

Lignite and Biomass Waste Hydrothermal Liquefaction Crude Upgrading by Hydrotreatment

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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-04170031

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
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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 (and in the world) and deeply impacted the food and energetic markets and climate issues ¹. For 31 32 instance, the European Union (E.U.) is the first market for diesel fuel and must import 20% of its consumption. Half of this imported diesel was coming from Russia. Despite E.U. policy attempts to 33 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 2024². 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 generation³. 40 Even if its production has strongly decreased since the 90's in Europe, the inland consumption of brown coal by E.U. member states was estimated, in 2021, at 300 Mt⁴. An alternative pathway to 41 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 or gazification⁵⁻⁷. These studies led to the establishment of the hydrothermal dewatering (HTD) 47 48 process, a pretreatment (developed at pilot scale) of lignite with no particular address regarding the crude oil formed ⁸. This was only tackled more recently by Hartman et al., which investigated the HTL 49 50 of selected coal feedstocks providing a high liquid yield (21%) and concluded that high-value petroleum-like products could be obtained ⁹. Liu et al. used HTL as a pretreatment before pyrolysis of 51 Xiaolongtan lignite and suggested three reaction steps discussed hereafter¹⁰. Like HTL of biomass, 52 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 these can impact the liquid yield and composition¹¹. They also suggested that HTL promotes the transfer from polycyclic aromatic hydrocarbons to monocyclic aromatic hydrocarbons. All these studies indicate that HTL of lignite can potentially provide some fuel. However, no one attempted to upgrade lignite HTL oil like it was done with the HTL biocrudes of biomass or wastes.

In the present work, we investigated the HTL conversion of a Polish lignite and the catalytic upgrading of the HTL lignite oil obtained. A detailed study of the upgrading operating conditions and their impact on the nature of the products was performed. After upgrading, a diesel fraction was obtained, showing that a preliminary HTL stage can provide a fraction of a diesel source and increase the HHV of the 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 N₂ (~2 bar) and then heated to 360 °C (reaction temperature) with a constant heating rate 10 °C/min and maintained at this 76 77 temperature for 30 min (HTL reaction time). The pressure in the reactor vessel was self-generated.

After completion of the reaction, the autoclave was cooled to ambient temperature, and the gas samples were taken for analysis by micro-GC SRA instruments equipped with the following three modules: MolSieve 5 Å with backflush, PoraPLOT U, and Plot Al₂O₃/KCl. The HTL products mixture (crude oil, aqueous phase, and char) were then recovered from the reaction vessel. The separation of the products mixture obtained after the HTL processes was performed using a vacuum filtration technique. The post-reaction mixture was filtered on glass microfiber filters. The aqueous phase obtained was separated from the char. The reactor vessel and the char were washed with acetone,

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

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Table 1. Physicochemical properties of lignite feedstock.

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

91 ^b 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 Crude oil yield (wt. %) = $\frac{m_{crude}}{m_{lignite}}$ 100 97 Equation 1 98 Char yield (wt. %) = $\frac{m_{char}}{m_{lignite}}$ 100 99 Equation 2 Gas yield (wt. %) = $\frac{\sum^{i} Mw_{i}y_{i}PV}{RTm_{Lignite}}$ 100 100 Equation 3

101 Aqueous phase solubles yield (wt. %) = 100 - gas yield - char yield - crude oil yield
 102 Equation 4

103

- 104 Where:
- 105 m_{crude}, m_{char}, and m_{lignite} are the mass of recovered crude oil, recovered char, and initial lignite feedstock
- 106 on a dry, ash-free (daf) basis;
- 107 Mw_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 performed under batch conditions using a 300 mL reactor from Parr (Model 4566). The hydrothermal 115 116 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/Al₂O₃ 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 (≈ 700 rpm) and, consequently, facilitate the contact between HTL oil, hydrogen, and catalyst. Before 119 120 reaction, the catalyst was activated through sulfidation carried at 400 °C for 3 h, under a continuous 121 flow (4 L/h) of H_2S (15%) in H_2 . After being sulfided, the catalyst is kept under an inert atmosphere (N_2) 122 until being transferred into the reactor.

123 At room temperature and after flushing with H₂, the reactor was pressurized with 10 bar of H₂ 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 H₂ was introduced into the reactor, reaching a reaction pressure of \approx 100 bar. After the second H₂ introduction in the reactor, the crude oil hydrotreatment was performed 127 128 for 1 h or 3 h leading to a pseudo-WHSV (Equation 5) of 3 h^{-1} and 1 h^{-1} , respectively. Additionally, a test 129 where the reaction was stopped after introducing the 50 bar of H₂ was also performed, denominated 130 t = 0 h, as a reference.

