Sustainable Energy & Fuels

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Journal:	*Sustainable Energy & Fuels*
Manuscript ID	SE-ART-06-2020-000903
Article Type:	Paper
Date Submitted by the Author:	19-Jun-2020
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Renewable Diesel Blendstocks and Bioprivileged Chemicals Distilled from Algal Biocrude Oil Converted via Hydrothermal Liquefaction

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Abstract

Hydrothermal liquefaction (HTL) has been demonstrated as a promising technology to convert algae into biocrude oil. However, the knowledge gaps of 1) biocrude oil upgrading and 2) process/energy optimization and design of an algal biorefinery producing valuable bioproducts need to be bridged. In this study, *Spirulina* (SP) was converted into biocrude oil via HTL. Next, fractional distillation was used to separate SP-derived biocrude oil. It was found that 62% of the viscous SP-derived biocrude oil can be separated into oil and water-soluble products at about 270ºC. Density, viscosity, acidity, elemental compositions, higher heating values and chemical compositions were carried out with the distillates separated from SP-derived biocrude oil. These analyses showed that 15% distillates could be used as renewable diesel because they have similar heating values (43-46 MJ/kg) and carbon numbers (ranging from C8 to C18) to petroleum diesel. In addition, GC-MS analysis indicates that some distillates contain bioprivileged chemicals like aromatics, phenols and fatty nitriles that can be used as commodity chemicals. Energy efficiency analysis also demonstrates that the fractional distillation has a lower energy consumption ratio than other HTL biocrude oil upgrading methods. An algal biorefinery roadmap was proposed based on the analyses of different distillates from the SP-derived biocrude oil. Finally, the fuel specification analysis was conducted with the drop-in renewable diesel, which was prepared with 10 vol.% (HTL10) distillates and 90 vol.% petroleum diesel. According to the fuel specification analysis, HTL10 exhibited a qualified lubricity (<520 µm), acidity (<0.3 mg KOH/g) and oxidation stability (>6 hr) to those of petroleum diesel. Ultimately, it is expected that this study can provide insights for potential application of algal biocrude oil converted via HTL and improve the process/energy efficiency of an algal biorefinery via HTL.

Key Words: Biofuel; Biorefinery; Bioprivileged Chemicals; Hydrothermal Liquefaction; Algae; Distillation

1. Introduction

Microalgae are superior feedstocks for biofuels and chemicals because of their fast growth, high lipid content (20-70%), and a relatively low environmental impact.[1, 2] However, due to the high water content (80-99%) of microalgae, these energy and chemical resources have not been cost-effectively harvested at industrial scale. Over 75% of the total energy input toward refinement comes from the drying process.[3]

Among the current available conversions for wet biomass, hydrothermal liquefaction (HTL), involving direct liquefaction of biomass with water, has been demonstrated as an energetically favorable approach.[4] Previous studies have also proven that HTL can effectively convert wet biomass into biocrude oil, which contains closer higher heating values (HHV) to heavy crude.[2, 5] This conversion of wet biomass to biocrude oil has been accomplished at temperatures (<305^{o}C), retention times (15-60 min), water contents (70-90%), ash contents (0-40%), and various feedstock combinations.[5-9]

Although HTL appears to serve as a promising method for converting wet biomass into biofuel, practical applications of biocrude oil remains as a critical bottleneck. Biocrude oil converted from wet biomass generally contains 10-20% oxygen, 3-7 % nitrogen, and up to 20% moisture contents.[4-7, 10] These impurities will result in corrosion of the engine when the biocrude oil is used as transportation fuels.[11] Further upgrading or separation of the biocrude oil is needed.

Current available techniques for upgrading HTL biocrude oil includes steam reforming,[12] sub-/super-critical fluid treatment (*e.g.,* sub-/super-critical water or alcohols),[13, 14] hydrocracking,[15, 16] zeolite cracking,[12, 16, 17] thermal cracking,[15, 18] hydrotreating,[19] solvent addition,[20] chemical extraction from HTL biocrude oil,[21-23] emulsification,[11, 24] and distillation,[21, 25] Cracking reactions and hydrotreating are primary methods to upgrade petroleum crude. Cracking reactions fragment one heavy molecule into two light molecules while hydrotreating saturates olefins to achieve hydrodeoxygenation (remove O as H_2O), hydrodenitrogenation (remove N as NH_3), or hydrodesulfurization (remove S as H_2S). However, cracking reactions typically need catalysts to enhance their efficiency and several studies have demonstrated that commercially available catalysts (*e.g.,* zeolites) had little effect on upgrading the quality of biocrude oil when the upgrading reaction temperature was below 450°C. [14] Hydrotreating requires excessive amounts of hydrogen to accelerate the heteroatom removal efficiency and thus is not favored in terms of energy efficiency.[13, 26, 27]

On the other hand, it was reported that after proper separations, such as distillation, the oxygen content in the biocrude oil could be reduced to 5% and the heating values could be increased to 41-45 MJ/kg.[21] Moreover, the viscosity of the distillates separated from HTL biocrude oil was significantly reduced.[25] The reduced viscosity indicates that there is a high potential to utilize these distillates as drop-in fuels, or a blendstock for petroleum fuels.[25] Most importantly, distillation can be operated at ambient pressures and moderate temperatures (typically below 400°C) and could be a potentially energy-efficient method to upgrade algal biocrude oil.

A highly desirable feature of biocrude oil application in practice is to produce a blendable product with properties that fall within international standards so that conventional distribution capabilities could be used.[25] However, fuel specification analyses of algal biocrude oil were limited. As a consequence, the feasibility of algal biocrude oil as an alternative transportation fuel was unknown.

This study aims to effectively separate algal biocrude oil converted via HTL for fuel applications via fractional distillation. *Spirulina platensis* (SP) was used as an algal representative biomass for HTL conversion because SP can sustain in stress conditions such as nutrient deprivation environments or wastewater.[2] It is anticipated that the results from this study can provide insights to upgrade the biocrude oil converted from other kinds of algae such as mixed-culture algae from wastewater treatment plants, which has been demonstrated as a more cost-effective and sustainable algal biomass.[1, 2, 5, 9]

Physicochemical characterizations of various distillates were conducted to understand the similarity between algal biocrude oil and petroleum fuels. The density, viscosity, acidity, elemental and chemical compositions of different distillates were characterized. Results were compared to petroleum fuels. Selective distillates that share the closest fuel properties to petroleum diesel were used to formulate the drop-in renewable diesel, which was prepared with 10 vol.% distillates and 90 vol.% petroleum diesel (HTL 10). The fuel specification analysis was conducted with the HTL 10 to evaluate their potential use as an alternative transportation fuel. In addition, the chemical composition analysis of different distillates was also used to assess the potential of using these distillates as bioprivileged molecules, which are bio-derived chemicals that can be readily converted to a variety of chemical products or used as drop-in replacements.[28] Finally, the energy recovery from the SP-derived biocrude oil to different distillates as well as the energy consumption ratio of the fractional distillation were also evaluated for improving the overall energy efficiency of algal biorefinery via HTL.

To the best of our knowledge, this present study appears to be the first of its kind to use fractional distillation to separate algal biocrude oil converted via a continuous HTL reactor and carry out a comprehensive fuel specification analysis on the distillates. With fractional distillation, the viscosity and the impurity of algal biocrude oil are anticipated to be reduced so that the separated distillates can be used as drop-in fuels. Results from this study would expedite the downstream application of algal biocrude oil for biofuels and bioprivileged chemicals. In particular, the physicochemical properties of various distillates will contribute to the process optimization (*e.g.,* energy efficiency optimization) and process design of algal biorefinery via HTL. Ultimately, this study will bridge the knowledge gaps of 1) HTL biocrude oil upgrading and 2) process/energy optimization and design of an algal biorefinery via HTL.

2. Methods

2.1 Feedstock

Spirulina platensis (SP) were purchased in dry powder from Cyanotech (Kailua-Kona, HI). The feedstock used in this study (more than 10kg) were all stored in a refrigerator at 4°C before HTL tests. The total solid content of feedstock was measured as the dry residue at 105°C for 24 h. The ash content was measured as the residual fraction after combustion at 550°C for 3 h. The contents of crude protein (AOAC 990.03), crude fat (AOAC 954.02), and lignin (AOAC 973.18) were measured using AOAC standard methods while acid and neutral detergent fibers were determined by Ankom Technology standard methods. Elemental analysis of feedstock was operated by a CHN analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA) and duplicate analyses were conducted for each sample. The average value was reported. ICP analysis was employed to measure the contents of total sulfur, phosphorus, potassium, magnesium, calcium, sodium, iron, manganese, copper, and zinc in the feedstocks following AOAC 985.01. Chemical and elemental compositions of SP biomass were summarized in **Table 1.** Results from ICP analysis were also available in **Table S1** in the **supplementary data**.

Table 1. Chemical and elemental compositions of *Spirulina* used in this study

Compositions (d.w.%)[a]	Spirulina
Crude protein	64.4
Crude fat	5.1
Hemicellulose[b]	1.4
Cellulose[c]	0.5
Lignin	0.2
Non-fiber carbohydrates[d]	18.9
Ash content[e]	9.5
C	49.3
H	6.4
N	11.0
O[b]	33.3

[a]Reported by dry weight basis.

[b]Neutral detergent fiber (NDF) is generally considered as the sum of hemicellulose, celluloses and lignin, while acid detergent fiber (ADF) usually indicates the sum of cellulose and lignin. Here, the content of hemicellulose was estimated by subtracting ADF from NDF.[29]

[c]The content of cellulose was estimated by subtracting the lignin from ADF.

