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Impact of iron porphyrin complexes when hydroprocessing algal HTL biocrude

Jacqueline M. Jarvis [a], Nilusha M. Sudasinghe [a], Karl O. Albrecht [b], Andrew J. Schmidt [b], Richard T. Hallen [b], Daniel B. Anderson [b], Justin M. Billing [b], Tanner M. Schaub [a,*]

[a] Chemical Analysis and Instrumentation Laboratory, College of Agricultural, Consumer and Environmental Sciences, New Mexico State University, 945 College Avenue, Las Cruces, NM 88003, USA
[b] Chemical and Biological Processes Development Group, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA

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ABSTRACT

We apply Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) for direct characterization of iron-porphyrins in hydrothermal liquefaction (HTL) biocrude oils derived from two algae: *Tetraselmis* sp. and cyanobacteria. The iron porphyrin compounds are shown to cause catalyst bed plugging during hydroprocessing due to iron deposition. Inductively-coupled plasma optical emission spectrometry (ICP-OES) was utilized for iron quantitation in the plugged catalyst beds formed through hydroprocessing of the two HTL biocrudes and identifies an enrichment of iron in the upper five centimeters of the catalyst bed for *Tetraselmis* sp. (Fe = 100,728 ppm) and cyanobacteria (Fe = 115,450 ppm). Direct infusion FT-ICR MS analysis of the two HTL biocrudes with optimized instrument conditions facilitates rapid screening and identification of iron porphyrins without prior chromatographic separation. With FT-ICR MS we identify 138 unique iron porphyrin compounds in the two HTL biocrudes that have similar carbon number and double bond equivalent distributions to the metal porphyrins (e.g. Ni and V) reported for petroleum. No iron porphyrins are observed in the cyanobacteria HTL biocrude after hydroprocessing, which indicates that iron porphyrin structures in the HTL biocrude are degraded during hydrotreatment. Hydrodemetallization reactions that occur through hydroprocessing of HTL biocrudes could be responsible for the decomposition of iron porphyrin structures leading to metal deposition in the catalyst bed that result in catalyst deactivation and bed plugging, and must be addressed for effective upgrading of algal HTL biocrudes.

1. Introduction

Hydrothermal liquefaction (HTL) technology is a current forerunner for biomass-to-oil conversion for high-moisture feedstock. Algal HTL biocrude is substantially more complex than directly-harvested plant oils such as vegetable or palm oil and has elevated heteroatom content (i.e., N, O, P, S) that is addressed by hydroprocessing. Detailed characterization of all algal HTL products and process intermediates has been identified as a critical research need for technology advancement [1].

Unlike other thermochemical processes (e.g., pyrolysis, gasification), the HTL approach eliminates the energy requirement for water removal/drying of wet feedstock [2]. Through the HTL process biomass slurry at ~5–20% solids [3] is subjected to elevated temperature (280–370 °C) and pressure (10–25 MPa) to produce liquid hydrocarbon oil as a principal product with biochar solids, aqueous- and gas-phase by-products [4]. Algal hydrothermal liquefaction oil has an energy density comparable to that of petroleum crude (42 MJ/kg) with reported heating values of 40–50 MJ/kg (*Botryococcus brauni*) [5].

Catalytic hydrotreatment is the preferred method for removal of polar heteroatomic species from HTL biocrude. The process involves treatment of HTL biocrude with hydrogen (35–170 bar H_2) in the presence of heterogeneous catalysts (e.g. sulfided Co–Mo, Ni–Mo) at high temperature (300–450 °C) and liquid hourly space-velocity of 0.2–10 h^{-1} [6]. Catalytic hydrotreatment, though expensive, is also used by the petroleum industry for the removal of sulfur, nitrogen, oxygen, and metals from heavy petroleum fractions, and to saturate olefins and aromatic compounds. Catalytic hydrotreatment appears likely for commercial-scale biofuel production where existing infrastructure can be utilized for bio-oil treatment [6].

* Corresponding author.
E-mail address: tschaub@nmsu.edu (T.M. Schaub).

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Fast pyrolysis bio-oils are thermally unstable and plug hydrotreatment reactors unless they are first stabilized [7,8]. In contrast, HTL oils are thermally stable and can be directly upgraded without prior low-temperature stabilization [8]. Recently at Pacific Northwest National Laboratory (PNNL), continuous hydrotreatment of HTL biocrudes from lignocellulosic feedstocks (e.g., wood and corn stover where iron content is less than 35 ppm) has been performed for hundreds of hours on-stream without catalyst bed plugging necessitating run termination [9,10]. However, catalyst beds used to hydrotreat algal-derived HTL biocrudes (Fe > 700 ppm) have been found to plug after only tens of hours of continuous processing. Analysis of the catalyst reactor has shown unexpectedly high concentration of iron near the head of the catalyst beds in all cases.

Metal-containing species (e.g., porphyrins) in petroleum cause bed plugging, increase coke formation, deactivate catalysts during upgrading and stabilize water-in-oil emulsions [11–13]. Porphyrins have high thermal stability which makes them difficult to eliminate [13] and metals within porphyrin complexes rapidly degrade catalysts. Nickel and vanadium are the two most abundant metals found in porphyrin structures in petroleum crude oil and concentration of 20–100 ppm and 50–250 ppm, are observed [13–15]. Iron is also present at high concentration (150–1000 ppm) within petroleum-based oils. However, high iron content largely originates from pipeline rust and is not of geochemical significance [13].

