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Catalytic Hydrotreatment of Microalgae Biocrude from Continuous Hydrothermal Liquefaction: Heteroatom Removal and their Distribution in Distillation Cuts

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Abstract: To obtain drop-in fuel properties from non-feed biomass, we herein report the catalytic hydrotreatment of microalgae biocrude, produced from hydrothermal liquefaction (HTL) of Spirulina. Our contribution focuses on the effect of temperature, initial H_2 pressure, and residence time on the removal of heteroatoms (O and N). In contrast to common hydrotreating experimental protocols at batch scale, we devised a set of two-level factorial experiments and studied the most influential parameters affecting the removal of heteroatoms. It was found that up to 350 °C, the degree of deoxygenation (de-O) is mainly driven by temperature, whereas the degree of denitrogenation (de-N) also relies on initial H_2 pressure and temperature-pressure interaction.Based on this, complete deoxygenation was obtained at mild operating conditions (350 °C), reaching a concurrent 47 % denitrogenation. Moreover, three optimized experiments are reported with 100 % removal of oxygen. In addition, the analysis by GC-MS and Sim-Dis gives insight to the fuel quality. The distribution of heteroatom N in lower (<340 °C) and higher (>340 °C) fractional cuts is studied by a fractional distillation unit following ASTM D-1160. Final results show that 63-68 % of nitrogen is concentrated in higher fractional cuts.

Keywords: Hydrothermal liquefaction (HTL), Spirulina, Hydroprocessing, Hydrotreating, Upgrading, Hydrodeoxygenation (HDO), Hydrodenitrogenation (HDN), Fractional distillation, Drop-in biofuels and Nitrogen distribution.

1. Introduction

Unprecedented climate shift and brisk depletion of conventional resources have raised socioeconomic and environmental concerns; thus the pursuit of clean, independent and alternative renewable and sustainable commercialized solutions for fuels has been expedited [1]. Fuels produced from so-called 2nd and 3rd generation biomass feedstock, such as sewage sludge and microalgae, offer the advantage of a potentially favorable carbon footprint and a lower risk of negative ILUC (indirect land use change) [2–4].

Microalgae have been identified as an attractive energy source for the production of biofuels due to their ability to accumulate relatively large amount of lipids along with carbohydrates, and proteins [5]. Microalgae show higher photosynthetic efficiencies compared to terrestrial plants which could be beneficial in terms of environmental impact [6]. High growth rates and non-competition with arable land and fresh water resources, trigger escalating interests to convert microalgae into liquid fuels, which engage researchers to develop environment-friendly methods with remarkable potential roots for mass production [7,8].

Out of all available energy valorization techniques at our disposal, hydrothermal liquefaction (HTL) is considered as one of the most promising technology for the production of biocrude oil, due to its advantages in rapid reaction, using all types of wet or dry feedstocks with no lipid-content

restriction [9–11]. Recent techno-economic analyses and life cycle assessments on the conversion of microalgae into liquid fuels show that HTL has lower GHG emissions and higher economic potential, with a better energy return on investment as compared to conventional lipid extraction and transesterification technologies [12–15].

At temperatures around 300-420 °C and pressure above the saturation pressure of water the HTL process produces a viscous and energetically dense black liquid usually referred as biocrude. This biocrude contains ~ 10-15 wt. % of heteroatoms (primarily O and N) with a high heating value (HHV) of 32-38 MJ/kg [8,11,16]. Biocrude as such cannot be directly utilized in the transportation sector. To produce fungible on-specification transportation fuel, further upgrading processes such as deoxygenation, denitrogenation, etc. are required. Over the years, researchers have investigated both heterogeneous and homogeneous in-situ catalysts to achieve improved bio-diesel [17,18]. Catalytic upgrading of biocrude through hydroprocessing is the most promising pathway for the conversion of polar compounds into hydrocarbon-rich mixtures [19]. During hydroprocessing, undesirable materials such as metals, oxygen, sulfur, nitrogen, olefins, and aromatics are removed from biocrude by selectively reacting these materials in the presence of a heterogeneous catalyst, at relatively high pressure (30-170 bar H_2) and at high temperature 300-450 °C [20].

Biller et al. [21] investigated the hydroprocessing of biocrude obtained from Chlorella microalgae, by using sulfided CoMo and NiMo catalysts at 350 °C and 405 °C, with an initial H_2 pressure between 60-66 bar and a residence time of 2 h. Relatively low yields (41-69 %) were observed at high temperature, and 86 and 91 % reduction of O, along with 60 and 55 % of reduction of N, were obtained with NiMo and CoMo catalyst respectively. Both catalysts showed no difference in their catalytic activity at batch scale; furthermore, after pentane extraction the oil analysis indicated that the majority of remaining O is contained in high molecular weight compounds, while no adequate reduction of nitrogen was achieved. Bai et al. [22] carried out the catalytic hydrothermal processing of biocrude in the presence of 15 different catalysts in a batch reactor. By using a combination of Ru/C and Raney Ni catalyst they were able to obtain 2 wt. % O and 2 wt. % N with a yield of 77 %. Duan et al. [23] observed, 90 % of O and 59 % of N removal after the catalytic hydrothermal upgrading of microalgae biocrude by using a mixture of Ru/C and Mo_2/C as catalyst at 400 °C for 4 h. Savage et al. [24] explored the degree of deoxygenation and denitrogenation by using an acidic cracking catalyst (HZSM-5) in the presence of H_2 at 400, 450 and 500 °C. They found that the upgraded oil yield was reduced from 75 to 42 % as the temperature increases. Elliott et al. [25] reported the continuous hydrotreatment of biocrudes from four different microalgae in a bench-scale trickle bed reactor in the presence of sulfided Co-Mo/γ-Al_2O_3 catalyst at 405 °C and operating pressure of 136 bar. They obtained oil yields of 80-85 % with final O and N levels of ~ 1 and ~ 0.1 wt. % respectively. However, the authors also highlighted the difficulty to compare results from continuous and batch system, because the products from batch system are equilibrium limited.

