydrogen-to-carbon ratio, but it showed no effects on the product gas composition or the pH of the water phase. The successful operation demonstrated the technical feasibility of a continuous production of high quality biocrude.

Keywords: Biofuel, Continuous processing, Biocrude, Biomass, Hydrothermal liquefaction, Sustainability

*Corresponding author

Email address: lar@et.aau.dk

14 1. Introduction

15 Hydrothermal conversion of biomass in hot-compressed water is a viable, scalable, and
16 energy-efficient thermo-chemical route for converting biomass into synthetic solid, liquid, or
17 gaseous fuels and chemicals. At near and supercritical water conditions, biomass fragments
18 into a bulk liquid phase, better known as biocrude. It consists of low molecular weight
19 and deoxygenated chemical species compared to the original biomass macromolecules. The
20 biocrude may be further processed into platform chemicals or infrastructure-compatible fuels.
21 Hydrothermal conversion of biomass has been widely studied experimentally, mostly in batch
22 reactors and less so in continuous systems, and has been reviewed in the many process aspects,
23 such as near-critical water synthesis properties [1, 2], the effects of various process conditions
24 [3], effects of biomass composition [4–7], process developments [8–10], and upgrading of the
25 biocrude [11–13].

26 Although the vast majority of research is carried out in batch reactors, development of
27 continuous operation and technology upscaling of near-critical water technologies has been
28 ongoing since the mid-seventies - but has not yet reached commercialization [9]. The con-
29 tinuous process was first demonstrated at a bench scale system at the Pittsburgh Energy
30 Research Center (PERC) which was later scaled to the Albany plant, Oregon [14]. The
31 production facility utilized a recycle concept in which wood (Douglas fir) was slurried in re-
32 cycled process water and initially in anthracene oil and eventually in recycled biocrude as it
33 became available. The following three aspects of the process were identified as critical: 1) the
34 energy intensive pre-drying and grinding step required for wood flour preparation, 2) wood-
35 biocrude-water slurries could not be fed at concentrations greater than 10 % without causing
36 system plugging, 3) high recycle ratios of biocrude (up to 19:1) required excessive heat [15].
37 Many process improvements have since been done, and it is believed that the critical aspects
38 can be overcome or greatly reduced to an extent for the process to become feasible. One
39 aspect of the process optimization is to maximize the biocrude whilst decreasing the amount
40 of solid byproducts. During liquefaction, reactive biomass fragments rearrange to biocrude
41 compounds through condensation, cyclization, and re-polymerization, and for prolonged pro-
42 cess severity a solid fraction insoluble in most solvents is formed, which is generally termed
43 char.

44 In a lignocellulosic context, char formation results primarily from two counteracting mech-
45 anisms; 1) dehydration reactions of free sugars favored at intermediate temperatures, high
46 feed concentrations [16], and acidic conditions [17], and 2) radical formation during lignin
47 degradation leading to retrogressive char formation [18]. Char formation from carbohy-
48 drates can be suppressed by applying high heating rates to reach high reaction temperatures,
49 preferably above supercritical conditions, and alkaline conditions [16, 19, 20]. Lignin radi-
50 cal formation purely a thermal effect, hence supercritical conditions tends to enhance lignin
51 char formation [21]. Means of overcoming these counteracting thermal effects includes the
52 addition of a reducing agent such hydrogen or carbon monoxide, or by the addition of a sta-
53 bilizing co-solvent acting as a radical scavenger through hydrogen donation. Alcohols may
54 undergo thermal scission causing hydrogen abstraction in the form of $\cdot\text{H}$, $\cdot\text{OH}$, or $\cdot\text{CH}_2\text{OH}$
55 radicals, amenable to cap lignin radicals and hence preventing lignin repolymerization [22–
56 24]. Low molecular weight co-solvents such as phenol [25], propanol [26], ethanol [27, 28],
57 methanol [29], and glycerol [30, 31] have been applied, and are preferable in order to obtain

58 low molecular weight product compounds, when transport fuel precursors are targeted.

59 Among co-solvents, glycerol is of particular interest since it is already produced in large
60 quantities. Today, glycerol is mainly a refined bio-based by-product from biodiesel produc-
61 tion, and its market value has been declining since the market entry of biodiesel production,
62 making it economically interesting. Xiu et al. investigated in batch the potential of utilizing
63 crude glycerol, the unrefined by-product, as a co-substrate in hydrothermal processing of
64 swine manure. It was found that crude glycerol enhanced both the yield and the quality
65 of the biocrude based on the elemental composition [32–37]. In the same studies it was at-
66 tempted to understand the conversion chemistry involved through model studies using pure
67 glycerol, methanol, and fatty acids as model co-substrates, but the reaction mechanisms of
68 the different organic compounds in the crude glycerol on the biocrude production were not
69 fully established. Moreover, in house, but yet unpublished, model studies in batch reactors
70 have shown that by hydrothermally liquefying aspen wood in the presence of glycerol or crude
71 glycerol, char formation can be significantly reduced whilst maintaining a high yield of high
72 quality biocrude [38].

73 The objective and novelty of the present study is to investigate and demonstrate con-
74 tinuous co-liquefaction at bench scale conditions of aspen wood and glycerol as a co-solvent
75 as a viable route to process lignocellulose at high organic concentrations in the feed. The
76 technical feasibility of process water phase recirculation is incorporated to evaluate benefits
77 and eventual complications of such procedure. The process is evaluated based on system per-
78 formance, recirculation effects on phase characteristics, and a product assessment to examine
79 the quality of the obtained biocrude.

80 2. Materials and Methods

81 2.1. Materials

82 Supercritical co-liquefaction of aspen wood and glycerol was demonstrated in the con-
83 tinuous bench scale reactor unit (CBS1) at the Department of Energy Technology, Aalborg
84 University. In total, four batches of approximately 100 kg of feed each were processed, all
85 prepared from the same recipe. Table 1 shows the properties of the aspen wood. Glycerol
86 (99.5 %), potassium carbonate (K_2CO_3), and carboxymethyl cellulose (CMC) were purchased
87 from Brenntag Nordic A/S.

88 2.2. Process feed composition

89 Table 2 shows the feed composition used in the experimental campaign. Aspen wood
90 and glycerol were mixed in nearly 50/50 ratios in recycled water phase together with K_2CO_3
91 and CMC. In the absence of product water phase, the feed for Batch #1 was prepared using
92 distilled water.

93 2.3. Description of the Continuous Bench-Scale Unit (CBS1)

94 A process flow diagram (PFD) of the CBS1 is presented in Figure 1. Pretreatment and
95 feed slurry preparation is done in a stand-alone mixer, where aspen wood, glycerol, water
96 phase and catalyst are mixed. Steady state conditions at the preset operating conditions
97 are reached by circulating hot-compressed water (HCW) through the plant. Once reached,
98 the water is replaced by a batch of the prepared feed and continuous biocrude production

Table 1: ^aUltimate analysis was carried out in a Perkin Elmer 2400 Series II CHNS/O system. ^bFibre composition was determined by the Van Soest method in a FOSS Fibertec M6 unit. ^cAsh content measured by heating a sample to 850 °C and held isothermally for 2 hours. daf = dry, ash-free. N.D. = Not Determined

Elemental and ^a ultimate mass analyses (% , daf.)	
C	50.39 (±0.86)
H	6.19 (±0.08)
N	0.19 (±0.02)
S	N.D.
O (by difference)	43.23 (±0.08)
^b Fibre mass composition (% , db.)	
Cellulose	47.14 (±0.86)
Hemicellulose	19.64 (±0.11)
Lignin	22.11 (±0.17)
Extractives (by difference)	6.63 (±0.01)
^c Ash	0.46 (±0.02)

99 commences. After each batch of approximately 100 kg, HCW is again recirculated to main-
100 tain process conditions. The feed barrel is reloaded with new premixed feed and processed
101 continuously, and so on. Small amounts of CMC are added to the feed slurry (0.8 % on a
102 mass basis) to prevent feed slurry sedimentation while processing a batch. In a single stage,
103 the feed slurry is pressurized to process pressure (300 bar) by a high pressure piston pump.
104 Hereafter the feed is heated in two serial heaters to process temperature (400 °C) with a heat
105 ramp in the range of 200-400 °C/min. Two 5 L, heat-traced, serial reactors accommodate
106 the reaction residence time. Reactor effluent phases are pre-cooled in a concentric-tube heat
107 exchanger prior entering two parallel high-pressure filters. Depressurization and feed slurry
108 mass flow is controlled by serial capillary tubes of various lengths and various diameters.
109 Finally, the product phases are cooled to ambient conditions in a secondary cooler before
110 separation.