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

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
- a gas bag and analyzed with a micro-GC (SRA instruments) equipped with three modules: Molsieve 5Å
- 137 (H2, CO, CH4), Hayesep A (CO2, C2 hydrocarbons), PLOT Al2O3/KCl (C3-C4 hydrocarbons).

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

The yields of the products obtained from the HDT reaction, i.e., liquid, solid, gas, H₂O, and H₂S were
 calculated through the following equations:

146 Liquid yield (wt. %) =
$$\frac{m_{liquid}}{m_{crude \ oil}} 100$$
 Equation 6
147

148solid yield (wt. %) =
$$\frac{m_{solid}}{m_{crude oil}}$$
100Equation 7149Gas yield (wt. %) = $\frac{\sum^{i} Mw_{i}y_{i}PV}{RTm_{orde oil}}$ 100Equation 8

150
$$H_2O(wt.\%) = (O_{crude\ oil} - Gas\ yield\left(\frac{\%CO}{28} + 2\frac{\%CO_2}{44}\right)16 - Liquid\ yield.\ O_{liquid})\frac{18}{16}$$
 Equation 9
151 $H_2S(wt.\%) = (S_{crude\ oil} - Liquid\ yield.\ S_{liquid})\frac{34}{32}$ Equation 10

- 152
- 153 Where:
- m_{crude oil}, m_{solid}, and m_{liquid} are, respectively, the mass of crude oil to be hydrotreated, the excess of mass found in the catalyst after reaction (m_{spent catalyst}-m_{fresh catalyst}), and the mass liquid obtained after evaporation of n-heptane;
- 157 Mw_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 (≈ 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_{crude oil}) and liquid (O_{liquid}) determined by elemental
- 163 analysis.
- 164 %CO and %CO₂, are the weight fraction of CO and CO₂, respectively, in the gas
- 165 S, is the weight fraction of Sulfur in the crude oil (S_{crude oil}) and liquid (S_{liquid}).
- 166

167 2.3. Characterization methods

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

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

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 HPLC equipped with two PLgel Columns (50 and 500 Å), a refractive index detector (RID), and a diode 178 array detector (DAD). The analysis was carried out at 35 °C using tetrahydrofuran (THF – 1 mL/min) as 179 180 the eluent. Before analysis, the samples were diluted to a concentration of ≈1 wt.% in THF and filtered 181 (0.45 µm). 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_{HC} 183 data.

The ¹³C-NMR analysis of the liquid samples was performed in a Bruker AVANCE 400 MHZ spectrometer and analyzed using the software TopSpin 3.0. The measurements were performed at room temperature with an accumulation of 4700 scans for approximately 15 h. The samples (≈100 mg) were diluted with deuterated chloroform (CDCl₃) (0.6 mL). Table S2 includes the chemical shifts attributed to each functional group.

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

and TOF parameters are described in Tables S3 and S4. The GC×GC/FID was equipped with a switch valve modulator (Agilent G3486A CFT modulator), and modulation parameters were optimized according to ref ¹². The parameters used for product separation are described in Table S3. The quantification of the compounds detected by GC×GC-FID was performed using the relative responsive factor method (RRF)¹³ with cyclohexanol as the reference. The data obtained from comprehensive GCxGC-FID was also used to provide the distillation curve of the HDT liquid products by using a mixture of n-alkanes (C₇ to C₄₀) 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 was transformed into this product with char (48.8 wt.%daf), gas (23wt.% daf), and aqueous phase 204 205 organics (15.9 wt.%daf) representing the main fractions. Liu et al. ²¹ studied the optimal conditions for maximizing crude oil yield from lignite HTL and found that short residence times, i.e., ~5 min, and high 206 temperatures, i.e., ~400 °C, are necessary. In this study²¹, the authors found a maximum crude yield 207 of 34 wt.%. Hence, the high residence time (30 min) and low temperature (360 °C) presently used can 208 explain the low crude oil yield. Another important parameter known to affect the yield and quality of 209 crude oil in HTL is the amount of ash ^{25–29}. On biogenic feedstocks, such as algae, high ash contents 210 have been reported to decrease the yield and quality of the crude product ^{25–27}. Although no reference 211 applied to the conversion of lignite under HTL conditions was found, a direct analogy with biomass 212 213 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.%). Indeed, Liu et al. ²¹ used lignite with 7.14 wt.% of ash. It should be mentioned that Oner et al. 215 216 demonstrated that ash positively enhances the crude oil product in lignite liquefaction under organic solvents, like tetraline, and under H₂ pressure ³⁰. However, the positive effects were attributed to the 217 capacity of certain elements in ash to promote hydrogenation by H₂ or hydrogen transfer from the 218

