New insights into the effect of pressure on catalytic hydrolysis of biomass

Stummann, Magnus Zingler; Høj, Martin; Hansen, Asger Baltzer; Davidsen, Bente; Wiwel, Peter; Gabrielsen, Jostein; Jensen, Peter Arendt; Jensen, Anker Degn

Published in:
Fuel Processing Technology

Link to article, DOI:
[10.1016/j.fuproc.2019.05.037](https://doi.org/10.1016/j.fuproc.2019.05.037)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Stummann, M. Z., Høj, M., Hansen, A. B., Davidsen, B., Wiwel, P., Gabrielsen, J., Jensen, P. A., & Jensen, A. D. (2019). New insights into the effect of pressure on catalytic hydrolysis of biomass. *Fuel Processing Technology*, 193, 392-403. <https://doi.org/10.1016/j.fuproc.2019.05.037>

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

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

New insights into the effect of pressure on catalytic hydrolysis of biomass

Magnus Zingler Stummann^a, Martin Høj^a, Asger Baltzer Hansen^b, Bente Davidsen^b, Peter Wiwel^b, Jostein Gabrielsen^b, Peter Arendt Jensen^a, Anker Degn Jensen^{a*}

^a*Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), 2800 Kgs. Lyngby (Denmark)*

^b*Haldor Topsøe A/S, 2800 Kgs. Lyngby (Denmark)*

*aj@kt.dtu.dk

Abstract

Catalytic hydrolysis of beech wood has been conducted in a fluid bed reactor at 450 °C with a sulfided CoMo catalyst followed by a fixed bed hydrodeoxygenation (HDO) reactor with a sulfided NiMo catalyst at hydrogen pressures between 3.0 and 35.8 bar. Using both reactors the condensable organic yield (condensed organic and C₄₊ in gas) varied between 18.7 and 21.5 wt.% dry ash free basis (daf) and was independent of the hydrogen pressure. At 15.9 bar hydrogen or higher the condensed organic phase was essentially oxygen free (<0.01 wt.% dry basis (db)), but decreasing the hydrogen pressure to 3.0 bar increased the oxygen content to 7.8 wt.% db. The char and coke yield was close to constant (11.0-12.7 wt.% daf) at hydrogen pressures between 15.9 and 35.8 bar, but increased to 15.7 wt.% at 3.0 bar hydrogen due to an increase in the polymerization of pyrolysis vapors. The measured carbon content on the spent catalysts from both the fluid bed and HDO reactor showed that coking of the catalysts increased when the hydrogen pressure was decreased below 15.9 bar. The increased coking at low hydrogen pressure (<15.9 bar) was ascribed to the polymerization of the more reactive oxygenates produced in the fluid bed reactor.

Keywords

- Catalytic hydrolysis

- 24 • Deactivation
- 25 • Biofuel
- 26 • Low pressure
- 27 • Hydrodeoxygenation
- 28 • Oil characterization
- 29

30 **Abbreviations**

AED	Atomic emission detector
conc	Concentration
daf	Dry, ash free basis
db	Dry basis
diAro	Diaromatics
DMDS	Dimethyl disulfide
EDS	Energy dispersive X-ray spectroscopy
FB	Fluid bed
FID	Flame ionization detector
ToF	Time of flight
GC	Gas chromatograph
HDO	Hydrodeoxygenation
mAro	Monoaromatics
MS	Mass spectrometry
Naph	Naphthenes
O-Ali	Oxygenated aliphatics
O-Aro	Larger oxygenated aromatics
Par	Paraffins
PhOH	Phenols
Ph(OH) ₂	Dihydroxybenzene
TAN	Total acid number
Temp.	Temperature
tetAro+	Tetra- and higher aromatics

triAro Triaromatics

31

1 Introduction

Recent research have shown that catalytic hydropyrolysis of biomass is an efficient method for production of renewable liquid fuels with a low carbon footprint [1–4]. In this process pyrolysis takes place in a hydrogen atmosphere and a catalyst is used as heat carrier. This enables the hydrogenation of the oxygenates as soon as they are formed by the pyrolysis process, thus decreasing the extent of polymerization reactions [5]. Since catalytic hydropyrolysis is exothermic, as opposed to inert pyrolysis, additional heat to the fluid bed reactor is not required.

In GTI's process called IH² catalytic hydropyrolysis takes place in a fluid bed reactor at temperatures between 336–469°C and the produced vapors are sent to a fixed bed hydrodeoxygenation (HDO) reactor operated at 343–399°C and the total pressure is between 19.5 and 24.1 bar [1,2]. Using maple and pine wood the IH² process has been running continuously for 750 hours with a feeding rate of 50 kg/h at a hydrogen pressure of 24 bar with a condensable organic (condensed organics + C₄₊ in gas) of 26 wt.% dry as free (daf) [2].

Dayton et al.[6–8] also investigated catalytic hydropyrolysis of wood in a fluid bed reactor. Using a reduced NiMo hydrotreating catalyst they investigated the effect of the pressure by varying the total pressure between 10.3 and 20.7 bar and varying the hydrogen concentration between 20 and 60 % [8]. They found that the char yield increased at low hydrogen partial pressure and that higher partial pressure of hydrogen decreased the oxygen content and increased the carbon content in the organic phase favoring the formation of hydrocarbons [8]. Furthermore, conducting catalytic hydropyrolysis at 450°C and using hydrogen at atmospheric pressure with a molybdenum based reduced metal oxide catalyst resulted in a carbon recovery in the organic phases and C₄₊ of 43 % and an oxygen content of 6.2 wt.% [7]. The results show that catalytic hydropyrolysis can be conducted at low pressure with a high yield and reasonable degree of deoxygenation.

55 Several groups have investigated catalytic hydropyrolysis using Pyroprobe reactors and H-ZSM-5, often
56 impregnated with Ni [9–15]. Melligan et al.[15] investigated the effect of hydrogen pressure at 600 °C using
57 a Ni/H-ZSM-5 catalyst and found that increasing the hydrogen pressure increased the higher heating value
58 (HHV) of the products, due to an increased degree of deoxygenation. Other groups have investigated
59 hydropyrolysis either using a cyclone reactor or fluid bed reactor followed by a fixed bed catalytic HDO
60 reactor [16–19].

61 In our previous study [20] we investigated the effect of pressure and temperature on catalytic
62 hydropyrolysis of beech wood using a two-reactor system, where the catalytic hydropyrolysis took place in
63 a fluid bed reactor with a sulfided CoMo/MgAl₂O₄ catalyst followed by a fixed bed reactor with a sulfided
64 NiMo/Al₂O₃ catalyst. Operating the fluid bed reactor at 450 °C and varying the total pressure between 16
65 and 36 bar did not have an impact on the condensed organics and C₄₊ gas yield [20]. The spent catalysts
66 were not investigated. In this study we have conducted a more thorough investigation of the effect of the
67 total pressure and the hydrogen partial pressure. The total pressure has been varied between 5.0 and 36
68 bar and the hydrogen partial pressure has been varied between 3.0 and 35.8 bar. The liquid products have
69 been extensively characterized and the carbon content on the spent catalysts from both the HDO reactor
70 and fluid bed reactor has been measured to indicate catalyst deactivation by coking.

71 **2 Material and methods**

72 **2.1 Biomass feedstock**

73 Bark free beech wood was used as biomass feedstock and was supplied by Dansk Træmel (Product number:
74 10000251250390). The moisture and ash contents were 6.72 wt.% (dried at 105 °C) and 0.59 wt.% on dry
75 basis (db), respectively. The particle sizes were between 200-700 µm. The beech wood was analyzed by
76 Celnis Analytical (analysis P10) and consisted of 24 wt.% db lignin, 40 wt.% db cellulose, 18 wt.% db
77 hemicellulose, 3 wt.% db other polysaccharides, 3 wt.% db extractives and 12 wt.% db unknown. A detailed
78 elemental composition of the biomass, including the ash composition, can be found elsewhere [20].

79 **2.2 Catalysts**

80 A CoMo/MgAl₂O₄ catalyst was used in the fluid bed reactor. The catalyst was received as extrudates and
81 was crushed and sieved to a particle size between 180 and 355 µm. An extruded NiMo/Al₂O₃ catalyst was
82 used in the HDO reactor, and was used as received. Both catalysts were supplied by Haldor Topsøe A/S and
83 were also used in our previous work [20]. These two catalysts were chosen due to their well-known activity
84 in HDO reactions [21–30], where the NiMo catalyst mainly promotes the removal of oxygen from phenols
85 after it has saturated the aromatics (HDO pathway), while the CoMo to a larger extent promotes the direct
86 removal of oxygen from phenol (DDO pathway) [27,31–34]. At the applied temperatures in the fluid bed
87 reactor the hydrogenation/deoxygenation of phenols are controlled by the thermodynamic equilibrium
88 [20], thus it has been shown that the CoMo catalyst is the best choice for the fluid bed reactor [35]. In
89 addition a catalyst with MgAl₂O₄ as support material was chosen for the fluid bed reactor because of its
90 relatively high mechanical strength, which decreases the catalyst loss due to attrition.

