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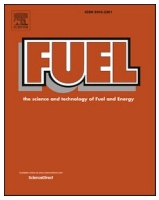

Full Length Article

Understanding the demetallization of nitrogen-rich hydrothermal liquefaction biocrudes by FTICR mass spectrometry: Recalcitrant effect of metalloporphyrins and basic nitrogenates

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ABSTRACT

Higher metallic content in nitrogen-rich hydrothermal liquefaction (HTL) biocrudes is a bottleneck during downstream hydroprocessing, which is necessary for producing drop-in biofuels from urban residues and algal feedstocks. Therefore, this work explores a non-catalytic pathway for effective demetallization of nitrogen-rich HTL biocrudes obtained from sewage sludge and cyanobacteria (generally referred as *Spirulina* algae). Herein, we utilized five different organic/inorganic acids and comprehensively documented the effect of acid washing on basic nitrogen containing compounds (NCCs), oxygenates and organometallics. HTL biocrudes before and after acid washing were characterized by Fourier transform ion cyclotron resonance (FTICR) mass spectrometry (MS). FTICR MS showed the presence of iron porphyrins in cyanobacteria biocrude, whereas no sign of metalloporphyrins was observed in sludge biocrude. Moreover, cyanobacteria biocrude mostly contains basic NCCs (N_1 and N_2 species), whereas sludge biocrude apart from basic NCCs mostly contain fatty acids (O_2 and O_4 species). Due to the presence and absence of metalloporphyrins, acid washing (0.1 M H_2SO_4) showed ineffective demetallization (3.2 %) for cyanobacteria and effective demetallization 89.2 % for sludge biocrude. For cyanobacteria, 66.3 % demetallization was achieved at 10 M H_2SO_4 which not only degrades the biocrude but also accounts for 35 % organic loss. However, O_1-O_4 species in sludge biocrude represent acidic groups such as carboxyl groups; thereby, 20.1 % organic loss is encountered even at 0.1 M H_2SO_4. For both biocrudes denitrogenation via acid washing remains unfeasible due to high organic loss. Present results indicate that a priori information about organometallics, NCCs, and oxygenates in a given biocrude could provide guidance to select and further optimize the demetallization process.

1. Introduction

Elevating concerns regarding climate change and global warming have raised environmental awareness and an impulse to reduce the overall carbon footprint by exploring sustainable alternatives for long–haul transportation. The pursuit of energy security and production of renewable liquid fuels opens up a unique opportunity, where liquid fuels derived from diverse biomass feedstocks is one way to move forward [1,2].

In recent years, hydrothermal liquefaction (HTL) has proved to be a promising valorization pathway for the production of energetically dense biocrude oils from wet feedstocks without any pre-drying [3,4], for example from algal feedstocks and organic urban residues. Notably, the properties of HTL biocrudes are strongly dependent on the properties of the biomass feedstock, but in general HTL biocrudes contain heteroatoms primarily in the form of oxygen (~5–25 %), nitrogen (~0.1–7 %) and sulfur (~0–2 %), along with an elevated ash content (~0.1–38 %) [5–8]. Moreover, the presence of complex oxygenated chemical entities (i.e. alcohols, carboxylic acids, fatty acids, aldehydes, phenolics, and many more) [9–11], and nitrogen containing compounds (e.g. indoles, pyrazine, etc.) [11–16] in HTL biocrudes also makes them highly polar.

The presence of high inorganic content (due to mineral solids) in HTL biocrudes led PNNL [17] to successfully adopt an in–situ approach, involving high–temperature (350 °C) and high-pressure (20.7 MPa)

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in–line filters (≤10 μm) for the removal of inorganics and carbonaceous solids during the HTL reaction. This in–situ separation of solids prevents the formation of emulsions between biocrude and aqueous phase, which can be costly to separate and decrease the effectiveness of downstream processing. Furthermore, polar solvents like acetone [18], methyl ethyl ketone [19] and methanol–dichloromethane (1:1) [6,20] were also utilized to break the emulsion and remove filterable solids from HTL biocrude before further downstream processing. Despite its high quality, considerable amounts of inorganics still remain associated with the filtered HTL biocrudes [6,21,22]. Besides all this, Mathieu et al. [23] proposed the use of flash distillation to break the HTL oil–water emulsion along with the removal of inorganic solids in the water phase.

However, regardless of its origin, HTL biocrudes contain significant amounts of inorganic contaminants (~0.1–0.6 %) possibly in the form of organometallics [6,21,22,24,25], which could become a bottleneck if not removed before hydroprocessing [26]. These organometallics not only cause catalyst fouling and reactor plugging [27,28], but could also react with the catalyst at high temperatures and form low melting eutectic phases which can either block catalytic active sites or reduce the high surface area of the catalyst by sintering [29]. All these drawbacks suggest removing the organometallics before catalytic hydrotreatment. Demetallization of fossil crude oil by utilizing organic and inorganic acids is widely reported and quite well–established [29,30]. Jensen [19] and Steeper Energy ApS [31] have explored the solvent assisted (methyl ethyl ketone) acid washing (0.1 M solution of acetic acid, citric acid, and hydrochloric acid) of lignocellulosic HTL biocrude and reduced the metallic and ash content up to 41 μg/g and 300 μg/g respectively. Furthermore, Haider et al. [18] reported successful demineralization (i.e., solvent-assisted filtration with subsequent acid washing) of *Miscanthus* HTL biocrude. Out of all six utilized acids, they achieved up to 92.7 % demineralization and documented organic loss in terms of total nitrogen (0.017–0.059 wt%) and total organic carbon (0.6–1.7 wt%).

Moreover, the deleterious effects (such as catalyst poisoning [28], polymerization on catalyst surface [27], lower reactivity [32,33], and lower hydrogen activation process [34] etc.) of nitrogen–containing compounds (NCCs) are extensively reported in fossil crude literature. The availability of lone pair of electrons on the nitrogen atom makes them highly basic (i.e. strong nucleophiles) [35–38]. According to the presence or absence of lone pair of electrons, NCCs in crude oils are conventionally classified as basic (e.g. amine, pyridine, quinoline, and azine derivatives) and non–basic (e.g. pyrrole, indole, and carbazole derivatives) [39,40] respectively. These basic and non-basic NCCs are present in abundance in nitrogen-rich HTL biocrudes [22,41]. Basic NCCs can readily neutralize the acid sites of the hydroprocessing catalysts [28,34] and could also cause fouling of the process equipment because of the formation of organic salts due to acid–base reactions [42]. Consequently, several methods including organic solvents [43], acidic washing [44–48] and ionic liquids [49] have been extensively investigated for the removal of nitrogen compounds from crude oil. Furthermore, Chen et al. [50] reported the extraction of NCCs from *Spirulina*, *Chlorella* and swine manure HTL biocrude by utilizing water as a green solvent. Therefore, it is imperative to not only explore the possible viable options for the extraction of NCCs from nitrogen–rich HTL biocrudes, but also the removal of organometallics which indeed is a pressing issue to be dealt with.

Catalytic hydrotreatment is indispensable to upgrade HTL biocrude into drop-in fuels (i.e., diesel, jet fuel etc.). To avoid catalyst fouling and/or deactivation leading to reactor plugging or ineffective upgrading, it is necessary to not only reduce inorganics (particularly metals, to ppm/ppb level) but also NCCs. To do so, it is essential to explore if it is possible to remove metal contaminants and NCCs from HTL biocrude via chemical treatment. Moreover, it is also vital to understand how metal removal during chemical treatment is affected by heteroatoms, in particular nitrogen.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR MS) offers a powerful tool for the characterization of petroleum and biocrude samples at the molecular level. The correlation of this analytical approach together with others techniques such as Infrared Spectroscopy (FTIR) and nuclear magnetic resonance (NMR) and the properties of oil and its derivatives is the main subject of the field known as petroleomics [51]. Different ion sources in direct infusion mode like electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) [52] coupled with FTICR MS have been applied to make a molecular characterization of HTL biocrudes [53,54]. Basic NCCs and acid/non-basic NCCs are routinely characterized employing ESI in the positive ion mode and negative ion mode respectively [41]. Regarding HTL biocrudes, NCCs are formed by reaction of carbohydrates and protein derivatives through Maillard reaction [55]. These compounds are detected more efficiently by using ESI in the positive ion mode, due to their basic nature [22,41]. Moreover, Jarvis et al. [24] demonstrated that ESI in the positive (+) ion mode is effective for the determination of iron porphyrins, employing specific ion source conditions.

