



## Full Length Article

# Continuous low pressure decarboxylation of fatty acids to fuel-range hydrocarbons with *in situ* hydrogen production



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## ABSTRACT

Fatty acids are considered as a renewable feedstock for the production of high value products such as fuel-range hydrocarbons. Decarboxylation can produce high quality fuels from fatty acids, although either high pressure or additional hydrogen is required. This study investigated a low pressure (< 500 psi) continuous decarboxylation process examining oleic acid in a continuous fixed bed reactor using activated carbon, which gave surprisingly high quality fuel-like hydrocarbons with no external hydrogen. The results showed that activated carbon performed as a catalyst for both decarboxylation and *in situ* hydrogen production. The reaction parameters for maximum degree of decarboxylation (91%) was found to be 400 °C, 2 h and water-to-oleic acid ratio of 4:1. To determine the degree of decarboxylation and reaction mechanism, the formed liquid products were examined by ATR-FTIR, Raman and GC-FID analysis, respectively. The liquid product was found to consist of mainly saturated hydrocarbons containing heptadecane (89.3% selectivity) as the major compound. The liquid product was found to have a similar density and higher heating value (HHV) to commercial diesel and jet fuel. The mechanism for decarboxylation reaction along with *in situ* hydrogen formation was proposed in this study.

## 1. Introduction

Energy security, sustainability and global climate change concerns resulting from society's energy consumption has increased our need to find renewable energy resources [1]. The large scale substitution of petroleum based fuels and products with those obtained from renewable sources is a major driving force towards sustainable development. Foremost among these concerns is the issue of the release and accumulation in the atmosphere of CO<sub>2</sub> and other climate-changing gases. Transportation fuel derived from renewable resources can be an alternative to reduce CO<sub>2</sub> emissions significantly since the largest source (27% in the United States [2]) of greenhouse gas emissions is from the burning of fossil fuels by transportation vehicles. Biodiesel (produced by the transesterification of triglycerides with methanol) is one of the most popular renewable transportation fuels which is currently used either as is, or blended with petroleum feedstocks. The chemical composition and physicochemical properties are very important for identifying the performance and emission characteristics of any fuel. Biodiesel is composed of a significant amount of oxygen containing molecules compared to conventional petroleum fuels [3]. Higher viscosity, cloud point and acid number of biodiesel can cause engine problems which prevent their usability in cold areas such as the northern

US and Canada [4]. Biodiesel has much higher kinematic viscosity [5], NO<sub>x</sub> emissions, oxidative stability and poor cold flow properties compared to conventional diesel [6,7].

On the other hand, green diesel, which is essentially free of oxygen, is almost identical to petroleum diesel. Green diesel has higher heating value, higher energy density, and a very high Cetane number (80–90) compared to biodiesel [8,9]. Fuel properties of biodiesel completely depend on the feedstock source and process configuration. In comparison, green diesel is independent of feedstock and the oxygen free liquid hydrocarbon fuel that is ready to use with conventional diesel fuel. UOP/ENI Ecofining™ process was the first commercial hydrodeoxygenation (HDO) technology to produce green diesel from biologically derived feedstocks [9]. Although HDO technology has been widely used to remove oxygen from various feedstocks to produce hydrocarbon fuels, it consumes expensive hydrogen gas [10,11]. Additionally, HDO often requires expensive platinum or palladium catalysts [12–14].

As an alternative to HDO to produce oxygen free fuel range hydrocarbons, decarboxylation can be used. Decarboxylation is simply the removal of CO<sub>2</sub> from a fatty acid chain, normally with the assistance of a catalyst. Depending on the reaction media and type of catalyst used [15–17], decarboxylation can potentially produce *in situ* hydrogen,

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although the mechanism is unclear. Although decarboxylation has mainly been studied using noble metal catalysts such as Pd or Pt in supercritical water [18–20], no report was available for complete decarboxylation until our previous study [15]. We showed that commercial activated carbon (AC) was an efficient and inexpensive catalyst for complete decarboxylation of oleic acid in a larger 300 mL stirred batch reactor. The final products were mainly straight chain hydrocarbons without an external source of hydrogen. This result motivated us to proceed to investigate this system in a continuous flow reactor, which would be required for commercial implementation.

The goal of the present study was to explore the one-step continuous decarboxylation of oleic acid (OA) into fuel range hydrocarbons in subcritical water using a fixed bed tubular reactor at relatively low operating pressure (< 500 psi) with no added hydrogen. This study also investigates the source of *in situ* hydrogen required for carbon saturation. The quality of the liquid fuel products was measured and compared to commercial fuels.

## 2. Experimental section

### 2.1. Materials

90% pure oleic acid, powder activated carbon (AC-DARCO G-60, 100–325 mesh particle size), granular activated carbon (4–14 mesh particle size) and hexanes (ACS Grade) were obtained from Sigma-Aldrich, Oakville, ON, Canada, and are used as received. De-ionized water (18.2 MΩ) was taken from a compact ultrapure water system (EASY pure LF, Mandel Scientific Co., model BDI-D7381).

