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# Lignite and Biomass Waste Hydrothermal Liquefaction Crude Upgrading by Hydrotreatment

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► **To cite this version:**

N. Batalha, R. Checa, C. Lorentz, P. Afanasiev, K. Stanczyk, et al.. Lignite and Biomass Waste Hydrothermal Liquefaction Crude Upgrading by Hydrotreatment. *Energy & Fuels*, 2023, 10.1021/acs.energyfuels.3c01550 . hal-04170031

**HAL Id: hal-04170031**

**<https://hal.science/hal-04170031v1>**

Submitted on 24 Nov 2023

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1 Hydrocarbon fuels from sequential hydrothermal liquefaction (HTL) of lignite  
2 and catalytic upgrading of crude oil

3  
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11  
12 **ABSTRACT**

13 Lignite from Belchatów in Poland was converted to hydrocarbon fuels, particularly in the kerosene  
14 and diesel range, through sequential hydrothermal liquefaction (HTL) and hydrotreatment (HDT) of  
15 the obtained crude oil. Different HDT temperatures were investigated (from 350°C up to 390°C).  
16 Despite the highly aromatic nature and high heteroatom content, the HTL lignite crude oil could  
17 undergo deep hydrodesulfurization (HDS = 99 %) and hydrodeoxygenation (HDO =98 %) in a single  
18 HDT treatment stage, yielding a liquid product rich in aliphatic and aromatic, particularly  
19 monoaromatic, hydrocarbons. The hydrotreatment and hydrogenating capacity of the lignite crude oil  
20 was linked to the low presence of refractory compounds in lignite and, consequently, lignite's crude  
21 oil, permitting the easy transformation of the crude oil into hydrocarbon fuel.

22 In addition to the crude oil, the HTL of lignite yielded a stream of char, which displayed a higher  
23 calorific value and lower heteroatom content than the original lignite feedstock, thus having a high  
24 potential for electricity production, the common use of lignite. Thus, introducing an HTL stage to  
25 extract crude oil before lignite use in electricity production could provide an alternative fuel source

26 used as a strategy to increase multiple countries' energetic independence before the transition to  
27 renewable fuels.

28 Keywords: Lignite; hydrotreatment; Crude oil; liquid fuels; coal valorization

## 29 **1. INTRODUCTION**

30 The Russian invasion of Ukraine in February 2022 has redistributed the energetic policy in Europe  
31 (and in the world) and deeply impacted the food and energetic markets and climate issues <sup>1</sup>. For  
32 instance, the European Union (E.U.) is the first market for diesel fuel and must import 20% of its  
33 consumption. Half of this imported diesel was coming from Russia. Despite E.U. policy attempts to  
34 eliminate fossil resources, with a new target of 45% of renewables in 2030, energetic transition and  
35 evolution of energetic policies are challenging to manage, and a portfolio of options must be  
36 investigated. Biofuels and biodiesel are slowly increasing their production. However, these are only  
37 expected to cover 4.6% of transport fuel demand in 2024<sup>2</sup>. Therefore, there might be a need for a local  
38 diesel resource in the E.U. before vehicles electrification and green fuels are fully implemented.

39 Despite its relatively low heat content, almost 80% of lignite is used for electricity generation<sup>3</sup>.  
40 Even if its production has strongly decreased since the 90's in Europe, the inland consumption of  
41 brown coal by E.U. member states was estimated, in 2021, at 300 Mt <sup>4</sup>. An alternative pathway to  
42 valorize lignite, pure or mixed with waste biomass, is hydrothermal liquefaction. In the absence of  
43 oxygen, subcritical or supercritical water as a reaction medium converts organic matter,  
44 independently of the origin, into a liquid of high heating value (HHV). In early works, Deshpande et al.,  
45 Kershaw et al., and Hu et al. extracted brown coals or Dayan lignites, respectively, with sub and  
46 supercritical water and claimed that the extraction residue would be a good feedstock for combustion  
47 or gazification<sup>5-7</sup>. These studies led to the establishment of the hydrothermal dewatering (HTD)  
48 process, a pretreatment (developed at pilot scale) of lignite with no particular address regarding the  
49 crude oil formed <sup>8</sup>. This was only tackled more recently by Hartman et al., which investigated the HTL  
50 of selected coal feedstocks providing a high liquid yield (21%) and concluded that high-value  
51 petroleum-like products could be obtained <sup>9</sup>. Liu et al. used HTL as a pretreatment before pyrolysis of  
52 Xiaolongtan lignite and suggested three reaction steps discussed hereafter<sup>10</sup>. Like HTL of biomass,  
53 numerous reactions occurring during HTL are favorable for deoxygenation and monomer formation,  
54 even if condensation reactions may co-occur. Due to the complexity of the HTL process, the  
55 optimization of operating conditions, i.e., the impact of lignite nature and the understanding of the  
56 formation of the product, have yet to be deeply investigated. Recently, Li et al. attempted to optimize  
57 HTL process parameters for the transformation of demineralized and pretreated lignite, observing

58 these can impact the liquid yield and composition<sup>11</sup>. They also suggested that HTL promotes the  
59 transfer from polycyclic aromatic hydrocarbons to monocyclic aromatic hydrocarbons. All these  
60 studies indicate that HTL of lignite can potentially provide some fuel. However, no one attempted to  
61 upgrade lignite HTL oil like it was done with the HTL biocrudes of biomass or wastes.

62 In the present work, we investigated the HTL conversion of a Polish lignite and the catalytic upgrading  
63 of the HTL lignite oil obtained. A detailed study of the upgrading operating conditions and their impact  
64 on the nature of the products was performed. After upgrading, a diesel fraction was obtained, showing  
65 that a preliminary HTL stage can provide a fraction of a diesel source and increase the HHV of the  
66 fraction used for electricity generation.

67

## 68 **2. EXPERIMENTAL**

### 69 *2.1. Hydrothermal liquefaction of lignite*

70 Lignite from the coal mine of Bełchatów in Poland was used as feedstock. The physicochemical  
71 characteristics of the feedstock are presented in Table 1. The HTL experiments were conducted in a  
72 batch type 1000 ml stainless steel autoclave reactor (Autoclave Engineers, USA), equipped with a  
73 magnetically coupled mechanical stirrer. In each of the HTL experiments, 600 g of 10 wt% of lignite in  
74 water solution was used. After loading the reactor, the residual air was removed by nitrogen purging  
75 and vacuuming four times. Subsequently, the vessel was pressurized with N<sub>2</sub> (~2 bar) and then heated  
76 to 360 °C (reaction temperature) with a constant heating rate 10 °C/min and maintained at this  
77 temperature for 30 min (HTL reaction time). The pressure in the reactor vessel was self-generated.

78 After completion of the reaction, the autoclave was cooled to ambient temperature, and the gas  
79 samples were taken for analysis by micro-GC SRA instruments equipped with the following three  
80 modules: MoISieve 5 Å with backflush, PoraPLOT U, and Plot Al<sub>2</sub>O<sub>3</sub>/KCl. The HTL products mixture  
81 (crude oil, aqueous phase, and char) were then recovered from the reaction vessel. The separation of  
82 the products mixture obtained after the HTL processes was performed using a vacuum filtration  
83 technique. The post-reaction mixture was filtered on glass microfiber filters. The aqueous phase  
84 obtained was separated from the char. The reactor vessel and the char were washed with acetone,

85 and the solid fraction and the liquid organic fraction (crude oil) solution in acetone were separated by  
 86 vacuum filtration. Next, the solid fraction was dried to constant weight in the laboratory drying oven  
 87 at 105 °C. The filtered crude oil solution was concentrated using a rotary vacuum evaporator. The  
 88 scheme of the process is presented in Figure S1.

89 Table 1. Physicochemical properties of lignite feedstock.

Proximate Analysis	Moisture <sub>total</sub> (wt.%)	50.59
	Organic matter (wt.% dry) <sup>a</sup>	72.48
	Volatiles (wt.% dry) <sup>b</sup>	41.99
	Ash (wt.% dry)	25.94
Ultimate analysis	C (wt.% dry)	50.53
	H (wt.% dry)	4.55
	N (wt.% dry)	0.56
	O (wt.% dry)	15.99
	S total (wt.% dry)	3.78
	Calorific value <sub>as received</sub> (kJ/kg)	8 130
Calorific value <sub>dry</sub> (kJ/mol)	18 960	

90 <sup>a</sup> Weight loss of dry sample upon combustion under air atmosphere (T = 575 °C).

91 <sup>b</sup> Weight loss of dry sample under inert atmosphere (T=950 °C)

92  
93

94 The yields of the products were calculated based on dry, ash-free (daf) initial lignite using the following  
 95 formulas:

96

$$97 \text{ Crude oil yield (wt. \%)} = \frac{m_{\text{crude}}}{m_{\text{lignite}}} 100 \quad \text{Equation 1}$$

98

$$99 \text{ Char yield (wt. \%)} = \frac{m_{\text{char}}}{m_{\text{lignite}}} 100 \quad \text{Equation 2}$$

$$100 \text{ Gas yield (wt. \%)} = \frac{\sum^i M w_i y_i P V}{R T m_{\text{lignite}}} 100 \quad \text{Equation 3}$$

$$101 \text{ Aqueous phase solubles yield (wt. \%)} = 100 - \text{gas yield} - \text{char yield} - \text{crude oil yield}$$

102 Equation 4

103

104 Where:

105  $m_{\text{crude}}$ ,  $m_{\text{char}}$ , and  $m_{\text{lignite}}$  are the mass of recovered crude oil, recovered char, and initial lignite feedstock  
 106 on a dry, ash-free (daf) basis;

107  $M w_i$  and  $y_i$  are the molecular weight and gas composition of compound  $i$ , respectively.

