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Catalytic hydroconversion of HTL micro-algal bio-oil into biofuel over NiWS/Al₂O₃

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1. Introduction

The global demand for energy in the world and the environmental concerns to supplying this energy are constantly increasing. Consequently, the production of transportation fuel from renewable resources is receiving more attention from the scientific community. Among the species that constitute the biomass, microalgae display extremely varied biodiversity and are rich sources of new molecules and lipidic materials. Microalgae represent an almost untapped resource (It is estimated that there are about 200,000-800,000 species in many different genera, of which only about 50,000 species are described.) This feedstock seems to be a potential raw material for third-generation fuel production due to its high growth rate and its abundant production that exceeds the best oilseed crops, e.g., biodiesel yield of 58,700 L/ha for microalgae containing only 30% oil by wt.% compared with 1190 L/ha for rapeseed or Canola. Besides, this microorganism has the potential for CO₂ fixation through photosynthesis, storing this carbon in energy rich-compounds such as lipids, carbohydrates, and proteins. Its high lipid content can be converted into drop-in fuels for diesel and jet fuel. Life cycle assessment has shown a reduction in greenhouse gas emission by 76% for algal bio-jet fuel production, compared to conventional jet fuel [1–4].

Hydrothermal liquefaction of microalgae is one of the most promising alternatives for producing biofuels as this process is performed in water, it does not require any algae drying and leads to an interesting yield of liquid. Nevertheless, the biocrude obtained still contains nitrogen and oxygen compounds. The total acid number (TAN) tends to be approximately 60 mg KOH/g oil which comes from the fatty acids [5]. Besides, the density is around 0.96 g/mL and the viscosity can vary from 40 to 400 cSt @ 40 °C. Thus, requires an upgrading stage to obtain a compatible transport fuel. Upgraded algal HTL oils showed a TAN close to zero, density and viscosity roughly 0.77 g/mL and 4 cSt @ 40 °C, respectively [6–8]. In 2016, Lopez Barreiro *et al.* [9] reviewed the literature on upgrading biocrude oils obtained by HTL of microalgae and concluded the need to improve processes, catalysts, and underlined the

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importance of algae species. Xu *et al.* [10] and Djanda *et al.* [11] complemented this review by adding technico-economic studies which also suggest that algae composition strongly impacts the economics of the process. Catalytic upgrading is usually performed by using either hydrotreatment catalysts or acid catalysts active for catalytic cracking (or both functions in hydrocracking). However, sulfur and nitrogen compounds present in the biocrude require robust thio- and azo-resistant, and low-cost catalysts. Metal sulfide hydrotreating catalysts are often considered for industrial application in bio-oil hydroconversion. The most recent studies in this domain use either NiMo or NiW supported on alumina catalysts [12–17]. The scalability of HDT unit for HTL bio-oil upgrading was recently demonstrated at Pacific Northwest National Laboratory (PNNL), as well as two-stage upgrading [18,19], and the feasibility of co-processing in FCC unit was also assessed [20]. However, there is still a significant challenge in the growth and algae strain selection with an obvious target of high lipid contents since they will provide ideally long-chain alkanes after upgrading. However, the complexity of the microalgae bio-oils obtained by HTL makes difficult the understanding of their reactivity during upgrading. Catalysts have various roles in the conversion of bio-oils [21]. Regarding the upgrading stage, the hydrogenolysis properties for removing oxygen from oxygenated compounds (mostly phenols) are similarly required for algae HTL oils. As compared with pyrolytic oils, algae biocrude contains different species. The presence of nitrogen-containing compounds in the algal bio-oils constitutes another challenge since an almost complete removal of nitrogen is required for a fuel application. This denitrogenation issue was underlined by Leng *et al.* [22]. Other specific components of algae feedstocks might be problematic. For instance, using FT-ICR-MS, Jarvis *et al.* [23] evidenced that iron porphyrins can remain after HTL, and like porphyrins in petroleum, it may cause catalyst deactivation. A model molecule study demonstrated that chlorophyll, which can represent up to 5 wt% of algae content, can release, during the HTL process, phytols that are further converted into several unsaturated compounds [24]. After upgrading, these molecules can also produce long-chain alkanes (C₂₀). A detailed semi-quantitative analysis by comprehensive GC of the hydrogenation products of an algal biocrude was provided by Rathsack *et al.* [12]. These authors underlined the possibility of converting phenols but difficulties to further reduce nitrogen compounds such as indoles or anilines. In the present work, the reactivity of HTL micro-algal bio-oil over a NiW/Al₂O₃ sulfided catalyst will be investigated at different temperatures and characterized with several analytic tools such as ¹³C-NMR, GPC-RID/DAD, Sim-Dis, and GCxGC-MS/FID. Thus, we will describe the behavior of compounds and families of compounds identified in the bio-oil and quantify them. Removal of heteroatomic compounds (O, N, and S), which can significantly

affect the quality of the biofuel, is also considered. Careful attention is given to lipids and the evolution of long-chain compounds on different stages, from the initial microalga until final biofuel. Lastly, the transfer of the metal present in the microalga to the used hydrotreating catalysts will be also discussed.

2. Materials and methods

2.1. Microalgae production

The microalga strain consists of *Chlorella sorokiniana* NIES 2173 and was grown at MicroAlgae Processes Platform, CEA Cadarache, France.

Table 1. *Chlorella sorokiniana* feedstock analysis.

Component	Content (%)
Moisture	41.2
Ash ^a	2.4
Carbohydrates ^a	31.4
Lipids ^a	13.3
Proteins ^{a,b}	16.5

^a Based on dry algae

^b Calculated using a nitrogen-to-protein conversion factor of 5.0 as reported by Templeton and Laurens [25].

The amino acids profile of a batch of microalgae grown under similar conditions is given in supplementary material Table S1.

2.2. Extraction and transesterification of lipids.

Lipids extraction from dry microalga was performed with a mixture of chloroform and methanol (volume ratio 2:1) in an automatic solvent extractor VELP Scientifica SRE 158, following the Bligh and Dyer method. As Ryckebosch *et al.* [26] mentioned, two extractions in series could be performed to ensure that all lipids are extracted, irrespective of the microalgae species. Therefore, after two extractions, 11 wt.% (dry-ash-free basis) of extract were recovered from nearly 8 g of dry microalga. The transesterification reaction was performed with a mixture

of methanol, sulfuric acid, and THF at 60°C for 2h using a stirring of 500 rpm according to the procedure described by Nguyen *et al.* [27]. This analysis aims to qualify and quantify carbon chains.

2.3. HTL bio-oil production

Hydrothermal liquefaction reaction was performed in a 300 mL Parr stainless steel reactor. The reactor was loaded with the microalga and water (20 wt.% - dry-ash-free basis) and purged with N₂ to remove the air inside. Subsequently, 0.1 MPa of N₂ pressure was applied, and the reactor was heated to 300 °C with a heating rate of approximately 10 °C/min. When the target temperature was reached, the stirring (370 rpm) was started, and the reaction was performed for 30 min. The reactor total pressure at 300°C was approximately 10 MPa. After the reaction, the biocrude and the aqueous phase were separated by filtration, and the reactor was washed with ethyl acetate to recover the residual biocrude. Then, all the biocrude was mixed with ethyl acetate and heated until 40 °C for 1h to favor the solubilization and extraction of the bio-oil. The bio-oil and char were separated by vacuum filtration, and the solvent was removed using a rotary evaporator. This protocol was repeated ten times to produce enough bio-oil for upgrading experiments. The total bio-oil mass was approximately 50 g, and the average yield over the HTL reactions was 24% (dry-ash-free basis).

