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1 Hydrogen assisted catalytic biomass 2 pyrolysis. Effect of temperature and 3 pressure

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11 Highlights

- 12 - Catalytic hydropyrolysis of beech wood was studied at 365-511 °C and 1.6-3.6 MPa.
- 13 - Up to 22 % mass yield of condensed organics and C₄₊ gasses has been obtained.
- 14 - Up to 53 % of the energy in biomass was recovered in the condensed organics and C₄₊.
- 15 - The organic liquid was essentially oxygen free.
- 16 - The organic liquid consisted of a volume fraction of 20-40 % naphtha and 60-80 % diesel.

17

18   **Abstract**

19   Beech wood has been converted into a mixture of oxygen-free naphtha and diesel boiling point range
20   hydrocarbons by using catalytic hydropyrolysis in a fluid bed reactor with a CoMoS/MgAl₂O₄ catalyst,
21   followed by deep hydrodeoxygenation (HDO) in a fixed bed reactor loaded with a NiMoS/Al₂O₃ catalyst. The
22   effect of varying the temperature (365-511 °C) and hydrogen pressure (1.6-3.6 MPa) on the product yield
23   and organic composition was studied. The mass balance closed by a mass fraction between 90 and 101 %
24   dry ash free basis (daf). The yield of the combined condensed organics and C₄₊ varied between a mass
25   fraction of 17 and 22 % daf, corresponding to an energy recovery of between 40 and 53 % in the organic
26   product. The yield of the non-condensable gases varied between a mass fraction of 24 and 32 % daf and the
27   char yield varied between 9.6 and 18 % daf. The condensed organics contained a mass fraction of 42 to 75
28   % aromatics, based on GC×GC-FID chromatographic peak area, and the remainder was primarily
29   naphthenes with minor amounts of paraffins. The condensed organics were essentially oxygen free (mass
30   fraction below 0.001 %) when both reactors were used. Bypassing the HDO reactor increased the oxygen
31   concentration in the condensed liquid to a mass fraction of 1.8 %. The results show that catalytic
32   hydropyrolysis may be a viable way to process solid biomass into liquid and gaseous fuels.

33   **Keywords**

34   Catalytic hydropyrolysis

35   Fluid bed

36   Oil characterization

37   Hydrodeoxygenation

38   Biofuel

39

40   **Abbreviations**

AED	Atomic emission detector
conc	Concentration
daf	Dry ash free basis
diAro	Diaromatics
DMDS	Dimethyl disulfide
FID	Flame ionization detector
GC	Gas chromatograph
HDO	Hydrodexoxygenation
HHV	Higher heating value
mAro	Monoaromatics
MS	Mass spectrometry
Naph	Naphthenes
O-Ali	Oxygenated aliphatics
Par	Paraffins
PhO-	Oxygenated aromatics
SIMDIS	Simulated distillation by GC
Temp.	Temperature
tetAro+	Tetraaromatics
triAro	Triaromatics

41

42

43   **1   Introduction**

44   Recent research has shown that catalytic hydropyrolysis is an efficient process for producing diesel and
45   gasoline hydrocarbons from biomass [1,2]. The reactive molecules formed by fast pyrolysis are immediately
46   hydrogenated, thus inhibiting polymerization and other undesired properties of conventional fast pyrolysis
47   bio-oil. In this process, the pyrolysis takes place at an elevated hydrogen pressure and in the presence of a
48   HDO catalyst. The basic concept of hydropyrolysis share similarities with the Bergius process (high
49   temperature and high hydrogen pressure) [3–5], however in the Bergius process coal and heavy oil is mixed
50   into a slurry, while hydropyrolysis is a gas phase process. Steinberg et al. [6] showed in 1985 that using fast
51   hydropyrolysis of wood at high temperatures (600-1000 °C) over 90 % of the carbon can be converted into
52   hydrocarbons, mainly methane and other gases. It has also been shown that catalytic hydropyrolysis of
53   lignin can give oil mass yields up to 80 % [7]. Despite that hydropyrolysis is not a new concept it has first in
54   the recent years become a popular method for producing liquid fuels from biomass. Using a pyroprobe
55   reactor, Melligan et al.[8] showed that conducting the pyrolysis of Miscanthus in an atmosphere of H₂
56   instead of He decreased the concentration of ethanoic acids in bio-oil. It has also been shown that zeolites
57   impregnated with reduced transition metals increase the hydrocarbon yield and decrease the molecular
58   size of the phenols [8–10]. Other groups have been pursuing the high pressure, non-catalytic hydropyrolysis
59   of biomass in an inverted cyclone or fluid bed reactors followed by downstream catalytic HDO of the
60   product vapors prior to oil and water condensation [11–13]. Marker et al.[1,2] have proposed a process
61   called Integrated Hydropyrolysis and Hydroconversion (IH²®). Their process consists of a fluid bed reactor,
62   where the catalytic hydropyrolysis takes place, and a fixed bed hydroconversion reactor, where the deep
63   HDO takes place. Different types of biomass were tested, and the yield of condensed organic liquid and C₄₊
64   hydrocarbons in the product gas phase varied between a mass fraction of 20.6 and 46.3 %. The IH²® process
65   has been able to run continuously for 750 h in a pilot plant with a biomass feeding rate of 50 kg per day.
66   The composition of the catalyst used in the IH²® process has not been reported. Carbon footprint analysis
67   of the IH²® process showed that producing liquid fuels from this process, when compared to conventional

68 production from fossil fuels, decreases the emission of greenhouse gases with 67-86 % [14]. Dayton et al.
69 [15–17] also conducted several studies on catalytic hydropyrolysis using loblolly pine with a setup that did
70 not include an additional HDO reactor after the fluid bed catalytic hydropyrolysis reactor. Using a
71 commercially available hydrotreating catalyst gave an initial low oil yield (mass fraction below 5 %), but the
72 oil yield increased over time to a mass fraction of 12.5 % as the catalyst deactivated [15]. Several
73 experiments at different temperatures and hydrogen pressures with a commercially available NiMo
74 hydrotreating catalyst have also been conducted with the same setup [16]. The catalyst was reduced in
75 hydrogen and not sulfided prior to the experiments. Liquid organic yields between a mass fraction of 12.6
76 and 25.6 % with an oxygen mass fraction between 2.4 and 11.9 % and a char yield between 7.4 and 26 %
77 were obtained depending on temperature, total pressure and hydrogen partial pressure. The carbon
78 recovery in the organic liquid and C₄₊ gases varied between 34.8 and 42.0 %, thus being significantly higher
79 than for zeolite based catalytic pyrolysis [16]. These results indicate that catalytic hydropyrolysis is a
80 potential technology for converting solid biomass to liquid transportation fuels. The knowledge base on this
81 type of process in the open literature is however still scarce. Often the catalyst composition is not reported
82 and the liquid oil produced is not characterized in depth. Furthermore the combination of catalytic
83 hydropyrolysis followed by HDO is not fully understood.