108  $P$  is the residual reactor pressure at room temperature

109 V is the reactor volume occupied by gas (400 mL)  
110 R, is the ideal gas constant  
111 T, is the room temperature  
112

## 113 2.2. Hydrotreatment of lignite crude oil

114 The hydrotreatment of the crude oil obtained from the hydrothermal liquefaction of lignite was  
115 performed under batch conditions using a 300 mL reactor from Parr (Model 4566). The hydrothermal  
116 conversion of 3 g of crude oil was performed in the presence of 25 g of n-heptane (solvent) and 1 g of  
117 sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst (See main properties in Table S1). Heptane was considered inert during  
118 the reaction and is used to provide enough volume inside the reactor to enable continuous stirring (≈  
119 700 rpm) and, consequently, facilitate the contact between HTL oil, hydrogen, and catalyst. Before  
120 reaction, the catalyst was activated through sulfidation carried at 400 °C for 3 h, under a continuous  
121 flow (4 L/h) of H<sub>2</sub>S (15%) in H<sub>2</sub>. After being sulfided, the catalyst is kept under an inert atmosphere (N<sub>2</sub>)  
122 until being transferred into the reactor.

123 At room temperature and after flushing with H<sub>2</sub>, the reactor was pressurized with 10 bar of H<sub>2</sub> to  
124 prevent catalyst deactivation during heating. After, the reactor was heated up to the reaction  
125 temperature, i.e., 350 °C, 375 °C, or 390 °C. Once the reaction temperature is attained (20 min), an  
126 additional pressure of 50 bar of H<sub>2</sub> was introduced into the reactor, reaching a reaction pressure of ≈  
127 100 bar. After the second H<sub>2</sub> introduction in the reactor, the crude oil hydrotreatment was performed  
128 for 1 h or 3 h leading to a pseudo-WHSV (Equation 5) of 3 h<sup>-1</sup> and 1 h<sup>-1</sup>, respectively. Additionally, a test  
129 where the reaction was stopped after introducing the 50 bar of H<sub>2</sub> was also performed, denominated  
130 t = 0 h, as a reference.

$$131 \text{ (Pseudo - WHSV}(h^{-1}) = \frac{m_{oil}}{m_{cat}t_{reaction}} \quad \text{Equation 5}$$

132 Where:

133  $m_{oil}$  and  $m_{cat}$  are the mass of crude oil and catalyst, respectively,

134  $t_{reaction}$  is the reaction time.

135 After the reaction, the reactor was cooled to room temperature, and the residual gas was collected in  
136 a gas bag and analyzed with a micro-GC (SRA instruments) equipped with three modules: Molsieve 5Å  
137 (H<sub>2</sub>, CO, CH<sub>4</sub>), Hayesep A (CO<sub>2</sub>, C<sub>2</sub> hydrocarbons), PLOT Al<sub>2</sub>O<sub>3</sub>/KCl (C<sub>3</sub>-C<sub>4</sub> hydrocarbons).

138 The liquid and spent catalyst were separated through filtration, and the heptane in the liquid was  
139 evaporated, using a rotovapor apparatus, for 2 h at a pressure of 30 mBar and temperature of 40°C.  
140 The liquid remaining after evaporation was considered to be the liquid product from hydrotreatment.  
141 Elemental analysis was used to determine the coke deposited in the catalyst, i.e., coke equivalent to  
142 carbon in the spent catalyst.

143 The yields of the products obtained from the HDT reaction, i.e., liquid, solid, gas, H<sub>2</sub>O, and H<sub>2</sub>S were  
144 calculated through the following equations:

145  
146 
$$Liquid\ yield\ (wt.\ \%) = \frac{m_{liquid}}{m_{crude\ oil}} 100 \quad \text{Equation 6}$$

147  
148 
$$solid\ yield\ (wt.\ \%) = \frac{m_{solid}}{m_{crude\ oil}} 100 \quad \text{Equation 7}$$

149 
$$Gas\ yield\ (wt.\ \%) = \frac{\sum^i M w_i y_i P V}{RT m_{crude\ oil}} 100 \quad \text{Equation 8}$$

150 
$$H_2O\ (wt.\ \%) = (O_{crude\ oil} - Gas\ yield\ (\frac{\%CO}{28} + 2\frac{\%CO_2}{44})) 16 - Liquid\ yield.\ O_{liquid}) \frac{18}{16} \quad \text{Equation 9}$$

151 
$$H_2S\ (wt.\ \%) = (S_{crude\ oil} - Liquid\ yield.\ S_{liquid}) \frac{34}{32} \quad \text{Equation 10}$$

152

153 Where:

154  $m_{crude\ oil}$ ,  $m_{solid}$ , and  $m_{liquid}$  are, respectively, the mass of crude oil to be hydrotreated, the excess of  
155 mass found in the catalyst after reaction ( $m_{spent\ catalyst} - m_{fresh\ catalyst}$ ), and the mass liquid obtained after  
156 evaporation of n-heptane;

157  $M w_i$  and  $y_i$  are the molecular weight and gas composition of compound  $i$ , respectively.

158  $P$  is the residual reactor pressure at room temperature

159  $V$  is the reactor volume occupied by gas ( $\approx 263$  mL)

160  $R$ , is the ideal gas constant

161 T, is the room temperature  
162 O, is the weight fraction of oxygen in the crude oil ( $O_{\text{crude oil}}$ ) and liquid ( $O_{\text{liquid}}$ ) determined by elemental  
163 analysis.  
164 %CO and %CO<sub>2</sub>, are the weight fraction of CO and CO<sub>2</sub>, respectively, in the gas  
165 S, is the weight fraction of Sulfur in the crude oil ( $S_{\text{crude oil}}$ ) and liquid ( $S_{\text{liquid}}$ ).

166

### 167 2.3. Characterization methods

168 Elemental compositions (CHNS-O) of lignite, crude oil, hydrotreatment liquid, and spent catalyst were  
169 analyzed on a Thermo Scientific FLASH 2000 Organic Elemental Analyzer (accuracy of  $\pm 0.1$  wt%).  
170 Additionally, the S composition of the crude oil and hydrotreatment liquid samples were also  
171 quantified using ANTEK 9000NS apparatus, which is more precise (from few ppm until percent levels)  
172 and accurate. Prior to analysis, the samples were diluted in THF ( $\approx 5$  wt.%).

173 The boiling point of the sulfur-containing compounds in the crude oil was estimated by using a Agilent  
174 7890A GC coupled with an FPD+ detector and fitted with a CP-SimDist GC column (10 m  $\times$  0.53mm  $\times$   
175 2.65  $\mu$ m).

176 The molecular weight distribution of the compounds in the lignite crude oil and the hydrotreatment  
177 liquid was obtained by size exclusion chromatography (SEC) performed using an Agilent 1200 series  
178 HPLC equipped with two PLgel Columns (50 and 500 Å), a refractive index detector (RID), and a diode  
179 array detector (DAD). The analysis was carried out at 35 °C using tetrahydrofuran (THF – 1 mL/min) as  
180 the eluent. Before analysis, the samples were diluted to a concentration of  $\approx 1$  wt.% in THF and filtered  
181 (0.45  $\mu$ m). A mixture composed of hydrocarbons (Mw from 86 to 1000 g/mol) was used as standard  
182 to convert elution time into molecular weight (hydrocarbons equivalent) leading to an average  $Mw_{\text{HC}}$   
183 data.

184 The <sup>13</sup>C-NMR analysis of the liquid samples was performed in a Bruker AVANCE 400 MHz spectrometer  
185 and analyzed using the software TopSpin 3.0. The measurements were performed at room  
186 temperature with an accumulation of 4700 scans for approximately 15 h. The samples ( $\approx 100$  mg) were  
187 diluted with deuterated chloroform (CDCl<sub>3</sub>) (0.6 mL). Table S2 includes the chemical shifts attributed  
188 to each functional group.

189 Comprehensive GC $\times$ GC-TOF MS and GC $\times$ GC-FID were used to identify and quantify the compounds in  
190 the lignite crude oil and HDT liquid. The GC $\times$ GC/TOF system was equipped with a cryogenic modulator  
191 from Zoex Corporation (USA) and a BenchTOF 2 TI spectrometer from Sepsolve. The chromatograph



192 and TOF parameters are described in Tables S3 and S4. The GC×GC/FID was equipped with a switch  
193 valve modulator (Agilent G3486A CFT modulator), and modulation parameters were optimized  
194 according to ref <sup>12</sup>. The parameters used for product separation are described in Table S3. The  
195 quantification of the compounds detected by GC×GC-FID was performed using the relative responsive  
196 factor method (RRF)<sup>13</sup> with cyclohexanol as the reference. The data obtained from comprehensive  
197 GC×GC-FID was also used to provide the distillation curve of the HDT liquid products by using a mixture  
198 of n-alkanes (C<sub>7</sub> to C<sub>40</sub>) as a reference.

199

### 200 **3. RESULTS AND DISCUSSION**

#### 201 ***3.1. Hydrothermal liquefaction of lignite***

##### 202 ***3.1.1. Crude oil***

203 While the primary target product for liquid fuel production is crude oil, only 12.3 wt.%daf of lignite  
204 was transformed into this product with char (48.8 wt.%daf), gas (23wt.% daf), and aqueous phase  
205 organics (15.9 wt.%daf) representing the main fractions. Liu et al. <sup>21</sup> studied the optimal conditions for  
206 maximizing crude oil yield from lignite HTL and found that short residence times, i.e., ~5 min, and high  
207 temperatures, i.e., ~400 °C, are necessary. In this study<sup>21</sup>, the authors found a maximum crude yield  
208 of 34 wt.%. Hence, the high residence time (30 min) and low temperature (360 °C) presently used can  
209 explain the low crude oil yield. Another important parameter known to affect the yield and quality of  
210 crude oil in HTL is the amount of ash <sup>25–29</sup>. On biogenic feedstocks, such as algae, high ash contents  
211 have been reported to decrease the yield and quality of the crude product <sup>25–27</sup>. Although no reference  
212 applied to the conversion of lignite under HTL conditions was found, a direct analogy with biomass  
213 feedstocks suggests that high-ash in lignite might have a similar effect. Thus, a high concentration of  
214 ash found in lignite (25.94 wt.%) could also be responsible for the low crude oil yield (12.3 wt.%).  
215 Indeed, Liu et al. <sup>21</sup> used lignite with 7.14 wt.% of ash. It should be mentioned that Oner et al.  
216 demonstrated that ash positively enhances the crude oil product in lignite liquefaction under organic  
217 solvents, like tetraline, and under H<sub>2</sub> pressure <sup>30</sup>. However, the positive effects were attributed to the  
218 capacity of certain elements in ash to promote hydrogenation by H<sub>2</sub> or hydrogen transfer from the

219 solvent, a reaction not likely to occur under HTL conditions. While ash is bound to affect lignite HTL  
220 conversion, the chemical composition of lignite and lignite's ash is substantially different from that of  
221 biomass feedstocks like algae. Thus, further studies, out of the scope of this work, should be  
222 performed to infer the impact of this component.