111 2.4. Process conditions for liquefaction experiments

112 Process conditions were kept constant at 400 °C and 300 bar. Mass flow rate was ap-
113 proximately 9 kg/hr for Batch #1 and approximately 14 kg/hr for Batch #2, #3, and #4.
114 During each batch run, mass balance samples were collected to evaluate process yields. In
115 total, 14 mass balances were collected over the four batches.

116 2.5. Product separation procedure

117 Product phases (water phase and biocrude phase) were separated gravimetrically in a
118 separation funnel. In contrast to small scale lab-experiments, using only a gravimetric sep-
119 aration procedure alleviates the need for expensive solvents and provides a more realistic

Table 2: Feed slurry composition of the four batches.

Feed composition						
Compound	Aspen wood	Glycerol	Water phase	K ₂ CO ₃	CMC	SUM
Mass fraction [%]	16.9	15.7	62.3	4.2	0.8	100

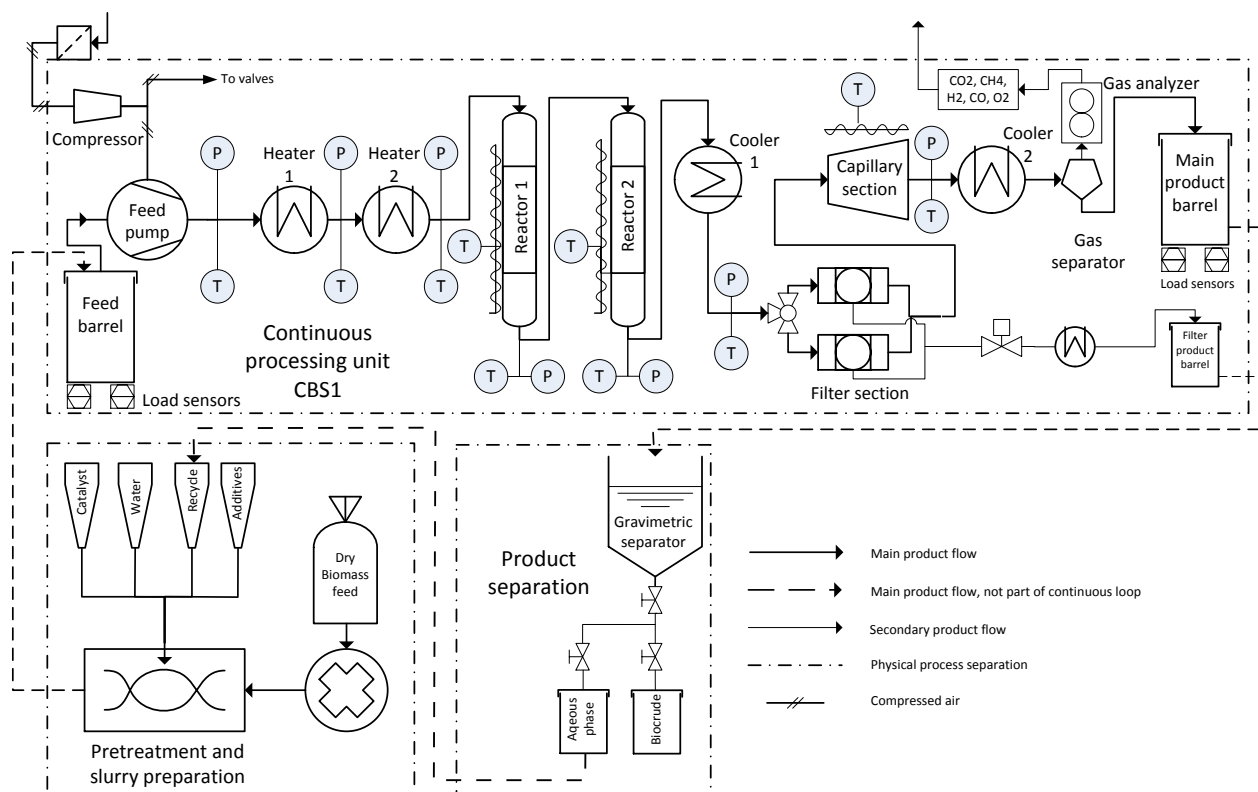


Figure 1: PFD of the CBS1 unit.

120 picture of economically viable yields. The biocrude and water phases were left to settle (30-
 121 60 minutes) before the water phase was tapped from the bottom of the funnel. Biocrude
 122 yields were measured right after the gravimetric separation. Product gases were collected
 123 and analyzed online for H₂, CO₂, CO, CH₄, and O₂.

124 2.6. Methods for biocrude and water phase analyses

125 Prior to biocrude analyses, the biocrude was centrifuged in a Sigma 6-16 HS centrifuge
 126 (2153 RCF) for 60 minutes to extract free water. Bound water was determined by Karl
 127 Fischer titration using a TitroLine 7500 KF. Elemental composition was measured using a
 128 Perkin Elmer 2400 Series II CHNS/O system (ASTM D5291). Calorific values were measured
 129 using an IKA C2000 oxygen combustion calorimeter (ASTM D2015). Qualitative analyses
 130 of all biocrude samples were carried out on a Thermo Scientific Trace 1300 ISQ GC-MS
 131 system, using a TG-SQC column (Length: 15 m., i.d.: 0.25 mm., film: 0.25 μm film). Prior
 132 to analysis, all samples were diluted in diethyl ether (DEE) and subjected to the following
 133 oven temperature profile: 40 °C was held for 3 minutes, then ramped to 325 °C at 8 °C/min
 134 and finally kept at this temperature for 4 minutes. Injector and ion source temperatures
 135 were 280 °C, split ratio was 1:20, and flow rate of the carrier gas (helium) was 1.0 mL/min.
 136 Compounds were identified by mass spectra comparison with the NIST mass spectral data
 137 library. Identification of all compounds by GC-MS is challenged by the complexity of the
 138 mixture and due to the fact only the volatile fraction is identifiable (roughly 50 % of the
 139 bulk biocrude). The identification of the reported compounds on the specific instrument was

140 confirmed by a round robin test. Total organic carbon (TOC) and potassium analyses of the
141 water phases were performed on a Hach Lange Spectrophotometer with RFID.

Energy Recovery (ER), Carbon Recovery (CR), and the effective hydrogen-to-carbon ratio (H/C_{eff}) were calculated according to Eq. 1, 2, and 3:

$$ER = \frac{\text{HHV of biocrude} \cdot \text{mass of biocrude}}{\text{HHV of feedstock} \cdot \text{mass of feedstock}} \quad (1)$$

$$CR = \frac{\text{mass of C in the biocrude}}{\text{mass of C in the feedstock}} \quad (2)$$

$$H/C_{eff} = \frac{H - 2O}{C} \quad (3)$$

142 3. Results and Discussion

143 3.1. CBS1 performance

144 The performance and process stability in terms of process temperature, pressure, and
145 mass flow rate of the CBS1 system is illustrated in Figure 2. The figure displays trend curves
146 for a typical batch run, operating at a flow rate of approximately 14 kg/hr. It is readily
147 observed that process conditions remains stable throughout the entire batch. Small pressure
148 fluctuations in the beginning and in the end of a batch are observed, but these are explained
149 by viscosity changes when feed is pumped into the system instead of HCW, and vice versa.
150 The tiny oscillations in the pressure profile are due to the use of a piston pump.

