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Upgrading of non-dewatered non-demetalized lignocellulosic bio-crude from hydrothermal liquefaction using supercritical carbon dioxide

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Abstract

Supercritical carbon dioxide (sCO_2) extraction was applied on a raw bio-crude, obtained by hydrothermal liquefaction of pinewood. The extractions were carried out in semicontinuous mode, in the range 80 to 150 °C and 330 to 450 bar. Extraction yields from 44 to 53 wt% were achieved. The extracts were richer in lower molecular weight (MW) compounds, with fatty acids and aromatic hydrocarbons concentrated up to 14 and 24 wt%, respectively. For comparable MWs, lower polarity compounds concentrated in the extracts. Compared to the feed, the extracts exhibited lower density (from 1030 kg/m^3 down to 914 kg/m^3), lower water content (from 5.7 wt% down to 1.3 wt%) and lower oxygen content (from 10.0 wt% down to 5.0 wt%). In addition, the metal content was drastically reduced (from 8500 mg/kg down to 170 mg/kg on average). In the context of biofuel production, the sCO_2 extracts are a better feed for catalytic hydrotreating.

1. Introduction

Hydrothermal liquefaction (HTL) is a promising thermochemical process to produce liquid fuel from biomass. The process entails the depolymerisation of biomass in an aqueous medium at high temperature (e.g. 250 – 450 °C) and pressure (e.g. 100 – 350 bar).[1] One of the major advantages of HTL involves the flexibility of feedstocks that can be processed, which include both dry and wet biomasses.[2] The utilization of lignocellulosic biomass, an example of so-called second generation biomass, is particularly appealing due to lack of direct competition with food production. Wood residue and excess lignin from the paper pulp industry are examples of lignocellulosic by-products produced in large quantities, which can be valorised to liquid fuels via HTL.[3–5]

Besides the water medium, the HTL process is typically carried out in the presence of homogeneous catalysts and pH adjusters, such as potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH).[1,6] The main products of HTL are a CO_2-rich gas phase (typically around 90 wt% CO_2),[7,8] a solid phase (i.e. char) and two liquid phases. The liquid products are an aqueous phase saturated of water-soluble organics and an oil, namely the HTL bio-crude.[1]

The HTL bio-crude obtained by gravimetric separation of the products is a tight water-in-oil emulsion, with water content in the range 5 to 15 wt%.[9–12] Typical ash content values are reported broadly ranging from 0.01 wt% up to 5 wt%.[4,10,13] Individual values of the content of alkali and earth metals (e.g. potassium and iron) are typically not reported, except for a few cases.[3,4] In comparison to fossil crude oils, HTL bio-crudes have relatively high oxygen content, typically in the range 10 to 20 wt%.[10,12,14,15] The high oxygen content is caused by a variety of oxygenated components, such as ketones, fatty acids and different one-ring phenols (e.g. phenol, guaiacols, catechols). Moreover, oxygen is also expected to be contained in a complex large fraction of high boiling components,

including phenolic oligomers derived from the lignin fraction.[16] The presence of a relatively large heavy fraction, essentially non-volatile, is evident from previous works reporting vacuum distillation of lignocellulosic HTL bio-crudes. It was observed that approximately 50 wt% of the oil cannot be distilled even at very high vacuum (i.e. 1.3 mbar) at temperatures between 130 °C and 160 °C. The atmospheric equivalent boiling point of this heavy fraction was above 400 °C.[17,18] In the reported distillation experiments, the bio-crude was dewatered prior the process, since the presence of water would reduce the distillation efficiency, result to unsteady boiling and create control issues.[17] In addition to the above, HTL lignocellulosic bio-crudes have high viscosity (typically in the range 10^3 to 10^6 cP)[19–21] and high density (typically above 1000 kg/m^3)[5,7,20,22].

In order to utilize HTL bio-crudes as drop-in biofuels, the oxygen content has to be drastically reduced. The state of the art method for this purpose is catalytic hydrotreating (i.e. hydrodeoxygenation, HDO).[23] However, hydrotreating of raw HTL bio-crudes can lead to accelerated deactivation of the catalytic bed due to high metal content, which originates from the alkali catalysts used in the HTL process and, to some extent, from the biomass itself.[21,24] These metals deposit on the active sites of the catalyst and promote sintering during catalyst regeneration.[25] Both of these mechanisms are irreversible. Even at low concentrations, metals can drastically reduce the lifetime of the catalyst, which needs to be replaced when the deposition of 3 – 4 wt% of metals is reached.[26] In addition, water can reduce catalyst activity by modifying its surface or the pore structure.[25] Less water and oxygen in the HDO feed is therefore beneficial due to the lower hydrogen requirement of the process and the lower amount of water in the HDO reactor. In addition, reduced density values for the bio-crude are desirable in order to increase the drop-in potential with different types of petroleum fuels, such as kerosene (775 to 840 kg/m^3),[27] diesel (820 to 845 kg/m^3)[28] and marine fuels (up to 991 kg/m^3).[29]

63 The application of a separation process upstream the hydrotreating, aimed at obtaining a large fraction
64 of HTL bio-crude exhibiting favourable properties for the hydrotreating process itself (especially low
65 water, oxygen and metal content), is worth analysing. Among alternative separation processes,
66 supercritical carbon dioxide (sCO_2) extraction is appealing for a number of reasons: i) it is an
67 environmentally friendly process, thus suitable by nature for the sustainability paradigm that should
68 characterize biofuel production; ii) CO_2 is internally generated in the HTL process; iii) it is a process
69 competitive to distillation in the presence of high boiling point oils, as temperatures required in
70 distillation may be too high even at high vacuum.[30] The separation of high boiling point liquid mixtures
71 using sCO_2 is at industrial level for the fractionation of perfluoropolyether oligomers[31] and it has been
72 applied at pilot or demonstration scale in a number of cases. Some representative examples include the
73 separation of fish oil ethyl esters,[32,33] or the removal of fatty acids from rice bran oil,[34] wheat germ oil[35]
74 and olive oil deodorizer distillate.[36]

75 In previous works, sCO_2 was reported capable of extracting a large fraction of a dewatered and
76 demetalized lignocellulosic bio-crude (extraction yields up to 49 wt%).[22,37] The procedure used for the
77 dewatering and demetalization of the bio-crude used in the mentioned previous works[22,37] is based on
78 dilution of the bio-crude in methyl ethyl ketone followed by washing in citric acid aqueous solutions.
79 Details on the procedure are available in the PhD Thesis of Jensen.[38] The previous works[22,37]
80 demonstrated problem-free operation above 80 °C (i.e. 80 – 120 °C), while the extractions were not
81 smooth and sometimes characterized by equipment clogging at 40 °C and 60 °C. The only other works
82 found on extraction of lignocellulosic bio-crudes refer to pyrolysis oils, where the extracts
83 demonstrated lower viscosity,[39] and lower water content than the corresponding feeds.[40,41]

The aim of this work is to assess the sCO_2 extraction process on a raw HTL bio-crude, which is to say a non-dewatered non-demetalized bio-crude obtained by gravimetric separation downstream the HTL reactor and without any further treatment. The specific objective of this work is therefore to assess the potential of sCO_2 extraction in carrying out dewatering, demetalization and bio-crude separation in a single process step, as well as to compare the characteristics of the sCO_2 separation on this raw bio-crude with the separation reported in previous works referring to a dewatered and demetalized bio-crude[22,37]. In addition, the tested operating conditions were expanded to higher pressures (up to 450 bar) and temperatures (up to 150 °C), as the previous works[22,37] indicated a positive effect with increasing these parameters. Extraction temperatures below 80 °C were instead not considered, due to the above-mentioned operating problems.

2. Materials and methods

2.1. Materials

2.1.1. Feed bio-crude

The feed HTL bio-crude was produced by continuous-flow hydrothermal liquefaction of pinewood at 400 °C and 300 bar using potassium carbonate as a catalyst and sodium hydroxide for pH adjustment, as previously reported in the literature.[22] Details on the effect of the operating parameters on the hydrothermal liquefaction process can be found in the work of Jensen et al.[6] As a difference compared to the previous work where sCO_2 was used to fractionate the bio-crude obtained in this thermochemical process, in the present work the bio-crude underwent neither dewatering nor demetalization. Therefore, it is a raw bio-crude simply obtained by gravimetric separation from the aqueous phase downstream of the HTL reactor. It appears as a black high-viscosity liquid (Figure 1a), even though less viscous than

the bio-crude of the previous work,[22] and as a stable emulsion of water in oil, since no phase separation was observed during 6 months of storage.

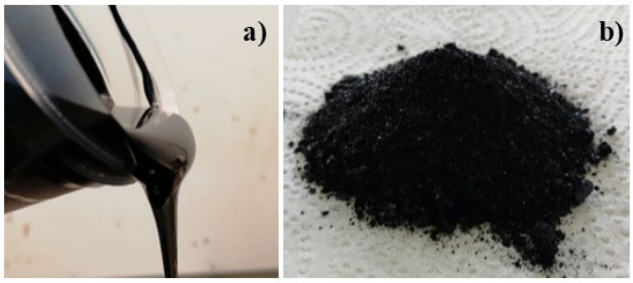


Figure 1. a) The HTL bio-crude used in this work; b) Example of the residue after sCO_2 extraction, tetrahydrofuran evaporation and mortar grinding. The example refers to the run at 450 bar and 100 °C.