223 When compared to the lignite feedstock, the crude oil stream contains a higher concentration of  
224 carbon (77.7 wt.% vs. 50.5 wt.%dry) and hydrogen (8.9 wt.% vs. 4.6 wt.%dry) (Tables 1 and 2).  
225 Additionally, the crude oil displayed a lower concentration of oxygen (10.8 wt.% vs. 16.0 wt.%dry) and  
226 sulfur (2.4 wt.% vs. 3.78 wt.%dry) than the parent lignite sample. However, it is essential to mention  
227 that the sulfur content in crude oil is still well above the specifications for liquid hydrocarbon fuels,  
228 e.g., diesel specification < 10 ppm. Thus, significant desulfurization must take place during upgrading.  
229 In the case of nitrogen, no specification states a maximum N concentration in hydrocarbon fossil  
230 fuels<sup>31</sup>. Still, nitrogen compounds impact other regulated properties, such as gum content, storage  
231 stability, and thermal stability<sup>33</sup>. However, synthetic aviation fuels (SAF) have a nitrogen  
232 concentration inferior to 2 ppm<sup>32</sup>. It is worth mentioning that there is still no regulation concerning  
233 HTL-derived fuels.

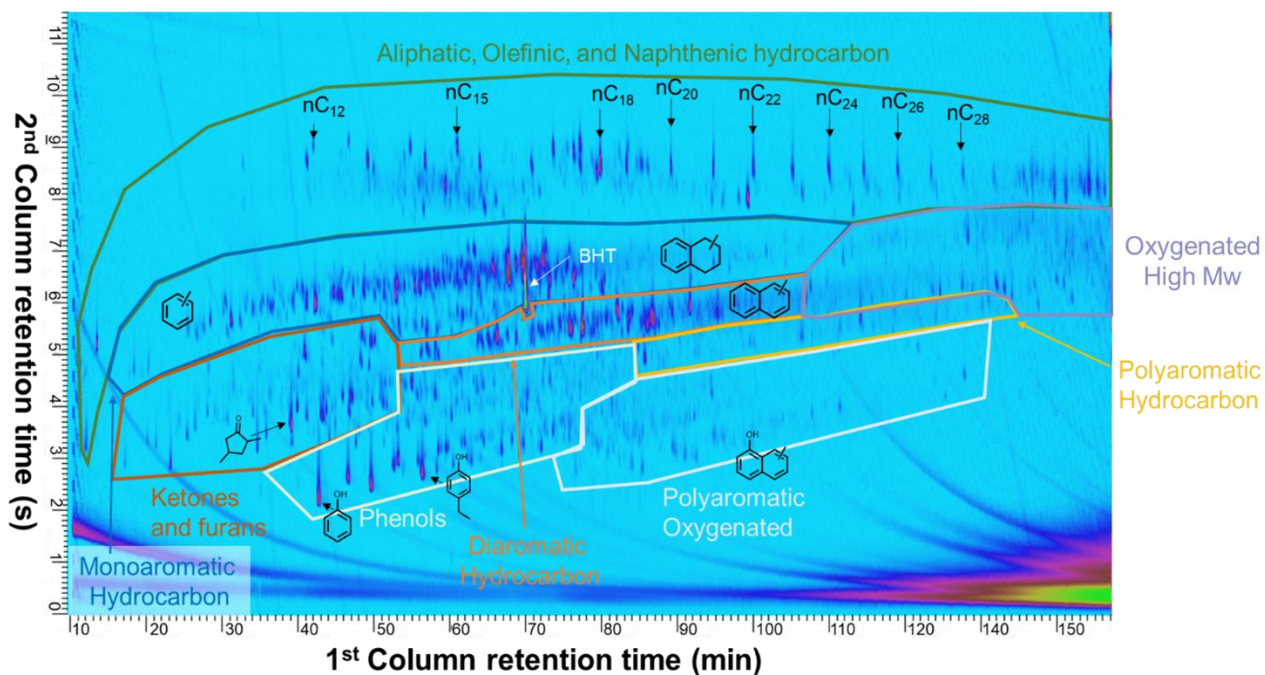
234 The functional group's composition, determined by <sup>13</sup>C NMR, of the crude oil is shown in Table 2. The  
235 crude oil is mainly composed of aliphatic (53.6%) and aromatic (40.3%) carbon. Among the aromatic  
236 carbon, 24.0% corresponded to C-H bonds, 9.6% to C-C bonds, and 6.8% to C-O bonds (chemical shift  
237 and NMR Spectrum in Table S2 and Figure S2, respectively). Alkyl groups or polyaromatics compounds  
238 in crude oil can explain the occurrence of C-C bonds in aromatic fraction. Additionally, the high  
239 incidence of aromatic C-O and carbonyl C=O, compared to the methoxy, aliphatic, carboxylic acid, and  
240 esters, indicates that phenolic compounds and ketones represent a significant portion of the crude oil  
241 oxygen. Indeed, the crude oil composition analysis by comprehensive GC×GC-TOFMS (Figure 1)  
242 showed the presence of ketones, furans, phenols, and naphthols. A small amount of mono-aromatic  
243 and di-aromatic hydrocarbons and non-aromatic cyclic hydrocarbons, possibly derived from

244 biomarkers typically present in lignites<sup>34</sup>, were also found. The quantification performed by GCxGC-  
 245 FID is shown in Table 3. Only 16.7 wt.% of the crude oil sample was detectable by GCxGC-FID analysis.  
 246 The non-detected compounds were too heavy to be analyzed by gas chromatography. Indeed, Liu et  
 247 al. analyzed the heteroatom-containing compounds obtained from the ethanolysis of lignite via  
 248 Fourier transform ion cyclotron resonance mass spectroscopy (FTICR-MS), observing a significant  
 249 number of oxygenated compounds with up to 6 aromatic rings with the particular occurrence of  
 250 oxygenated molecules with carbon number between 17 and 26 carbons and two oxygen atoms, like  
 251 organic acids and diols<sup>35</sup>. In the same study, authors characterized the sulfur-containing compounds,  
 252 mostly ranging above C<sub>20</sub> and associated in the same molecule with another S or several O atoms.<sup>35</sup>  
 253 The relatively large carbon number of the sulfur-containing compounds in crude oil can explain the  
 254 few S compounds detected in the products by comprehensive GCxGC-TOFMS (Figure 1). Indeed, the  
 255 analysis of the sulfur content of the crude oil sample by GC-FPD<sup>+</sup> using a Simdis chromatography  
 256 method equivalent to ASTM D2887 reveals that such molecules have a retention time higher than  
 257 hexatriacontane (C<sub>36</sub> - Bp = 497 °C) (Figure S3), which defines the upper detection limit of the GCxGC  
 258 analysis. The same explanation can be given for the few nitrogen-containing compounds among the  
 259 GCxGC detected compounds in the crude oil (Figure 1).

260 Table 2. Composition of crude oil obtained from the HTL of Bełchatów lignite

Composition		Carbon chemical composition ( <sup>13</sup> C NMR) <sup>a</sup>	
C (wt.%)	77.7 ± 0.1	C <sub>Aliphatic</sub>	53.6
H (wt.)	8.9 ± 0.3	C <sub>Methoxy (-O-CH<sub>3</sub>)</sub>	0.1
O (wt.%)	10.8 ± 1.0	C <sub>Aliphatic-O (-O-(CH<sub>2</sub>)<sub>n</sub>)</sub>	0.8
S (ppm)	2.4 ± 0.1	C <sub>Aromatic</sub>	40.3
N (ppm)	0.5 ± 0.1	C <sub>Carboxylic/Amide</sub>	0.8
TAN (mg <sub>KOH</sub> /g)	29.2 ± 0.2	C <sub>Aldehyde/Ketone</sub>	4.4
HHV (MJ/kg)	31.8		

261 <sup>a</sup>Chemical shift range in Table S1 and NMR spectra in Figure S2



262

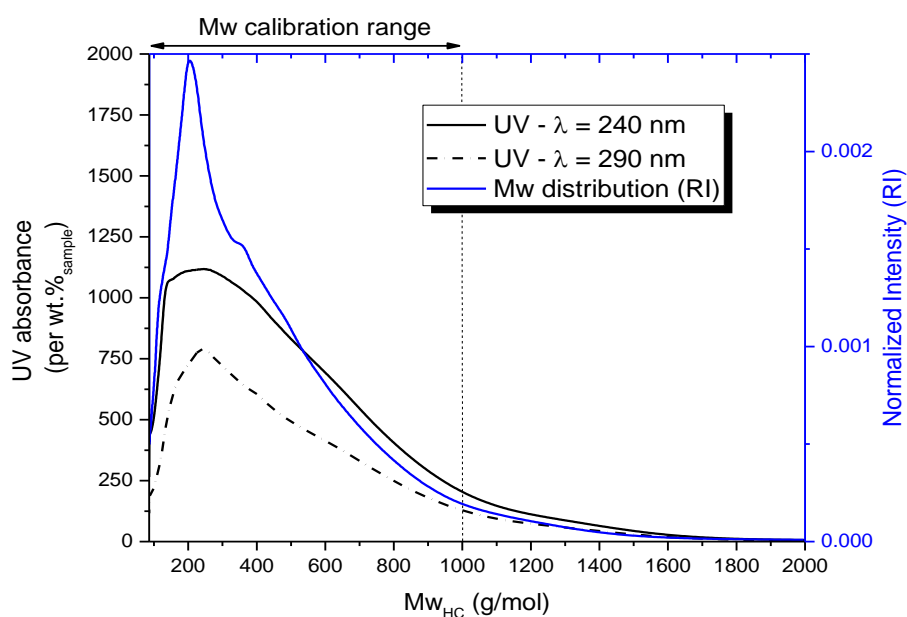
263 Figure 1. GCxGC-TOF MS chromatogram of the crude oil obtained from the HTL of lignite. BHT  
 264 (butylated hydroxytoluene) originates from THF solvent, where it serves as a stabilizer.