solvent, a reaction not likely to occur under HTL conditions. While ash is bound to affect lignite HTL conversion, the chemical composition of lignite and lignite's ash is substantially different from that of biomass feedstocks like algae. Thus, further studies, out of the scope of this work, should be 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 fuels³¹. Still, nitrogen compounds impact other regulated properties, such as gum content, storage 231 stability, and thermal stability ³³. However, synthetic aviation fuels (SAF) have a nitrogen concentration inferior to 2 ppm³². It is worth mentioning that there is still no regulation concerning 232 233 HTL-derived fuels.

234 The functional group's composition, determined by ¹³C 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 lignites³⁴, 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 diols³⁵. In the same study, authors characterized the sulfur-containing compounds, 252 mostly ranging above C₂₀ and associated in the same molecule with another S or several O atoms. ³⁵. 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⁺ using a Simdis chromatography 256 method equivalent to ASTM D2887 reveals that such molecules have a retention time higher than 257 hexatriacontane (C_{36} - 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 GC×GC detected compounds in the crude oil (Figure 1).

Composition		Carbon chemical composition (¹³ C NMR) ^a	
C (wt.%)	77.7±0.1		53.6
H (wt.)	8.9 ± 0.3	C _{Methoxy} (-O-CH ₃₎	0.1
O (wt.%)	10.8 ± 1.0	C _{Aliphatic-O} (-O-(CH ₂) _n)	0.8
S (ppm)	2.4 ± 0.1	Caromatic	40.3
N (ppm)	0.5 ± 0.1	C _{Carboxylic} /Amide	0.8
TAN (mgкон/g)	29.2 ± 0.2	CAldehyde/Ketone	4.4
HHV (MJ/kg)	31.8		

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

²61 ^aChemical shift range in Table S1 and NMR spectra in Figure S2



262

1st Column retention time (min)

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

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

Compounds	Oil composition	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 Oyxgenated	2.2
Polyaromatic HC	1.2	Aliphatic Oxygenated	6.5



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271

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

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 λ > 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 λ (Figures S6 and S7). Therefore, in the crude 291 oil (Figure 2-A), the wide absorption band at 250 > λ > 400 nm indicates the presence of compounds 292 with at least 3 and 4 conjugated aromatic rings.

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

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298

3.1.2. Char, gas, and aqueous phase

The hydrothermal liquefaction of lignite (soft Miocene lignite) obtained in the Bełchatów coal mine in Poland led to four product streams, i.e., gas, char, crude oil, and an aqueous phase rich in organic 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 MJ/kg_{Dry} vs. 19.0 MJ/kg_{Dry}, respectively. P. Liu and D. Zhang¹⁴ studied the transformation of lignite 306 under hydrothermal conditions, observing that, at T=260 °C, significant removals of oxygen and 307 308 hydrogen occur. Similar observations were made by Z. Shi et al. ¹⁵, 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 CH₂ and CH₃ 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 as CO, CO₂, and light hydrocarbons^{14,15}. Like O and H, the sulfur in char was significantly smaller than 313 314 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 contain more substantial amounts of sulfides and thiols than other types of coal¹⁶, which are more 317 easily transformed under hydrothermal conditions^{17,18}. 318

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

The composition of the gas stream formed during the hydrothermal liquefaction of lignite is shown in Table S5. CO₂ was the majority product in the gas phase, corresponding to 92.6 wt.% of all the produced gases. The high CO₂ selectivity in the gas products obtained from lignite HTL had already been reported previously^{15,21}, indicating that decarboxylation is one of the primary processes responsible for oxygen removal during the reaction. Indeed, CO only represented 1.4 wt.% of the 328 gases, suggesting decarbonylation is significantly less favored. H₂S 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_2S . The significant formation of H_2S reflects the 331 transformation of organic, i.e., thiol and sulfide, and inorganic sulfur, i.e., pyrite, compounds in lignite promoted by H radicals under hydrothermal conditions ^{17,18,22}. In addition to CO₂, CO, and H₂S, small 332 333 amounts of light hydrocarbons and H₂ (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 H₂ formation are not the main ones responsible for the elimination of hydrogen in the lignite as proposed by Z. Shi et al., and P. Liu and D. Zhang ^{14,15}. Instead, the 336 337 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.