[d]Calculated by difference (*e.g.,* non-fibrous carbohydrate (%) =100 – crude fat (%) – crude protein(%) – hemicellulose(%) – cellulose(%) –lignin(%) – ash content (%).

[e]The ash content was measured as the residual fraction after combustion at 550°C for 3 h.

2.2 Hydrothermal Liquefaction (HTL)

The HTL experiments were conducted according to the previously reported methods using a continuous stir reactor (CSTR).[4, 30] The solid content of the feedstock was adjusted to 20% for the HTL tests. The size of the CSTR reactor was 2 L and it had the capacity to process 48 kg of feedstock per day. This CSTR system continuously operated for 16 h per test.[4, 30] The HTL reaction was carried out at the previously determined optimum conditions for converting SP into biocrude oil (300°C and 0.5 h reaction time).[4, 31] The reactor was sealed and purged with nitrogen gas at least three times to remove the residual air in the reactor. Nitrogen gas was again added to the reactor to build a 0.69 MPa gauge initial pressure inside the reactor to prevent water boiling during the tests. After the HTL reaction at the designated temperature and reaction time, the reactor was cooled down to approximately 60°C by the heat exchangers. The biocrude oil was naturally selfseparated from the aqueous fraction by decanting. [30, 32] More details were available in previous studies.[30, 32]

2.3 Distillation

The distillation was conducted according to the previously reported standard methods.[21, 25] and the distillation curves were measured. For each distillation test, approximately 200 g algal biocrude oil was loaded into a 300 ml round-bottom flask, which was heated with a stirring heating mantle (Azzota SHM-250, LabShops, Claymont, DE). To avoid quick distillations that may cause ineffective separation and safety issues, the heating rate was set at about 1°C/min. The biocrude in the flask was homogenized with a stir bar to enhance the heat transfer. In order to reduce the heat loss, glass wool was wrapped around the distillation equipment. The distillation was conducted under atmospheric pressure. The vapor distillate was condensed by circulating tap water. Distillate fractions at a weight of 10 g (~5 wt.% of feed biocrude) each were collected at different distillation temperatures in sequence.[21, 25] Distillation experiments were conducted for at least three independent tests and average values were reported. The distillation set-up is available in **Figure S1** (supplementary data).

2.4 Analysis of biocrude oil, distillates and distillation residues (atmospheric residue)

Elemental compositions of biocrude oil and distillates were determined using a CE 440 elemental analyzer (Exeter Analytical). The higher heating values (HHV) of biocrude oil and distillates were calculated by using the *Dulong* formula based on the elemental composition: $\text{HHV}= 0.3383 \times \text{C}+1.422 \times (\text{H-O}/8)$.[5, 7] Carbon, hydrogen, nitrogen, and energy recoveries were defined as the carbon, hydrogen, nitrogen, and HHV of the distillate divided by those of the biocrude oil. The detailed equations of elemental recoveries were also available in literature.[5, 10, 33]

The chemical compositions of distillates (extracted with hexane) were analyzed using GC-MS (Agilent Technologies). The internal standard, pentadecanoic acid methyl ester (0.5μM), was used. Detailed analytical methods were also described in previous literature.[10, 25] Briefly, samples were analyzed using a GC-MS system consisting of an Agilent 7890 gas chromatograph, an Agilent 5975 mass selective detector, and a HP 7683B autosampler. Gas chromatography was performed on a ZB-5MS capillary column. The inlet and MS interface temperatures were 250°C and the ion source temperature was adjusted to 230°C. The helium carrier gas was kept at a constant flow rate of 2 mL/min. The temperature program was 5-min isothermal heating at 70°C followed by an oven temperature increase of 5°C /min to 310°C and a final 10 min at 310°C. The mass spectrometer was operated in positive electron impact (EI) mode at 69.9 eV ionization energy and a scan range of m/z 50-800. The spectra of all chromatogram peaks were compared with electron impact mass spectrum libraries (NIST08 and W8N08). To allow comparison between samples, all data were normalized to the internal standard. The instrument variability was within the standard acceptance limit (5%).

2.5 Energy Consumption Ratio and Reaction Severity of Upgrading Processes

The energy consumption ratio (ECR) was calculated for different upgrading methods using equation (1),

$$\mathrm{ECR}_{\mathrm{upgrading}} = \frac{E_{upgrading}}{E_{biocrude\ oil-upgraded}} = \frac{[W_i C_{pw} \Delta T + (1 - W_i) C_{pw} \Delta T][1 - R_h]}{[Y\ (HHV)(1 - W_i) R_C} \tag{1}$$

where W_i is the moisture content of the initial feedstock prior to upgrading, C_{pw} is the specific heat of water (4.18 kJ/kg·K), C_{pm} is the specific heat of HTL biocrude oil (assumed to be similar to petroleum, 2.13 kJ/ kg·K) [34, 35], ΔT is the difference between the designated reaction temperature and the initial temperature (assumed to be 25°C), Y is the upgraded HTL biocrude oil yield (*i.e.,* the yield of useful fractions), HHV is the higher heating value of upgraded HTL biocrude oil, R_h is the efficiency of heat recovery assumed to be 0.5, and R_c is the efficiency of available combustion energy assumed to be 0.6.[4, 7] Notably, the numerator of equation (1) includes all the process energy (*e.g.,* energy for distillation, esterification, hydrotreating, energy of hydrogen consumed, *etc.*) required to upgrade HTL biocrude oil, while the denominator indicates how much energy of the biocrude oil is retained in the useable fraction after upgrading (*e.g.,* distillation, hydrotreating, *etc.*). An ECR of less than 1.0 indicates a net energy gain for the system.[7]

The reaction severity was estimated for different upgrading methods using equation (2),

$$R_0 = \int_{t_1}^{t_2} \exp \frac{T_r(t) - T_b}{14.75} dt \tag{2}$$

where T_r (°C) is the reaction temperature, T_b is the base temperature (assumed to be 100°C) [36, 37], and t_1/t_2 is the initial/final holding time. Reaction severity combines the effect of reaction temperature and time into a single parameter [36, 37].

2.6 Drop-in fuel preparation and fuel specification analysis

Distillates derived from SP were added into diesel to obtain a 10 vol.% drop-in biodiesel. The fuel specifications, including viscosity, density, acidity, net heat of combustion, existent gum content, lubricity, and oxidation stability of drop-in renewable diesel were measured and compared to those of transportation fuel standards. The characterizations of fuel specifications were conducted by ASTM D 7467 standard and previously reported methods.[25, 38]

3. Results and Discussion

3.1 Distillation of HTL Biocrude Oil Converted from Spirulina

After HTL, the solid phase product was defined as the biocrude oil. The elemental compositions and the heating value of the SP-derived biocrude oil are available in supplementary data (**Table S2**). The SP-derived biocrude oil contains heating values (26.4 MJ/kg) similar to other algal biocrude oils converted from continuous-flow reactors (25-30 MJ/kg).[39] The SP-derived biocrude oil had a high viscosity at room temperature and contained 28% oxygen contents that need to be removed to reach the same level as petroleum fuels (<1 wt.% oxygen content).[25] This feature also makes the algal biocrude oil inappropriate to be used as drop-in fuels—diffusion of the algal biocrude oil to transportation fuel would be challenging.

Fractional distillation was then conducted to separate the SP-derived biocrude oil into several distillates. Overall, fractional distillation separated 62% distillates and 30% atmospheric residue from the SP-derived HTL biocrude oil (8% was lost). The majority of this 8% was lost in gaseous fraction (leaking out from the distillation set-up), while some of this 8% was lost during the transfer of the distillates. A comparable yield was also reported in literature. For instance, Nam et al (2016) recovered 95% (by weight) distillates by fractionally distilling pyrolytic microalgae bio-oil at ambient pressure.[40]

As **Fig.1** shows, 31% of the distillates were first distilled at around 100°C. Afterwards, another 31% of the distillates were distilled at 100-270°C. This indicates that half of the distillates may be water and water-soluble compounds because they have similar boiling points as water. On the other hand, the other half of the distillates (distilled at 100-270°C) may be used as fuels because they showed comparable distillation temperatures to jet fuels (205-300°C) and diesel (<343°C).[38, 41]

Compared to the biocrude oil converted from other feedstocks (swine manure and woody biomass), fractional distillation can separate 9-20 wt.% more distillates from SP-derived biocrude oil.[22, 25, 42] This indicates that the SP-derived biocrude oil was more volatile than the biocrude oil converted from other feedstocks. This also suggests that the biocrude oil characteristics are highly dependent on the compositions of the biomass feedstock.