265

266 Table 3. Quantification of the lignite HTL oil compounds detected by GCxGC-FID using the relative  
 267 response factor method (supporting information). The chromatogram and the areas attributed to  
 268 each compound family are represented in Figure 1.

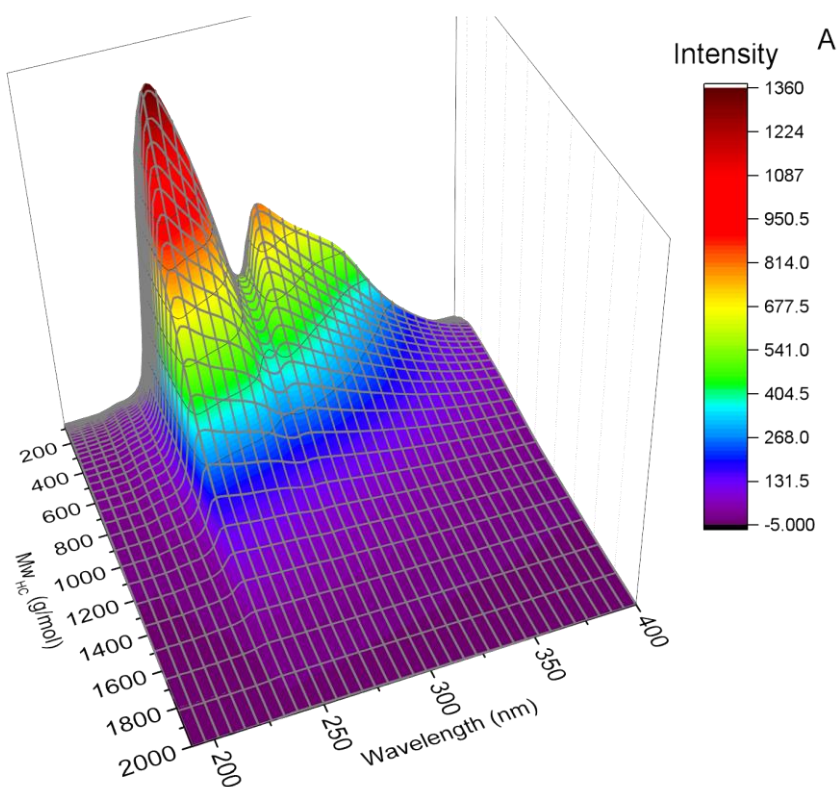
Compounds	Oil composition (wt.%)	Compounds	Oil composition (wt.%)
Aliphatic HC	1.6	Ketones and furans	0.6
Monoaromatic HC	1.6	Phenols	1.4
Diaromatic HC	1.6	Polyaromatic Oxygenated	2.2
Polyaromatic HC	1.2	Aliphatic Oxygenated	6.5

269



B

270



A

271

272 **Figure 2.** A) Compounds in the liquid product molecular weight ( $Mw_{HC}$ ) distribution determined by  
 273 refractive index (RI) (blue curve) and UV absorbance ( $\lambda = 240$  nm and 290 nm) as a function of the  
 274 compounds Mw. Average Mw = 297 g/mol. B) DAD spectrum ( $\lambda = 190 - 400$  nm) of crude oil as a  
 275 function of molecular weight ( $Mw_{HC}$ ).

276

277 A better insight into heavy molecules is given by SEC. The molecular weight distribution of the crude  
278 oil components (Figure 2-A) reveals a large range of compounds, with a molecular weight of up to  
279 ~1,800 g/mol in HC eq. and an average molecular weight of 297 g/mol in HC eq. The significant  
280 presence of large Mw molecules, which are expected to have a high boiling point, agrees with the  
281 small detection level observed in the GCxGC analysis. The evolution of the DAD spectra as a function  
282 of molecular weight (Figure 2-B) reveals an intense absorption between 240 and 400 nm, reflecting  
283 the high aromatic nature of the compounds in the crude oil. The presence of two absorption  
284 maximums, 245 nm and 293, and a shoulder at 316 nm indicates that polyaromatic compounds are  
285 abundant in the crude oil sample. Indeed, as exemplified in Figure S4, monoaromatic compounds like  
286 benzene generate a DAD band at ~250 nm. In opposition, polyaromatic compounds with two or more  
287 conjugated aromatic rings present a second absorption band at  $\lambda > 290$  nm (Figures S5, S6, and S7). In  
288 the particular case of naphthalene, a second sharp peak was observed at 290 nm, with identical  
289 intensity to the peak centered at 250 nm (Figure S5), while in anthracene and pyrene, this band is  
290 significantly broader, extending to significantly higher  $\lambda$  (Figures S6 and S7). Therefore, in the crude  
291 oil (Figure 2-A), the wide absorption band at  $250 > \lambda > 400$  nm indicates the presence of compounds  
292 with at least 3 and 4 conjugated aromatic rings.

293 The comparison of the Mw distribution and the UV absorbance at  $\lambda=240$  nm and 290 nm as a function  
294 of the Mw reveals that both RI and UV curves have a maximum at Mw ~ 230 g/mol (Figure 2-A).  
295 However, the UV spectra absorption distribution is shifted to higher Mw, evidencing heavier  
296 molecules with high aromaticity presence.

297

### 298 **3.1.2. Char, gas, and aqueous phase**

299 The hydrothermal liquefaction of lignite (soft Miocene lignite) obtained in the Bełchatów coal mine in  
300 Poland led to four product streams, i.e., gas, char, crude oil, and an aqueous phase rich in organic  
301 matter. Char was the most abundant among the product streams, representing 48.8 wt.% of the lignite

302 feedstock yield. Even though char and lignite are both solids, the former displayed a higher carbon  
303 content with lower oxygen, nitrogen, hydrogen, and sulfur (Table S4). Hence, char displayed O/C and  
304 H/C ratios of 0.1 and 0.4, respectively, while lignite O/C was 0.2 and H/C was 1.1. The different solid  
305 composition explains char's slightly higher heating value compared with the lignite feedstock, i.e., 22.6  
306 MJ/kg<sub>Dry</sub> vs. 19.0 MJ/kg<sub>Dry</sub>, respectively. P. Liu and D. Zhang<sup>14</sup> studied the transformation of lignite  
307 under hydrothermal conditions, observing that, at T=260 °C, significant removals of oxygen and  
308 hydrogen occur. Similar observations were made by Z. Shi et al.<sup>15</sup>, who, like P. Liu and D. Zhang,  
309 observed a significant reduction of carboxyl, carbonyl, and oxygenated aliphatic carbon in the solid  
310 after HTL treatment. These authors also observed a reduction of the aliphatic CH<sub>2</sub> and CH<sub>3</sub> groups after  
311 hydrothermal treatment, which justifies the decrease in the H/C ratio. The authors linked the  
312 elimination of oxygen and hydrogen from the lignite structure to the production of light gases, such  
313 as CO, CO<sub>2</sub>, and light hydrocarbons<sup>14,15</sup>. Like O and H, the sulfur in char was significantly smaller than  
314 in the lignite feedstock, i.e., 1.1 wt.% vs. 3.78 wt.%, respectively, indicating only 14.2 % of sulfur  
315 remained in the solid phase after hydrothermal liquefaction. The significant extent of desulfurization  
316 is directly related to the nature of the sulfur compounds in lignite. As low-ranking coals, lignites  
317 contain more substantial amounts of sulfides and thiols than other types of coal<sup>16</sup>, which are more  
318 easily transformed under hydrothermal conditions<sup>17,18</sup>.

319 The lower impurities content, i.e., O, N, and S, and increased calorific value indicate that char is a  
320 higher quality coal than the original lignite. Indeed, the treatment of coal samples through  
321 hydrothermal liquefaction has been demonstrated to increase the quality of coal samples, both by  
322 eliminating impurities and improving hydrophobicity<sup>11,15,19,20</sup>.

323 The composition of the gas stream formed during the hydrothermal liquefaction of lignite is shown in  
324 Table S5. CO<sub>2</sub> was the majority product in the gas phase, corresponding to 92.6 wt.% of all the  
325 produced gases. The high CO<sub>2</sub> selectivity in the gas products obtained from lignite HTL had already  
326 been reported previously<sup>15,21</sup>, indicating that decarboxylation is one of the primary processes  
327 responsible for oxygen removal during the reaction. Indeed, CO only represented 1.4 wt.% of the

328 gases, suggesting decarbonylation is significantly less favored. H<sub>2</sub>S represents the second most  
329 abundant compound in the gas stream, representing 3.4 wt.% of all gases. Furthermore, 19.4% of the  
330 sulfur in the lignite feedstock was transformed into H<sub>2</sub>S. The significant formation of H<sub>2</sub>S reflects the  
331 transformation of organic, i.e., thiol and sulfide, and inorganic sulfur, i.e., pyrite, compounds in lignite  
332 promoted by H radicals under hydrothermal conditions<sup>17,18,22</sup>. In addition to CO<sub>2</sub>, CO, and H<sub>2</sub>S, small  
333 amounts of light hydrocarbons and H<sub>2</sub> (Table S5) were also observed. Nonetheless, the amount of such  
334 compounds is not enough to justify alone the small H/C observed in the char, thus suggesting that  
335 light hydrocarbons and H<sub>2</sub> formation are not the main ones responsible for the elimination of  
336 hydrogen in the lignite as proposed by Z. Shi et al., and P. Liu and D. Zhang<sup>14,15</sup>. Instead, the  
337 transformation of lighter fractions of lignite into aqueous and crude organic compounds is more likely  
338 to cause the low H/C of char compared to lignite.