The overarching goal of the present study is to develop an understanding about organometallics and explore the synergetic effect of basic NCCs and organometallics during the acid based demetallization of HTL biocrudes (i.e., primary sewage sludge (~3% N) and cyanobacteria (~7% N)). The specific objective of this work is to explore the acid washing of HTL biocrudes in the presence of five different organic and inorganic acids. The aim is to identify: (i) the extent of metal removal in an acidic environment; (ii) effect of acid washing on highly polar nitrogen–rich HTL biocrudes; (iii) loss of organics from HTL biocrudes; (iv) metalloporphyrins, basic NCCs, and oxygenates in HTL biocrudes by utilizing FTICR MS; and (v) the suitability of diverse nitrogen–rich HTL biocrudes for demetallization which in turn strictly depends on the presence of different types of organometallics, basic NCCs, and oxygenates. This research is an attempt to categorize the complex highly nitrogenous HTL biocrudes into different classes of nitrogenates, oxygenates and organometallics, and based on this classification a comprehensive interplay during acid washing was studied.

2. Materials and methods

2.1. Materials

Primary sewage sludge and cyanobacteria (genus *Arthrospira platensis* and generally referred as *Spirulina* algae) biomass feedstocks were obtained from Energi Viborg A/S. (wastewater treatment plant at Viborg, Denmark) and Rejuve Biotech Co. ltd. (Otog, Ordos, Inner Mongolia, China), and further processed under sub–critical HTL conditions (22 MPa, 350 °C) in a pilot–scale continuous facility at Aarhus University, Denmark. Details related to the properties of feedstock and HTL biocrude are reported elsewhere [7].

Five different organic (acetic acid, maleic acid, and citric acid containing one, two and three carboxyl groups (COOH), respectively) and inorganic acids (phosphoric acid and sulfuric acid) were utilized during acid washing. Citric acid (CA) and maleic acid (MA) were purchased from Sigma Aldrich with a purity of ≥ 99.5 % and ≥ 99 %. Acetic acid (AA) and phosphoric acid (PA) were acquired from Borup Kemi (32 %) and VWR Chemicals (≥85 %) respectively. 98 % sulfuric acid (SA) was bought from Honeywell Fluka™.

2.2. Physical separation of inorganics

In order to continue with the physical separation of the inorganic solids from HTL biocrude, the choice of a suitable solvent [56] (e.g. availability, volatility, oil miscibility, density difference with respect to the oil etc.) for filtration is indeed a crucial step. In the present study, acetone is used as a solvent of choice [57,58]. Polar solvents [6,19] are already reported in literature for the removal of filterable solids. Filtration was carried out by diluting the HTL biocrudes with acetone (1:3) and then filtering them under vacuum over VWR filter papers (5–13 μm). Solvent and associated water content were evaporated at

60 °C and ~ 8 kPa, with a rotary evaporator (Büchi AG). At the end, filtered biocrudes were ready for acid washing.

2.3. Demetallization procedure

The chemical treatment procedure described in the work by Haider et al. [18] was adopted. The filtered biocrudes were first diluted with acetone in 1:1 (w/w ratio) to lower the density and viscosity of biocrudes during acid washing. Five different aqueous solutions of organic and inorganic (mineral) acids with 0.1 M were prepared, using deionized water. Subsequently, 1:3 (w/w ratio) of biocrude to demetallization agents were utilized for the removal of organometallics. These mixtures (samples) were then magnetically stirred at 25 °C and 1000 rpm for 4 hr. After demetallization, acetone was removed by rotary evaporation at 60 °C and 40 kPa. The two resulting phases, i.e., demineralized biocrude and washing agent, were separated by gravity in a separatory funnel. The two phases were clearly separated in such a way that the demineralized biocrude was in the bottom phase and the washing agent was on the top phase of the separatory funnel. Besides the five acidic solutions (0.1 M), a further experiment using only deionized water was also conducted, to serve as a reference for demetallization. Additionally, three confirmatory experiments (CB7-CB9 in Table 1) were carried out to record the demetallization of cyanobacteria biocrude under severe conditions. These severe conditions were employed because cyanobacteria biocrude showed ineffective demetallization at 0.1 M acidic solution.

In order to assure reproducibility, all experiments were performed in duplicates. Mean values of the results are reported along with their errors (i.e., difference of mean values from the actual values). Errors are reported to highlight the accuracy of experimental results. A detailed list of the experimental runs carried out at different molar concentration (M) of given acids are reported in Table 1.

2.4. Characterization and analytical techniques

The elemental composition of the biocrudes (raw, separated and demetallized) was analyzed according to ASTM D5291 [59], using an elemental analyzer (PerkinElmer® 2400 Series II) operating under CHN-O mode. Here, oxygen was calculated by difference. Ash content was determined through incineration at 775 °C in a Protherm electric muffle furnace, according to ASTM D482 [60]. Based on the elemental composition, the higher heating value (HHV) was estimated by using the correlation proposed by Channiwala and Parikh [61].

$$\mathrm{HHV}\left(\mathrm{MJ\,kg^{-1}}\right) = 0.3491\mathrm{C} + 1.1783\mathrm{H} - 0.1034\mathrm{O} - 0.0151\mathrm{N} \quad (1)$$

The concentration of metals along with sulfur and phosphorous content in both biocrudes and acid washed samples were determined by using Agilent 715 inductively coupled plasma – optical emission spectrometry (ICP–OES). Prior to ICP–OES, ~0.1 g of each sample was digested in 2 mL of nitric acid (Sigma–Aldrich). For this purpose, Anton Paar Multiwave 3000 microwave digestion system was utilized. After digestion samples were diluted to 50 mL with Milli-Q water. Ash content of the demetallized biocrudes was also reported, because ICP–OES results do not account for all the inorganic elements that could be present in sludge and cyanobacteria biocrude. Total organic carbon (TOC) and total nitrogen (TN) in the aqueous phase were measured after the acid washing by using LCK386 and LCK138 kits in a Hach DR3900 VIS Spectrophotometer. For samples involving organic acids, the reported TOC values are calculated by subtracting the TOC of the aqueous acidic solution before and after demetallization. Moreover, the organic loss was measured as a difference of biocrude used before and after acid treatment.

2.4.1. ESI FTICR MS direct flow injection analysis

Biocrude samples were diluted to a final concentration of 1 mg/ml with a 1:4 DCM:Methanol solvent mixture, 0.05 mg/ml of caffeine (Sigma Aldrich) was added as internal standard. Mass spectrometry analysis were performed on a 7 T FTICR MS (LTQ-FT Ultra Thermo Scientific), equipped with ESI (Electrospray) ion source. The mass spectra were collected in positive and negative mode. The samples were infused at a flow rate of 10 L $\mathrm{min^{-1}}$; typical ESI (+) conditions were as follows: source voltage 3.5 kV, capillary voltage 43 V, tube lens voltage 160 V, capillary temperature at 275 °C, sheath gas 10 arbitrary units, auxiliary gas 5 arbitrary units. The high value of tube lens voltage was set following the experimental setup used by Jarvis [24], that allows to ionize the iron porphyrins compounds.

The spectra were acquired with a 7 T ultrahigh resolution FTICR cell with a mass range of *m/z* 100–1000. The resolution was set to 400.000 (at *m/z* 400). The ion accumulation time was defined by the automatic gain control (AGC), which was set to 10^6. 360 scans were collected and averaged for each analysis to improve the signal to noise ratio using a Booster Elite instrument (Spectroswiss). Data were then processed by the peak-by-peak petroleomic software (Spectroswiss). The elaboration procedure consisted of transient averaging, noise thresholding, peak picking (about 10 thousand peaks for each mass spectrum), and internal recalibration using caffeine internal standard exact mass. The molecular formulas were assigned to approximately 90 % of the detected peaks. The relevant signals were then categorized according to different parameters, such as the number of heteroatoms (N, O and S) and the number of unsaturations expressed as DBE (Double Bond Equivalents). For each molecular formula the DBE was calculated according to the following equation (for $C_cH_hN_nO_oS_s$);

$$DBE = c - \frac{h}{2} + \frac{n}{2} + 1 \quad (2)$$

Table 1
Summary of performed demetallization tests for primary sewage sludge and cyanobacteria biocrude; along with the three confirmatory experiments for cyanobacteria biocrude.