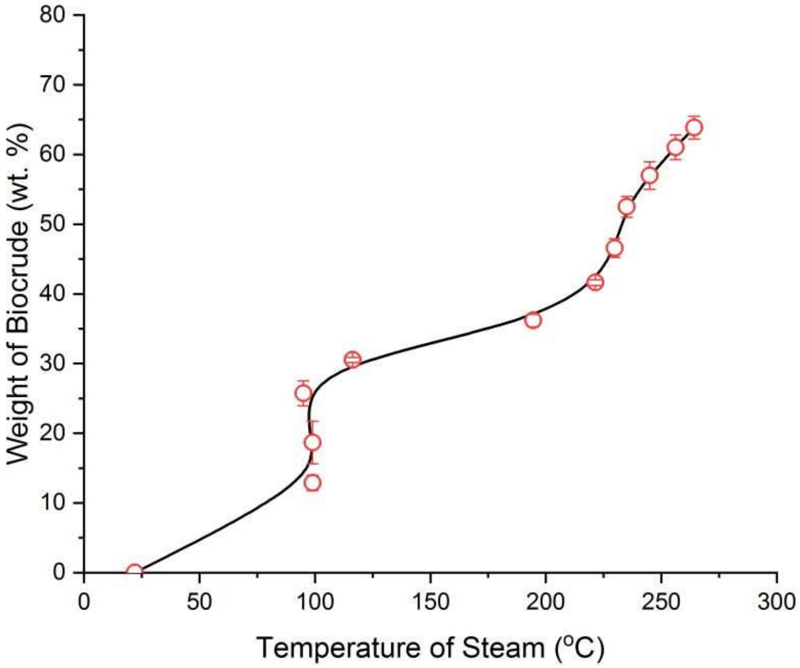


Figure 1. Distillation curves of the biocrude converted from *Spirulina* via HTL

3.2 Characterization of the Distillate from SP-Derived Biocrude Oil

3.2.1 Density, viscosity, and acidity of different distillates

The distillates separated from the SP-derived biocrude oil were characterized to explore their potential applications. As **Fig. 2** shows, the x-axis represents the steam temperature that the distillates were collected, while the y-axis displays the density, viscosity and acidity of different distillates separated from the SP-derived biocrude oil. The density of the fractions distilled below 185℃ was close to 1 g/mL (**Fig. 2a**), suggesting that the first three fractions may be primarily composed of water. The density of the fractions distilled at 185-256℃ (~0.9 g/mL) was lighter than that of water (1 g/mL) but heavier than jet fuel (~0.8 g/mL) and diesel (~0.85 g/mL). These distillates may contain compounds heavier than petroleum fuels. For instance, the density of pyridine, a nitrogen-containing compound present in algal biocrude oil, is 0.982 cm/kg^3, which is heavier than petroleum fuels.[43]

In order to confirm if the fractions distilled below 185℃ were mainly water, another distillation apparatus (according to ASTM D95-99) was used to measure the moisture content in those distillates.[44] Because the distillates collected below 185℃ contained 89-99 wt.% moisture content according to this ASTM method, their viscosity and acidity were not measured. Instead, this study focused more on the fractions distilled at 185-256℃, which shows a closer boiling point distribution and density to those of diesel and jet fuel.

Viscosity plays an important role in the fuel injection, atomization, and combustion processes.[45] **Fig. 2b** reports the average value along with the standard deviation of the viscosity of different distillates. The viscosity of the distillates increased from 3 mm^2/s to 13 mm^2/s when the distillation temperature increased from 185°C to 256°C. Apparently, the amount of large molecules increased with the distillation temperature.[45] However, the viscosity of the distillates separated at 225°C is much higher than those separated at 219°C and 230°C. This could be that the distillate separated at 225°C contained a high concentration of nitrogen-containing compounds such as n-heterocyclic compounds (see **Table S3** in the supplementary data). In general, aliphatic and aromatic hydrocarbons have low viscosities because they have no heteroatoms (*e.g.,* oxygen).[46] Similar change of viscosity was also reported when distilling the biocrude oil converted from swine manure via HTL.[25] Compared to diesel and jet fuel, the distillates from SP-derived biocrude oil have a higher viscosity, possibly due to the heteroatoms (*e.g.,* oxygen and nitrogen). The compositions of HTL distillates are generally more complex than conventional biofuels (*e.g.,* bioethanol) and petroleum fuels.[47] Further investigation is suggested to understand if the relatively high viscosity of HTL distillates would affect the fuel injection, atomization, or combustion processes.

Fig. 2c shows the acidity of the distillates separated at 185-256°C. The acidity of the distillates first increased from 185°C to 219°C and then decreased from 219°C to 256°C. This could be that the distillate separated at 219°C contained more phenols than the fractions distilled at 219-256°C. Furthermore, the fraction distilled at 219°C contains less nitrogen-containing compounds to neutralize the acidity than the fraction distilled at 185°C (see **Table S3** in the supplementary data).[48] In contrast to the distillates separated from the biocrude oil converted from swine manure (≤80 mg KOH/g), food processing waste (≤200 mg KOH/g), and woody biomass (≤ 71 mg KOH/g), the distillates from SP-derived biocrude oil have a much lower acidity (≤7 mg KOH/g).[25, 42] This could be as a result of a higher nitrogen content and lower fatty acids in the algal biocrude oil. Although the acidity of the distillates from SP-derived biocrude oil is still higher than that of biodiesel (≤ 0.3 mg KOH/g), these distillates could be readily used as a blendstock for diesel. For instance, mixing 10% of the fractions distilled at 230-256°C with another 90% of regular diesel (presuming no fatty acids present in petroleum diesel so the acidity is 0) would lead to an acidity of 0.14 mg KOH/g, which would meet the ASTM criteria (≤ 0.3 mg KOH/g).

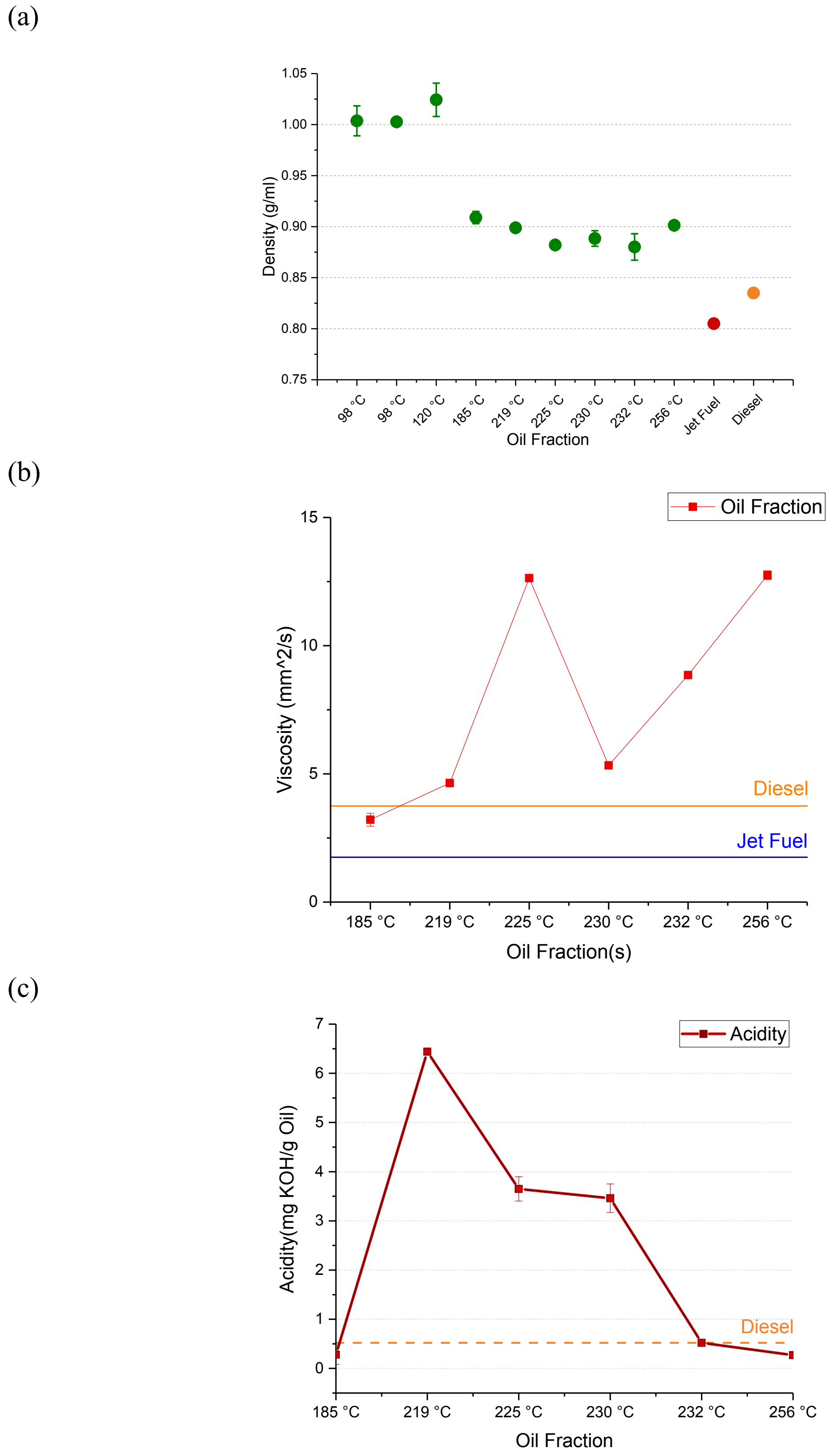


Figure 2. Physicochemical properties of SP-distillates: (a) density, (b) viscosity, and (c) acidity (n≥2).