84 In this study, catalytic hydropyrolysis of beech wood has been performed in a fluid bed reactor with a
85 sulfided commercial CoMo/MgAl₂O₄ catalyst followed by a HDO reactor loaded with a sulfided commercial
86 NiMo/Al₂O₃ catalyst. The concept is thus similar to the IH²® process [1]. With this reactor combination it is
87 expected that the biomass can be converted into a mixture of naphtha and diesel. It is well-known that the
88 temperature is an important parameter in pyrolysis [18], thus the effect of the temperature is investigated
89 in the range relevant for catalytic hydropyrolysis (365 to 511 °C). There is also a lack of knowledge of the
90 effect of hydrogen pressure on catalytic hydropyrolysis of wood, and the effect of pressure is therefore
91 investigated in the range 1.6 to 3.6 MPa. Furthermore equilibrium calculations indicate that the liquid
92 product composition changes in the tested temperature and pressure range. This is to our knowledge the

first study in the open literature of hydropyrolysis of wood using a sulfided hydrotreating catalyst. In order to get a comprehensive understanding of the effect of the temperature and pressure the produced oil is extensively characterized.

2 Material and methods

2.1 Biomass feedstock

Bark free beech wood supplied by Dansk Træmel (Product number: 10000251250390) was used as biomass. The particle size was approximately 200-700 µm. The moisture mass fraction was 6.72 % (dried at 105 °C) and the ash mass fraction was 0.59 % dry basis. The composition and the higher heating value (HHV) of the beech wood are shown in Table 1.

Table 1. Composition of bark free beech wood

C	499	g kg ⁻¹ dry
H	60	g kg ⁻¹ dry
N	1.3	g kg ⁻¹ dry
O	430	g kg ⁻¹ dry
K	1.2	g kg ⁻¹ dry
Ca	1.3	g kg ⁻¹ dry
S	48	mg kg ⁻¹ dry
Na	9.9	mg kg ⁻¹ dry
Mg	350	mg kg ⁻¹ dry
Si	140	mg kg ⁻¹ dry
P	75	mg kg ⁻¹ dry
Cl	2.0	mg kg ⁻¹ dry
Mn	170	mg kg ⁻¹ dry
Fe	24	mg kg ⁻¹ dry
Cu	2.1	mg kg ⁻¹ dry
Zn	4.9	mg kg ⁻¹ dry
Sr	4.6	mg kg ⁻¹ dry
HHV*	19.7	MJ kg ⁻¹

*Calculated from Milne formula: $0.341 \times C + 1.322 \times H - 0.12 \times O - 0.12 \times N + 0.0686 \times S - 0.0153 \times \text{ash}$ [19]

2.2 Catalysts

The catalyst used in the fluid bed reactor was a CoMo/MgAl₂O₄ catalyst supplied by Haldor Topsøe A/S. The active CoMo phase was chosen because it is an efficient hydrodeoxygenation catalyst [20–27], and MgAl₂O₄

107 was chosen as support due to its mechanical strength and moderate acidity, anticipating it would lead to
108 less attrition and char formation in the fluidized bed. The catalyst was received as extrudates and was
109 crushed and sieved to obtain a particle size between 180-355 μm . This particle size distribution was chosen
110 to obtain a good fluidization of the bed. A fresh load of 50 g catalyst was used in each experiment. The fixed
111 bed reactor was loaded with 173 g NiMo/Al₂O₃ catalyst supplied by Haldor Topsøe A/S. The catalyst was
112 shaped as extrudates and was used as received. To ensure a high degree of deoxygenation in all
113 experiments the catalyst in the fixed bed reactor was replaced between experiment 5 and 6. The catalysts
114 in both reactors were sulfided prior to each experiment to obtain the most active phase.

115 **2.3 Experimental setup**

116 A bench scale setup was constructed and a simplified piping and instruction (PI) diagram is shown in Figure
117 1. The feeding system consists of a gas mixing system (H₂, H₂S, N₂), where the gas flows are controlled by
118 Brooks mass flow controllers (Model: SLA5850). A liquid feeding system supplying dimethyl disulfide
119 (DMDS; Sigma-Aldrich $\geq 99\%$) with a pump and evaporator (operating temperature: 200 °C) was used for
120 sulfidation of the catalysts. Because of the relatively high cost of bottled H₂S, DMDS was used during the
121 sulfidation. A pressurized vessel with a volume of 4 L was used for biomass feeding. A screw placed at the
122 bottom of the vessel was used to push the biomass to the feeding tube, where it was rapidly transported by
123 a flow of hydrogen to the reactor. The biomass was preheated before entering the fluid bed reactor by
124 heating the feeding tube to approximately 200 °C. To ensure a steady biomass feeding rate the biomass in
125 the vessel was continually stirred by an impeller.

126

127 **Figure 1. Simplified piping and instrumentation diagram of the used setup**

128 The reactor system consisted of a fluid bed hydrolysis reactor, a filter, and a fixed bed
 129 hydrodeoxygenation (HDO) reactor. The basic principle of the used setup is similar to the IH²® process [1].
 130 The fluid bed reactor was made of Incoloy 800 HT and the HDO reactor and filter were made of 316L
 131 stainless steel. The fluid bed consisted of an electrical gas preheater, a gas distribution tube, a reaction
 132 zone, and a disengagement zone. In order to ensure that the gas was well distributed a sintered metal plate
 133 (GKN Sinter Metals SIKA-IL 10 IS, 5 mm height) was placed between the gas distribution tube and the
 134 reaction zone. The reaction zone consisted of a 200 mm long tube with an inner diameter of 29.46 mm. The
 135 disengagement zone was a 200 mm long tube with an inner diameter of 49.25 mm. The products exited
 136 through a tube (inner diameter: 3.87 mm) located 3.6 cm from the start of the disengagement zone,
 137 however this distance was increased to 8.6 cm after experiment 1. The reactor is designed in such a way
 138 that the char will be entrained out of the disengagement zone while the catalyst primarily will stay in the

139 reaction zone. A multipoint thermocouple measured the temperature every 80 mm in the reaction zone.
140 The entrained solids (char and catalyst fines) were captured with a heated (350 °C) filter. The vapors and
141 gas were further upgraded in a fixed bed HDO reactor. This reactor consisted of a tube and a flange with a
142 total length of 642 mm and an inner diameter of 32.46 mm. The top part (200 mm) of the reactor was filled
143 with glass beads and the next 360 mm of the reactor was loaded with the NiMo/Al₂O₃ catalyst. In order to
144 keep the catalyst in position, 20 mm of quartz wool and a 60 mm holder were placed below the catalyst
145 bed. A multipoint thermocouple (4 points) measured the temperature through the catalyst bed. In order to
146 avoid condensation of the vapors the tubing between the fluid bed, filter, and HDO reactor were heat
147 traced to approximately 350 °C.