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

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345 **3.2. Hydro**

3.2. Hydrotreatment of lignite HTL crude oil

The significant concentration of heteroatoms and polyaromatic compounds in the crude oil stream clearly demonstrates the necessity of further upgrading for the production of hydrocarbon fuels. Therefore, this section will focus on the hydrotreatment of the crude oil stream obtained from the hydrothermal liquefaction of lignite. The hydrotreatment of the lignite crude oil was performed at three different temperatures, i.e., 350 °C, 375 °C, and 390°C, and at two different reaction times, 1 h and 3 h. An additional residence time, where the reaction was stopped after the reaction temperature was attained (t_{heating} = 20 min), designated t = 0 h, was also performed at each temperature. The crude oil conversion occurring before t = 0 h are caused primarily by thermal processes. For each operating
 condition, five product streams (Figure 3-A) were obtained, i.e., gas, liquid, solid, and H₂S and H₂O
 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 –19.6wt.%, 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 spent catalyst was found in the reactor. Consequently, at least part of the solid product is represented 361 362 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 °C and 390 366 °C after 3 h, the carbon deposition on the spent catalyst was \approx 5 wt.%, which is compatible with the typical coke loadings observed in the early stages of operating HDT catalysts³⁶. Hence, the crude oil 367 368 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 ³⁷.

370 **3.2.2.** Gas product

The yield and composition of the gas products are shown in Figure 3-B. In general, the yield of gas increases with the reaction temperature and reaction time, achieving a maximum of 4.7 wt.% for the reaction conditions of 390 °C and 3 h. Still, the yield of gas products like CO and CO₂, which result from decarboxylation and decarbonylation reactions, was found to stay constant, between 0.4-0.6 wt.% and 0.6 - 0.8 wt.%, respectively, after 1 h of reaction independently of the temperature (Figure 3-B). The low yield of CO and CO₂ is attributed to the minor contribution of aliphatic C-O, methoxy, and acid groups in the crude oil (Table 2). Indeed, the oxygen in the crude oil was primarily eliminated as H₂O,

378 whose yield is between 7.5 wt.% and 10.0 wt.%. Light hydrocarbons, like CH_4 , C_2H_6 (C_2), C_3H_8 (C_3), and 379 C_4H_{10} (C₄), 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 bound cleavage caused by hydrogenolysis, which is favored at higher temperatures, heptane hydrogenolysis does not seem to contribute significantly to the gas products since the $\frac{C_3}{C_4}$ ratio 382 is significantly higher than 1 (Figure 3-B). Instead, light hydrocarbons most likely result from the 383 384 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.





391

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

395

396 **3.2.3.** Liquid product

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

The elemental composition of the HDT liquid product is shown in Figure 4. When compared with the crude oil feedstock (Table 2), the HDT liquid products contained a higher concentration of carbon and hydrogen (Figure 4) even at $t_{reaction} = 0$ h. Similarly, the concentration of heteroatoms in the liquid product was also significantly smaller at $t_{reaction} = 0$ 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_2 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 compounds, i.e., polyaromatic sulfur and nitrogen compounds³⁸, as indicated by Liu et al.³⁵. It is 416 417 relevant to mention that most HTL crude oils from bio-sourced feedstocks, like algae, food waste, and sewage sludge, require two stages of upgrading to remove heteroatoms effectively^{23,39,40}. Yet, nearly 418 419 all lignite crude oil's sulfur, nitrogen, and oxygen were removed after a single hydrotreatment step on 420 NiMoS/P-Al₂O₃ 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.



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

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The evolution of the functional groups upon HDT, determined by ¹³C NMR, is shown in Figure 5. In 427 428 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 $t_{reaction} = 0$ h, it can be observed that the concentration of aromatic C-H and C-C increases with temperature. In contrast, the occurrence of 432 functional groups containing oxygen and aliphatic C follows the opposite trend (Figure 5). The increase 433 434 of aromatic carbon in the liquid with the reaction temperature for $t_{reaction} = 0$ h suggests that thermal 435 phenomena cause transformations during reactor heating. Indeed, the UV absorption at λ =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 consequence of hydrogenation, as confirmed by the H/C ratio increase from ≈1.5 at 0 h to >1.6 after 439 3 h for reaction (Figure 4). Additionally, the $\frac{C_{Aliphatic}}{C_{Aromatic}}$ ratio increases more with the reaction time for 440 441 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 $\frac{c-c_{aromatic}}{c}$. 6 (where 6 refers to the number of carbon atoms in one aromatic ring), which accounts 444 $C_{Aromatic}$ 445 for the average number of C-C_{Aromatic} bonds per aromatic ring, increased from 1.5 at 0 h to 2.0 after 3 h of reaction. It should be mentioned that aromatic C-C bounds can result from polyaromatic 446 hydrocarbons, partially hydrogenated polycyclic-aromatics, like tetraline, and alkylated aromatics, 447 448 such as toluene. Aromatic ring hydrogenation in polyaromatic compounds decreases for each ring already hydrogenated in the molecule ^{38,41,42}. Indeed, our previous work screening the upgrading of 449

various HTL oils has already demonstrated that lignite crude oils were particularly rich in aromatic
 compounds, which results in a significant concentration of naphthenes and cyclic monoaromatic
 compounds after HDT⁴³.