339 Finally, the organic matter solubilized in the aqueous reaction media, i.e., the aqueous phase,  
340 represented 15.9 wt.% of feedstock lignite. In hydrothermal liquefaction processes, the aqueous  
341 phase is typically composed of organic acids, e.g., acetic acid, oxygenated aromatics, aromatic, like  
342 phenols, nitrogenated compounds, and oxidized sulfur compounds<sup>18,23,24</sup>, thus justifying this stream's  
343 acidic pH of 5.2.

344

### 345 **3.2. Hydrotreatment of lignite HTL crude oil**

346 The significant concentration of heteroatoms and polyaromatic compounds in the crude oil stream  
347 clearly demonstrates the necessity of further upgrading for the production of hydrocarbon fuels.  
348 Therefore, this section will focus on the hydrotreatment of the crude oil stream obtained from the  
349 hydrothermal liquefaction of lignite. The hydrotreatment of the lignite crude oil was performed at  
350 three different temperatures, i.e., 350 °C, 375 °C, and 390°C, and at two different reaction times, 1 h  
351 and 3 h. An additional residence time, where the reaction was stopped after the reaction temperature  
352 was attained ( $t_{\text{heating}} = 20 \text{ min}$ ), designated  $t = 0 \text{ h}$ , was also performed at each temperature. The crude



353 oil conversion occurring before  $t = 0$  h are caused primarily by thermal processes. For each operating  
354 condition, five product streams (Figure 3-A) were obtained, i.e., gas, liquid, solid, and  $H_2S$  and  $H_2O$   
355 estimated using equations 9 and 10.

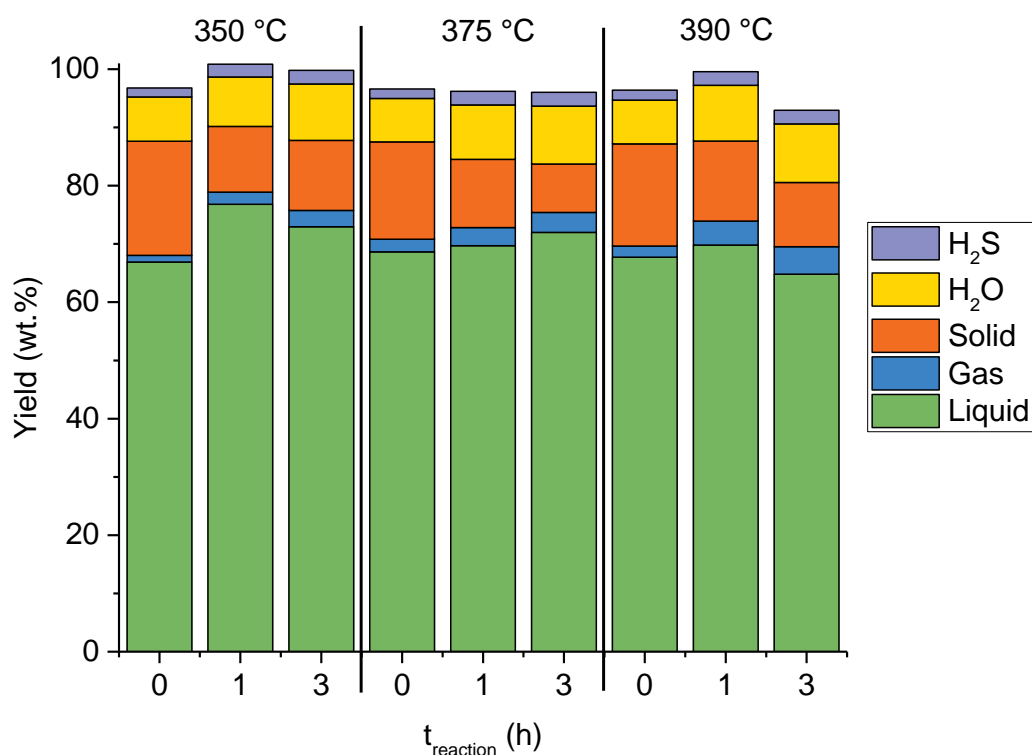
### 356 **3.2.1. Solid product**

357 The solid product, which was determined through the difference in the catalyst weight before and  
358 after the reaction (equation 7), was found to decrease as a function of the reaction time. Indeed, for  
359 the  $t = 0$  h experiments, the solid fraction yield was  $\approx 16.7 - 19.6$  wt.%, while the solid yield decreased  
360 to  $\approx 9 - 12$  wt.% for longer residence time. It should be mentioned that no solid matter other than the  
361 spent catalyst was found in the reactor. Consequently, at least part of the solid product is represented  
362 by heavy asphaltene-like products that can be converted under the reaction conditions but are not  
363 soluble in heptane and stay with the catalyst after the reaction. Table S6 contains the carbon loading  
364 of the spent catalyst after the reaction, showing that higher reaction time and temperatures lead to  
365 lower carbon deposition on the catalyst's surface. Furthermore, at the temperature of  $375^\circ C$  and  $390$   
366  $^\circ C$  after 3 h, the carbon deposition on the spent catalyst was  $\approx 5$  wt.%, which is compatible with the  
367 typical coke loadings observed in the early stages of operating HDT catalysts<sup>36</sup>. Hence, the crude oil  
368 feedstock did not lead to enhanced deactivation by coke deposition of the sulfided catalyst, as  
369 observed for HTL crude oils from other sources, like sewage sludge<sup>37</sup>.

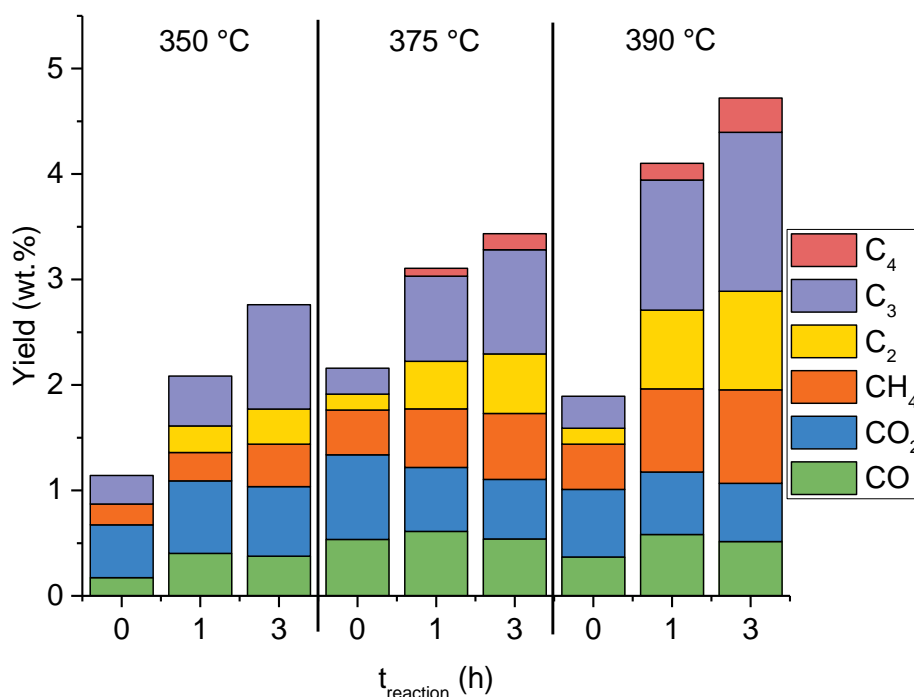
### 370 **3.2.2. Gas product**

371 The yield and composition of the gas products are shown in Figure 3-B. In general, the yield of gas  
372 increases with the reaction temperature and reaction time, achieving a maximum of 4.7 wt.% for the  
373 reaction conditions of  $390^\circ C$  and 3 h. Still, the yield of gas products like CO and  $CO_2$ , which result from  
374 decarboxylation and decarbonylation reactions, was found to stay constant, between 0.4-0.6 wt.%  
375 and 0.6 – 0.8 wt.%, respectively, after 1 h of reaction independently of the temperature (Figure 3-B).  
376 The low yield of CO and  $CO_2$  is attributed to the minor contribution of aliphatic C-O, methoxy, and acid  
377 groups in the crude oil (Table 2). Indeed, the oxygen in the crude oil was primarily eliminated as  $H_2O$ ,

378 whose yield is between 7.5 wt.% and 10.0 wt.%. Light hydrocarbons, like CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> (C<sub>2</sub>), C<sub>3</sub>H<sub>8</sub> (C<sub>3</sub>), and  
 379 C<sub>4</sub>H<sub>10</sub> (C<sub>4</sub>), were the main compounds responsible for the gas yield increase observed at higher  
 380 temperature and reaction time (Figure 3-B). While the formation of light hydrocarbons can be  
 381 explained by C-C bond cleavage caused by hydrogenolysis, which is favored at higher temperatures,  
 382 heptane hydrogenolysis does not seem to contribute significantly to the gas products since the  $\frac{C_3}{C_4}$  ratio  
 383 is significantly higher than 1 (Figure 3-B). Instead, light hydrocarbons most likely result from the  
 384 cleavage of larger molecules from the crude oil during the hydrotreatment reaction. However, it is  
 385 worth mentioning that, after 3 h of reaction, the O content in the liquid product is quite low for the  
 386 catalytic tests performed at 375 °C and 390 °C (Figure 4), and the contribution of light hydrocarbons  
 387 to the gas yield is significantly higher at 390°C. Hence, the occurrence of C-C hydrogenolysis and its  
 388 contribution to the gas yield cannot be discarded entirely.