2.4. Catalytic hydrotreating (HDT) of HTL bio-oil

The hydrotreating step was performed using the same reactor than for the HTL experiments. The commercial NiW/Al₂O₃ catalyst (WO₃: 25.7 wt.%, NiO: 3.8 wt.%, specific surface area: 179 m²/g, and total pore volume: 0.40 cm³/g) was previously sulfided at 400°C for 3h under a 15% H₂S/H₂ flow (4 NL/h) [28]. Firstly, the reactor was loaded with 3.0 g of bio-oil, 0.6 g of pre-sulfided catalyst, and 25 g of n-heptane, which was used to enable an efficient agitation during the experiment. Then, the reactor was purged three times with N₂ and was pressurized until 6 MPa for a leak test. Subsequently, the N₂ was removed, and the reactor was purged three times with H₂. At room temperature, 1 MPa of H₂ was added, and the reactor was heated until the desired temperature. Three different upgrading temperatures were used to study the reactivity of the compounds in the HTL micro-algal bio-oil: 350, 375, and 400 °C. Once the desired temperature had been reached, 5 MPa of H₂ was added to get a total pressure of 10 MPa

at the reaction temperature. All experiments were performed for 5h. After that, the reactor was cooled down, and the catalyst and hydrotreated bio-oil were separated by filtration. The reactor was washed with n-heptane to remove the residual oil and catalyst. The n-heptane was later removed using a vacuum rotary evaporator, and the oil was characterized with different analytical techniques described after.

2.5. Characterization and analytical techniques

2.5.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of dry microalga (2-7 mg) was carried out under air or N₂ (60 mL/min) from 30 °C until 800 °C (10 °C/min) on a Mettler Toledo TGA/DSC 1 as described in the literature by Cheng *et al.* [29].

2.5.2. Metals, phosphorus, and sulfur content

The metals, phosphorus, and sulfur were firstly identified by X-ray fluorescence (XRF) analysis performed on a Panalytical Epsilon 4 instrument and, subsequently, the metals and phosphorus were quantified using inductively coupled plasma optical emission spectrometry (ICP-OES) performed on an Activa (Jobin Yvon) apparatus.

2.5.3. Elemental analysis (CHONS)

The C, H, O, N, and S mass fractions were analyzed in a Thermo Scientific Flash 2000 Apparatus. The formed gas was analyzed via a TCD detector. For the analysis of low S and N concentrations in liquid products, ANTEK 9000NS apparatus, which is more precise (from low ppb until percent levels) and accurate, was also used. The bio-oil and HDT-oil were diluted using THF to a concentration of ≈ 5 wt.% and ≈ 10 wt.%, respectively, then injected at 1050 °C. The sample was burned, and S and N were converted into SO₂ and NO₂, respectively, and analyzed by two detectors in series. Two calibration curves, one with thiophene and another with pyridine, for S and N analysis, were made to convert the signal response into concentration (ppm).

The degree of deoxygenation (de-O), denitrogenation (de-N), and desulfurization (de-S) were calculated by the following equation (1):

$$\text{de - I (\%)} = \left(1 - \frac{I_{\text{HDT-oil}}}{I_{\text{bio-oil}}}\right) \times 100 \quad (1)$$

where “I = O, N, and S”, “de-I” is the degree of deoxygenation, denitrogenation, or desulfurization, “ $I_{\text{HDT-oil}}$ ”, and “ $I_{\text{bio-oil}}$ ” is the heteroatoms content of hydrotreated oil (HDT-oil) and bio-oil, respectively.

The higher heating value (HHV), equation (2), based on the elemental mass fraction, was estimated through the correlation proposed by Channiwala and Parikh [30]:

$$\text{HHV} \left(\frac{\text{MJ}}{\text{kg}}\right) = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} \quad (2)$$

2.5.4. Gel permeation chromatography (GPC)

The GPC analysis was performed using an Agilent 1200 series HPLC equipped with two PLgel Columns (50 and 500 Å), a refractive index detector (RID), and a diode array detector (DAD). The analysis was carried out at 35 °C using tetrahydrofuran (THF) as eluent with a 1 mL/min flow rate. The samples were diluted to a concentration of ≈1 wt.% in THF and filtered (0.45 μm) before analysis. Two molecular weight (Mw) standards are available to convert the elution time into Mw: hydrocarbon mixture (Mw from 86 to 1000 g/mol) or polystyrene mixture (Mw from 162 to 55100 g/mol). The hydrocarbon mixture was used as a calibration curve to present more remarkable similarities with the analyzed samples and the chromatograms were normalized to the highest peak intensity. When the DAD detector was used, the signal was normalized per mass unit of sample to compare different samples.

2.5.5. Simulated distillation (Sim-Dis)

The boiling point distributions were determined utilizing Sim-Dis, according to the standard ASTM D2887 [31]. The analysis were performed on an Agilent 7890A series gas

chromatograph fitted with an Agilent J&W GC column (dimensions 10 m × 0.53 mm × 2.65 μm P/N: CP7582) and two detectors: flame ionization detector (FID) and flame photometric detector (FPD Plus), specific for sulfur compounds. The instrument was calibrated with a reference gas oil sample (initial boiling point of 114 °C and final boiling point of 475 °C) and a calibration mix (mixture of C₆-C₄₄) following the standard method. The liquid products were defined by five boiling point ranges: gasoline (< 175 °C), jet-fuel (175-250 °C), diesel (250-350 °C), heavy gas oil (350-500 °C), and residual (> 500 °C).

2.5.6. ¹³C nuclear magnetic resonance (¹³C-NMR)

¹³C-NMR spectra were recorded with a Bruker AVANCE 400 MHz spectrometer and analyzed using the software TopSpin 3.0. The measurements were performed at room temperature with an accumulation of 4700 scans for approximately 15 h. The samples (60 mg) were diluted with deuterated chloroform (CDCl₃).

2.5.7. Comprehensive two-dimensional gas chromatography (GCxGC)

Two GCxGC analytical systems have been used: a cryogenic modulator from Zoex Corporation (USA), described in the supplementary material (Table S2), connected to a mass spectrometry (MS) for the identification of compounds (up to C₃₂), as reported elsewhere [32], and a flow modulator connected to an FID for quantification (up to C₄₀). Modulation parameters were optimized according to Lelevic *et al.* [33]. The same column set of reversed polarity, consisting of a polar column in the first dimension and apolar in the second dimension, were utilized for both systems. Such configuration allows a better separation of the families of polar compounds [34–36].

Both analytical tools were used to analyze the extracts from microalga, transesterified lipids, HTL bio-oil and HDT-oils obtained at various temperatures. The samples were diluted in THF with a concentration of ≈ 10wt.% and ≈ 5wt.% for MS and FID analysis, respectively. Besides, an internal standard, 3,3'-dimethylbiphenyl (3,3-DMBP), ≈ 200 ppm, was also added for quantification purposes. For better discrimination of double bonds position in the transesterified lipids, a specific column ZB-FAME (30 m x 0.25 mm x 0.20 μm) was used.

