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Hydrothermal liquefaction of high- and low-lipid algae: Bio-crude oil chemistry

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HIGHLIGHTS

- Algal lipid and protein content affect the composition and upgrading of HTL oils.
- *N. salina* bio-crude oils contain more fatty acids, amides, and aliphatic molecules.
- *G. sulphuraria* bio-crude oils have more N- and O-heteroatom aromatic molecules.
- Bio-crude oils recovered with lower-polarity solvents are better for upgrading.
- Carbohydrates should be removed prior to HTL, but N removed by catalytic upgrading.

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ABSTRACT

The bio-crude oil produced from hydrothermal liquefaction (HTL) of a high-protein microalgae useful for wastewater treatment, *Galdieria sulphuraria,* was comprehensively characterized, and compared to that of a high-lipid microalgae useful for biofuel production, *Nannochloropsis salina*. HTL was conducted in a batch reactor at temperatures of 310–350 °C and reaction times of 5–60 min. Characterization methods included high-resolution Fourier transform ion cyclotron resonance mass spectroscopy (FT-ICR MS), fatty acid methyl ester (FAME) analysis by gas chromatography mass spectroscopy (GC/MS), proton nuclear magnetic resonance spectroscopy (^{1}H NMR), and Fourier transform infrared spectroscopy (FT-IR). Milder reaction conditions favored bio-crude oil yield and quality for *N. salina*, while more severe conditions (350 °C) were needed for *G. sulphuraria*. *N. salina*-derived bio-crude oil contained mainly C_{14}-C_{18} fatty acid amides, while *G. sulphuraria*-derived bio-crude-oil had many $N_{1\text{-}3}O_{0\text{-}2}$ hetero-atom compounds. FT-ICR MS showed that the aromaticity of hetero-compounds in *N. salina* bio-crude oil was higher due to *N. salina*'s higher carbohydrate content and the tendency of carbohydrate-derived molecules to condense at HTL conditions. FAME-GC/MS and ^{1}H-NMR results showed that stable fatty acid amides increased in *G. sulphuraria* bio-crude oil at higher temperatures as more protein-derived compounds combined with lipid-derived compounds. While N-containing and high molecular weight compounds are a concern for the upgrading of bio-crude oils obtained from high-protein algal biomass, removal of carbohydrates rather than removal of proteins as a pretreatment to HTL is recommended since carbohydrate-derived compounds are more likely to create highly aromatic hetero-compounds that are much more difficult to upgrade.

1. Introduction

Hydrothermal processing is one of the most competitive thermochemical conversion methods for wet biomass. Hydrothermal carbonization produces char-like solid at low temperatures (170–250 °C) [1], hydrothermal liquefaction (HTL) produces bio-crude oil at moderate temperatures (250–370 °C), and hydrothermal gasification produces energy-rich gases at high temperatures (370–750 °C) [2]. As liquid fuels have higher energy density relative to solid fuels or syngas [3], many researchers have used HTL for conversion of wet biomass into bio-oils.

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Most components (lipids, proteins and carbohydrates) in algae can contribute to the formation of bio-crude oil, so bio-crude oil yields can exceed the original lipid content of the algae [4].

To date, most studies on the HTL of algae have focused on the optimization of operating conditions to improve bio-crude oil yields [5] and energy content/energy recovery [6]. Few studies have focused on the chemistry of bio-crude oils, which is imperative for upgrading the highly complex mixtures into finished products. Of particular concern for upgrading are oxygen, nitrogen, and ash [7]. Although bio-crude oils from HTL of algae generally have lower oxygen contents, lower moisture contents [8], and higher heating values (HHV) [9] than fast pyrolysis bio-oils from the conversion of lignocellulose biomass, algae contain more protein and, therefore, more nitrogen. Homogeneous [10] and heterogeneous [11] catalysts, and organic solvents [12], have be used in HTL to remove hetero-atoms in bio-crude oils, however, the yield and quality of the bio-crude oil is generally more influenced by the water itself [13]. As it nears its critical point at 374 °C and 22 MPa, water acts more like a non-polar solvent with lower density, a lower dielectric constant, and enhanced mass transfer. Under subcritical conditions (180–370 °C and 5–21 MPa), a variety of HTL reactions are catalyzed by H^+or OH^- ions generated from the water molecules [8]. These reactions include hydrolysis, dehydration, decarboxylation, repolymerization, deamination [8], and Maillard reactions [14], which convert macromolecules (e.g. lipids, proteins [15] and carbohydrates [16]) into water-insoluble molecules, water-soluble molecules, non-condensable gases, and solid char) [17].

The influences of algal composition on HTL have been well studied [18]. At HTL temperatures below 250 °C, lipids are hydrolyzed into various free fatty acids that make up the organic product phase. With increasing temperatures and reaction times, algal cell walls break, and proteins and some carbohydrates undergo deamination, decarboxylation, deoxygenation, and repolymerization. These reactions add heteroatom-containing organic compounds to the bio-crude oil phase [19]. Torri et al. [20] found that the HTL temperature for the highest bio-crude oil yield is much lower for high-lipid algal biomass than for high-protein or high-carbohydrate biomass. Higher temperatures also favor the transfer of heteroatom-containing compounds into the bio-crude oil.