2.1.2. Chemicals

Carbon dioxide (CO_2, 99.7 %) used for the supercritical extractions was purchased from Air Liquide (Denmark). Diethyl ether (DEE, 99 %) from VWR and pyridine (ACS grade) from Hach were used as solvents for the GC-MS analysis, while vanillin (99.8 %) and myristic acid (99 %) from Sigma Aldrich were used as internal standards. N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA, 98.5 %) from Sigma Aldrich was used to derivatize samples. HYDRANAL Titrant 2 and Solvent oil from Fluka, as well as the Aquastar 1 % standard from Merck were used for the Karl Fischer titrations (KF). The elemental analyser was calibrated with the PerkinElmer Cystine 4G powder. Tetrahydrofuran (THF, 99.9 %) from VWR was used as solvent for retrieving the residue inside the sCO_2 extractor at the end of each extraction. Ethylene glycol (glycol, 98%) from VWR was used to prepare the aqueous solution (1:1 by mass) employed as cooling fluid in the cold trap described in Section 2.2. Tetrabutyl-ammonium-hydroxide (TBAOH) 0.1 M in 2-propanol/methanol from Merck and tetraethyl ammonium bromide (TEABr) 0.4 M in ethylene glycol (Metrohm) were used as titrant and electrode electrolyte for

the total acid number (TAN) measurements. Toluene (99.5 %) and 2-propanol (99.8 %) from VWR were used as solvents for the TAN measurements. NIST traceable Metrohm buffers (i.e. pH 4, 7, 9) were used for calibration of the TAN electrode. Methyl ethyl ketone (MEK, 99 %) and methyl isobutyl ketone (MIBK, 99 %) from VWR, as well as THF, were used as solvents to estimate the density of the bio-crude. A 7 M nitric acid aqueous solution was used for acid digestion and the PlasmaCAL multi-element standard from SCP Science was used for the calibration of the ICP-OES instrument.

2.2. Supercritical CO_2 Extraction

The experimental setup was described in detail in a previous publication.[22] Therefore, only a short description of the setup and the experimental method used in this work, together with notes about modifications, is provided here. The apparatus consists of a high-pressure extraction vessel (i.e. the extractor) with a 178 cm^3 basket insert, where approximately 50 g of bio-crude were charged prior to an extraction. The basket insert was packed with 6 mm soda-lime glass beads up to approximately 1/3 of its height. The glass beads were chosen as an inert packing material that can disperse the bio-crude feed and improve its contact with the flowing sCO_2. A cylindrical filter (pore size 10 μm) is used at the top of the basket in order to prevent entrainment of particles. An automatically controlled heating jacket maintained the extraction temperature, which in this work was in the range 80 to 150 °C. The temperature indication was within ± 0.5 °C of the set value in all extractions. Liquid CO_2 from a dip-tube cylinder was subcooled by means of a heat exchanger fed with cold water (approx. 5 °C), which was provided by a thermostatic bath (Braun Frigomix U) and erogated by an immersion circulator (Julabo ED). Subsequently the CO_2 was compressed by a high-pressure pneumatic pump and fed to the entry port at the bottom of the extractor. The extraction pressure and the solvent flow rate were regulated manually by the pressure of the air supply of the pump and by a micrometering valve

downstream the extractor. The extraction pressures selected for this study were 330 bar and 450 bar. At the tested conditions the extractions were smooth, with pressure gauge readings within ± 3 bar of the set value in all runs. The micrometering valve was heated by hot air. The extract was collected in a 20 ml sampling vial inserted in a washing bottle immersed in a cold bath that was kept at approximately -10 °C by means of a refrigerating circulator (Lab Companion RW3-0525P). A subsequent gas-washing bottle immersed in the cold bath was packed with 3 – 4 g of cotton wool and aimed at collecting any further condensate, or retaining fine droplets or particles that might be entrained with the CO_2, in order to protect the downstream gas meter. The cotton wool was weighed after each extraction to account in the mass balance. The weight difference of the cotton before and after an extraction was on average 0.1 g, while there was no condensate observed in the corresponding gas washing bottle. The gas meter (Ritter TG3, max flow: 6 L/min; min flow: 0.1 L/min; accuracy: 0.5 %) measured the volume of CO_2 flowing through it and was equipped with a thermometer for measuring the gas temperature. The CO_2 flow rate in this work was in the range 3 to 4 L/min at gas meter conditions, corresponding to mass flow rates in the range 4 to 6 g/min. After the completion of each extraction, the apparatus was depressurized and let to cool down to about 80 °C, the basket insert dismounted and washed with 100 – 150 mL of THF in order to retrieve the residue. Preliminary tests showed that allowing the system to cool down to ambient temperature was unfeasible, since the residue solidified incorporating the glass beads and making its own retrieval problematic even with large amounts of THF. The drawback of the recovery of the residue at 80 °C consisted in THF evaporation, together with losses of water contained in the residue, which increased the uncertainty in the mass balance of water, as discussed in Section 3. For extraction D (see Section 3.2), a small sample (approx. 1 g) of the mixture THF + residue was saved for KF analysis, prior to solvent evaporation. THF was then separated from the residue by rotary vacuum evaporation at 50 °C. The amount of THF in the mixture was estimated by subtracting the

mass of the residue after evaporation from the mixture THF + residue before evaporation. After the evaporation of THF, the residue appeared as a dry solid. It was ground in a mortar to obtain a fine powder (Figure 1b) and to ensure representative sampling for analysis.

2.3. Analytical characterization

2.3.1. Elemental analysis

Elemental analysis (EA) was performed with a PerkinElmer 2400 Series II CHNS/O analyser coupled with a PerkinElmer AD-6 Autobalance. Carbon, hydrogen and nitrogen were measured while oxygen was calculated by difference. Sulphur was in all measurements under the detection limit of the instrument and was omitted, since it is not expected to be present in this type of bio-crude. The instrument was calibrated by the Cystine standard (single point calibration) prior to each series of measurements, which were performed at least in triplicate. The Absolute Relative Deviation (ARD) between the measured elemental mass fractions of the standard compared to the theoretical values for C, H, and N was on average 0.4 %. The Relative Standard Deviation (RSD) on oxygen was 17 % for the feed bio-crude, whereas it was on average 21 % for the extracts and 6.4 % for the residues.

2.3.2. Water content

A Metrohm 870 KF Titrino Plus, coupled with a Metrohm 860 KF Thermoprep, was used for the KF water determination. The instrument was calibrated regularly with the Aquastar 1 % standard, as well as controlled with the standard prior to daily measurements. The ARD between the measured mass fraction of water of the standard and its theoretical value was always below 3 %. Approximately 0.1 g of bio-crude, extracts and residue (after solvent evaporation) were analysed. A sample of approximately 0.1 g was titrated also for the residue + THF mixture sample, in the case of Extraction D

189 (see Section 3.2). In this case, however, also the pure THF used for retrieving the residue was titrated in
190 order to account for water already contained in the solvent. All KF measurements were performed at
191 least in triplicate. The RSD for the feed bio-crude was 4.9 %, whereas it was on average 4.8 % for the
192 extracts and 1.4 % for the residues.

193 2.3.3. Acid number measurements

194 The acid number measurements were carried out by potentiometric titration on a Metrohm Titrando
195 888 equipped with a Metrohm Solvotrode, following a procedure based on a modification of ASTM
196 D664 test method B, which was developed in a previous work.[22] The titration solvent was a mixture of
197 toluene, 2-propanol and demineralized water (100:99:0.5, by volume), instead of pure 2-propanol,[42] as
198 this mixture proved more effective in dissolving the bio-crude and its extracts of this work.
199 Approximately 0.1 g of bio-crude, extract or residue were diluted in 50 ml of the titration solvent and
200 titrated. The method allows for determination of two acid numbers: the carboxylic acid number (CAN)
201 and the total acid number (TAN), both expressed as mg KOH/g. The difference between TAN and
202 CAN is the acid number that corresponds to the phenolic nature of acidity (PhAN), which is an
203 important factor in lignocellulosic bio-crudes. The electrode was calibrated with 3 NIST traceable
204 buffers (i.e. pH 4, 7, 9) and the calibration always demonstrated an R-squared (R^2) of at least 0.999
205 between pH and the measured electrical potential. According to the method, two inflection points are
206 observed during the titration, which correspond to CAN and TAN, respectively. All TAN
207 measurements were performed at least in triplicate. The RSD on TAN, CAN and PhAN for the feed
208 bio-crude was 2.1 %, 1.4 % and 2.9 %, respectively. The average RSD on TAN, CAN and PhAN for
209 the extracts was 1.6 %, 1.0 % and 1.6 %, respectively. The average RSD on TAN, CAN and PhAN for
210 the residues was 1.3 %, 0.8 % and 1.0 %, respectively.

2.3.4. Density measurement

The density measurements were performed following a procedure developed before.[22] The bio-crude density was measured with an Anton Parr DMA 35 Ex densitometer after dilution in three solvents (THF, MIBK and MEK), 1:1 by mass in each. Due to the small quantity of the sCO_2 extracts, their density was calculated by accurately measuring the mass of a volume displaced by a precision pipette (Gilson Microman M1000). The mass was weighed on an analytical balance (OHAUS PA224C) and the capillary piston used for each measurement was calibrated with distilled water in order to calculate accurately the displaced volume. The relative standard deviation (RSD) of triplicate pipetting of distilled water was always lower than 1 %. Density of pure water at the laboratory ambient conditions was taken from NIST.[43] All density measurements were performed in triplicate. The RSD for the feed bio-crude was 0.9 %, whereas it was on average 1.4 % for the extracts.