389  
 390



391

392 Figure 3. A) Product yields, determined according to equations 6 to 10, obtained from the HDT of the  
 393 lignite HTL crude oil. B) Gas products yield as a function of reaction temperature and time, obtained  
 394 from the HDT of the lignite HTL crude oil.

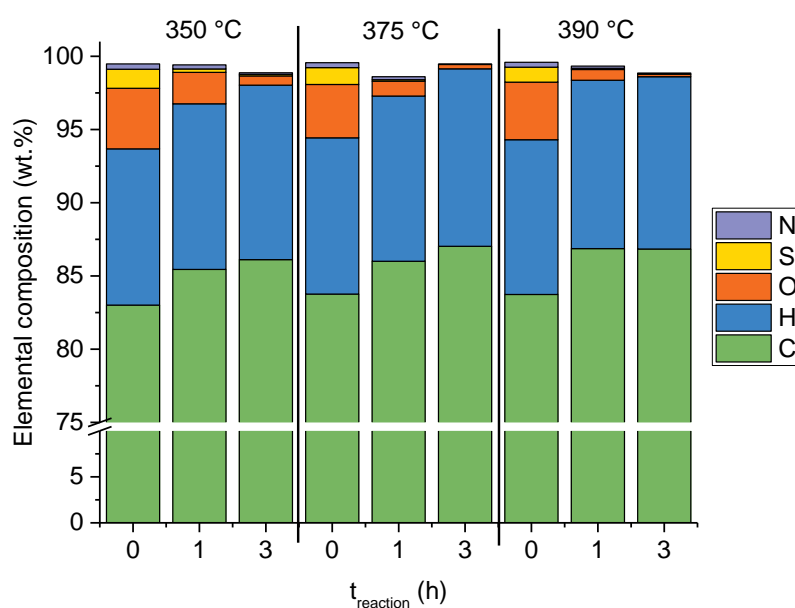
395

### 396 3.2.3. Liquid product

397 After upgrading, the liquid product yield varied between 65 wt.% and 77 wt.% depending on the  
 398 reaction temperature and time (Figure 3-A). In all cases, the liquid yield was higher after 1 h of reaction  
 399 as compared to  $t_{\text{reaction}} = 0$  h, which agrees with the hypothesis previously stated on the conversion of  
 400 solid products existing at the early stages of the reaction (section 3.2.1). After 3h of reaction, the liquid  
 401 produced stabilized at 375 °C or slightly decreased at 350 °C and 390 °C due to the lower amount of  
 402 solid converted in this time (Figure 3-A and Table S6) and the HDT reactions.

403 The elemental composition of the HDT liquid product is shown in Figure 4. When compared with the  
 404 crude oil feedstock (Table 2), the HDT liquid products contained a higher concentration of carbon and  
 405 hydrogen (Figure 4) even at  $t_{\text{reaction}} = 0$  h. Similarly, the concentration of heteroatoms in the liquid  
 406 product was also significantly smaller at  $t_{\text{reaction}} = 0$  h than on the parent crude oil sample, with

407 deoxygenation, denitrogenation, and desulfurization in the range of 60%, 30% and 50% respectively  
 408 (Tables S7 to S9). It should be mentioned during heating, H<sub>2</sub> pressure is reduced (10 bar, at room  
 409 temperature) and that heating up to the reaction temperature takes 20 min. Thus, the significant  
 410 elimination of heteroatoms during heating suggests these be easily removable under relatively mild  
 411 conditions or by thermal degradation. Furthermore, HDO, HDS, and, to a lesser extent, HDN (Tables  
 412 S7 to S9) significantly increased with the reaction time, reaching above 94 %, 96 %, and 78%,  
 413 respectively, after 3 h of reaction. High denitrogenation levels requires a higher temperature 390 °C,  
 414 HDN rate was significantly favored at higher temperatures. The efficient removal of heteroatoms  
 415 suggests that the hetero-compounds in the crude oil feedstock are not in the form of refractory  
 416 compounds, i.e., polyaromatic sulfur and nitrogen compounds<sup>38</sup>, as indicated by Liu et al.<sup>35</sup>. It is  
 417 relevant to mention that most HTL crude oils from bio-sourced feedstocks, like algae, food waste, and  
 418 sewage sludge, require two stages of upgrading to remove heteroatoms effectively<sup>23,39,40</sup>. Yet, nearly  
 419 all lignite crude oil's sulfur, nitrogen, and oxygen were removed after a single hydrotreatment step on  
 420 NiMoS/P-Al<sub>2</sub>O<sub>3</sub> catalyst. Still, in the best-case scenario, 30 ppm of sulfur was found in the liquid,  
 421 indicating further desulfurization via a second HDT stage, harsher conditions, or blending is necessary  
 422 to meet the minimum requirements of a drop-in fuel from lignite crude oil.



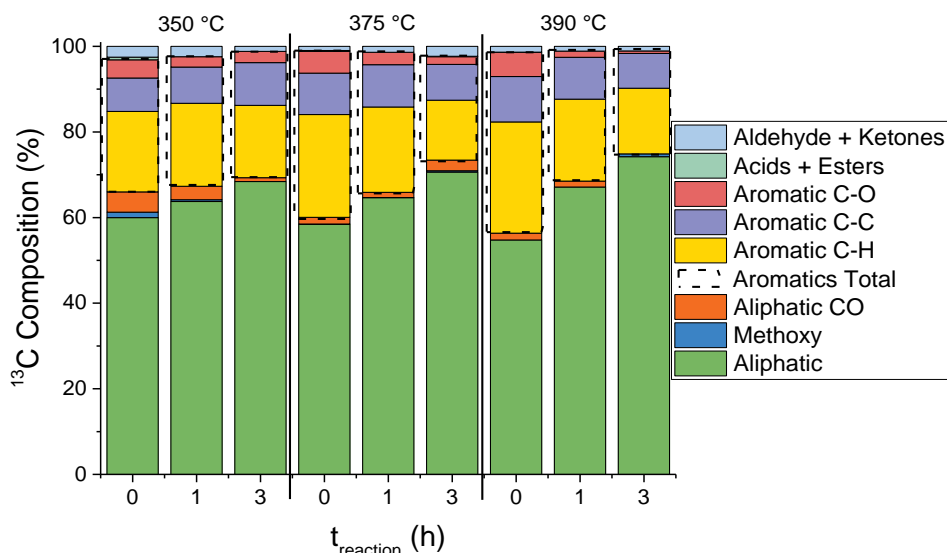
423

424 Figure 4. Elemental analysis of the liquid product obtained from HDT of lignite crude oil at different  
425 reaction temperatures (350 °C, 375 °C, and 390 °C) and reaction times ( $t_{\text{reaction}}$ ).

426

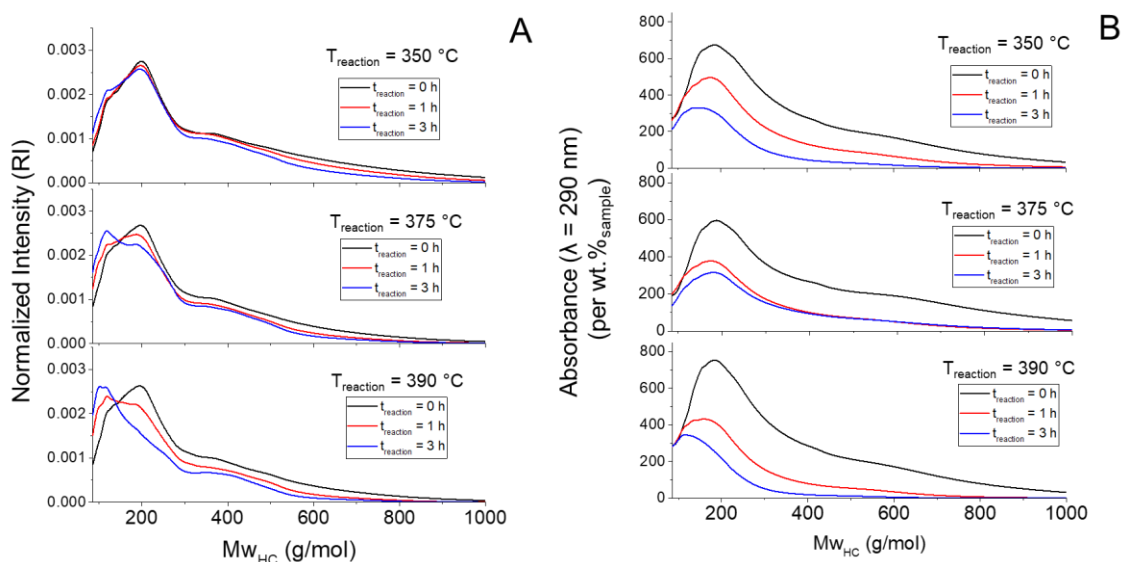
427 The evolution of the functional groups upon HDT, determined by  $^{13}\text{C}$  NMR, is shown in Figure 5. In  
428 comparison with the crude oil, the distribution of the functional groups of the liquid product clearly  
429 shows a significant increase in the aliphatic carbon, i.e., from 40.1%, in crude oil, to 54.8 – 74.2% in  
430 the liquid, accompanied by a reduction of the aromatic carbon, i.e., 54.3% to 42.3 – 24.0%. When  
431 comparing the HDT liquids composition obtained at  $t_{\text{reaction}} = 0$  h, it can be observed that the  
432 concentration of aromatic C-H and C-C increases with temperature. In contrast, the occurrence of  
433 functional groups containing oxygen and aliphatic C follows the opposite trend (Figure 5). The increase  
434 of aromatic carbon in the liquid with the reaction temperature for  $t_{\text{reaction}} = 0$  h suggests that thermal  
435 phenomena cause transformations during reactor heating. Indeed, the UV absorption at  $\lambda=290$  nm  
436 (Figure 6-B), characteristic of polyaromatic compounds, which can be formed by unstable products in  
437 the crude oil during heating, clearly increases as a function of temperature for  $T = 0$  h. As the reaction  
438 time increases, the concentration of aliphatic C increases together with a reduction of aromatic C as a  
439 consequence of hydrogenation, as confirmed by the H/C ratio increase from  $\approx 1.5$  at 0 h to  $>1.6$  after  
440 3 h for reaction (Figure 4). Additionally, the  $\frac{C_{\text{Aliphatic}}}{C_{\text{Aromatic}}}$  ratio increases more with the reaction time for  
441 higher temperatures due to the faster kinetics of the HDT reactions promoted by the catalyst. While  
442 HDT significantly reduced the aromatic C-H bonds concentration, the concentration of aromatic C-C  
443 only decreased slightly at 375 °C and 390°C and even increased at 350 °C (Figure 5). Additionally, the  
444  $\frac{C-C_{\text{Aromatic}}}{C_{\text{Aromatic}}}$  . 6 (where 6 refers to the number of carbon atoms in one aromatic ring), which accounts  
445 for the average number of C-C<sub>Aromatic</sub> bonds per aromatic ring, increased from 1.5 at 0 h to 2.0 after 3  
446 h of reaction. It should be mentioned that aromatic C-C bounds can result from polyaromatic  
447 hydrocarbons, partially hydrogenated polycyclic-aromatics, like tetraline, and alkylated aromatics,  
448 such as toluene. Aromatic ring hydrogenation in polyaromatic compounds decreases for each ring  
449 already hydrogenated in the molecule<sup>38,41,42</sup>. Indeed, our previous work screening the upgrading of