3.2.2 Elemental compositions and HHV of different distillates

In order to understand the carbon, hydrogen, nitrogen, oxygen, and energy contents of different distillates, the elemental compositions of the fractions distilled at 98-256°C and the atmospheric residue were measured. **Fig. 3** displays the relationship between the distillation fractions with the elemental component (left y-axis) and the higher heating value (right y-axis). As **Fig. 3** shows, the distillates collected below 185°C contained lower carbon but higher oxygen contents than those obtained over 185 °C. This could be that the main component of the distillates collected below 185°C was water or water-soluble compounds, while the majority of the distillates collected over 185°C was hydrocarbon or nitrogen-containing compounds. In addition, the distillates separated between 185-256°C contained around 80% carbon, 10% hydrogen, 5-8% nitrogen, and 2-5% oxygen. While the carbon and hydrogen contents of the distillates remained constant, the oxygen content decreased by 57% (from 6.1 to 2.6 wt.%) and the nitrogen content fluctuated (ranged from 4.9-6.3 wt.%) when the distillation temperature increased from 185 to 256°C.

The light blue curve with square dot in **Fig. 3** represents the higher heating value (HHV) of distillates. Because the distillates sampled below 185°C contained mainly water, the HHV of these distillates were extremely low (around zero). On the other hand, the HHV of the distillates separated over 185°C was in the range of 41-44 MJ/kg, which equals to 89-96% energy content of diesel (46 MJ/kg, plotted in the red dot-line in **Fig. 3)**. About 24 wt.% of the distillates shows a comparable HHV to that of diesel and could be suitable for transportation fuel applications. This HHV is also higher than those obtained from other upgrading methods such as catalytic hydrotreating or thermal cracking.[47]

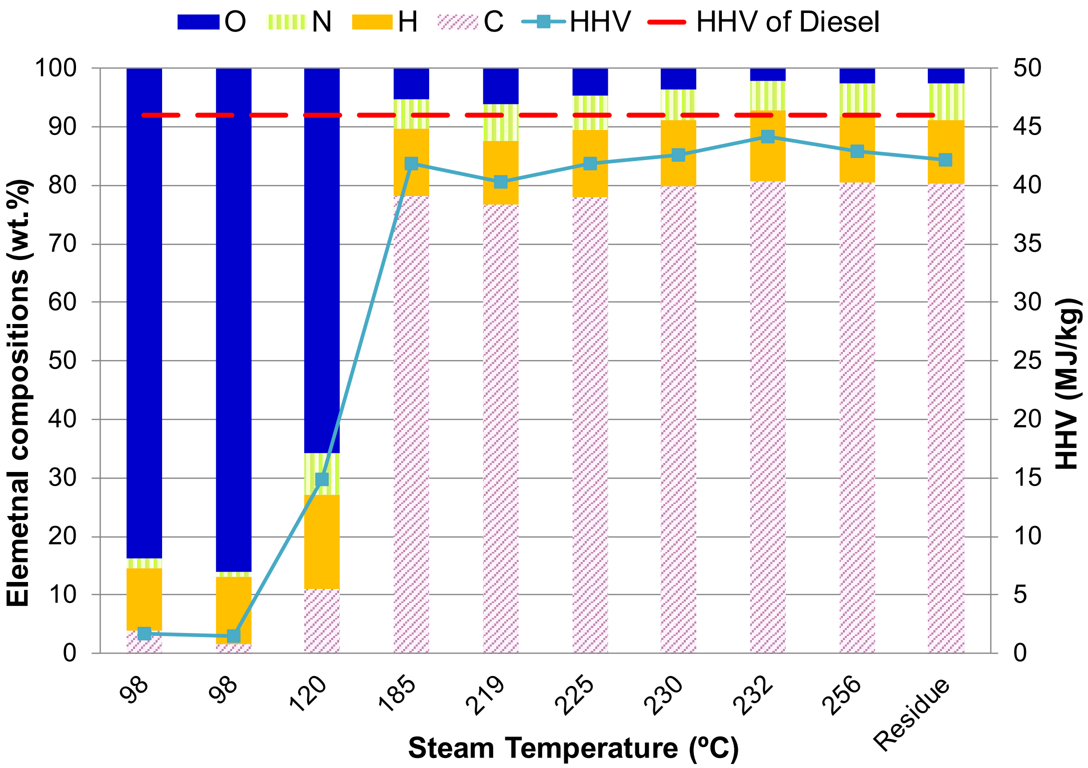


Figure 3. Elemental compositions and higher heating values (HHV) of different SP-distillates

To investigate the change of the atomic ratio across distillation temperatures of 185-256°C, the Van Krevelan diagrams were plotted in **Fig. 4**. The atomic ratios of transportation fuels—Jet Fuel (red dot) and Diesel (orange dot)—were also plotted for comparison. **Fig. 4a** cross-plots the O:C ratio as a function of the N:C ratio. The distillates can be split into two clusters. The distillates collected at 185-225°C had a higher O:C atomic ratio (0.06-0.04) than those collected at 230-256°C (0.03-0.02). A 53-64% decrease in O:C atomic ratio was observed as the distillation temperature increased from 185 to 256°C. Furthermore, the N:C atomic ratio decreased by 29% (from 0.07 to 0.05) as the distillation temperature increased from 219 to 232°C. Deoxygenation and denitrogenation occurred when distillation temperature increased.

Fig. 4b cross-plots the O:C atomic ratio as a function of the H:C ratio. Similarly, the distillates can be split into two clusters, 185-225°C and 230-256°C. When the temperature increased, the O:C atomic ratio decreased by 54% and the H:C atomic ratio remained constant. Compared to jet fuel and diesel, the distillates separated from the SP-derived biocrude oil had a lower hydrogen content. To reduce the difference, further upgrading such as hydrogenation may be required.

Overall, the Van Krevalen diagrams (**Fig. 4**) suggest that the fractional distillation effectively achieves deoxygenation (54%) and denitrogenation (28%) of the SP-derived biocrude oil. This denitrogenation efficiency was comparable to the algal biocrude oil upgraded with high pressure of hydrogen (40 MPa) at high temperature (350°C) for a long reaction time (2-4 hr).[49] With a fractional distillation, the nitrogen content was reduced from 5% to 2-3% in the distillates. This could benefit the following upgrading steps such as catalytic denitrogenation.

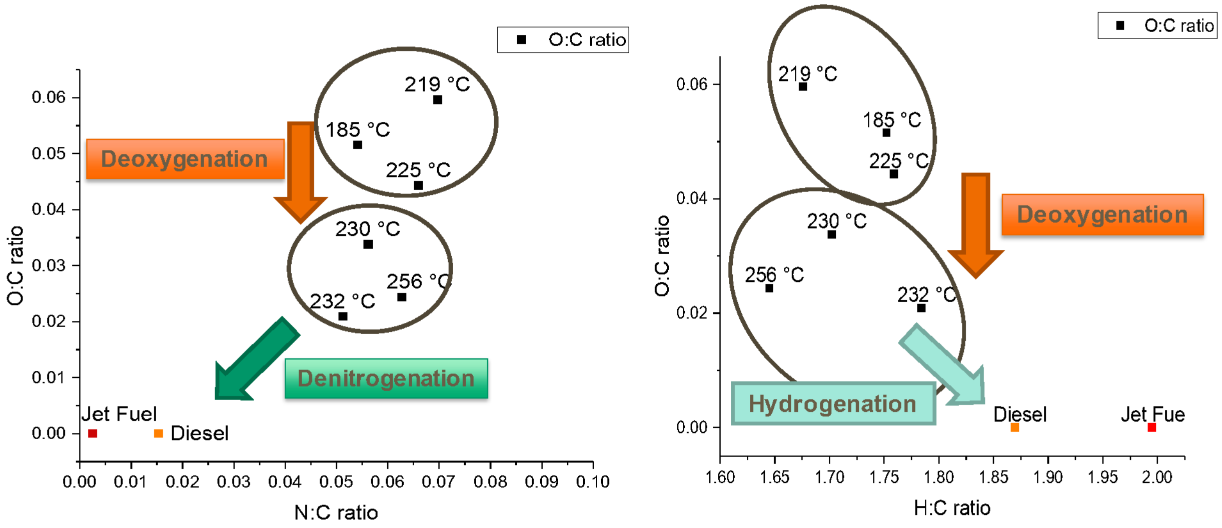


Figure 4. Van Krevelan diagram of SP-distillates: (a) O/C vs N/C and (b) O/C vs H/C atomic ratio.

3.2.3 Chemical compositions of different distillates

GC-MS analysis was conducted to understand how the distillation temperature affects the chemical compositions of different distillates. **Fig. 5** summarizes the chemical compositions of the distillates from the SP-derived biocrude. More details about the identified compounds were also available in supplementary data (**Table S3**). Components characterized by GC-MS were categorized into several major chemical groups including hydrocarbons, cyclic hydrocarbons, fatty nitriles, nitrogen-heterocyclic compounds, phenols, and amino acids. GC-MS analysis was not conducted for the fractions distilled at 98°C because they mainly contain water.

As **Fig. 5a** shows, the relative concentration of hydrocarbons increased from 120°C to 230°C and then decreased from 230°C to 256°C. This indicates that the middle fractions (219-256°C) of the SP-derived biocrude, which were mostly composed of straight-chain alkanes and alkenes with carbon numbers of 10-18, are more suitable for fuel application. Different from the biocrude oil converted from swine manure or food processing waste,[25] the SP-derived distillates also contained branched alkanes and alkenes (*e.g.,* tetramethylhexadecane), which are possibly converted from Chlorophyll.[50] **Fig. 5a** also shows that the fractional distillation can effectively separate hydrocarbons from the viscous algal biocrude oil. The concentrations of hydrocarbons were highly refined after fractional distillation. However, when the temperature increased from 230°C to 256°C, the carbon numbers of hydrocarbons may have increased as well. High-molecular weight hydrocarbons may not be distillable from algal biocrude oil and thus the concentration of hydrocarbons decreased from 230°C to 256°C.

