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Hydrotreatment of Supercritical Carbon Dioxide Extracts of Hydrothermal Liquefaction Lignocellulosic Biocrude

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4 1 Hydrotreatment of supercritical carbon dioxide extract of hydrothermal
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7 2 liquefaction lignocellulosic biocrude
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40 14 Abstract
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43 15 Raw lignocellulosic biocrude produced by hydrothermal liquefaction and its supercritical carbon
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45 16 dioxide extract (SE) were hydrotreated at 350-405 °C and for 2-6 h utilizing commercial CoMo and
46
47 17 NiMo catalysts. The hydrotreatment reduced the oxygen content of the SE down to 1.6 wt %, while
48
49 18 the minimum oxygen content of the hydrotreated biocrude (HBC) was 3.1 wt %. No coke formation
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52 19 was observed in the hydrotreatment of the SE, while the yield of coke was 13 wt % when
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54 20 processing the raw biocrude. The hydrotreated SE (HSE) samples exhibited molecular weights 24-
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56 21 61 % lower than the HBC samples, with larger low-boiling fractions (up to diesel). The better
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59 22 quality of the HSE and the absence of coke, together with the lower metal content of SE (0.2 g/kg)
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23 vs. BC (8.5 g/kg), suggest that the implementation of hydrotreatment on supercritical CO₂ extracts,
24 instead of raw lignocellulosic biocrude, is a promising option.

25
26 Keywords: Hydroprocessing, hydrodeoxygenation, catalytic hydrotreatment, supercritical carbon
27 dioxide extraction, bio-oil fractionation, biocrude upgrading

29 1. Introduction

30 The utilization of biocrudes produced by hydrothermal liquefaction (HTL) is one of the promising
31 pathways to produce liquid fuel from biomass.¹ This is particularly true for lignocellulosic biomass,
32 which can be obtained without direct competition with food production regarding the use of land
33 and water as in the case of agricultural, forest and industrial residues (e.g., sugarcane bagasse,
34 lumbermill saw dust).² The estimation of the quantitative potential of such biomass depends on
35 many variables, but it is considerable.³ For example, it is estimated that approximately 419 Mt per
36 year of residual lignocellulosic biomass is produced by the agricultural sector in the European
37 Union (EU),⁴ which is comparable to the approximately 350 Mt of crude oil consumed in the EU
38 per year.⁵ Comparable is the estimation for crop residues in the USA as well, expected to exceed
39 250 Mt per year by 2025.⁶ In order to unlock this potential, in the last couple of decades a large
40 scientific effort has taken place in developing and optimizing the HTL process on lignocellulosic
41 feedstocks.^{2,7} HTL proved to produce a biocrude with remarkable fuel-related properties, such as
42 higher heating values (HHV) in the range 25-36 MJ/kg, which are larger than the corresponding
43 biomass HHVs ranging 16-20 MJ/kg. This is the result of the improved elemental composition of
44 the HTL biocrude compared to the biomass, with oxygen to carbon ratio largely reduced (e.g., from
45 0.6 to 0.3).⁷⁻⁹ The abovementioned research effort brought the production of HTL lignocellulosic

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4 46 biocrudes up to pilot scale and soon to demonstration level.^{7,9} At the same time, it is established that
5
6 47 HTL lignocellulosic biocrudes cannot be utilized as a liquid fuel and further upgrading is required.
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9 48 Chemical properties such as high oxygen (e.g., 10-36 wt %) and water content (e.g., 4-15 wt %),
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11 49 low hydrogen to carbon (H/C) ratio (e.g., <1.6), high content of polar species, high acidity (>100
12
13 50 mg KOH/g TAN), and in some cases high levels of metals (up to 5 wt %), as well as physical
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15 51 properties such as high viscosity (up to several thousand cP) and high density (>1000 kg/m³) render
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17 52 these biocrudes incompatible with modern combustion engines and only partially miscible with
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20 53 conventional fuel.^{7,10-12}

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23 54 One of the most important and challenging improvements required for the utilization of HTL
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25 55 lignocellulosic biocrudes is the reduction of the oxygen content. The oxygen reduction is naturally
26
27 56 connected to increased HHV, reduced amount of polar substances and acidity, as well as reduced
28
29 57 molecular weight, density and viscosity.^{13,14} An effective technology for oxygen removal and
30
31 58 hydrogenation of liquid feedstocks is catalytic hydrotreatment. It is well established in the crude oil
32
33 59 refining. However, the marked differences between lignocellulosic biocrudes and crude oils make
34
35 60 this process problematic on the biocrude feedstock. In detail, the hydrotreatment of lignocellulosic
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37 61 biocrudes suffers from: (i) high hydrogen requirements, due to the high oxygen content of the feed;
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39 62 (ii) catalyst deactivation due to coking, particularly pronounced when processing biocrudes owning
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41 63 a large high boiling fraction and phenolic species (coke precursors);^{15,16} (iii) catalyst deactivation
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43 64 due to deposition and sintering of metals present in certain biocrudes;¹⁷ (iv) catalyst deactivation
44
45 65 caused by surface alteration induced by water, which is present at high mass fractions in the feed;¹⁵
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47 66 (v) corrosion, caused by the acidity of lignocellulosic biocrudes; and (vi) operational problems due
48
49 67 to high viscosity of the feed, requiring additional equipment costs (e.g., larger high pressure pipes,
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51 68 heat tracing).¹¹

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4 69 For the abovementioned reasons, the hydrotreatment of HTL lignocellulosic biocrudes is currently
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6 70 not feasible on industrial scale. To unlock the potential of HTL lignocellulosic biocrudes, one
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9 71 possible strategy is the separation of the raw biocrude aimed at obtaining one fraction with
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11 72 physicochemical properties suitable for hydrotreatment. On research level, a few studies observed
12
13 73 that the heavy fraction of lignocellulosic and microalgae biocrudes is difficult to hydrotreat and it
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15 74 was postulated that a pre-fractionation step prior to hydrotreatment can be a viable strategy to
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17
18 75 achieve biocrude utilization.^{18,19} Pedersen et al.²⁰ performed hydrotreatment on the distillate fraction
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20 76 of a lignocellulosic biocrude, instead of the whole biocrude, in an attempt to use milder conditions
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22 77 (i.e., 360 °C, 1.5 h) than those typically used for such biocrudes. In addition, on industrial scale the
23
24 78 concept of pre-separation is common in crude oil refining as liquid-liquid extraction (LLE) is
25
26 79 utilized to remove heavy (e.g., asphaltene) fractions that are known to induce catalyst
27
28 80 deactivation.²¹ However, to the best of our knowledge no literature works report a comparison
29
30 81 between the hydrotreatment of a biocrude and its fraction obtained by a pre-separation step.
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34 82 Possible separation processes for the HTL lignocellulosic biocrudes prior to hydrotreatment are
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36 83 distillation, LLE, and supercritical extraction. The feasibility of supercritical carbon dioxide (sCO₂)
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38 84 extraction was proved at laboratory scale in recent works.²²⁻²⁴ Operating on woody lignocellulosic
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40 85 biocrudes, the process was found to achieve extract yields exceeding 50 wt %. The sCO₂ extract
41
42 86 was hypothesized to be a better feed for hydrotreatment compared to the raw HTL biocrude, due to
43
44 87 the remarkable reduction in metals (from 8500 to 170 mg/kg), water (from 6 to 2 wt %) and oxygen
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46 88 content (from 10 to 5 wt %) along with lower density (from 1030 to 914 kg/m³).²² In addition, the
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48 89 volatile fraction of the sCO₂ extract showed a lower O/C ratio than the raw HTL biocrude, with a
49
50 90 higher content of fatty acids,²²⁻²⁴ which are easy to convert to alkanes via hydrotreating.²⁵ The
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52 91 extraction yields achieved are comparable to the distillate fraction obtained by vacuum distillation
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54 92 at very low vacuum (e.g., 1 mbar),^{26,27} as well as single stage lab scale LLE with organic
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93 solvents.^{18,19} sCO₂ extraction requires no solvent separation step compared to LLE and CO₂ is a
94 green solvent compared to the commonly petroleum derived organic solvents used in LLE. The
95 main energy requirement of the process is for the compression of the CO₂ as opposed to the heating
96 and vacuum requirement of distillation. Furthermore, the major gas product of HTL is CO₂ at high
97 pressure, which can be directly utilized as make-up solvent for the supercritical separation
98 downstream of the HTL reactor.

