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Full Length Article

Extraction, characterization, purification and catalytic upgrading of algae lipids to fuel-like hydrocarbons

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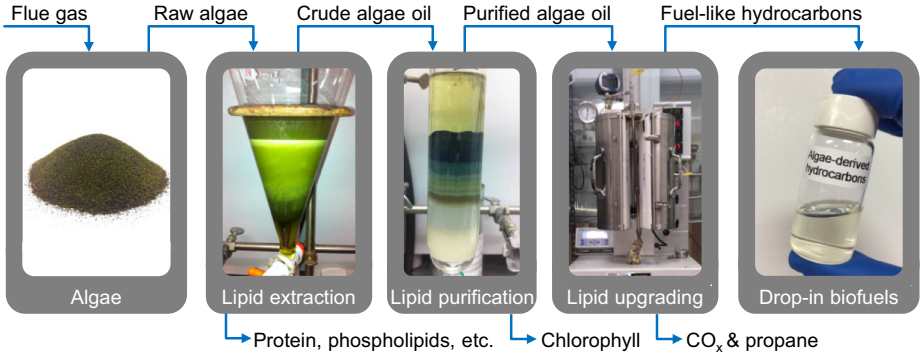
HIGHLIGHTS

- Lipids were extracted from algae grown with flue gas from a coal-fired power plant.
- Extracted lipids were purified via column chromatography using low-cost adsorbents.
- Purified lipids were catalytically deoxygenated to afford fuel-like hydrocarbons.
- Catalyst deactivation due to polyunsaturated lipids in the feed was observed at 260 °C.
- Upgrading at 300 °C resulted in increased catalyst stability and diesel yields >75%.

GRAPHICAL ABSTRACT



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ABSTRACT

The extraction, characterization, purification and upgrading of algal lipids was examined, utilizing *Scenedesmus acutus* microalgae grown with flue gas from a coal-fired power plant. Lipid extraction was achieved using a procedure based on the Bligh–Dyer method, modified so as to utilize a significantly decreased solvent:biomass ratio than the original protocol. Both activated carbon and K10 montmorillonite were found to function as efficient adsorbents for the removal of chlorophyll, phospholipids and sterols from the crude algae oil. The yield of purified lipids using this approach was similar to that obtained by in situ transesterification of the lipids in *S. acutus*, confirming that adsorption is an effective method for the removal of non-esterifiable lipids. During the deoxygenation of the purified algae oil at 260 °C over a Ni–Al layered double hydroxide catalyst, deactivation of the catalyst was observed, attributed to the presence of highly unsaturated lipid chains which can act as poisons by adsorbing strongly to the catalyst surface and/or acting as precursors to coke formation. However, upgrading at 300 °C gave better results, the liquid product consisting of ~99 wt% hydrocarbons, diesel-like (C10–C20) hydrocarbons constituting 76 wt% of the liquid after 4 h on stream.

1. Introduction

Microalgae present a variety of advantages over terrestrial plants for the production of renewable fuels and chemicals. Chief among these is the fact that many species of algae exhibit high

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growth rates and can be grown on non-arable land using wastewater, thus avoiding undesirable competition with food crops for land and water resources [1]. Of late, the genetic manipulation of algae has also attracted interest as a means of making these organisms a better feedstock for the manufacture of a wide range of industrial products, including pharmaceuticals, aquaculture feed and biofuels [2].

Microalgae can be processed through a variety of methods to yield a diverse set of products depending on local demand and profitability. One approach involves the hydrothermal liquefaction (HTL) of whole algal biomass to produce bio-oil – a viscous, corrosive and unstable mixture of organic compounds that can be subsequently upgraded into liquid fuels. HTL has the advantage of utilizing wet algal biomass with little to no pre-processing [3]; however, if microalgae are to become a financially viable feedstock for the production of fuels, fractionation must be undertaken to extract high value components which are typically destroyed during HTL. These compounds include protein, pigments such as carotenoids, and nutraceuticals such as polyunsaturated fatty acids (PUFAs). Given the valuable nature of many of these compounds, any viable biofuel production process must be accompanied by the isolation and monetization of these commodities [1].

Another important step in the development of an economically sound algal fuel production scheme is the implementation of an efficient and cost-effective lipid extraction methodology. Various techniques have been utilized to isolate lipids from algal biomass, including solvent extraction, supercritical fluid extraction, ultrasonication, and expelling/pressing [4]. Among the assortment of both emerging and mature extraction technologies, solvent-based extraction is still the most prevalently utilized technique for isolating lipids from oleaginous biomass. This type of process is considered attractive not only due to its simplicity and effectiveness, but also because the extraction solvent can typically be recycled. Remarkably, the extraction method first published by Bligh and Dyer in 1959 [5] which utilizes a chloroform–methanol-water solvent system, is still in widespread use today – along with its several variants [6,7]. However, while the Bligh–Dyer method is considered a standard method for total lipid determination [8], it is not used at commercial scale due to the large amounts of solvent required and that fact that it is only effective for dry algal biomass.