The current study differs from those by Elliott et al. [25], Biller et al. [21] and Bai et al. [22], as the lower temperature of 350 °C is considered as the highest operating temperature. In previous studies, researchers did not investigate the overall effect of temperature, pressure and time on the heteroatom removal. In the current work, a set of two-level factorial experimental design was developed and the hydrotreating of HTL microalgae biocrude, obtained from Spirulina was evaluated. The effect of temperature, H_2 pressure, and residence time on the hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), and hydrogen consumption is discussed as response variables. At the end, three optimized experiments are performed at high temperatures to understand the significance of heteroatom removal. Moreover, after the complete HDO of hydrotreated oil, a small fractional distillation unit following ASTM D-1160 is used to investigate the concentration of heteroatom N and its distribution in lower (< 340 °C) and higher (>340 °C) fractional cuts. Comprehensive analysis is carried out on the upgraded fuel and distilled fractional cuts.

2. Materials and methods

2.1. Materials

The biocrude used in this research was obtained from Aarhus University (Denmark), after the processing of Spirulina microalgae under sub-critical condition at 220 bar and 350 °C. In the frame of work HyFlexFuel project a pilot-scale continuous HTL facility was used to produce biocrude with a throughput of up to 100 L/h [26]. Properties of the feedstock and HTL biocrude are listed in Table 1.

Table 1. Spirulina feedstock and HTL biocrude analysis. All on wt. % dry basis and oxygen by difference.

Materials	Elemental composition (wt. %)					HHV (MJ/kg)	Ash content (wt. %)	Water content (wt. %)
	C	H	N	S	O			
Spirulina	53.5	7.2	12.6	-	26.6	24.0	5.8	6.4
Biocrude	78.1	10.4	8.0	-	3.5	38.0	0.2	3.8

A pre-activated commercial Ni-Mo/γ-Al$_2$O$_3$ hydrotreating catalyst in the form of extrudates was provided by Shell Denmark A/S. This pre-sulfided catalyst was activated at 340 °C and 60 bar in the Shell refinery in Fredericia, Denmark.

2.2. Experimental methods

2.2.1. Design of experiments

In order to understand the most influential process parameters during hydrotreating, a factorial two-level experimental design with three factors on two levels (2^3), as stated in Table 2, was used to investigate further [27].

Table 2. Test factors for hydrotreating experiments.

Factor	Name	Unit	Low level (-)	High level (+)
A	Temperature	°C	250	350
B	H$_2$ pressure	bar	40	80
C	Residence time	h	2	4

Complete experimental matrix with obtained responses is stated in Table 3. Even though, hydrotreating is affected by a large number of factors, but during this study only reaction temperature, initial H$_2$ pressure, and residence time were considered and thus, the oxygen and nitrogen contents were measured as response variables.

Table 3. Two-level factorial experimental matrix (1-8) along with three optimized experiments (9-11) at high temperatures.

Exp.	Factor A Temperature	Factor B Initial H$_2$ pressure	Factor C Reaction time
1	250 (-)	40 (-)	2 (-)
2	350 (+)	40 (-)	2 (-)
3	250 (-)	40 (-)	4 (+)
4	350 (+)	40 (-)	4 (+)
5	250 (-)	80 (+)	2 (-)
6	350 (+)	80 (+)	2 (-)
7	250 (-)	80 (+)	4 (+)
8	350 (+)	80 (+)	4 (+)
9	375(+)	70 (+)	3 (+)
10	400 (+)	65 (+)	2.5 (+)
11	400 (+)	70 (+)	2 (-)

2.2.2. Experimental set-up

Hydrotreatment was carried out in a pair of 25 mL Swagelok micro-batch stainless steel reactors. To confirm reproducibility and comparability of results, experiments were measured in duplicates. For each experiment, 4 g of biocrude were loaded inside the reactor, along with 2 g of pre-sulfided catalyst and 3 stainless steel spheres (4 mm dia.) to enhance mixing. Both reactors were purged with N_2 and H_2 twice at 80 bar, leak tested and filled with a certain H_2 pressure. In order to obtain high temperatures and efficient mixing a Techne SBL-2D fluidized sand-bath and an agitation device with a frequency of 450 min^{-1} was used. Pressure was continuously measured with a Wika A-10 pressure transducer and recorded in a data logger connected to LabVIEW™ programme. After desired reaction time, both reactors were quenched in a water bath prior to gas venting and product separation. The gas was released in the fume-hood and the hydrotreated liquid products were separated into oil phase and water phase, by centrifuging (Sigma 6-16 HS centrifuge (2153 RCF)) at 4000 rpm for 5 min.