99 The aim of this work is to investigate the hydrotreatment on a sCO₂ extract of a woody biocrude
100 obtained by means of HTL. To our knowledge, the hydrotreatment on this type of feed has not been
101 investigated so far. The hydrotreatment experiments were carried out in batch mode on laboratory
102 scale equipment (11 and 40 cm³), for different reaction times, temperatures and with two
103 commercial sulfided metal catalysts (sulfided NiMo/Al₂O₃ and sulfided CoMo/Al₂O₃). The process
104 was also carried out on the woody biocrude as is (i.e., not subjected to preliminary sCO₂ extraction)
105 for benchmarking. Extensive analysis of the hydrotreated liquid product of the two feedstocks was
106 carried out, including elemental composition, molecular weight and boiling point distribution as
107 well as analytical determination of the composition of the volatile fraction, to highlight similarities
108 and differences of the products obtained with the two feedstocks.

2. Materials and methods

2.1 Materials

112 The biocrude (BC) used in this work was produced by hydrothermal liquefaction (HTL) of
113 pinewood at 400 °C and 300 bar with potassium carbonate and sodium hydroxide as catalyst and
114 pH adjuster, respectively.²² The supercritical carbon dioxide (sCO₂) extract (SE) was produced
115 utilizing a semicontinuous extractor described elsewhere,²³ following the procedure reported in the

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4 116 literature.²² In total, six extractions at 450 bar and 150 °C were performed and the extracts were
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7 117 combined to a total volume of approximately 200 cm³. The extract constitutes 53 wt % of the raw
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9 118 HTL biocrude. The catalysts used for hydrotreating were cobalt molybdenum (CoMo) and nickel
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11 119 molybdenum (NiMo) on alumina (Al₂O₃) support in beads of 1-2 mm size (Johnson Matthey,
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13 120 London, UK), which were sulfided before use. Details of the sulfidation procedure are reported in a
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15
16 121 previous work,¹⁹ and is in line with the typical methods reported in literature.^{28,29} In the following,
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18 122 the sulfided catalysts are indicated as CoMo and NiMo for brevity. Tetrahydrofuran (THF, 99.9 %)
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20 123 and dichloromethane (DCM, 99.9 %) were used as solvents. Hydrogen (H₂, 99.9 %) from Airgas
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23 124 was used for hydrotreating.

25 125 2.2 Hydrotreatment

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28 126 The hydrotreatment was performed in stainless steel tube reactors. The bottom part of the reactor
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31 127 was sealed by a stainless-steel cap while the top was connected to a capillary closed by an on/off
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33 128 valve. The valve was used to connect with a line for pressurizing with hydrogen (H₂) as well as to
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35 129 connect with a pressure gauge before and after the reaction to determine the initial and final
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38 130 pressure. The total volume of the reactor of this setup was approximately 11 cm³. 1 g of the feed
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40 131 (BC or SE) and 0.2 g of catalyst were charged in the reactor prior to each reaction. To improve
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42 132 mixing of the feed and catalyst, the tube was shaken for 30 minutes at 40 °C and 700 rpm. The tubes
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45 133 were then connected to the on/off valve. Consequently, the reactor was purged with nitrogen and
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47 134 then with H₂, followed by pressurizing the reactor system with H₂ to 45 bar (at ambient
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49 135 temperature). The pressure provided an excess of hydrogen with respect to the oxygen in the feed
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52 136 on a molar basis (i.e., at least threefold), and it is in line with typical literature values that range
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54 137 from 40 to 80 bar (at ambient temperature).^{28,30–32} The reactor tube was then inserted in a preheated
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56 138 metal clay kiln (Everheat Kingpin 88). The hydrotreatment reaction was investigated at three
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58 139 temperature levels between 350 °C and 405 °C. The H₂ pressure at the reaction temperatures,
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4 140 estimated using the ideal gas equation of state, resulted to be around 100 bar. The reaction
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7 141 temperature was monitored by a thermocouple wire wrapped tightly around the reactor tube and
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9 142 was recorded regularly. A period of approximately 50 min was required for the tube reactor to reach
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11 143 the desired temperature, which is considered as the start of the reaction (time $t = 0$). Experiments
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14 144 with both the BC and SE were performed for reaction times of 2 h, 4 h, and 6 h. The experimental
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16 145 conditions of each experiment are reported in Table S1 in the supplementary information. After the
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18 146 reaction time was elapsed, the reactor was removed from the kiln and quenched in ice for 30
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20
21 147 minutes. The final pressure at ambient temperature was measured and the reactor depressurized by
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23 148 opening the on/off valve. The final pressure was in the range 25 to 40 bar. In a single experiment
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25 149 (SE at 399 °C and 4 h with CoMo catalyst), a gas sample was taken during depressurization for
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28 150 qualitative characterization of the produced gas.

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30 151 The reactor tube was dismantled, and the free-flowing part of the liquid product (direct liquid) was
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33 152 poured in a pre-weighed vial for subsequent analysis. In the following, the direct liquid obtained
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35 153 from the BC and the SE is indicated as hydrotreated biocrude (HBC) and hydrotreated supercritical
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37 154 extract (HSE), respectively. After the hydrotreatment, the mass-based yield of the direct liquid with
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40 155 respect to the feed charged (i.e., BC or SE), was in the range 36-56 % and 32-69 % for BC and SE,
41
42 156 respectively. Individual mass data for each experiment are reported in Tables S2 and S3 in the
43
44 157 supplementary information. Solvent (i.e., DCM for SE or THF for BC) was used to recover the
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47 158 remaining liquid product as well as the spent catalyst and any solids produced (i.e., coke) during the
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49 159 reaction. The liquid product recovered with DCM/THF, the spent catalyst and the produced coke
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51 160 were filtrated under vacuum using a Büchner funnel and filter paper (2.5 μm or 11 μm pore size for
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54 161 SE and BC, respectively). The retained solids were dried, and the amount of coke was calculated
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56 162 after subtracting the weight of the catalyst charged. An overview of the experimental protocol is
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58 163 presented in Figure 1.
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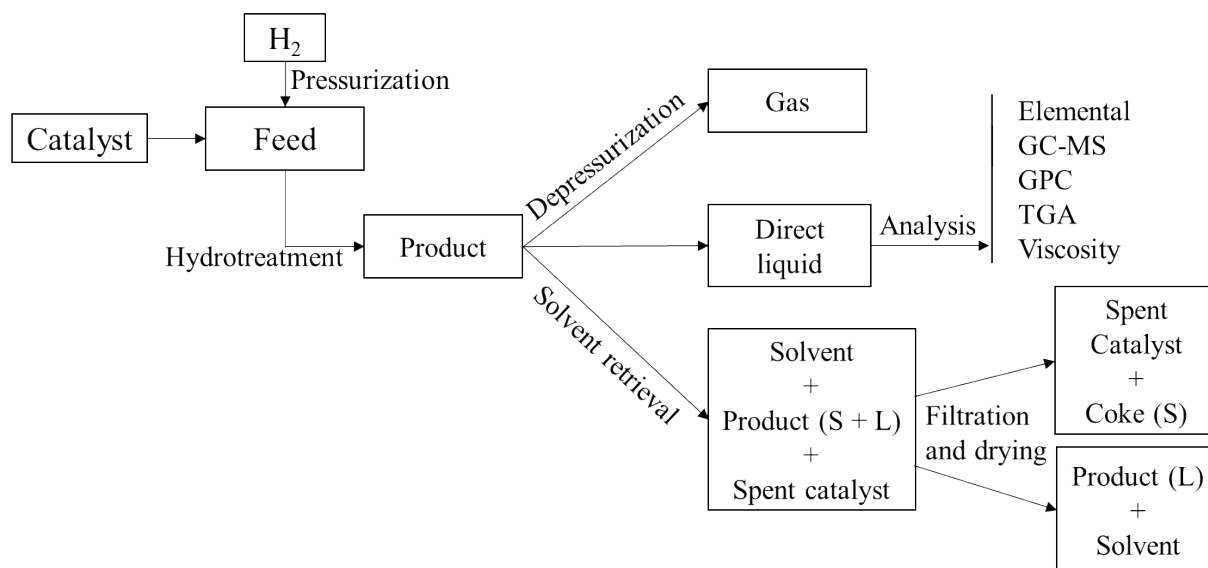