450 various HTL oils has already demonstrated that lignite crude oils were particularly rich in aromatic  
 451 compounds, which results in a significant concentration of naphthenes and cyclic monoaromatic  
 452 compounds after HDT<sup>43</sup>.



453  
 454 Figure 5. <sup>13</sup>C functional group composition of the liquid product obtained from HDT of lignite crude oil  
 455 at different reaction temperatures (350 °C, 375 °C, and 390 °C) and reaction times ( $t_{\text{reaction}}$ ).

456



457  
 458 **Figure 6.** A) Liquid product molecular weight ( $Mw_{\text{HC}}$ ) distribution determined by refraction index (RI),  
 459 and B) UV absorbance ( $\lambda = 290 \text{ nm}$ ) as a function of the compounds Mw. A hydrocarbon mixture with  
 460 Mw comprised between 86 g/mol and 1000 g/mol was used as a standard to determine  $Mw_{\text{HC}}$ .

461

462 The molecular weight ( $M_{w_{HC}}$ ) distribution of the HDT liquid products is shown in Figure 6A. At low  
463 reaction time, the  $M_{w_{HC}}$  distribution presented a maximum centered at  $\approx 200$  g/mol and a maximum  
464 molecular weight of 1 000 g/mol. As the reaction time increased, the compounds centered at 200  
465 g/mol progressively decreased as a new group of compounds centered at  $\approx 120$  g/mol appeared.  
466 Similarly, the higher molecular weight compounds progressively disappeared, and at 390 °C after 3 h  
467 of reaction, no compounds above 800 g/mol were detected. Indeed, the degree of  $M_{w_{HC}}$  reduction  
468 observed in the liquid products after HDT highly depended on the reaction time and temperature,  
469 with the average  $M_{w_{HC}}$  (Table S10) ranging from 243 g/mol to 160 g/mol. The average molecular  
470 weight of the liquid products is reported in Table S10.

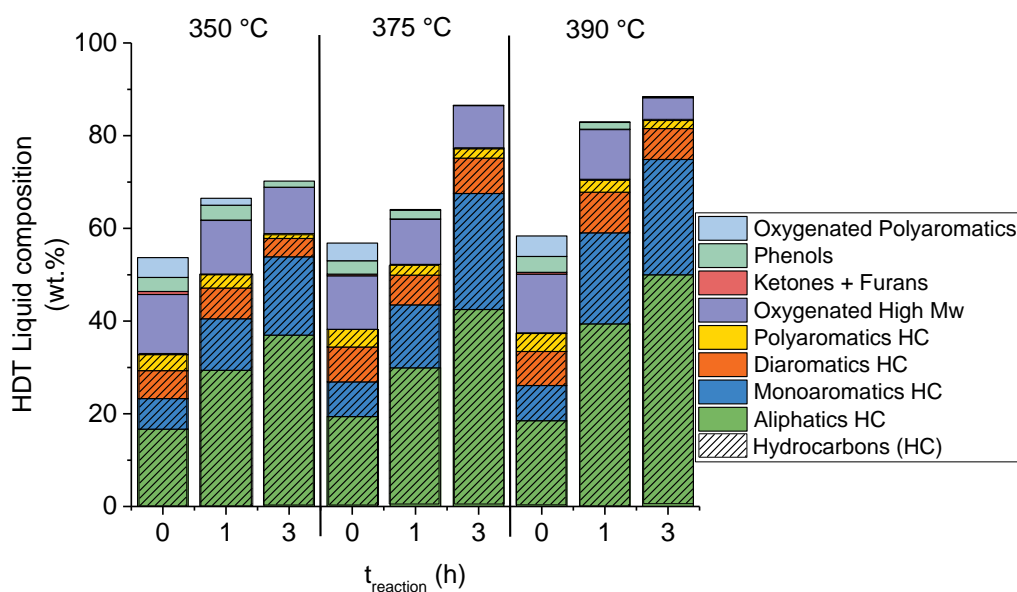
471 The removal of the heteroatom elements, i.e., O, N, and S, is considered to be the main responsible  
472 for the significant  $M_{w_{HC}}$  reduction since the cleavage of C-C bonds via hydrogenolysis is not  
473 predominant under the reaction conditions used in this study.

474 Figure 6B shows the absorbance at  $\lambda=290$  nm, characteristic of conjugated polyaromatic compounds,  
475 as a function  $M_{w_{HC}}$ . The absorbance decreases as a function of the reaction time due to the full or  
476 partial hydrogenation of the polyaromatic compounds. Still, Figure 6B clearly shows that  
477 polyaromatics undergo faster conversion in the first hour of a reaction than in the subsequent 2 h, a  
478 phenomenon explained by the more straightforward conversion of certain compounds in the oil. Also,  
479 at all temperatures, the UV absorption for  $M_{w_{HC}} > 300$  g/mol decreases fast during HDT, with nearly all  
480 polyaromatics in this range being converted at  $T = 390$  °C after 3 h of reaction. However, the refraction  
481 index detector (RID – Figure 6A) clearly shows that the amount of compounds with a  $M_{w_{HC}} > 300$   
482 g/mol are only reduced slightly during HDT. The difference between the two detectors suggests that  
483 higher  $M_{w_{HC}}$  polyaromatic compounds undergo hydrogenation faster. Indeed, Korre et al. studied the  
484 hydrogenation kinetic of multiple polyaromatic compounds identifying that the higher the number of  
485 conjugated rings, the faster the hydrogenation reaction rate<sup>44</sup>.

486 The composition of the liquid product, quantified by comprehensive GC×GC/FID (Figure 7), shows a  
487 progressive increase in the concentration of aliphatic and mono-aromatic hydrocarbon under harsher  
488 reaction conditions, as already suggested by <sup>13</sup>C NMR (Figure 5), SEC-DAD (Figure 6B), and elemental  
489 analysis (Figure 4) results. At the same time, the oxygenated compounds, such as phenols, ketones,  
490 furans, and other high molecular weight compounds, are progressively transformed. Furthermore, the  
491 concentration of compounds in the comprehensive GC×GC-FID analysis detection range, i.e., up to  
492 ≈C<sub>40</sub>, progressively increased with HDT reaction time and temperature, which is a consequence of the  
493 reduction of the Mw of the samples (Figure 6A). At 390 °C and 3 h of reaction, 88.4 wt.% of the HDT  
494 liquid product composition was quantified, with aliphatic and monoaromatic hydrocarbon, mainly  
495 composed of naphthenes and partially hydrogenated aromatics, respectively, contributing to ≈75%  
496 of the sample. Additionally, 9 wt.% of the liquid was composed of polyaromatic hydrocarbons with  
497 two or more aromatic rings. The high concentration of cyclic hydrocarbons in the liquid is a direct  
498 consequence of the aromatic nature of the products in the crude oil and, by extension, in lignite.  
499 Indeed, in our previous work, we demonstrated that the nature of the feedstock was crucial in  
500 determining the composition of the HDT liquid product and that lignite led to an HDT liquid rich in  
501 cyclic hydrocarbons<sup>43</sup>.

502 As mentioned before, lignite crude oil was already transformed during the 20 min heating stage of the  
503 reactor, as easily observable by the comprehensive GC×GC's significant compound detection boost,  
504 i.e., 16.7 wt.% to >56.7 wt.%. While the increase in aromatic content in the liquid showed that thermal  
505 phenomena caused at least part of the transformation, the rise in detectable aliphatic and  
506 monoaromatic hydrocarbon compounds suggests that catalytic HDT was also responsible for the  
507 transformation of the feedstock during the heating stage, indicating that lignite crude oil can undergo  
508 significant heteroatoms removal, even under relatively mild conditions.