151 For each mass balance sample roughly 20 kg of product (biocrude and water phase) was
152 loaded into the funnel and left to separate gravimetrically before the water phase was tapped
153 off at the bottom of the funnel. Figure 3 clearly shows a resulting hydrophobic supernatant
154 biocrude. The yields of biocrude were based on this initial gravimetric separation, where
155 bound water was not included. Furthermore, later centrifugal runs of the biocrude samples
156 revealed yet unsettled water which naturally introduced unaccounted experimental errors on
157 the biocrude yields. Figure 3 shows the yield calculations based on the mass balance samples
158 obtained from the four batches. Due to significant yield variations within each batch, effects
159 of water phase recirculation on the biocrude yields are somewhat inconclusive. As a result
160 it is concluded that the separation procedure was not adequate for producing reliable yield
161 results and a more robust and standardized separation procedure is under evaluation. Based
162 on analysis of variations (ANOVA) calculations, it can only be concluded that yields from
163 batch #3 are statistically higher than the yields from batch #4 (on a 95% confidence interval).
164 During the liquefaction process water-soluble organics (WSO) are formed and contained in
165 the aqueous phase. For batch #1, for which the feed slurry was prepared using demineralized
166 water, it appears from Table 3 that the total organic carbon (TOC) content of the aqueous
167 phase reaches a value of 54.1 g/L. after the first batch. Due to the recirculation procedure
168 adopted, commenced after batch #1, it is observed that the TOC of the aqueous phase
169 increases almost linearly to 136.2 g/L after the last batch. As the fraction of WSO in the
170 aqueous phase increases, the biocrude and aqueous phase separation weakens since WSO act
171 as co-solvents, leading ultimately to a single phase mixture, as it was found by Oasmaa et
172 al. in a study on pyrolysis biooil separation [39]. As the amount of WSO increases, biocrude

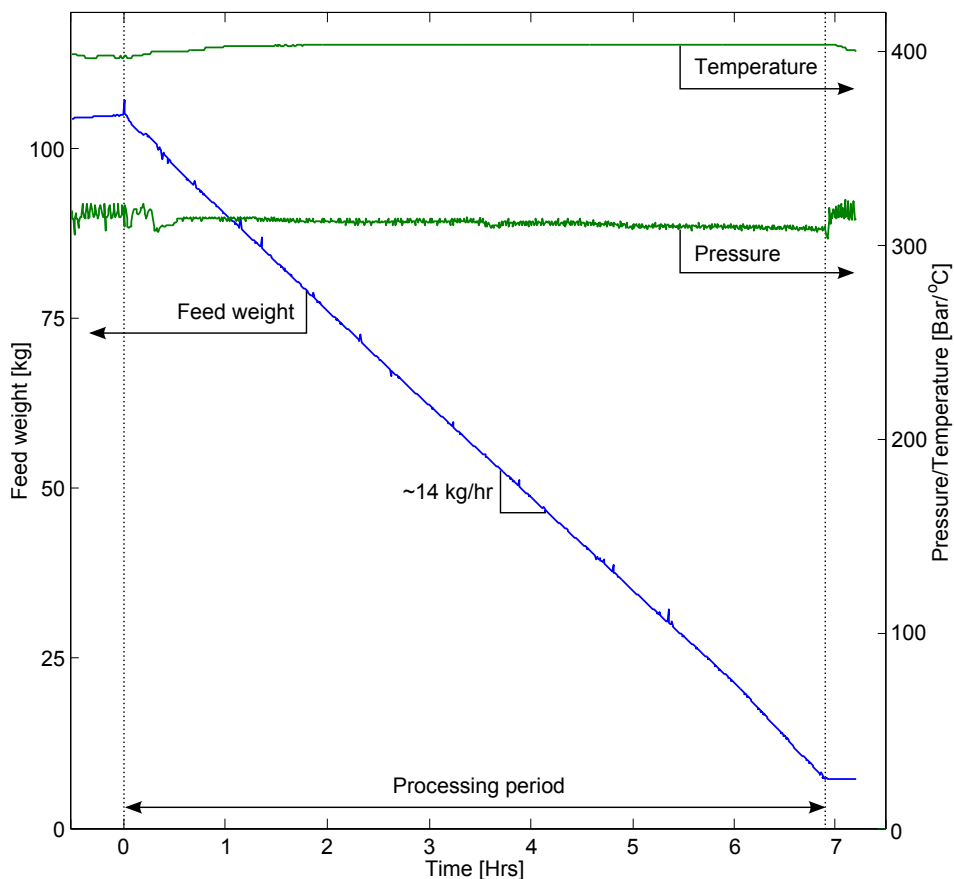


Figure 2: Process conditions, temperature, pressure, and feed barrel weight during a continuous batch run.

173 compounds become more soluble in the aqueous phase which could explain the tendency to
 174 a lower biocrude yield. The yield fluctuations also cause fluctuations in the energy (ER)
 175 and carbon recovery (CR) in the biocrude. In the present experiments, biocrude ER and
 176 CR ranges from 39-62 % and 42-66 %, respectively. Due to the fact that glycerol forms
 177 mostly WSO or gaseous products, the ER and CR are generally penalized when including
 178 the co-solvent fraction in the ER and CR calculations, which is only measured with respect
 179 to the biocrude.

180 Table 3 also shows that accompanying the accumulation of WSO in the aqueous phase,
 181 ash is likewise observed to accumulate as an equal amount of K_2CO_3 is added for each
 182 batch. Starting at an aqueous phase ash content of 6.2 %, resembling that of the original
 183 feed composition, the ash content is increasing linearly to a final value of 12.6 % after three
 184 recycles. Tracing the potassium in the water phase, it is observed that potassium accumulates
 185 linearly in the water phase. The mass fraction of potassium to the total water phase is
 186 almost half of the mass fraction of the TOC to the total water phase. It is also evident
 187 that after four batches (3 recycles) steady state values of the water phase has yet not been
 188 reaches. During hydrothermal processing of glycerol, glycerol is mainly converted into WSO
 189 and hence the observation of WSO accumulation is likely to be a contribution from the
 190 high amount of glycerol added for each batch. Möller and Vogel investigated hydrothermal
 191 conversion of glycerol at 400 °C [16]. Even after 60 minutes, more than 10 % of the glycerol was

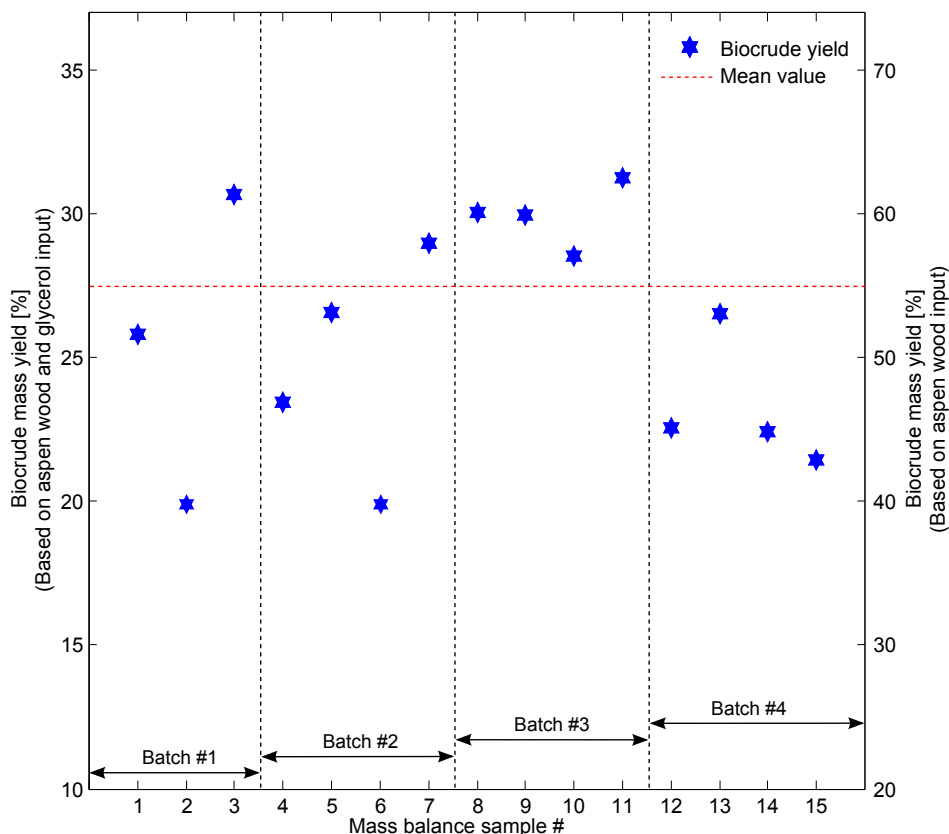


Figure 3: Biocrude yields obtained from mass balance samples during the four batches. Mean value of all the mass balance samples are presented. In the plot; display of a typical supernatant biocrude and water phase sample. The hydrophobic biocrude readily separates gravimetrically.