2.6. Quantification of compounds and families

A quantification of the compounds on the different steps, from extracts of initial microalga until HDT-oil upgraded at different temperatures, was performed to evaluate the evolution of lipids chains and conversion of refractory nitrogen and oxygen compounds present in the bio-oil. Standard compounds such as hexadecane, oleamide, stearic acid, methyl stearate, and cholesterol were analyzed, and a calibration curve was done. However, due to the complexity of bio-oil, some standards could not be easily purchased or synthesized in the lab [37]. Moreover, a calibration curve preparation could be time-consuming and costly. For the compounds that did not have a calibration curve, the relative response factor (RRF) for FID analysis could be estimated from their chemical structure. A methodology to predict the RRF was proposed by Sternberg *et al.* [38], introducing the effective carbon number (ECN) concept. They showed that the effect of heteroatoms on the ECN of a molecule depended on the functional group's nature and empirically quantified each functional group's contribution to the ECN. These values were also reported by Scanlon *et al.* [39] and used in this work to calculate the ECN value. The ECN value was calculated by equation (3), and the relationship between RRF and ECN is given by equation (4), as reported in [40]:

$$ECN = \sum_i (N_i \times Cnt_i) \quad (3)$$

where “N” is the number of atoms or functional groups in the compound i, and “Cnt” is the ECN contribution coefficient reported by Scanlon *et al* [39].

$$RRF = \frac{ECN_i \times MW_{IS}}{MW_i \times ECN_{IS}} \quad (4)$$

where “ECN_i” is the effective carbon number of a compound or family i, “MW_{IS}” is the molecular weight of the internal standard, “MW_i” is the molecular weight of compound or family i, and “ECN_{IS}” is the effective carbon number of internal standard.

Note that the theoretical contribution of nitrogen for ECN in cyclic compounds can be difficult to estimate. For this reason, the quantification of cyclic nitrogen compounds, such as pyrrole, indole, and carbazoles, was made considering the experimental ECN value reported by Jorgensen *et al.* [41].

3. Results and discussion

3.1. Algal composition

The thermogravimetric curves and their derivatives under N₂ and air are given in supplementary material (Figure S1).

Lipids that can be extracted from dry microalga correspond to many compounds such as neutral lipids (triacylglycerol and free fatty acid), polar lipids (glycolipids and phospholipids), unsaponifiable matters, chlorophylls (and related metabolites), and others [42]. Therefore, liquid extraction with chloroform-methanol mixture led to a large distribution of compounds containing heavy and lighter compounds, as illustrated by the GPC analysis reported in Figure 1. Extracted lipids exhibit three main contributions, which can be attributed, respectively, from the highest to the lowest Mw, to triglycerides, diglycerides, and free fatty acids or other compounds. These assumptions are comforted by using tristearin and methyl stearate as references. The extracted lipids were converted into fatty acid methyl esters (Fame) during the transesterification reaction in the presence of methanol and sulfuric acid. The GPC curve obtained for the Fame was shifted to the lower masses and close to the methyl stearate reference, which can be associated with the presence of C18 methyl esters and also C16 methyl esters, as will be discussed further.

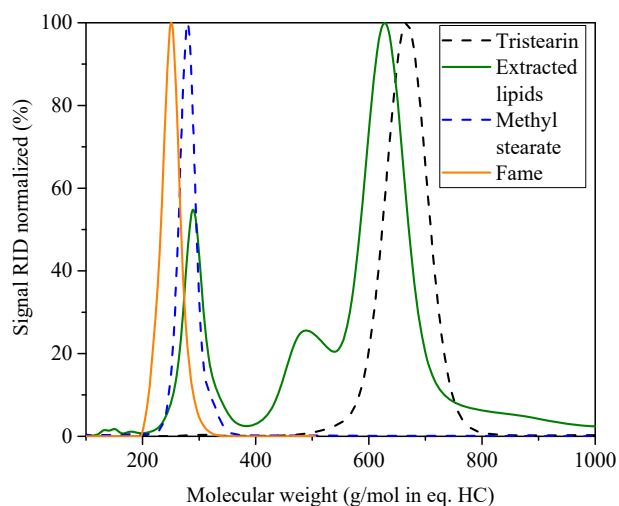


Figure 1. GPC-RID analysis (in HC calibration) of extracted lipids, Fame, and reference compounds (tristearin and methyl stearate).

The average M_w of extracted lipids, Fame, and tristearin and methyl stearate references are reported in Table 2. It is worth emphasizing that the M_w values calculated with the hydrocarbon calibration present a deviation of 7% for methyl stearate ($M_w = 298.5$ g/mol) and 26% for tristearin ($M_w = 841.5$ g/mol). Although this error is not negligible, the average M_w values are reported to compare different samples.

Table 2. Molecular weight for extracted lipids, fame, and reference compounds (tristearin and methyl stearate) using RID detector (in HC equivalent).

Sample	Weight average mass M_w (g/mol)
Tristearin	659
Extracted lipids	504
Methyl stearate	279
Fame	250

GPC with hydrocarbon calibration is also helpful to indicate the fraction of compounds that can be observed by gas chromatography (typically below 450 g/mol), thus corresponding to the first contribution of GPC analysis. Figure S2(a) illustrates the nature of extracted lipids identified by GC×GC-FID/MS. The compounds with high Mw (diglycerides and triglycerides, per example), observed with GPC, cannot be analyzed with this GC system as they are too heavy.

We observed the C16 and C18 fatty acids as the main components in the extraction liquid, as well as the presence of methyl esters of these fatty acids. During the chloroform and methanol extraction, some free fatty acids might be converted into C16 and C18 methyl esters by transesterification reaction, as already reported by Biller *et al.* [43]. These authors mentioned that esterification reactions could occur under these moderate conditions, due to the presence of alkali salts that can act as a catalyst in the microalgae and are expected to esterify free fatty acids only. Phytosterols and phytol derivatives were also found in the extract. Figure S2(b) presents the Fame chromatogram after the transesterification reaction. As reported in Table 3, in the micro-algae, the lipids are composed basically of C16 and C18 chains. C16 chains are mainly saturated, while C18 chains are unsaturated, as reported by Qiu *et al.* [44] for the same algae.

Table 3. Fatty acid profiles of microalga *Chlorella sorokiniana* (%).

	C16:0	C16:1	C16:2	C16:3	C18:0	C18:1	C18:2	C18:3
Fatty acids (%)	26.9	7.2	7.1	2.8	1.8	12.4	31.2	5.0

3.2. HTL micro-algal bio-oil composition

Hydrothermal liquefaction of microalgae involves many reactions. Hietala and Savage [45] recently proposed a kinetic model based on 16 reaction pathways illustrating the complexity of families of compounds reacting together, leading to a viscous bio-oil. C, H, O, N, S atoms are redistributed between gas, liquid (aqueous and organic phase) and solid phases during the process.

The lightest compounds of the bio-oil obtained by HTL were characterized by GC×GC-MS/FID (Figure 2). Several families of compounds can be identified, similar to those listed by Torri *et*

al. [46] and Madsen *et al.* [47], such as C16 and C18 carboxylic acids, amides, and esters, phytosterols, cyclic nitrogen and oxygen compounds. The HTL yield was 24%, approximately two times higher than lipids content in microalga, indicating that carbohydrates and proteins were also converted into an organic phase during HTL reaction. This hypothesis is confirmed by GCxGC chromatogram, where compounds such as phenols, pyrroles, indoles, carbazoles, and its alkyl-substituted homologues formed from the decomposition of carbohydrates and proteins, for example by Maillard reaction can be found [48]. Diketopiperazines (DKPs) that are coming from the degradation of proteins and their recombination were also detected in the bio-oil [49]. These compounds would affect biofuel quality and must be removed during the hydrotreatment step. The C16 and C18 carboxylic acids formed from the hydrolysis of di- and tri-glycerides represent 41% of HTL bio-oil. Fatty amides were also formed obviously from the reaction between fatty acids and ammonia coming from proteins degradation. The products coming from the hydrothermal transformation of phytol, such as phytane and dihydrophytol, were also found. As reported by Changi *et al.* [24], chlorophyll is a complex molecule, usually formed by a hydrophilic chlorine ring and the hydrophobic ester-linked to the phytol side chain, which can be readily hydrolyzed to release a phytol and products during HTL conditions [50]. A family of compounds with polarity close to C16 and C18 carboxylic acids and amides, but with a higher boiling point was also observed in the GCxGC-FID chromatogram. However, their identification was not possible with MS detector due to the fragmentation of the molecule and low probability using the NIST MS data base.