Exp.	Washing agent	Concentration (M)	Exp.	Washing agent	Concentration (M)
Primary sewage sludge (SS) biocrude			Cyanobacteria (CB) biocrude		
SS1	Water (W)	–	CB1	W	–
SS2	Acetic acid (AA)	0.1	CB2	AA	0.1
SS3	Maleic acid (MA)	0.1	CB3	MA	0.1
SS4	Citric acid (CA)	0.1	CB4	CA	0.1
SS5	Phosphoric acid (PA)	0.1	CB5	PA	0.1
SS6	Sulfuric acid (SA)	0.1	CB6	SA	0.1
			Confirmatory experiments		
			CB7	1:3 of AL to SA	0.5
			CB8	1:10 of AL to SA	0.5
			CB9	1:3 of AL to SA	10

3. Results and discussion

3.1. Demetallization

Physical filtration of raw sludge and cyanobacteria biocrude resulted in 99.7 % and 18.1 % decrease in ash content, and 99.5 % and 5.8 % removal of inorganic solids respectively (Table 2). Even though, the filtered biocrudes still contains a significant amount of metallic content primarily in the form of iron (Fe). However, small amounts of zinc (Zn), calcium (Ca) and nickel (Ni) are also present in both biocrudes.

Table 2 shows interesting results and summarizes the impact of demetallization on both biocrudes, when treated with 0.1 M acidic

Table 2
ICP OES results of primary sewage sludge and cyanobacteria HTL biocrude before and after physical filtration and chemical treatment (acid washing). Ash content was measured by following the ASTM D482 55.

Sample	S	Al	Ca	Cu	Fe	K	Mg	Mn	Ni	P	Zn	Ash
	(μg/g)											
Primary sewage sludge (SS) biocrude												
SS-Raw	4025	5636	72534	70.6	3202	1041	3644	200	90.3	33231	487	285742
SS-Sep	5464	<100	<15	<30	335	n.d.	<1	n.d.	n.d.	n.d.	19.8	659
SS1	5241	<100	<15	<30	331	n.d.	<1	n.d.	n.d.	n.d.	20.3	701
SS2	4317	<100	<15	<30	283	n.d.	<1	n.d.	n.d.	n.d.	17.5	592
SS3	4868	<100	<15	<30	153	n.d.	<1	n.d.	n.d.	n.d.	9.73	301
SS4	4376	<100	<15	<30	171	n.d.	<1	n.d.	n.d.	n.d.	7.85	329
SS5	4798	<100	<15	<30	77.8	n.d.	<1	n.d.	n.d.	932	12.6	214
SS6	8431	<100	<15	<30	<15	n.d.	<1	n.d.	n.d.	n.d.	7.65	71
Cyanobacteria (CB) biocrude												
CB-Raw	12214	<100	20	<30	951	n.d.	4.75	<3	76.7	n.d.	46.8	1682
CB-Sep	11532	<100	<15	<30	918	n.d.	<1	n.d.	59.3	n.d.	37.1	1378
CB1	11439	<100	<15	<30	895	n.d.	<1	n.d.	75.2	n.d.	41.3	1612
CB2	11622	<100	21	<30	1118	n.d.	<1	n.d.	78.4	n.d.	48.1	1641
CB3	11193	<100	57.5	<30	1123	n.d.	<1	n.d.	77.0	n.d.	48.0	1563
CB4	11333	<100	<15	<30	1111	n.d.	<1	n.d.	78.6	n.d.	42.2	1589
CB5	11356	<100	<15	<30	1100	n.d.	<1	n.d.	73.7	350	43.8	1627
CB6	13755	<100	31.8	<30	868	n.d.	<1	n.d.	75.7	n.d.	38.6	1164
CB7	21355	<100	<15	<30	761	n.d.	<1	n.d.	78.4	n.d.	25.1	927
CB8	31132	<100	67	<30	641	n.d.	<1	n.d.	<100	n.d.	25	753
CB9	259903	<100	<15	<30	230	n.d.	<1	n.d.	<100	n.d.	<12	380

solution. Under the given acidic concentration (0.1 M), significant reduction of ash content (deashing) and metal removal was observed during the acid washing of sludge biocrude. However, for cyanobacteria biocrude ash and metals content remain the same with all washing agents, except for 0.1 M sulfuric acid (CB6), where slight deashing and demetallization was observed. Moreover, for both biocrudes deionized water does not exhibit any effect on deashing and demetallization. Table 2 indicates that mineral acids, and especially sulfuric acid, have a strong effect on the demetallization of sludge biocrude and successfully reduced the Fe content to < 15 μg/g (96 % removal), Zn content to 7.7 μg/g (61 % removal) and ash content to 71 μg/g (89 % deashing). Fig. 1a illustrates that 89.2 % of metal and 93.6 % of ash content was removed when sludge biocrude was subjected to 0.1 M SA. It can also be observed that organic acids are less effective for both biocrudes, when compared with the demetallization achieved in the presence of inorganic acids. Moreover, it is also apparent that citric acid and maleic acid are superior to acetic acid when it comes to the demetallization and deashing of sludge biocrude via organic acids. This is plausible as acetic acid has only one carboxyl functional group as compared to maleic acid (dicarboxylic) and citric acid (tricarboxylic). Even though citric acid has more functional groups than maleic acid, the degree of demetallization almost remains the same (54.1 % for 0.1 M MA and 49.6 % for 0.1 M CA). This is due to the fact that the degree of ionization in water (acidic strength) for both acids is almost similar [62,63]. The degree of ionization is reflected by the pH of the washing solution: 2.0 for citric acid and 1.5 for maleic acid. In general, it can be observed that the efficiency of demetallization increases with the decrease of the pH of the acidic solution. For example, demetallization extent is maximum for sulfuric acid (pH = 0.7) and minimum for acetic acid (pH = 2.9).

Two possible explanations can be found to the fact that demetallization at 0.1 M SA works for sludge biocrude but not for cyanobacteria biocrude: (i) molecular structure of organometallics (i.e. metal carboxylates [64–66] or metalloporphyrins [29,30,67]); (ii) classification of NCCs (basic and non–basic) on the basis of lone pair of electrons associated with nitrogen atom [39,68]. These points are quite well documented in the fossil crude chemistry. During the desalting of crude oil, metal carboxylates are easily demetallized in the presence of acids [64,65]. On the contrary, metalloporphyrins with a metal center are chemically stable complex aromatic compounds [69–73]. Therefore, metalloporphyrins are difficult to remove and need strong oxidizing agents for demetallization [29,30]. In addition, the basic NCCs are strong nucleophiles and readily react with acids (strong electrophiles) by an acid–base reaction and form water soluble salt complexes [35,36,74,75]. Thereby, acid solutions are extensively used for the removal of basic NCCs from fossil crude oil [44–46].

As far as the chemistry of nitrogen–rich algae biocrudes is concerned, Sun et al. [16] documented the presence of pyridine–, pyrazine–, and quinoline– base compounds which are highly basic NCCs. Similarly,

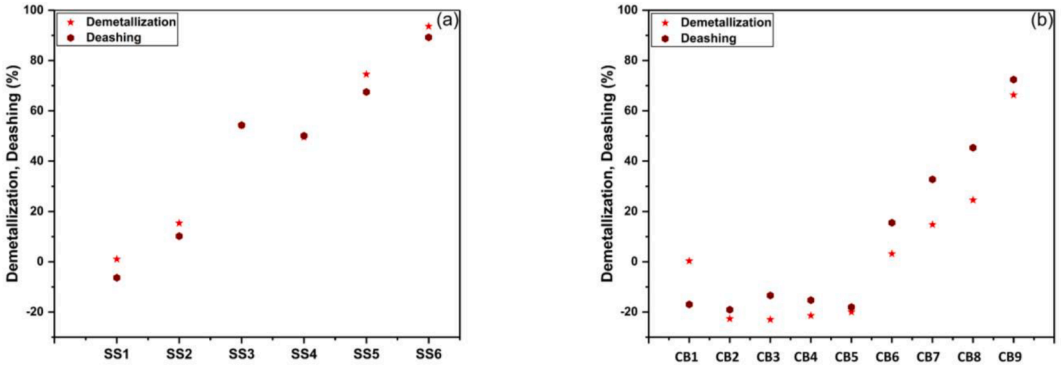

Fig. 1. Demetallization and deashing of primary sewage sludge biocrude (1a) and cyanobacteria biocrude (1b).