Recently, FT-ICR MS has been used to identify problematic compounds for petroleum refining operations [16–19]. The isolation of organometallic complexes from heavy crude oil has been reported [20–24] along with subsequent characterization by mass spectrometry [25–28]. FT-ICR MS coupled with atmospheric pressure photoionization (APPI) or electrospray ionization (ESI) has been used to characterize nickel and vanadyl porphyrins from heavy petroleum crude oil and natural seeps [12,15,29–34]. Here, we apply electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) to identify organometallic complexes, specifically iron-containing porphyrins, for the first time within algal HTL biocrudes. These compounds are responsible for bed plugging observed during hydrotreatment of the algae HTL biocrude.

2. Materials and methods

2.1. HTL biocrude production

HTL biocrudes were produced in one of two bench-scale continuous flow reactor systems (see Fig. A1). The *Tetraselmis* sp. composite biocrude was derived from a series of five HTL tests performed in a hybrid reactor system that combines plug flow reactor (PFR) components with a small continuous stirred tank reactor (CSTR) [33]. The cyanobacteria feedstock was processed in a single test in a recently commissioned reactor system that was configured to bypass the CSTR and rely solely on a plug flow tubular reactor. For both systems, the feedstock slurry (17.0–27.3 wt.% DAF *Tetraselmis* sp., 14.7 wt.% DAF cyanobacteria) is brought to operating pressure (3000 psig target, actual pressure 2910–3070, average 2970 psig *Tetraselmis*, 2930 psig cyanobacteria) and continuously fed to the reactor system using dual Teledyne Isco syringe pumps. In the hybrid configuration, the slurry is heated in a tube-in-tube, oil jacketed heat exchanger, then brought to HTL reactor temperature (350 °C target, actual temperatures 339–350 °C, average 346 °C Tetraselmis, 344 °C cyanobacteria) in the CSTR. Rapid mixing in the CSTR facilitates heat transfer and accommodates product slurry swelling. The liquefied slurry then proceeds to a tubular reactor that provides the requisite residence time (liquid hourly space velocity (LHSV) was 2.2 L/L/h for *Tetraselmis* sp.). In the PFR-only system, the CSTR is bypassed and the first heat exchanger is used to increase the temperature to 325 °C before entering the main tubular reactor (LHSV was 2.5 L/L/h for cyanobacteria). Downstream of the reactors, solids are removed from the product stream in a settling and filtration vessel where precipitated minerals settle to the bottom while liquids pass overhead through a stainless steel filter. After solids removal, the product is cooled to 40–70 °C and collected in one of two oil jacketed separators/collection vessels. At timed intervals, one vessel is isolated from the system and product collection is directed to the other vessel. The isolated vessel is depressurized, the product is retrieved, and the gravity separable HTL biocrude is separated from the aqueous phase. The yield of gravity separable biocrude (no solvent extraction) as a percentage of the mass of DAF feed solids ranged from 34 to 45 wt.% for the *Tetraselmis* sp. tests and was 27 wt.% for the cyanobacteria test.

2.2. HTL biocrude hydroprocessing

HTL biocrude samples were hydroprocessed in a continuous mini-hydrotreater system at PNNL, as previously described by Elliott et al. [35]. Two HTL biocrudes (*Tetraselmis* sp. and cyanobacteria) were hydroprocessed in separate runs. The catalyst was identical for both tests, but the bed was configured differently in each case. The $CoMo/Al_2O_3$ catalyst (Alfa Aesar, Ward Hill, MA, USA. Product No. 45579) was supplied as extrudates in the oxide form and reported by the supplier to consist of 3.4–4.5% cobalt oxide and 11.5–14.5% molybdenum oxide on alumina. For the *Tetraselmis* sp. test, 20 mL/14.4 g of catalyst was ground and sieved to −30/+60 mesh and loaded into the reactor. On top of the catalyst bed, ~4 mL/2.1 g of catalyst was loaded as unground extrudate. For the cyanobacteria test, 12 mL/7.7 g of catalyst was ground to −30/+60 mesh on top of which another 12 mL/8.7 g of unground extrudate was added.

The catalyst was sulfided with 35 wt.% di-tertbutyl disulfide (DTBDS, Sigma Aldrich, St. Louis, MO, USA) in decane prior to the introduction of HTL biocrude for both tests. Next, the reactor was pressurized to 1500 psig with H_2 and the H_2 flow was allowed to stabilize prior to heating the reactor to 150 °C. The DTBDS/decane solution was introduced with a nominal flow rate of 0.16 mL solution/mL catalyst/h (volumetric flow rate determined at 21 °C). The volume of the extrudate and sized material was included in the catalyst volume calculation. Hydrogen gas was added at nominally 2000 SCCM/mL sulfiding solution. The temperature was then ramped at 1.4 °C/min to 400 °C and held for 4 h. The HTL biocrude was introduced to the reactor immediately after sulfiding.

Reactor conditions for the *Tetraselmis* sp. HTL biocrude hydrotreatment were nominally 400 °C and 1500 psig. The temperature profile of the bed was measured periodically at 2.5 cm intervals during the run via an internal thermowell. The volumetric feed rate of the HTL biocrude was 0.1 mL/min (measured at 40 °C). The mass flow rate of the HTL biocrude was 0.093 g/min (dry basis). Hydrogen gas was co-fed to the system at 125 SCCM. The *Tetraselmis* sp. HTL biocrude was processed for 102 h, after which a buildup of system pressure led to system shutdown. The system was then cooled, depressurized and the catalyst bed recovered. The observed plug was characterized as a hardened section of the catalyst bed that was solidified to the point that drilling was required to remove it. Extrudate above and sized catalyst below the plug were free flowing upon catalyst bed recovery.

The cyanobacteria hydroprocessing test utilized separate heat zones for the extrudate and sized portions of the catalyst bed. The nominal temperature for the extrudate bed portion was 370 °C. The temperature in the portion of the catalyst bed consisting of the sized catalyst particles was 400 °C. The temperature