Extracted algal lipids contain typically a number of compounds that are unsuitable for upgrading to fuels, as well as potentially valuable compounds which ideally should be isolated prior to catalytic upgrading. The most prevalent of these undesirable compounds in crude algae oil is chlorophyll, a magnesium-porphyrin complex. Similar metallic complexes have been demonstrated to poison the type of metal-based deoxygenation catalysts typically used to upgrade lipids to fuels through the adsorption of the metal center, which is followed by accelerated coke formation due to the highly aromatic nature of the chelating porphyrin ring [9]. As a result, the development of a lipid purification strategy is essential to render algal lipids a viable feedstock for deoxygenation processes.

While liquid transportation fuels can be obtained from lipid-based feeds by converting the latter to the Fatty Acid Methyl Esters (FAMEs) that constitute biodiesel, the high oxygen content of FAMEs results in a number of undesirable properties that make biodiesel a less than ideal biofuel. Consequently, attention has shifted to deoxygenation processes capable of converting lipids to drop-in hydrocarbon fuels [1,10]. Hydrotreating – a process mostly based on the hydrodeoxygenation (HDO) reaction – represents the most commonly used approach to achieve this transformation. However, this approach has a number of disadvantages, as it requires high pressures of hydrogen and employs problematic sulfided catalysts that risk contaminating the products with sulfur and which deactivate in the presence of water, the latter being a product of the HDO reaction. Interestingly, it has recently been reported that supported iron nanoparticles constitute an efficient and sulfur-free catalyst for converting algae oil to green diesel [11]. However, the reaction proceeds mostly via HDO, meaning that this approach still has the drawback of high hydrogen consumption. Deoxygenation via decarboxylation/decarbonylation ($deCO_x$) represents a promising alternative to hydrotreating, since this reaction can proceed at lower temperatures over simple (non-sulfided) metal catalysts and under lower pressures of hydrogen [1,10], thereby minimizing the process costs for fuel production from algae [12]. It is also worth noting that both the energy balance and the techno-economic analysis of $deCO_x$-based processes to convert lipids to fuel-like hydrocarbons have been performed, these processes being found to be 89.6% energy efficient, more economically competitive than hydroprocessing-based approaches and potentially competitive with petroleum depending on the relative prices of the lipid and petroleum feedstocks [13]. Admittedly, most work to date on the $deCO_x$ of lipids to fuel-like hydrocarbons has focused on catalysts based on precious metals such as Pd and Pt, the cost of which may limit their industrial application [1]. However, recent work has shown that comparable yields of fuel-like hydrocarbons can be obtained over inexpensive and recyclable Ni-based catalysts [14–17], the transformation of triglycerides and related compounds to green diesel over these formulations being the subject of a recent critical review by Kordulis et al. [18]. In addition, these catalysts have shown promise in the upgrading of algal lipids in both batch [19–21] and continuous mode [21–24].

While recent contributions from our group focused on the cultivation of microalgae using flue gas from a coal-fired power plant [22] and on the study of Ni-based catalysts capable of upgrading model and algal lipids to fuel-like hydrocarbons via $deCO_x$ [23,24], details of the extraction, purification and characterization of the algae oil fell outside of the scope of these articles. In this contribution, the extraction, characterization, purification and upgrading of algal lipids is presented, utilizing *Scenedesmus acutus* grown with flue gas as the CO_2 source. Lipid extraction was conveniently accomplished using the Bligh–Dyer method, albeit this cannot be considered an industrially viable method for the reasons indicated above. Rather, emphasis is placed on demonstrating the technical feasibility of using low-cost adsorbents to afford purified algal lipids amenable to catalytic upgrading. Finally, we report the continuous catalytic upgrading of the purified algae lipids to fuel-like hydrocarbons via $deCO_x$ over a Ni–Al layered double hydroxide (LDH) catalyst.

2. Materials and methods

2.1. Reagents

The Ni–Al LDH catalyst employed was prepared using a previously described method [25] and was determined to be $[Ni_{0.67}Al_{0.33}(OH)_2][CO_3]_{0.17}\cdot mH_2O$ by elemental analysis. Reagents purchased from Fisher Scientific included chloroform (HPLC grade), acetone (histological grade) and diethyl ether (laboratory grade). Dodecane (>99%) and cyclohexanone (>99%) were obtained from Alfa Aesar. Silica gel (SiliaFlash® P60) was purchased from SiliCycle. The Supelco® 37 Component FAME Mix, activated charcoal (Darco® KB-G), K10 montomorillonite, toluene (anhydrous, 99.8%), methanol (anhydrous, 99.8%), glyceryl heptadecanoate (⩾99%), methyl nonadecanoate (analytical standard), potassium methoxide (95%) and chloroform-d were procured from Sigma Aldrich. Phytol (distilled) was obtained from MP Biomedicals, LLC. D_2O was purchased from Cambridge Isotopes Laboratories, Inc.