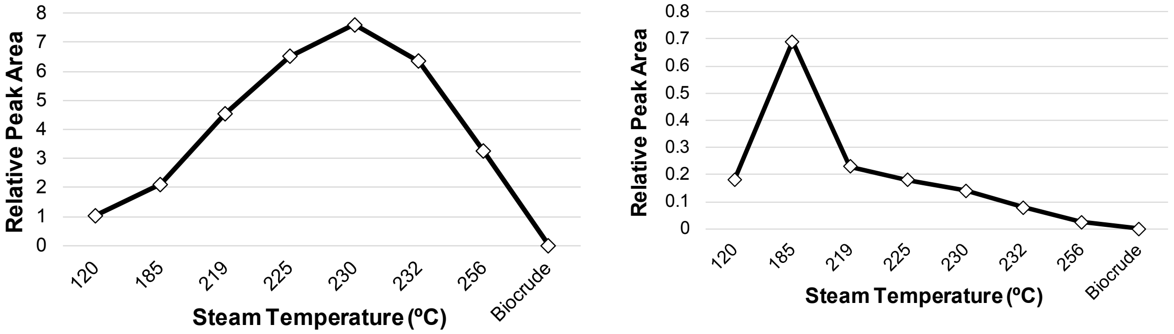
Fig. 5b summarizes the relative concentration of cyclic hydrocarbons in the distillates. It is found that the concentration of cyclic hydrocarbons peaked at 185°C and then decreased. The primary cyclic hydrocarbon found in the distillate separated at 185°C was ionene (trimethyltetralin). Further quantitative analysis of the cyclic hydrocarbons is recommended if one would like to refine tetralin from algal distillates. Similar to the trend found in **Fig. 5a**, the concentration of cyclic hydrocarbons was significantly refined as compared to that in the biocrude oil before distillation.

Fig. 5c shows the relative concentration of fatty nitriles in the distillates. The concentration of fatty nitriles increased as the distillation temperature increased and peaked at the highest distillation temperature (256°C). The major fatty nitrile identified in the distillates is hexadecanenitrile. Fatty nitrile generally is used as a precursor to synthesize fatty amines,[52] which are commonly used in a variety of cosmetic applications (*e.g.,* fabric softeners).[53] It is worth noting that the unit price of fatty nitriles is typically higher than that of fuels, although fuels have a larger market size. Further integration of producing valuable chemicals and fuels from the same source of biomass is thereby suggested.

Fig. 5d and 5e display the relative concentration of n-heterocyclic compounds and amino acids in the distillates. The concentrations of n-heterocyclic compounds and amino acids were much lower in the distillates than in the biocrude oil. N-heterocyclic compounds and amino acids tend to partition into the aqueous phase rather than the oil phase.[23] A majority of the n-heterocyclic compounds and amino acids could exist in the aqueous phase distilled at 98-120°C.

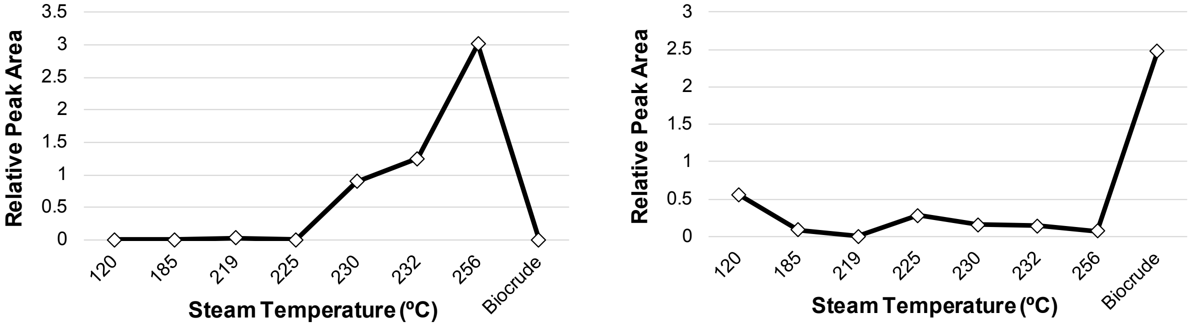
Fig. 5f illustrates the relative concentration of phenolic compounds in the distillates. The concentration of phenols increased as the distillation temperature increased from 120°C to 185°C and decreased from 185°C to 225°C. Then, its concentration increased again from 225°C to 230°C and decreased from 230°C to 256°C. The separation of phenol (with the boiling point of 182°C) and methyl phenol (*i.e.,* cresol) probably led to the first increase of phenols, while the second increase of phenols was possibly from the separation of dimethyl phenol (*i.e.,* xylenol).[54] Notably, methyl phenol has three isomers (with the boiling point range of 191-202°C) and dimethyl phenol has six isomers (with the boiling point range of 203-227°C).[54] Because these isomers may be distilled at a wide range of temperatures, using fractional distillation to separate phenols from algal biocrude oil was ineffective. This is also reflected upon the similar concentration of phenols in the biocrude oil (before fractional distillation) and in the distillates (after fractional distillation).

Other upgrading strategies, such as neutralization (removing phenols as a salt, *e.g.,* sodium phenoxide),[47] solvent extraction,[55, 56] steam distillation,[57] hydrotreating,[58] or catalytic upgrading.[59-61] are needed for the removal of phenols from HTL biocrude oil. Neutralization was proven to be an effective method to remove phenols from distillation from swine manure-derived biocrude oil and enable the upgraded distillates for diesel blendstock application with qualified ASTM stardanrds.[47] In addition, steam distillation appears to be a logical and cost-effective strategy to recover phenol isomers.[34] Steam distillation uses water to purify or isolate temperature-sensitive materials by lowering the partial pressure of the mixture and thereby reducing the boiling point of components.[62] For instance, Murwanashyaka et al (2001) has separated syringol from woody pyrolytic bio-oil using a steam distillation. On the other hand, it was found that dehydroxylation of phenols was difficult. Prior studies found that catalysts ($Ni/Mo/\gamma Al_2O_3$) enable the altering of the side chain structure of phenol but not dehydroxylation, probably due to the higher energy required to break the C-O bond.[61]



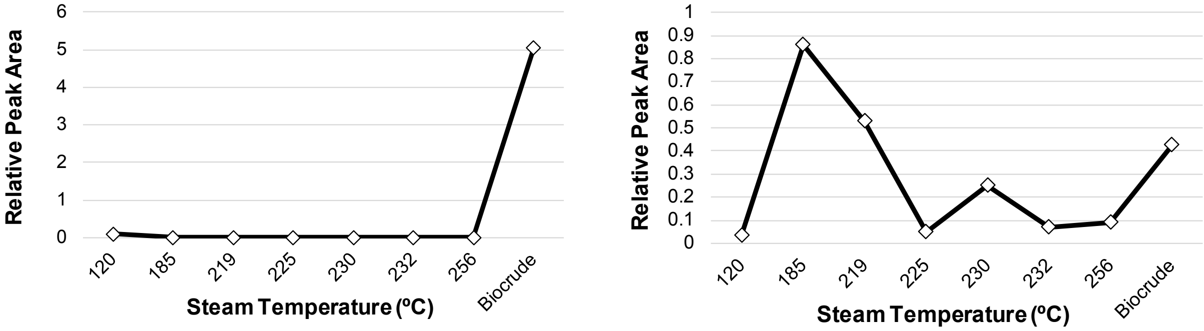
(a) Hydrocarbons

(b) Cyclic hydrocarbons



(c) Fatty nitriles

(d) N-Heterocyclic compounds



(e) Amino acids

(f) Phenols

Figure 5. Chemical compositions of the SP-derived distillates obtained at different temperatures: (a) Hydrocarbons, (b) Cyclic hydrocarbons, (c) Fatty nitriles, (d) N-Heterocyclic compounds, (e) Amino acids, and (f) Phenols. (Note: the y-axis represents the peak area of a chemical groups divided by that of an internal standard, pentadecanoic acid methyl ester, 0.5μM).

3.3 Elemental and energy recovery of biocrude oil to different distillates

Knowing the fractional distillation yields and elemental compositions of each distillate allows the estimation of the elemental and energy recoveries from the SP-derived biocrude oil (**Fig. 6**).[5, 10, 33] As **Fig. 6** shows, about 3% of carbon was distributed in the first three distillates (sampled between 98-120°C). Then, about 7-8% carbon was recovered into each distillate separated at 185-256°C. About 30% carbon was distributed to the atmospheric residue (the fraction denoted as >256°C), while another 24% was lost in the gas phase. During distillation, small molecules (*e.g.,* propane and butane formed by the cracking reactions occurring at high temperatures during distillation) could be lost due to a fast and abrupt evaporation of gas vapor.[40] The cracking reactions were indicated by the white smoke in the flask during the distillation.[22] Similar observation was also reported when fractionally distilling the biocrude oil converted from lignocellulosic biomass,[22, 63] food processing waste,[25] swine manure,[21, 47] and duckweed,[64] via HTL. In addition, the loss of small molecules was also found with vacuum or atmospheric distillations of the pyrolytic bio-oil converted from corn stover.[65]

Hydrogen balance is also performed to track how much hydrogen from the SP-derived biocrude oil went to various distillates. About 47% hydrogen was recovered in the first three distillates (sampled between 98-120°C). This is because that the first three distillates separated from the SP-derived biocrude oil primarily contained water and water-soluble compounds (as other characterizations demonstrated earlier). Subsequently, another 7-8% hydrogen was recovered into each distillate separated at 185-256°C. Another 7% hydrogen was distributed to the atmospheric residue. Only about 2% of hydrogen was lost in the gas phase. This analysis of hydrogen recovery indicates that the fractional distillation can efficiently recover the majority of hydrogen in the distillation products.

