# Continuous catalytic deoxygenation of model and algal lipids to fuel-like hydrocarbons over Ni–Al layered double hydroxide

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## ARTICLE INFO

## ABSTRACT

The deoxygenation of lipid-based feeds to diesel-like hydrocarbons was investigated over a series of oxide-supported Ni catalysts. Catalyst screening in a semi-batch reactor revealed that a Ni–Al layered double hydroxide formulation afforded a higher yield of hydrocarbons in the diesel range than 20 wt% $Ni/Al_2O_3$, 20 wt% $Ni/ZrO_2$, 20 wt% and $Ni/La-CeO_2$ (lanthanum-stabilized ceria). Through a series of fixed bed reactor experiments involving model lipids in which reaction conditions – including temperature, hydrogen partial pressure and feed to catalyst ratio – were systematically changed, the effects of these variables on catalyst performance were elucidated. Based on the results of these experiments the optimum set of conditions was identified and applied to the conversion of realistic feeds, including the oil extracted from algae cultured using flue gas from a coal-fired power plant. Catalyst stability studies showed Ni–Al layered double hydroxide to be a stable formulation, no significant loss of activity being observed between 6 and 72 h on stream under conditions known to promote catalyst deactivation, namely the use of an unsaturated feed – comprising both a triglyceride and a considerable amount of free fatty acids – in high concentration.

## 1. Introduction

Dwindling petroleum deposits and environmental concerns have spurred the search for alternatives to fossil fuels. Biofuels represent a renewable alternative with the potential of closing the carbon cycle without disrupting the food supply if the use of arable land and deforestation are avoided, which is why waste and non-edible biomass sources are preferred [1,2]. Due to their similarity to diesel fuel, lipid feeds have attracted a great deal of interest, waste and non-edible streams – such as brown grease, yellow grease, tall oil, tallow and algae oil – being particularly favored [3].

Traditionally, lipid feeds have been converted to the mixture of fatty acid esters commonly known as biodiesel. However, biodiesel is a less than ideal fuel due to a number of issues stemming from its high oxygen content. Therefore, attention has shifted to catalytic methods capable of deoxygenating lipid-based feeds to afford hydrocarbons that are entirely fungible with petroleum-derived fuels and thus are compatible with existing infrastructure [4]. Hydrotreating – a process mostly based on hydrodeoxygenation

(HDO) in which oxygen is eliminated as $H_2O$ – represents one of these catalytic methods. Unfortunately, this approach requires sulfided catalysts that risk contaminating the products with sulfur and high hydrogen pressures that are typically only available in centralized facilities. However, an alternative approach in which deoxygenation is accomplished via decarboxylation ($-CO_2$) and/or decarbonylation ($-CO$) has recently been reported [5].

Compared to HDO, decarboxylation/decarbonylation ($deCO_x$) has the advantage of proceeding under considerably lower hydrogen pressures and over simple supported metal catalysts. Admittedly, most $deCO_x$ work reported to date in the literature involves catalysts based on either Pd or Pt, the cost of which may be prohibitive. Nevertheless, recent results indicate that Ni-based catalysts can display comparable performance to precious metal catalysts in the conversion of lipids to fuel-like hydrocarbons via $deCO_x$ [6,7], which is particularly promising due to the fact that the cost of Ni is thousands of times lower than that of Pd or Pt. However, studies of lipid $deCO_x$ over Ni-based catalysts in continuous mode are limited in number [8–11], and to date continuous studies involving triglyceride model compounds are virtually nonexistent. Continuous processes are favored by industry and thus, the use of continuous reactors is critical both for scale up efforts and to assess the effect of long reaction times on catalyst performance [12]. Additionally, triglycerides represent one of the main constituents within the lipid-based feeds used for biofuel synthesis and the use of pure

model triglycerides stands to greatly facilitate the interpretation of results from catalytic tests. Parenthetically, some recent studies have investigated the continuous deoxygenation of fatty acid methyl esters (FAMEs) over Ni-based catalysts [13–15]; however, Gosselink et al. [4] have concluded that FAMEs are unsuitable as triglyceride models due to the different reaction pathways followed by these two families of compounds.

In this contribution, we report the continuous deoxygenation via deCO$_x$ of a model unsaturated triglyceride over a Ni-based catalyst and the effect of key reaction variables – including temperature, hydrogen partial pressure, feed to catalyst ratio, purity of the feed (free fatty acid content) and time-on-stream – on catalyst performance. In addition, the spent catalysts from representative tests are characterized in an effort to rationalize the effect of these variables, and the optimum reaction conditions identified using the model compound are applied to the continuous deoxygenation of realistic lipid-based feeds, including algal lipids.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

A layered double hydroxide (LDH) catalyst with the formula [Ni$_{0.67}$Al$_{0.33}$(OH)$_2$][CO$_3$]$_{0.17}$·mH$_2$O was prepared via co-precipitation using previously described materials and methods [16]. For simplicity, this material will be henceforth referred to as Ni–Al LDH. 20 wt% Ni/Al$_2$O$_3$, 20 wt% Ni/ZrO$_2$, 20 wt% Ni/La-CeO$_2$ (lanthanum-stabilized ceria) were all prepared via excess wetness impregnation – using an aqueous solution (unless otherwise indicated) of Ni(NO$_3$)$_2$·6H$_2$O as the metal precursor – followed by a calcination step in static air at 500 °C for 3 h. Ni(NO$_3$)$_2$·6H$_2$O (98%) was purchased from Alfa Aesar. Al$_2$O$_3$ (S.A. = 216 m$^2$/g) was obtained from Sasol. ZrO$_2$ (S.A. = 97 m$^2$/g) was supplied by Saint-Gobain NorPro. La-CeO$_2$ (S.A. = 119 m$^2$/g) was provided by Advanced Material Resources.