91 **2.3 Experimental setup**

92 The catalytic hydropyrolysis experiments were conducted in a bench scale setup shown in Figure 1. The
93 setup is described in detail elsewhere [20]. The setup consisted of a feeding system, which included a gas
94 mixing system and a screw feeder for biomass feeding, a fluid bed hydropyrolysis reactor, a filter for char
95 removal, a fixed bed hydrotreating reactor, which can be bypassed, and a three stage condensation system
96 (20°C, 2°C, and -40°C). The temperature in the last step in the condensation system was in some
97 experiments increased to -20°C, to avoid plugging of the heat exchanger due to formation of wax. The
98 uncondensed gases were sent to a flare. A small fraction of the gas was sent to an online gas
99 chromatograph (GC), which measured the gas composition (H₂, N₂, H₂S, CO, CO₂, C₁ to C₅ and C₆₊
100 hydrocarbons) every 10 min. The tubes between the fluid bed, filter and condensation section were heated
101 to 350°C in order to avoid condensation. The biomass feeding tube was preheated to approximately 200°C
102 to preheat the biomass and carrier gas while avoiding premature pyrolysis.

103 The total mass of the condensed liquid was determined by weighing and the organic phase and the
 104 aqueous phase were separated with a separation funnel. In experiment 1-4 the mass of the condensed
 105 organics and aqueous were determined as described in ref. [20], while in experiment 5-8 the mass of the
 106 aqueous phase was measured and the mass of the organic phase was determined by subtracting the mass
 107 of the aqueous phase from the total mass of condensed liquid. The differences between these two
 108 methods are below the experimental uncertainty. The H_2S dissolved in the liquid phases was for safety
 109 reasons removed by bubbling with N_2 until hydrogen sulfide test strips (Sigma Aldrich) showed no sign of
 110 H_2S . This lead to a mass loss between 1.2 and 7.9 wt.% for the organic phase and between 0.43 and 5.1
 111 wt.% of the aqueous phase. The mass loss in the organic phase was mainly due to vaporization of light
 112 hydrocarbons while the mass loss in the aqueous phase was mainly due to vaporization of water.

113
 114 **Figure 1. Simplified piping and instrumentation diagram of the catalytic hydropyrolysis setup**

115 After each experiment the catalyst and the remaining char was removed from the fluid bed, and replaced
 116 with fresh catalyst for the subsequent experiment. The same catalyst was used in the HDO reactor in
 117 experiments 1 to 4, but the catalyst in the HDO reactor was replaced before experiments 5, 6, and 7. The

solid yield was defined as the sum of the char (un-vaporized biomass particles) and coke (carbon on the catalyst) yield, and was calculated by subtracting the mass of loaded catalyst from the total mass of solids collected from the filter and fluid bed.

In experiments 1 to 4 a liquid feeding system consisting of a pump and evaporator was used to supply the setup with dimethyl disulfide (DMDS) during the sulfidation of the catalysts, more information can be found in ref. [20]. However, DMDS lead to coking of the gas preheater and bottled H₂S was therefore used in experiments 5 to 8. The catalysts were sulfided at 26 bar by heating the reactors from 180 to 350 °C with 1.8 mol % H₂S, 11 mol % N₂ in 87 % H₂ by feeding 2 % H₂S in H₂ (flow: 4 NL/min) and N₂ (flow: 0.5 NL/min). The temperature ramp was 10 °C/min and the holding time was 3 hours, when both reactors were used and 2 hours when only the fluid bed reactor was used.

The experimental error is less than 0.2 wt.% daf for the C₁-C₃ yield, 0.5 wt.% daf for the total CO and CO₂ yield, 0.5 wt.% daf for the char and coke yield, 0.5 wt.% daf for the condensable organic yield (condensed organics and C₄₊ in the gas), and 1.5 wt.% daf for the aqueous phase yield, when the mass balance closes within 99 wt.% daf [36]. However, it should be noted that the experimental uncertainty increases with decreasing mass balance closure.

2.4 Analysis methods

2.4.1 Organic phase

The produced organic phases were analyzed with several different methods and a detailed description of the methods can be found elsewhere[20]. The hydrogen and sulfur content was measured with ASTM method D7171 and ASTM method D4294, respectively. The viscosity at 40 °C was measured with ASTM method D7042, the density at 40 °C was measured with ASTM method D4052. The water content was measured with Karl Fisher titration. The total acid number (TAN) was measured at DB lab by titration with KOH.

141 For the organic phases with less than 2 wt.% oxygen, the oxygen content was measured using a GC with an
142 atomic emission detector (AED). The GC was an Agilent 7890 coupled to a JAS 2370 AED in oxygen selective
143 mode. The total amount of oxygen in the samples was quantified by adding a known amount of 4-
144 fluorophenol to the sample. For organic phases with more than 2 wt.% oxygen, the oxygen content was
145 analyzed at DB Lab A/S using a Flash 2000 elemental analyzer (Thermo Scientific). The uncertainty of this
146 measurement was 3.0 %, defined as two standard deviations for the measurement uncertainty,
147 corresponding to a confidence interval of 95 %.

148 Selective analysis of the sulfur containing compounds in the condensed oil was conducted using the above
149 described GC with the AED detector in sulfur specific mode. Quantification was done by adding known
150 amounts of benzothiophene, dibenzothiophene and 4-methyl-dibenzothiophene to the sample.

151 The condensed organic liquid samples were characterized by GC×GC-time of flight (ToF)/ mass
152 spectrometry (MS) or –flame ionization detector (FID) using a LECO® Pegasus 4D™ instrument. The
153 instrument included an Agilent 7890A GC equipped with a Gerstel® CIS 4 PTV inlet, a secondary oven, a
154 quad-jet, dual-stage cryogenic (liquid N₂) modulator, a ToF/MS, and a FID detector. The primary (1D) and
155 secondary (2D) columns were Restek® Rxi-5Sil MS and Restek® Rxi-17Sil MS, respectively. Based on the
156 GC×GC-ToF/MS analysis the compounds were classified into eleven classes: naphthenes, monoaromatics,
157 diaromatics, triaromatics, larger aromatics, phenols, dihydroxybenzenes, larger oxygenated aromatics,
158 oxygenated aliphatics, paraffins, and sterols. Based on the paraffins retention time on the 1D column the
159 component classes were divided into subgroups on the basis on the number of carbon atoms in the
160 molecules : -C10, C11-C15, C16-C20, and C20+. However, it should be noted that other component classes
161 do not necessarily have the same carbon number distribution as the paraffins, thus caution is needed when
162 correlating the relative amount of each subgroup with its carbon number distribution. The relative amount
163 (FID area-%) of each compound class was estimated as the sum of areas of all detected peaks in that class

164 divided by the total peak area of all compound classes. All data was processed using the ChromaTof® 4.50
165 software.

166 **2.4.2 Aqueous phase**

167 The carbon content in the aqueous phase was determined with GC-AED. The quantification was done by
168 external standards using benzyl alcohol dissolved in water. Calibration concentrations ranged from 10 ppm
169 to 1100 ppm carbon. No identification of individual compounds was done and the total detected carbon
170 was taken as a figure of the total carbon content in the aqueous sample. No sample pretreatment was done
171 prior to analysis. A more thorough description of the method can be found elsewhere[36].

172 The aqueous phase was also analyzed on a Shimadzu GC-MS/FID with a Supelco Equity-5 column. The
173 compounds were identified on the MS and quantified using the parallel FID. Based on the GC-FID/MS
174 analysis the components were classified into 8 groups: unidentified, ethers, ketones, alcohols, sugars,
175 phenols, acids and furans. The relative amount (FID area-%) of each component class was estimated as the
176 sum of all the detected peaks in that class divided by the total peak area.

177 **2.4.3 Catalyst characterization**

178 The carbon content on the spent NiMo/Al₂O₃ catalyst from the HDO reactor was measured with a LECO CS-
179 200. The sample was combusted in an O₂ atmosphere and the formed CO₂ was measured with IR-
180 absorption.

181 The catalyst in the fluid bed reactor was during the experiment mixed with char particles, which makes it
182 difficult to measure that carbon content on the spent catalyst from the fluid bed by combustion. The
183 carbon content on the spent catalysts from the fluid bed reactor was therefore measured with scanning
184 electron microscopy (SEM) combined with an energy-dispersive detector (EDS), and a detailed description
185 of the method can be found elsewhere [36]. A FEI QUANTA600 scanning electron microscope with tungsten
186 filament and equipped with a liquid nitrogen cooled EDAX EDS detector was used for these measurements.
187 EDS element quantification was conducted at four different acceleration voltages: 3 kV, 5 kV, 10 kV, and 15

188 kV to probe different interaction volumes between the incident electron beam and the sample. The
189 maximum penetration depth for MgAl_2O_4 was estimated with CASINO Monte Carlo Software to be
190 approximately 0.170 μm for 3 kV and 1.60 μm for 15 kV [36], thus mainly probing the composition close to
191 the catalyst surface. The standard deviation for the measurement was 1.5 wt.% at 3 kV, 0.8 wt.% at 5 kV,
192 1.0 wt.% at 10 kV and 1.5 wt.% at 15 kV.