Figure 1. Experimental protocol for the hydrotreatment, product work-up and analytical characterization. S: solid products (coke); L: liquid.

The same experimental procedure was used for one scaled-up experiment with each feed. In this case, a 40 cm³ reactor tube was used, with the amount of feed and catalyst being 10 g and 2 g, respectively. These experiments served to provide larger amount of samples for characterization, more accurate coke quantification, as well as to verify the results obtained on the smaller scale.

2.3 Characterization of feedstocks and hydrotreated products

2.3.1 Density and viscosity

The density of the SE and its hydrotreated liquid (obtained in the two hydrotreatment runs with the 40 cm³ reactor) was determined in triplicate by weighing the mass of a volume of sample displaced by a precision pipette calibrated with deionized water, according to a procedure reported elsewhere.²³ The kinematic viscosity of the SE and the hydrotreated supercritical extract (HSE) was measured in triplicate on a Cannon-Fenske viscometer according to the ASTM D446-12 standard.³³ The density and viscosity of the BC were reported elsewhere.³⁴

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179 2.3.2 Elemental composition

180 Elemental analysis for the feedstocks and their hydrotreated products, as well as for the residue of
181 the sCO₂ extraction, was performed using a Perkin Elmer 2440, Series II CHN analyzer. Carbon
182 (C), hydrogen (H) and nitrogen (N) were measured, while oxygen (O) was calculated by difference.
183 All samples were analyzed in duplicate. The elemental composition was also used to estimate the
184 higher heating value (HHV) using the equation proposed by Oasmaa et al.³⁵

185 2.3.3 Molecular weight distribution

186 The molecular weight (MW) distribution of the feedstocks, their hydrotreated products, as well as
187 the residue of the sCO₂ extraction, was determined by gel permeation chromatography (GPC) on a
188 Waters 2695 separation system described in literature.³⁶ Samples were prepared by dissolving
189 approximately 0.06 g of sample in 1.8 ml THF. The mixture was filtrated with PTFE syringe filters
190 (0.45 µm pore size) and the filtrate was analyzed. THF was used as carrier with a flow rate of 1
191 mL/min. For each analysis, 20 µL of sample were injected and the resulting data were processed
192 with a MatLab program as reported in the literature.³⁶ All samples were analyzed in duplicate.

193 2.3.4 Boiling point distribution

194 The boiling point (BP) distribution of the feedstocks (BC and SE) and the hydrotreated biocrude
195 (HBC) produced at 359 °C, 4 h, and CoMo as well as the HSE produced at 397 °C, 6 h, and NiMo
196 was determined by thermogravimetric analysis (TGA), using a method inspired by the literature.^{37,38}
197 The method assumes a linear relation between the temperature corresponding to the maximum rate
198 of mass loss on the TGA curve with the boiling point of pure components. The standard
199 components chosen for this work were naphthalene, fluorene, phenanthrene, pyrene, and chrysene,
200 with normal boiling points (NBP) of 218 °C, 298 °C, 336 °C, 394 °C, and 448 °C. The linear
201 regression of the maximum rate of mass loss on the NBP of the standard components provided a

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4 202 calibration straight-line ($R^2=0.989$), which was used to estimate the boiling points of the feeds and
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6 203 the hydrotreated liquid products from their TGA curves, considering the temperatures of maximum
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9 204 rate of mass loss for these samples.
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12 205 2.3.5 Chemical composition

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15 206 Qualitative characterization by GC-MS analysis was performed on the feedstocks and selected
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17 207 hydrotreatment experimental runs. An Agilent 7890A GC, coupled with a 5975C MS was utilized.
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20 208 The analytes were separated in a Phenomenex ZB-5MS column (60 m x 320 μm x 0.25 μm). The
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22 209 temperature program was 2 min at 40 $^{\circ}\text{C}$ and ramp of 10 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$ held for 2 min. The
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24 210 temperature of the injector was maintained at 300 $^{\circ}\text{C}$. Helium was used as carrier gas at 2.4
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26 211 mL/min. All samples were dissolved in DCM (1:20) prior to analysis. In the case of the BC and
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29 212 HBC, a filtration step with a 0.45 μm syringe filter was added because they were not fully soluble in
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31 213 DCM. The single gas sample obtained for the reaction experiment on the SE (i.e., 399 $^{\circ}\text{C}$, 4 h,
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34 214 CoMo) was also analyzed with the GC-MS. Light hydrocarbons (C1-C4) and CO_2 were separated in
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36 215 a S-GasPro GC Column (15 m, 0.32 mm, 7-inch cage). The temperature program was 40 $^{\circ}\text{C}$ initial
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38 216 temperature and 10 $^{\circ}\text{C}/\text{min}$ ramp to 100 $^{\circ}\text{C}$. The injector was maintained at 200 $^{\circ}\text{C}$ and helium was
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41 217 used as carrier gas at 1.2 mL/min.
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44 218 3. Results and discussion

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47 219 3.1 Characterization of the feedstocks

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50 220 The properties of the BC and SE, as well as of the residue of the sCO_2 extraction (R), are reported
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52 221 in Table 1. The elemental composition of the BC is in line with typical woody biocrudes, and it is
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54 222 also in good agreement with the values determined in a previous work for the same biocrude.²² It
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57 223 has one of the lowest oxygen mass fractions among biocrudes from woody biomass reported in the
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4 224 literature.^{8,39} In comparison, the SE has a slightly higher carbon and hydrogen content, as well as a
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7 225 lower oxygen content. A large difference in the MW distribution is observed with the number
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9 226 average MW of the SE being around four times lower than that of the BC. Consistently, the residual
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11 227 fraction (R) exhibits a higher MW than the BC. Also considering the lower polydispersity of the SE
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14 228 and R, it is obvious that the sCO₂ extraction effectively separates biocrude compounds on a
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16 229 molecular weight basis. Regarding the chemical nature of the residue, the higher oxygen content
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18 230 can be explained by the higher content of high molecular weight phenolics. In line with this, our
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21 231 previous work on the same biocrude showed increased phenolic acidity in the sCO₂ extraction
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23 232 residue.²² In addition, it has been recently shown by NMR and FT-IR analysis that the heavy
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25 233 fraction of HTL wood biocrudes is characterized by higher aromaticity, partly due to high
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27 234 molecular weight phenolics.⁴⁰ It is expected that the heavy aromatic residue originates from the
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30 235 repolymerization of the lignin fraction of the biomass during the HTL process, which has been
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32 236 shown to occur after only a few minutes of reaction time.^{41,42}
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35 237 The lighter nature of the SE is reflected in its physical properties as its density is moderately lower
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37 238 (i.e., 5 %) and its viscosity is more than 50 times lower than that of the BC, providing a much less
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40 239 viscous feed for a downstream hydrotreater. Furthermore, the water content of the SE is
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42 240 approximately a quarter of that of the BC. The oxygen content in the sCO₂ separated fraction, the
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44 241 slight increase of the H/C ratio (i.e., 1.4 to 1.5), as well as the moderate density decrease lead to
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46 242 properties comparable to batch vacuum distillate fractions reported in literature.^{26,27}
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Table 1. Elemental composition, density, viscosity, water mass fraction, weight and number average molecular weight (MW), and polydispersity index of biocrude (BC), sCO₂ extract (SE) and the extraction residue (R). ND: Not determined.