2.3.5. Metal content determination by ICP-OES

The metal content of the feed and of all the extracts, together with the metal content of the residue of selected extractions, was determined by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES), utilizing a PerkinElmer Optima 8000 system. The content of Potassium (K) and Sodium (Na) was measured, since they were expected due to the use of K_2CO_3 as catalyst and NaOH as pH adjuster in the HTL process. Additional metals subjected to quantitation were Aluminium (Al), Iron (Fe), Magnesium (Mg) and Titanium (Ti), since they are expected to derive from wear of equipment and natural presence in the pinewood biomass.[24] Samples were prepared by acid digestion and dilution. Approximately 0.5 g of sample were digested in an autoclave in 20 ml of 7 M aqueous nitric acid for 30 minutes at 120 °C and 2 bar. A blank of the nitric acid solution was digested as well for each set of samples and non-zero concentrations were subtracted from the sample measurement in order to account

for baseline errors. The digested samples were diluted with distilled water in a volumetric flask (Class A), and filtered by filter paper (pore size 4-12 μm). Dilution to 50 ml was performed for the bio-crude and the residues, while dilution to 25 ml was applied for the extracts. In case of visually observed turbidity of the solution, which was assumed to be due to organic particles, a second filtration was performed to acquire a transparent fluid to protect the plasma torch. In order to ascertain the reproducibility of the sample preparation procedure, eight samples of different mass of the feed bio-crude (i.e. 0.4 to 1 g) were digested and analyzed. The extracts and residues were measured in duplicate. The standards solutions used for calibration were prepared by diluting the PlasmaCAL standard in demineralized water and measured in triplicate. The range was 0.2 to 2 mg/L for all the metals, with the exception of Fe (0.2 to 10 mg/L), K (2 to 100 mg/L) and Na (2 to 10 mg/L). The R^2 for all elements was always above 0.999 except for Na, which was however always above 0.988. The Relative Standard Deviation (RSD) of the triplicate measurements of the calibration standards was always lower than 1 %, while the ARD with respect to the analyzed standard value was always between 0 and 4 % for all metals except Na. In fact, Na had a higher ARD (always lower than 20 %) which is assumed to be an inherent instrument inaccuracy for Na measurement. High uncertainty in Na concentration by ICP measurements has been reported in literature for fast pyrolysis oil of woody biomass.[44]

2.3.6. Component identification by GC-MS

GC-MS analysis was performed for the identification and quantitation of the GC-detectable fraction (i.e. the volatile fraction) of the bio-crude feed and the extracts. In addition, GC-MS after silylation was performed to identify and quantify free fatty acids and a few phenolic components for which the ion peaks had better resolution than in the non-silylated samples. The analysis was performed on a

PerkinElmer Clarus 680 GC coupled with a PerkinElmer Clarus SQ 8T MS. For the analysis of the feed, the bio-crude was extracted with DEE (bio-crude to solvent ratio approximately 1:50 by mass) and the resulting DEE-rich mixture was filtered with a syringe filter (pore size 0.45 μm). The amount of the DEE-soluble fraction of the bio-crude was determined gravimetrically from the filtrate, after evaporation of the solvent overnight in a fumehood. All sCO_2 extracts were instead fully soluble at a 1:10 extract to DEE ratio (mass basis). GC-MS samples were prepared by mixing approximately 0.1 g of the DEE-soluble fraction of the feed, or approximately 0.1 g of extract, with approximately 0.7 g a of a DEE solution containing a known amount of vanillin (1 wt%) as internal standard (IS). Vanillin was selected as IS as most of the identified components were oxygenated aromatics with some degree of similarity to vanillin, with vanillin being however not present in the bio-crude samples, not overlapping with chromatographic peaks of species contained in the bio-crude samples. With regard to the GC-MS after silylation, the feed and extract samples were silylated as follows: about 0.1 g of each sample were dried in a heating cabinet for 2 h at 120 °C, then diluted in pyridine, which contained a known amount of myristic acid (1 wt%) as IS, and derivatized with BSTFA at 60 °C for 20 minutes. Myristic acid was selected as IS as the GC-MS analysis after silylation was aimed at fatty acids, with myristic acid being howver not present in the bio-crude and not overlapping with chromatographic peaks of species contained in the bio-crude samples. The mixture ratio of sample – pyridine – BSTFA was 1:1:1 in mass basis. The derivatized samples were further diluted in DEE (1:25 by mass). For all samples, 1 μl was injected in a PerkinElmer Elite 5 column (30 m, 0.25 mm ID, 0.1 μm), with the temperature ramping from 40 °C to 250 °C at a rate of 10 °C/min. The initial temperature was held for 3 min while the final temperature was held for 6 min. The injector was maintained at 300 °C and the helium carrier gas at 1.0 ml/min. The mass fraction of the identified analytes i was calculated as: $w_i = w_{IS} \cdot A_i/A_{IS}$, where A_i and A_{IS} are the chromatographic areas of the analyte i and the IS, respectively,

278 whereas w_{IS} is the mass fraction of the internal standard (vanillin for pure samples, myristic acid for
279 derivatized samples). Triplicate GC-MS measurements were performed for all samples in random
280 consecution in order to account for random GC response differences.

281 # 3. Results and discussion

282 ## 3.1. Characterization of the feed bio-crude

283 Table 1 reports the measured bulk properties of the bio-crude feed, including the DEE-soluble fraction,
284 density, TAN, CAN, PhAN, water and metal content. In addition, the elemental carbon (C), hydrogen
285 (H), nitrogen (N) and oxygen (O) mass fractions, as well as the H/C and O/C ratios, are reported on a
286 water-free basis. As can be seen, the density of this bio-crude is approximately 1030 kg/m^3, which is in
287 line with values reported for HTL bio-crudes from lignocellulosic biomass, reported in the range 970 to
288 1140 kg/m^3.[5,17,20] The TAN value of 97 mg KOH/g is within the values reported in literatures, which
289 range from 30 to 150 mg KOH/g for HTL lignocellulosic bio-crudes.[5,18,45] With regard to the elemental
290 composition, the mass fractions are also in line with typical woody HTL bio-crudes (i.e. C: 0.76 – 0.84;
291 H: 0.07 – 0.10; N: 0.002 – 0.030; O: 0.05 – 0.15).[5,7,17,18]

292 **Table 1**. Bulk properties at ambient conditions, elemental composition on a water-free basis and metal
293 mass fraction of the feed bio-crude with standard deviations.

Property		Metal content (mg/kg)	
DEE soluble fraction	0.70 ± 0.03	Al	40 ± 9
Density (kg/m^3)	1030 ± 9	Fe	190 ± 20
TAN (mg KOH/g)	97 ± 2	K	3400 ± 400

CAN (mg KOH/g)	42 ± 1	Mg	96 ± 20
PhAN (mg KOH/g)	56 ± 2	Na	3800 ± 500
Water content (wt%)	5.7 ± 0.4	Ti	40 ± 3
C mass fraction	0.80 ± 0.01	Total metals	8500 ± 800
H mass fraction	0.08 ± 0.01		
O mass fraction	0.10 ± 0.02		
N mass fraction	0.017 ± 0.005		
H/C	1.2 ± 0.1		
O/C	0.09 ± 0.02		

294

295 As can be seen in Table 1, the bio-crude exhibits a water content of almost 6 wt%, which is at the lower
296 range of typical reported values for HTL lignocellulosic bio-crudes (i.e. 5 – 15 wt%).[4,5,7,17] In addition,
297 the bio-crude exhibits a high metal content of around 0.85 wt%, with potassium (K) and sodium (Na)
298 constituting more than 90 % of the total. The metal content is dependent on the biomass ash content,
299 but since woody biomass has typically low ash,[46] the high metal content mostly originates from the
300 chemicals used in the HTL process. This behaviour was observed by Déniel et al.[21], who performed
301 HTL of blackcurrant pomace and observed ash contents in the bio-crude increasing (i.e. from 0.1 to 5.3
302 wt%) with sodium hydroxide added (i.e. from 0 to 9 wt%). With regard to Mg, it is known to bind with
303 organic molecules in biomass,[47] while Al and Fe are typically introduced during the harvest and
304 processing of the biomass.[24] Ti is one of the less abundant metals in biomass,[47] which is assumed to be
305 introduced by equipment wear. The presence of Mg, Al, Fe, Ti, although in relatively small amount
306 (0.03 wt% in total), is confirmed in this work.

In total, 46 components were identified by GC-MS in the DEE-soluble fraction of the feed. Detailed list of the components along with retention time (RT), classification, molecular weight (MW), chemical formula, CAS registry number and their mass fraction (wt%) in the feed bio-crude is reported in the supporting information (Table S1). The identified components constitute 19.3 wt% of the feed bio-crude. The unidentified components of this volatile fraction correspond to a chromatographic area that is about twice as large as the identified fraction, which means that, as a rough estimation, about 60 wt% of the bio-crude can be assumed as volatile. The identified components were lumped into 10 categories according to their chemical functionalities: 1) Cyclic aliphatic (C6 – C9) ketones, saturated or monounsaturated (Ketones, K); 2) Alkylbenzenes (AB); 3) Phenol and alkylphenols (Phenols, P); 4) Guaiacol and alkylguaiacols (Guaiacols, G); 5) Benzenediols and acetyl derivatives of benzenediols (BD); 6) 2- and 3-ring aromatic hydrocarbons (PAH); 7) Dehydroabeityl alcohol (ArAl); 8) Short chain fatty acids, in the range C2 – C8 (SFA); 9) Long chain fatty acids, in the range C16 – C18 (LFA); 10) Dehydroabietic acid (ArAcid).