192 unconverted. During the present experiments, product analysis showed intact glycerol, but it
 193 was not clear how much glycerol was actually converted during processing. For continuous
 194 industrial operation with water phase recycling, ash accumulation presents an operational
 195 challenge to be addressed, as failing to do so may lead to operational malfunction. It has yet
 196 not been investigated, if the WSO containing water phase possess similar effects as glycerol on
 197 retardation of char formation. If so, glycerol may gradually be phased out as a feed additive as
 198 a work around for limiting the accumulation of WSO and still obtaining a stable process. The
 199 polarity of water as a solvent is known to diminish as it approaches near and supercritical
 200 water conditions, leading to solubility reduction for some salts, causing precipitation and
 201 ultimately plugging of the system. For the experiments reported here plugging was not
 202 experienced, nor did the campaign show signs of impending blockage, which would manifest
 203 itself as an increased pressure drop across the system.

204 Table 3 shows that after conversion the water phase is noticed to be acidic despite of the
 205 significant addition of alkaline catalyst. Lignocellulose and glycerol are known to form acidic
 206 compounds under hydrothermal processing, especially under alkaline conditions, which first
 207 neutralizes the K_2CO_3 , then later acidifies the water phase [16, 40]. Over the four batches
 208 the water phase pH appears almost invariant to the recirculation of aqueous phase.

209 To investigate if the aqueous recirculation affects the quality of the obtained biocrudes,
 210 an effective hydrogen-to-carbon ratio (H/C_{eff}) was calculated as a quality measure. Figure 4

Table 3: Aqueous phase analyses: Mass fraction of ash, total organic carbon (TOC), pH and potassium (K) content of the four different batches.

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

211 shows the results. Like for the biocrude yields, some variations within the individual batches
 212 are noticed blurring a clear trend to be observed. However, when excluding Batch #1, it
 213 seems as the quality in terms of H/C_{eff} is increasing as water phase is recirculated. The
 214 improvement in biocrude quality by aqueous phase recycling has also been demonstrated by
 215 Elliott et al. [10]. A hypothesis is that WSO act as hydrogen-donors. By aqueous phase
 216 recirculation, the concentration of WSO increases, which in turn increases the concentration
 217 of hydrogen-donors.

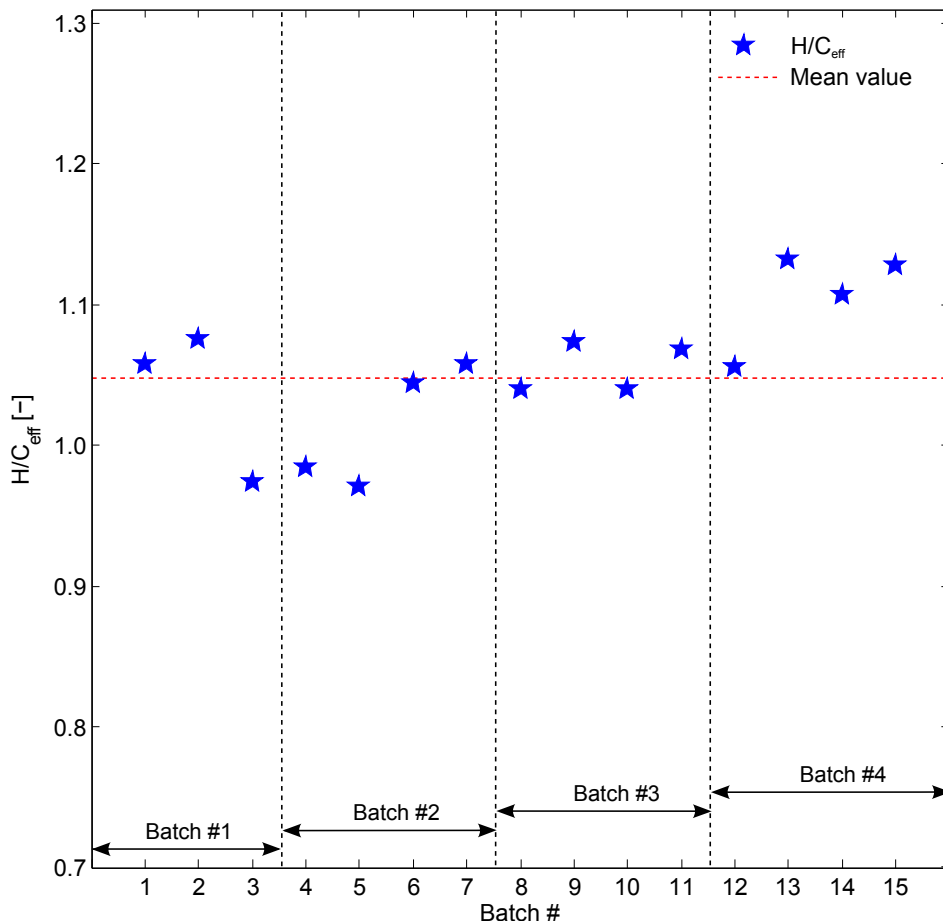


Figure 4: H/C_{eff} of the biocrude obtained from mass balance samples during the four batches. Mean value of all the mass balance samples are presented.

218 Gas phase composition was monitored continuously for carbon dioxide, hydrogen, methane,
 219 carbon monoxide, and oxygen throughout each batch. Figure 5 displays typical gas trends.

Initially, oxygen is diluted by producer gases and ultimately vanishes. It must be stated that the gas composition measured prior and in between batches is not precise, since gas detectors are calibrated only in a narrow band resembling process gas composition. It is noticed that the volume fractions CO_2 and H_2 reach steady state values of approximately 62 % and 30 %, respectively, and hence being the most abundant gases. The volume fractions of CH_4 and CO are 4-5 % and 2-3 %, respectively. During each mass balance samples, product gases are involuntarily exposed to surrounding conditions, allowing air to enter the gas stream. This is observed by an increased oxygen concentration, followed by decreasing product gases. After each mass balance sample steady state process conditions are reestablished as soon as the system is resealed. The gas mass flows were registered to approximately 0.6-0.7 kg/hr., amounting to a mass fraction of approximately 12-15 % of the input organic fraction. In terms of energy and carbon recoveries, this corresponds to approximately 2.4 % and 8.8 % in the gas phase. At best, the carbon balance across input and output phases was established at a 96 % closure.

Gas compositions obtained from the four batches are presented in Table 4, where the gas compositions have been normalized to exclude oxygen. It appears that the gas compositions are relatively invariant over the four runs and hence not affected by the water phase recirculation, although ashes and WS are observed to accumulate. The significant and insignificant shares of H_2 and CO , respectively, relative to uncatalyzed hydrothermal processing of lignocellulosic materials, indicate alternative chemical pathways [41–43]. Alkali catalysts have previously been found to enhance water-gas shift reactions, which can explain the high and low shares of H_2 and CO , respectively [44]. Steam reforming reactions may also be secondary contributors, but they proceed usually at much higher temperatures and in the presence of a transition metal catalyst [45]. A more speculative explanation is hydrogen abstraction reactions catalyzed by alkaline conditions. Glycerol deprotonation derives dihydroxyacetone, glyceraldehyde, and lactic acid, commonly observed WSO compounds, in addition to gaseous hydrogen [46].