Nitrogen balance is carried out to understand how nitrogen from SP was distributed into various distillates. About 15% nitrogen was recovered in the first three distillates (sampled between 98-120°C). This could be that the first three distillates separated from the SP-derived biocrude oil mainly contained water-soluble compounds. Many of the nitrogen-containing compounds (*e.g.,* amines) are water-soluble. Next, nitrogen was averagely recovered into several fractions distilled at 185-256°C (4-6%). Another 32% nitrogen was distributed into the atmospheric residue. This suggests that the atmospheric residue may contain nitrogen-doped carbonaceous material, which may be suitable for electrochemical applications with proper modification.[47] For instance, nitrogen-rich microalgae have been used to synthesize microporous carbons for electrochemical capacitors with a combination of low-cost hydrothermal carbonization and industry-adopted KOH activation processes.[66] Last, about 23% of nitrogen was lost in the gas phase. This is probably due to the loss of light amines. For instance, the SP-derived biocrude oil contains propylamine and butylamine that have boiling points below 80°C.[23]

Energy recovery from the SP-derived biocrude oil to different distillates were also conducted. About 1% energy was distributed in the first two distillates (sampled between 98-99°C). This is expected because the first two distillates mainly contained water. The third distillate (separated at 120°C) has 5% energy recovery, as a result of the recovery of nitrogen-containing compounds and some light hydrocarbons (see more details in **Table S3** in the supplementary data). Subsequently, energy was averagely recovered into the distillates separated at 185-256°C (8-9%), while another 18% energy was distributed into the atmospheric residue. Finally, about 25% of energy was lost in the gas phase, possibly due to the loss of small molecules (*e.g.,* propane and butane) that may contain high energy contents.

There are two possible reasons for this 25% energy loss. First, the distillation set-up used in this study is connected by multiple pieces of glassware. The gaseous products could be leaked out from the connection joint during distillation. It is expected that this 25% energy loss can be minimized when an advanced fractional distillation set-up is used. For instance, Hoffmann et al. (2016) fractionated woody biocrude oil using vacuum distillation, which can reduce the required heating temperature and thereby reduce the formation of gaseous compounds. In addition, the distillation set-up was also made by one-piece of glass to avoid possible leaking.[22] With this advanced fractional distillation set up, Hoffmann et al. recovered 98 wt.% distillates from the woody biocrude oil. Second, it could be due to a fast and abrupt evaporation of gas vapor, which can be avoided by optimizing the distillation process (*e.g.,* using a slower heating rate, increasing the length of the fractional column).[40] In short, in order to enhance the energy recovery and minimize the energy lost during fractional distillation, it is recommended to improve the distillation set-up or optimize the distillation process in the future.

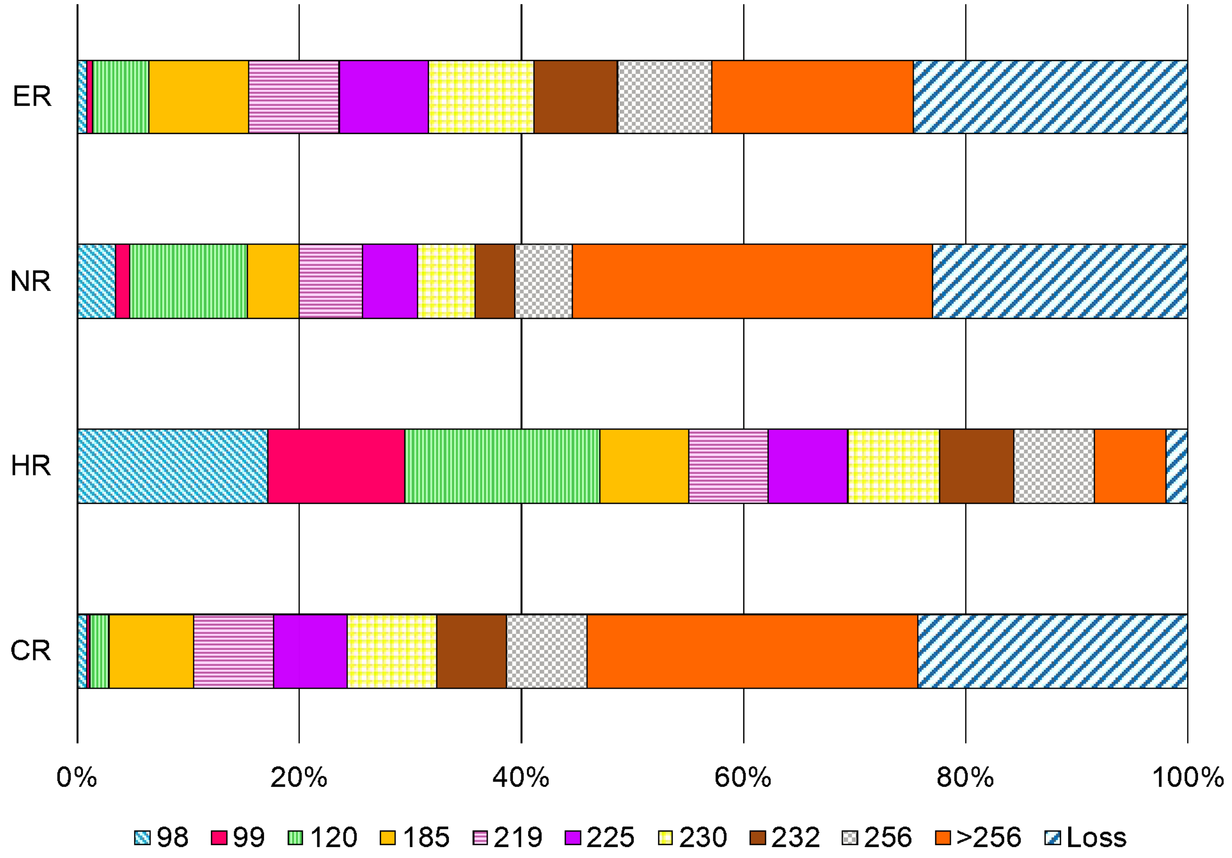


Figure 6. Carbon recovery (CR), hydrogen recovery (HR), nitrogen recovery (NR), and energy recovery (ER) of biocrude oil to different distillates, where elemental and energy recoveries were defined as the elements or the HHV of the distillate divided by those of the biocrude oil.[5, 10, 33] (Note: each color block represents the element or energy recovery fractions in the distillate temperature range)

3.4 Energy Consumption Ratio and Reaction Severity of Fractional Distillation

In addition to studying the energy recovery from the SP-derived biocrude oil to different distillates, understanding the energy consumption ratio of the fractional distillation is also important for improving the overall energy efficiency of wet biomass conversion. **Fig. 7** compares the energy consumption ratio and the reaction severity of different available upgrading methods. Energy consumption ratio (ECR) can be considered as the energy required for upgrading against the energy that can be recovered from combusting the upgraded HTL biocrude oil (*i.e.,* the energy of the biocrude oil retained in the useable fraction after upgrading). Fractional distillation demonstrates a competitive energy consumption ratio (0.03-0.06 with 50% heat recovery) to zeolite cracking (0.07 with 50% heat recovery), supercritical water (SCW) treatment (0.17 with 50% heat recovery), and hydrotreating (0.24 with 50% hear recovery).[13, 14, 17, 26] This is because that zeolite cracking and SCW treatment typically occur at relatively high temperatures (400-425°C) and only lead to an HHV of 40-43 MJ/kg of the upgraded HTL biocrude. Similarly, hydrotreating also happens at high temperatures (~400°C) and under high pressures of hydrogen (*e.g.,* 6 MPa H_2 under batch conditions, 0.043g H_2/g HTL biocrude oil or 85 L/hr H_2 under continuous conditions).[13, 26, 27] Typically, the yield and HHV of hydrotreated HTL biocrude oil can be as high as 82 wt.% and 47 MJ/kg, respectively. However, the large consumption of hydrogen and pressurized equipment may raise issues for energy efficiency, up-scaling, and cost-effectiveness, given hydrogen gas is also a valuable energy source (120-142 MJ/kg).

Reaction severity (R_o) is a metric combining the effect of reaction temperature and time of a process and can be used to evaluate the severity of different upgrading processes.[36, 37] As **Fig. 7** shows, the fractional distillation (with log R_o of 5.9-9.5) presents a much lower reaction severity than zeolite cracking (with log R_o of 11.0), SCW treatment (with log R_o of 10.6), and hydrotreating (with log R_o 11.5). This is mainly due to that zeolite cracking, SCW treatment, and hydrotreating occur at higher temperatures (400-425°C) than those for the fractional distillation (220-330°C).

Considering the energy consumption ratio and reaction severity of different upgrading approaches, the fractional distillation is an advantageous method to upgrade HTL biocrude oil into transportation fuels.