148 The liquid product was collected in a cooling section with 3 stage cooling (20 °C, 2 °C, and -40 °C). The
149 pressure was controlled with a backpressure regulator, and the remaining gas was sent to a flare. A small
150 fraction of the gas was pumped through a filter to an online gas chromatograph (GC) with a flame
151 ionization detector (FID) and two thermal conductivity detectors (TCD), which measured the gas
152 composition (H₂, H₂S, N₂, CO, CO₂, C₁ to C₅, and C₆₊ hydrocarbons) every 10 minutes. The total mass of the
153 collected liquid products was determined. The amount of aqueous phase was determined by measuring the
154 volume in a 500 cm³ graduated cylinder and assuming the density was 996.5 kg m⁻³, corresponding to the
155 density of water at 25 °C and atmospheric pressure. GC-MS of the aqueous phase showed that it was
156 essentially pure water. The amount of organic phase was then determined by subtracting the mass of the
157 aqueous phase from the mass of the condensed liquids. The aqueous phase was separated from the
158 organic phase using a separation funnel. The H₂S dissolved in the organic phase was removed by bubbling
159 with N₂ for approximately one hour, which lead to a mass loss between 2 and 7 %, mostly due to
160 vaporization of light hydrocarbons.

161 After each experiment, the catalyst and remaining char was removed from the fluid bed, and replaced by a
162 fresh batch of catalyst to be used in the subsequent experiment. The catalyst was initially sulfided at 2.6

163 MPa, 350 °C with 2-7.5 mole % H₂S, 5 mole % N₂ in 87.5-93 mole % H₂ by feeding DMDS (flow: 0.710-2.770
164 cm³ min⁻¹) to the system. After sulfidation, the system was depressurized and the unconverted DMDS was
165 collected. Then the reaction conditions listed in Table 2 were established. When the temperature in the
166 reactors reached steady state, the experiment was started by turning on the screw feeder. The total gas
167 inlet flow at the reaction temperature and pressure corresponded to approximately three times the
168 minimum fluidization velocity for the used catalyst particles.

169 **2.4 Analysis methods**

170 **2.4.1 Liquid products**

171 Several different methods were used to analyze the condensed organic phase. The hydrogen content was
172 measured with H-NMR on a Bruker minispec mq20. The samples were preheated to 50 °C for 25 minutes
173 and then moved to the measuring cell, also heated to 50 °C. The procedure followed the ASTM method
174 D7171. The sulfur content was measured by energy dispersive X-ray fluorescence using an X-Supreme8000
175 instrument from Oxford Instruments, according to ASTM D4294. The simulated distillation (SIMDIS) curves
176 were measured on two different GC's: Agilent 7890 A and Agilent 6890N. The ASTM D86 distillation curve
177 was then calculated according to ASTM D 7213 C.

178 The condensed organic liquid samples were characterized by GC×GC-ToF/MS or -FID using a LECO® Pegasus
179 4D™ instrument. The instrument included an Agilent 7890A GC equipped with a Gerstel® CIS 4 PTV inlet, a
180 secondary oven, a quad-jet, dual-stage cryogenic-based (liquid N₂) modulator, a time-of-flight (ToF) mass
181 spectrometer (MS) and a flame ionization detector (FID). The primary (1D) and secondary (2D) columns
182 were Restek® Rxi-5Sil MS and Restek® Rxi-17Sil MS, respectively.

183 0.3 mm³ sample was injected in pulsed split mode (split ratio 1:50) into the PVT inlet at 40°C, and then
184 raised to 300°C (10K s⁻¹), with a total hold up time of 1.5 min. The main oven with the 1D column was held
185 at 40°C for 1.5 min and then ramped to 290°C at 2.5 K min⁻¹; the secondary oven and modulator were run

186 with offsets to the main oven of +5°C and +20°C, respectively; total run time was 101.5 min. Helium (He)
187 was used as carrier gas at constant flow rate of 1.5 cm³ min⁻¹, and the modulation period was 9 sec. For
188 selected samples, compounds in the condensed organic phase were identified using the ToF/MS detector.
189 The transfer line and ion source were operated at constant temperatures of 250°C and 225°C, respectively.
190 The ToF/MS was run in EI mode at 70 eV and an acquisition rate of 100 spectra sec⁻¹ for m z⁻¹ = 41 to 441.
191 The NIST2008 mass spectral database was used as reference. For group quantification, the FID was used.
192 The detector was operated at 300°C and with a sampling rate of 100 Hz. Based on the GC×GC-ToF/MS
193 analysis the compounds were classified into six groups: paraffins, naphthenes, mono-, di- and tri- and
194 higher aromatics, phenolics, and in some samples oxygenated aliphatics. The relative amount (FID area-%)
195 of each compound class was estimated as the sum of areas of all detected peaks in that class divided by the
196 total peak area of all compound classes. All data was processed using the ChromaTof® 4.50 software.

197 Selective analysis of oxygenates was conducted using a GC with an atomic emission detector (AED). An
198 Agilent 7890A GC was coupled to a JAS 2370 AED in oxygen selective mode. The oxygen emission line at
199 171nm was used in combination with reaction gases of 10% methane in nitrogen and pure hydrogen and
200 with a makeup helium gas flow of 80 ml min⁻¹. Cavity and transfer line were heated to 320°C. The GC
201 column was a Phenomenex ZB-50 (60m X 0.25mm X 0.25µm) in connection with a JAS PTV inlet in split
202 mode (1:5) and 0.5 mm³ injection. The oven was held at 40°C for 1 min and then ramped to 340°C @ 7 K
203 min⁻¹.

204 Quantification was done by adding known amounts of 4-fluorophenol (CAS number: 371-41-5) to known
205 amounts of the sample. The signal for the internal standard was used for calibration of the other
206 oxygenates in the sample. To increase the sensitivity of the method and to remove potential interferences
207 from the sample matrix the polar compounds were extracted from the sample by use of Solid Phase
208 Extraction on silica based cartridges. The weighted sample including the internal standard was transferred
209 to the Si-SPE cartridge with n-heptane and the non-polar fraction eluted from the cartridge with 10

absorbent volumes of n-heptane. The polar compounds were subsequently eluted with 3 absorbent volumes of acetone. The acetone fraction containing the polar compounds were reduced over nitrogen to about 300 mm³ and injected in the GC for oxygen selective detection. Identification of individual compounds was done after analysis of pure compounds.

Selective analysis of sulfur containing compounds was also conducted using GC-AED using the sulfur emission line at 181nm. The GC column was a Phenomenex ZB-1 (30m X 0.25mm X 1.0μm) in connection with a JAS split/splitless inlet in split mode (1:10) and 0.5 mm³ injection. The oven was held at 40°C for 5 min and then ramped to 340°C @ 10 K min⁻¹ and a final time of 10 min.

Quantification was done using an external standard sample containing known amounts of benzothiophene, dibenzothiophene and 4-methyl-dibenzothiophene. Identification of individual compounds was done after analysis of pure compounds. The samples were diluted if necessary in a suitable solvent prior to GC analysis.

The aqueous phase was analyzed on a Shimadzu GC-MS/FID with a Supelco Equity-5 column. The compounds were identified on the MS and quantified using the parallel FID. The concentration of phenol was determined by use of external standards. The concentration of the remaining hydrocarbons was determined from the FID signal using the effective carbon number method [28].