	BC	SE	R
C (wt %)	76.0 ± 0.2	79.1 ± 0.1	76.7 ± 0.7
H (wt %)	9.1 ± 0.1	10.1 ± 0.01	7.6 ± 0.1
N (wt %)	0.3 ± 0.1	0.4 ± 0.02	0.6 ± 0.01
O (wt %)	14.6 ± 0.1	10.4 ± 0.2	15.1 ± 0.6
Water (wt %)	5.7 ± 0.3	1.5 ± 0.2	ND
Density (kg/m ³)	1030* ²²	979 ± 7	ND
Viscosity (cP)	7700* ³⁴	140**	solid
Number average MW (g/mol)	797 ± 47	198 ± 1	1665 ± 9
Weight average MW (g/mol)	4218 ± 756	476 ± 3	7120 ± 624
Polydispersity index	5.3 ± 0.1	2.4 ± 0.1	4.3 ± 0.4

*Taken from the literature; **Calculated from kinematic viscosity (143 ± 2 mm²/s)

In total, 50 components were identified in the volatile fraction of the BC and SE. The identified chemical components comprise mostly oxygenated functionalities including ketones, phenols, guaiacols, benzenediols, long chain fatty acids (LFA: C₁₆-C₁₈), and a single aromatic acid (dehydroabiatic acid). A few single-ring (benzenes) and several 2- and 3-ring aromatic hydrocarbons (PAH) were also found. In general, these chemical classes are common in HTL biocrudes produced from woody biomass.⁴³⁻⁴⁵ The results are in good agreement with previous works, where more detailed discussion on the chemical characterization is presented together with quantitative data.²²⁻²⁴ The relative distribution of these chemical classes is similar in the two feeds

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4 257 (Table S4 in supplementary information). However, it is important to note that the mass fraction of
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6 258 the volatile (GC-MS detectable) fraction of the SE can be up to twice as large as that of the
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9 259 biocrude (e.g., 19 wt % and 40 wt % for BC and SE respectively).^{22,23}
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12 260 In the feeds used in the current work, the LFA and the PAH are dominating chromatographic area,
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14 261 overall accounting for 71 % and 77 % for the BC and SE, respectively. Phenolic components
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16 262 namely, phenols, guaiacols and benzenediols correspond to 8 % and 10 % for the BC and SE,
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19 263 respectively. Single-ring aromatic hydrocarbons correspond to 4 % and ketones to 3 % in both
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21 264 feeds. Dehydroabietic acid was found reduced from a chromatographic area of 11 % in the BC to 5
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24 265 % in the SE. The higher concentration of the LFA and the PAH in the SE is partly responsible for
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26 266 the lower oxygen content compared to the BC.
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29 267 3.2 Hydrotreatment activities 30 31

32 268 The NiMo and CoMo catalysts tested in this work are common commercial hydrotreatment
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34 269 catalysts for fossil feedstocks and are typically used in research work of hydrotreatment of
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36 270 lignocellulosic biocrudes,^{9,15} microalgae,^{19,29} and various types of wastes.⁴⁶ The comparison was
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39 271 performed on the SE feed and data for the two catalysts are reported in Figure S1 in the
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41 272 supplementary information. No remarkable difference was observed with respect to
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43 273 hydrodeoxygenation (HDO) and molecular weight (MW) reduction between the NiMo and CoMo
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46 274 catalysts. The similar effectiveness of these two catalysts was also reported in the literature.¹⁹
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49 275 3.2.1 Hydrodeoxygenation (HDO) 50 51

52 276 The reaction temperatures studied were 353 °C ± 3 °C, 384 °C ± 2 °C and 398 °C ± 3 °C, while the
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54 277 reaction times were 2, 4 and 6 h as the literature indicates that these ranges are required for
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56 278 significant oxygen removal for lignocellulosic biocrudes.^{26,28,30,31,47} Duplicate experiments were
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59 279 performed for most of the reaction conditions. In addition, single hydrotreatment reactions were
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performed on the SE for a few reaction times lower than 2 h (i.e., 0 h, 0.5 h and 1 h) at 398 °C since the experiments at 2 h showed considerable deoxygenation for this feed. In total, 31 hydrotreatment experiments were performed in this work.

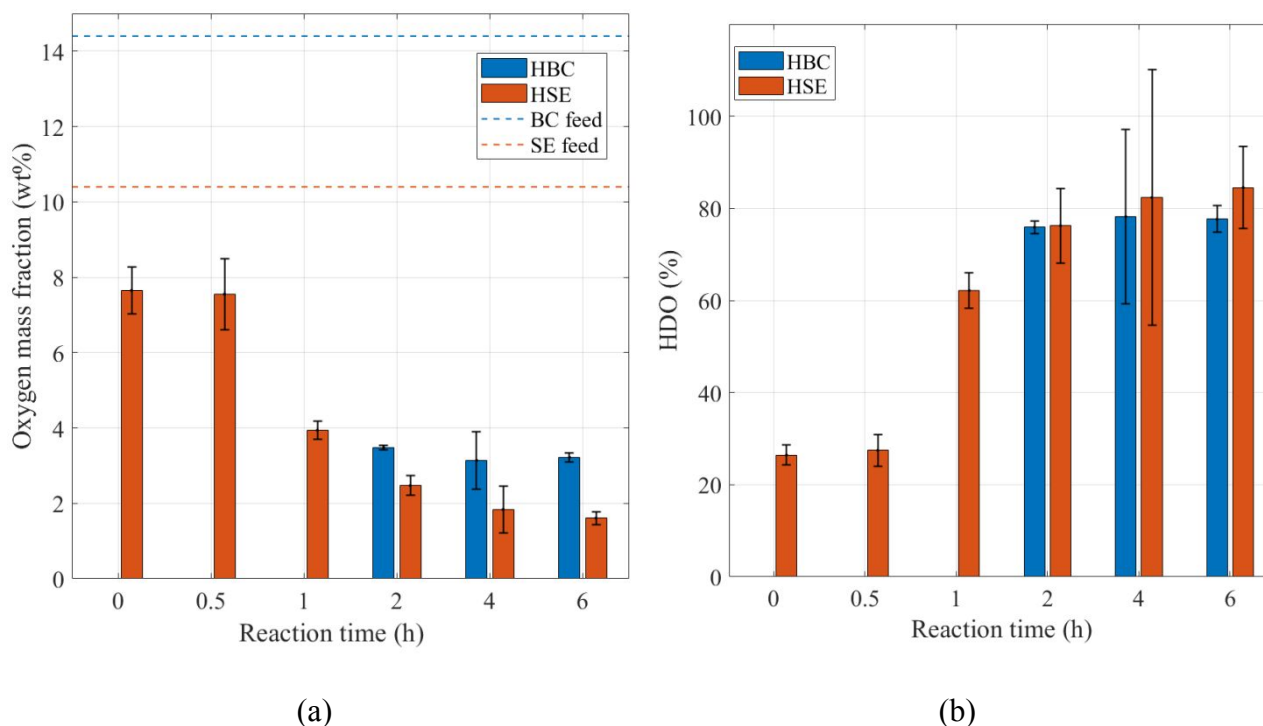


Figure 2. (a) Oxygen content for biocrude (BC), sCO₂ extract (SE) and their hydrotreated products (HBC and HSE, respectively); (b) hydrodeoxygenation. Experiments carried out at 398 °C ± 3 °C in the small-scale reactor (11 cm³) at different reaction times. The error bars in Figure 2a indicate the standard deviation for the oxygen mass fractions resulting from duplicate elemental analysis of samples from duplicate or single hydrotreatment experiments. The error bars in Figure 2b indicate the standard uncertainty for the HDO.