### 2.2. Experimental set-up

Hydrothermal decarboxylation of OA was conducted using a bench top continuous flow through reactor (BTRS-JR, Autoclave Engineers, Erie, PA) with a maximum operating pressure 2900 psi at 650 °C. A simplified sketch of the BTRS-JR reaction system is shown in Fig. 1. The system mainly consists of a fixed bed tubular reactor (I) with a furnace assembly (J), an oven (O) and a gas liquid separator (M). The reactor (316 stainless steel reactor tube with type 316 stainless steel fittings) dimension is 0.312" I.D. × 0.562" O.D. × 11" L. The reactor was loaded with AC in each catalytic experiment. The reactor is connected to four feed lines i.e. a total of four gases or two liquids or combination of both can be entered into the reactor. This study used only three feed lines (two for liquids such as OA and water, one for N<sub>2</sub> gas) which are shown in Fig. 1. Two Isco 260 DM syringe pumps (C) were used to feed OA (A) and water (B) continuously to the reactor. N<sub>2</sub> gas (D) was used only during the heating up the reactor with AC to prevent oxidation of

carbon. A minimum flow of N<sub>2</sub> gas was maintained using metering valve because high flow rate of N<sub>2</sub> may blow out the catalyst which can plug the reactor system. N<sub>2</sub> flow was stopped after reaching the desired reaction temperature and kept the outlet valve open for few minutes to release N<sub>2</sub> before feeding the reactants. The feeds next enter the mixer vaporizer (H) where they are homogeneously mixed and vaporized. The furnace was used to heat up the reactor to obtain desired reaction temperature. The reactor with furnace assembly, feed mixture and system tubing and switching valves are all placed in a heated, insulated, stainless steel oven which allows good temperature control via the oven temperature set-point. The maximum operating temperature is 250 °C. For this study, the oven temperature was maintained at 200 °C. The gas-liquid separator (150 mL) is located outside the oven. The reactant/product gas enters the gas-liquid separator through a dip tube in the top with the product gas exiting through a tee in the top. The product gas was passed through a mass flow controller with totalizer (Q) (Omega Engineering Inc.) to quantify the amount of gas produced during decarboxylation of OA and stored in an air tight Tedlar gas bag (S) obtained from SKC Inc. (PA, USA) for further analysis. The separator was wrapped with copper coils for water cooling. A metering valve and air operated valve are connected to the bottom of the reactor to drain the liquid to a glass vial (T). After leaving the gas-liquid separator, the reactant/product stream passes through a back pressure regulator (N) to maintain the pressure set-point. System pressure was monitored by an isolated pressure gauge/transducer. System has a pressure sensor (K) at the top which helps for a sudden release of pressure through rupture disc (L) if the operating pressure exceeds the maximum allowable pressure of the system.

Before starting any experiment, the reactor and gas-liquid separator were washed thoroughly by injecting a minimum of 100 mL of hexanes to remove residuals from previous experiment and then purging with N<sub>2</sub> gas for a minimum of 15 min. Before feeding the reactants to the reactor, the outlet valve of the gas-liquid separator was opened several times during reactor heating (with nitrogen) to remove residual hexanes from the system to avoid contamination with the product.

The flow rates of reactants such as OA and water were determined for catalytic experiments by using the tapped density of powder AC (0.4 g/mL), space time (15 min to 2.5 h) and a water-to-OA ratio (v/v) (2:1–5:1) during the investigation. The space time is defined as follows:

$$\text{Space time } (\tau) = \frac{\text{Volume of catalyst used in the reactor}}{\text{Volumetric flow rate of OA and water}} \quad (1)$$

Volume of the reactor was used to calculate the space time for the noncatalytic experiments. AC loading for each of the catalytic experiments was 4 g, which is the maximum loading capacity of the fixed bed reactor. Spent catalyst was removed from the reactor after each run and

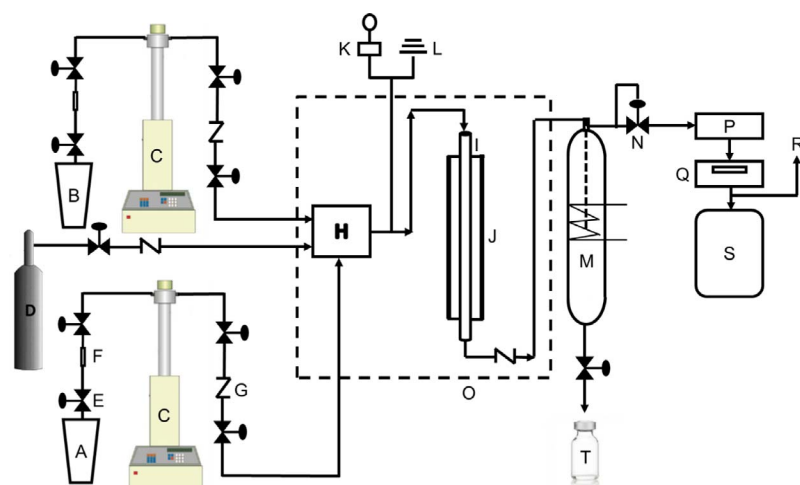


Fig. 1. Schematic of Continuous Reactor Setup: (A) oleic acid tank, (B) H<sub>2</sub>O tank, (C) Isco 260 DM syringe pump, (D) N<sub>2</sub> cylinder, (E) gate valve, (F) & (P) filters, (G) check valve, (H) mixer vaporizer, (I) tubular reactor, (J) electric furnace, (K) pressure sensor, (L) rupture disk, (M) gas-liquid separator, (N) back pressure regulator, (O) oven, (Q) mass flow controller, (R) vent, (S) gas bag, (T) glass vial.

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