2.4.2 Solid sample analysis

The elemental composition (CHNS) of the biomass was analyzed on a Eurovector EA-3000 elemental analyzer and the oxygen content was determined by difference. The elemental composition (CHNSO) of the produced char was analyzed at DB Lab A/S using a Flash 2000 elemental analyzer from Thermo Fisher. The relative uncertainty for the C, H, N, O, and S on the char was 1.0, 2.0, 2.0, 3.0, 2.0 %, respectively. In order to obtain a more homogeneous sample the char was crushed prior to this analysis. Other elements were determined by wavelength dispersive X-ray fluorescence using a Supermini 200 XRF instrument from Rigaku. Samples were ashed and the ash fused to a bead with lithium metaborate (BO₂Li) prior to analysis.

234 The ash and catalyst content in the produced char was measured by combusting the samples at 600 °C in
235 air. The ash content in char was calculated by assuming that all the ash in the biomass ends in the char and
236 the catalyst content was calculated by difference.

237 **3 Results and Discussion**

238 **3.1 Effect of temperature and pressure on the product distribution**

239 The effect of operating conditions on catalytic hydrolysis of beech wood was studied by varying the
240 total pressure and the temperature in the fluid bed and the HDO reactor as shown in Table 2. The
241 temperature in the fluid bed was between 365 and 511 °C and the temperature in the HDO reactor was
242 between 345 and 400 °C. The total pressure was varied between 1.6 and 3.6 MPa. In experiments 1 to 8 the
243 H₂S concentration was 460×10^{-6} mole fraction, while it was approximately 50×10^{-6} mole fraction in
244 experiments 9 to 11. Due to the short experimental time (1.2-4 hours) the catalysts have most likely
245 remained sulfided during the experiments with low H₂S concentration. The obtained mass balances varied
246 between 90 and 101 % daf on the basis of the used biomass. In experiment 6 the entrance to the fluid bed
247 plugged, thus stopping the experiment after only 1.2 hours, which is the reason for the poor mass balance
248 of 90 daf. The short operation time of experiment 6 is part of the reason for the low obtained yields, with
249 exception of the char yield. The organic yield (mass fraction daf basis) including condensed organics and C₄₊
250 gases varied between 16.6 to 22.5 % daf, the C₁-C₃ gas yield varied between 10.6 to 15.5 %, the CO+CO₂
251 yield varied between 13.2 to 17.5 %, the char yield varied between 9.56 to 18.5 %, and the aqueous yield
252 varied between 31.2 to 37.8 %. The carbon recovery for the condensed organics and C₄₊ gases varied
253 between 28.0 and 38.4 %, and for the C₁-C₃ gases the carbon recovery was 19.0-24.3 %. An overview of
254 hydrogen and oxygen recovery compared to the biomass input is shown in Table S.1. The yields of
255 condensed organics and C₄₊ are lower than what has been reported for the IH²® process, where the yield
256 was between a mass fraction of 26 and 30 % daf, when using wood [1,2]. The reason for this difference may

257 be due to a different biomass or the use of a different catalyst. The repeatability was tested in experiment
258 4 and 5, where the process conditions were similar. The product distribution in experiment 5 was quite
259 similar to experiment 4 with yields deviating less than a mass fraction of 1 % points, indicating that
260 experiments were reproducible. Depending on the applied test conditions between 2.6 and 33 % of the
261 catalyst loaded in the fluid bed was transported to the filter during the experiments. The biomass feeding
262 rate was difficult to control and varied between 161 and 300 g h⁻¹. However, due to the large excess of
263 hydrogen it is expected that the feeding rate and weight hourly space velocity (g biomass (g catalyst hr)⁻¹)
264 did not have an impact on the results, and this is also supported by the experimental results.

265

Table 2. Summary of reaction conditions and mass balances for catalytic hydropyrolysis of beech wood

Test:	1	2	3	4	5	6	7	8	9	10	11
Test conditions											
Hydropyrolysis T. (°C)	430	400	400	470	468	365	451	511	453	449	450
HDO T. (°C)	370	345	400	390	394	395	371	363	370	364	-
Pressure (MPa)	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	1.6	3.6	2.6
Feed time (h)	3.5	2.6	4.0	4	3.6	1.2	4.0	3.0	4.0	4.0	3.9
Feeding rate (g h ⁻¹)	282	194	212	233	300	239	250	171	161	159	174
H ₂ S (mole frac. × 10 ⁶)	460	460	460	460	460	460	460	460	47	50	48
H ₂ flow (mole min ⁻¹)	3.35	3.27	3.27	3.35	3.35	3.35	3.35	3.35	2.14	5.08	3.57
N ₂ flow (mole min ⁻¹)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.02	0.03	0.03
H ₂ consumed (g)	44	42	39	47	47	33	46	45	35	46	35
Biomass used (kg)											
Yields (mass fraction % daf)											
Gas	30.0	25.8	28.8	32.3	31.3	23.9	31.5	32.2	30.3	26.3	27.4
Char	14.2	14.6	15.0	11.4	11.9	18.5	11.4	9.56	11.0	12.7	12.2
Aqueous phase	35.7	37.8	35.9	36.1	36.0	31.2	35.2	35.6	33.2	37.7	37.0
Organics	11.6	8.8	9.9	11.4	12.7	7.9	12.4	11.1	11.0	10.6	12.0
C ₄₊ in the gas	8.6	10.1	11.5	10.3	8.7	8.8	9.1	11.3	8.7	10.3	8.4
Organics + C ₄₊	20.2	18.9	21.4	21.7	21.4	16.7	21.5	22.4	19.7	20.9	20.4
Mass balance	100.1	97.1	101.1	101.5	100.6	90.3	99.6	99.8	94.2	97.6	97.0
Carbon recovery (%)											
C ₁ -C ₃	21.5	19.7	23.1	22.9	21.6	19.4	22.5	24.3	18.9	20.7	19.0
C ₄₊	14.2	16.8	18.9	16.9	14.5	14.4	15.1	18.8	14.4	17.1	13.9
CO+CO ₂	11.4	9.3	10.1	12.7	12.5	8.2	12.1	12.7	13.3	10.3	12.6
Char	20.9	21.0	22.0	17.3	18.2	26.4	17.2	15.5	15.5	18.9	18.4
Organics	19.9	15.1	17.2	20.3	22.6	13.6	21.4	19.6	19.4	18.6	20.9
Aqueous phase	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6
Sum	87.9	82.0	91.3	90.1	89.5	82.0	88.4	90.9	81.4	85.5	85.4
Organic composition (mass fraction %)											
C*	87.5	87.7	88.3	88.8	88.2	88.2	88.0	88.32	88.4	88.1	89.5
H	12.5	12.3	11.7	11.2	11.7	11.8	11.9	10.89	11.2	11.6	10.2
O	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	1.8
S	0.0699	0.34	ND	0.113	0.0909	ND	0.117	0.794	0.417	0.246	0.302
Aqueous phase composition (mass fraction %)											
Organics	0	0	0	0	0	0	0	0	0	0	1.15
Gas composition (mass fraction % daf)											
CO	8.01	6.76	8.31	10.4	9.64	6.48	9.74	11.7	10.8	9.92	11.1
CO ₂	8.27	6.51	5.60	6.90	7.88	4.83	7.96	5.05	7.55	3.26	5.71
C ₁ -C ₃	13.7	12.5	14.8	14.7	13.8	12.4	12.9	15.5	12.0	13.2	12.1
C ₄₊	8.58	10.1	11.5	10.3	8.74	8.78	8.83	11.3	8.67	10.3	8.35
Char composition (mass fraction %)											
C	71	69	73	72	68	67	72	76	67	70	72
H	3.7	3.8	3.9	3.4	3.4	4.0	3.7	3.4	3.5	3.5	3.4
N	0.54	0.54	0.56	0.45	0.37	0.45	0.41	0.39	0.40	0.40	0.41
S	0.50	0.55	0.48	0.66	0.63	0.49	0.53	0.77	1.13	0.62	0.61
O	20	21	21	18	16	22	18	13	23	19	19
Ash	4.0	5.0	4.4	5.6	5.3	6.5	5.0	6.5	4.6	5.5	4.8