2.2.3. Fractional distillation

Selected samples of the produced oil underwent fractional distillation in a small unit, complying with ASTM D-1160 [28]. The set-up was bought from Ace Glass Inc., and involves a 10 ml pot flask in the bottom of the distillation column along with 3 lower graduated distillation receiver tubes having a volume of 3 ml each. This unit is able to reach the operating pressure of 10 mbar after connecting the vacuum pump to the top of the condenser. Water circulation in the distillation column was done at 5 °C by using Julabo 200F thermal circulation bath, in order to achieve better condensation and to reduce losses in the cold trap. To provide adiabatic conditions and avoid heat losses the column was surrounded by a HS - 450°C NiCr heating cable from Horst GmbH with a 4 mm winding radius. Furthermore, the heating tape was insulated from outside and a K-type thermocouples were used to measure the vapor temperature and the column head skin temperature. To ensure the adiabatic conditions, the temperature of the heating cable has been kept 5-10 °C below vapor temperature. Pressure, vapor temperature, and pot flask skin temperature were continuously monitored, in order to obtain the desired fractional cuts (lower (<340 °C) and higher (>340 °C)).

ASTM D-1160 was used as a guideline to produce fractions with a final cut temperature of 340 °C, which lies up to diesel range [28]. To avoid cracking and thermal degradation of hydrotreated biocrude, due to the presence of possible heteroatoms, the pot flask temperature and skin temperature should not exceed 310 °C [29]. Gasoline cut was attained and collected at <190 °C under atmospheric conditions. Subsequently, the vacuum was lowered to 20 mbar and the fractional cuts at 168 °C and 203 °C vapour temperature, corresponding to AET of jet fuel (190-290 °C) and diesel (290-340 ℃) were obtained. The observed column head temperature was converted into AET by using a relation described by Maxwell & Bonnel [30].

2.3. Characterization and analytical techniques

A CHN-O analyzer from Perkin Elmer 2400 Series II system (ASTM D-5291) with a detection limit of 100 ppm was used to determine the elemental composition of the hydrotreated oil in terms of C, H, and N. Oxygen was calculated by difference. Furthermore, the degree of deoxygenation (de-O) and denitrogenation (de-N) was measured according to Eq. 1 and Eq. 2.

$$de\text{-}O = \left(1 - \frac{O_{upgr.oil}}{O_{biocrude}}\right).100 \tag{1}$$

$$de\text{-}N = \left(1 - \frac{N_{upgr.oil}}{N_{biocrude}}\right).100 \tag{2}$$

The higher heating value (HHV) of the biocrudes and the upgraded samples was estimated through the correlation proposed by Channiwala and Parikh [31].

$$HHV\ (MJ/kg) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \tag{3}$$

The ideal gas law was used to estimate the H_2 consumption based on initial and final H_2 pressure in the reactor, under the hypothesis of negligible production of other gases.

$$n_{H_2\ consumed} = \frac{P_{initial}\,V}{RT} - \frac{P_{final}\,V}{RT} \tag{4}$$

The boiling range distribution of biocrudes and upgraded oil was determined by means of simulated distillation (Sim-Dis) following ASTM D-7169. Sim-Dis was equipped with a Zebron ZB-1XT column by Phenomenex, and a gas chromatography - flame ionization detector (GC-FID) from Shimadzu Corporation. To determine the chemical composition, the biocrude and the upgraded samples were analyzed by GC-MS (Thermo Scientific Trace 1300 ISQ QD - Single Quadrupole) with temperature range 40 to 300 °C as described previously [32].

3. Results and discussion

Hereby, the hydrotreating of Spirulina biocrude is conducted as described in Section 2. The results of the single experiments are presented in terms of degree of deoxygenation (de-O), degree of denitrogenation (de-N), and hydrogen consumption as response variables. After the identification of influencing factors, the characterization of upgraded biocrude is discussed in terms of elemental composition, chemical structure and boiling point distribution.

3.1. The effect of the process parameters on heteroatoms removal

In order to identify the most influencing parameters during hydrotreating, a two-level factorial design of experiments with varying reaction temperature, initial H_2 pressure, and residence time was performed until experiment 8 as described in Table 3. To check the influence of these varying parameters on bio-oil properties, the effect and the interaction between each parameter have been calculated based on the elemental composition of the upgraded oil as shown in Table 4. Furthermore, the half-normal probability plot is used to assess which factors are important and which are of no significance.

Table 4: Elemental composition (wt. %) along with the obtained responses (de-O and de-N) and their calculated effects until experiment 8. Oxygen is calculated by difference.