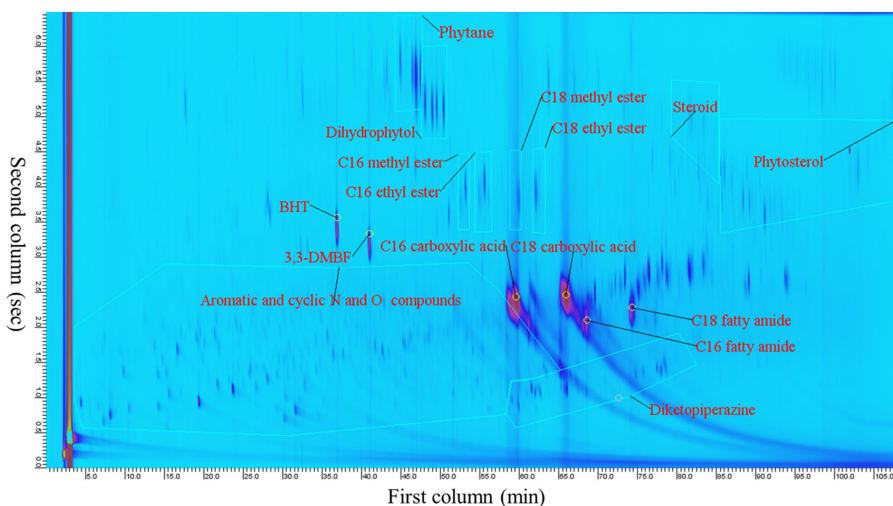


Figure 2. Comprehensive GCxGC-FID/MS chromatogram of HTL bio-oil.

3.3. Hydroconversion of HTL bio-oil

In order to improve the quality of the organic phase, the HTL bio-oil was upgraded under hydrogen pressure at 350, 375, and 400 °C for 5h over sulfide NiW/Al₂O₃ catalyst. A section considering the transfer of the metal present in the microalga to the hydrotreating catalysts used is reported in the supplementary material.

The upgraded oil yield, deoxygenation, denitrogenation and desulfurization degree are reported in Figure 3 for the three temperatures. The yield in upgraded oil is around 70% at 350°C and decreases slightly to 65% at 375 and 58% at 400°C, which can be associated to cracking reactions, that form gases, as reported by Haider *et al.* [16], who worked with sulfide NiMo and under close operating conditions. High conversion of oxygenated compounds was already achieved (90%) at 350 °C, while barely 40% of nitrogenated compounds were converted. However, after a hydroconversion performed at 400 °C, more than 90% of de-oxygenation, denitrogenation, and desulfurization was achieved, indicating that a higher temperature is required to convert nitrogen compounds.

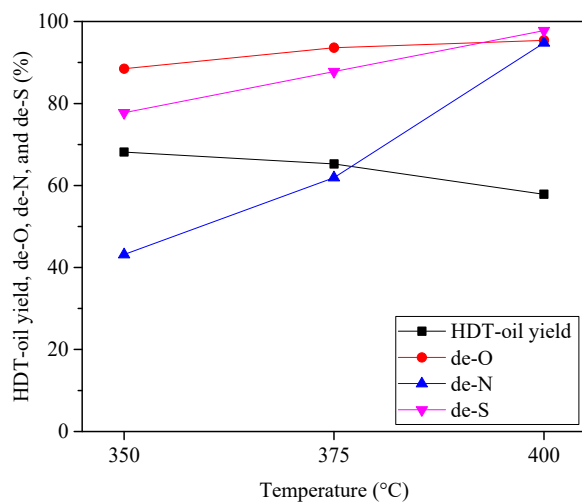


Figure 3. HDT-oil yield, degree of deoxygenation (de-O), denitrogenation (de-N), and desulfurization (de-S) in the function of temperature.

The elemental analysis of microalga, HTL, and HDT-oils at different temperatures is presented in Table 4.

Table 4. Elemental analysis of microalga, HTL, and HDT-oils at different temperatures.

Sample	C	H	O	N	S	H/C			HHV
						O/C	N/C	(MJ/kg)	
	(wt.% or ppm*)					(Atomic ratio)			
Microalga	50.4	6.8	33.6	3.2	0.2	1.61	0.50	0.05	22.5
HTL bio-oil	74.5	9.4	11.6	3.3	0.3	1.52	0.12	0.04	35.9
HDT – 350 °C	83.5	13.7	1.3	1.9	613*	1.97	0.01	0.02	45.2
HDT – 375 °C	83.8	14.0	0.7	1.2	337*	2.00	0.01	0.01	45.6
HDT – 400 °C	84.4	14.4	0.5	0.2	61*	2.05	0.00	0.00	46.4

As expected, the H/C increased in the function of temperature due to the promotion of hydrogenation reaction. On the other hand, O/C and N/C decreased due to the conversion of oxygenated and nitrogenated compounds. The HHV was significantly improved after an

upgrading step, which is indicative that hydrotreatment can be used to ameliorate the quality of HTL bio-oil from microalgae. Guo *et al.* [13] reported a *C. vulgaris* HTL bio-oil hydroconversion using close operating conditions and the same type of catalyst (sulfide NiW and NiMo). Although the HHV of microalga and HTL bio-oil were similar to the one reported in this work, the HHV of HDT-oil was lower, approximately 43 MJ/kg after upgrading at 400 °C. This difference in HHV can be associated with the high nitrogen content in the *C. vulgaris* bio-oil (6.9 wt.%), that is two times higher than the value reported in this paper for the bio-oil from *C. sorokiniana*, and that can inhibit the catalytic activity. The difference could also come from the effect of the supercritical state of n-heptane solvent, in used operating conditions. According to Xu *et al.* [51], the use of supercritical fluid (SCF) can improve the diffusion rates in catalyst pore mouth and hence minimize the mass-transfer limitations and coke formation. Besides, hydrocarbons in the supercritical state have the "hydrogen-shuttling" ability and enhanced solvent effects. Recently, Fang *et al.* [52] showed that the catalyst's performance was superior in SCF of n-hexane than in the conventional media for the hydrogenation of hexadecanoic acid, which is, with octadecanoic acid, the main compounds in HTL bio-oil.

The broad distribution of compounds in the HTL bio-oil is illustrated by the distribution of molar masses given by the GPC analysis of the bio-oil (Figure 4). The prominent peak is close to 300 g/mol, attributed to the contribution of C16 and C18 carboxylic acids, which represent a considerable fraction of HTL bio-oil and will be discussed further with GCxGC-MS/FID analysis. The Mw was reduced when the upgrading temperature was increased, as reported in Table 5. Consequently, the distribution is shifted to the left. As written before, this Mw reduction can be associated with carboxylic acid and amides converting into alkanes and cracking reactions. Moreover, it was also possible to observe the conversion of heavy molecules. However, even after an upgrading step at 400 °C, molecules with Mw higher than C₃₂, GCxGC-MS instrument limit, can be still found in the HDT-oils. This is in agreement with the studies of Jarvis *et al.* [8] and Zuber *et al.* [53], which mentioned the presence of heavy molecules by FT-ICR-MS analysis after an upgrading step of algal bio-oil under severe reaction conditions.