*By difference

267 The temperature in the two reactors was varied simultaneously in experiments 1 to 8. The results from
268 experiment 2 and 3 show that increasing the temperature in the HDO reactor increased the yield of C₁-C₃
269 slightly, but in general only had a minor effect on the product distribution. Varying the temperature in the
270 fluid bed reactor changed the product distribution as shown in Figure 2. Increasing the temperature in the

271 fluid bed reactor mainly decreased the char yield, while increasing the gas yield, in agreement with the
272 general observations in the pyrolysis literature [29–32] and with the results obtained with IH²® process [1].
273 The organic yield including condensed organics and C₄₊ gases increased when the fluid bed temperature
274 increased from 365 to 400 °C above which it remained constant within the experimental uncertainty. The
275 aqueous mass yield increased from 31 to 36 % daf when the fluid bed temperature increased from 365 to
276 400 °C, while further increasing the fluid bed temperature had a negligible impact on the aqueous yield.
277 Hydrocarbons were not observed in the aqueous phase for experiments 1 to 10 where the HDO reactor was
278 used. Interestingly, Dayton et al.[16] using a reduced NiMo catalyst observed an increase in char yield from
279 10.8 to 26.0 and a decreased yield of condensed organics from 25.6 to 16.8 when the temperature
280 increased from 375 to 475°C. Their results indicate accelerated cracking over the applied catalyst at
281 elevated temperatures, which was not observed in our study.

282

283 Figure 2. Effect of temperature on the yield of condensed organic liquid and C₄₊ gases (A), yield of light gases (B), char yield (C),
 284 and aqueous yield (D). Conditions: pressure: 2.6 MPa, H₂ flow: 3.27-3.35 mole min⁻¹, N₂ flow: 0.20 mole min⁻¹, biomass feeding
 285 rate: 212-300 g h⁻¹, H₂S concentration: 460 × 10⁻⁶ mole fraction.

286 A small decrease in the yield of condensed organic liquid and C₄₊ gases and an increase in the aqueous yield
 287 was observed when the HDO reactor was bypassed as seen by comparison of experiments 7 and 11 in Table
 288 2. GC-FID/MS of the aqueous phase from experiment 11 showed that it contained small amounts of
 289 oxygenated aliphatics and phenols, with a total organic mass fraction of 1.15 % corresponding to an organic
 290 yield of a mass fraction of 0.51 % daf. The dissolved oxygenates in the aqueous phase can partly explain the
 291 observed decrease in yield of condensed organics and C₄₊ when comparing experiment 11 with experiment
 292 7. The total CO and CO₂ yield did not decrease when the HDO reactor was bypassed, but a decrease in the
 293 C₁-C₃ yield was observed. This indicates that the remaining oxygen is mainly removed by hydrogenation in
 294 the HDO reactor, but hydrocracking also takes place in the HDO reactor. However, the CO₂ mass yield

295 decreased from 7.96 % daf in the experiment with the HDO reactor (experiment 7) to 5.71 % daf when the
296 HDO reactor was bypassed (experiment 11), while the CO yield increased from 9.71 to 11.1 % daf.
297 Considering that the aqueous phase yield also increased when the HDO reactor was bypassed, this
298 indicates that the water gas shift reaction takes place in the HDO reactor. In the experiments where the
299 HDO reactor was used no olefins were detected in the gaseous products. However, when the HDO reactor
300 was bypassed, olefins accounted for 26 % of the C₂-C₅ hydrocarbons in the gas phase. The hydrogen to
301 biomass consumption also decreased from 46 g kg⁻¹ to 35 g kg⁻¹ when the HDO reactor was bypassed.

302 The influence of pressure on the product distribution is shown in Figure 3, by comparison of experiment 7,
303 9, and 10 in Table 2. Increasing the total pressure did not affect the liquid organic yield, but it increased the
304 aqueous yield, while decreasing the CO and CO₂ yield. This was most likely due to the increase in hydrogen
305 partial pressure, which makes oxygen removal by hydrodeoxygenation more favorable compared to
306 cracking. The hydrogen to biomass consumption also increased from 35 g kg⁻¹ at 1.6 MPa to 46 g kg⁻¹ at 3.6
307 MPa, but did not increase further when the pressure increased to 3.6 MPa. The char yield also increased
308 slightly with increasing pressure; however this is within the experimental uncertainty. Dayton et al.[16]
309 observed an increase in the hydrogen to biomass consumption from between 20 to 25 g kg⁻¹ at a H₂ volume
310 fraction of 20 %, to between 35 to 38 g kg⁻¹ at 40 % at 2.168 MPa. However, they did not observe a related
311 increase in the aqueous yield, thus indicating that hydrogenation of the olefins increased with increasing
312 hydrogen partial pressure [16].

Figure 3. Effect of pressure on the organic liquid and C₄₊ gases yield (A), gas yield (B), char yield (C), and aqueous liquid yield (D). Conditions: Fluid bed temperature: 453-449 °C, HDO temperature: 364-371 °C, H₂ flow: 2.14-5.08 mole min⁻¹, N₂ flow: 0.02-0.03 mole min⁻¹, biomass feeding rate: 159-250 g h⁻¹, H₂S concentration: 47-460 × 10⁻⁶ mole fraction.

3.2 Chemical composition of the condensed organics

In the experiments where the HDO reactor was used the hydrogen mass fraction of the condensed organics was between 10.9 % and 12.5 %. When the HDO reactor was bypassed the hydrogen mass fraction decreased to 10.2 %, indicating that olefins and aromatics are saturated in the HDO reactor. The simulated distillation curves for the condensed organics are shown in Figure 4. As can be seen, a volume fraction of 20 to 40 % was naphtha, while the rest were in the diesel boiling point range. However, the uncondensed C₄₊ organics, that were detected in the gas phase, are most likely mainly naphtha, making a total naphtha mass fraction of 50-70 % of the condensed organics and C₄₊ in the gas. Comparing the simulated distillation

324 curves for experiment 7 and 11 shows that the boiling point for the condensed organics increased when the
 325 HDO reactor was bypassed (see supplementary material Figure S.1), this was due to the increased oxygen
 326 concentration in the product. For the condensed organics from experiment 8, a volume fraction of 99.5 %
 327 of the organics had a boiling point below 308 °C, thus indicating that increasing the fluid bed temperature
 328 to 511 °C decreased the boiling point, possibly due to increased cracking of the vapors. Varying the
 329 pressure only had a small effect on the distillation curves (experiment: 7,9 and 10) that was within the
 330 experimental uncertainty.