193 **3 Results and Discussion**

194 The tested process conditions and their effect on the product distribution are shown in Table 1. It should be
195 noted that experiment 1-4 has previously been published [20]. However, in this work the produced liquid
196 phases and the spent catalysts have been more extensively characterized and combining the previous
197 obtained results with the new results gives a more in-depth understanding of the effect of pressure. The
198 feed time varied between 1.4 and 4.0 hours and the mass balance closed between 99.5 and 92.1 wt.% daf.
199 The reason for the short feeding time of 1.4 hours in experiment 6 is that the tube between fluid bed
200 reactor and filter plugged. This was probably due to condensation and polymerization of heavy oxygenates
201 in the tube. The mass balance in experiment 8 only closed with 92.1 wt.% daf. In this experiment the HDO
202 reactor was bypassed, the total pressure was 10 bar and the hydrogen partial pressure only 3.0 bar. The
203 produced organic phase was thus heavier than the aqueous phase and part of the reason for the poor mass
204 balance in experiment 8, is therefore most likely due to accumulation of organics in the setup. The biomass
205 feeding rate was difficult to control and varied between 161 and 389 g/h, but only had a limited influence
206 on the results [20].

207

Table 1 Summary of the reactions conditions and mass balances for catalytic hydropyrolysis of beech wood at different total and hydrogen partial pressures.

Test	1	2	3	4	5	6	7	8
Test conditions								
	With HDO	Without HDO	With HDO	With HDO	With HDO	With HDO	With HDO	Without HDO
FB temperature (°C)	451	450	447	449	452	450	450	454
FB catalyst amount (g)	50.1	49.6	49.7	50.2	50.0	50.0	50.1	50.0
HDO temperature (°C)	371	-	370	364	386	383	376	-
HDO catalyst mass (g)	173	-	173	173	175	175	171	-
Total pressure (bar)	26	26	16	36	10	5	10	10
H ₂ pressure (bar)	24.5	25.8	15.9	35.8	8.2	3.0	3.0	3.0
Feed time (h)	4.0	3.9	4.0	4.0	2.6	1.4	2.8	2.8
Feeding rate (g/h)	250	174	161	159	354	389	350	350
H ₂ S conc.(ppm)	460	48	47	50	475	460	464	464
H ₂ flow (NL/min)	82	87	52.4	124.2	30.9	10.4	11.4	11.4
N ₂ flow (NL/min)	5.0	0.62	0.37	0.62	7.0	7.0	26.5	26.5
H ₂ consumed (g)	46	35	35	46	34	20	19	9.4
Biomass used (kg)								
Yields (wt. daf %)								
Gas	31.5	27.4	30.3	26.3	32.1	33.2	33.5	24.0
Solid	11.4	12.3	11.0	12.7	13.2	13.6	15.7	15.3
Aqueous phase	35.2	37.0	33.2	37.7	32.3	29.0	28.8	27.5
Organic phase	12.3	12.0	11.0	10.6	13.0	10.1	12.6	23.0
C ₄₊ in the gas	9.1	8.3	8.7	10.3	7.9	8.5	7.6	2.3
Organics + C ₄₊	21.5	20.3	19.7	20.9	20.9	18.7	20.2	25.3
Mass balance	99.5	96.9	94.2	97.6	97.5	94.5	98.2	92.1
Carbon recovery (%)								
C ₁ -C ₃	23	19	19	21	22	21	21	8
C ₄₊	15	14	14	17	13	15	13	4
CO+CO ₂	12	13	13	10	13	15	16	13
Organic phase	21	21	19	19	23	16	19	30
Aqueous phase	0.014	1.1	<0.008	<0.009	0.51	0.59	0.47	8.5
Organic phase + C ₄₊	37	35	34	36	36	31	32	34
Organic phase composition								
Water (wt.%)	ND	0.35	ND	ND	0.36	3.32	1.6	11.3
C* (wt.% db)	88	88	88	88	87	84	83	74
H (wt.% db)	11.9	10.2	11.2	11.6	9.58	9.55	9.56	7.60
O (wt.% db)	0.003	1.8	0.0009	0.0001	3.3	6.0	7.8	18.3
S (wt.% db)	0.117	0.303	0.417	0.246	0.036	0.045	0.033	0.093
Organic phase physical properties								
Density at 40°C (g/ml)	0.827	0.889	0.852	0.843	0.863	.0936	0.944	1.06
Viscosity (Pa s)	8.70×10 ⁻⁴	1.43×10 ⁻³	1.04×10 ⁻³	1.01×10 ⁻³	9.81×10 ⁻⁴	2.69×10 ⁻³	3.39×10 ⁻³	9.29×10 ⁻³
TAN (mg _{KOH} /g)	-	-	-	-	-	-	0.25	88.60
Aqueous phase composition (wt.%)								
C	0.017	1.3	<0.01	<0.01	0.66	0.81	0.7	12.3
Gas composition (wt.% daf)								
CO	9.0	11.1	10.8	9.9	8.8	10.0	10.0	8.7
CO ₂	8.1	5.7	7.6	3.3	10.3	12.4	12.9	10.8
C ₁ -C ₃	14.3	12.1	12.0	13.2	13.0	10.9	10.6	4.5
C ₄₊	9.1	8.3	8.7	10.3	7.9	8.5	7.6	2.3

*By difference

210 **3.1 Product distribution**

211 The main effect on the product distribution by increasing the hydrogen partial pressure was that it
212 increased the aqueous phase yield and decreased the CO and CO₂ yield. This shows that when the hydrogen
213 pressure is increased the hydrodeoxygenation activity increases while the carboxylation/carbonylation
214 decreases. In addition, decreasing the hydrogen partial pressure to below 15.9 bar hydrogen (experiment 5-
215 8) lead to an increase in the char and coke yield, which indicates that at low hydrogen pressure the catalyst
216 is not active enough to suppress polymerization reactions. Varying the total pressure at constant hydrogen
217 partial pressure (experiment 6 and 7) did not have a significant impact on the product distribution, thus the
218 observed effects are due to the variations in hydrogen pressure.

219 In the experiments where both reactors were used the condensable organic yield (condensed organics + C₄+
220 in the gas) varied between 18.7 and 21.5 wt.% daf, as shown in Figure 2(A), with no apparent correlation
221 between the hydrogen pressure and condensable organic yield. However, when the HDO reactor was
222 bypassed the condensable organic yield was 20.3 wt.% daf at 25.8 bar hydrogen and increased to 25.3 wt.%
223 daf at 3.0 bar hydrogen. The reason for the increased condensable organic yield is due to increased oxygen
224 content in the organic phase. Using the HDO reactor, the total gas yield (Figure 2(B)) decreased from 33.5
225 to 26.3 wt.% daf when partial pressure of hydrogen was increased from 3.0 to 35.8 bar. This was due to a
226 decrease in the CO and CO₂ yield, which decreased from 22.9 wt.% daf at 3.0 bar to 13.2 wt.% daf at 35.8
227 bar, while the C₁-C₃ yield varied between 10.6 and 14.3 wt.% daf. The CO and CO₂ yield most likely
228 decreased due to a higher hydrodeoxygenation activity at higher hydrogen partial pressure, which is a
229 competing reaction with decarbonylation and decarboxylation. The lower C₁-C₃ yield when the HDO reactor
230 is bypassed, 4.5 wt.% daf at 3.0 bar hydrogen and 10.6 wt.% at 25.8 bar hydrogen, could be due to cracking
231 of the vapors in the HDO reactor, but it is probably also due to deoxygenation of C₁-C₃ oxygenates, which
232 are recovered in the aqueous and organic phases when the HDO reactor is bypassed. Interestingly, the CO
233 and CO₂ yield is unchanged when the HDO reactor is bypassed at 25.8 bar hydrogen, but decreased from
234 22.9 to 19.6 wt.% daf at 3.0 bar hydrogen.

235 As shown in Figure 2(C) the solid yield decreased from 15.7 wt.% daf at 3.0 bar hydrogen to 11 wt.% at 15.9
236 bar hydrogen. Furthermore, at 3.0 bar hydrogen it was observed that coke builds up on the filter and the
237 filter cake was approximately 0.5 cm thick (see supplementary material Figure S.1). Similarly Dayton et al.
238 [8] observed that decreasing the hydrogen concentration from 40 to 20 % (at 20.7 bar total pressure and
239 425 °C) increased the solid yield from 8.9 to 14.1 wt.%. This indicates that the catalyst in the fluid bed
240 reactor is not able to sufficiently fast remove the reactive oxygenates, leading to increased polymerization
241 reactions. Furthermore, the solid yield increased to 12.7 wt.% daf when the hydrogen pressure was
242 increased to 35.8 bar, which could indicate that too high pressure also increases the solid yield. However,
243 the increase is close to the experimental uncertainty. The aqueous phase yield increased with increasing
244 hydrogen pressure from 28.8 wt.% daf at 3.0 bar hydrogen to 37.7 wt.% daf at 35.8 bar hydrogen, see
245 Figure 2(D). This increase is both due to an increased degree of hydrogenation and hydrodeoxygenation of
246 the organics, and decreased carboxylation/carbonylation reactions. The change in aqueous phase yield,
247 when the HDO reactor is bypassed is within the experimental uncertainty, however, bypassing the HDO
248 reactor increased the carbon content in the aqueous phase, which is discussed in section 3.2.