Table 4: Normalized gas composition of CO_2 , CO , CH_4 , and H_2

	Gas phase volume fractions [%]			
	CO_2	CO	CH_4	H_2
Batch #1	62.1	2.9	4.6	30.5
Batch #2	62.1	2.9	4.6	30.5
Batch #3	60.8	2.7	4.5	32.0
Batch #4	63.6	3.3	4.2	28.8

3.2. Analyses of the biocrude

The biocrude was analyzed for determining the system performance in terms of biocrude quality. Table 5 compiles the bulk analysis obtained. First of all, it is observed that the mass fraction of oxygen in the biocrude (15.8 %) is significantly lower as compared to that of the feedstock (47 %, aspen wood plus glycerol). Secondly, the course of deoxygenation resulted in a hydrophobic, easily separable biocrude, with an increased gross calorific value (34.3 MJ/kg). The hydrophobicity of the biocrude is quantified by the low mass fraction of bound water in the biocrude (3.8 %). It is further observed that the ash content of the

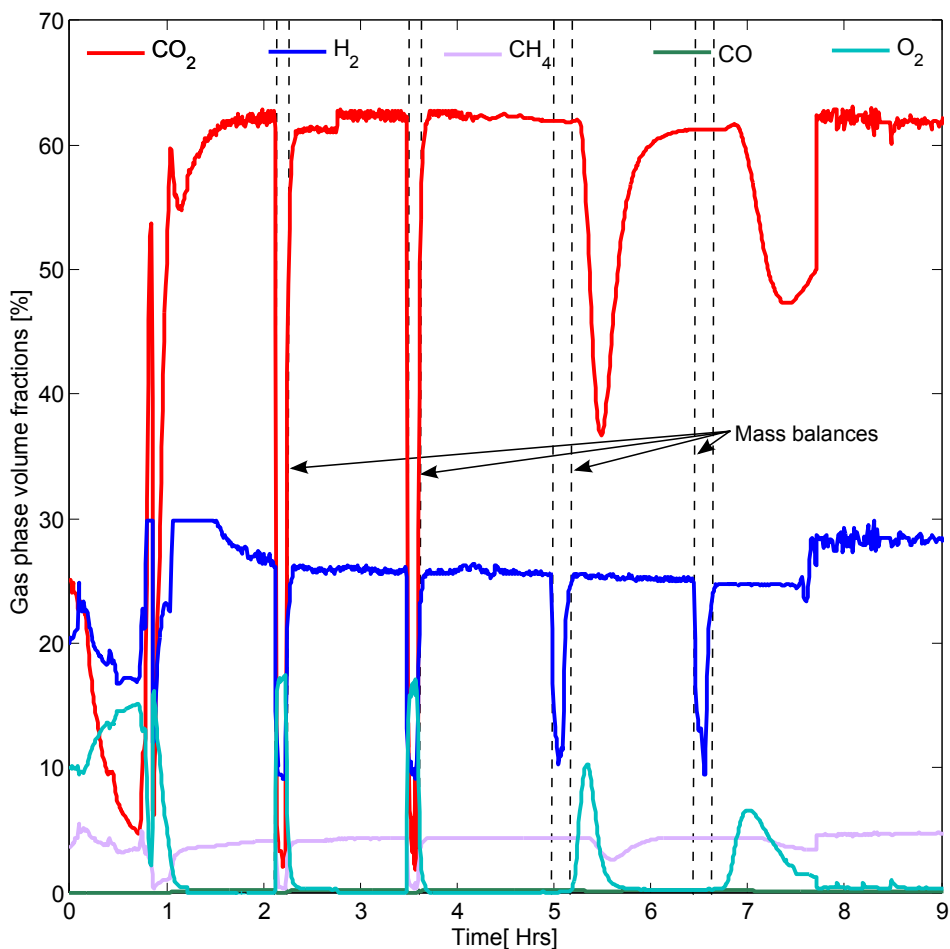


Figure 5: Continuous process gas composition. Initiations of mass balances are indicated in the figure.

255 biocrude is fairly high. The recycling effect of the ash content in the biocrude was not
 256 evaluated, but following the trends of the water phase, it is expected to increase from each
 257 aqueous phase recycle. A mass fraction of 0.48 % of undesirable inorganics poses a potential
 258 challenge, as inorganics mount a concern from a downstream point of view. A significant
 259 part of the inorganics is alkali metals, carried over by the high amount of K_2CO_3 added for
 260 each batch cycle. If the biocrude is to be refined, inorganics may decompose and deposit
 261 in refinery hardware or even poison expensive refining catalysts. If the biocrude is to be
 262 combusted directly, inorganics can cause corrosion, wear, and deposit in pumps, injectors,
 263 burners, turbines, *etc.* Hence, if the aqueous phase is to be recycled, procedure amendments
 264 have to be implemented. Accumulation of inorganics is of particular concern, which is why
 265 an inorganic removal step of the aqueous phase may have to be implemented downstream.
 266 A supercritical salt separator has previously been proposed as a means for precipitation vari-
 267 ous salts with high separation efficiency [47]. Furthermore, the accumulation of WSO in the
 268 aqueous phase must be investigated in greater details to understand, 1) the impact of WSO
 269 on the conversion mechanisms in terms of yields and product quality, and 2) the impact of
 270 WSO on the phase separation of the aqueous phase and the biocrude.

271

Table 5: Elemental mass analysis, higher heating value (HHV), mass fractions of ash and bound water of the biocrude, and biocrude ash composition.

Elemental analysis [% (daf)]		Metals [mg/g]	
C	75.2	Al	0.054
H	8.2	Cr	0.035
N	0.5	Fe	0.037
S	0.3	K	1.78
O	15.8	Mg	0.136
HHV [MJ/kg]	34.3	Zn	0.01
Ash content [%]	0.48	P	0.015
Bound water [%]	3.8	Ca	0.97
		S	0.1

272 The volatile fraction of the biocrude was further characterized to investigate the chemical
 273 composition. Table 6 presents the identified compounds by GC-MS analysis together with
 274 their chemical formulas, relative peak area, and number of carbon atoms (C#). It is readily
 275 observed that the biocrude is a complex mixture of chemical compounds for which the major-
 276 ity of compounds are oxygenated cyclic structures having carbon atoms in the range of C₆-C₂₁.
 277 Unsaturated hydrocarbons compounds with higher number of carbon atoms, including fused
 278 ring structures, were also identified but in minor quantities. The major denominators for all
 279 of the compounds are cyclic C₅ or aromatic C₆ backbones, substituted with various functional
 280 groups (ketonic, aldehyde, phenolic). Ketonic functionalities are mainly observed on pentane
 281 and pentene backbones having only single heteroatoms, and are believed to be formed by
 282 condensation reactions between Retro-Aldol derived carbohydrate intermediates. A broad
 283 collection of aromatics are also observed having mainly phenolic functionalities with single,
 284 double or even triple heteroatom formulas. Despite the fact that the compound mixture is
 285 complex and diverse, the range of numbers of carbon atoms is relatively narrow. The dis-
 286 tribution of number of carbon atoms based on the identified compounds has been calculated
 287 semi-quantitatively by total ion count. The distribution is plotted in Figure 6, together with
 288 the common number of carbon atom ranges of conventional gasoline, kerosene-type jet fuel,
 289 and diesel. It appears that the majority of compounds lump into the C₆-C₁₂ region, mainly
 290 representing gasoline range and 'low cut' jet fuel. Based only on carbon range, the diesel
 291 range is hardly represented in the biocrude.