331

332 **Figure 4. GC simulated distillation curves for the condensed organics. The curves are calculated using D86 according to ASTM D**
 333 **7213 C.**

334 GC×GC-FID and GC-AED was used to gain a deeper insight into composition of the condensed organics. GC-
 335 AED was used to selectively identify the sulfur and oxygen containing compound classes in the condensed
 336 organics. GC×GC-FID was used to measure the concentration of the different types of hydrocarbons and an
 337 example of a chromatogram is shown in Figure 5.

Figure 5. GCxGC-FID contour plot of the condensed organics from experiment 4. Conditions: Fluid bed

temperature: 470 °C, HDO temperature: 390 °C, pressure: 2.6 MPa, H₂ flow: 3.35 mole min⁻¹, N₂ flow: 0.20 mole min⁻¹, biomass feeding rate: 233 g h⁻¹, H₂S concentration: 4.6×10^{-6} mole fraction.

The concentration of paraffins was between 2.5 and 5.1 % peak area. The concentration of aromatics and naphthenes are shown as a function of the fluid bed temperature and the total pressure in Figure 6. Between 35 % (experiment 1) and 60 % area-FID (experiment 4) of the aromatics were monoaromatics, but considerable amounts of diaromatics were also present (up to 13 %), while only low concentrations (below 4.5 %) of tri- and larger aromatics were observed. The concentration of aromatics decreased when the temperature in the fluid bed was increased from 365 to 430 °C, but increased when the temperature was further increased. Equilibrium calculations for monoaromatics show that they are favored over the corresponding naphthenes when the temperature is above 405 °C (see supplementary material Figure S.2 and Figure S.3). This indicates that the hydrogenation of aromatics to naphthenes was kinetically controlled below 430 °C and equilibrium controlled at higher temperatures. The HDO reactor has only a minor influence on the aromatic concentration. In experiments 2 and 3 the fluid bed temperature was 400 °C, and the temperature in the HDO reactor was 345 and 400 °C respectively, but the concentration of aromatics did not change. As shown in Figure 6B, increasing the total pressure at 450 °C in the fluid bed decreased the aromatic concentration and increased the naphthenes concentration, which is most likely due to the

increased hydrogen pressure shifting the equilibrium towards the saturated products and increasing the rate of hydrogenation (see supplementary material Figure S.4).

Figure 6. The effect of temperature at 2.6 MPa (A) and pressure at 450 °C (B) on the aromatic (including phenols) and naphthene content in the condensed organic liquid. Conditions: H₂ flow: 2.14-5.08 mole min⁻¹, N₂ flow: 0.02-0.20 mole min⁻¹, biomass feeding rate: 159-300 g h⁻¹, H₂S concentration: 47-460 × 10⁻⁶ mole fraction.

The result of the GC×GC-FID/MS analysis of the condensed organics in experiment 7 and 11 is shown in Figure 7. The reaction conditions in these two experiments were the same except that the HDO reactor was bypassed in experiment 11. When the HDO reactor was bypassed (experiment 11) the relative area of hydrocarbons with less than 10 carbon atoms was 41 % and hydrocarbons between 10 and 15 carbon atoms was 43 %. When the HDO reactor was used (experiment 7) the relative area for hydrocarbons with less than 10 carbon atoms increased to 53 %, while it decreased to 33 % for hydrocarbons with between 10 and 15 carbon atoms. This decrease in carbon number mainly decreased the concentration of diaromatics. For both experiment 7 and 11 alkyl benzenes with between 15 and 20 carbon atoms were detected. In the experiment without the HDO reactor, oxygenated aliphatics and phenols were detected in the product, but they were hydrodeoxygenated in the experiment with the HDO reactor. Oxygen specific GC-AED showed that when the HDO reactor was bypassed the total oxygen mass fraction in the condensed organics was 1.8 % and that the main oxygenates were different phenols (see supplementary material Figure S.5.). When the

373 HDO reactor was used the oxygen mass fraction was below 0.001 % and only traces of phenols, naphthol,
 374 and dibenzofurans were detected in the condensed organics.

375 **Figure 7. The composition of the condensed organic phase from experiment 7 (with HDO reactor) (A) and experiment 11**
 376 **(without HDO reactor) (B). Conditions: H₂ flow: 3.35-3.57 mole min⁻¹, N₂ flow: 0.20-0.02 mole min⁻¹, biomass feeding rate: 174-**
 377 **250 g h⁻¹, H₂S concentration: 48-460 × 10⁻⁶ mole fraction. The components in the condensed organics is divided into paraffins**
 378 **(Par), naphthenes (Naph), monoaromatics (mAro), diaromatics (diAro), triaromatics (triAro), tetraaromatics and larger aromatics**
 379 **(tetAro+), oxygenated aliphatics (O-Ali) and oxygenated aromatics (PhO-). The components are also divided into the following**
 380 **groups based on the number of carbon atoms in the components: less than 10 carbons atoms (-C10) between 10 and 15 carbons**
 381 **atoms (C10-C15), between 15 and 20 carbon atoms (C15-C20), more than 20 carbon atoms (C20+).**

382 The sulfur mass fraction in the condensed organics phase varied between 0.06 and 0.8 %, which is very high
 383 for oil produced from biomass. Therefore, the condensed organics from experiment 7 was analyzed with
 384 sulfur specific GC-AED. This showed that a large part of the sulfur was H₂S, which was not properly stripped
 385 from the condensed organic phase. DMDS was also detected, thus indicating that part of the DMDS used in
 386 the sulfidation of the catalyst ended up in the condensed organics. Trimethylthiophen (S mass fraction:
 387 0.036 %), benzothiophen (S mass fraction: 0.003 %), and a S mass fraction of 0.45 % from larger unknown
 388 sulfur containing components were also detected. It is possible that part of the sulfur from the H₂S added
 389 to the gas phase is incorporated into the organics. The detected sulfur compounds are commonly
 390 encountered in petrochemical refining and can be removed by further hydrotreating – either in the online

391 HDO reactor by increasing the residence time, or in a separate reactor. This would slightly increase the
 392 hydrogen consumption.

393 3.3 Chemical composition of the char

394 The carbon mass fraction in the produced char varied between 71 and 81 % and increased with increasing
 395 temperature in the fluid bed reactor as shown in Figure 8. The oxygen mass fraction varied between 14 and
 396 24 % and decreased with increasing temperature in the fluid bed reactor. The carbon mass fraction
 397 increased and the oxygen mass fraction decreased when the pressure increased from 1.6 to 2.6 MPa, but
 398 further increasing the pressure to 3.6 MPa did not have a substantial impact on the carbon and oxygen
 399 concentration. The hydrogen mass fraction decreased from 4.3 % at 365 °C to 3.7 at 511 °C. The sulfur mass
 400 fraction varied between 0.39 and 1.13 % and the nitrogen mass fraction varied between 0.39 and 0.56 %.