Exp.	C	H	N	O	de-O [%]	de-N [%]	H_2 Consumption [kg $_{H2}$/kg $_{feed}$]	H/C [-]	HHV [MJ/kg]
Biocrude	75.01 ±0.31	10.40 ±0.09	7.65 ±0.10	6.94 ±0.12	-	-	-	1.66	37.59
1	76.94 ±0.49	10.79 ±0.10	7.19 ±0.05	5.11 ±0.61	26	6	0.0025	1.68	38.93
2	81.24 ±0.12	11.18 ±0.03	5.55 ±0.04	1.95 ±0.11	72	27	0.0060	1.65	41.42
3	77.72 ±0.10	10.76 ±0.05	6.53 ±0.05	5.00 ±0.20	28	15	0.0033	1.66	39.18
4	82.24 ±0.22	11.05 ±0.08	5.44 ±0.04	1.28 ±0.35	82	29	0.0058	1.61	41.51
5	77.16 ±0.19	10.66 ±0.02	6.66 ±0.50	5.53 ±0.69	24	10	0.0033	1.66	37.59
6	82.62 ±0.17	11.87 ±0.04	4.35 ±0.12	1.17 ±0.09	83	43	0.0108	1.72	42.64
7	76.82 ±0.03	10.98 ±0.03	6.36 ±0.03	6.13 ±0.03	12	17	0.0045	1.67	38.68
8	84.31	12.13	4.03	0.00	100	47	0.0125	1.73	43.70

	±0.35	±0.06	±0.17	±0.23					
9	84.55	12.66	3.09	0.00	100	60	0.0103	1.80	44.38
	±0.16	±0.10	±0.05	±0.01					
10	84.17	11.99	3.84	0.00	100	50	0.0080	1.71	43.45
	±0.02	±0.05	±0.11	±0.04					
11	84.37	12.44	3.19	0.00	100	58	0.0093	1.77	44.05
	±0.11	±0.02	±0.04	±0.01					

Potential coke and product gases during hydrotreatment were considered negligible as compared to the losses during liquid (oil plus water) recovery in a micro-batch reactor. Thus, the overall yield (wt. %) of upgraded oil is not reported in present study in order not to present an inaccurate picture. Though, the liquid recovered was around ~ 90 wt. % ±5 during all experiments which is similar to other works in the literature, for example [21]. Current study focuses on the removal of heteroatoms (O and N) by varying the initial H_2 pressure and reaction time at considerably low operating temperatures (250 °C and 350 °C).

Table 4 shows intriguing results in case of heteroatom removal. Within the detection limit of CHN/O, 100 % O content is removed from algal biocrude at 350 °C, 80 bar and 4 h of reaction time. At these severe conditions of present experimental matrix N content is reduced up to 47 %. Till now, the most prominent studies on heteroatom removal by Elliott et al. [25], Biller et al. [21] and Bai et al. [22] showed the removal of O and N up to ~ 90 % and ~ 99 % respectively at ~ 400 °C. Biller et al. [21] and Duan et al. [23] reported 91 and 90 % reduction of O along with 60 and 59 % reduction of N at 405 °C and 400 °C. Furthermore, Elliott et al. [25] was able to reduce final O and N levels down to ~ 1 and ~ 0.05 wt. % (99 %) at 405 °C in a continuous flow catalytic fixed bed reactor. Lower denitrogenation rates until experiment 8 from above study are evidence that high temperatures are vital for the removal of nitrogen. It also seems obvious, that mild conditions relating with each variable factor just slightly affect the O content, whereas the N content almost remain intact.

Based on this knowledge, an optimized set of three confirmation experiments (exp. 9, 10 and 11) were performed as shown in Table 4. They are based on the anticipation that N content will reduced further with the 100 % removal of O at high temperatures. Subsequently, the results presented in Table 4 show complete deoxygenation for experiment 9, 10 and 11, while at best the denitrogenation was only achieved up to 60 % at 375 °C and 70 bar initial H_2 for three hours. However, 50 % and 58 % of denitrogenation is achieved at 400 °C by changing H_2 pressure and reaction time.

The absolute values from Table 5 indicate the most relevant factors affecting the responses (R_1 and R_2). Moreover, half-normal probability graph as shown in Figure 1 is used to assess the significant and insignificant factors for de-O (R_1) and de-N (R_2).

Table 5. Selected process parameters (factors) and their measured effects on de-O (R_1) and de-N (R_2) from experiment 1-8.

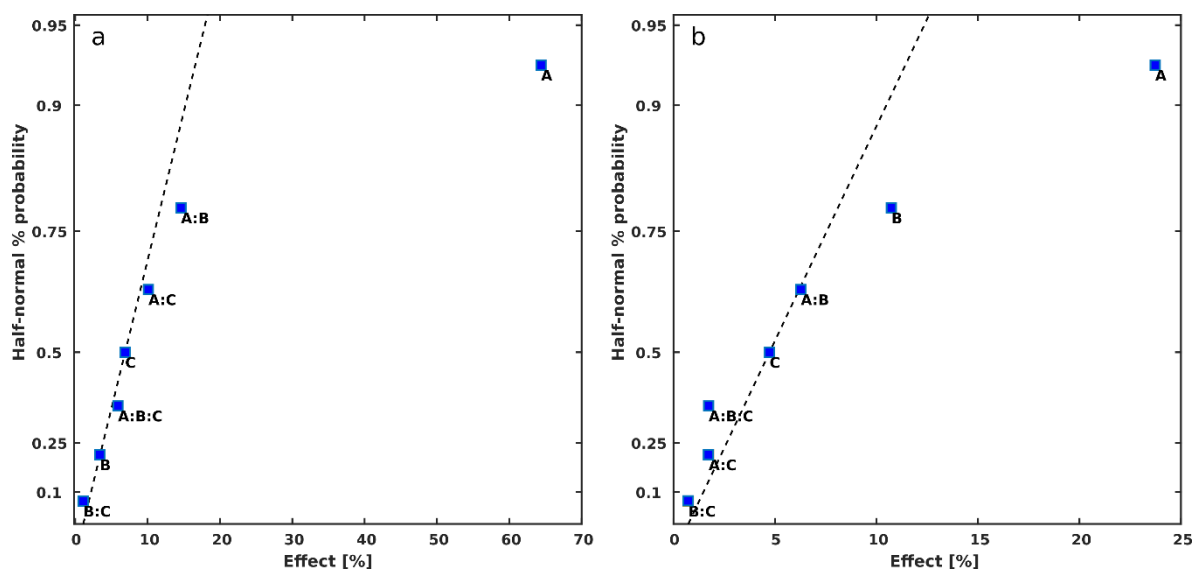|	Factor A	Factor B	Factor C	Factor AB	Factor AC	Factor BC	Factor ABC
Effect R_1 [%]	64.24	3.51	6.50	14.63	10.06	0.88	6.03
Effect R_2 [%]	24.07	10.80	4.53	6.29	-1.75	-0.51	1.85