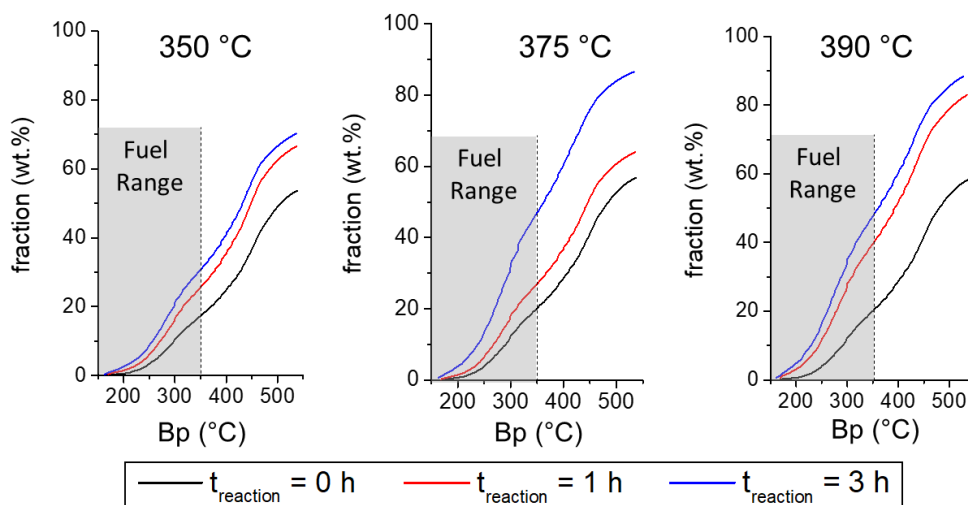
509

510 Figure 7. Composition of HDT liquid as a function of the reaction temperature (350 °C, 375 °C, and 390  
 511 °C) and reaction time ( $t_{\text{reaction}}$ ) detected by GCxGC-TOFMS and quantified by GCxGC-FID

512

513 The distillation curves for the HDT liquid products are shown in Figure 8. As expected SEC results, the  
 514 number of products in the fuel range increases with the reaction temperature and time. While at 0h,  
 515 the fuel range products concentration is quite similar at all temperatures (17-20 wt.%), fuel yield  
 516 quickly rises with the reaction time (Table S11). It is worth mentioning that oxygenated products, like  
 517 phenols, are present in the fuel product in all cases, except for the experiments performed at 375°C  
 518 and 390 °C after 3 h of reaction, which are exclusively composed of hydrocarbon molecules.  
 519 Additionally, diaromatic hydrocarbons are present in all cases and makeup  $\approx$  5 wt.% of the fuel range  
 520 products obtained at 375°C and 390 °C after 3 h of reaction. Additionally, the maximum fuel yield  
 521 obtained at 375°C and 390°C was 47.0 wt.% and 47.6 wt.%, respectively, showing that increasing the  
 522 HDT temperature has little effect on the overall fuel yield after the elimination of most heteroatoms

523 (Figure 4). Still, a slight variation in the composition of the fuel range products was observed (Tables  
 524 S12 and S13), with the test at 375°C yielding more products, i.e., 33.5 wt.% Vs 30.8 wt.%, in the middle  
 525 distillates range (Bp between 250°C and 350°C) and the test at test at 390°C being more selective for  
 526 kerosene (Bp between 175°C and 250 °C), i.e., 14.7 wt.% Vs. 11.9 wt.%. The increase in lower Bp  
 527 products observed at 390 °C might be associated with C-C hydrogenolysis, favored by a higher  
 528 temperature.



529

530 Figure 8. Distillation curve of the hydrotreatment liquid product as a function of reaction time ( $t_{\text{reaction}}$ ).  
 531 Fuel range: Bp < 350°C.

532

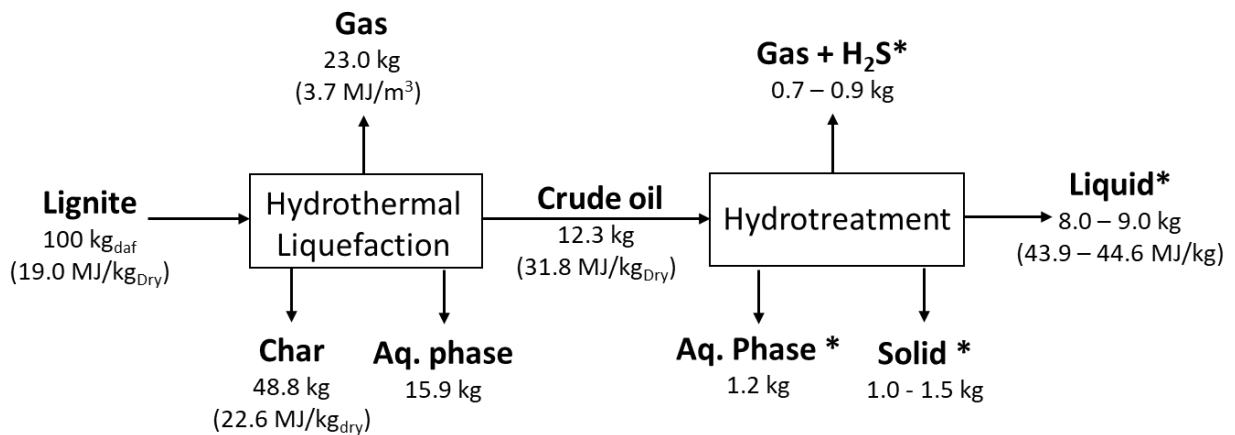
#### 533 4. CONCLUSION

534 In several European countries, gross electricity is partly generated by the combustion of lignite. Here,  
 535 we propose diverting one fraction of the lignite to produce kerosene and diesel through a HTL and  
 536 single-stage HDT sequence. The overall mass balance of the process, shown in Figure 9, indicates that  
 537 the HDT liquid yield obtained from lignite under the HTL and HDT conditions used in this study is 8-9  
 538 wt.% and 47 wt.% of HDT liquid products have a boiling point in the range of standard fuels, i.e., Bp <  
 539 350°C (Figure 8). The unsatisfactory production of crude oil during HTL, i.e., 12.3%, is responsible for  
 540 the low overall conversion of lignite into fuel. Indeed, the HDT liquid yield obtained in this study, i.e.,

541 65-73 wt.%, was comparable to that in the literature when upgrading HTL biocrudes produced from  
 542 different feedstocks<sup>45-49</sup>. The low crude oil yield can be explained by the experimental conditions used  
 543 in the HTL process, as Liu et al. were able to increase the crude oil production to 34 wt.% by using a  
 544 lower HTL reaction time (5 min) and higher temperature (440 °C). Additionally, the use of catalysts<sup>50</sup>  
 545 and recycling the aqueous phase<sup>51</sup> are known to increase crude yield during HTL. Therefore, adequate  
 546 process optimization can orient a more significant fraction of lignite towards fuel generation.

547

548



549

550 Figure 9. Block flow diagram of the transformation of lignite through hydrothermal liquefaction (HDT)  
 551 and subsequent hydrotreatment of the HTL crude oil. Mass basis = 100 kg of dry ash-free lignite (kg<sub>daf</sub>).  
 552 The values in brackets refer to the calorific value of the respective streams and were determined by  
 553 using the expression from <sup>52</sup>. \*values determined using the data from HDT performed during 3 h at  
 554 temperatures of 375°C and 390°C (Figures 3-A and 4).

555

556 The hydrotreatment experiments showed lignite's crude oil to be quite easily hydrotreated. Near  
 557 complete heteroatom removal was attained with a single HDT stage and using a milder pseudo-WHSV  
 558 (equation 5) than those reported in the literature for pilot-scale bio-based crude oil HDT<sup>47,53</sup>. After  
 559 HDT, despite a significant improvement in fuel quality, i.e., heteroatom removal and hydrogenation,  
 560 substantial amounts of aromatic compounds, particularly monoaromatic and diaromatic compounds  
 561 (≈45% of fuel range products), are still present in all products. This suggests that further upgrading or

562 harsher conditions, i.e., higher contact time and H<sub>2</sub> pressure, are required. Indeed, aromatics have low  
563 cetane numbers, which can be detrimental for using the middle distillate in diesel fuels<sup>54</sup>. In addition  
564 to decreasing the aromatic content in the liquid product, our results showed that harshening HDT  
565 conditions did not significantly augment the fuel range products, suggesting that subsequent  
566 hydrocracking or using an HDT catalyst with acid properties might be necessary. Nevertheless, the  
567 crude oil obtained from the hydrothermal liquefaction of lignite has an excellent potential for  
568 producing hydrocarbon fuels, particularly when compared with other feedstocks typically used in the  
569 HTL process, like sewage sludge and algae<sup>39,55</sup>. Finally, it is important to mention that the presence of  
570 this aromatic fraction can be a benefit, acting as a polar solvent in the case of co-processing between  
571 HTL of lignite and less proper biogenic feedstocks, such as biomass or sewage sludge.

572 While lignite is not a green feedstock, its easily upgradable products obtained during HTL can be  
573 beneficial under mixed hydrothermal liquefaction with greener feedstocks, like lignocellulosic  
574 biomass, sewage sludge or algae, which yield crude oils more difficult to upgrade as proposed, for  
575 instance, by Wang et al.<sup>56</sup>. Indeed, it was shown that the hydrothermal liquefaction of a mixture of  
576 Jingou lignite, wheat straw, and plastic waste could provide a synergetic effect on oil yields. Synergetic  
577 effects were also observed in the co-liquefaction of coal and polymers (polypropylene and  
578 polystyrene) by Y. Shen et al.<sup>57</sup>. Finally, it is worth mentioning that the char from lignite HTL can be  
579 further used for electricity production, the original purpose of lignite.

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## 581 **5. Acknowledgements**

582 The authors gratefully acknowledge the financial support of the European Commission Research  
583 Programme of the Research Fund for Coal and Steel for the project HyCon (Grant agreement: 899471).  
584 In the case of Polish authors, this scientific work is published as part of an international project co-  
585 financed by the program of the Ministry of Science and Higher Education entitled "PMW" in the years  
586 2020 -2023 agreement No. 5157/FBWiS/2020/2021/2

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