249 In both experiments 6 and 7 the hydrogen partial pressure was 3.0 bar, but in experiment 6 the total
250 pressure was 5 bar, while it was 10 bar in experiment 7. The difference in the condensable organic,
251 CO+CO₂, C₁-C₃, and aqueous phase yields in these two experiments were 0.6 wt.% daf or lower. The
252 largest difference was in the solid yield, which was 13.6 wt.% daf in experiment 6 (5 bar) and 15.7 wt.% daf
253 in experiment 7 (10 bar). However, the reason for the lower solid yield in experiment 6 compared to 7 is
254 that the tube between the fluid bed and filter blocked in experiment 6, thus leading to a solid build up in
255 the tube, which was therefore not accounted for in the mass balance. Therefore, considering the relatively
256 large difference in the product distribution (>2 wt.% for CO+CO₂, C₁-C₃, solid and aqueous phase yield)
257 between experiment 5 (10 bar pressure, 8.2 bar hydrogen) and 7 (10 bar pressure, 3 bar hydrogen), the
258 experiments show that the product distribution is mainly dependent on the hydrogen partial pressure, and
259 not on the total pressure.

260 Figure 2 Effect of hydrogen partial pressure on the condensable organic yield (A), gas yield (B), char yield (C), and aqueous phase
 261 yield (D). The lines provided are trend lines. Conditions: fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C,
 262 biomass feeding rate: 159-389 g/min, H_2S concentration: 47-475 ppm, H_2 flow: 11.4-124.4 NL/min, N_2 flow: 0.37-26.5 NL/min.

263 The CO and CO_2 yield is shown in Figure 3(A). The CO yield varied between 8.8 and 11.1 wt.% daf, and no
 264 correlation between the CO yield and the hydrogen pressure was observed. While the CO_2 yield decreased
 265 from 12.9 wt.% daf at 3.0 bar hydrogen to 3.3 wt.% daf at 35.8 bar hydrogen. The reason for the decreasing
 266 CO_2 yield might be that when the hydrogen pressure is increased, the CO_2 is converted through the reverse
 267 water gas shift reaction (R.1).

268 The C_2-C_3 paraffin and olefin yields in Figure 3(B) show that when the HDO is used at hydrogen pressures
 269 between 15.9 and 35.8 bar all the olefins were converted into paraffins. However, at lower hydrogen
 270 pressures the olefin conversion decreased, thus at 8.2 bar hydrogen the C_2-C_3 olefin yield was 0.8 wt.% daf

and at 3.0 bar hydrogen the olefin yield was 3.1-3.3 wt.% daf. Bypassing the HDO reactor increased the olefin yield to 1.5 wt.% at 25.8 bar hydrogen, which shows that the olefins are removed in the HDO reactor at this pressure. However, bypassing the HDO reactor at 3.0 bar hydrogen decreased the olefin yield to 1.7 wt.% daf, which is probably due to a higher yield of light oxygenates, which are not deoxygenated.

Figure 3 Effect of hydrogen partial pressure on the CO and CO₂ yield (A) and the C₂-C₃ paraffin and olefin yield (B). The lines provided are trend lines. Conditions: fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C, biomass feeding rate: 159-389 g/min, H₂S concentration: 47-475 ppm, H₂ flow: 11.4-124.4 NL/min, N₂ flow: 0.37-26.5 NL/min.

3.2 Chemical composition of the condensed liquids

3.2.1 Oxygen and hydrogen content

The oxygen and hydrogen content in the condensed organic phase are shown in Figure 4. When the HDO reactor was used the oxygen content was close to 0 wt.% at hydrogen pressures between 15.9 and 25.8 bar; however, decreasing the hydrogen pressure to 8.2 increased the oxygen content to 3.3 wt.% db and further decreasing the hydrogen pressure to 3.0 bar increased the oxygen content to between 6.0 and 7.8 wt.% db. This shows that in order to produce oxygen free oil the hydrogen pressure should be above about 8.2 bar with the used catalysts. Bypassing the HDO reactor when the hydrogen pressure was 25.8 bar increased the oxygen content in the organic phase to 1.8 wt.% db, showing that at this hydrogen pressure most of the deoxygenation takes place in the fluid bed reactor. However, bypassing the HDO reactor at 3.0 bar hydrogen pressure increased the oxygen content to 18.3 wt.% db, thus under these conditions most of the oxygen must be removed in the HDO reactor.

Using the HDO reactor and increasing the hydrogen pressure from 3.0 to 24.5 bar increased the hydrogen content in the organic phase from 9.55 to 11.9 wt.% db, while further increasing the hydrogen pressure to 35.8 bar decreased the hydrogen content to 11.6 wt.% db. However, this decrease is most likely due to the experimental uncertainty. Bypassing the HDO reactor also decreased the hydrogen content in the condensed organic phase to 10.2 wt.% db at 25.8 bar hydrogen and 7.60 wt.% db at 3.0 bar hydrogen. The lower hydrogenation activity could also be seen on the lower hydrogen consumption at low hydrogen pressures, thus the hydrogen consumption was between 19 and 20 g H₂/kg biomass at 3.0 bar hydrogen which increased to 34 g H₂/kg biomass at 15.9 bar hydrogen and further increased to 46 g H₂/kg biomass at 24.5 and 35.8 bar hydrogen. The hydrogen consumption also decreased with approximately 10 g H₂/kg biomass when the HDO reactor was bypassed at both 3.0 and 25.8 bar hydrogen, indicating that the hydrogen consumed in the HDO reactor is independent of the pressure in the tested range. Dayton et al. [8] observed that the hydrogen consumption was between 20 to 25 g H₂/kg biomass when operating at 4.1 bar hydrogen and between 35 to 38 g H₂/kg biomass when operating at 8.2 bar hydrogen. The reason for the higher hydrogen consumption in the work by Dayton et al. is most likely that they used a reduced NiMo catalyst, while sulfided catalysts are used in this study, and reduced Ni is known for its high hydrogenation activity.

Figure 4 Effect of the hydrogen partial pressure on the oxygen (A) and hydrogen (B) content of the condensed organic phase. The lines provided are trend lines. Conditions: fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C, biomass feeding rate: 159-389 g/min, H₂S concentration: 47-475 ppm, H₂ flow: 11.4-124.4 NL/min, N₂ flow: 0.37-26.5 NL/min.

3.2.2 Physical properties of the organic phase

The density and the viscosity of the condensed organic phase were measured at 40 °C and are shown in Figure 5(A) and (B), respectively. Using the HDO reactor the density was between 0.936 and 0.944 g/ml at 3.0 bar hydrogen, and increasing the hydrogen pressure to 24.5-35.8 bar decreased the density to 0.827-0.843 g/ml. Bypassing the HDO reactor increased the density to 1.0589 g/ml at 3.0 bar hydrogen and 0.889 g/ml at 25.8 bar hydrogen. The viscosity varied between 9.81×10^{-4} and 1.01×10^{-3} Pa s when the hydrogen pressure was between 8.2 and 35.8 bar and the HDO reactor was used. Decreasing the hydrogen pressure to 3.0 increased the viscosity to between 2.69×10^{-3} and 3.39×10^{-3} Pa S, and bypassing the HDO reactor increased the viscosity to 1.43×10^{-3} Pa s at 25.8 bar hydrogen and 9.29×10^{-3} Pa s at 3.0 bar. The density of fast pyrolysis oil is typically between 1.1 and 1.3 g/ml and the viscosity is between 0.014 and 0.13 Pa s [5]. Therefore, and despite that both the density and viscosity increased significantly when the HDO reactor was bypassed at 3.0 bar they were still significantly lower than typical values for untreated fast pyrolysis oil. Furthermore, the density and viscosity of diesel is 0.82-0.85 g/ml and $1.56\text{-}1.83 \times 10^{-3}$ Pa s, respectively [5]. This shows that the organic phases from the experiments with the HDO reactor were more similar to light gas oil than pyrolysis oil and due to the fairly low oxygen content in the organic phase it is most likely possible to co-feed into a refinery diesel hydrotreater.

Figure 5 Effect of the hydrogen partial pressure on the density (A) and viscosity (B) of the condensed organic phase. The lines provided are trend lines. Conditions: fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C, biomass feeding rate: 159-389 g/min, H_2S concentration: 47-475 ppm, H_2 flow: 11.4-124.4 NL/min, N_2 flow: 0.37-26.5 NL/min.

328 The TAN number was also measured for the condensed organic phase from the experiments conducted at
329 3.0 bar hydrogen with (exp. 7) and without the HDO reactor (exp. 8). This showed that the TAN number for
330 organic phase was 0.25 mg_{KOH}/g when the HDO reactor was used and 88.60 mg_{KOH}/g when it was bypassed,
331 indicating the HDO reactor is able to remove the acids, which are known for their ability to deactivate HDO
332 catalysts by polymerization [37].