Figure 1. Half normal plot of effects [%], de-O (a) and de-N (b).

Assuming that the estimated effects of each factor and each interaction term on the de-O follow a normal distribution, the absolute estimated effects will then follow a half-normal distribution. By plotting the ranked estimated effects against the cumulative percent contribution (the contribution to the total sum of squares) of each factor, significant (and insignificant) factors can be identified. Insignificant factors are those having small estimated effects and tend to fall on a straight line starting at the origin (0:0).

From Figure 1 (a), it is clear that the only significant factor influencing the de-O is the temperature. Obviously, the half-normal plot show only positive effects (absolute estimated effects). By examining Table 4 it is evident that temperature indeed has a positive effect on the de-O. At the lower level temperature, the higher degree of deoxygenation obtained was 28 % (Exp. 3), whereas the de-O range from 72-100 % at the higher level. Likewise, a similar identification of the significant factors influencing the de-N can be observed in in Figure 1 (b). It is apparent that temperature is also significantly influencing the de-N along with the hydrogen pressure. Thus, the highest de-N was obtained in Exp. 8 (all factors set at high level) yielding a de-N of 47 %, which is only marginally higher than Exp. 6 (de-N = 43 %) for which the reaction time was only 2 hours. As for the de-O, any interaction effects seem insignificant.

The hydrotreated oil after all 11 experiments has a higher C and a lower O and N content. However, H/C molar ratio remains more or less stable with the algal biocrude at lower temperatures and lower pressures. While, at higher temperatures (350-400 °C) and higher pressures (80 bar) overall H/C molar ratio increases and thus the aromatics in the oil decreases. In addition, a negligible effect of reaction time is observed on the molar H/C ratio. However, at 400 °C lower H/C is observed as compared to 375 °C, which is anticipated as a result of cracking reaction. Subsequently, after the complete deoxygenation and 60 % of N reduction the HHV increases from 37.6 MJ/kg of the algal biocrude to 44.4 MJ/kg. Higher temperatures are needed for complete denitrogenation, but both H/C and HHV decrease at higher temperature of 400 °C in relation with 375 °C, which means that we are getting higher degree of denitrogenation with a loss of fuel quality. This may be caused by the formation of coke, as HTL biocrude due to high polarity are unstable and prone toward the polymerization and deactivation of NiMo catalyst. This complete deoxygenated oil with reduced N content is considered more stable and thus reduces the possibility of catalyst deactivation during further upgrading for on-specification fuel.

3.2. Analysis of the up-graded oil

Simulated distillation (Sim-Dis) was used to evaluate the boiling point distribution of the catalytically upgraded oil samples and then compared with the untreated biocrude. Five different

boiling point ranges are defined and described as gasoline (>190 °C), jet fuel (190-290 °C), diesel (290-340 °C), vacuum gas oil (340-538 °C) and vacuum residue (>538 °C). Table 6 along with Figure 2 shows yield of different fractions and boiling point distribution of all the experiments with complete degree of deoxygenation along with the biocrude and experiment 1 with the lowest possible operating range (250 °C, 40 bar H_2 for 2 h). The biocrude shows large fractions in high molecular weight compounds and therefore, it associates with the higher residual cuts (72.7 % above 340 °C). In addition, the overall recovery at 720 °C increases from 72 % to 92 %, thus the amount of potential distillable products also increases. Furthermore, after 100 % HDO more than 32 % and 14 % oil is in jet fuel and diesel range and around 15 % is confined in residue. High temperatures and high initial H_2 pressures are vital for the cracking of biocrude into lower fractional cuts. Present study shows that at 350 °C and 80 bar initial H_2 pressure highest boiling point distribution above diesel is obtained with minimum residual fraction cut of 12.5 %. This looks very promising as by just tuning operating conditions at mild temperature (350 °C) high production of diesel drop-in fuel could be achieved (Table 6 and Figure 2).

Table 6. Sim-Dis analysis of biocrude and selected hydrotreated samples.