Jarvis et al. [22] and Sudasinghe et al. [41] utilized ESI^+ and observed amines and broad range pyridinic, and quinazolinic highly basic NCCs in microalga *Chlorella* sp. and *Nannochloropsis salina* biocrude respectively. Moreover, they [22,41] also reported non-basic NCCs (i.e. pyrrole, indole and carbazole) derivatives in microalgae *Chlorella* sp. and *Nannochloropsis salina* biocrude. In another work, Jarvis et al. [24] reported that iron porphyrins are intrinsic to algal HTL biocrudes. However, sludge HTL biocrude is predominantly composed of long chain fatty acids [7,22] (i.e. aliphatic carboxylic and hydroxy acids [22]). Additionally, Jarvis et al. [22] also found out that sludge biocrude contains non–basic N_1 species from C_{12}–C_{23} along with the basic N_2 species (possibly the derivatives of imidazole/azaindole) which ranges from C_{10}–C_{46}. Furthermore, sewage sludge also contains non–basic amides [41,76] in the form of N_1O_1 species from C_{10}–C_{40} [22].

Table 2 shows no sign of metal removal for cyanobacteria biocrude when treated with acid solutions at 0.1 M. Moreover, from Fig. 3 it can be evidently noticed that negative values of demetallization and deashing were obtained (CB2, CB3, CB4 and CB5). This confirms that the metals were not removed but the concentration of cyanobacteria biocrude was considerably decreased after acid washing. Certainly, the basic NCCs in cyanobacteria biocrude underwent undesired protonation because of the acid– base reaction. Being strong nucleophiles, basic NCCs have a higher tendency to get protonated when reacting with the acid. Consequently, either the strength or the quantity of acid is not enough to demetallize the organometallics present in cyanobacteria biocrude. Based on this speculation, three confirmatory demetallization experiments (CB7, CB8 and CB9) were performed as described in Table 1.

From Fig. 1b, higher degrees of demetallization (3.2 % to 14.8 %) and deashing (15.5 % to 32.7 %) were achieved when the concentration of sulfuric acid solution was increased from 0.1 M (CB6) to 0.5 M (CB7). Likewise, it is also apparent that the excess amount of acid (1:10 in CB8, instead of 1:3 in CB7) has a positive effect on demetallization and deashing. By doing so, 24.5 % of metal and 45.4 % of ash content was successfully removed. Table 2 and Fig. 1b shows that highest level of demetallization (66.3 %) and deashing (72.4 %) of cyanobacteria biocrude was attained when 10 M SA (CB9) was utilized. These results suggest that demetallization of cyanobacteria biocrude is possible and needs higher concentration as well as excess amount of acid.

Acids also have a tendency to contaminate the organic moieties [35,38,77–83]. After examining Table 2 this phenomenon becomes quite evident, especially, after the demetallization of HTL biocrudes in the presence of inorganic acids. After acid washing, ICP–OES results (Table 2) substantiate the presence of phosphorous and sulfur in both HTL biocrudes. As a general trend, the concentration of sulfur was considerably increased when the acidic concentration (CB7 and CB9) or the amount of sulfuric acid (CB8) was increased. Electrophilic addition and electrophilic substitution of unsaturated aliphatic (olefins) and heterocyclic aromatic structures in the presence of acids [36,38,77,78,80,81,83] not only add impurities (i.e. sulfuric acid reacts and could possibly form sulfates, sulfones, polysulfones, and aromatic sulfonic acids etc.), but also this could increase the amphiphilicity of organic structure after demetallization. Due to this, the demetallized HTL biocrude could become more polar and more acidic in nature. Under the conditions studied, the results from ICP–OES suggest that adequate demetallization in sludge biocrude was already achieved at lower acidic strength, while much stronger acids in excess amounts are required for the removal of metals in cyanobacteria biocrude. Therefore, it is reasonable to assume that undesired side reactions can possibly be restrained while operating at lower concentration of acidic solution.

3.2. Organic loss and extraction of nitrogen

To evaluate the effect of acid based demetallization, organic losses (loss of biocrude before and after acid washing) from both biocrudes were compared with the loss of organic carbon (TOC) and loss of nitrogen (TN) from biocrude to washing agents after each experiment. As it can be visualized in Fig. 2, organic losses are directly related to the type, concentration and quantity of the acid utilized during acid washing. When deionized water was used for the removal of metals from sludge (SS1) and cyanobacteria (CB1) biocrudes, demetallization was ineffective and it corresponded to the lowest organic loss (8.1 % and 7.5 %, respectively), along with the least TOC (1.2 % and 2.9 %) and TN (0.6 % and 0.16 %) in the washing agent. Although sulfuric acid under given concentration (0.1 M) is the strongest demetallization agent (Fig. 1), both citric acid and sulfuric acid have a comparable effect on organic losses (sewage sludge: 18.7 % and 20.1 %; cyanobacteria: 14.1 % and 12.6 %, respectively) as well as on TOC and TN. Primarily, this might be caused because citric acid has three carboxyl functional groups which could take part in unwanted side reactions, such as electrophilic substitution of unsaturated aliphatic and heterocyclic aromatic structures [84,85].

Sulfuric acid is the strongest acid among those investigated, therefore it accounts for high organic losses together with significant TOC and TN in the aqueous phase. Indeed, the increase in acidic strength and its quantity strongly affect the removal of organics from cyanobacteria biocrude. Fig. 2b shows a remarkable increase in organic loss when the concentration of sulfuric acid was increased from 0.1 M (13 %) to 0.5 M (17 %) and 10 M (35 %). Under these conditions, higher TOC (5.9 %, 6.3 %, and 9.5 %) and TN (0.4 %, 0.6 %, and 1.2 %) were also observed, respectively.

Loss of organics in deionized water (SS1 and CB1) is possibly due to the presence highly polar oxygen (e.g. carboxylic acids, phenolic derivatives etc.) and nitrogen (e.g. indoles, pyrazines etc.) containing compounds [9,11,14,22]. As a rule of thumb, polarity of organic compounds is inversely dependent on the molecular weight, chain length, and carbon number [86]. However, in the presence of acids not only does the solubility increase (like dissolves like) but also the organic loss is inherent due to the formation of water soluble salt complexes with basic NCCs [35,36,47] and the oxidation of non–basic NCCs [87]. The fact that acids react with organic moieties and promote unwanted side reactions is a draw-back. These side reactions not only require higher quantity and higher strength of acids, but also result in lower biocrude recoveries due to inherent organic loss.

10 M SA strongly affected the appearance of the cyanobacteria biocrude, as illustrated in Fig. 3. Indeed, the untreated biocrude is black in color and flowable at room temperature (Fig. 3a). Extensive side reactions (such as element incorporation, cracking, oxidation, polymerization etc.) and biocrude contamination remove significant amounts of organics during demetallization and cause a dramatic increase in viscosity, thus degrading the biocrude (Fig. 3b). These results are in line with the findings of Kukes et al. [88] and Michlmayr [89] with fossil oil. From the perspective of organic loss vs demetallization, 0.1 M SA was the best choice for sludge biocrude. In the whole scenario, 10 M SA accounts for the highest metal removal, but, at the same time, it imparts unprecedented organic loss (Fig. 2b) and accounts for excessive sulfur incorporation (Table 2) in cyanobacteria biocrude. Thereby, an excess amount of 0.5 M SA was more effective within three confirmatory experiments.