401 Comparing the char composition in Figure 8 with the biomass composition in Table 1 shows an enrichment
 402 of carbon and nitrogen in the char, which is an well-known phenomenon for pyrolysis [33]. The significant
 403 sulfur enrichment in the char, indicates that part of the sulfur in the char comes from H₂S that is
 404 incorporated into the char. The retention of nitrogen, carbon, oxygen and hydrogen in the char decreased
 405 when the fluid bed temperature increased (see supplementary material Figure S.6). The variations in the
 406 carbon content with pressure is within the experimental uncertainty.

407 Figure 8. The effect of temperature at 2.6 MPa (A) and pressure at 450 °C (B) on the CHNSO composition of the char in the filter.
408 Conditions: H₂ flow: 2.14-5.08 mole min⁻¹, N₂ flow: 0.02-0.2 mole min⁻¹, biomass feeding rate: 159-300 g h⁻¹, H₂S concentration:
409 47-460 × 10⁻⁶ mole fraction.

410 **3.4 Energy recovery**

411 The energy recovery was calculated on the basis of the higher heating value (HHV) of the biomass fed to
412 the setup and the HHV of the different phases. The heating value of the char was calculated from the Milne
413 formula (see section 2.1), the heating value for the gas was calculated on the basis of the heating value of
414 the different compounds detected in the gas, and the heating value of the condensed organics was
415 calculated from their elemental (CHNSO) composition according to ref. [34]. The resulting energy
416 recoveries for each product are shown in Figure 9. The energy recovery for the condensed organics and C₄₊
417 was between 40 and 53 %, the energy recovery for the gas was between 36 and 45 %, and the energy
418 recovery for the char was between 14 and 19 %. The total energy recovery for all of the experiments was
419 more than 100 %, which is due to incorporation of hydrogen that increases the heating value of the
420 products. The energy added to the products by hydrogen corresponded to between 0.26 and 0.34 MJ MJ⁻¹
421 biomass used. The exothermic hydrogenation reactions decrease the energy recovery in the products
422 compared to the energy in the consumed biomass and hydrogen. The energy recovery for the condensed
423 organics and C₄₊ was directly proportional to the yield indicating that the oil quality was rather constant. At
424 1.6 MPa the energy recovery was 46 %, while it was 51 and 50 % at 2.6 and 3.6 MPa, respectively. This is
425 because the condensed organics and C₄₊ yield and hydrogen content were slightly lower at 1.6 MPa
426 compared to 2.6 and 3.6 MPa. Thus the differences in the energy recovery at the different pressures are
427 not statistically significant.

Figure 9. The effect of the process conditions on the energy recovery. Conditions: H₂ flow: 2.14-5.08 mole min⁻¹, N₂ flow: 0.02-0.2 mole min⁻¹, biomass feeding rate: 159-250 g h⁻¹, H₂S concentration: 47-460 × 10⁻⁶ mole fraction.

Trinh et al. [35] achieved a bio-oil mass yield from fast pyrolysis of wood of 68 % daf, corresponding to an energy recovery of 74 %, which is significantly higher than the energy recovery achieved in this study. However, the bio-oil had an oxygen mass fraction of 35.3 % dry basis. Baldauf et al. [36] tested the ability of a commercial CoMoS catalyst to upgrade pyrolysis oil in a fixed bed reactor and showed that it is possible to achieve a degree of deoxygenation of 99.9 % with an oil mass yield of 33 %. This shows that a total oil mass yield of 22 % daf and energy recovery of 53 % is possible with fast pyrolysis followed by HDO, which is comparable with the results from experiment 8. This indicates that catalytic hydrolypyrolysis is competitive with fast pyrolysis followed by HDO. Furthermore, Baldauf et al. [36] experienced problems with rapid

439 catalyst deactivation and operational problems due to the instability and coking potential of the used bio-
440 oil, which are problems that were not encountered in this study.

441 The produced gas could through steam reforming be used to generate the hydrogen needed in the
442 hydropyrolysis and HDO reactor, as proposed by Marker et al. [2]. The process could also be combined with
443 other renewable energy technologies. For instance, electricity produced from wind turbines could be used
444 to generate the hydrogen needed in the process by electrolysis, and the produced gas could instead be
445 converted fully to substitute natural gas by methanation of CO and CO₂. Since the amount of hydrogen
446 added to the products depend on the applied process conditions the process could be adjusted to
447 correspond to the energy available from excess renewable electricity, resulting in energy storage in the
448 form of liquid and gaseous fuels. Our experimental results confirm and expand on the positive results
449 obtained by Marker et al. [1,2] by a similar combined catalytic hydropyrolysis and downstream
450 hydrotreating process.

451 **4 Conclusion**

452 In this work, beech wood was converted into liquid fuels by catalytic hydropyrolysis in a fluid bed reactor
453 with a sulfided CoMo/MgAl₂O₄ catalyst followed by a deep hydrodeoxygenation in a fixed bed reactor with
454 a sulfided NiMo/Al₂O₃ catalyst. The char yield decreased and the gas yield increased with increasing fluid
455 bed temperature, while the condensable organic yield was less affected by the temperature. Increasing the
456 total pressure mainly increased the aqueous phase yield and decreased the CO and CO₂ yield, while only
457 negligible changes in the yields of condensable organics and char yield were observed. Detailed analysis of
458 the condensed organics showed that it consisted of species in the diesel and naphtha boiling point range.
459 The condensed organics had a high concentration of aromatics and the concentration was mainly
460 controlled by the fluid bed temperature and the total pressure. Comparing the experimental results with
461 equilibrium calculations indicated that the aromatic to naphthene ratio was controlled by the
462 thermodynamic equilibrium at high temperatures, but was kinetically controlled at low temperatures.

463 When using both reactors the condensed organics were essentially oxygen free. Bypassing the HDO reactor
464 increased the oxygen content in the organics, however, the oxygen content was still significantly lower than
465 the oxygen content in normal pyrolysis oil and the oxygen was mainly different phenols, but minor amounts
466 of oxygenated aliphatics were also observed. Overall, the present experimental results indicate that
467 catalytic hydrolysis of biomass may be a viable path to green transportation fuels.

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Supplementary material

Masse balances on elemental basis

An overview of the carbon, hydrogen and oxygen recovery is shown in Table S.1.