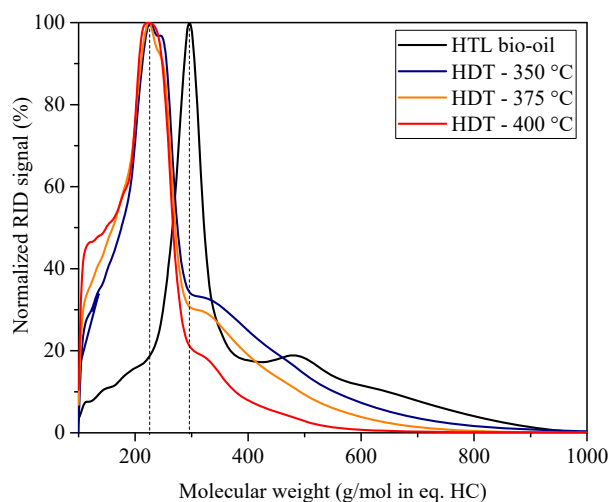


Figure 4. GPC-RID analysis of the HTL bio-oil and HDT-oil at various temperatures.

Table 5. Molecular weight for HTL bio-oil and HDT-oils at different temperatures using a RID detector (in HC equivalent).

Sample	Weight average mass M_w (g/mol)
HTL bio-oil	333
HDT – 350 °C	250
HDT – 375 °C	229
HDT – 400 °C	203

GPC-DAD gives information on the aromaticity of the compounds. Higher molecular weight compounds of the biocrude partly consist of thousands of molecules with a wide range of aromaticity [54]. These poly-aromatic compounds provide a UV response between 190 and 450 nm, depending on the condensation and functionalization of the rings. GPC-DAD chromatograms reveal the presence of mostly poly-aromatic molecules in the HTL bio-oil, as illustrated by Figure 5(a). Upon hydroconversion, the degree of aromaticity of HDT-oils is drastically reduced (see Figure 5(b)). This can be attributed to the conversion of cyclic nitrogen and oxygen compounds as already observed by FT-ICR-MS [53]. Besides, in the 2D GPC-

DAD projection, the temperature increase during the upgrading step led to a shift of intensity for a higher retention time (Figure S3).

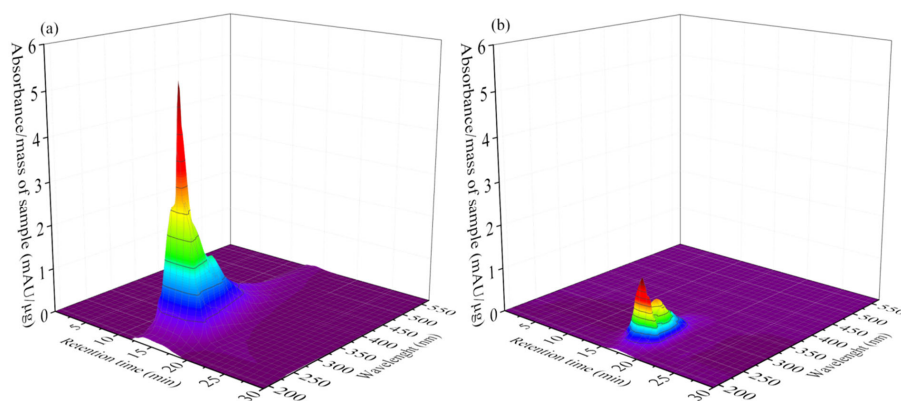


Figure 5. 3D projection of GPC-DAD signals for (a) HTL bio-oil and (b) HDT-oil at 400 °C.

The ^{13}C -NMR gives information about the functional group distribution in the HTL bio-oil and HDT-oils (Figure S4). Carboxylic groups are present in the HTL bio-oil and can be associated with the carboxylic acids formed by hydrolyses of di and triglycerides during the HTL reaction [43]. Then, these compounds were converted during the upgrading step, probably related to the significant decrease in oxygen content in the HDT-oils compared to the HTL bio-oil, as reported by elemental analysis. The carboxylic acids can be easily converted during the upgrading step under the reaction conditions employed, as reported by Toba *et al.* [55], which achieved approximately 100% of HDO of waste vegetable oil using the same type of sulfide catalyst at 300 °C. Moreover, the degree of aromaticity reduced when the temperature was increased as confirmed by GPC-DAD analysis and can be correlated to the H/C. The conversion of aromatics compounds during the hydrotreatment step is essential since these compounds have a negative effect on the diesel's cetane number.

Figure 6 shows the simulated distillation profiles of oils hydrotreated at different temperatures, and the fractional cuts are presented in Table 6. The hydrotreated oil from microalga falls primarily in the diesel range corresponding to approximately 60% of the biofuel, in agreement with Elliot *et al.* [6], who mentioned that about 80-85% of hydrotreated HTL bio-oil would be

blendable into the diesel pool. Furthermore, within the diesel range, four distinct steps are present in the Sim-Dis curves, which are associated, respectively, with the n-alkanes C15, C16, C17, and C18, as will be discussed further. The increase in the upgrading temperature enhanced cracking reactions, promoting the formation of compounds with lower boiling points, such as jet-fuel, and favored the conversion of heavier compounds like heavy gas oil and residual. This tendency is corroborated by the GPC results, which showed an Mw reduction when the temperature was increased, in accordance with the works of Castelo *et al.* [56] and Biller *et al.* [57], who reported similar results.

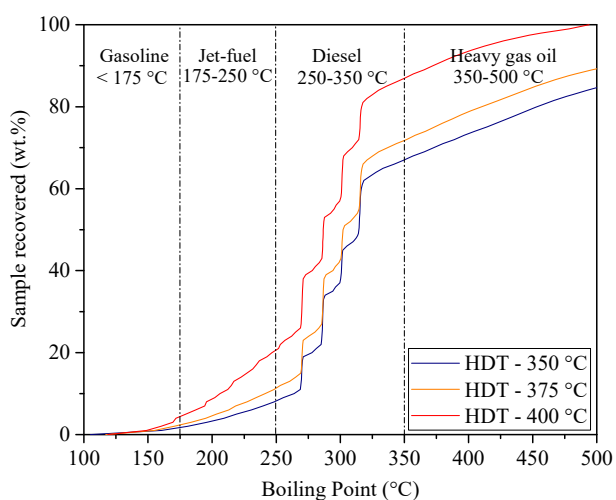


Figure 6. Simulated distillation profiles of oils hydrotreated at different temperatures.

Table 6. Fractional cuts obtained from the simulated distillation of HDT-oil at different temperatures.