Table 3 shows the results of elemental composition, HHV, and H/C atomic ratio of raw, acetone filtered, and demetallized HTL biocrude. As compared to cyanobacteria biocrude, the quality of sludge biocrude in content of carbon, hydrogen and HHV was significantly increased after the physical separation of inorganics. For both biocrudes, extractive denitrogenation with deionized water seems to be ineffective. This outcome corresponds to the work reported by Chen et al. [50], where water was used as a green solvent for the extraction of NCCs from *Chlorella* and cyanobacteria HTL biocrudes. Their results indicate that the use of water was ineffective as it merely removed highly polar short chain carbon compounds preferably containing oxygen (phenols, fatty acids, and fatty alcohols etc.) and nitrogen (indoles, pyrazine, and amides etc.) [50]. Furthermore, when it comes to the elemental

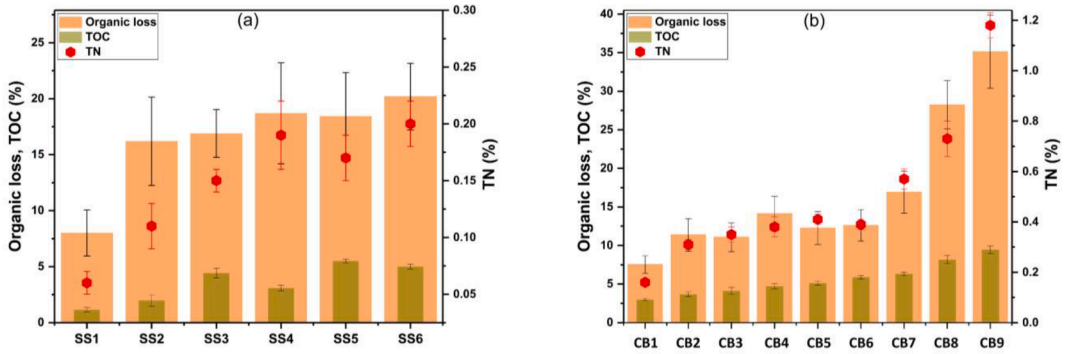

Fig. 2. Organic loss along with the total organic carbon (TOC) and total nitrogen (TN) in the aqueous phase after the demetallization of primary sewage sludge (2a) and cyanobacteria (2b) biocrude from hydrothermal liquefaction.

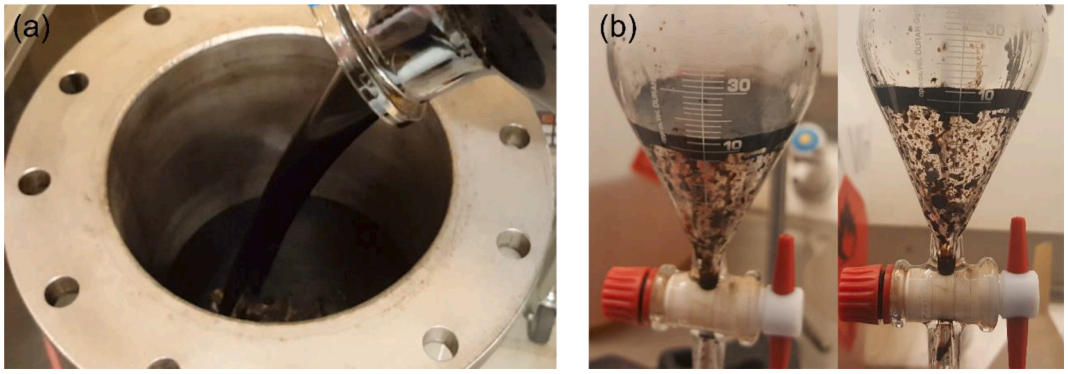

Fig. 3. Picture of untreated (3a) and treated (3b) cyanobacteria biocrude after the demetallization under 10 M sulfuric acid solution.

composition, comparable results (Table 3) were obtained after the acid washing of filtered HTL biocrudes (sludge and cyanobacteria) at 0.1 M acidic solution. However, a very high acid concentration (10 M SA) has a noticeable impact on the nitrogen removal.

If the sole purpose is to remove NCCs from nitrogen–rich HTL biocrudes then neither water nor acids could possibly provide good enough results. The results indicate that the use of water was ineffective. However, after employing acids, observable amounts of NCCs were extracted (Fig. 2b and Table 3), especially when the concentration of acid was increased tremendously. Increased acid concentration significantly removed nitrogen at the cost of extensive organic losses. In parallel, the extraction of NCCs has been extensively studied and reported in fossil crude literature. In any case, the extraction of NCCs via chemical treatment (acids [35,36,47,74,75], ionic liquids [49,90] etc.) or adsorption (either chemisorption [91–93] or physisorption [94–96]) results in carbon losses, because the whole molecular structure is removed along with nitrogen. Due to this, innovative solution are of dire need, such as using a catalyst which could remove most of the nitrogen in the form of gas during the hydrothermal processing of nitrogen–rich biomasses or better extracting most of the nitrogen [97] prior to HTL.

3.3. FTICR MS analysis of HTL biocrudes

3.3.1. Cyanobacteria biocrude samples

Cyanobacteria biocrude samples were analyzed with ESI positive (+) ion FTICR MS. A wide distribution of protonated peaks in the mass range *m/z* 130–500, are present and mainly related to basic NCCs. This is due to the ion source used, and ionization mode (ESI^+) that is particularly suitable for basic NCCs. Indeed, the ionization of the molecules involves a proton exchange from the solvent to the organic compounds, and each compound is ionized with a different ionization yield dependent on its specific proton affinity, that is proportional to its basicity. Therefore, by ESI^+ FTICR MS a very detailed determination of basic NCCs is obtained, but in the meantime non-basic NCCs cannot be efficiently ionized and determined.

The mass spectra in Fig. 4 revealed the presence of very intense peaks (*m/z* ~ 500–570) related to iron porphyrins (N_4Fe). The two main N_4Fe species at *m/z* of 504.20 and 530.21 corresponds to $C_{30}H_{32}N_4Fe$ and $C_{32}H_{34}N_4Fe$, respectively. The presence of iron porphyrins in cyanobacteria biocrude consolidates the previous findings reported by Jarvis et al. [24], where they found out that iron porphyrins structures are intrinsic to HTL biocrudes from algae. Moreover, comparing the initial biocrude sample and the one obtained after acid washing, these iron porphyrins are still present and least affected, even after treating with 0.5 M H_2SO_4 (CB7). Here, the relative abundance of peaks (around *m/z* 500) related to iron porphyrin is slightly reduced. This incorporates the results obtained from ICP–OES (Table 2), which show 17.1 % of iron removal in experiment CB7. Meanwhile, a slight variation in the distribution of the other peaks related to nitrogen and oxygen-containing compounds is also found in the mass spectrum (Fig. 5).

The FTICR MS derived heteroatom class distributions before and after acid washing of cyanobacteria biocrude is illustrated in Fig. 6. This shows that basic NCCs related to N_1 and N_2 classes seem to be more affected after acid washing, as compared to N_3 and oxygenated (O_1N_1, O_2N_1, O_1N_2, O_2N_2, and O_1N_3) classes. This is probably because N_1 and N_2 heteroatom classes are mostly concentrated in lower molecular weight compounds with higher N/C ratios, in contrast to heteroatom classes related to N_3 and oxygenated NCCs. After observing N_3, O_2N_2, and O_1N_3, it becomes quite evident that their concentration after acid washing increases because of the considerable organic loss. The high organic loss (Fig. 2) is due to the removal of low molecular weight compounds with high polarity and strong basicity (high N/C ratio).

Moreover, in Fig. 7 the attribution of class N_2 species before and after acid washing are plotted against C_n and DBE. The C_n vs DBE plot shows

Table 3
Elemental composition (%) of primary sewage sludge and cyanobacteria biocrude before and after physical filtration and acid washing. Oxygen was calculated by difference.