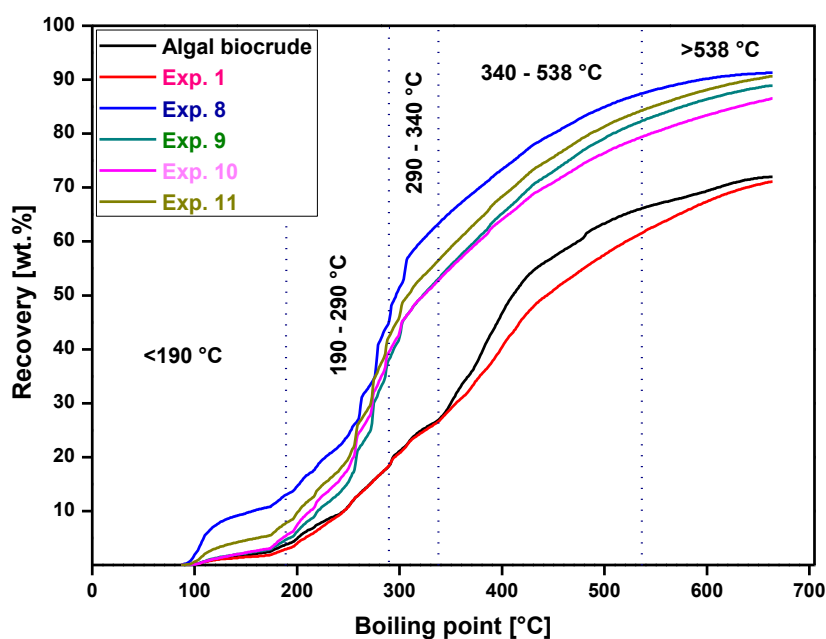| Fractional cuts	Boiling point range	Composition [wt. %]					
		Biocrude	Exp. 1	Exp. 8	Exp. 9	Exp. 10	Exp. 11
Gasoline	<190 °C	3.9	3	13.1	4.8	5.6	7.9
Jet fuel	190-290 °C	14.5	15.5	32.2	33.4	34	34.5
Diesel	290-340 °C	8.9	8.5	18.4	15.3	13.6	14.5
Vacuum gas oil	340-538 °C	38.9	34.7	23.8	29	26.3	27.5
Vacuum residue	>538 °C	33.8	38.3	12.5	17.5	20.5	15.6

Figure 2. Boiling point distribution of biocrude and upgraded oil samples, obtained by simulated distillation.

Figure 3a and 3b show the GC-MS chromatograms of the HTL biocrude and the complete deoxygenated oils at 350 °C (47 % HDN). The untreated biocrude (Figure 3 a) shows a complex mixture of numerous different hydrocarbons and heteroatoms (mainly O and N), as expected from the elemental analysis. The oxygen containing compounds are mainly saturated fatty acids (hexadecanoic acid) and phenol derivatives such as p- and m-cresol. Moreover, fatty alcohols such as dodecanol are also observed in small amounts. Whereas, nitrogen-containing compounds are mostly found in the form of non-heterocyclic high molecular weight compounds such as various amides.

However, N compounds are also present in the form of ring type structures with either one N atom, such as indoles and pyrroles, or two N atoms, such as pyrazines. The sole purpose of hydrotreating is to convert heteroatoms into their respective hydrocarbons along with the saturation of double bonds and cracking of high molecular weight compounds. Figure 3 b shows a chromatogram of upgraded oil (exp. 8) after the complete removal of O atoms at 350 °C and reveal the presence of dominating aliphatic hydrocarbons ranging from C_{14} to C_{21}. Aromatic hydrocarbons such as ethylbenzene and toluene are also present in the upgraded oil. At the same time, N is observed in the GC-MS spectrum, such as the presence of amides in Figure 3 b at the retention time of 25.51 min and 27.09 min. However, the GC-MS spectrum also indicates minor presence of amine, indole, nitrile, pyrrole, pyrazine, pyridine and quinoline in the hydrotreated oil.
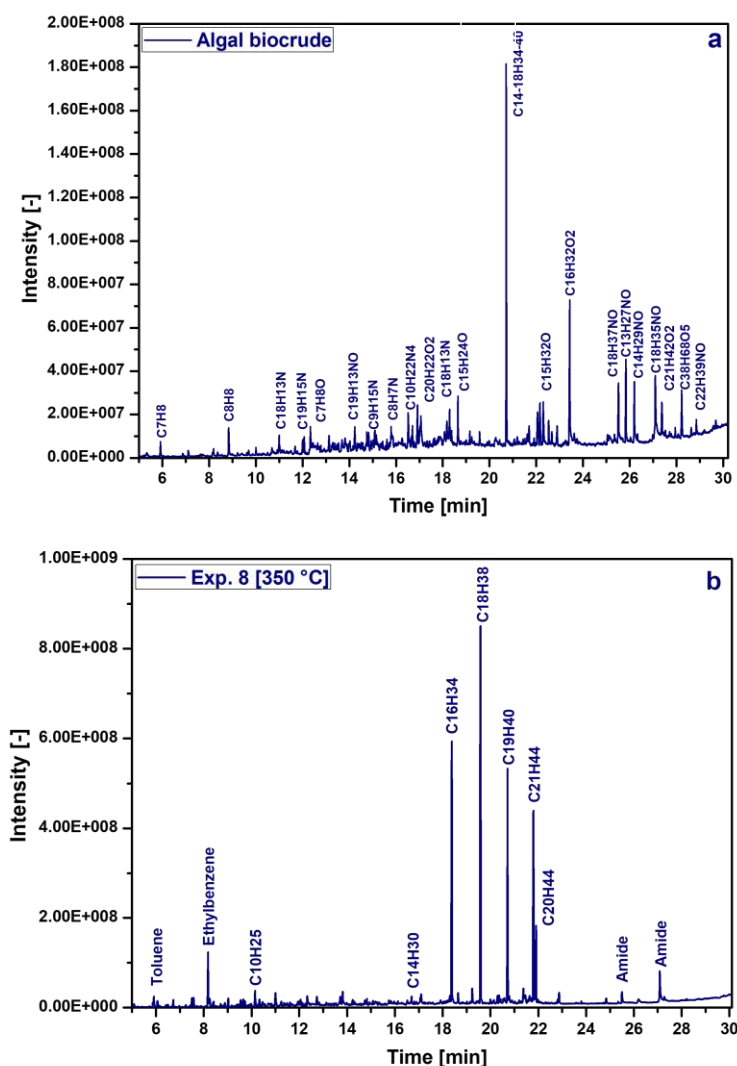