453

454 Figure 5. ¹³C 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 ($t_{reaction}$).

456



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

The molecular weight (Mw_{HC}) distribution of the HDT liquid products is shown in Figure 6A. At low 462 463 reaction time, the Mw_{HC} distribution presented a maximum centered at ≈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 ≈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 Mw_{HC} reduction 468 observed in the liquid products after HDT highly depended on the reaction time and temperature, with the average Mw_{HC} (Table S10) ranging from 243 g/mol to 160 g/mol. The average molecular 469 470 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 Mw_{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 λ =290 nm, characteristic of conjugated polyaromatic compounds, 475 as a function Mw_{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 Mw_{HC} > 300 g/mol decreases fast during HDT, with nealy 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 $Mw_{HC} > 300$ 482 g/mol are only reduced slightly during HDT. The difference between the two detectors suggests that 483 higher Mw_{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 rate⁴⁴.

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 ¹³C 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 $\approx C_{40}$, 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 cyclic hydrocarbons⁴³. 501

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



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Figure 7. Composition of HDT liquid as a function of the reaction temperature (350 °C, 375 °C, and 390
°C) and reaction time (t_{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 ≈ 5 wt.% of the fuel range products obtained at 375°C and 390 °C after 3 h of reaction. Additionally, the maximum fuel yield 520 521 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 (Figure 4). Still, a slight variation in the composition of the fuel range products was observed (Tables S12 and S13), with the test at 375°C yielding more products, i.e., 33.5 wt.% Vs 30..8 wt.%, in the middle distillates range (Bp between 250°C and 350°C) and the test at test at 390°C being more selective for kerosene (Bp between 175°C and 250 °C), i.e., 14.7 wt.% Vs. 11.9 wt.%. The increase in lower Bp products observed at 390 °C might be associated with C-C hydrogenolysis, favored by a higher temperature.



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

532

533 **4. CONCLUSION**

In several European countries, gross electricity is partly generated by the combustion of lignite. Here, we propose diverting one fraction of the lignite to produce kerosene and diesel through a HTL and single-stage HDT sequence. The overall mass balance of the process, shown in Figure 9, indicates that the HDT liquid yield obtained from lignite under the HTL and HDT conditions used in this study is 8-9 wt.% and 47 wt.% of HDT liquid products have a boiling point in the range of standard fuels, i.e., Bp < 350°C (Figure 8). The unsatisfactory production of crude oil during HTL, i.e., 12.3%, is responsible for 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^{45–49}. 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 catalysts⁵⁰ 545 and recycling the aqueous phase⁵¹ are known to increase crude yield during HTL. Therefore, adequate 546 process optimization can orient a more significant fraction of lignite towards fuel generation.

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548



549

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

555

The hydrotreatment experiments showed lignite's crude oil to be quite easily hydrotreated. Near complete heteroatom removal was attained with a single HDT stage and using a milder pseudo-WHSV (equation 5) than those reported in the literature for pilot-scale bio-based crude oil HDT^{47,53}. After HDT, despite a significant improvement in fuel quality, i.e., heteroatom removal and hydrogenation, substantial amounts of aromatic compounds, particularly monoaromatic and diaromatic compounds (\approx 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 H₂ pressure, are required. Indeed, aromatics have low cetane numbers, which can be detrimental for using the middle distillate in diesel fuels⁵⁴. In addition 563 564 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 producing hydrocarbon fuels, particularly when compared with other feedstocks typically used in the 568 HTL process, like sewage sludge and algae^{39,55}. Finally, it is important to mention that the presence of 569 570 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 biomass, sewage sludge or algae, which yield crude oils more difficult to upgrade as proposed, for 574 instance, by Wang et al. ⁵⁶. Indeed, it was shown that the hydrothermal liquefaction of a mixture of 575 576 Jingou lignite, wheat straw, and plastic waste could provide a synergetic effect on oil yields. Synergetic effects were also observed in the co-liquefaction of coal and polymers (polypropylene and 577 578 polystyrene) by Y. Shen et al.⁵⁷. 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

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

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