Sample	Biocrude elemental composition (%)				H/C (-)	HHV (MJ kg^{-1})
	C	H	N	O		
Primary sewage sludge (SS) biocrude						
SS-Raw	76.7 ± 0.6	8.9 ± 0.3	2.3 ± 0.5	12.1 ± 0.9	1.38	35.9
SS-Sep	78.5 ± 0.8	10.6 ± 0.2	2.8 ± 0.1	8.1 ± 0.8	1.62	39.1
SS1	79.8 ± 2.2	10.5 ± 0.4	2.6 ± 0.7	7.1 ± 2.4	1.57	39.5
SS2	81.2 ± 1.8	10.7 ± 0.3	2.9 ± 0.1	5.2 ± 1.9	1.57	40.4
SS3	77.4 ± 1.8	10.5 ± 0.4	2.6 ± 0.1	9.5 ± 1.8	1.62	38.4
SS4	84.8 ± 2.5	10.4 ± 0.3	3.1 ± 0.3	1.7 ± 2.5	1.47	41.7
SS5	84.7 ± 5.5	10.6 ± 1.5	2.4 ± 0.2	2.3 ± 5.7	1.50	41.6
SS6	80.1 ± 3.2	10.6 ± 0.6	2.5 ± 0.2	6.8 ± 3.3	1.58	39.7
Cyanobacteria (CB) biocrude						
CB-Raw	74.4 ± 0.2	10.2 ± 0.1	6.6 ± 0.4	8.9 ± 0.4	1.64	36.8
CB-Sep	76.3 ± 0.1	10.2 ± 0.1	6.5 ± 0.1	6.9 ± 0.2	1.61	37.8
CB1	76.1 ± 0.2	10.0 ± 0.1	7.3 ± 0.1	6.6 ± 0.3	1.58	37.6
CB2	76.8 ± 0.4	10.2 ± 0.1	7.4 ± 0.1	5.6 ± 0.4	1.59	38.1
CB3	76.1 ± 0.2	10.1 ± 0.0	6.8 ± 0.2	7.1 ± 0.3	1.59	37.6
CB4	72.1 ± 0.1	10.3 ± 0.0	6.2 ± 0.2	11.4 ± 0.2	1.71	36.1
CB5	76.9 ± 0.3	10.3 ± 0.0	6.7 ± 0.2	6.0 ± 0.3	1.61	38.2
CB6	74.4 ± 0.2	10.2 ± 0.0	6.1 ± 0.1	9.3 ± 0.2	1.64	36.9
CB7	73.3 ± 0.3	10.2 ± 0.0	5.8 ± 0.4	10.8 ± 0.5	1.66	36.3
CB8	74.4 ± 0.0	9.7 ± 0.1	5.9 ± 0.0	10.0 ± 0.1	1.57	36.3
CB9	70.4 ± 0.2	9.3 ± 0.4	4.2 ± 0.5	16.1 ± 0.7	1.58	33.7

that N_2 species are widely distributed and almost cover the entire mass spectrum. In filtered cyanobacteria biocrude (CB-Sep) the most intense species are in the C*n* range 10–23 and in the DBE range 7–12, with DBE 8–9 as the most intense ions (probably related to condensed pyridinic rings with short alkyl side substituents). After acidic washing (CB7), these species are dramatically reduced and the most intense species are in the C_n range 15–30, but with similar DBE range. This proves that acidic washing removes the most basic compounds (with low C_n), that are the ones with the highest N/C ratio. Similar results are also obtained for NCCs related to N_1 species.

3.3.2. Sewage sludge biocrude samples

The primary sewage sludge biocrude samples before (SS-Sep) and after (SS6) acid washing were analyzed by ESI in both positive (+) and negative (-) ion mode (Fig. 8). The ESI^+ mass spectra comparison of the mass range *m/z* 100–420 is shown in Fig. 8b. Again, the strong effect of acid washing is observed in relatively low molecular weight compounds (with higher N/C ratios), which is in accordance with the results obtained after the acid washing of cyanobacteria biocrude. Regarding the inorganic content, and specifically iron, no iron porphyrin ions were detected in sludge biocrude. Certainly, these structures are specific to cyanobacteria biocrude because of the presence of chlorophyll in cyanobacteria biomass.

Sewage sludge HTL biocrudes are generally associated with high concentrations of carboxyl group. Therefore, ESI^- mass spectra were acquired to detect acidic organic compounds and record oxygen heteroatom species with higher sensitivity. ESI^- (i.e. deprotonation) selectively shows acidic compounds [41] (strong acids (i.e. carboxyl group) and weak acids (i.e. hydroxyl group)), primarily oxygenates with different classes. After ESI^- FTICR MS analysis, the resulting sludge biocrude mass spectra exhibits the domination of fatty acid (FAs) ions with class O_2 and O_4 [41]. In case of class O_2 (Fig. 9), intense signals were detected for C_{16} (at DBE 1) and C_{18} (at DBE 1, 2, 3 and 4) saturated and monounsaturated FAs. In the class O_2, compounds with aromatic nature are also found at low to medium intensities.

In Fig. 10, the compound distribution belonging to the class O_4 is plotted against C_n and DBE for both washed and unwashed primary sewage sludge biocrude. The most abundant compounds show C_n of 16 and 18 and low DBE of 1–3. These might be related to oxidized FAs (cheto-acids) or hydroxylated FAs. The other compounds with DBE 8–11 and C_n 13–20 might be related to aromatic dicarboxylic acids (with two carboxyl groups). From the comparison of the plots, a general reduction of these species is found after acid washing, and this is particularly evident for low DBE species, and to less extent for high DBE species. This proves that acid washing also removes the long chain FAs with low DBE due to their affinity (i.e., like dissolve like) with acids, which arises because of the presence of oxygenates (i.e., two carboxyl groups or possible one carboxyl and two hydroxyl groups).

By comparing Fig. 2, Fig. 7, and Fig. 8 this phenomenon become easy to comprehend; because even at lower acidic concentration (0.1 M H_2SO_4) higher organic losses were observed for sludge biocrude (20.1 %) as compared to cyanobacteria biocrude (13 %). The DBE 8 compound homologues series could be related to this hypothetic molecular structure (with R as methyl or longer alkyl chain) represented in Fig. 11.

Unlike cyanobacteria biocrude, ESI^+ FTICR mass spectra shows that metalloporphyrins (i.e., iron porphyrins) are not present in sludge biocrude. Moreover, it indicates that the oxygen in sludge biocrude is predominantly present in the form of carboxylic acids (saturated/monounsaturated FAs and aromatic FAs (with higher DBE)). Furthermore, ICP–OES results show that sewage sludge biocrude contains substantial amounts of iron (Table 2). From these facts we can infer that most probably the iron is present in the form of iron carboxylates [98] or metallic aromatic complexes [99]. As sludge biocrude exhibits complex mixture of acids with vast variations in molecular weight; therefore, the carboxyl/hydroxyl/aromatic groups could possibly form complexes with metal ions in varied structural formulations.

The absence of metalloporphyrins and possible presence of metallic salt complexes corresponds to the results obtained after the demetallization (89.2 %) of sludge biocrude in lower concentration (0.1 M) of H_2SO_4. This outcome confirms that the prospects of successful demetallization directly relates to the presence or absence of metalloporphyrins in HTL biocrudes. In addition to demetallization, the organic loss is directly dependent on polarity and affinity of (carboxyl groups) and basicity (basic NCCs) of HTL biocrudes. For sludge biocrude, not showing metalloporphyrins, further optimization including first the distillation of HTL biocrude and accompanying demetallization on heavier fractional cut (~>300 ± 50 °C) could possibly suppress the inherent organic losses. However, one should also be aware and select the optimal distillation temperatures under the vacuum - because exposure to high temperatures could possibly cause condensation/polymerization within the heavier fraction of the biocrude and make it difficult for hydroprocessing.

4. Conclusions

A high amount of metals (inorganic content) in nitrogen–rich HTL biocrudes is currently a challenge. In downstream processing, the integration of acid washing could be associated with effective demetallization and potential denitrogenation. However, the effectiveness of this