Figure 2a reports the oxygen content of the hydrotreated biocrude (HBC) and the hydrotreated sCO₂ extract (HSE) for the reactions performed at 398 °C and at different reaction times. The complete elemental analysis data are reported in the supplementary information (Tables S5 and S6). Figure

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2b presents these results in terms of the reduction of oxygen that can be conveniently described as hydrodeoxygenation (HDO):³¹

$$HDO, \% = \frac{\text{oxygen wt \% in feed} - \text{oxygen wt \% in product}}{\text{oxygen wt \% in feed}} \times 100$$

As can be seen at a constant reaction temperature of 398 °C the HDO is similar for the two feeds and only slightly higher for the SE at long times (4 h and 6 h). However, the lower oxygen content of the SE feed (i.e., 10.4 wt %) compared to the BC feed (i.e., 14.6 wt %) leads to the HSE showing lower values of oxygen content (down to 1.6 wt %) compared to the HBC (down to 3.1 wt %).

The hydrotreatment runs on the SE at different reaction times, i.e., 0.5 to 6 hours, showed that most of the deoxygenation takes place between 30-60 minutes of reaction (approx. 60 %), with further deoxygenation being progressively slower and reaching values up to 85 % at 6 hours. The rate of deoxygenation reduces with the reaction time as both the oxygen and hydrogen are depleted. In addition, the reduction of HDO rate for the BC feed can also be attributed to the rapid adsorption of coke precursors on the acidic sites of the catalytic support, which leads to plugging of the small pores, and covering of the acidic sites, resulting in loss of surface area.⁴⁸

The temperature effect on the reduction of oxygen and HDO can be observed in Figure 3, where the oxygen content and the HDO of the samples are shown for experiments at 4 h and different reaction temperatures. For both feeds the increase of temperature leads to higher extent of deoxygenation.

As can be seen, the oxygen content of the HSE is approximately half of that of the HBC. In addition, in all runs at same operating conditions, the extent of HDO using the SE feed is slightly higher than the BC. In the case of the large-scale experiments, the exact same temperature was not achieved when working with these two feedstocks (i.e., BC and SE). However, a much higher extent of HDO (78 %) was achieved using the SE feed compared to the 54 % HDO on the BC feed.

This appears not to be explained by the different temperature only and indicates that the

deoxygenation of the SE feed is more effective than the BC feed. The latter observation is also supported by the lower mass fraction of oxygen in the HSE (i.e., 1.6-2.5 wt %) compared to the HBC (i.e., 3.1-6.6 wt %) under similar conditions (384 °C 4 h; and 398 °C 2, 4 and 6 h), which is also corresponding to higher average HDO values for the SE feed compared to the BC feed, in spite of the lower oxygen content of the SE feed as a starting point.

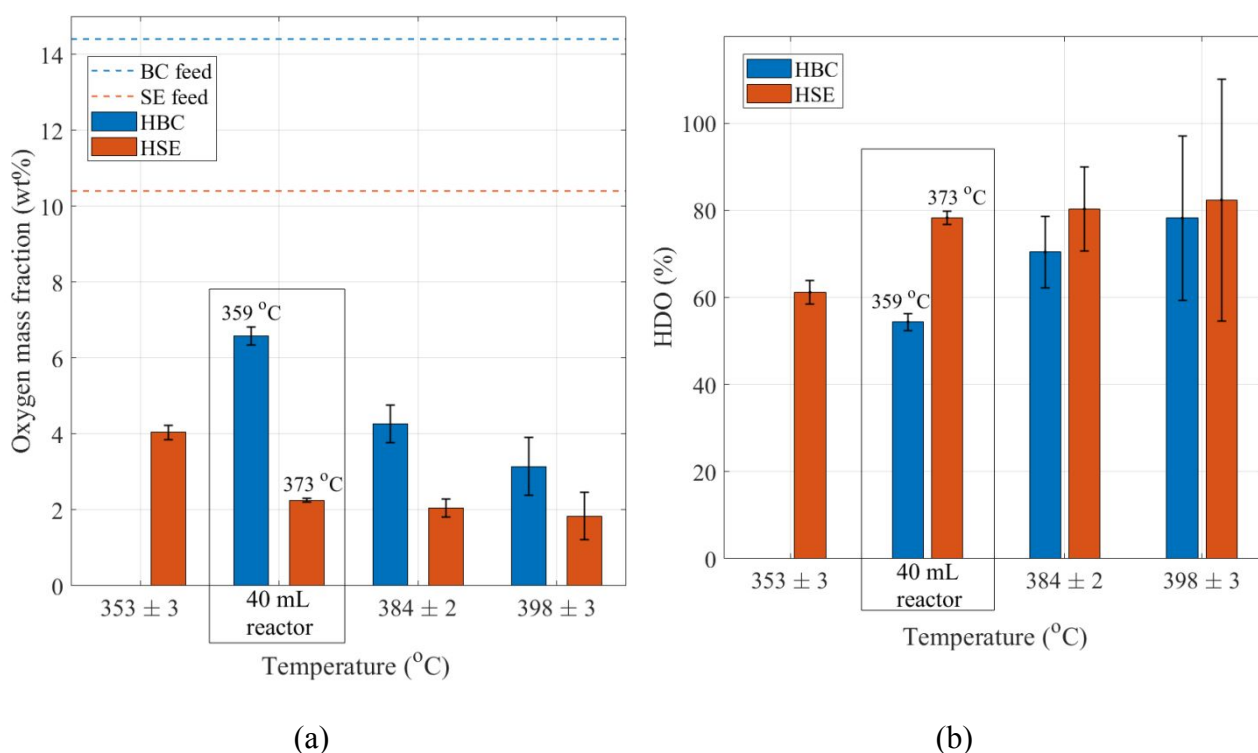
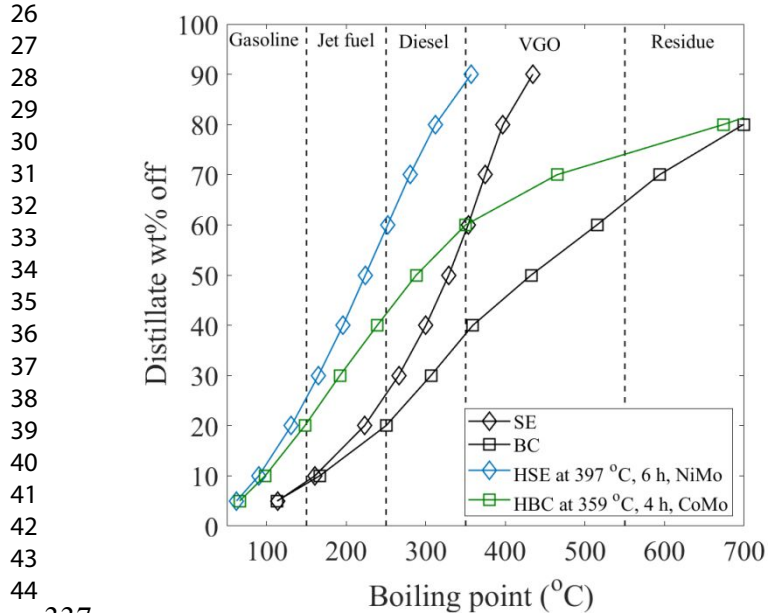


Figure 3. (a) Oxygen content for biocrude (BC), sCO₂ extract (SE) and their hydrotreated products; (b) hydrodeoxygenation (HDO). Experiments carried out for 4 hours reaction time and different temperatures. The error bars in Figure 3a indicate the standard deviation for the oxygen mass fractions resulting from duplicate elemental analysis of samples from duplicate or single hydrotreatment experiments. The error bars in Figure 3b indicate the standard uncertainty for the HDO.