333 3.2.3 GC×GC-MS/FID

334 In order to gain a deeper insight into the condensed organic phases they were analyzed with GC×GC-
335 MS/FID and the detected components were divided into eleven groups naphthenes, monoaromatics,
336 diaromatics, triaromatics, larger aromatics, phenols, dihydroxybenzenes, larger oxygenated aromatics,
337 oxygenated aliphatics, paraffins, and sterols. The most important observation was that when the HDO
338 reactor was used most of the oxygenates were phenols, showing that even at low hydrogen partial
339 pressures the HDO reactor was able to remove the most reactive oxygenates (experiment 5-7). Bypassing
340 the HDO reactor showed that the obtained bio-oil at 3 bar hydrogen (experiment 8) contained many
341 reactive oxygenates and multifunctional phenols, thus likely making it more difficult to further upgrade in a
342 refinery.

343 Using the HDO reactor the concentration of paraffins was between 1.2 and 4.6 % area-FID, and the
344 concentration of oxygenated aliphatics was between 1.5 and 2.6 % area-FID when the hydrogen pressure
345 was below 15.9 bar, but 0 % area-FID at higher hydrogen pressures (see supplementary material Figure
346 S.2). This indicates that even at low hydrogen pressures most of the reactive oxygenates are removed. The
347 concentration of phenols and larger oxygenated aromatics are shown in Figure 6(A). The concentration of
348 phenols was between 44 and 45 % area-FID at 3.0 bar hydrogen, but decreased to 12 % area-FID at 8.2 bar
349 hydrogen and further increasing the hydrogen pressure lead to an almost complete removal of the phenols
350 (non-detected). Similarly, the concentration of larger oxygenated aromatics decreased from between 4.5
351 and 5.4 % area-FID at 3.0 bar hydrogen to 1.5 % area-FID at 8.2 bar hydrogen; none were detected at
352 higher hydrogen pressures. The concentration of naphthenes increased from 17 % area-FID at 3.0 bar

hydrogen to 38 % area-FID at 35.8 bar hydrogen, while the concentration of diaromatics decreased from between 15 and 17 % area-FID at 3.0 bar hydrogen to 7.8 % area-FID at 35.8 bar hydrogen, see Figure 6(A). Interestingly, the concentration of monoaromatics increased from between 12 and 14 % area-FID at 3.0 bar hydrogen to 57 % area-FID at 15.9 bar hydrogen, but further increasing the hydrogen pressure to 35.8 bar decreased the concentration to 48 % area-FID. This indicates an optimum hydrogen pressure for the production of monoaromatics. At hydrogen pressures below the 15.9 bar the reaction rate of HDO is too low to efficiently deoxygenate the phenols and larger oxygenated aromatics despite that benzene is favored by the equilibrium [5]. At hydrogen pressures above the 15.9 bar the oxygenates are converted, and the naphthenes are favored by the thermodynamics [20], hence the aromatics are also hydrogenated which decreases the concentration of mono- and di-aromatics. This indicates that the concentration of monoaromatics is kinetically controlled at low hydrogen pressures (<15.9 bar), but controlled by the equilibrium at high hydrogen pressure (>15.9 bar).

Figure 6 Effect of the hydrogen partial pressure on the concentration of naphthenes (Naph), monoaromatics (mAro), diaromatics (diAro), phenols (PhOH), and larger oxygenated aromatics (O-Aro) (A), and on the concentration of hydrocarbons with 10 or fewer carbon atoms (-C10), between 11 and 15 carbon atoms (C11-C15), between 16 and 20 carbon atoms (C16-C20), and more than 20 carbon atoms (C20+) (B). The lines provided are trend lines. Conditions: fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C, biomass feeding rate: 159-389 g/min, H_2S concentration: 47-475 ppm, H_2 flow: 11.4-124.4 NL/min, N_2 flow: 0.37-26.5 NL/min.

Based on the paraffins retention time on the 1D column it was possible to estimate the number of carbon atoms in the products. However, it should be noted that other component classes do not necessarily have the same carbon number distribution as the paraffins and caution is needed when correlating the results.

374 As shown in Figure 6B the molecules were divided into 4 groups: less than 10 carbon atoms (-C10),
375 between 11 and 15 carbon atoms (C11-C15), between 16 and 20 carbon atoms (C16-C20), and more than
376 20 carbon atoms (C20+). The concentration of molecules with less than 10 carbon atoms increased from
377 between 19 and 23 % area-FID at 3.0 bar hydrogen to 49 % area-FID at 8.2 bar, further increasing the
378 hydrogen pressure to 35.8 bar increased the concentration to 52 % area-FID. The reverse trend was
379 observed for molecules with between 11 and 15 carbon atoms for which the concentration decreased from
380 between 60 and 61 % area-FID at 3.0 bar to 39 % area-FID at 8.2 bar, and to 35 % area-FID at 35.8 bar. This
381 indicates that increasing the hydrogen pressure from 3.0 to 8.2 bar significantly increases the hydrocracking
382 activity, while further increasing the hydrogen pressure has less effect on the hydrocracking activity. It
383 should be noted that the concentration of molecules with between 16 and 20 carbon atoms was between
384 12 and 15 % area-FID at 3.0 bar hydrogen and decreased to 9.9 % area-FID at 35.8 bar hydrogen. This
385 indicates that hydrogen pressure only has a limited effect on the concentration of larger molecules and the
386 concentration of molecules with more 20 carbon atoms was 3.9 % area-FID at 3.0 bar hydrogen and 3.6 %
387 area-FID at 35.8 bar hydrogen.

388 The chromatograms and composition of the organic phases from the experiments where the HDO reactor
389 was bypassed (#2 and #8) are shown in Figure 7. The organic phases from the two experiments are very
390 different. At 3.0 bar hydrogen 77 % area-FID of the organics are oxygenates, while only 26 % area-FID is
391 oxygenates at 25.8 bar hydrogen. At 3.0 bar hydrogen the concentration of oxygenated aliphatics was 33 %
392 area-FID, while it was 4.0 % area-FID at 25.8 bar hydrogen, which shows that at the low hydrogen pressure
393 (3.0 bar) the rate of HDO is too low to convert even simple and reactive oxygenates. Likewise, the
394 concentration of larger oxygenated aromatics and dihydroxybenzenes was 18 and 5.2 % area-FID,
395 respectively, at 3.0 bar hydrogen. Increasing the hydrogen pressure to 25.8 bar decreased the
396 concentration of larger oxygenated aromatics to 0.1 % area-FID and dihydroxybenzenes were not detected
397 at this hydrogen pressure. Traces of sterols (0.1 % area-FID) were also detected at 3.0 bar hydrogen, but
398 not at 25.8 bar hydrogen. These results indicate that the organic phase produced at 25.8 bar hydrogen is

399 more stable and less reactive than the organic phase produced at 3.0 bar hydrogen. It is therefore likely
400 that the organic phase produced at 25.8 bar hydrogen can easily be co-feed into an existing refinery unit,
401 while co-feeding the organic phase produced at 3.0 bar will most likely lead to catalyst deactivation due to
402 the furans and multifunctional phenols present in the organic phase. Furthermore, the organic phase
403 produced at 3.0 bar is most likely less miscible with fossil oil due to its high oxygen content. However, it
404 should also be noted that dihydroxybenzenes were not detected in any of the experiments with the HDO
405 reactor, thus multifunctional phenols were only detected at 3.0 bar hydrogen when the HDO reactor was
406 bypassed. Furthermore, the molecular size distribution was also very different for produced organics when
407 the HDO reactor was bypassed. 32 % area-FID of the molecules contains less than 10 carbon atoms at 3.0
408 bar hydrogen, while 41 % contains less than 10 carbon atoms at 25.8 bar hydrogen, showing that
409 decreasing the hydrogen pressure leads to a heavier organic phase.

410

Figure 7 Composition of the organic phase when the HDO reactor is bypassed at 3.0 bar hydrogen (A,B) and at 25.8 bar hydrogen (C,D). The components in the condensed organics are divided into paraffins (Par), naphthenes (Naph), monoaromatics (mAro), diaromatics (diAro), triaromatics (triAro), tetraaromatics and larger aromatics (tetAro+), oxygenated aliphatics (O-ali), phenols (PhOH), dihydroxybenzenes (Ph(OH)₂), and larger oxygenated aromatics (O-aro). Conditions: fluid bed temperature 450-454 °C, biomass feeding rate: 174-350 g/min, H₂S concentration: 48-475 ppm, H₂ flow: 11.4-87 NL/min, N₂ flow: 0.62-26.5 NL/min.