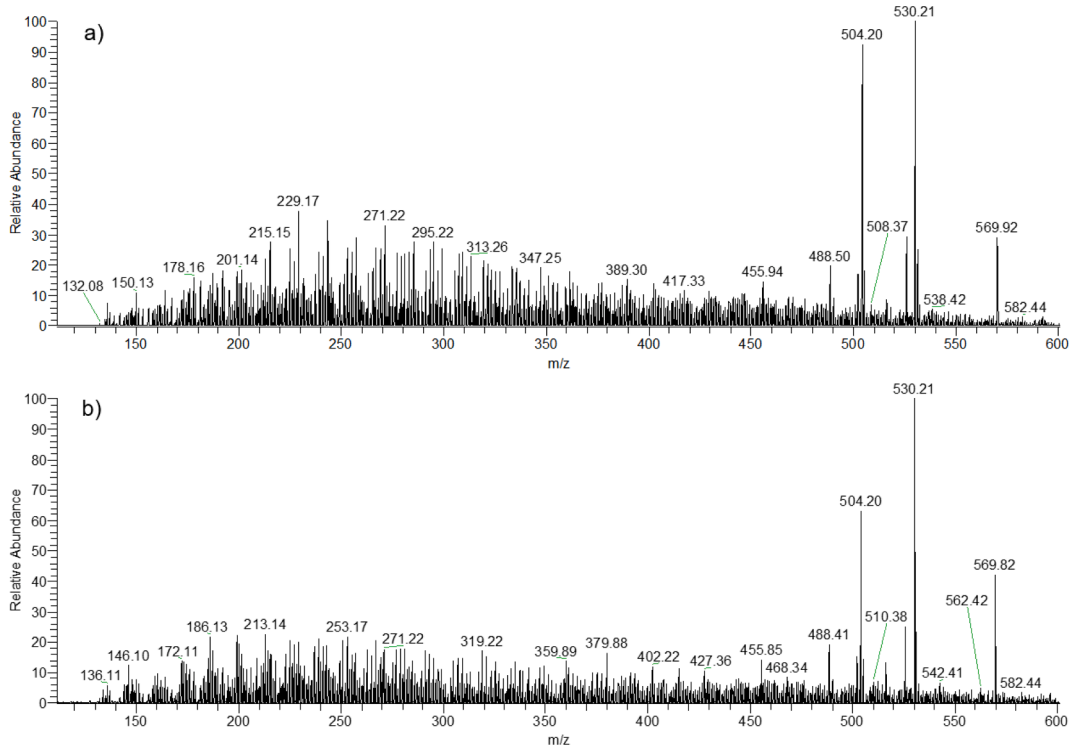

Fig. 4. ESI$^+$ FTICR MS mass spectra comparison of acetone separated (CB-Sep) cyanobacteria biocrude (a) and acid washed (CB7) cyanobacteria biocrude (b).

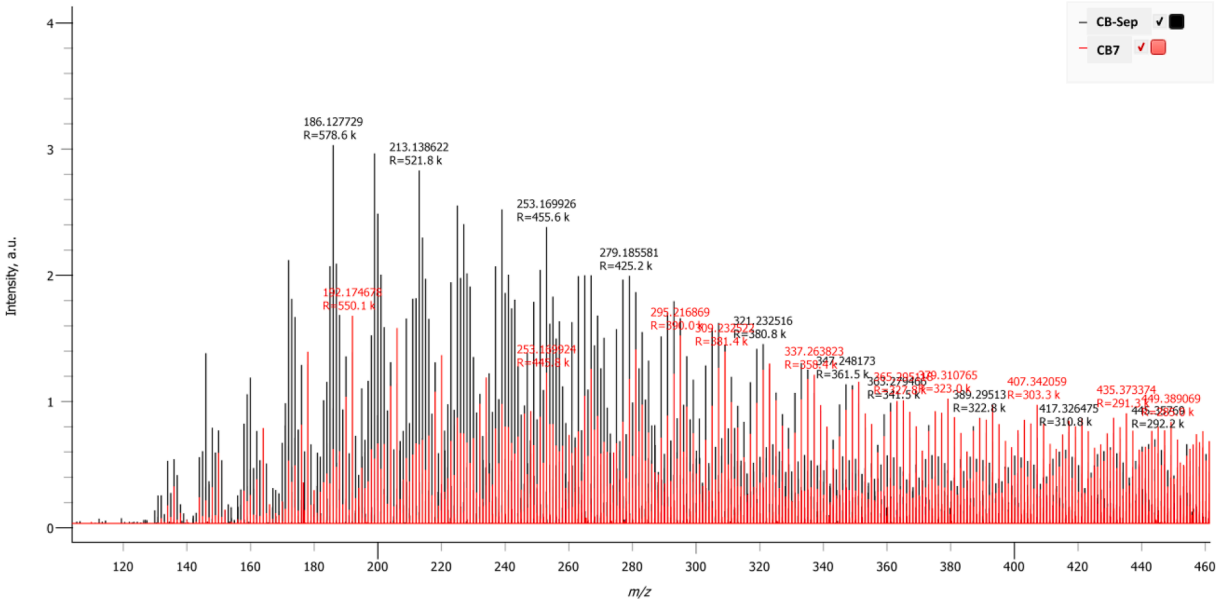

Fig. 5. ESI$^+$ FTICR MS mass spectra comparison of cyanobacteria biocrude (CB-Sep) with black peaks and acid washed cyanobacteria biocrude (CB7) with red peaks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

chemical treatment is strongly dependent on the type of organometallics and NCCs. Therefore, a more dynamic approach is followed, in which not only the effect of different organic/inorganic acid on demetallization but also the removal of basic NCCs/oxygenates and the residual effect on demetallization and organic loss is comprehensively studied.

Experimental results suggest that chemically stable metalloporphyrins in nitrogen–rich cyanobacteria (generally referred as *Spirulina* algae) biocrude limit the demetallization at lower acid concentrations (i.e., 0.1 M). Primarily, this is due to the presence of basic NCCs (mainly N_1, N_2 species with low carbon number or higher N/C ratio) which readily neutralizes the oxidizing agents and form metallic salt complexes during acid washing. The utilization of a strong acid (H_2SO_4) at elevated concentrations results in appreciable demetallization (24.5 % and 66.3 %) and denitrogenation (9.2 % and 35.4 %). However, this severe treatment causes up to 35 % of organic losses and degrades the cyanobacteria biocrude due to extensive side reactions, therefore not representing a viable option.

The results after the acid washing of primary sewage sludge HTL biocrude supplements the interplay of different organometallics along with different types of NCCs. In this study, via FTICR MS it was found

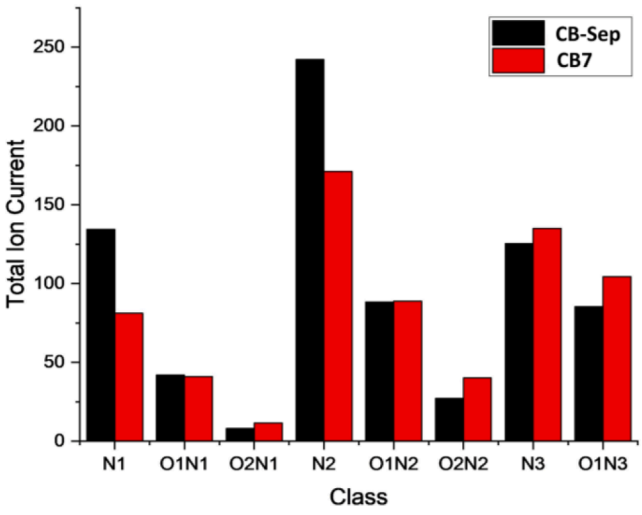

Fig. 6. ESI$^+$ FTICR MS derived heteroatom class distribution for cyanobacteria biocrude (CB-Sep) and acid washed cyanobacteria biocrude (CB7). N_x and O_x denotes the number of nitrogen and oxygen atoms in the detected ions.

that metalloporphyrins are not present in sludge biocrude, and it is mainly composed of carboxylic acids with class O_2 and O_4. Primarily, due to polarity and affinity of carboxylic groups, acid washing also removes organic compounds low DBE and longer carbon chains (up to C_{18}). This comprehension was confirmed during acid treatment, where 89.2 % of demetallization and 10.7 % of denitrogenation was achieved with an organic loss of 20.1 %.

FTICR MS analysis not only consolidates the experimental findings, but also shows that the fractions of both cyanobacteria and sludge biocrudes with mass-to-charge ratio (m/z) of below 300 are prone to higher organic loss. Above 300 m/z, the polarity of the organic compounds decreases (due to considerable increase in carbon number and its chain length) thus, the organic loss decreases. Even though some denitrogenation occurs along with demetallization, overall results indicate that the denitrogenation during acid treatment is negligible. This is mainly because the removal of nitrogen is associated with the removal of whole organic compound. Acid washing not only decreases the amount of nitrogen but also decreases the organic concentration and therefore, at the end the denitrogenation remains unaffected.