The largest fraction of the identified components is constituted by PAHs, which account for 9 wt% of the bio-crude. Even though such components are not often reported often, some have been reported by Pedersen et al.[18] in the distillation residue of woody HTL bio-crude. Retene has been reported in the HTL bio-crude of softwood lignin.[48] Retene and phenanthrenes are possibly the degradation products of dehydroabietic acid in the biomass, since they are typically found as products of its thermal degradation (e.g. wood smoke).[49,50]

Single-ring aromatic hydrocarbons (alkylbenzenes, AB) are also found, albeit in lower amount (1 wt%). Aliphatic hydrocarbons are not observed. Fatty acids (SFA + LFA) are the second most abundant group, accounting for almost 4 wt% of the oil, with the LFA being largely predominant (3.75

wt%). Fatty acids are typically one of the most abundant classes in bio-crudes,[51] although their mass fractions are not often reported. Dehydroabietic acid and dehydroabeytil alcohol are also observed in remarkable amount, 1.8 wt% and 0.4 wt%, respectively. Abietane skeleton diterpenoids are major structures of conifers such as pine,[50] and dehydroabietic acid is therefore expected to be present in the pine biomass of the bio-crude used in this work. The presence of dehydroabietic acid in the bio-crude suggests that it remains unconverted, to some extent, during the HTL process. Ketones are always present in lignocellulosic bio-crudes. However, even though they are numerous, they are in low amount, summing up to 0.5 wt% of this oil. Single-ring phenolics (alkylphenols, catechols and other types of benzenediols, and guaiacol) account altogether for 2.6 % of the bio-crude. Alkylphenols, catechols and guaiacols are typically observed in HTL of softwood lignin,[3,14,48] with the ratio catechols to guaiacols increasing with the HTL reaction temperature.[14,48] Their presence and the low guaiacols/catechols ratio is therefore qualitatively in line with the high-temperature hydrothermal decomposition of the lignin contained in the original biomass of this work.

3.2. Extraction conditions and yields

The experimental conditions and mass balances for each supercritical extraction are reported in Table 2. Four different extraction temperatures (i.e. 80, 100, 120 and 150 °C) were tested at two pressures (i.e. 330 and 450 bar). The lower pressure (330 bar) was chosen to be within the typical pressure range of the HTL process,[19] therefore allowing the investigation of the sCO_2 extraction at pressure levels comparable to the HTL reactor, as higher pressures in the downstream separation would be less favourable for process economics. The higher pressure (450 bar) was selected on the basis of previous works,[22,37] which showed promising results in terms of attainment of high extraction yields. The duration of the extractions was between 5.3 and 6.4 hours. Table 2 also reports: the density of pure CO_2

351 at the operating conditions of the extraction (ρ); the average solvent mass flow rate (Q); the mass of
352 feed bio-crude charged in the extractor at the beginning of an experiment (F); the mass of the four
353 extracts collected in each extraction (E1, E2, E3 and E4), with the exception of run A where only three
354 extracts were collected. Run A was the extraction with the lowest yield and the third sampling vial (i.e.
355 E3) was maintained for a longer period to avoid ending up with E4 sample mass inadequate for
356 analysis. The mass balance discrepancy (losses, L) of each run is also reported, together with the total
357 solvent-to-feed ratio (i.e. at the end of the run) and the total extraction yield. The total extraction yield
358 is defined as the ratio of the total mass of the collected extracts to the mass of the feed. It is therefore
359 determined gravimetrically. Data from Table 2 were also used to calculate the Vapour Phase Loading
360 (VPL) as the extractions progress. VPL is defined as the ratio of the mass of extract in a given time
361 interval over the mass of solvent flowed in the same interval. VPL values were also used to evaluate
362 the reproducibility of the extraction procedure. In this regard, six repetitions of Run H were carried out
363 and the RSD on VPLs were found to be: 7.1 % for extract 1 (E1); 11.6 % for extract 2 (E2); 14.0 % for
364 extract 3 (E3); 11.3 % for extract 4 (E4).

365

366 **Table 2**: Experimental extraction conditions and results. Temperature (T); pressure (P); CO_2 density
367 (ρ); average CO_2 mass flow rate (Q); mass of feed (F); mass of extract samples (E1, E2, E3, E4); mass
368 of residue (R); losses (L); solvent-to-feed ratio (S/F); total yield (Y_T).

Run ID	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
T (°C)	80	100	120	150	80	100	120	150
P (bar)	330	330	330	330	450	450	450	450

ρ (kg/m^3)[a]	773	696	623	531	851	790	731	650
Q (g/min)	5.2	5.5	5.0	4.7	5.7	5.9	5.0	4.8
F (g)	48.9	52.6	51.3	53.6	53.9	51.5	54.2	51.9
E1 (g)	6.6	5.7	7.7	5.4	5.3	8.4	6.9	6.6
E2 (g)	6.1	5.9	5.3	6.9	5.3	5.8	6.4	7.6
E3 (g)	8.9	6.0	5.6	5.0	5.3	5.5	6.9	6.2
E4 (g)	-	6.2	5.0	7.5	8.1	7.2	7.8	7.3
R (g)	23.1	24.4	22.8	23.8	23.9	21.0	22.2	18.0
L (%)	8.2	6.5	9.4	9.0	9.4	7.0	8.5	12.0
S/F (g/g)	30.2	36.5	36.3	31.6	32.4	36.7	33.3	30.0
Y_T (%)	44.1	45.1	46.0	46.3	47.3	52.4	51.5	53.4

[a] Taken from NIST [43];

In Table 2, it can be seen that the highest extraction yield of 53.4 % is not achieved at the highest solvent density, but in fact at the highest temperature and in combination with high pressure. This observation highlights the importance of high temperatures for sCO_2 separation of bio-crudes and it is in line with previous works,[22,37] where extraction yields up to 48.9 % have been achieved at 448 bar and 120 °C while low efficiency and bad operability were observed below 80 °C. Importantly, not only was Run H characterized by the highest yield but also by the lowest S/F (i.e. 30 g/g). These results indicate that operating conditions of the downstream sCO_2 separation at pressures higher than the pressure of the HTL reactor should not be discarded a priori in the design of the process.

In Figure 2, the extraction yield is plotted vs. the solvent to feed ratio at the four different temperatures and the two pressures. In all cases, the effect of pressure is beneficial for the extraction efficiency,

showing higher extraction yields at given S/F values. This is a general feature in sCO_2 separation processes, since higher pressures at given temperatures lead to higher solvent density and increased solvent power. The perusal of Figure 2 also shows that the increase in process efficiency with pressure at given temperature is more pronounced at higher temperatures. This is due to the isothermal variation of the solvent density, which is monotonically increasing with temperature, ranging from 78 to 119 kg/m^3 as temperature increases from 80 to 150 °C. The increase of the yield for given S/F as pressure increases at constant temperature, which is to say the increased extract to solvent ratio (E/S) with pressure, is typically observed in sCO_2 extraction processes. The primary reason is the increase in solubility of extractable species in the supercritical solvent. However, it is recognised that the extraction yield is affected by both the solubility of extractable species and by mass transfer parameters .[52]