Table S.1. Mass balances on elemental basis for carbon, hydrogen and oxygen

Test	1	2	3	4	5	6	7	8	9	10	11
Carbon recovery (%)											
C ₁ -C ₃	21.5	19.7	23.1	22.9	21.6	19.4	22.5	24.3	18.9	20.7	19.0
C ₄ +	14.2	16.8	18.9	16.9	14.5	14.4	15.1	18.8	14.4	17.1	13.9
CO+CO ₂	11.4	9.3	10.1	12.7	12.5	8.2	12.1	12.7	13.3	10.3	12.6
Char	20.9	21.0	22.0	17.3	18.2	26.4	17.2	15.5	15.5	18.9	18.4
Organics	19.9	15.1	17.2	20.3	22.6	13.6	21.4	19.6	19.4	18.6	20.9
Aqueous phase	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6
Sum	87.9	82.0	91.3	90.1	89.5	82.0	88.4	90.9	81.4	85.5	85.4
Hydrogen recovery (%)											
C ₁ -C ₃	48.3	44.1	51.7	52.0	49.0	43.3	50.7	55.3	42.8	46.8	43.0
C ₄ +	24.0	28.3	31.8	28.4	24.5	24.3	25.5	31.6	24.2	28.7	23.3
CO+CO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Char	9.2	9.7	9.9	6.8	7.6	13.3	7.3	5.8	6.7	7.9	7.3
Organics	23.7	17.8	19.1	21.6	25.0	15.1	24.3	20.2	20.5	20.5	20.4
Aqueous phase	66.5	70.2	66.8	67.1	67.2	58.0	65.7	66.5	62.0	70.4	69.1
Sum	171.8	170.3	179.3	175.8	173.3	153.9	173.5	179.4	156.2	174.3	163.1
Oxygen recovery (%)											
C ₁ -C ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ +	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO+CO ₂	24.2	19.7	20.2	25.1	25.7	16.5	25.3	23.7	26.6	18.4	24.0
Char	6.9	7.5	7.3	5.1	5.0	9.8	5.0	3.0	6.1	6.0	5.4
Organics	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Aqueous phase	72.3	76.4	72.7	73.0	73.1	63.0	71.4	72.3	67.5	76.5	75.1
Sum	103.4	103.5	100.2	103.2	103.8	89.3	101.7	99.0	100.2	100.9	104.5

583 GC simulated distillation curves for the condensed organics

584 The effect of bypassing the HDO reactor is shown in Figure S.1, where the simulated distillation curve for
 585 experiment 7 and 11 are shown. Bypassing the HDO reactor clearly increases the final boiling point of the
 586 condensed organics; this is most likely due to the increase in the oxygen content. The effect of the
 587 temperature and pressure on the simulated distillation curve is shown in Figure S.1 B and Figure S.1 C.
 588 Increasing the fluid bed temperature decreases the final boiling point, this is because more cracking takes
 589 place at higher temperatures. No significant effect of varying the pressure on the distillation curve is
 590 observed.

591 **Figure S.1.** GC simulated distillation curves for the condensed organics with and without HDO reactor (A), at different fluid bed
 592 and HDO reactor temperatures (B), and different total pressure (C). The curves are calculated using D86 according to ASTM D
 593 7213 C.

594 Equilibrium calculations

595 Equilibrium concentrations were calculated using the HSC Chemistry 9 software package. GC×GC-MS shows
 596 that the produced oil is a very complex mixture and in our calculations we have therefore on the basis of
 597 the results from GC×GC-MS reduced the amount of hydrocarbons to 9 (shown in Figure S.2).

598 **Figure S.2 .** Model compounds used to calculate equilibrium concentrations

599 The used initial molar distribution is shown in Table S.2.

600   **Table S.2. Hydrogen free mole fraction of molecules used in equilibrium calculations**

	Hydrogen free mole fraction
Benzene + cyclohexane	20 %
Toluene + methylcyclohexane	20 %
o-xylene +1,2-dimethylcyclohexane	20 %
Naphthalene+ 1,2,3,4-tetrahydronaphthalene +decahydronaphthalene	40 %

601   The equilibrium concentration of the molecules as a function of temperature at different hydrogen partial
602   pressures is shown in Figure S.3. The naphthenes are favored at lower temperature. At temperatures above
603   approximately 405 °C at 99% H₂ the monoaromatics become the main components. When the hydrogen
604   partial pressure is increased the naphthenes becomes more dominating. The fraction of diaromatics is close
605   to zero at temperatures below 450 °C and when the gas consists of 99 % hydrogen.

606
607   **Figure S.3. The influence of temperature and hydrogen partial pressure on the equilibrium distribution between the molecules**
608   **shown in Figure S.2. The calculations were conducted in HSC Chemistry 9 at 2.5 MPa.**

609   The effect of varying the total pressure on naphthenes, monoaromatics, and diaromatics is shown in Figure
610   S.4. The aromatics are more thermodynamically favored at a low total pressure. The monoaromatics have
611   a maximum at 0.5 to 1 MPa. The concentration of diaromatics decreases with the total pressure and is
612   close to zero when the pressure increases to above 1 MPa. The reason for the peak in monoaromatics is
613   that at low pressure naphthalene is more equilibrium favorable than 1,2,3,4-tetrahydronaphthalene.

Figure S.4. The influence of the total pressure on the equilibrium distribution between the molecules shown in Figure S.2. The calculations were conducted in HSC Chemistry 9 at 450 °C with 99 % H₂ in the gas.

Chromatograms

The chromatograms for GC-AED on the condensed oil from experiment 7 and 11 are shown in Figure S.5. In the analysis of the condensed organics from experiment 7, 2-ethyl-phenol was used as internal standard (ISTD) and 4-fluoro-phenol was used as ISTD in the analysis of the condensed organics from experiment 11.

Figure S.5. Chromatograms for GC-AED of the condensed oil in experiment 7 (A) and experiment 11 (B). Conditions: Fluid bed temperature: 450 °C, HDO temperature in experiment 7: 371 °C, the HDO reactor was bypassed in experiment 11, pressure: 2.6 MPa, H₂ flow: 82-87.4, N₂ flow: 0.62-5 NL/min, biomass feeding rate: 174-250 g/h, H₂S concentration: 48-460 ppm.

Retention of organic Elements in the char

The retention of the elements is defined as:

$$Retention = \frac{\text{element wt.\% daf in char}}{\text{element wt.\% daf in beech wood}} \times \text{char yield wt.\% daf} \quad (1)$$

The retention of nitrogen, carbon, hydrogen and oxygen is shown in Figure S.6.

Figure S.6. Retention of nitrogen, carbon, hydrogen, and oxygen as a function fluid bed temperature (A) and pressure (B). Conditions: H₂ flow: 2.14-5.08 mole/min, N₂ flow: 0.02-0.2 mole/min, biomass feeding rate: 159-300 g/h, H₂S concentration: $0.47-4.6 \times 10^{-3}$ mole fraction.

Gas residence time in setup

The vapor residence time in the different parts of the setup is shown in Table S.3. The first condenser was located directly after the HDO reactor, thus the residence time between these two is below 1 s.

Table S.3. Vapor residence time in setup

	Residence time
Flow screw feeder to fluid bed	~2 s
Fluid bed reaction zone	~1 s
Fluid bed disengagement zone	~2 s
Pipes between fluid bed, filter and HDO reactor	< 1 s
Filter	Up to 16 s
HDO reactor	~2 s