3.2.4 Sulfur specific GC-AED

The sulfur content in the condensed organic phases was measured to be between 0.033 and 0.417 wt.% db with energy dispersive X-ray fluorescence, which indicates an incorporation of sulfur into the produced organics. The sulfur content in the organic phase therefore needs to be reduced before it can be used as transportation fuel for cars. Since the reactivity of sulfur molecules is highly dependent on the type of molecules, for instance dibenzothiophene is very difficult to desulfurize [38], it is important to investigate the type of sulfur compounds in the organic phase. Therefore, 5 of the condensed organic phases were analyzed with sulfur specific GC-AED and the detected compounds were divided into thiols, thiophenes, benzothiophenes, other sulfur containing hydrocarbons such as DMDS and carbonylsulfide, and

unidentified. Detailed lists of the detected compounds are shown in supplementary material Tables S.1 - S.5. This showed that the samples contained between 17 and 232 wt-ppm S as H₂S, which was not properly removed during the stripping. When the HDO reactor was bypassed at 3.0 bar hydrogen the concentration of thiols was 23 wt-ppm S, but between 0 and 3 wt-ppm S when the HDO reactor was used, see Figure 8, showing that even at low hydrogen pressures the thiols were removed in the HDO reactor. The concentration of thiophenes was 220 wt-ppm S at 3.0 bar hydrogen without the HDO reactor, but 298 wt-ppm S at 3.0 bar hydrogen (10 bar total pressure) with HDO reactor, indicating that thiophenes are formed in the HDO reactor. However, it should be noted that the concentration of unidentified compounds was 96 wt-ppm S when the HDO reactor was bypassed and 34 wt-ppm S when the HDO reactor was used, thus it is likely that the organic phase from experiments without the HDO reactor contains some unidentified thiophenes or benzothiophenes.

Figure 8 Effect of the hydrogen partial pressure and the total pressure on the concentration of organic sulfur species in the condensed organic phase. Conditions: fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C, biomass feeding rate: 159-389 g/min, H₂S concentration: 47-475 ppm, H₂ flow: 11.4-124.4 NL/min, N₂ flow: 0.37-26.5 NL/min.

Interestingly, the concentration of thiophenes was 463 wt-ppm S when the total pressure was 5 bar (3.0 bar hydrogen), but 298 wt-ppm S when the total pressure was 10 bar (3.0 bar hydrogen), both with the HDO reactor, indicating that the total pressure influences the thiophene concentration. The thiophene concentration was 38 wt-ppm S both at 8.2 and 24.5 bar hydrogen, indicating that varying the hydrogen pressure in this interval only has a limited effect on the thiophene concentration. However, the

445 concentration of benzothiophenes was 16 wt-ppm S at 8.2 bar hydrogen, but was not detected at 24.5 bar
446 hydrogen. Furthermore, the total concentration of sulfur containing compounds was 109 wt-ppm S at 8.2
447 bar hydrogen and 84 wt-ppm S at 24.5 bar hydrogen. This therefore shows that the sulfur compounds in
448 the produced organic phase are fairly similar to the sulfur compounds produced in fluid catalytic cracking
449 [39] and does not contain the very stable dibenzothiophenes [38], thus the sulfur can relatively easily be
450 removed in a modern refinery.

451 **3.2.5 Aqueous phase composition**

452 The carbon content in the aqueous phases was below 0.02 wt.% in the experiments where the HDO reactor
453 was used and the hydrogen pressure was 15.9 bar or higher, see Table 1. Decreasing the hydrogen pressure
454 to 8.2 bar increased the carbon content in the aqueous phase to 0.66 wt.% and further decreasing the
455 hydrogen pressure to 3.0 bar increased the carbon content to between 0.70 and 0.81 wt.%, depending on
456 the total pressure. Furthermore, bypassing the HDO reactor at 3.0 bar hydrogen the carbon content in the
457 aqueous phase was 12.3 wt.%, while it was 1.3 wt.% at 25.8 bar hydrogen. This shows that conducting
458 catalytic hydropyrolysis at low hydrogen pressures (<15.8 bar) even with a HDO reactor lead to higher
459 carbon content in the aqueous phase, which could increase the operating expenses for waste water
460 treatment.

461 In order to obtain a more thorough understanding of the oxygenates the aqueous phase, the aqueous
462 phases with more than 0.02 wt.% carbon were analyzed with GC-MS/FID. The detected oxygenates were
463 divided into 8 groups: alcohols, furans, acids, ketones, phenols, sugars, esters, aldehydes and unidentified.
464 Lists of the detected compounds can be found in supplementary material Tables S.6-S.10. To compare the
465 concentrations in the different aqueous phases the relative FID area (the FID area of one group divided
466 with total area) was multiplied with the concentration of carbon in the aqueous phase, as shown in Figure
467 9. When the HDO reactor was used most of the aqueous phase oxygenates were phenols and the phenol
468 concentration increased from 0.11 to 0.31 wt.% when the hydrogen pressure was decreased from 8.2 to 3.0
469 bar (10 bar total pressure). At 8.2 bar hydrogen no acids were detected, but at 3.0 bar hydrogen (10 bar

total pressure) acetic acid, propanoic acid, and butanoic acid were detected, corresponding to a total concentration of 0.009 wt.%. Ketones were also observed at 3.0 bar hydrogen at both 5 and 10 bar total pressure, showing that at 3.0 bar hydrogen the rate of HDO is too low to convert even the more reactive oxygenates. However, the concentration of alcohols was below 0.1 wt.% in all the experiments with the HDO reactor.

Figure 9 Effect of the hydrogen partial pressure and total pressure on composition of the aqueous phase. The concentration is calculated by multiplying the total concentration of the carbon in the aqueous phase with the fraction (area-FID) of the different compounds.

Bypassing the HDO reactor increased the concentration of alcohols to 1.0 wt.% at 3.0 bar hydrogen and 0.66 wt.% at 25.8 bar hydrogen. Likewise, the phenols concentration increased to 0.53 wt.% at 3.0 bar hydrogen and 0.36 wt.% at 25.8 bar hydrogen and the concentration of ketones increased to 3.6 wt.% at 3.0 bar hydrogen and 0.24 wt.% at 25.8 bar hydrogen. At 3.0 bar hydrogen furans (0.12 wt.%), sugars (0.34 wt.%), esters (0.073 wt.%), aldehydes (0.024 wt.%) were also observed, none of these compounds were detected at 25.8 bar hydrogen, showing that the aqueous phase formed at 3.0 bar hydrogen contains much more reactive oxygenates than the aqueous phase formed at 25.8 bar.

3.3 Characterization of the spent catalysts

3.3.1 Fluid bed reactor

The carbon content on the spent catalysts from the fluid bed reactor was investigated with SEM-EDS and the acceleration voltage was varied between 3 and 15 kV. At 3 kV the carbon concentration at the surface

490 was measured and at 15 kV a concentration closer to the bulk was measured, as described in detail in ref.
491 [36]. In order to account for the background carbon measurement, the carbon content on the catalysts was
492 calculated by subtracting the measured carbon content on the fresh catalyst from the carbon on the spent
493 catalysts (see supplementary material equation S.1). The measured carbon content on the catalysts is
494 shown at different acceleration voltages in supplementary material Table S.11. Figure 10 shows the
495 measured concentration of carbon at 15 kV as a function of the hydrogen pressure. It can be seen that at
496 hydrogen pressures between 15.9 and 35.8 bar the carbon concentration varied between 4.8 and 6.2 wt.%,
497 differences within the measurement uncertainty, and hence the coke formation was unaffected by the
498 hydrogen pressure in this range. However, decreasing the hydrogen pressure to 8.2 bar increased the
499 carbon concentration to 8.8 wt.% and further decreasing the hydrogen pressure to 3.0 increased the
500 carbon content to between 12.2 and 20.7 wt.%. Part of the reason for the large variation in the carbon
501 content at 3.0 bar hydrogen is that different amounts of biomass were used. When 513 g daf biomass was
502 used the carbon content was 12.2 wt.%, while it was 16.0 wt.% when 972 g daf was used and 20.7 wt.%
503 when 899 g daf was used. As shown in supplementary material Figure S.3 the carbon content on the
504 catalysts, which had a bulk carbon content of 16.0 and 20.7 wt.% (measured at 15 kV), had a higher carbon
505 concentration at surface (between 20.8 and 25.6 wt.%). This indicates that carbon was building up on the
506 surface of the catalyst, which over time could lead to blocking of the pores. The carbon content on the
507 spent catalysts from the fluid bed reactor therefore indicates that at hydrogen pressures of 15.9 bar and
508 above there is sufficient hydrogen for the catalyst to stabilize the reactive molecules before they can
509 participate in polymerization reactions on the surface. These observations are therefore in alignment with
510 the knowledge from hydrotreating of fossil oil, where it is well-known that high hydrogen pressure
511 decreases the degree of coking due to stabilization of coke precursors [40].

512

513 **Figure 10** Carbon content on the spent catalysts from the fluid bed (FB) reactor, measured with SEM-EDS at 15 kV. Conditions:
 514 fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C, biomass feeding rate: 159-389 g/min, H₂S concentration: 47-
 515 475 ppm, H₂ flow: 11.4-124.4 NL/min, N₂ flow: 0.37-26.5 NL/min.