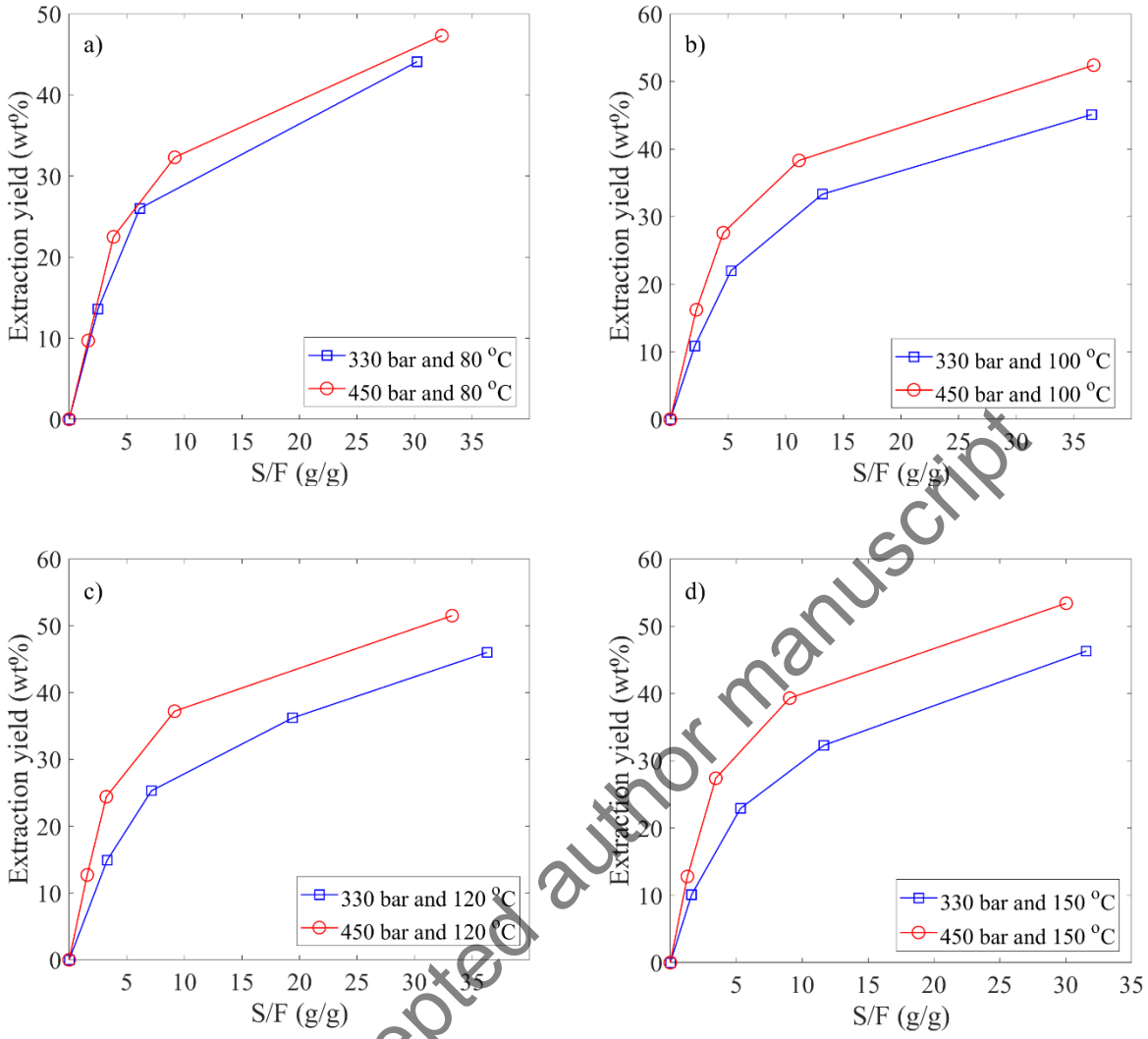
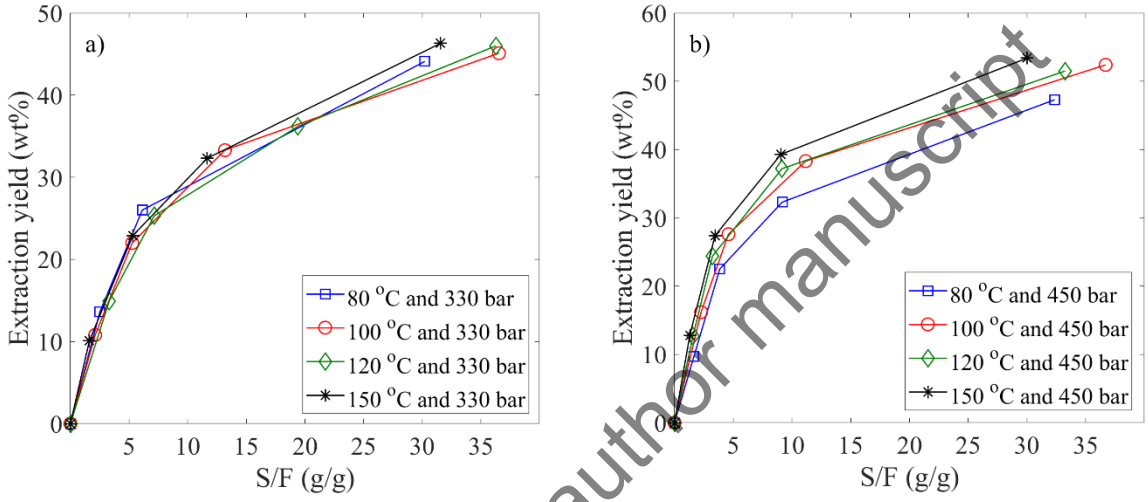


Figure 2. Pressure effect on the extraction yield vs. solvent to feed ratio (S/F) at: a) 80 °C; b) 100 °C; c) 120 °C and d) 150 °C.

In order to visualize this combined effect, Figure 3 shows the extraction yield against S/F at the two studied pressures (i.e. 330 and 450 bar). At 330 bar it is observed that, even though the increase of temperature decreases the solvent density, the extraction yields are comparable for all temperatures. This could indicate that the solubility of the bio-crude at this pressure reduces with temperature, but the mass transfer parameters improve enough to counteract the reducing solubility. Contrary to the

399 behaviour at 330 bar, at 450 bar the extraction yield slightly increases with temperature. This could be
400 either due to a crossover pressure between 330 and 450 bar that results to solubility increasing with
401 temperature, or due to mass transfer improvements prevailing to the solubility decrease with
402 temperature. Phase equilibrium measurements of the solubility of this type of bio-crude in sCO_2 are not
403 available in the literature and they would be needed to prove the above-mentioned hypotheses.



404

405 **Figure 3.** Temperature effect on the extraction yield vs. solvent to feed ratio (S/F) at: a) 330 bar and b)
406 450 bar.

407 In theory, the slope of the curves in Figure 2 and Figure 3 (dE/dS) indicates the Vapour Phase Loading
408 (VPL), i.e. the instantaneous value of the mass of components extracted per unit mass of solvent. The
409 collection of a number of extracts per each run allowed to estimate average VPL values (ΔE/ΔS) as the
410 extraction proceeds. Results are presented for the extractions at 100 °C (Figure 4a) and 150 °C (Figure
411 4b) and at 330 (Figure 5a) and 450 bar (Figure 5b). Similar trends as Figure 4 are observed at all
412 temperatures studied.

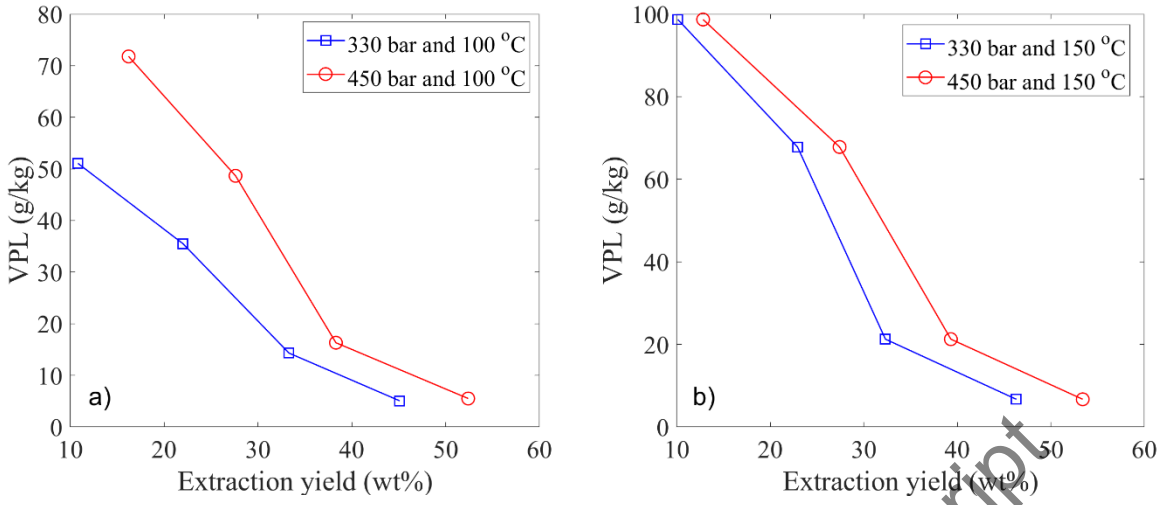
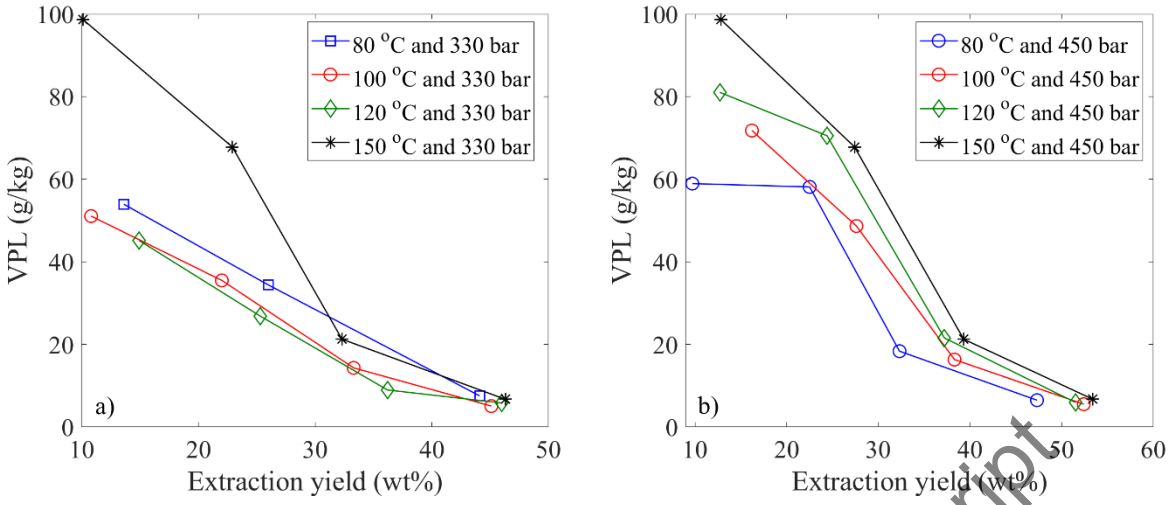


Figure 4. Pressure effect on the vapour phase loading (VPL) vs. extraction yield at: a) 100 °C; b) 150 °C.

As usual, VPL values decrease during the extraction, as the unextracted bio-crude remaining inside the extractor becomes progressively heavier. As can be seen from Figure 4, higher pressure at given temperature leads to higher VPL values, which resulted to the highest extraction yield with the least solvent used in Run H. On the other hand, the effect of temperature is more complex as can be seen in Figure 5. Figure 5b shows that higher temperatures affect positively the VPL at 450 bar, especially in the early stages of the extraction. Whereas at 330 bar (Figure 5a) this effect is only observed at the highest temperature (i.e. 150 °C) and for extraction yields below approximately 30 wt%.



423

424 **Figure 5**. Temperature effect on the vapour phase loading (VPL) vs. extraction yield at: a) 330 bar and

425 b) 450 bar.