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4 328 3.2.2 Hydrocracking

7 329 The boiling point distribution of the feedstocks (BC and SE) and the hydrotreated liquid products,
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10 330 i.e., HBC (359 °C, 4 h and CoMo catalyst) and HSE (397 °C, 6 h and NiMo catalyst), is reported in
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12 331 Figure 4. It is observed that approximately 60 wt % of the SE corresponds to fuel fractions up to
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14 332 diesel (i.e., < 350 °C), while for the biocrude that fraction correspond to around 40 wt %. The latter
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16 333 values are in line with BP distribution reported in literature for similar biocrudes, determined by
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19 334 true boiling point analysis (TBP) and simulated distillation (SimDis) methods.^{26,27} In addition, the
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21 335 total SE boils in the range between gasoline and vacuum gas oil (VGO), whereas approximately 40
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23 336 wt % of the biocrude is vacuum residue (> 550 °C).



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47 338 Figure 4. Boiling point distribution of the biocrude (BC), sCO₂ extract (SE) and their hydrotreated
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49 339 products. HBC at 359 °C, 4 h using CoMo catalyst; HSE at 397 °C, 6 h using NiMo catalyst.

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56 341 Regarding the improvement of the boiling point profile in the hydrotreated products, a 2- to 3-fold
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58 342 increase of the gasoline (< 150 °C) and jet fractions (150-250 °C) is observed. More specifically,
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4 343 the gasoline fraction in the HSE increases from 9 to 25 wt % and in the HBC from 6 to 20 wt %
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6 344 compared to the corresponding feeds. The jet fuel fraction increases from 17 to 34 wt % and from
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8 345 11 to 22 wt % in the HSE and HBC compared to the SE and BC, respectively. The diesel fraction
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11 346 remains approximately the same between the feeds and their hydrotreatment products i.e.,
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13 347 approximately 30 wt % and 20 wt % for the SE and BC, respectively. The considerable increase of
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16 348 the gasoline and jet fractions in the HSE is also reflected in the number average MW of this sample
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18 349 that is one of the lowest values found in this work (i.e., 90 g/mol). The increase in the lighter
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20 350 fractions corresponds to the decrease of the VGO and residual fractions indicating that the heavy
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23 351 fractions were subjected to cracking reactions. Specifically, the 40 wt % VGO fraction of SE is
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25 352 reduced to 10 wt % in the HSE. The VGO and residue fractions of BC are reduced from 29 to 15 wt
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27 353 % and from 37 to 25 wt % in the HBC. Overall, the hydrotreatment of SE qualitatively leads to
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30 354 larger improvement in the lower boiling fractions compared to the hydrotreatment of BC.

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33 355 The coke formation was quantified for the hydrotreatment experiments in the 40 mL reactors. In the
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35 356 case of the BC hydrotreatment experiment, it was 13 wt % of the biocrude treated. Similar value has
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37 357 been reported in the literature for a lignocellulosic biocrude from miscanthus at similar conditions
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39 358 (350 °C and 108 bar).³¹ On the other hand, no quantifiable coke was observed after the
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42 359 hydrotreatment of the SE. The absence of observable coking propensity for the SE is attributed to
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44 360 the removal of the high MW fraction attained in the sCO₂ extraction process. As a matter of fact, it
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46 361 is known that the extensive cracking reactions of the high MW fractions are one of the major causes
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49 362 of coking.¹⁶ In addition, as also discussed in Section 3.1, previous studies indicated that the heavy
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51 363 fraction of the HTL lignocellulosic biocrudes is largely constituted of phenolic structures which are
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53 364 coke precursors.^{22,40} Therefore, the removal of the heavy phenolic fraction is expected to be the
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56 365 main reason for the limited coking propensity of the SE feed. This is particularly important for the
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58 366 potential of the SE as feed for a hydrotreater, since coke formation and deposition on the catalytic
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4 367 bed is the major reversible deactivation mechanism that dictates how often regeneration cycles are
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6 368 performed.^{15,25} An increased H₂ pressure when hydrotreating the BC feed would possibly improve
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9 369 the catalyst stability and reduce coking, in line with the methods applied in industrial applications
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11 370 on residual hydrocarbon fractions.⁴⁹ In this regard, the abovementioned work of Castello et al.,³¹
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13 371 focused on the hydrotreatment of lignocellulosic HTL biocrudes, shows a coke reduction from 14
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16 372 wt % to 6 wt % when increasing the reaction pressure from 108 bar to 156 bar at 350 °C.
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18 373 Nevertheless, the coke yield on the raw HTL biocrude was still rather high, whereas the absence of
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21 374 coke during the hydrotreatment of the SE feed suggests a pathway to reduce the H₂ consumption by
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23 375 performing a milder hydrotreatment without compromising the catalyst performance and increasing
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25 376 its regeneration interval.

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28 377 The abovementioned data can be used for calculating mass-based yields of the most valuable
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30 378 fractions (gasoline, jet fuel, and diesel). Considering 100 kg of biocrude as a basis of calculation, its
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33 379 direct hydrotreatment yields 87 kg HBC (on a coke-free basis), which consist of 17 kg of gasoline,
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35 380 19 kg of jet fuel, and 17 kg of diesel. On the other hand, considering that 53 kg of SE were obtained
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37 381 from 100 kg of biocrude, the two-step process (i.e., sCO₂ extraction followed by hydrotreatment)
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40 382 leads to 13 kg of gasoline, 18 kg of jet fuel, and 16 kg of diesel. Therefore, the sum of these three
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42 383 fractions accounts for 53 kg starting from the biocrude, while it is 47 kg starting from the
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44 384 supercritical extract. This means that part of the initial loss of materials due to the sCO₂ extraction
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46 385 process (53 kg extracted from 100 kg of biocrude) is compensated by a more efficient
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49 386 hydrotreatment process, with the amount of light fractions obtained in the two-step process being 88
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51 387 % of the amount obtained from the direct hydrotreatment of the biocrude. Even though there is a
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53 388 yield loss, three aspects must be considered: (i) the direct hydrotreating of the HTL lignocellulosic
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56 389 biocrudes is currently considered not feasible at industrial level, due to the problems caused to the
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58 390 catalysts by these biocrudes. Therefore, the application of a preliminary extraction step can be the
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4 391 only way to make the process viable on currently available commercial catalysts, thus within short
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6 392 development times; (ii) same boiling point fractions do not imply same product quality; (iii) the
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9 393 extraction yield used in this calculation (53 kg extracted from 100 kg of biocrude) is based on the
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11 394 execution of sCO₂ extraction in a single-stage semicontinuous process operated on a laboratory
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13 395 equipment.²² The application of the supercritical extraction process in a continuous-flow
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16 396 countercurrent column operated with reflux is expected to give a better separation and higher
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18 397 extraction yields. Another aspect to be considered regarding the two-step process (i.e., sCO₂
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20 398 extraction + hydrotreatment) is the increase of the throughput for the same hydrotreater size. In fact,
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23 399 taking 100 kg of feed to the hydrotreater as a basis of calculation, 53 kg of light fractions are
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25 400 produced from the direct hydrotreatment of biocrude, while 89 kg are produced from the two-step
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27 401 process (68 % increase of product) while feeding 189 kg of biocrude to the sCO₂ extractor (89 %
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30 402 increase of throughput for the same hydrotreater size). Therefore, it has to be considered that the
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32 403 additional costs for the installation and operation of the sCO₂ separation unit is counterbalanced by
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34 404 the increase of throughput of the process for the same hydrotreater size.