Sample	Gasoline	Jet-fuel	Diesel	Heavy gas oil	Residual
	< 175 °C (wt.%)	175-250 °C (wt.%)	250-350 °C (wt.%)	350-500 °C (wt.%)	> 500 °C (wt.%)
HDT – 350 °C	1	7	59	21	12
HDT – 375 °C	2	9	61	20	8
HDT – 400 °C	4	17	66	12	1

The GCxGC coupled to an MS and FID detector was used to identify and quantify different families presented in the hydrotreated oil (Figure 7). A family of aliphatic hydrocarbons formed by n-, iso-, and cycloalkanes from C8 until C37 was observed in agreement with Rathsack *et al.* [12], who reported hydrocarbons chains from C7 until C30. The longer hydrocarbons are presumably formed by a sequence of reactions beginning with a ketonization reaction between two fatty acids involving CO₂ removal and leading to larger ketones. In the next step, ketones are hydrogenated toward hydrocarbons. C16 and C18 carboxylic acids were easily converted using the employed conditions, as observed by ¹³C-NMR analysis, and corroborated by Castello *et al.* [56], who mentioned that this type of compound is relatively easy to upgrade into the corresponding paraffin, even at mild conditions. Mono, di, poly-aromatics, phytosterols and phenols, and cyclic nitrogen compounds, such as pyrroles, indoles, and carbazoles, were identified in the HDT bio-oil, and their concentration changed in function of the temperature employed during the experiment. C16 and C18 alcohols and nitriles were also found in the hydrotreated bio-oil obtained at 350 °C. As reported by Senol *et al.* [58] with a model molecule, the carboxylic acid can be hydrogenated to aldehyde, subsequently to alcohol, and finally to alkane. The fatty amides can be rapidly hydrogenated to nitriles and then converted to imine, amine, and alkane, as reported by Pongsiriyakul *et al.* [59], over NiRe catalyst. It is worth emphasizing that no imine or amine were found during our experiments, suggesting that maybe those intermediates are rapidly converted or not detected with our GC system. Therefore, a higher temperature (≥ 375 °C) was required for the total conversion of C16 and C18 alcohols and nitriles. Although nitriles were not found in the experiments at 375 °C and 400 °C, fatty amides are still present after upgrading even if higher temperatures are employed. The 3D GCxGC-FID/MS chromatograms of bio-oil and HDT-oils that illustrate better the concentration of the various families are shown in the supplementary material (Figure S5).

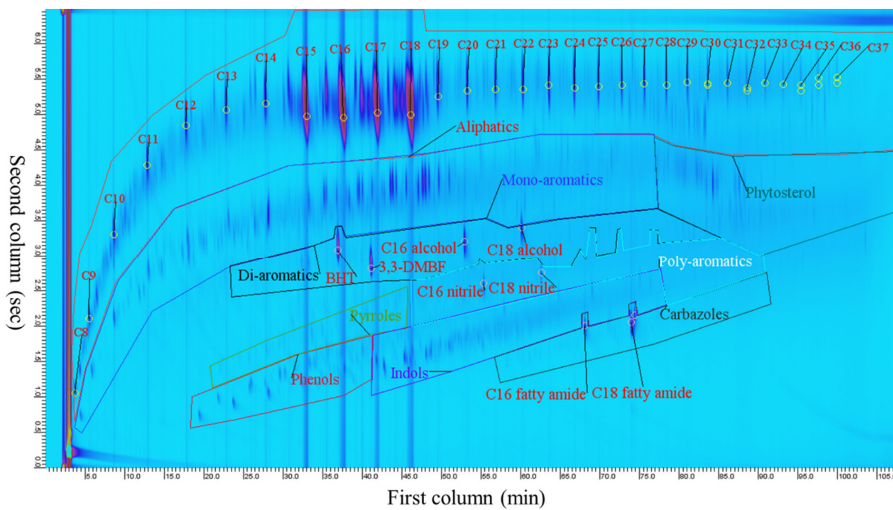


Figure 7. Comprehensive GCxGC-FID/MS chromatogram of HDT-oil at 350 °C.

During the hydrotreatment step, the C16 and C18 carboxylic acids can be converted mainly via two pathways: decarboxylation/decarbonylation (DCO), which implies the loss of carbon by eliminating CO or CO₂ in the gas phase and forming C15 and C17 n-alkanes in the liquid phase, or hydrogenation (HDO), which preserves the number of carbon leading to C16 and C18 n-alkanes by removing water, but consumes more hydrogen [60,61]. Effectively, the main n-alkanes in the hydrotreated oil were C15, C16, C17, and C18 (Figure 8), in accordance with previous works [12,56]. These results are also consistent with the Sim-Dis analyses that showed that approximately 60% of biofuel from microalga is in the diesel range (Figure 6). Temperature increases during the hydrotreatment step promoted cracking reactions, leading to the formation of lighter n-alkanes (below C14) and the reduction of C16 and C18 n-alkanes (also reported in Figure 8). This trend can be explained by the fact that increasing temperature favors the decarbonation pathway, as reported by Arora *et al.*[62]. This is also confirmed by the C16/C15 and C18/C17 n-alkanes ratio that decreases slightly from 350°C to 375°C and more strongly after 375°C (Figure 9). Therefore, it is possible to vary the distribution of n-alkanes by changing the operating conditions.

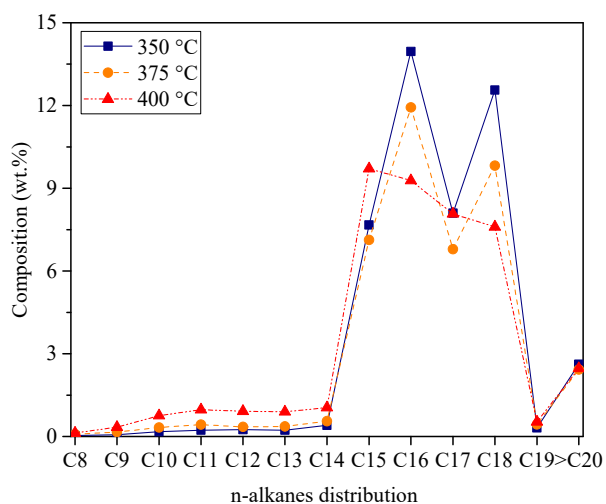


Figure 8. n-Alkanes distribution of bio-oil hydrotreated at different temperatures.

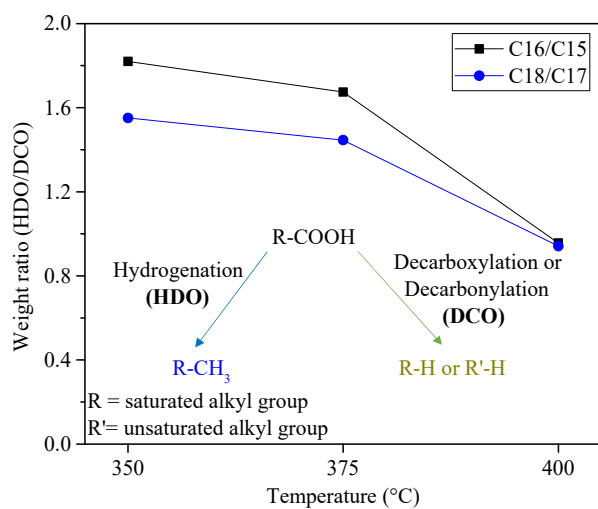


Figure 9. HDO/DCO ratio in function of upgrading temperature.

Oxygenated compounds, such as phenols and phytosterols, and nitrogen compounds were also highly affected by upgrading temperature, as shown in Figure 10. From those O- or N-compounds, we can expect the products of hydrodeoxygenation (HDO) or hydrodenitrogenation (HDN) reactions that are shown in Figure 11.