426 An interesting observation arises when the results of this work at 120 °C and 450 bar are compared

427 with an extraction run carried out at basically same conditions (120 °C and 448 bar) on a dewatered

428 bio-crude (water content 2.7 %), presented in a previous work.[37] In Figure 6a, the cumulative extract is

429 plotted against S/F for a normalized feed mass (i.e. 50 g). It can be seen that the extraction is more

430 efficient for the non-dewatered bio-crude of this work. The results of this work show an increase of

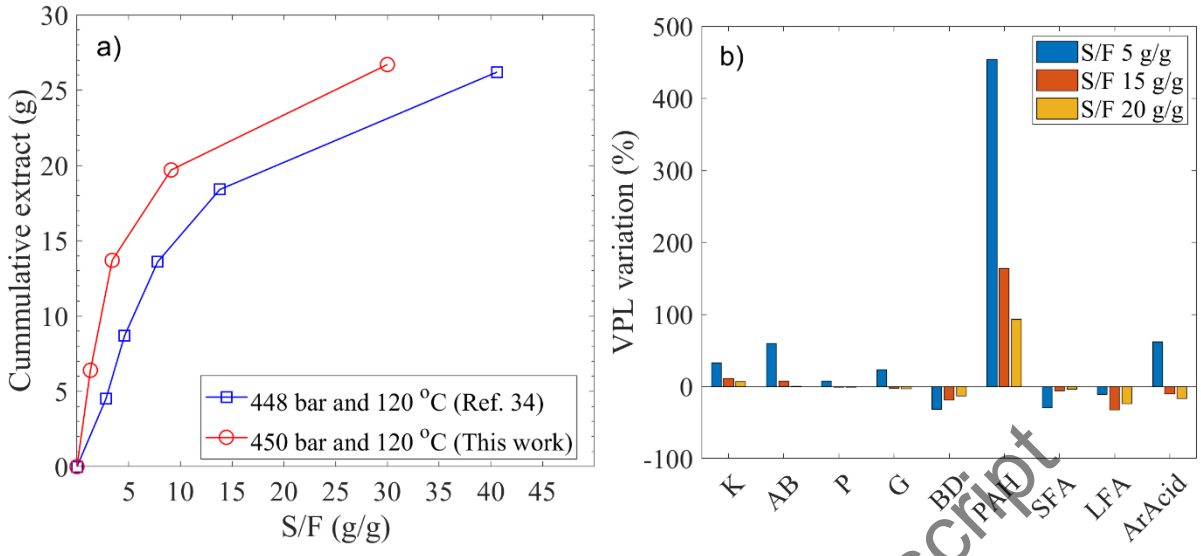
431 extract in the range 3 to 6 g, for given S/F values ranging from 1.3 to 30. The difference in water

432 content for 50 g of the two bio-crudes is 1.5 g. Considering that the variation of the extract mass is 2 to

433 4 times higher than the water content in the feed, it is apparent that the increase in the extract cannot be

434 entirely attributed to the extraction of water itself. Therefore, the presence of water actually enhances

435 the extraction of other molecules contained in the bio-crude feed.



436

437 **Figure 6.** a) Cumulative extract mass (normalized to 50 g feed) vs. S/F for extraction of dewatered bio-
438 crude (2.7 wt% water)[37] and the bio-crude of this work (5.7 wt% water); b) Vapour phase loading
439 (VPL) variation of chemical classes between dewatered bio-crude[37] and the bio-crude studied in this
440 work. Ketones (K); Alkylbenzenes (AB); Phenols (P); Guaiacols (G); Benzenediols (BD); 2- and 3-ring
441 aromatic hydrocarbons (PAH); Short chain fatty acids, in the range C2 – C8 (SFA); Long chain fatty
442 acids, in the range C16 – C18 (LFA); Dehydroabietic acid (ArAcid).

443 This enhancement can be discussed in further detail with the aid of Figure 6b, where the variation of
444 VPL, in the two above-mentioned experiments, is shown for specific chemical classes at different S/F
445 ratios. In Figure 6b, nine out of the ten classes defined in this work are represented, since no aromatic
446 alcohols were reported in the previous work. The major observation from Figure 6b is that the higher
447 water content enhances dramatically the VPL of the non-polar hydrocarbons (i.e. AB and PAH). In
448 addition, components of low polarity (e.g. K, P, G) are extracted more efficiently. The more polar
449 components (i.e. BD, SFA and LFA) have in general higher VPL for the bio-crude with the lower
450 initial water content. In all cases the benefit of the presence of water is reduced while the extraction

progresses, which is in line with the slope in the curves of Figure 6a, and suggests that this effect becomes less pronounced as the unextracted residue becomes drier. The above indicates that the application of sCO_2 extraction on the non-dewatered bio-crude leads to both increased VPL and selectivity with respect to polar and apolar components.

3.3. Bulk properties and elemental composition

The values of CAN and PhAN for the extracts increase with the extraction yields (E/F) at all conditions. As an example, the CAN and PhAN values of the extractions at 150 °C are plotted vs. the extraction yield and shown in Figure 7.

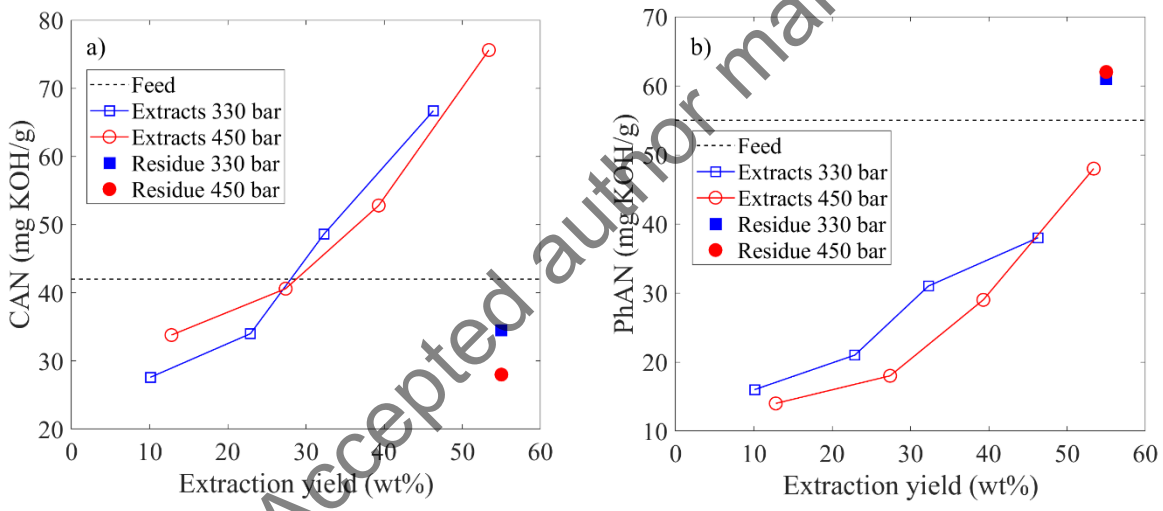


Figure 7. Effect of pressure on a) CAN vs. extraction yield and b) PhAN vs extraction yield at 150 °C

CAN values of the first extracts range from 28 to 41 mg KOH/g, which are values always lower than the CAN value of the feed (42 mg KOH/g). This observation indicates that fatty acids are not preferentially extracted at the beginning of the batch separation process. As the extraction proceeds, the CAN value of the extracts increases, with values ranging from 34 to 41 mg KOH/g for E2, 49 to 53 mg KOH/g for E3 and 67 to 76 for E4 mg KOH/g. The trend of the CAN indicates that fatty acids are

progressively more extracted as the extraction proceeds. CAN of the residues ranges from 28 to 35 mg KOH/g, which means that, in most of the cases, the residue is partially depleted of carboxylic acids. When CAN values in this work are compared to those of previous work on a dewatered bio-crude,[22] it is observed that in the early stages of the extraction (S/F up to 5 g/g), the literature CAN values are higher (i.e. 37 – 47 mg KOH/g) than those of this work (at similar conditions 80 -120 °C and 255 – 400 bar). This further indicates that, at the beginning of the separation process, the fatty acids are less extracted in the presence of higher water content.

On the other hand, PhAN values of the extracts are always lower than the value of the feed (55 mg KOH/g). In this case, the values ranges from 14 to 16 mg KOH/g for E1, 18 to 21 mg KOH/g for E2, 29 to 31 mg KOH/g for E3 and 38 to 48 mg KOH/g for E4. Consistently, the PhAN value of the residue is higher than the feed, resulting to be in the range 61 to 62 mg KOH/g. Overall, the reduced CAN and increased PhAN in the residue indicates that its type of acidity is shifted towards phenolic nature. The highest value of CAN was observed for extract E4 at 450 bar and 150 °C (i.e. 76 mg KOH/g), while the lowest PhAN was observed for extract E1 for the same extraction (i.e. 14 mg KOH/g). A high CAN and low PhAN is advantageous for hydrotreating since HDO of fatty acids is easier than opening aromatic rings.[53,54] In addition, the increased PhAN indicates that high molecular weight phenolic components remain in the residue. This fraction is expected to be resistant to HDO, as it was similarly shown for the residue of n-pentane extraction of lignocellulosic bio-crude.[55]

The density of the extracts was found in the range of 914 to 1034 kg/m^3, increasing with the extraction progression. Most of the sCO_2 extracts exhibit a moderate reduction compared to the feed, with the maximum being a 10 % reduction for early extracts (i.e. E1, E2). The later extracts show a density comparable to the feed, with only the final extracts (i.e. E4) at 80 °C and 300 bar and 100 °C and 450

bar exhibiting a density slightly higher than the feed (see example in Figure 8b). The extraction conditions show negligible influence on the density of the extracts. As in the case of acidity, also in the case of density the trends were similar at all experimental conditions. Figure 8a shows an example referred to the extractions at 150 °C, whereas Figure 8b shows two cases at 450 bar.