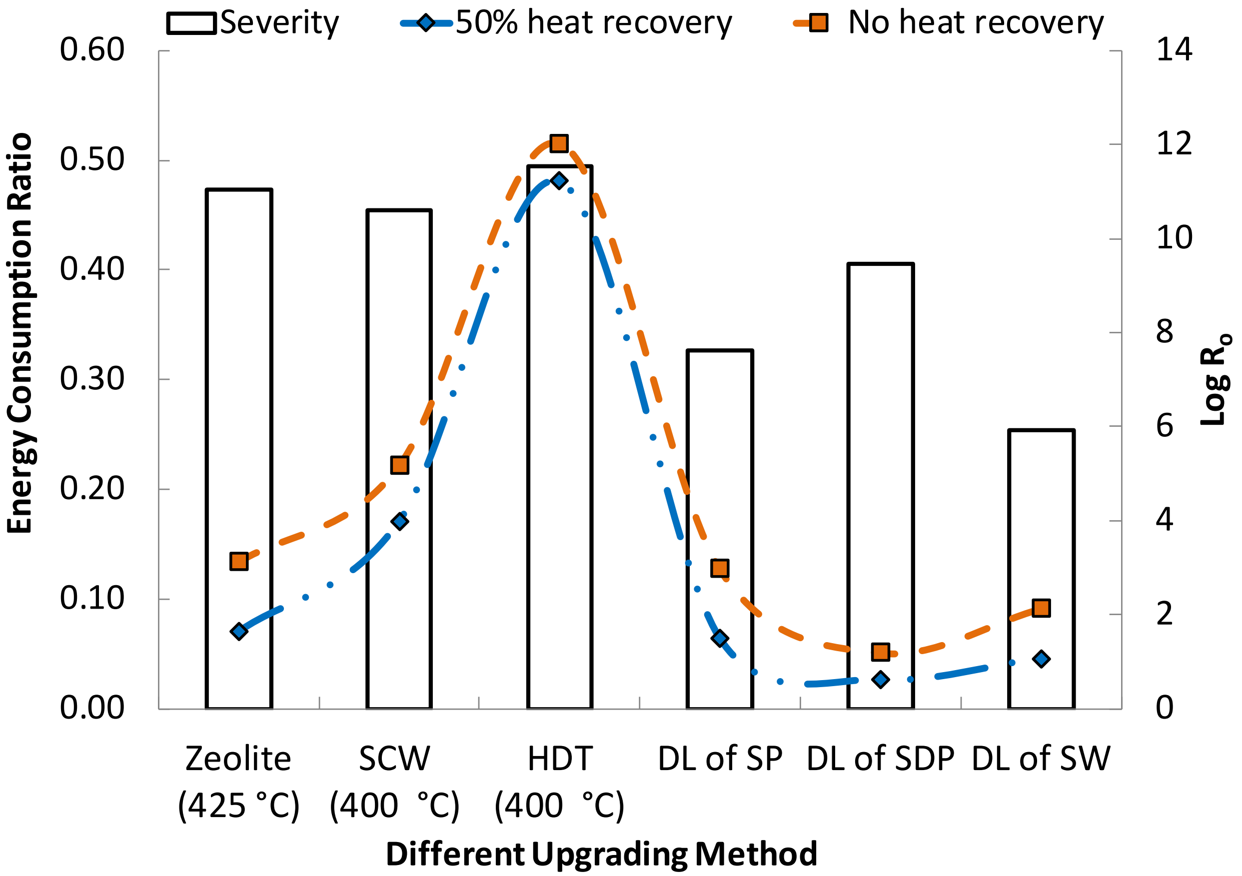


Figure 7. Energy consumption ratio and reaction severity of using different strategies to upgrade HTL biocrude oil (the data for zeolite cracking, supercritical water (SCW) treatment, and hydrotreating (HDT) is adapted from Cheng et al (2014),[17] Duan et al (2013), [13], Elliott et al (2013), and Jones et al (2014),[26, 27] respectively; the data for upgrading the HTL biocrude oil converted from salad-dressing plant (SDP) waste (including fractional distillation (DL) and esterification) is from Chen et al (2018)[25]; and the data for upgrading the HTL biocrude oil converted from swine manure ((DL plus neutralization) is adapted from Chen (2017).[47]

3.5 Fuel Specification Analysis of the Distillate from the SP-Derived Biocrude Oil

Based on the density, viscosity, acidity, elemental and chemical compositions of the distillates from the SP-derived biocrude oil, the distillates separated at 185-232°C had the closest properties to petroleum fuels and thus were used for further fuel specification analysis. The distillates separated at 185-232°C were used to synthesize the drop-in renewable diesel, which was formulated with 10 vol.% distillates and 90 vol.% petroleum diesel (namely HTL10). Fuel specification analyses, including viscosity, acidity, net heat of combustion, existent gum content, ash content, lubricity and oxidation stability, were subjected to the drop-in renewable diesel.

As **Table 2** shows, the fuel specification of SP-HTL10 met the ASTM criteria for biodiesel application and was comparable to the performance of petroleum diesel. For instance, SP-HTL10 presents a satisfactory acidity (0.3 mg KOH/g) that meets the ASTM standards.[38] This is very different as compared to those from salad-dressing plant (SDP) waste or swine manure (SW) derived biocrude oil, which typically contains an excessively high acidity.[25]

Existent gum contents and ash contents of the drop-in renewable diesel were also measured to investigate if additional upgrading processes are needed to remove compounds that cannot stably mix with petroleum diesel. **Table 2** also demonstrates that SP-HTL 10 had a comparable performance to petroleum diesel, indicating that the SP-derived distillates can be used as stable drop-in blendstocks.

Heat of combustion is mainly affected by the elemental compositions of fuel samples.[38, 41] Compared to petroleum diesel, SP-HTL10 had a slightly lower heat of combustion. This is probably due to a higher oxygen content in SP than in petroleum diesel. Although this higher oxygen contents lead to a lower heat of combustion, they may make the drop-in renewable diesel combust more completely.[67] For instance, a recent study proves that the upgraded-SDP-HTL10 and HTL20 in **Table 2** can lead to a lower CO emission, which is typically caused by incomplete combustion under diesel engine combustion.[25]

SP-HTL10 showed a superior lubricity to that of upgraded-SDP-HTL10 and HTL20, as well as petroleum diesel. The distillates from the SP-derived biocrude oil contained more fatty nitriles (*e.g.,* heptadecanenitrile). Fatty nitriles may serve as a role of surfactants, acting as emulsifiers and dispersants in an oil-aqueous phase, and thus help improve the flowability and lubricity.[23] However, it has to point out that the presence of fatty nitriles could lead to the formation of NOx during combustion. Further combustion and rheology studies with SP-HTL10 or model compounds (*e.g.,* Heptadecanenitrile with diesel) are recommended to elaborate the effect of fatty nitriles on combustion and lubricity.

It is generally believed that the oxidation stability of biodiesel links to the presence of unsaturated compounds because they tend to degrade during storage.[68] Normally, oxidation stability for biodiesel is 4-12 hours.[68] In the present work, SP-HTL10 demonstrates an oxidation stability of more than 48 hours, which suggests that there was no rapid oxidation. According to the GC-MS results (**Table S3** in supplementary data), the major components in the distillates from SP-derived biocrude were alkanes. Furthermore, no fatty acids were identified in the SP-derived distillates under GC-MS.

Overall, SP-HTL10 shows comparable fuel properties to regular diesel without any chemical modification. It is also acknowledged that the effect of the excessive nitrogen contents on fuel properties and diesel engine combustion performance remains unknown. More research with SP-HTL10 would be needed to reveal the effect of different nitrogen-containing compounds on diesel combustion and engine performance.

Table 2. Fuel specification analysis of drop-in biodiesel (HTL10 and HTL 20 respectively represents 10 vol.% and 20 vol.% upgraded distillates plus 90 vol.% petroleum diesel)

Fuel Spec Property	SP	Upgraded-SDP (adapted from [25])		Diesel
	HTL10	HTL10	HTL20	
Viscosity @20°C (mm^2/s)[a]	3.1 ± 0.003	3.7 ± 0.01	3.1 ± 0.02	3.7 ± 0.02
Acidity (mg KOH/g)[b]	0.3 ± 0.0	0.1 ± 0.004	0.3 ± 0.05	0.3[e]
Existent Gum (wt.%)[c]	0.55 ± 0.03	0.17 ± 0.01	0.21 ± 0.02	0.63± 0.06
Ash Content (wt.%)[d]	0.05 ± 0.01	N/A[g]	N/A[g]	0.07 ± 0.002
Net Heat of Combustion (MJ/kg)[f]	45.4 ± 0.2	44.7 ± 0.3	44.2 ± 0.6	46.0 ± 0.3
Lubricity (μm)	314	364	324	<520[e]
Oxidation Stability (hrs)	48>	48>	48>	6>[e]

[a]Measured by Cannon-Fenske Viscometer (ASTM D445); [b]Measured by ASTM D664; [c]Modified by ASTM D381, heat the sample in the furnace from room temperature to 240°C for 60 minutes; [d] Measured by ASTM D482; [e] Adapted from ASTM D7467; [f]Measured by bomb Calorimeter (ASTM D4809); [g]Not applied because of the low existent gum contents.