516 3.3.2 HDO reactor

517 The carbon content on the spent catalysts from the HDO reactor was also measured as shown in Figure 11.

518 The catalyst in the HDO reactor was not exchanged between experiments 1 to 4, and had prior to

519 experiment 1 also been used in another experiment at 24.5 bar hydrogen. Despite that this catalyst had

520 been used for several experiments (at high hydrogen partial pressure), the carbon content was only 1.29

521 wt.%, while it was 2.94 wt.% on the catalyst that was tested at 8.2 bar hydrogen, 4.43 wt.% on the catalyst

522 tested at 3.0 bar hydrogen (0.51 kg daf biomass used), and 5.59 wt.% on the catalyst that was tested at 3.0

523 bar hydrogen (0.90 kg daf biomass used). This shows that the degree of coking of the catalyst in the HDO

524 reactor increased with decreasing hydrogen partial pressure. The reason for this observation is most likely a

525 combination of the low hydrogen pressure, the higher oxygen content in the hydrocarbons produced in the

526 fluid bed reactor and the more reactive and multifunctional oxygenates, as discussed in the Section 3.2.

527 These experiments therefore indicate that in order to minimize coking of the HDO reactor the hydrogen

528 pressure should be above 8.2 bar, when the herein applied catalyst combination is used.

Figure 11 Carbon content on the spent catalyst from the HDO reactor. Conditions: fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C, biomass feeding rate: 159-389 g/min, H_2S concentration: 47-475 ppm, H_2 flow: 11.4-124.4 NL/min, N_2 flow: 0.37-26.5 NL/min.

4 Conclusion

Catalytic hydropyrolysis of beech wood was conducted in a fluid bed reactor followed by a fixed bed HDO reactor, at a total pressure between 5 and 36 bar and a hydrogen pressure between 3.0 and 35.8 bar. At hydrogen pressures below 15.9 bar the solid yield increased from 11.0 wt.% daf at 15.9 bar hydrogen to 15.7 wt.% daf at 3.0 bar hydrogen, showing that at low hydrogen pressures the pyrolysis vapors are not sufficiently stabilized, leading to polymerization. The organic phase produced at between 15.9 and 35.8 bar hydrogen pressure was essentially oxygen free (<0.01 wt.%), but the oxygen content increased with decreasing pressure and an oxygen content up to 7.8 wt.% db was measured at 3.0 bar hydrogen, where the oxygenates were mainly phenols. In addition conducting the experiments at 3.0 and 25.8 bar hydrogen pressure without the HDO reactor, showed that the oxygenates in the condensed liquid phases at 25.8 bar hydrogen mainly consisted of phenols, while the oxygenates from the experiment conducted at 3.0 bar consisted of phenols, dihydroxybenzenes, larger aromatics, and a high concentration of oxygenated aliphatics.

The carbon content on the spent catalysts from both the fluid bed and HDO reactor was measured. Varying the hydrogen partial pressure between 15.9 and 35.8 bar did not have an impact on the carbon content on

the spent catalyst from the fluid bed, however further decreasing the hydrogen pressure increased the carbon content, indicating an increased deactivation of the catalyst. Similarly, a higher carbon content was observed on the spent catalyst from the HDO reactor when operating at below 15.9 bar hydrogen pressure. The higher carbon on the catalysts from experiments at low hydrogen pressures (15.9 bar) is because the oxygenates produced at low hydrogen pressures are more reactive, thus increasing the rate of coking. The results show, that despite being easier to feed biomass at low pressure, it may lead to a more reactive product, which can decrease the catalyst life time and may limit further processing in a refinery.

5 Acknowledgments

This work is part of the project “Hydrogen assisted catalytic pyrolysis for green fuels” conducted at The Department of Chemical and Biochemical Engineering at the Technical University of Denmark (DTU). The work was supported by The Danish Council for Strategic Research (now Innovation Fund Denmark, project 1305-00015B), The Programme Commission on Sustainable Energy and Environment. Funding from DTU is also gratefully acknowledged. The authors acknowledge the Organic Analysis Department at Haldor Topsøe A/S for analysis of the organic phase and the Inorganic Analysis Department at Haldor Topsøe A/S for carbon on the spent catalysts.

6 References

- [1] T.L. Marker, L.G. Felix, M.B. Linck, M.J. Roberts, Integrated hydrolysis and hydroconversion (IH²) for the direct production of gasoline and diesel fuels or blending components from biomass, Part 1: Proof of principle testing, *Environ. Prog. Sustain. Energy*. 31 (2012) 191–199. doi:10.1002/ep.10629.
- [2] T.L. Marker, L.G. Felix, M.B. Linck, M.J. Roberts, P. Ortiz-Toral, J. Wangerow, Integrated hydrolysis and hydroconversion (IH²) for the direct production of gasoline and diesel fuels or blending components from biomass, Part 2: Continuous testing, *Environ. Prog. Sustain. Energy*. 33

570 (2014) 762–768. doi:10.1002/ep.11906.

571 [3] E. Maleche, R. Glaser, T. Marker, D. Shonnard, A preliminary life cycle assessment of biofuels
572 produced by the IH²™ process, *Environ. Prog. Sustain. Energy*. 33 (2014) 322–329.
573 doi:10.1002/ep.11773.

574 [4] J. Fan, J. Gephart, T. Marker, D. Stover, B. Updike, D.R. Shonnard, Carbon Footprint Analysis of
575 Gasoline and Diesel from Forest Residues and Corn Stover using Integrated Hydropyrolysis and
576 Hydroconversion, *ACS Sustain. Chem. Eng.* 4 (2016) 284–290. doi:10.1021/acssuschemeng.5b01173.

577 [5] T.M.H. Dabros, M.Z. Stummann, M. Høj, P.A. Jensen, J.-D. Grunwaldt, J. Gabrielsen, P.M. Mortensen,
578 A.D. Jensen, Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and
579 catalytic fast hydropyrolysis, *Prog. Energy Combust. Sci.* 68 (2018) 268–309.
580 doi:10.1016/j.pecs.2018.05.002.

581 [6] D.C. Dayton, J. Carpenter, J. Farmer, B. Turk, R. Gupta, Biomass hydropyrolysis in a pressurized
582 fluidized bed reactor, *Energy & Fuels*. 27 (2013) 3778–3785. doi:10.1021/ef400355t.

583 [7] K. Wang, D.C. Dayton, J.E. Peters, O.D. Mante, Reactive catalytic fast pyrolysis of biomass to produce
584 high-quality bio-crude, *Green Chem.* 19 (2017) 3243–3251. doi:10.1039/C7GC01088E.

585 [8] D.C. Dayton, J. Hlebak, J.R. Carpenter, K. Wang, O.D. Mante, J.E. Peters, Biomass hydropyrolysis in a
586 fluidized bed reactor, *Energy & Fuels*. 30 (2016) 4879–4887. doi:10.1021/acs.energyfuels.6b00373.

587 [9] S. Thangalazhy-Gopakumar, S. Adhikari, R.B. Gupta, M. Tu, S. Taylor, Production of hydrocarbon
588 fuels from biomass using catalytic pyrolysis under helium and hydrogen environments., *Bioresour.*
589 *Technol.* 102 (2011) 6742–9. doi:10.1016/j.biortech.2011.03.104.

590 [10] S. Thangalazhy-Gopakumar, S. Adhikari, R.B. Gupta, Catalytic pyrolysis of biomass over H⁺ZSM-5
591 under hydrogen pressure, *Energy & Fuels*. 26 (2012) 5300–5306. doi:10.1021/ef3008213.

- 592 [11] O. Jan, R. Marchand, L.C.A. Anjos, G.V.S. Seufitelli, E. Nikolla, F.L.P. Resende, Hydropyrolysis of lignin
593 using Pd/HZSM-5, *Energy & Fuels*. 29 (2015) 1793–1800. doi:10.1021/ef502779s.
- 594 [12] F. Melligan, M.H.B. Hayes, W. Kwapinski, J.J. Leahy, Hydro-pyrolysis of biomass and online catalytic
595 vapor upgrading with Ni-ZSM-5 and Ni-MCM-41, *Energy & Fuels*. 26 (2012) 6080–6090.
596 doi:10.1021/ef301244h.
- 597 [13] P. Choudhary, A. Malik, K.K. Pant, Mass-Scale Algal Biomass Production Using Algal Biofilm Reactor
598 and Conversion to Energy and Chemical Precursors by Hydropyrolysis, *ACS Sustain. Chem. Eng.* 5
599 (2017) 4234–4242. doi:10.1021/acssuschemeng.7b00233.
- 600 [14] R.. Pindoria, A. Megaritis, A.. Herod, R. Kandiyoti, A two-stage fixed-bed reactor for direct
601 hydrotreatment of volatiles from the hydropyrolysis of biomass: effect of catalyst temperature,
602 pressure and catalyst ageing time on product characteristics, *Fuel*. 77 (1998) 1715–1726.
603 doi:10.1016/S0016-2361(98)00079-9.
- 604 [15] F. Melligan, M.H.B. Hayes, W. Kwapinski, J.J. Leahy, A study of hydrogen pressure during
605 hydropyrolysis of *Miscanthus x giganteus* and online catalytic vapour upgrading with Ni on ZSM-5, *J.*
606 *Anal. Appl. Pyrolysis*. 103 (2013) 369–377. doi:10.1016/j.jaap.2013.01.005.
- 607 [16] V.K. Venkatakrishnan, J.C. Degenstein, A.D. Smeltz, W.N. Delgass, R. Agrawal, F.H. Ribeiro, High-
608 pressure fast-pyrolysis, fast-hydropyrolysis and catalytic hydrodeoxygenation of cellulose:
609 Production of liquid fuel from biomass, *Green Chem.* 16 (2014) 792–802. doi:10.1039/c3gc41558a.
- 610 [17] V.K. Venkatakrishnan, W.N. Delgass, F.H. Ribeiro, R. Agrawal, Oxygen removal from intact biomass
611 to produce liquid fuel range hydrocarbons via fast-hydropyrolysis and vapor-phase catalytic
612 hydrodeoxygenation, *Green Chem.* 17 (2015) 178–183. doi:10.1039/c4gc01746c.
- 613 [18] L. Zhang, K. Gong, J. Lai, P. Alvey, Chemical composition and stability of renewable hydrocarbon