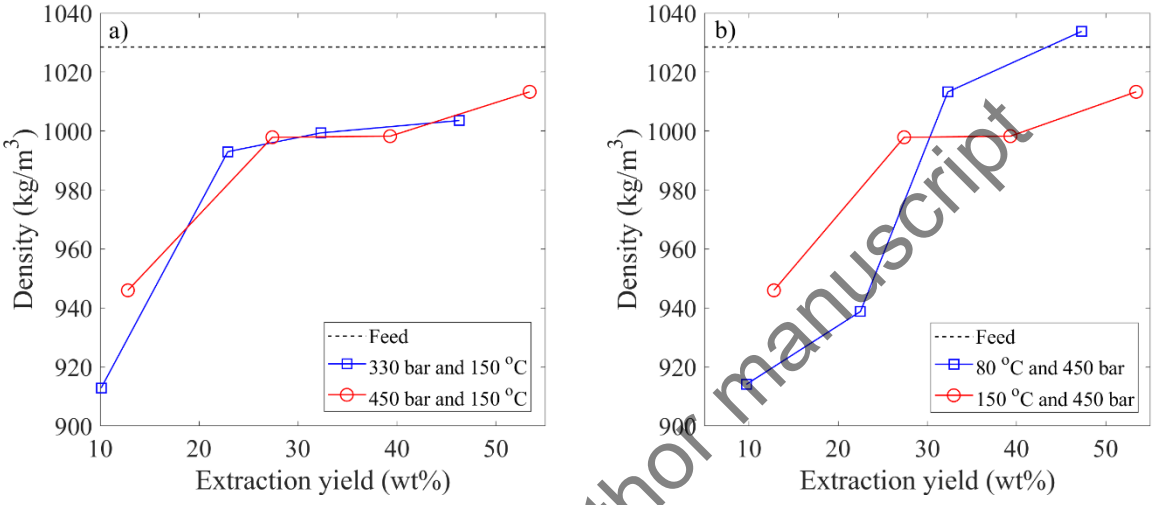
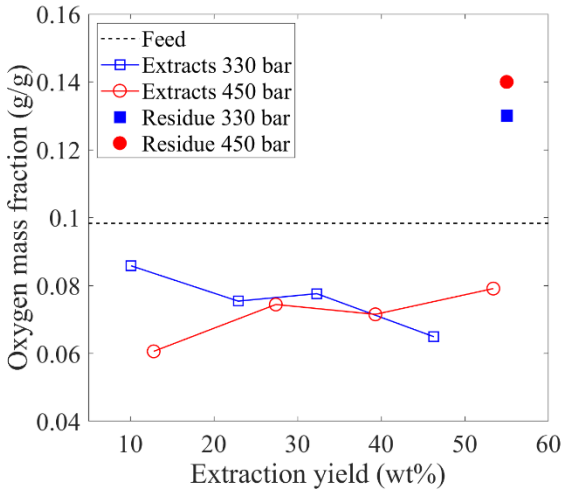


Figure 8. Density vs. extraction yield at: a) Constant temperature (150 °C); b) Constant pressure (450 bar).

The water content of the extracts was measured for the experimental runs B, E, D, and H and resulted to be in the range 1.3 to 1.8 wt%, with no clear trend with the extraction pressure and temperature. Importantly, the values are consistently and remarkably lower than the water content of the feed (i.e. 5.7 wt%). The water content of the residues of the same extractions was measured after evaporation of the solvent used for their recovery. The obtained values were in the range 0.9 to 1.6 wt%. The fact that the water content was observed to decrease both in the residue and in the extract clearly indicates that it was not possible to recover all the water from the system, due to lack of complete recovery in the cold trap and/or water losses during the recovery of the residue at the end of the extraction. The mass

balances indicate that approximately 50 % of the water originally in the feed was not retrieved in the extracts and in the residue. For extraction D, the water content of the residue was measured by means of direct KF titration of a sample of THF solution, i.e. before the solvent evaporation. The value was 1.2 wt%, while the corresponding value after solvent evaporation was 0.9 wt%. This means that about 2% of the water in the feed was lost during the vacuum evaporation, which is not significant with regard to the total water losses. Interestingly, the earlier extracts (i.e. E1, E2) exhibited spontaneous separation of water, with water droplets collecting at the bottom of the storage vials. This was not observed for the later extracts (i.e. E3, E4). This freely separated water was determined for extractions at 150 °C and it was 0.4 g and 0.6 g for extractions H and D, respectively, which corresponds to 13 % and 20 % of the original water in the feed. Even though it was not possible to close the mass balances on water, the results clearly indicate that sCO_2 process co-extracts water from the HTL bio-crude, induce the separation of water from the extracts and allows reducing the water content in the residue as well.

The carbon mass fraction in the extracts was in the range 0.80 to 0.81, which are values close to the values of the feed (i.e. 0.80) and the residue (0.78 – 0.79). The hydrogen content (on a water-free basis) is slightly increased in the extracts (0.09 – 0.11), with respect to the feed (i.e. 0.08) and the residues (range 0.07 – 0.08). The oxygen mass fraction of the extracts (on a water-free basis) was for all extractions lower than that of the feed, ranging from 0.05 to 0.07 (vs. 0.10 in the feed). In line with this, the mass fraction of oxygen of the residues increased, ranging from 0.13 and 0.15. The oxygen mass fraction of the extractions performed at 150 °C is plotted in Figure 9 as a function of the extraction yield. Similar trends are observed in all extractions.



524

525 **Figure 9**. Oxygen content on a water-free basis vs extraction yield for extractions at 150 °C.

526 3.4. Metal content of bio-crude extracts and residues

527 The metal content of extracts and residues was measured for extraction B, D, G and H. In all cases, the
528 extracts were found almost completely devoid of metals. The metal content was reduced from 95 % to
529 99 %, compared to the feed value. The analysis of the residues confirmed that the metals are
530 concentrated in the unextracted phase. The trends were very similar in all runs. As an example, the
531 results obtained with the extraction at 330 bar and 150 °C are reported in Figure 10.

532 As can be seen in Figure 10, potassium and sodium, which constitute more than 90 % of the metal
533 content of the feed, are reduced from 3400 mg/kg and 3800 mg/kg down to values ranging from 30 to
534 40 mg/kg and 70 to 100 mg/kg, respectively. Aluminium, iron and titanium are reduced in the extracts
535 down to values below 10 mg/kg in all extracts. Interestingly, magnesium remains unchanged, which
536 suggests that it may be in organometallic components [24] that can be solubilized by sCO_2. In all cases,
537 the total metal content was found to be drastically reduced from 8500 mg/kg down to an average value
538 of 170 mg/kg.