292 4. Conclusion

293 Continuous co-liquefaction of aspen wood and glycerol at supercritical water conditions
 294 was demonstrated successfully. High organic content feeds were prepared and processed for
 295 which a water phase recycling procedure was implemented. High process stability in terms
 296 of temperature, pressure, and mass flow rate was obtained and steady state conditions were
 297 achieved throughout all experiments. High hydrophobicity of the resulting biocrudes allowed
 298 for a simple, but commercially realistic, gravimetric separation between biocrudes and water
 299 phases. Unfortunately, significant yield variations obtained from mass balance samples within
 300 each batch obscured the identification of clear effects of the water phase recirculation on the

Table 6: List of compounds identified in the biocrude by gas chromatography-mass spectroscopy. The table includes compound name, formula, relative peak area, and number of carbon atoms (C#). No standards were used for compound verification.

RT (min)	Identified compound	Chemical Formula	Peak area (%)	C#
2.06	Cyclopentanone	C ₅ H ₈ O	0.30	5
2.59	3,5,5-trimethyl-2-hexene	C ₉ H ₁₈	0.39	9
2.94	2-methyl-cyclopentanone	C ₆ H ₁₀ O	2.28	6
3.37	ethylbenzene	C ₈ H ₁₀	0.39	8
3.56	p-xylene	C ₈ H ₁₀	0.62	8
3.87	2,5-dimethyl-cyclopentanone	C ₉ H ₁₆ O	0.86	9
4.04	3,4-dimethyl-3-penten-2-one	C ₇ H ₁₂ O	1.51	7
4.38	2-methyl-2-cyclopenten-1-one	C ₆ H ₈ O	1.58	6
5.04	1-cyclohexylethanol	C ₈ H ₁₆ O	2.84	7
5.19	1,2-dimethyl-cyclohexene	C ₈ H ₁₄	1.26	8
5.56	3-methyl-2-cyclopenten-1-one	C ₆ H ₈ O	1.83	6
6.93	2,3-dimethyl-2-cyclopenten-1-one	C ₇ H ₁₂ O	4.33	7
7.37	2,3,4-trimethyl-2-cyclopenten-1-one	C ₈ H ₁₂ O	4.32	8
7.65	p-cresol	C ₇ H ₈ O	1.75	7
8.12	2,3-dimethyl-phenol	C ₈ H ₁₀ O	2.71	8
8.50	2-ethylidenecyclohexanone	C ₈ H ₁₄ O	1.34	8
8.81	3,5-dimethyl-phenol	C ₈ H ₁₀ O	4.69	8
9.15	2,4,6-trimethyl-3-cyclohexen-1-carboxaldehyde	C ₁₀ H ₁₆ O	1.25	10
9.35	4-methyl-1-(1-methylethyl)-cyclohexene	C ₁₀ H ₁₈	1.32	10
9.44	4-methyl-1-(1-methylethyl)-cyclohexene	C ₁₀ H ₁₈	1.73	10
9.62	2,4,6-trimethyl-3-cyclohexen-1-carboxaldehyde	C ₁₀ H ₁₆ O	1.62	10
9.82	4-ethyl-3,4-dimethyl-2,5-cyclohexadien-1-one	C ₁₀ H ₁₄ O	1.31	10
10.14	2,4,6-trimethyl-3-cyclohexen-1-carboxaldehyde	C ₁₀ H ₁₆ O	1.50	10
10.71	2,6-dimethoxytoluene	C ₉ H ₁₂ O ₂	1.49	9
11.07	2,3-dihydroxy-3-methyl-1H-inden-1-one	C ₁₁ H ₁₂ O ₃	2.05	10
11.33	duroquinone	C ₁₀ H ₁₂ O ₂	0.86	11
11.71	2,6-dimethyl-1,4-benzenediol	C ₈ H ₁₀ O ₂	1.62	8
12.13	4-ethylcatechol	C ₈ H ₁₀ O ₂	1.92	8
12.42	2,5-dimethyl-1,4-benzenediol	C ₈ H ₁₀ O ₂	1.47	8
12.76	5-methoxy-2,3-dimethyl-phenol	C ₉ H ₁₂ O ₂	3.67	9
12.90	4-ethylguaiacol	C ₉ H ₁₂ O ₂	2.54	9
13.68	2,3,5-trimethyl-1,4-benzenediol	C ₉ H ₁₂ O ₂	4.21	9
13.97	3-tert-butyl-4-hydroxyanisole	C ₁₁ H ₁₆ O ₂	1.52	11
14.19	4-butoxybenzyl alcohol	C ₁₀ H ₁₆ O	0.93	10
14.81	2,3,5,6-tetramethyl-1,4-benzenediol	C ₁₀ H ₁₄ O ₂	1.52	10
15.30	2,6-dimethoxy-4-(2-propenyl)-phenol	C ₁₁ H ₁₄ O ₃	2.61	11
16.32	6-tert-butyl-2,4-dimethylphenol	C ₁₂ H ₁₈ O	1.20	12
16.44	Benzaldehyde, 3-hydroxy-4-methoxy-2-(2-propenyl)-	C ₁₁ H ₁₂ O ₃	0.81	12
16.63	4-(2,4,4-trimethyl-cyclohexa-1,5-dienyl)-but-3-en-2-one	C ₁₃ H ₁₈ O	0.64	13
18.82	methyl dehydroabietate	C ₂₁ H ₃₀ O ₂	0.36	21
19.79	10,18-bisnorabieta-5,7,9(10),11,13-pentene	C ₁₈ H ₂₂	0.74	18
20.82	retene	C ₁₈ H ₁₈	1.55	18

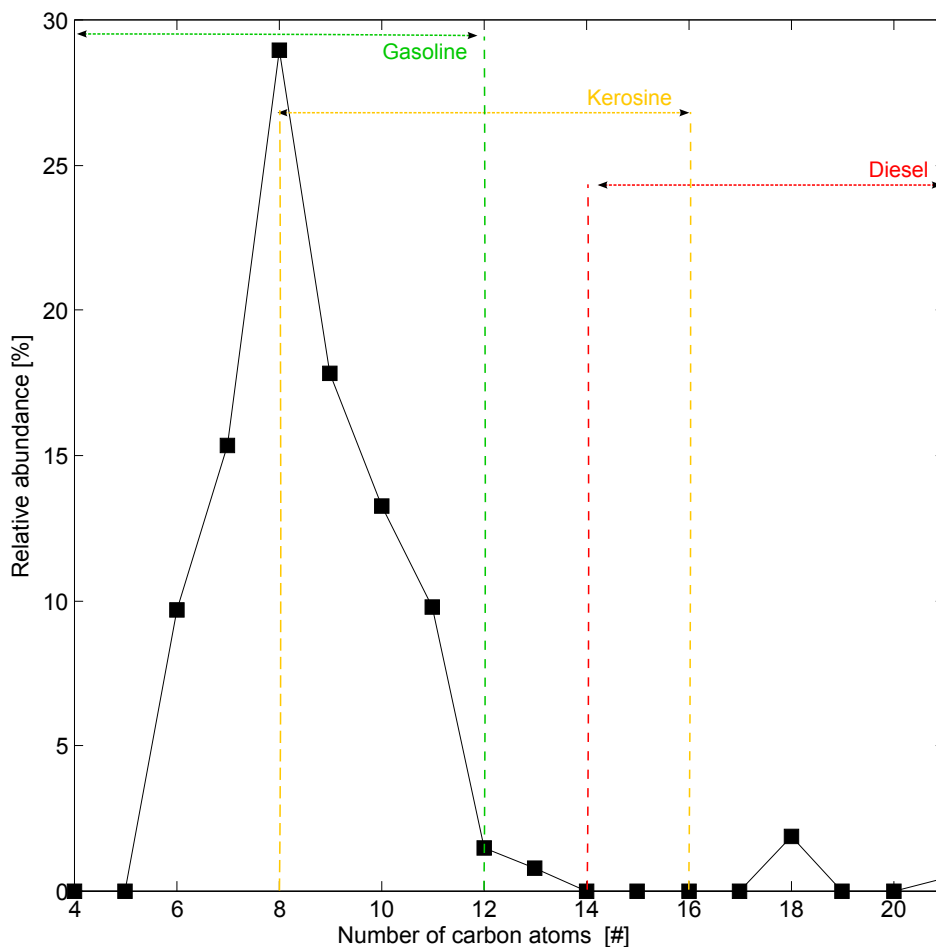


Figure 6: Relative distribution (by relative peak area) in numbers of carbon atoms in the compounds obtained from the identified in the biocrude. The relative abundance is calculated based on summed relative peak areas. The ranges of number of carbon atoms in conventional fuels are included.