The surface area, pore volume and average pore radius of the catalysts before and after deoxygenation reactions were determined by means of N$_2$ physisorption using instrumentation and methods described elsewhere [16]. Temperature Programmed Reduction (TPR) measurements were performed on 20 wt% Ni/Al$_2$O, 20 wt% Ni/ZrO$_2$, 20 wt% Ni/La-CeO$_2$ after calcination and on Ni–Al LDH as synthesized using an instrument and a procedure previously described [16]. In an effort to study the nature and the amount of the carbonaceous deposits on the surface of spent catalysts, the latter were subjected to thermogravimetric analysis (TGA) under flowing air or nitrogen (50 mL/min) on a TA instruments Discovery Series thermogravimetric analyzer. The temperature was ramped from room temperature to 800 °C at a rate of 10 °C/min.

### 2.2. Characterization of lipids

Tristearin (95%) was purchased from City Chemical. Practical grade triolein (glyceryl trioleate, ~65%) and pure triolein (glyceryl trioleate, ≥99%) were purchased from Sigma-Aldrich. Technical grade oleic acid (90%) was purchased from Alfa Aesar. Soybean oil (salad oil grade) was provided by Owensboro Grain (Owensboro, KY). Algal lipids were extracted from a sample of dry *Scenedesmus* sp. – grown in a photobioreactor fed with flue gas from a coal-fired power plant [17] – by the Bligh–Dyer method [18] and purified using a column containing both montmorillonite clay and silica gel. Experimental details on both algae culturing and the lipid extraction and purification are available elsewhere [17]. The total acid number (TAN) of these feeds was determined via titration with base using a standard method of the American Society for Testing and Materials (ASTM), namely ASTM D664. The identity of the fatty acid

chains in the lipids employed in this study was determined by converting the latter to the corresponding methyl esters (by means of base-catalyzed transesterification with methanol) followed by GC analysis using an Agilent 6890A gas chromatograph equipped with a HP-88 column (30 m × 0.25 mm × 0.2 μm) and a flame ionization detector. Helium was used as the carrier gas, the flow rate was set to 1 mL/min and a split of 20:1 was employed. The temperatures of the inlet and the detector were 250 and 300 °C, respectively. The temperature program included an initial temperature of 50 °C followed by a ramp of 20 °C/min to 140 °C, an isotherm at this temperature lasting 5 min, and a subsequent ramp of 3 °C/min to a final temperature of 240 °C. The results of these analyses are collected in Table 1.

### 2.3. Deoxygenation experiments

Tristearin deoxygenation experiments in semi-batch mode were performed utilizing previously reported materials and methods [7,19]. Representative semi-batch experiments were performed in duplicate to assess the repeatability of the results, the conversion and selectivity values typically being found to have a standard deviation (SD) below 4.25%. Lipid deoxygenation experiments in continuous mode were performed in a fixed bed stainless steel tubular reactor (1/2 in o.d.) equipped with an HPLC pump. 0.5 g of Ni–Al LDH catalyst (particle size 150–300 μm) was first reduced under flowing H$_2$ at 400 °C for 3 h. After reduction, the system was taken to the reaction temperature (either 260 or 300 °C) and pressurized with H$_2$ to 580 psi. A liquid solution of the feed in dodecane (either 1.33 or 13.3 wt% for triolein and 1.33 wt% for the algal lipids) was introduced to the system at a rate of 0.2 mL/min along with a flow of H$_2$ (50 mL/min). Samples were collected from a liquid gas separator (kept at 0 °C) placed downstream from the catalyst bed. Notably, these reaction conditions are almost identical to those used by Lercher and co-workers in a recent contribution [8], the similarities extending to the reactor system employed. Representative fixed bed experiments were also performed in duplicate to assess the repeatability of the results, the vast majority of conversion and selectivity values also having a SD < 4.25%. Notably, the SD values associated with the method used for product analysis have been determined to be ≤1.85%, which suggests that part of the variability observed in the results of both semi-batch and continuous experiments stems from the method employed in the analysis of the reaction products. Finally, it should be emphasized that all these reactions involved relatively high temperatures and pressures of hydrogen, and while no difficulties were experienced while performing these experiments, appropriate precautions should always be taken when working with pressurized hydrogen and hot surfaces.

### 2.4. Product analysis

Liquid feeds and reaction products were analyzed using an Agilent 7890A GC equipped with an Agilent Multimode inlet, a deactivated open ended helix liner and a flame ionization detector (FID). A 1 μL injection was employed and helium was used as the carrier gas. The FID was set to 350 °C with the following gas flow rates: H$_2$ = 30 mL/min; air = 400 mL/min; makeup = 5 mL/min. The inlet was ran in split mode (split ratio 25:1; split flow 50 mL/min) using an initial temperature of 100 °C. Immediately upon injection, inlet temperature was increased at a rate of 8 °C/min to a final temperature of 320 °C kept for the duration of the analysis. The oven temperature (initially 45 °C) was immediately increased upon injection first to 325 °C at rate of 4 °C/min and then to 400 °C at a rate of 10 °C/min. The maximum temperature was maintained for 12.5 min, total run time being 90 min. An Agilent J&W DB-5HT column (30 m × 250 μm × 0.1 μm) rated to 400 °C