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37 405 Figure 5 reports the number-average MW of the BC, SE, and their hydrotreated liquid product (i.e.,
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39 406 HBC and HSE, respectively). The complete set of data for the average molecular weights is
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42 407 reported in Table S7 in supplementary information.
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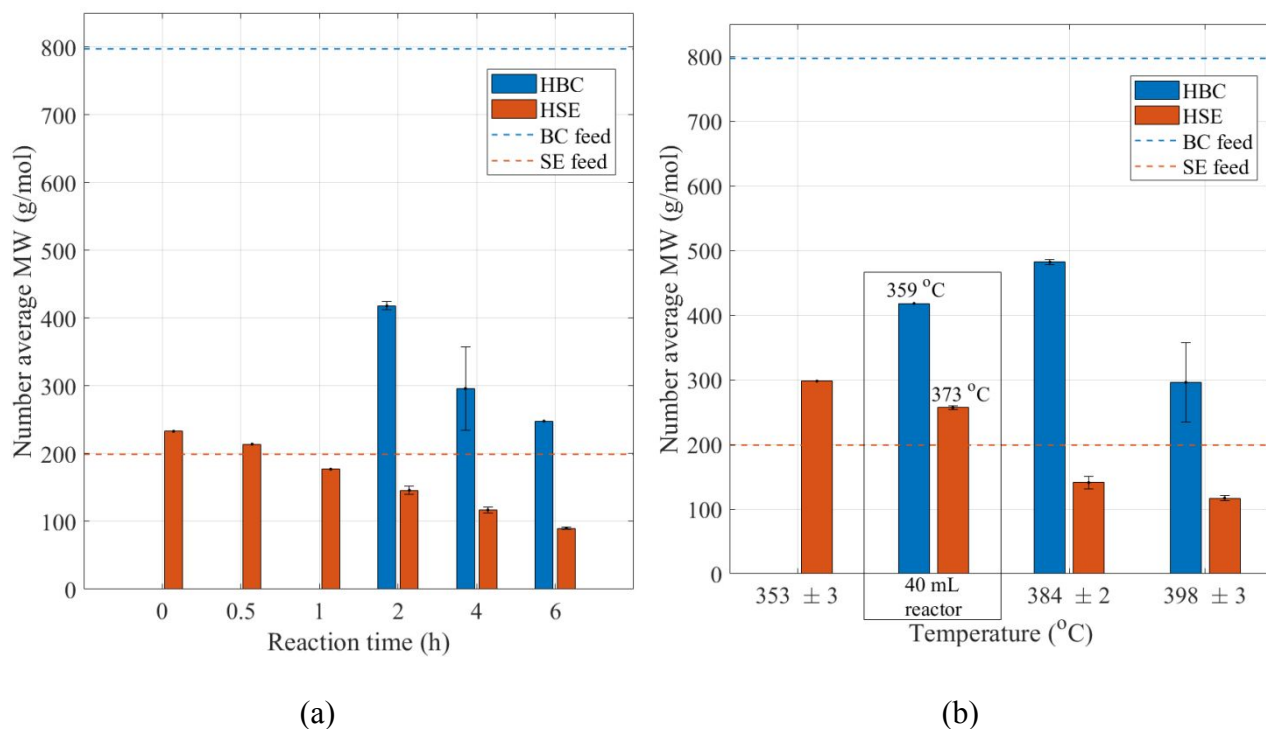
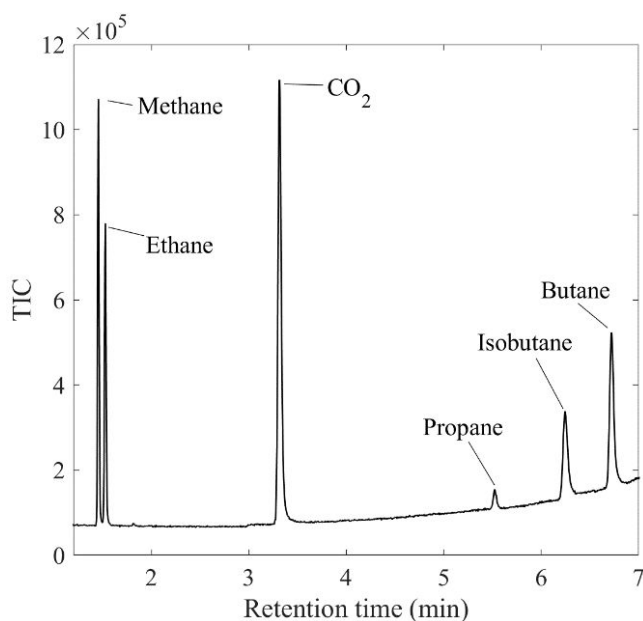


Figure 5. Number-average molecular weight of biocrude (BC), sCO₂ extract (SE) and their hydrotreated products at: (a) 398 °C ± 3 °C and different reaction times; (b) 4 h and different temperatures. The error bars indicate the standard deviation for the molecular weight determination resulting from duplicate GPC analysis of samples from duplicate or single hydrotreatment experiments.

A very large reduction of the MW of the BC is observed with around 50 % reduction in 2 h at 398 °C, compared to the BC feed (Figure 5a). The MW is further reduced at 4 h and consequently after 6 h. As can be seen from Figure 5a, the MW of the SE is reducing over time in the process carried out at 398 °C, reaching a maximum reduction of approximately 46 % after 6 h. The large reduction of the MW of the BC indicates the cracking reactions of the residual fraction, which significantly reduces during hydrotreatment. That is not the case for the SE as a large part of the heavy fraction is already removed by the sCO₂ extraction. The MW trends further support the explanation for the different coking propensity of the two feeds as determined by high MW species of aromatic nature.^{50,51}

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6 423 the reaction temperature is increased from 384 to 398 °C on the BC, a large MW reduction is
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9 424 observed as cracking reactions are more pronounced at temperatures close to 400 °C.^{19,31} Despite
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11 425 the large reduction of the MW for the BC, the MW of the HSE remains lower by 24-61 %. This
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14 426 means that the SE feed can be processed at less severe conditions to limit less desirable cracking
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16 427 reactions. The gas phase produced in the hydrotreatment of the SE at 400 °C and 4 h with CoMo
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18 428 was qualitatively analyzed and the chromatogram is shown in Figure 6. In majority, light
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21 429 hydrocarbons (i.e., C1-C4) were identified in the gas phase as well as carbon dioxide.
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52 53 434 3.3 Liquid product fuel properties

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56 435 Regarding the physical properties, the density of HSE was $972 \pm 12 \text{ kg/m}^3$ (at 24 °C), which is very
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58 436 close to the value of the SE feed. This corroborates the relatively unchanged MW of the HSE with
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4 437 respect to the SE. On the other hand, almost 30 % reduction was achieved for the viscosity, from
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6 438 140 cP of the SE feed down to 101 cP in the HSE (measured at 20 °C). These values are in line with
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9 439 low-sulfur residual marine fuel according to ISO 8217 (e.g., approximately 80 cP at 50 °C and 975
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11 440 kg/m³ at 15 °C).⁵²

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14 441 The HHV increases from 36 MJ/kg to 40-42 MJ/kg for the BC feed and from 38 MJ/kg to 42-44
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16 442 MJ/kg for the SE feed for reaction times of 2, 4 and 6 h at 398 °C. In both cases the increase is
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19 443 noteworthy with the HSE reaching values that are in the range of conventional diesel and jet
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21 444 fuel.^{53,54} The highest HHV was achieved with the CoMo catalyst at 398 °C for 6 h under H₂
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24 445 pressure of 45 bar for the SE.