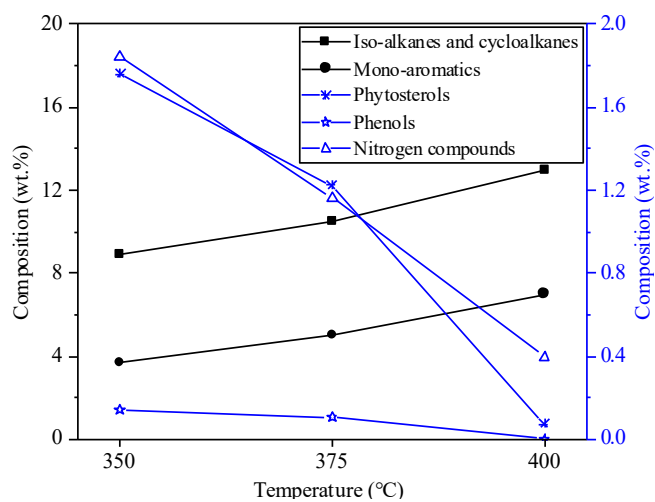


Figure 10. Concentration of families in the bio-oil hydrotreated at different temperatures.

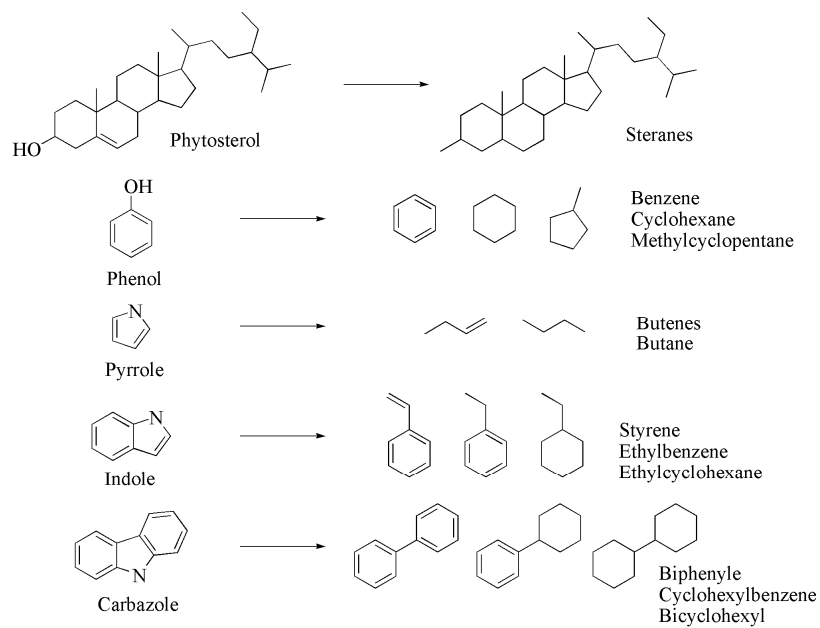


Figure 11. Illustration of the of HDO or HDN reactivity of the various families of compounds.

Metal sulfide catalysts are industrially used for their propensity to hydrogenolyse C-heteroatoms bonds (C-S, C-O, C-N and C-M with for instance M= V or Ni in fossil fuels but also Fe or Mg with algae) and hydrogenates aromatic rings (reaction sometimes required before hydrogenolysis) in the presence of poisoning molecules such as H₂S or NH₃ [63–65]. Therefore, in the case of algae crude oils sulfide catalysts are required for O and N removal. Considering the complexity of the algal oil we select below some characteristic molecules and describe their reactivity.

On metal sulfide catalysts, phenol can react by two routes: direct deoxygenation route (DDO) forming benzene, or by a consecutive route including hydrogenation (HYD) with sequent elimination of oxygen, to produce cyclohexene which can be further hydrogenated to cyclohexane or converted to methylcyclopentane, as shown by Bui *et al.* [66]. These compounds were fully converted at 400 °C, which agrees with Rathsack *et al.* [12]. These authors reported 2% of phenols after an upgrading step performed at 340 °C, and this value decreased to 0.1 when a temperature of 400 °C was employed. Concerning the hydrodeoxygenation of phytosterols, our results showed a similar tendency proposed by Anthonykutty *et al.* [67]. Sterane is the main product of this reaction and, like phenolics, more severe operating conditions are required for the deoxygenation of all phytosterols. Although more than 90% denitrogenation degree was achieved at 400 °C, some nitrogen compounds remain in the upgraded bio-oil. To better discuss the refractory compounds, the concentration of different nitrogen families was evaluated and reported in Figure 12. Diketopiperazines present in the algal bio-oil were not detected anymore in the upgraded bio-oil, indicating that these compounds were fully converted. As mentioned before, five-membered N-ring such as pyrroles, indoles, carbazoles, and their alkyl-substituted homologues were identified in the algal bio-oil. Usually, the HDN reaction of these types of compounds can proceed by hydrogenation of the aromatic ring to which the amino group is attached, followed by C-N bond scission [68,69]. Possible HDN products of N-containing heterocycles are shown in Figure 11. According to Stern [70], the conversion rates decrease as the five-membered ring of pyrroles is increasingly substituted; carbazoles being less reactive than indole and pyrrole, respectively, which is in agreement with the conversion range obtained for these families. Pyrroles and indoles concentration were reduced when a higher temperature was employed and they were almost entirely converted at 400 °C. However, carbazoles content was approximately the same when an upgrading step was performed at 350 °C and 375 °C and started to be converted just when more severe conditions (400°C) were employed. Surprisingly, fatty amides were found

in the hydrotreated bio-oil at 400 °C. These results contrast to the one reported by Rathsack *et al.* [12], who mentioned an almost total conversion of fatty amides at 380 °C. However, they used a much higher hydrogen pressure (249 bar) and found a low concentration of carbazoles in their upgraded oil.

In contrast to oxygenated and nitrogenated compounds, the concentration of mono-aromatics and iso- and cyclo-alkanes increased with temperature (Figure 11). As mentioned, cracking products were also observed. According to the literature, on acidic catalysts such as zeolites, zirconia, and tungsten oxide supported on zirconia, n-alkanes first isomerize to mono-branched isomers, then into di-branched isomers, and subsequently are hydrocracked into smaller chains [71]. The increase of iso-alkanes concentration can be attributed to the operating conditions (rising temperature) enabling cracking reactions. Moreover, cyclo-alkanes and aromatic compounds, such as decylcyclohexane and 2-phenylundecane, were also identified in the upgraded bio-oil chromatogram. According to Snare *et al.* [61], alkane chains can be cyclized and dehydrogenated to aromatics. Therefore, our results suggest that these reactions were promoted by temperature since the concentration of cyclo-alkanes and mono-aromatics increased (the latter compounds being also obtained by hydrogenation of polyaromatics). Lastly, HDO and HDN products and the conversion of heavy cyclic molecules into smaller compounds could also contribute to the increase of mono-aromatics concentration.

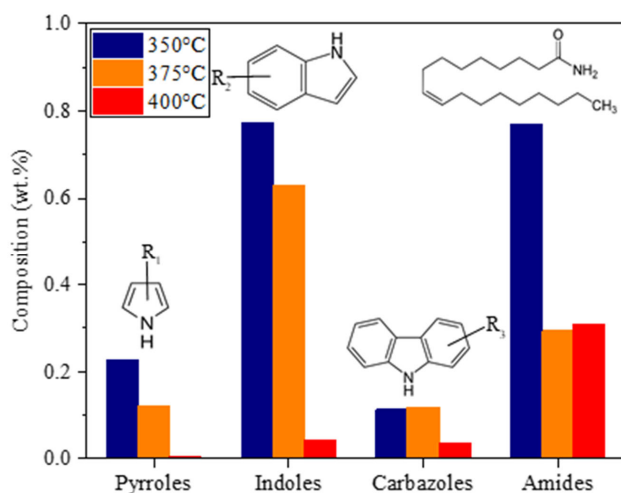


Figure 12. Nitrogen compounds concentration after hydrotreatment step at different temperatures.