- 614 products generated from a hydropyrolysis vapor upgrading process, *Green Chem.* 19 (2017) 3628–
 615 3641. doi:10.1039/c7gc01075c.
- 616 [19] J. Lai, L. Zhang, K. Gong, Nuclear magnetic resonance characterization of renewable products from a
 617 two-step ex-situ hydropyrolysis vapor upgrading process, *ChemistrySelect*. 3 (2018) 297–307.
 618 doi:10.1002/slct.201702431.
- 619 [20] M.Z. Stummann, M. Høj, C.B. Schandel, A.B. Hansen, P. Wiwel, J. Gabrielsen, P.A. Jensen, A.D.
 620 Jensen, Hydrogen assisted catalytic biomass pyrolysis. Effect of temperature and pressure, *Biomass*
 621 and Bioenergy. 115 (2018) 97–107. doi:10.1016/j.biombioe.2018.04.012.
- 622 [21] O.İ. Şenol, E.-M. Ryymin, T.-R. Viljava, A.O.I. Krause, Reactions of methyl heptanoate
 623 hydrodeoxygenation on sulphided catalysts, *J. Mol. Catal. A Chem.* 268 (2007) 1–8.
 624 doi:10.1016/j.molcata.2006.12.006.
- 625 [22] O.İ. Şenol, T.-R. Viljava, A.O.I. Krause, Hydrodeoxygenation of aliphatic esters on sulphided NiMo/ γ -
 626 Al_2O_3 and CoMo/ γ - Al_2O_3 catalyst: The effect of water, *Catal. Today*. 106 (2005) 186–189.
 627 doi:10.1016/j.cattod.2005.07.129.
- 628 [23] O.İ. Şenol, T.-R. Viljava, A.O.I. Krause, Effect of sulphiding agents on the hydrodeoxygenation of
 629 aliphatic esters on sulphided catalysts, *Appl. Catal. A Gen.* 326 (2007) 236–244.
 630 doi:10.1016/j.apcata.2007.04.022.
- 631 [24] E.-M. Ryymin, M.L. Honkela, T.-R. Viljava, A.O.I. Krause, Competitive reactions and mechanisms in
 632 the simultaneous HDO of phenol and methyl heptanoate over sulphided NiMo/ γ - Al_2O_3 , *Appl. Catal.*
 633 *A Gen.* 389 (2010) 114–121. doi:10.1016/j.apcata.2010.09.010.
- 634 [25] A. Gutierrez, E.-M. Turpeinen, T.-R. Viljava, O. Krause, Hydrodeoxygenation of model compounds on
 635 sulfided CoMo/ γ - Al_2O_3 and NiMo/ γ - Al_2O_3 catalysts; Role of sulfur-containing groups in reaction

636 networks, *Catal. Today*. 285 (2017) 125–134. doi:10.1016/j.cattod.2017.02.003.

637 [26] T.M.H. Dabros, A. Gaur, D.G. Pintos, P. Sprenger, M. Høj, T.W. Hansen, F. Studt, J. Gabrielsen, J.-D.
638 Grunwaldt, A.D. Jensen, Influence of H₂O and H₂S on the composition, activity, and stability of
639 sulfided Mo, CoMo, and NiMo supported on MgAl₂O₄ for hydrodeoxygenation of ethylene glycol,
640 *Appl. Catal. A Gen.* 551 (2018) 106–121. doi:10.1016/j.apcata.2017.12.008.

641 [27] V.N. Bui, D. Laurenti, P. Afanasiev, C. Geantet, Hydrodeoxygenation of guaiacol with CoMo catalysts.
642 Part I: Promoting effect of cobalt on HDO selectivity and activity, *Appl. Catal. B Environ.* 101 (2011)
643 239–245. doi:10.1016/j.apcatb.2010.10.025.

644 [28] A. Centeno, E. Laurent, B. Delmon, Influence of the support of CoMo sulfide catalysts and of the
645 addition of potassium and platinum on the catalytic performances for the hydrodeoxygenation of
646 carbonyl, carboxyl, and guaiacol-type molecules, *J. Catal.* 154 (1995) 288–298.
647 doi:10.1006/jcat.1995.1170.

648 [29] M. Badawi, J.-F. Paul, S. Cristol, E. Payen, Guaiacol derivatives and inhibiting species adsorption over
649 MoS₂ and CoMoS catalysts under HDO conditions: A DFT study, *Catal. Commun.* 12 (2011) 901–905.
650 doi:10.1016/j.catcom.2011.02.010.

651 [30] T.M.H. Dabros, H. Kramer, M. Høj, P. Sprenger, J.-D. Grunwaldt, J. Gabrielsen, A.D. Jensen, The
652 Influence of Active Phase Loading on the Hydrodeoxygenation (HDO) of Ethylene Glycol over
653 Promoted MoS₂/MgAl₂O₄ Catalysts, *Top. Catal.* (2019). doi:10.1007/s11244-019-01169-y.

654 [31] C. Bouvier, Y. Romero, F. Richard, S. Brunet, Effect of H₂S and CO on the transformation of 2-
655 ethylphenol as a model compound of bio-crude over sulfided Mo-based catalysts: propositions of
656 promoted active sites for deoxygenation pathways based on an experimental study, *Green Chem.* 13
657 (2011) 2441–2451. doi:10.1039/c1gc15181a.

- 658 [32] V.N. Bui, D. Laurenti, P. Delichère, C. Geantet, Hydrodeoxygenation of guaiacol. Part II: Support
659 effect for CoMoS catalysts on HDO activity and selectivity, *Appl. Catal. B Environ.* 101 (2011) 246–
660 255. doi:10.1016/j.apcatb.2010.10.031.
- 661 [33] V.O.O. Gonçalves, S. Brunet, F. Richard, Hydrodeoxygenation of cresols over Mo/Al₂O₃ and
662 CoMo/Al₂O₃ sulfided catalysts, *Catal. Letters.* 146 (2016) 1562–1573. doi:10.1007/s10562-016-1787-
663 5.
- 664 [34] E. Schachtl, J.S. Yoo, O.Y. Gutiérrez, F. Studt, J.A. Lercher, Impact of Ni promotion on the
665 hydrogenation pathways of phenanthrene on MoS₂/γ-Al₂O₃, *J. Catal.* 352 (2017) 171–181.
666 doi:10.1016/j.jcat.2017.05.003.
- 667 [35] M.Z. Stummann, A.B. Hansen, L.P. Hansen, B. Davidsen, S.B. Rasmussen, P. Wiwel, J. Gabrielsen, P.A.
668 Jensen, A.D. Jensen, M. Høj, Catalytic Hydropyrolysis of Biomass Using Molybdenum Sulfide Based
669 Catalyst. Effect of Promoters, *Energy & Fuels.* 33 (2019) 1302–1313.
670 doi:10.1021/acs.energyfuels.8b04191.
- 671 [36] M.Z. Stummann, M. Høj, B. Davidsen, A.B. Hansen, L.P. Hansen, P. Wiwel, C.B. Schandel, J.
672 Gabrielsen, P.A. Jensen, A.D. Jensen, Effect of the catalyst in fluid bed catalytic hydropyrolysis, *Catal.*
673 *Today.* (2019). doi:10.1016/j.cattod.2019.01.047.
- 674 [37] T.M.H. Dabros, A Step in Understanding and Optimizing Fuel Production from Solid Biomass PhD
675 Thesis, Technical University of Denmark, Dept. of Chemical and Biochemical Engineering, 2017.
- 676 [38] A. Stanislaus, A. Marafi, M.S. Rana, Recent advances in the science and technology of ultra low sulfur
677 diesel (ULSD) production, *Catal. Today.* 153 (2010) 1–68. doi:10.1016/j.cattod.2010.05.011.
- 678 [39] A. Corma, C. Martínez, G. Ketley, G. Blair, On the mechanism of sulfur removal during catalytic
679 cracking, *Appl. Catal. A Gen.* 208 (2001) 135–152. doi:10.1016/S0926-860X(00)00693-1.

680 [40] E. Furimsky, F.E. Massoth, Deactivation of hydroprocessing catalysts, Catal. Today. 52 (1999) 381–
681 495. doi:10.1016/S0920-5861(99)00096-6.

682