301 biocrude yields, but a slight decreasing tendency is observed. Conversely the biocrude yield
 302 trend, the biocrude quality in terms of an effective hydrogen-to-carbon ratio was observed
 303 to increase slightly when the water phase is recirculated. Gas phase yields and compositions
 304 were found almost invariant to the water phase recirculation. Some process inconveniences
 305 were observed with respect to water phase recirculation; TOC and ash contents of the water
 306 phase were observed to increase significantly with water phase recirculation, which may
 307 eventually lead to system failure due to salt precipitation. Moreover, the mass fraction
 308 of ash in the biocrude was found relatively high (0.48 %). From the biocrude analysis it
 309 was found that the major biocrude compounds were cyclic C_5 or aromatic C_6 backbones,
 310 substituted with various oxygenated functionalities. The number of carbon atoms range of
 311 the biocrude compounds is distributed mainly in the C_6 - C_{12} range similar to gasoline. In
 312 conclusion, the experimental campaign demonstrated an auspicious platform for continuous
 313 operation of hydrothermal liquefaction for the production of high quality biocrudes.

314 Acknowledgements

315 This work is part of the Flexifuel Project, a Sino-Danish collaboration, and C3BO (Center
316 for BioOil) at the Department of Energy Technology, Aalborg University. The research was
317 financially supported by The Danish Agency for Science, Technology and Innovation (grant
318 no. 10-094552) and The Danish Council for Strategic Research (grant no. 1305-00030B).

319 References

- 320 [1] Kruse, A., Dinjus, E.. Hot compressed water as reaction medium and reactant: Prop-
321 erties and synthesis reactions. *The Journal of Supercritical Fluids* 2007;39(3):362 – 380.
322 doi:10.1016/j.supflu.2006.03.016.
- 323 [2] Kruse, A., Dinjus, E.. Hot compressed water as reaction medium and reactant:
324 2. degradation reactions. *The Journal of Supercritical Fluids* 2007;41(3):361 – 379.
325 doi:10.1016/j.supflu.2006.12.006.
- 326 [3] Akhtar, J., Amin, N.A.S.. A review on process conditions for optimum bio-oil yield
327 in hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*
328 2011;15(3):1615 – 1624. doi:10.1016/j.rser.2010.11.054.
- 329 [4] Peterson, A.A., Vogel, F., Lachance, R.P., Froling, M., Antal Jr., M.J., Tester, J.W..
330 Thermochemical biofuel production in hydrothermal media: A review of sub- and super-
331 critical water technologies. *Energy Environ Sci* 2008;1:32–65. doi:10.1039/B810100K.
- 332 [5] Toor, S.S., Rosendahl, L., Rudolf, A.. Hydrothermal liquefaction of biomass:
333 A review of subcritical water technologies. *Energy* 2011;36(5):2328 – 2342.
334 doi:10.1016/j.energy.2011.03.013.
- 335 [6] Pedersen, T.H., Rosendahl, L.A.. Production of fuel range oxygenates by supercriti-
336 cal hydrothermal liquefaction of lignocellulosic model systems. *Biomass and Bioenergy*
337 2015;83:206 – 215. doi:10.1016/j.biombioe.2015.09.014.
- 338 [7] Toor, S., Rosendahl, L., Hoffmann, J., Pedersen, T., Nielsen, R., Søgaard, E.. chap.
339 Hydrothermal liquefaction of biomass. Springer Publishing Company. ISBN 978-3-642-
340 54457-6; 2014, p. 189–217. doi:10.1007/978-3-642-54458-3.
- 341 [8] Bouvier, J., Gelus, M., Maugendre, S.. Wood liquefaction - an overview. *Applied*
342 *Energy* 1988;30(2):85 – 98. doi:10.1016/0306-2619(88)90006-2.
- 343 [9] Elliott, D.C.. Historical developments in hydroprocessing bio-oils. *Energy & Fuels*
344 2007;21(3):1792–1815. doi:10.1021/ef070044u.
- 345 [10] Elliott, D.C., Biller, P., Ross, A.B., Schmidt, A.J., Jones, S.B.. Hydrothermal
346 liquefaction of biomass: Developments from batch to continuous process. *Bioresource*
347 *Technology* 2015;178(0):147–156. doi:10.1016/j.biortech.2014.09.132.
- 348 [11] Xiu, S., Shahbazi, A.. Bio-oil production and upgrading research: A review. *Renewable*
349 *and Sustainable Energy Reviews* 2012;16(7):4406 – 4414. doi:10.1016/j.rser.2012.04.028.

- 350 [12] Furimsky, E.. Catalytic hydrodeoxygenation. *Applied Catalysis A: General*
351 2000;199(2):147 – 190. doi:10.1016/S0926-860X(99)00555-4.
- 352 [13] Hoffmann J. Pedersen, T., Rosendahl, L.. chap. Hydrothermal Conversion in Near-
353 Critical Water A Sustainable Way of Producing Renewable Fuels. Springer Netherlands.
354 ISBN 978-94-017-8922-6; 2014, p. 373–400. doi:10.1007/978-94-017-8923-3.
- 355 [14] Lindemuth, T.. Carboxylolysis of biomass. In: Sofer, S.S., Zaborsky, O.R., editors.
356 Biomass Conversion Processes for Energy and Fuels. Springer US. ISBN 978-1-4757-
357 0303-0; 1981, p. 187–200. doi:10.1007/978-1-4757-0301-6_10.
- 358 [15] Schaleger, L.L., Figueroa, C., Davis, H.G.. Direct liquefaction of biomass: Results
359 from operation of continuous bench scale unit in liquefaction of water slurries of douglas
360 fir wood - report number: Lbl-14019. Tech. Rep.; Energy and Environment Division,
361 Lawrence Berkeley Laboratory; 1982.
- 362 [16] Müller, J.B., Vogel, F.. Tar and coke formation during hydrothermal processing of
363 glycerol and glucose. influence of temperature, residence time and feed concentration.
364 *The Journal of Supercritical Fluids* 2012;70:126 – 136. doi:10.1016/j.supflu.2012.06.016.
- 365 [17] Tran, A., Rogers, D.. Examination of alternative catalysts for biomass direct
366 liquefaction. 1985. URL: <http://www.osti.gov/scitech/servlets/purl/6316343>.
367 doi:10.2172/6316343.
- 368 [18] Saisu, M., Sato, T., Watanabe, M., Adschiri, T., Arai, K.. Conversion of
369 lignin with supercritical waterphenol mixtures. *Energy & Fuels* 2003;17(4):922–928.
370 doi:10.1021/ef0202844.
- 371 [19] Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y.. Hydrothermal upgrading of biomass:
372 Effect of K_2CO_3 concentration and biomass/water ratio on products distribution. *Biore-*
373 *source Technology* 2006;97(1):90 – 98. doi:10.1016/j.biortech.2005.02.051.
- 374 [20] Zhu, Z., Rosendahl, L., Toor, S.S., Yu, D., Chen, G.. Hydrothermal liquefaction of
375 barley straw to bio-crude oil: Effects of reaction temperature and aqueous phase recir-
376 culation. *Applied Energy* 2015;137(0):183 – 192. doi:10.1016/j.apenergy.2014.10.005.
- 377 [21] Yong, T.L.K., Matsumura, Y.. Kinetic analysis of lignin hydrothermal conver-
378 sion in sub- and supercritical water. *Industrial & Engineering Chemistry Research*
379 2013;52(16):5626–5639. doi:10.1021/ie400600x.
- 380 [22] Ross, D.S., Blessing, J.E.. Alcohols as h-donor media in coal conversion. 1.
381 base-promoted h-donation to coal by isopropyl alcohol. *Fuel* 1979;58(6):433 – 437.
382 doi:10.1016/0016-2361(79)90084-X.
- 383 [23] Ross, D.S., Blessing, J.E.. Alcohols as h-donor media in coal conversion. 2.
384 base-promoted h-donation to coal by methyl alcohol. *Fuel* 1979;58(6):438 – 442.
385 doi:10.1016/0016-2361(79)90085-1.