The sulfur level in the HTL bio-oil (0.3 wt.% in this study) is much higher than the values required by current environmental legislation for fuels [72]. These compounds are primarily derived from sulfur-containing amino acids, such as cysteine and methionine. They can be removed during the upgrading step by hydrodesulfurization reaction (HDS), forming sulfur-free compounds and hydrogen disulfide. The literature related to sulfur in HTL micro-algal bio-oil remains scarce and requires deep exploration. Duan and Savage [73] mentioned that the only sulfur-containing compound detected in the algal bio-oil, 1-methyl-2-piperidinethione, was removed after the upgrading process. No S compounds were identified during our analysis of bio-oil and hydrotreated oil with GCxGC-MS. Therefore, the samples were analyzed with a GC coupled with an FPD Plus detector, which is highly sensitive for sulfur compounds. Reference sulfur-bearing molecules, generally found in petroleum, like thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT), were injected to verify their retention time and enable a better identification. Figure 13(a) shows the sulfur speciation in HTL algal bio-oil and Figure 13(b) in the hydrotreated bio-oils. To estimate the volatility of sulfur compounds, the boiling point curve of n-paraffins, from C7 until C44 obtained with the FID detector, was also included in Figure 13. We observed that the sulfur compounds in initial and hydrotreated bio-oils are numerous and probably of various nature, as they are eluted between 2 and 15 min. Once the concentration of initial and hydrotreated oil samples is similar, we see that the intensity of the sulfur signal reduces after the upgrading step, indicating that part of the sulfur compounds was removed, as verified by ANTEK analysis. Furthermore, comparing the obtained signal with the retention time of sulfur model molecules, it can be concluded that sulfur compounds heavier than 4,6-DMDBT, with boiling point (bp) close to 500 °C as benzo[b]naphtho[1,2-d]thiophene (bp: 434 °C) and dinaphtho[1,2-b:2',1'-d]thiophene (bp: 523 °C), are present in the bio-oil. These are the most refractory molecules, as their signal is more intense than the signal of light sulfur compounds, and it remains intense even after upgrading step (Figure 13(b)). These observations shed light on the fact that these molecules are difficult to detect by GCxGC-MS due to their diversity, low concentration, and high molecular weight.

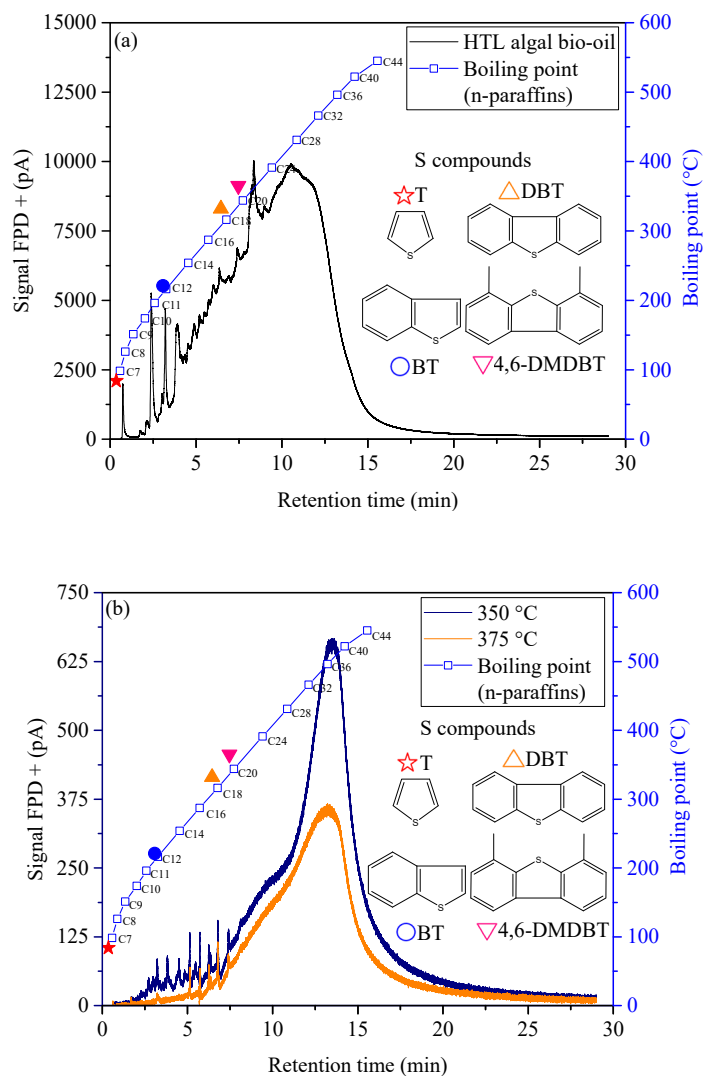


Figure 13. N-paraffin's boiling point curve obtained from FID detector and sulfur compounds signal obtained from FPD Plus detector: (a) HTL micro-algal bio-oil and (b) HDT-oil.

4. Conclusions

In this work, we performed the hydrothermal liquefaction of the microalga *Chlorella sorokiniana* and the HTL bio-oil was upgraded at different temperatures (350 °C, 375 °C, and

400 °C) over a NiW/Al₂O₃ sulfided catalyst. The initial bio-oil and its upgraded products were characterized by various techniques to understand the bio-oil composition, the reactivity of composing molecules, and quantification of the products up to C₃₂ is provided. The lipids, containing mostly C16 and C18 chains, are mainly converted during the HTL reaction into C16 and C18 carboxylic acids. The C16 and C18 fatty acids represent 41 wt.% of the HTL bio-oil. C16 and C18 amides were also identified in the bio-oil, as well as cyclic oxygen and nitrogen compounds such as phenols, indoles, pyrroles, and carbazoles, probably formed from the decomposition of carbohydrates and proteins. As expected, after catalytic upgrading, the C16 and C18 carboxylic acids were mainly converted into C15, C16, C17, and C18 n-alkanes by HDO and DCO classical pathways, the latter being promoted by temperature increase. The temperature increase also promoted cracking reactions, as observed by GPC-RID and Sim-Dis, and reduced the aromaticity degree, as confirmed by GPC-DAD and ¹³C-NMR analysis. GCxGC-MS/FID analysis of HDT-oils allowed to follow the conversion of nitrogen and oxygen compounds during the upgrading step. Phenols and phytosterols were almost totally removed. However, indoles, carbazoles, and fatty amides remain in the HDT-oil even after high-temperature hydroconversion. The results suggest that amides conversion can be affected by cyclic nitrogen compounds. Using a specific sulfur detector, we evidenced the presence of some refractory heavy sulfur compounds. Several metals found in the microalga, such as iron, potassium, and calcium, were transferred from microalga to the HTL bio-oil, as showed by ICP-OES analysis. XRF analysis of fresh and used catalysts showed an accumulation of iron in the used catalyst, suggesting that iron compounds (pigments) were converted during the upgrading step. Finally, more than 60% of upgraded oil at 400 °C falls in the diesel range, showing the potential of microalgae to produce biofuel. Therefore, catalytic hydrotreatment with NiW sulfide catalyst is a relevant technology for upgrading HTL micro-algal bio-oil but requires the use of either drastic operating conditions or more efficient catalysts with a particular emphasis on HDN performances.

CRedit authorship contribution statement

Bruno da Costa Magalhães: Investigation, Writing – original draft. **Ruben Checa:** Methodology. **Chantal Lorentz:** Methodology. **Pavel Afanasiev:** Writing – review & editing. **Dorothee Laurenti:** Writing – review & editing, Supervision. **Christophe Geantet:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

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.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at

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