25 26 446 3.4 Chemical composition of the volatile fractions

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29 447 76 components were identified by GC-MS in the hydrotreatment products. A few alkyl-phenols
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31 448 (e.g., phenol, 2,3-dimethyl-), low boiling point saturated/mono-unsaturated cyclic aliphatic ketones
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34 449 (e.g., cyclopentanone, 2,5-dimethyl-) and a few high MW oxygenates (i.e., aromatic alcohols and
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36 450 aldehydes with MW>200 g/mol) were found in the hydrotreatment products. Most of the multiple-
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39 451 ring aromatic hydrocarbons originally present in the feeds were found in the hydrotreatment
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41 452 products as well. The major chemical classes resulting from the hydrotreatment reactions were
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43 453 alkanes (6-24 carbon atoms) and cycloalkanes (6-9 carbon atoms), while the single benzene ring
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45 454 hydrocarbons (7-10 carbon atoms) showed a relative increase. As an example, these changes can be
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48 455 observed in Figure 7, where the distribution of the identified chemical classes in the two feeds and
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50 456 two of their hydrotreatment products is shown as a percentage of the total chromatographic area.

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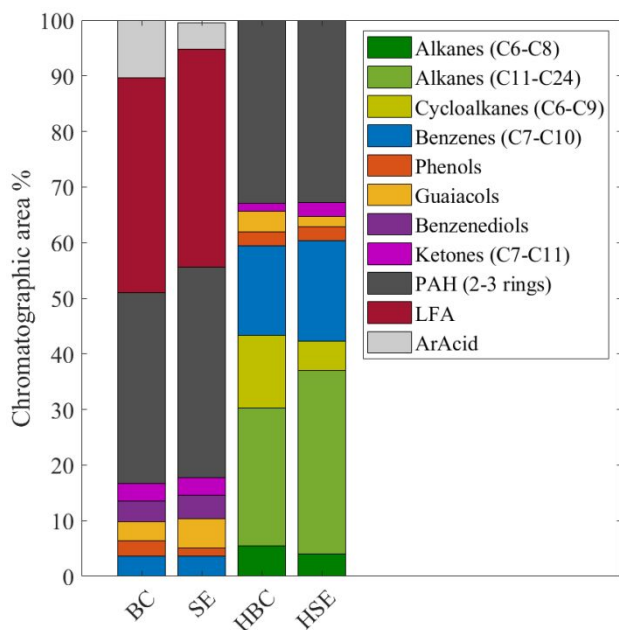


Figure 7. Gas chromatographic area percentage of identified chemical classes in the biocrude (BC), $s\text{CO}_2$ extract (SE) and their hydrotreated products (HBC, HSE, respectively) obtained with CoMo catalyst at 398 °C and 4 h. LFA: Long chain fatty acids; PAH: 2- and 3-ring aromatic hydrocarbons; ArAcid: Dehydroabietic acid.

The distribution of the components in the volatile fraction of the BC and the SE is rather similar.

This is expected as the GC-MS analysis only provides information on the fraction having appreciable volatility below approximately 350 °C, which is expected to be very similar for BC and SE. However, the mass fraction of the volatiles in the SE is relatively higher, as discussed in Section 3.1. As a relevant example, in a previous work we found that the LFA in the $s\text{CO}_2$ extracts can reach up to 14 wt %, while they were around 4 wt% in the biocrude before the extraction.²²

Regarding the effect of the hydrotreatment, although the change in the peak area percentage is not a quantitative determination of the change in the mass fraction of individual species in the sample, as it is influenced by the total volatile fraction, some clear compositional trends can be observed. It is evident that the long chain fatty acids (LFA) are effectively hydrotreated (through hydrodecarboxylation or hydrodecarbonylation) as they are completely converted at 400 °C with

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4 473 CoMo catalyst for both feeds. The high content of the LFA in the feeds results into the large
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6 474 chromatographic area percentage of long chain alkanes in the products. This is in line with literature
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9 475 findings and confirms that the fatty acids are relatively easy to convert to straight chain alkanes via
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11 476 hydrotreatment.^{25,31,49} The abovementioned larger mass fraction of LFA in the SE, compared to BC,
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13 477 is therefore one of the reasons of the increased suitability of the SE towards hydrotreatment.
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16 478 The fact that the PAH fraction is relatively unchanged, together with the increase of single ring
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18 479 aromatics (i.e., benzenes), indicates that no opening of aromatic rings takes place under these
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21 480 conditions. In addition, hydrogenation does not occur as polyaromatic components, such as retene
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23 481 that is an abundant component in the PAH fraction,^{22,31} remain unchanged in terms of
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32 484 4. Conclusion

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35 485 A sCO₂ extract (SE) of a HTL lignocellulosic biocrude (BC) was hydrotreated using conventional
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37 486 sulfided catalysts based on CoMo and NiMo typically used in petroleum refineries. No significant
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39 487 differences in the performance of these two catalysts on these feeds were observed. The differences
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42 488 in the reaction products, i.e., the hydrotreated biocrude (HBC) and the hydrotreated supercritical
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44 489 extract (HSE), were highlighted. The main advantages of the operation on the sCO₂ extract, as
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46 490 opposed to the operation on the raw HTL biocrude, can be summarized as: (i) lower oxygen of the
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48 491 HSE, with minimum value of 1.6 wt % vs. 3.1 wt % for HBC; (ii) lower number-average molecular
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51 492 weight of the HSE (in the range 90-298 g/mol), with values from 24 % to 61 % lower than the
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53 493 values for HBC; (iii) no coking when operating on SE, while approximately 13 % of the BC was
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56 494 converted into coke; (iv) complete conversion of the fatty acids, while unconverted fatty acids were
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58 495 observed in some experimental runs on the BC; (v) better boiling point distribution of the HSE,
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496 with no fractions above the diesel fuel range and larger amount of the low boiling fractions (e.g.,
497 gasoline and jet), while the HBC still retains a 25 % of residual fraction (boiling above 550 °C).

498 Overall, this work indicates that sCO₂ extracts of raw HTL biocrudes are by far more suitable for
499 hydrotreatment than the raw HTL biocrude. They may be of quality high enough to be run on
500 conventional industrial catalysts in use on fossil feeds without excessive problems of catalyst
501 deactivation. In addition, the products of the hydrotreatment of the sCO₂ extract have better fuel
502 properties. On the other hand, potential applications for the sCO₂ extraction residue should be
503 identified, such as production of adsorbents, renewable bio-coke, or component for asphalt.

504

505 Supporting Information

506 Hydrotreatment conditions (Table S1); Masses of feed, catalyst and hydrotreated samples (Tables
507 S2-S3); Chromatographic percentage area of chemical classes identified in the volatile fraction of
508 the feeds and hydrotreated samples (Table S4); Elemental composition of the feeds and the
509 hydrotreated samples (Tables S5-S6); Weight and number average molecular weight, and
510 polydispersity index of the feeds and the hydrotreated samples (Table S7); Comparison of CoMo
511 and NiMo catalyst effect on hydrotreatment of the sCO₂ extract (Figure S1); Total ion
512 chromatograms for the feeds and for some hydrotreated samples (Figure S2).

513

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518 Alexander Ulanov, Jamison Taylor Watson and Sarmila Katuwal for the gas chromatographic
519 analysis, viscosity, and density measurements, respectively.

520 Mention of trade names or commercial products in this article is solely for the purpose of providing
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525

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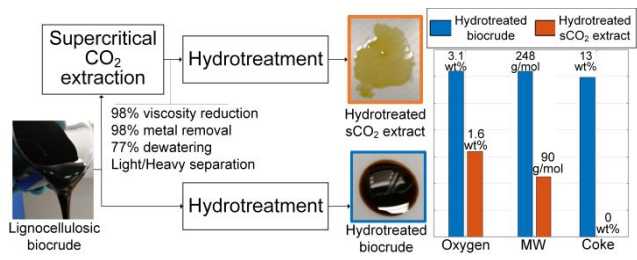
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