- 386 [24] Wolfson, A., Dlugy, C., Shotland, Y., Tavor, D.. Glycerol as solvent and hydro-
387 gen donor in transfer hydrogenation-dehydrogenation reactions. *Tetrahedron Letters*
388 2009;50(43):5951 – 5953. doi:10.1016/j.tetlet.2009.08.035.
- 389 [25] Zhang, Q.h., Zhao, G.j., Jie, S.j.. Liquefaction and product identification of
390 main chemical compositions of wood in phenol. *Forestry Studies in China* 2005;7(2).
391 doi:10.1007/s11632-005-0018-8.
- 392 [26] Ross, D.S., Blessing, J.E.. Isopropyl alcohol as a coal liquefaction agent. *Am Chem*
393 *Soc Fuel Div Prepr* 1977;22(6):208 – 213. doi:10.1016/0016-2361(79)90084-X.
- 394 [27] Cheng, S., Dacruz, I., Wang, M., Leitch, M., Xu, C.C.. Highly efficient lique-
395 faction of woody biomass in hot-compressed alcoholwater co-solvents. *Energy & Fuels*
396 2010;24(9):4659–4667. doi:10.1021/ef901218w.
- 397 [28] Zhang, J., Zhang, Y., Luo, Z.. Hydrothermal liquefaction of chlorella pyrenoi-
398 dosa in ethanol-water for bio-crude production. *Energy Procedia* 2014;61:1961 –
399 1964. doi:10.1016/j.egypro.2014.12.052; international Conference on Applied Energy,
400 {ICAE2014}.
- 401 [29] Long, J., Xu, Y., Wang, T., Yuan, Z., Shu, R., Zhang, Q.,
402 et al. Efficient base-catalyzed decomposition and in situ hydrogenolysis process for
403 lignin depolymerization and char elimination. *Applied Energy* 2015;141:70 – 79.
404 doi:10.1016/j.apenergy.2014.12.025.
- 405 [30] Demirbas, A.. Liquefaction of biomass using glycerol. *Energy Sources,*
406 *Part A: Recovery, Utilization, and Environmental Effects* 2008;30(12):1120–1126.
407 doi:10.1080/15567030601100654.
- 408 [31] Seljak, T., Oprešnik, S.R., Kunaver, M., Katrašnik, T.. Wood, liquefied in
409 polyhydroxy alcohols as a fuel for gas turbines. *Applied Energy* 2012;99:40 – 49.
410 doi:10.1016/j.apenergy.2012.04.043.
- 411 [32] Xiu, S., Shahbazi, A., Shirley, V., Mims, M.R., Wallace, C.W.. Effectiveness and
412 mechanisms of crude glycerol on the biofuel production from swine manure through
413 hydrothermal pyrolysis. *Journal of Analytical and Applied Pyrolysis* 2010;87(2):194 –
414 198. doi:10.1016/j.jaap.2009.12.002.
- 415 [33] Xiu, S., Shahbazi, A., Shirley, V.B., Wang, L.. Swine manure/crude glycerol co-
416 liquefaction: Physical properties and chemical analysis of bio-oil product. *Bioresource*
417 *Technology* 2011;102(2):1928 – 1932. doi:10.1016/j.biortech.2010.08.026.
- 418 [34] Xiu, S., Shahbazi, A., Wallace, C.W., Wang, L., Cheng, D.. Enhanced bio-oil
419 production from swine manure co-liquefaction with crude glycerol. *Energy Conversion*
420 *and Management* 2011;52(2):1004 – 1009. doi:10.1016/j.enconman.2010.08.028.
- 421 [35] Ye, Z., Xiu, S., Shahbazi, A., Zhu, S.. Co-liquefaction of swine manure and crude glycerol
422 to bio-oil: Model compound studies and reaction pathways. *Bioresource Technology*
423 2012;104(0):783 – 787. doi:10.1016/j.biortech.2011.09.126.

- 424 [36] Cheng, D., Wang, L., Shahbazi, A., Xiu, S., Zhang, B.. Characterization of
425 the physical and chemical properties of the distillate fractions of crude bio-oil pro-
426 duced by the glycerol-assisted liquefaction of swine manure. *Fuel* 2014;130:251 – 256.
427 doi:10.1016/j.fuel.2014.04.022.
- 428 [37] Cheng, D., Wang, L., Shahbazi, A., Xiu, S., Zhang, B.. Catalytic cracking of
429 crude bio-oil from glycerol-assisted liquefaction of swine manure. *Energy Conversion*
430 *and Management* 2014;87(0):378 – 384. doi:10.1016/j.enconman.2014.06.084.
- 431 [38] Pedersen, T.H., Jasiūnas, L., Casamassima, L., Singh, S., Rosendahl, L.A.. Synergetic
432 hydrothermal co-liquefaction of crude glycerol and aspen wood. *Energy Conversion and*
433 *Management* 2015;106:886 – 891. doi:10.1016/j.enconman.2015.10.017.
- 434 [39] Oasmaa, A., Sundqvist, T., Kuoppala, E., Garcia-Perez, M., Solantausta, Y.,
435 Lindfors, C., et al. Controlling the phase stability of biomass fast pyrolysis bio-oils.
436 *Energy Fuels* 2015;29(7):4373–4381. doi:10.1021/acs.energyfuels.5b00607.
- 437 [40] Yin, S., Tan, Z.. Hydrothermal liquefaction of cellulose to bio-oil un-
438 der acidic, neutral and alkaline conditions. *Applied Energy* 2012;92:234 – 239.
439 doi:10.1016/j.apenergy.2011.10.041.
- 440 [41] Mosteiro-Romero, M., Vogel, F., Wokaun, A.. Liquefaction of wood in hot compressed
441 water: Part 1 experimental results. *Chemical Engineering Science* 2014;109(0):111 –
442 122. doi:10.1016/j.ces.2013.12.038.
- 443 [42] Knezevic, D., van Swaaij, W.P.M., Kersten, S.R.A.. Hydrothermal conversion of
444 biomass: I, glucose conversion in hot compressed water. *Industrial & Engineering Chem-*
445 *istry Research* 2009;48(10):4731–4743. doi:10.1021/ie801387v.
- 446 [43] Knezevic, D., van Swaaij, W., Kersten, S.. Hydrothermal conversion of biomass. ii.
447 conversion of wood, pyrolysis oil, and glucose in hot compressed water. *Industrial &*
448 *Engineering Chemistry Research* 2010;49(1):104–112. doi:10.1021/ie900964u.
- 449 [44] Akgül, G., Kruse, A.. Influence of salts on the subcritical water-gas shift reaction. *The*
450 *Journal of Supercritical Fluids* 2012;66:207 – 214. doi:10.1016/j.supflu.2011.10.009.
- 451 [45] Guo, Y., Wang, S., Xu, D., Gong, Y., Ma, H., Tang, X.. Review of catalytic
452 supercritical water gasification for hydrogen production from biomass. *Renewable and*
453 *Sustainable Energy Reviews* 2010;14(1):334 – 343. doi:10.1016/j.rser.2009.08.012.
- 454 [46] Sharninghausen, L.S., Campos, J., Manas, M.G., Crabtree, R.H.. Efficient selective
455 and atom economic catalytic conversion of glycerol to lactic acid. *Nature Communica-*
456 *tions* 2014;5(0):1 – 9. doi:10.1038/ncomms6084.
- 457 [47] Schubert, M., Regler, J.W., Vogel, F.. Continuous salt precipitation and separation
458 from supercritical water. part 1: Type 1 salts. *The Journal of Supercritical Fluids*
459 2010;52(1):99 – 112. doi:10.1016/j.supflu.2009.10.002.