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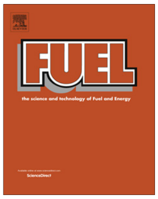

Water-washing to reduce metals in oils extracted from Nannochloropsis algae for potential FCC feedstock

Chengrong Wang [a,*], J. Scott Buchanan [b], Wayne R. Kliewer [b], Kuangnan Qian [b]

[a] *ExxonMobil Research and Engineering, 600 Billingsport Road, Paulsboro, NJ 08066, United States*
[b] *ExxonMobil Research and Engineering, 1545 Route 22, Annandale, NJ 08801, United States*

HIGHLIGHTS

- Organic oils can be extracted from algae using solvents such as ethanol.
- The oils metals levels are too high for inclusion in refinery cracker feedstock.
- Washing the extracted oil with water was ineffective at removing the metals.
- Washing the algae with water prior to solvent extraction greatly reduced metals.
- The resulting oil could be co-fed to a cracking unit at a 2% level in the feed.

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ABSTRACT

Algae cultivation offers the potential to produce biofuels with much higher productivity than conventional soil-based crops. Organic oils can be extracted from algae using solvents such as alcohols and paraffins. A challenge is to define the most economical means to process these extracted oils into products such as chemical intermediates and liquid fuels. One approach is to add algal oils directly into the petroleum-based feeds to existing refinery processes such as fluid catalytic cracking (FCC) or hydroprocessing. Maximum acceptable levels were defined for contaminants such as sodium, potassium, calcium, phosphorus, and nitrogen in the feed to an FCC unit, based on refinery experience. Cracking runs in a laboratory unit confirmed the large decrease in conversion for high levels of sodium and potassium. For a laboratory sample of Nannochloropsis algae, the level of metals was far too high in the whole algae or in oils extracted from the algae using ethanol or n-heptane to allow their inclusion in FCC feedstock, even at a level of 2% algal product in the FCC feed. Washing the extracted oil with water removed only modest amounts of metals. It was found that washing the algae with water first, and then doing solvent extractions, resulted in oils with metals levels low enough for co-feeding to an FCC unit at a level of 2%. The oil yields by mass from the starting algae from this route were 21% for ethanol solvent, and 10% for heptane solvent. If an FCC unit were completely dedicated to bio-feeds without the necessity of co-processing petroleum feedstocks, the unit might operate with a different catalyst and different set of operating constraints, but that is beyond the scope of this study.

1. Introduction

Algae are fast-growing organisms with the potential to produce high volumes of biofuels [1–4]. Some algae can grow on non-productive land and utilize brackish water to minimize concerns of competing with agriculture for limited natural resources [1,2].

To obtain fuels that are useful in application such as internal combustion engines, some sort of processing must typically be applied to the bulk algae. Various approaches have been proposed to transform the whole algae into useful liquid or gaseous fuels and chemicals. These approaches include hydrothermal processing with high pressure and high temperature, and organic solvent extraction to recover the algae oil. For solvent extraction process, algae cell membrane disruption, either via physical or chemical means, is typically necessary to achieve high oil recovery.

A typical initial processing step is to remove water (either via extraction or direct drying). The dried algae may then pass through a mechanical milling step to lyse the cell membrane. A solvent extraction may be carried out to recover the algae oil, which can

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* Corresponding author. Tel.: +1 856 224 2060; fax: +1 856 224 3633.
E-mail address: Chengrong.Wang@ExxonMobil.com (C. Wang).

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be further processed via polar and non-polar solvent partition to separate the non-polar lipids (glycerides) from polar components. In some cases, the algae cell membranes can be ruptured during the solvent extraction and thus the mechanical lysing step may be omitted.

Adding algal-derived materials to the feeds of existing refinery units offers a cost-effective means to insert bio-feeds into the existing system for producing fuels and chemicals. "Algal-derived materials" here could be whole algae (with or without rigorous dewatering), or some fraction or extract of the algae. Key conversion units in refineries include the fluidized catalytic cracking (FCC) and hydroprocessing (HDP) units, which utilize catalysts to promote desired reactions such as cracking and the removal of heteroatoms by hydrogen insertion.

A number of reviews have appeared on the catalytic processing of bio-derived feedstocks [5–8]. Idem et al. [9] cracked canola oil over various acidic and basic catalysts in a fixed-bed reactor, and compared reaction yields to those from an empty reactor (thermal cracking). The choice of catalyst had little impact on the initial cracking of canola oil to long chain hydrocarbons and oxygenates, but did affect the secondary reactions. Secondary cracking was enhanced by the catalysts which were amorphous and non-basic (silica, alumina, and silica–alumina), resulting in more gas and light liquid products. ZSM-5 catalysts, with no aluminum and with Si/Al = 56, moderated the secondary cracking, producing high yields (26–27 wt%) of aromatics. Basic catalysts (calcium and magnesium oxides) somewhat dampened secondary cracking, giving lower gas yields.