Figure 3. GC-MS Chromatographs of (a) bio crude and (b) Experiment 8 at 350 °C.

3.3. Distribution of nitrogen-containing compounds

GC-MS analysis is only able to investigate the volatile fraction of the sample, hence it does not account for all molecules in the oil. Therefore, in order to assess the distribution of N content in the light and heavy fractional cuts of the upgraded oil, a more relevant industrial approach following ASTM D-1160 is carried out. Biller et al. [21] reported inappreciable amounts of nitrogen-containing compounds through GC-MS; while, through elemental analysis they observed 1 - 1.5 % of O and 2.4 - 2.7 % of N. They performed C_5 (pentane) extraction of hydrotreated oil to investigate the distribution of O and N between C_5 soluble (flowable) and C_5 insoluble (asphaltene) fractions. They were able to completely remove O content in C_5 soluble fraction, but the removal of N content was

not satisfactory and it seems that it was almost homogenously distributed in C_5 soluble and insoluble fractions.

In order to determine the distribution of N content in lower and higher molecular weight compounds, the hydrotreated oil from experiments 8 (47 % HDN) and 9 (60 % HDN) were subjected to further investigation. Consequently, we performed true boiling point distillation following ASTM D-1160 to assess the concentration and the distribution of heteroatom content in low and high molecular weight fuel fractional cuts which correspond up to diesel (<340 °C) and vacuum residue (>340 °C). Results are shown in Table 7.

Table 7. Yields (%) and elemental analysis (N and O content in wt. %), H/C and N/C molar ratios of below and above diesel range fraction cuts.

Exp.	Light fraction (< 340 °C)					Heavy fraction (> 340 °C)				
	Yield [wt. %]	N [wt. %]	O [wt. %]	H/C [-]	N/C [-]	Yield [wt. %]	N [wt. %]	O [wt. %]	H/C [-]	N/C [-]
8	52	1.30	0	1.86	0.02	35	2.73	0.08	1.48	0.03
9	29	1.15	0	1.82	1.32	47	1.95	0.24	1.32	0.02

Table 7 shows, that 32 % and 37 % of N content is concentrated in the light fraction while vacuum residue contains 68 % and 63 % of N content for experiment 8 and 9 respectively. These results reveal that most of the nitrogen-containing compounds are distributed in the higher fractional cuts. Additionally, no O content is associated with the light fraction for both experiments while, 0.24 wt. % of O and 0.08 wt. % of O is incorporated in the vacuum residue obtained after the fractional distillation of experiment 8 and 9 respectively. The results indicate that oxygen is in fact concentrated in the heavy fraction, although in small amount. This means that when analyzing the total sample it is diluted to below the error associated with the CHN analyzer and therefore reported as zero. The presence of 0.08 wt. % of O in vacuum residue of hydrotreated oil (375 °C) as compared to the 0.24 wt. % of O (350 °C) also validate the statistical analysis, which showed that temperature is a main driver for O removal. Moreover, overall higher H/C molar ratio is observed for diesel range (>1.82) and very low H/C molar ratio (<1.48) was observed for vacuum residue in case of both experiment.