In summary, the integration of acid treatment before hydrotreatment is possible depending on the type of organometallics and of NCCs present in the given HTL biocrude. HTL biocrudes without recalcitrant organometallic compounds (e.g., metalloporphyrins) and with a low level of basic NCCs are suitable for a demetallization route via chemical

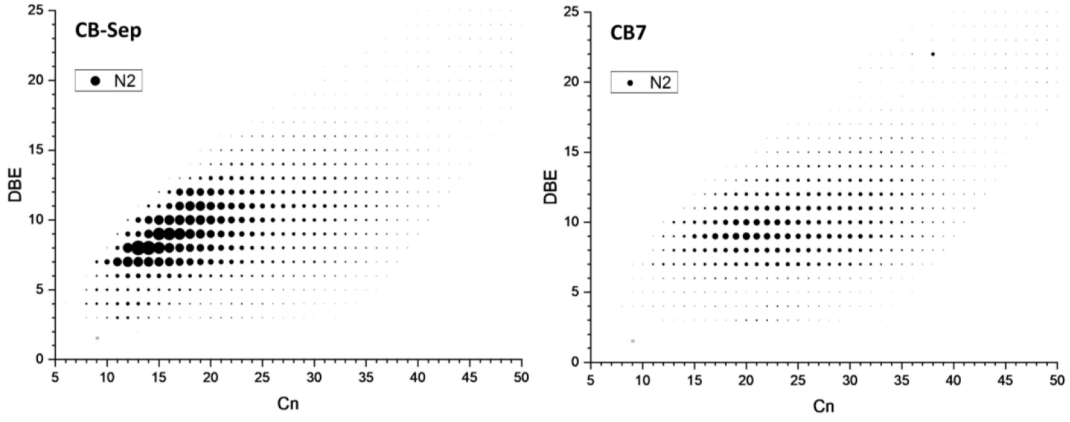

Fig. 7. ESI$^+$ FTICR MS derived isoabundance-contoured double bond equivalent (DBE) vs carbon number (C_n) plots for the heteroatom N_2 species of cyanobacteria biocrude (CB-Sep) on the left and acid washed cyanobacteria biocrude (CB7) on the right.

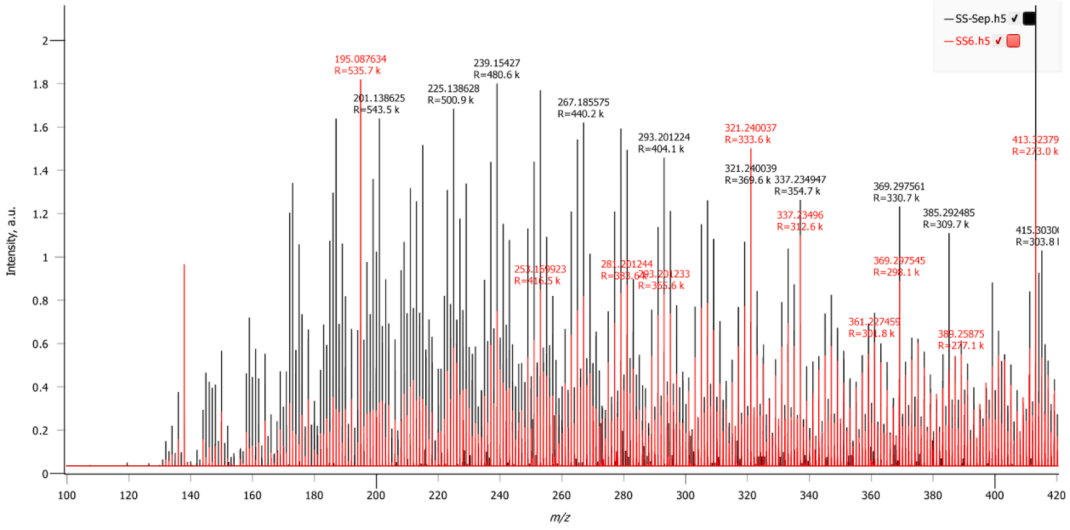

Fig. 8. ESI$^+$ FTICR MS mass spectra comparison of primary sewage sludge biocrude (SS-Sep) with black peaks and acid washed primary sewage sludge biocrude (SS6) with red peaks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

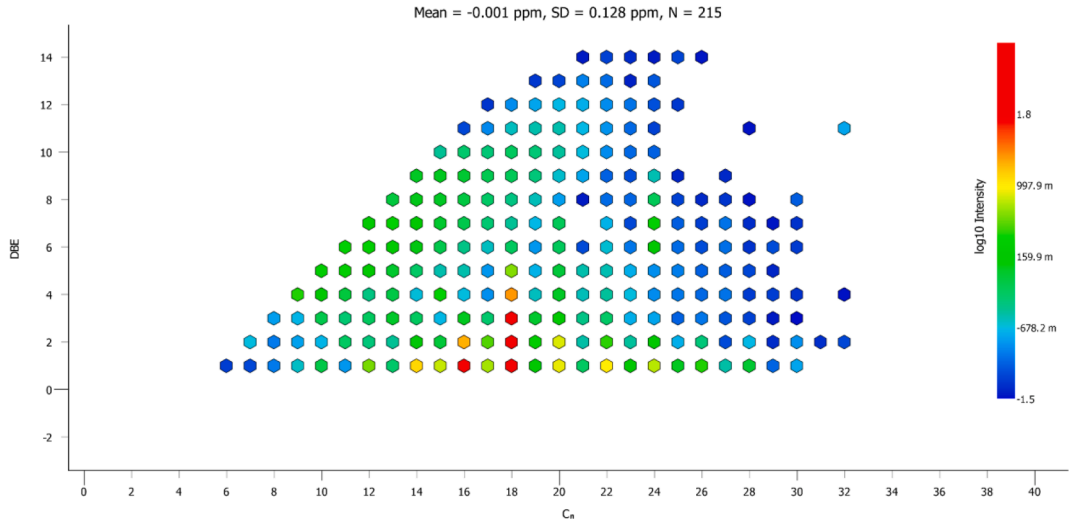

Fig. 9. ESI⁻ FTICR MS derived isoabundance-contoured double bond equivalent (DBE) vs carbon number (C_n) plot for the heteroatom O_2 species of sludge biocrude (SS-Sep).

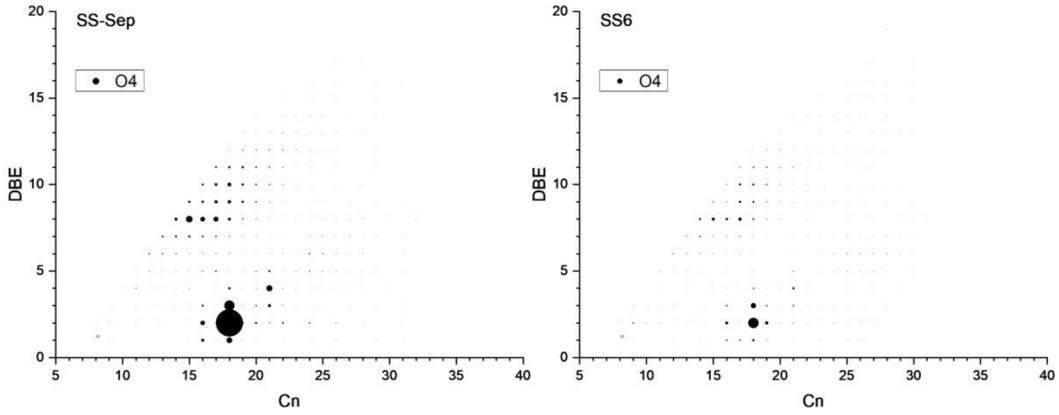

Fig. 10. ESI⁻ FTICR MS derived isoabundance-contoured double bond equivalent (DBE) vs carbon number (C_n) plots for the heteroatom O_4 species of sludge biocrude (SS-Sep) on the left and acid washed sludge biocrude (SS6) on the right.

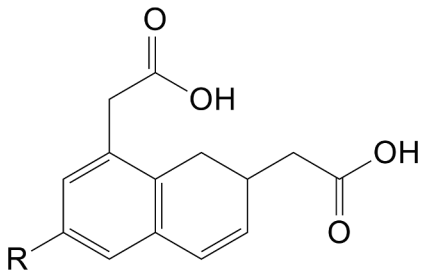

Fig. 11. Hypothetic molecular/chemical structure depending on DBE 8 and O_4.

treatment. Therefore, prior knowledge of organometallics, NCCs, and oxygenates in a given HTL biocrude is crucial to select an optimal demetallization strategy. This could possibly eliminate one of the bottlenecks for the commercial implementation of HTL for sustainable biofuels production.

CRediT authorship contribution statement

Muhammad Salman Haider: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Stefano Chiaberge:** Formal analysis, Software, Visualization, Writing – original draft, Writing – review & editing. **Andrea Siviero:** Formal analysis. **Mehmed Akif Isik:** Conceptualization, Data curation, Formal analysis, Investigation. **Daniele Castello:** Conceptualization, Writing – review & editing. **Thomas Helmer Pedersen:** Conceptualization, Resources, Supervision. **Lasse Aistrup Rosendahl:** Funding acquisition, Supervision, Resources, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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