Corma et al. [10] cracked biomass-derived oxygenates (glycerol, sorbitol) in a fixed-bed MAT unit. At a typical FCC MAT test temperature of 500 °C, glycerol gave relatively high yields of coke (e.g. about 40% coke at 80% conversion) with alumina and with commercial (faujasite-based) FCC catalysts. The highest yields in gases were: CO > propene > CO_2 > ethene. ZSM-5 catalyst gave lower coke and higher ethylene. Sorbitol gave similar yields as glycerol, except for higher CO. When glycerol was co-fed with a vacuum gasoil, both feed components were converted, with gas yields lower than expected from a simple additive effect.

Dupain et al. [11] cracked rapeseed oil in a riser-type reactor under realistic FCC conditions. At their short contact time conditions, they observed only water as an oxygenate product, not CO or CO_2. The triglycerides were largely converted to fatty acids within 50 ms through radical cracking reactions. The resulting unsaturated fatty acids from rapeseed rapidly aromatized, forming relatively stable heavy liquid products. When a fully-saturated stearic acid feed was used, the aromatics yield was lower, and there was more cracking down to gases and gasoline-range liquids.

These prior publications deal mainly with idealized or clean oxygenate feeds. This seems appropriate when treating vegetable oils or animal fats, which consist mainly of triglycerides with low metals contents.

Tran et al. [12] reviewed catalytic upgrading of oils from algae. The work discussed there typically involved short-term laboratory experiments. For longer-term runs, however, the oils extracted from algae can have levels of metals that are high enough to interfere with conventional refinery operations.

A constraint on these units is the amount of metals and phosphorus that can be tolerated by the catalyst while retaining acceptable catalytic activity and selectivity and longevity. If catalyst change-out intervals or rates are kept within the industry norms, this translates to effective maximum desirable levels of these contaminants in the feed. In typical petroleum operations, the metals in the feeds that are of most concern are nickel and vanadium. These metals are commonly present in algae at levels much lower than the alkalis, so our focus here is on the basic metals rather than nickel or vanadium. Bi and He [13] characterized five green and three brown microalgae for their potential application in biofuels. The brown algae, with high ash contents (up to 43.4 wt% on dry basis), were deemed less suitable for conversion to biofuels. Multiplying the ash contents by the mineral contents in the ashes, for the five green algae the average levels of sodium, potassium, and calcium in the dry algae were 1.4 wt%, 1.5 wt%, and 0.6 wt%, respectively.

For instance for FCC, some typical maximum contaminant values are shown in Table 1. At these levels of metals on catalyst, significant performance deterioration is expected, so normally metals levels are kept below these maximum values. The assumption here is that the catalyst consists of the faujasite-based acidic composite which has proven over many decades to be the most effective material for cracking the primary vacuum gasoil FCC feed. If an FCC unit were completely dedicated to bio-feeds without the necessity of co-processing the petroleum stock, the unit might operate with a much different set of constraints, including a non-faujasitic base catalyst, but that is beyond the scope of this study. Faujasite is a type of zeolite, with acidic sites formed on the walls of the micropores. Calcium and alkali metals can deactivate the catalyst by titrating these acid sites, and can also accelerate long-term structural breakdown of the zeolite in the FCC unit.

The translation in Table 1 from levels on catalyst to levels in feed assumes a relatively high catalyst make-up rate of 0.32 lb catalyst/bbl feed, such that 1 ppm metals in feed gives 1000 ppm (0.1%) on catalyst. For a given maximum level of a contaminant in the overall feed to the FCC, one can calculate the maximum acceptable level of that contaminant in some component of that feed. For instance, if an algal component was present in at a level of 5% by weight in the feed, then in order to maintain the level of sodium below 8 ppm in the overall feed, the sodium level would have to be less than 0.016% in the algal component. If the algal concentration in the feed were reduced from 5% to 2%, then a higher level (0.04%) of sodium could be tolerated in the algal component. These values are also listed in Table 1. They provide a target for metals reduction in the algal component, if that component is intended to be included in the feed to the FCC.

High levels of these contaminants are detrimental in hydroprocessing as well as in catalytic cracking. However, it can be more difficult to define specific levels of metals in hydroprocessing feeds that are acceptable or unacceptable than for FCC, since practices with guard bed change-out vary. Rapid change-out, especially with swing operation of two guard beds, can help protect the main catalyst bed from high levels of metals in the feed.

To quantify the effects in FCC of the high alkali levels associated with algal components, experiments were done in a laboratory FCC using catalyst which was spiked with sodium and potassium. These experiments verified the degradation of cracking performance with high levels of alkali. Accordingly, research was carried out to determine effective means to remove metals from algal components to prepare them as potential FCC feed extenders.

Table 1
Typical maximum acceptable levels of contaminants by weight on FCC catalyst and in FCC feed; corresponding maximum levels in an algal component in FCC feed, at two concentrations of algal component within the FCC feed.

	Typ. max. on FCC cat. (wt%)	Typ. max. in FCC feed (ppm)	Max. in algal for 5% algal in FCC feed (wt%)	Max. in algal for 2% algal in FCC feed (wt%)
Na	0.8	8	0.016	0.04
K	1	10	0.02	0.05
Ca	0.8	8	0.016	0.04
P	5	50	0.1	0.25
N	–	5000	10	25