Figure 4 illustrates a modified Van Krevelen plot as a function of H/C and N/C molar ratio for biocrude, hydrotreating experiments and distillation cut of upgraded oil from experiment 8 and 9. Starting from the same biomass composition, it is clear that both temperature and pressure have a significant effect on the removal of N heteroatoms. Thus, the N/C molar ratio decreases along with the increase of hydrocarbon content. This plot also elucidates the distribution of nitrogen-containing compounds in lower and higher fractional cuts for experiment 8 and 9; and shows, that the N/C molar ratio decreases in the hydrocarbon range (higher H/C molar ratio) but on the other hand N/C molar ratio increases as the aromatic content of the fractional cut increases.
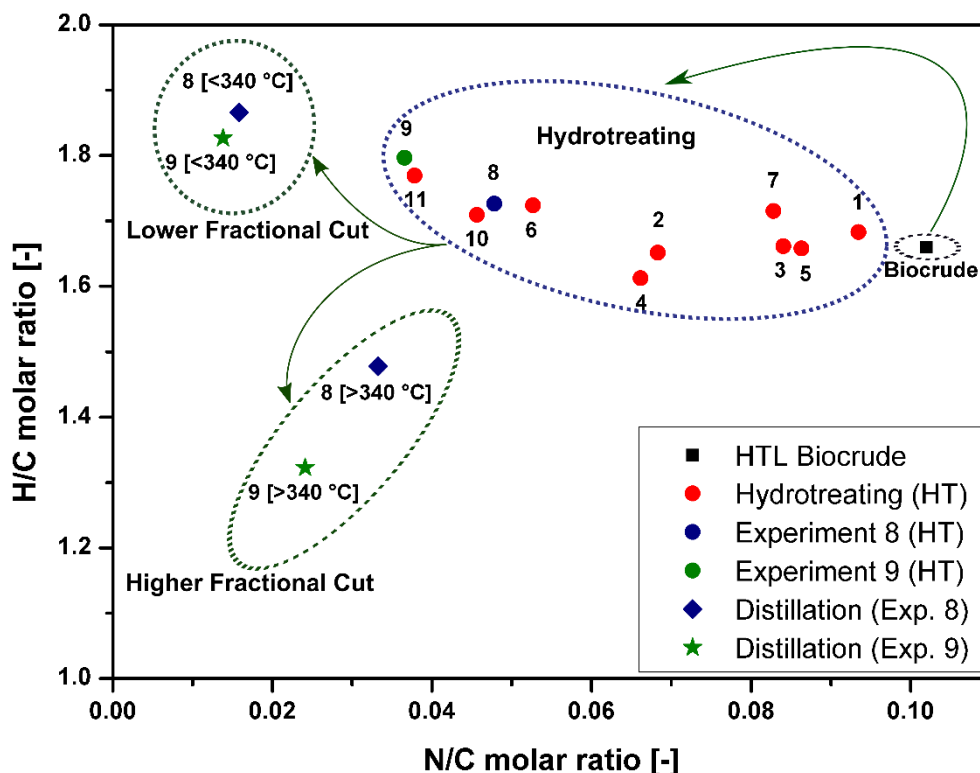
Figure 4. Modified Van Krevelen diagram showing molar ratio of H/C as a function of N/C for Spirulina feedstock, HTL biocrude, 11 hydrotreating experiments and fractional distillation cuts of experiment 8 and 9.

Furthermore, the yields of the small fractional distillation unit are also stated in Table 7. 2.76 g and 1.09 g of sample is used for the fractional distillation of experiment 8 and 9 respectively. Higher recovery of 87 wt. % is obtained after the fractional distillation of experiment 8 as compared to 76 wt. % for experiment 9. Vacuum residue cut for both experiments is in line with the Sim-Dis results. However, some losses in the light fractional cut (<340 °C) were observed after comparing it with Sim-Dis results, which may be due to the loss of lighter fraction in the distillation column and column head. From experiment 8 it is clear that the losses are less as compared to experiment 9 due to the use of higher amount of sample. Losses for lighter fractional cuts could be minimized by subjecting higher amount of sample to the fractional distillation unit.

Even though nitrogen-containing compounds are mostly found in the higher fractional cuts (>340 °C), still some nitrogen is found in the light fraction. Therefore, this could not be used directly as a fuel, because of the indirect regulations applied on the fuel specification due to the presence of N compounds. The reason for the presence of remaining N compounds could be found in thermodynamics and the reduction of partial H_2 pressure during hydrotreating. Thus, we suggest that hydrotreating of algal biocrude for the removal of heteroatom N either possibly requires higher temperatures (which will result in reduced yields due to the formation of volatiles) or multi-stage catalytic treatment, to partially stabilize the oil before further upgrading at higher temperatures in order to complete remove nitrogen-containing compounds.

4. Conclusion

The aim of this study was to investigate the most influential parameters affecting the hydrotreating of Spirulina (micro-algae) biocrude. In addition, the distribution of heteroatoms in lower and higher fractional cuts was explored by using a small fractional distillation unit following the ASTM D-1160. For this purpose, a parametric study following a factorial two-level experimental design with three subsequent optimized experiments was carried out in a micro-batch reactor using

conventional NiMo/Al$_2$O$_3$ catalyst. Operating temperature has a key influence on the degree of deoxygenation (de-O), whereas the operating pressure along with temperature-pressure interaction mainly affects the degree of denitrogenation (de-N). Complete deoxygenation of upgraded free flowing oil was observed at 350 °C. An optimized experiment at 375 °C, 70 bar initial H$_2$ and 3 h residence time leads toward 100 % de-O, 60 % de-N, 1.80 H/C ratio and maximum HHV of 44.38 MJ/kg. In addition, fractional distillation up to diesel (<340 °C) and vacuum residue (>340 °C) cut shows a significant concentration of 63-68 % of N content in the higher fractional cut. Emanating from these encouraging results, shows that oxygen could be completely removed from given biocrude with a high liquid recovery.

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