3.5 Roadmap for Renewable Diesel and Biopriveleged Chemical Synthesized from Microalgae

Combining the characterization results of different distillates and potential reaction pathways reported in literature,[5, 31] a roadmap for renewable fuels and biopriveleged chemicals synthesized from *Spirulina* is proposed in **Fig. 8**. Notably, the reaction pathways are slightly modified because the fractional distillation allows GC-MS to identify compounds that were not detectable when analyzing the biocrude oil solely. For instance, fatty nitriles and phosphate were not observed in the biocrude oil before.[8, 23] This could be that the signals of fatty nitriles and phosphate were relatively weak compared to the main compounds in the biocrude oil.[23] Similar findings were also reported when distilling the swine manure-derived biocrude oil.[25]

As **Fig. 8** shows, lipids in microalgae could be hydrolyzed into fatty acids, glycerol, or phosphate under HTL. The phosphate group was probably produced from hydrolysis of phosphate ester.[4] Phosphate ester is a key component of DNA, RNA, and ATP. In addition, *Spirulina* may contain cyanotoxins with the chemical structure of cyclic N-hydroxyguanine organophosphate, given *Spirulina* is a kind of cyanobacteria.[69] Then, fatty acids could be converted into hydrocarbons via decarboxylation.[4, 5, 31] Hydrocarbons could be further converted into cyclic hydrocarbons or aromatics via cyclization or aromatization.[70, 71]

Proteins and carbohydrates could also be hydrolyzed into amino acids and glucose, respectively. Upon heating, Maillard reaction may occur between amino acids and reducing sugar, forming n-heterocyclic compounds (*e.g.,* indole derivatives). Additionally, amino acids can also experience deamination and produce ammonia, which can further react with fatty acids and give fatty nitriles at high temperatures.[47, 52] Fatty nitriles are widely used as intermediate molecules in the chemical industries.[72] For instance, fatty nitriles are the precursor for synthesizing fatty amines, which are common surfactants and the basis for a variety of cosmetic formulations.[72, 73] Under HTL, lignin could also be degraded into phenols, which is an important industrial commodity.[5] For example, phenols are essential for the production of plastics such as polycarbonate and epoxy.[74]

In addition, **Fig. 8** suggests that it is possible to simultaneously produce renewable fuels (diesel blendstocks) and bioprivileged chemicals from the same source of biomass. In fact, it has been reported that biomass has the potential to fulfill the energy and chemical needs of society while minimizing environmental impact and increasing sustainability at the same time.[75] The petroleum industry operates on a refinery model yielding fuels and other value-added products from crude oil to maximize their economic profit. Analogously, a biorefinery is defined as "an integral unit that can accept various biological feedstocks and convert them to a range of useful products including chemicals, energy, and materials."[76] Analysis has shown that integrating co-products with biofuels offers a substantially higher return on investment while simultaneously meeting energy and economic goals.[77] For instance, as **Fig. 8** shows, the price of aromatics and fatty nitriles is 2-18 times higher than that of fuels, while fuels could have a larger market size than aromatics and commodity chemicals.

However, the majority of recent research involving biomass has been focused on fuels rather than on value-added products. More research focused on producing bioprivileged chemicals that can add value to biomass is thereby advocated.

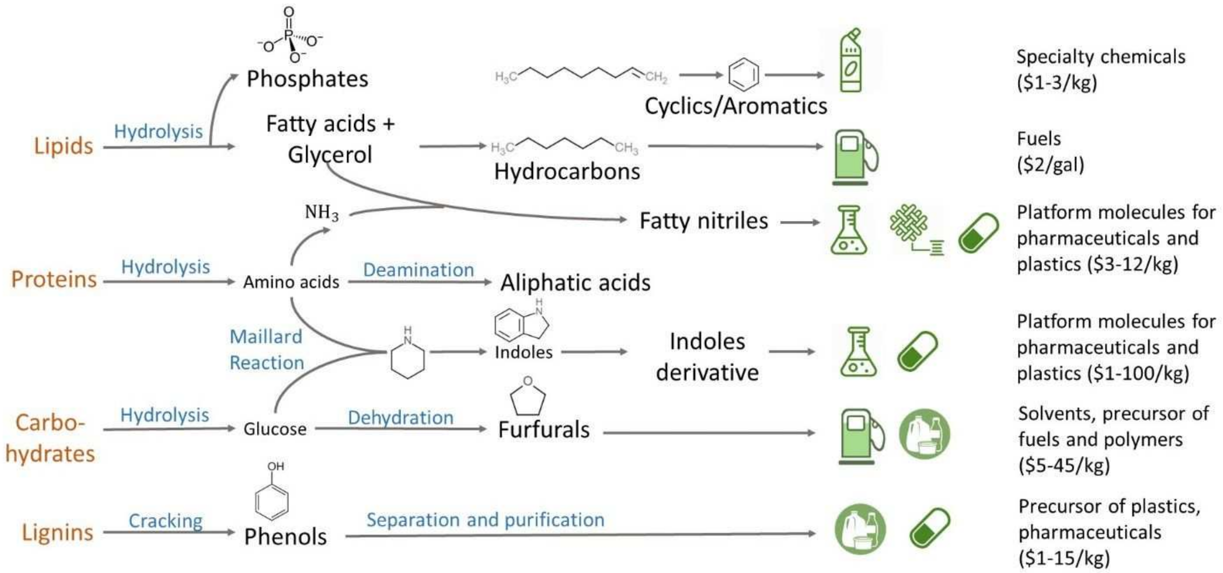


Figure 8. An algal biorefinery roadmap for producing renewable fuels and bioprivileged chemicals (the prices of fuels and chemicals are adapted from the USEIA and Alibaba.com, respectively). Note: the exact price is highly dependent on the purchase quantity--a small quantity of purchase usually leads to a high unit price and vice versa. For instance, buying 25-49 kg and >1000 kg of furfural costs $45/kg and $5/kg, respectively. Similar estimation is also used in literature.[71]

4. Conclusion

A fractional distillation was carried out to separate the biocrude oil converted from *Spirulina* (SP) via hydrothermal liquefaction (HTL). It was found that the fractional distillation can separate 62% of the biocrude oil into flowable liquids at about 270ºC. The acidity of the distillates was in the range of 0 to 6 mg KOH/g. The viscosity of these algal distillates was 3-12

mm^2/s with a higher heating value ranged from 39-44 MJ/kg. Compared to the fuel and chemical properties of petroleum fuels, about 15% of the algal distillates was suitable for fuel applications. The elemental composition analysis also shows that deoxygenation of algal biocrude oil was effectively achieved by fractional distillation. In addition, chemical composition analysis indicates that some distillates contained bioprivileged chemicals like aromatics, phenols, and fatty nitriles that can be used as commodity chemicals. Energy efficiency analysis also demonstrates that the fractional distillation has a lower energy consumption ratio than other upgrading methods. Finally, the fuel specification analysis was conducted with the drop-in renewable diesel (formulated with 10 vol.% distillates and 90 vol.% petroleum diesel, HTL10). According to the fuel specification analysis, HTL10 exhibited a qualified lubricity (<520 μm), acidity (<0.3 mg KOH/g), and oxidation stability (>6 h), as well as a comparable net heat of combustion (1% lower), ash content (29% lower) and viscosity (17% lower) to those of petroleum diesel. Ultimately, it is expected that results from this study can help bridge the knowledge gaps of 1) biocrude oil upgrading and 2) process/energy optimization and design of an algal biorefinery producing renewable diesel blendstocks and bioprivileged chemicals via HTL.

Data Availability

The data that supports the findings of this study are available from the corresponding author upon request.

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Acknowledgement

The authors thank USDA and the Snapshot Energy Gift Fund for providing experimental supplies for the research. The first author appreciates the Dissertation Fellowship provided by the University of Illinois.

The first author also would like to thank the University of Massachusetts Lowell for providing start-up funds and the Massachusetts Technology Transfer Center for providing the Acorn Innovation Awards. The authors thank Elizabeth Eves in the Microanalysis Laboratory (Urbana, IL) for their help on elemental analyses. The authors e also greatly appreciate Dr. Alexander Ulanov of the Roy J. Carver Biotechnology Center (Urbana, IL) for his help and discussion on GC-MS analysis. The authors would like to thank Ms. Kerry Candlen and Madison Reed (Department of Plastics Engineering, University of Massachusetts Lowell) for reading through this paper and providing useful suggestions.

Competing interests

The authors declare no competing interests.

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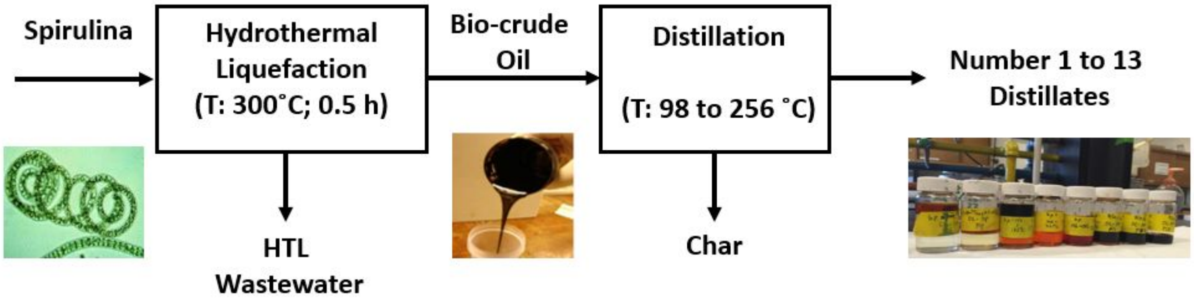
Spirulina
Hydrothermal Liquefaction (T: 300˚C; 0.5 h)
Bio-crude Oil
Distillation
(T: 98 to 256 ˚C)
Number 1 to 13 Distillates
HTL Wastewater
Char