Bio-crude oil's complexity has made it difficult to accurately describe and track changes in bio-crude oil chemistry. Ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been used to characterize the chemical composition of fossil oils [21], bio-oils [22], and algal lipid extracts [23] for compounds across a wide range of molecular weights, the vast majority of which cannot be detected by gas chromatography mass spectroscopy (GC/MS) due to low volatility and spectral complexity [24]. Specifically, FT-ICR MS provides exceptionally high mass resolving power (e.g., $m/\Delta m_{50\%}$ = 400,000 at m/z 400, where $\Delta m_{50\%}$ is the mass spectral peak width at half-peak height for mass m and charge z) and mass measurement accuracy in the range of 100–500 parts-per-billion [25]. This method enables the direct detection of thousands of organic compounds simultaneously and offers insight for feedstock selection, process optimization, and downstream processing [26]. Negative-ion mode FT-ICR MS has been used to characterize fast pyrolysis bio-oils [27] where highly oxygenated compounds (O_x and NO_x classes) are present [28]. By comparison, bio-crude oils from HTL of algae tend to contain fewer O-containing compounds but more N-containing compounds. In addition, highly oxygenated compounds tend to fractionate into the HTL aqueous phase, while nitrogen-containing compounds fractionate into the organic phase [24]. Therefore, positive-ion mode electrospray ionization (ESI) FT-ICR MS is beneficial for characterization of algal HTL bio-crude oils [29].

Nannochloropsis salina (hereafter *N. salina*) is one species of a genus of marine microalgae that has been well-studied for biofuel production due to its high lipid content [30]. *Galdieria sulphuraria* (hereafter *G. sulphuraria*) is an acidophilic red microalgae that recently has attracted attention as a potential species for wastewater treatment and biomass production due to its wide tolerances for growth conditions and mixotrophic metabolism [31]. *G. sulphuraria* represents a low-lipid, high-protein algal biomass that may be a good candidate for recovering energy as liquid fuel from wastewater treatment, but for which there is little existing conversion data.

This study is one component of a multi-part study to evaluate yields, energy recovery, and chemistry of bio-crude oil produced from HTL of a high-protein *G. sulphuraria* relative to other biofuel candidate microalgae. The goal of this study is to identify HTL reaction conditions to convert *G. sulphuraria* into bio-crude oil more suitable for upgrading into "drop-in" transportation bio-fuels, where suitability is a function of the molecular weight, aromaticity, and heteroatom content. This is done by using a comprehensive suite of characterization methods on HTL bio-crude oils produced under varying operating conditions. Data from this study represents the first time that HTL light and heavy bio-crude oil chemistries from a high-lipid and high-protein algae species are compared directly.

2. Materials and methods

2.1. Algae production and hydrothermal liquefaction

A starter culture of *Nannochloropsis salina* (CCMP1776) was obtained from the Provasoli-Guillard National Center for Culture of Marine Phytoplankton (CCMP). The starter culture was expanded in 20 L carboys then transferred to an outdoor photobioreactor system (Solix Algredients, Fort Collins, CO), located at the NMSU Algal Growth Facility in Las Cruces, NM. The algae were grown in 200 L batch cultures in f/2 growth medium with 2% ocean salts. *Galdieria sulphuraria* (CCMEE 5778.1) was identified by the Culture Collection of Microorganisms from Extreme Environments (University of Oregon). The strain was grown in a modified cyanidium medium where the pH was adjusted to 2.5 with 10 N H_2SO_4. The algae were grown in the same outdoor photobioreactor system using natural photoperiod and light intensity. The temperature in the enclosed growth bags was substantially hotter than the ambient air temperature. Algal cultures were harvested and concentrated by a custom-built high speed continuous centrifuge (AC26VHC, Type 265322CD, Pennwalt, India) at 15,000 rpm for 1–2 h with a flow rate of 8 L/min. Samples were stored at −20 °C prior to use. Algae biomass characterization methods and growth media composition are detailed in the supplemental information.

HTL experiments were performed in a 1.8 L Model 4572 stainless steel batch reactor with a Model 4848B controller unit (Parr Instrument Co., Moline, IL). Algae slurries of different solid concentrations (5 and 10 wt.%) were converted at temperatures of 310, 330 and 350 °C and reaction times of 5, 30, and 60 min. The HTL products: light bio-crude oil (LBO), heavy bio-crude oil (HBO), char, and aqueous phase, were recovered using a hexane extraction procedure, followed by char rinsing with dichloromethane (DCM), and then solvent evaporation at 50 °C using a rotary evaporator. The hexane-soluble product was designated as LBO; the hexane-insoluble, DCM-soluble fraction was designated as HBO. Both LBO and HBO fractions were stored in sealed glass containers at 4 °C prior to analysis. The hexane and DCM were analytical grade (Pharmco-Aaper, Shelbyville, KY). Yield and reaction ordinate calculations are shown in the supplemental information.

2.2. Characterization of bio-crude oils by FT-ICR-MS

Bio-crude oil samples were diluted in 1:1 chloroform:methanol (HPLC grade, Sigma-Aldrich, St. Louis, MO) to a concentration of 1 mg/mL, then to a final concentration of 250 μg/mL in 1:3 chloroform:methanol with 1% formic acid. Positive-ion electrospray ionization ((+) ESI) FT-ICR MS was performed with a hybrid linear ion trap, 7T FT-ICR mass spectrometer (LTQ FT, Thermo Fisher, San Jose, CA) equipped with an Advion TriVersa NanoMate system (Advion, Ithaca, NY). Multiple 300 individual time-domain transients were co-added,

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