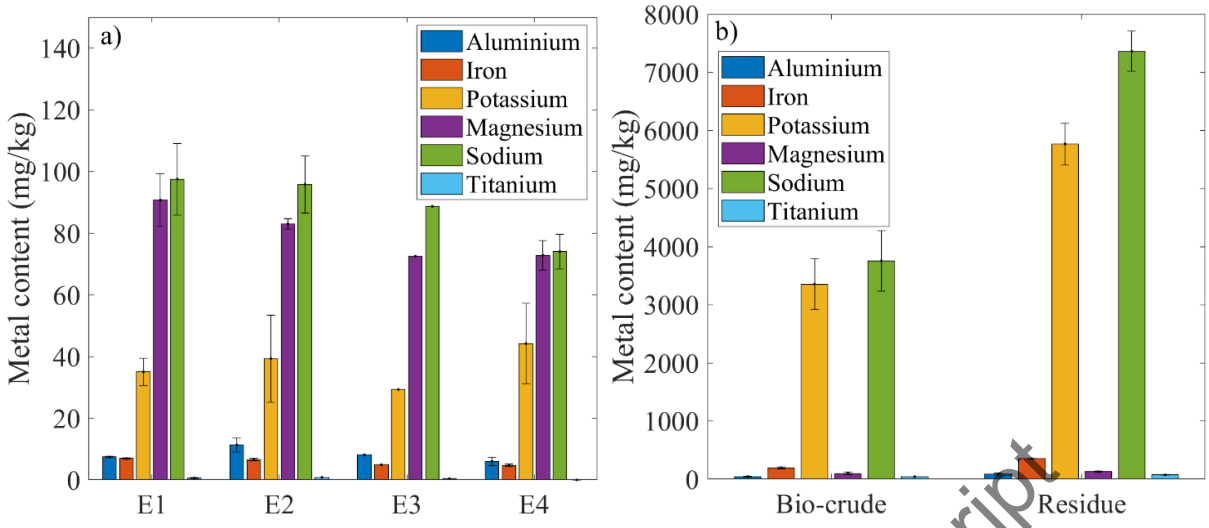


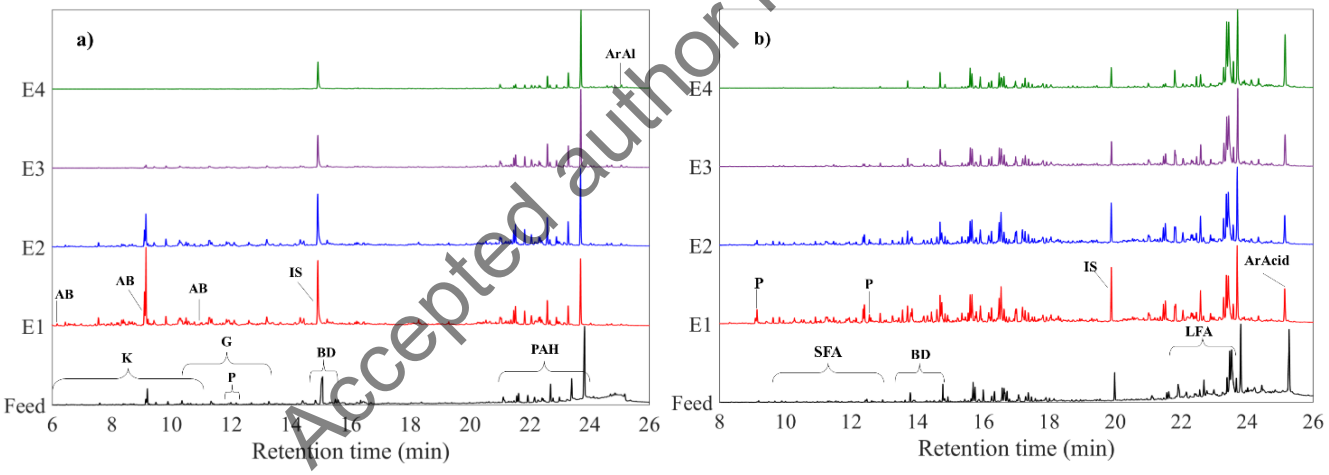
Figure 10: Metal distribution between bio-crude, extracts (i.e. E1, ..., E4) and residue for the extraction at 330 bar and 150 °C. Error bars represent the standard deviation of at least duplicate measurements.

The small amount of metals in the extracts indicates that either they can be entrained together with fine water droplets where they are dissolved in, or they are present, albeit in very small amount, as organometallic components that are soluble in sCO_2. The 10 μm filter at the top of the basket insert is expected to act as a factor limiting the entrainment of water droplets.

3.5. Chemical composition by GC-MS

Figure 11a shows the total ion chromatograms (normalized with respect to the highest peaks) of the non-derivatized samples of the feed bio-crude and the extracts obtained at 330 bar and 150 °C. Figure 11b shows the corresponding chromatograms for the derivatized (silylated) samples. The trends shown in Figure 11 are qualitatively representative of all extractions carried out in this work. It is noted that some classes of components exhibit overlapping Retention Time (RT) ranges, which does not allow assuming that all components in a certain RT range are expected to belong to a specific class. As can be seen in Figure 11a, the concentration of lower retention time components (up to 17 min) is increased in

554 the first extract, while it decreases in subsequent extracts. This indicates that these components are
555 preferentially extracted at the beginning of the process and depleted in the unextracted oil. The peak
556 areas of higher retention time components (21 – 25 min) increase over time, which is particularly
557 visible by the increasing difference between the largest peak of the chromatograms (retene at 23.8 min)
558 and the IS (vanillin at 15.1 min). This indicates that they are not preferentially extracted in the early
559 stages of the extraction, but are substantially extracted as their concentration in the residue increases.
560 Similar trend is observed in the derivatized sample (Figure 11b), with light components (RT up to 15
561 min) extracted preferentially in the early stages while gradually depleted. In this case, the heavy acids
562 (i.e. LFA and ArAcid, RT above 21 min) are progressively extracted in relatively higher amounts as the
563 extraction proceeds.

564 

565 **Figure 11**. Chromatograms of feed bio-crude and extracts E1 – E4 of the extraction at 330 bar and 150
566 °C. a) non-derivatized samples; b) derivatized (silylated) samples. Ketones (K); Alkylbenzenes (AB);
567 Phenols (P); Guaiacols (G); Benzenediols (BD); 2- and 3-ring aromatic hydrocarbons (PAH); Aromatic
568 alcohol (ArAl); Short chain fatty acids, in the range C2 – C8 (SFA); Long chain fatty acids, in the
569 range C16 – C18 (LFA); Dehydroabietic acid (ArAcid).

570 Figure 12 shows the progress of the mass fractions of the identified classes of components with the
571 extraction time with reference to the extractions at 150 °C, which are taken as a representative example
572 of all extractions. The total identified components in the sCO_2 extracts are in the range 27 wt% to 40
573 wt%, which are higher values compared to the feed (19 wt%). This observation, together with the
574 reduction in density (see Section 3.3) indicate that the extract has lower average molecular weight than
575 the feed. A lower average molecular weight is expected to reduce coking during catalytic
576 hydrotreatment, thus prolonging the lifecycle of the catalyst.[25]

577 Ketones, alkylbenzenes, phenols, guaiacols and short chain fatty acids are decreasing monotonically
578 with extraction progression, while benzenediols, polyaromatic hydrocarbons, long chain fatty acids and
579 the aromatic acid increase. The aromatic alcohol does not show any specific trend mostly being
580 unchanged between the extracts. In further detail, the mass fractions of the above-mentioned species in
581 the extracts were found in the ranges of: ketones (0.06 – 1.9 wt%); alkylbenzenes (0.05 – 6.6 wt%);
582 phenols (0.03 – 0.9 wt%); guaiacols (0.04 – 2.5 wt%); benzenediols (0.8 – 3.6 wt%); polyaromatic
583 hydrocarbons (8 – 23 wt%); dehydroabeityl alcohol (0.1 – 1.4 wt%); short chain fatty acids (0.09 – 0.3
584 wt%); long chain fatty acids (3 – 14 wt%); dehydroabietic acid (0.8 – 6 wt%).

585

586

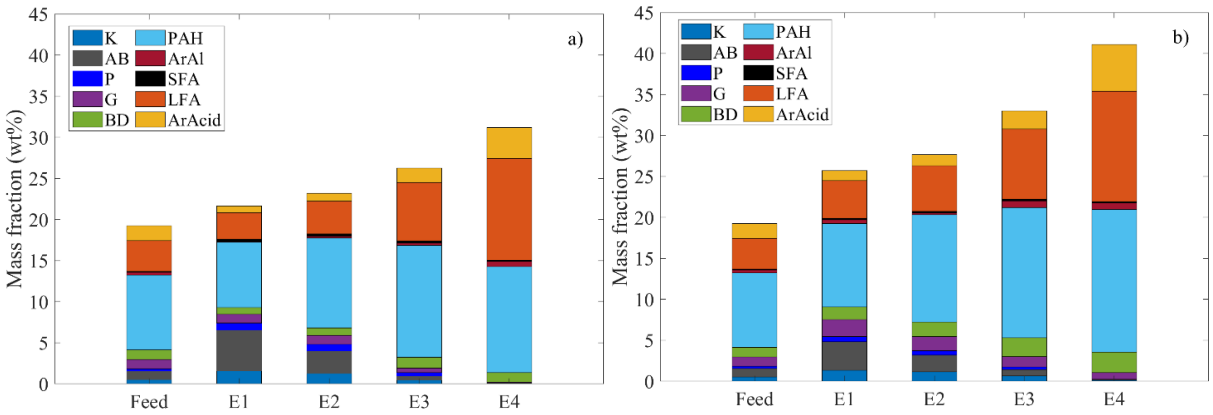


Figure 12. Mass fractions on a water-free basis of the feed and sCO_2 extracts for the experimental runs at: a) 330 bar and 150 °C; b) 450 bar and 150 °C. Ketones (K); Alkylbenzenes (AB); Phenols (P); Guaiacols (G); Benzenediols (BD); 2- and 3-ring aromatic hydrocarbons (PAH); Aromatic alcohol (ArAl); Short chain fatty acids, in the range C2 – C8 (SFA); Long chain fatty acids, in the range C16 – C18 (LFA); Dehydroabietic acid (ArAcid).

Overall, the GC-MS analysis shows that the trend of the separation is mainly determined by molecular weight, with the lighter components preferentially extracted in the early stages of the extraction. The polarity plays however an important role as well, as can be observed by the different behaviour between guaiacols, preferentially extracted in the early stages, and benzenediols, which are more polar and are extracted at later stages even though having a slightly lower molecular weight.

4. Conclusion

This work proves that sCO_2 extraction is an effective process for the separation of raw (i.e. non-dewatered and non-demetalized) HTL lignocellulosic bio-crude. The process is capable of extracting a large fraction of the bio-crude (yields of extract up to 53 wt%) with relatively low solvent-to-feed ratios (i.e. 30 to 37 g/g) compared to typical values for sCO_2 extractions. The extracts showed favorable

properties towards downstream catalytic hydrotreatment. More specifically, they were drastically demetalized (from 8500 mg/kg down to 170 mg/kg on average), substantially dewatered (from 6 wt% down to 1.3 wt% – 1.8 wt%), exhibited lower oxygen content (from 30 to 50 % reduction on a water-free basis), lower average molecular weight and their acidity was shifted towards carboxylic nature, with a reduction of the phenolic acidity. Interestingly, not only is the sCO_2 process capable of simultaneous demetalization, dewatering and upgrading of the bio-crude, but also the process efficiency was improved, compared to sCO_2 extractions at similar conditions on a dewatered bio-crude. Overall, these properties are expected to lead to longer catalyst life, lower hydrogen requirements and less coking. Experimental studies on hydrotreatment of sCO_2 extracts are needed to confirm the expectations and to provide data allowing to evaluate if the advantages that can be obtained in the hydrotreatment step prevail on the reduced yield of hydrotreatment feed with respect to the initial biomass.

Supporting information: List of GC-MS identified components (Table S1)

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