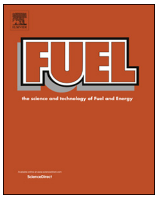
Fuel 231 (2018) 253–263

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



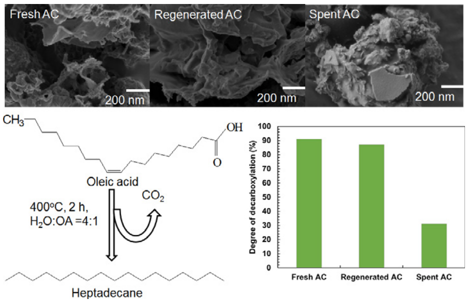
Full Length Article

Deactivation and regeneration studies of activated carbon during continuous decarboxylation of oleic acid in subcritical water

Md. Zakir Hossain, Anil Kumar Jhawar, Muhammad B.I. Chowdhury, William Z. Xu, Paul A. Charpentier*

Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario N6A 5B9, Canada

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Activated carbon
Fresh and spent catalyst
Deactivation
Catalyst stability
Regeneration
Decarboxylation

ABSTRACT

Decarboxylation of fatty acids using sub or supercritical water is a renewable pathway for producing fuel range hydrocarbons with high selectivity without an added external source of H_2. Activated carbon (AC) has been shown as an effective catalyst for decarboxylation of fatty acids to fuels but it has limited life and an unknown surface chemistry for this catalysis. This study investigates the stability (time on stream) and surface chemistry of AC for the decarboxylation of oleic acid in a bench scale continuous reactor system at 400 °C, 2 h of space time and water to oleic acid ratio of 4:1. AC was found to be effective until 30 h time on stream (out of 45 h), providing 91% degree of decarboxylation constantly. The degree of decarboxylation declined afterwards, dropping from 91 to 50% after 45 h time on stream due to deactivation. The thermal regeneration of deactivated AC was examined using potassium hydroxide (KOH) treatment at 750 °C which helped to regain the physical and catalytic properties of AC. The degree of decarboxylation of oleic acid using fresh and regenerated AC were 91% and 87%, respectively. On the other hand, the selectivity of heptadecane obtained using fresh and regenerated activated carbon was 89.3% and 81.2%, respectively. Decarboxylated liquid products using fresh and regenerated activated carbon gave a similar density and HHV's as commercial fuels, showing the utility of this approach.

1. Introduction

The increasing number of worldwide transportation vehicles and raising environmental concerns related to conventional fuels has led to an urgent need to find renewable fuels [1–3]. Transesterification of fats or oils to produce fatty acid methyl esters (FAME) is a well-known process for renewable biodiesel production [4]. However, biodiesel has limitations for use in cold countries because of its higher cloud point

---

* Corresponding author.
E-mail address: pcharpentier@eng.uwo.ca (P.A. Charpentier).

https://doi.org/10.1016/j.fuel.2018.05.068
Received 4 January 2018; Received in revised form 11 May 2018; Accepted 12 May 2018

and higher viscosity compared to convention fuels [5]. These poorer properties compared to conventional fuels is primarily due to the difference in molecular structure of biodiesel containing oxygen moieties (e.g. −COOH groups). Removal of oxygen from biodiesel can improve its stability for enhancing its integration into the fuel value chain. The hydrodeoxygenation (HDO) process was previously shown to remove oxygen from lipids but the process consumes excess hydrogen [6]. Decarboxylation is an alternative of HDO which does not require hydrogen [7–10].

The decarboxylation process normally requires a catalyst to produce higher selectivity of liquid hydrocarbons. The most efficient decarboxylation catalysts reported in the literature are precious metals such as Pt and Pd [11–15]. However, due to their rarity and high cost, alternatives such as metal catalysts or activated carbon are of interest. Transition metal catalysts have been shown to enhance mainly the cracking reactions instead of the decarboxylation reaction, leading to a lower liquid hydrocarbon yield [16,17]. Activated carbon (AC) has been found as a very effective low cost catalyst for hydrothermal decarboxylation of fatty acids and their derivatives [7,9,18]. Medina et al. [19] reported that the activity of AC depends on its surface area and surface based oxygenated functional groups. Popov and Kumar [18] had similar findings for hydrothermal decarboxylation of oleic acid in a continuous flow process in the presence of AC. Fu et al. [9] and Hossain et al. [7,20] demonstrated that the activity of AC is associated with its large surface area and narrow pore size distribution. However, very limited information is available in the literature for deactivation and regeneration studies of AC as catalyst. Hossain et al. [7] reported that deactivation of AC occurred mainly due to the deposition of impurities after the decarboxylation reaction. Some portion of fatty acids may polymerize and subsequently be deposited on the surface of AC, thus blocking the pores. On the other hand, AC is also known to participate in the steam reforming reaction to produce H_2 during decarboxylation, which may cause deactivation [20]. These phenomena are poorly understood and need to be carefully considered for potential scale-up purposes. In addition, to make the process feasible from an economic point of view, it is necessary to regenerate the deactivated catalysts and reuse them.

In this study, we examine the stability of AC and regeneration of deactivated (spent) AC from hydrothermal decarboxylation of oleic acid to both optimize this process and provide a better understanding of the catalytic mechanism. Different types of chemical activating agents for AC have been reported in the literature including $ZnCl_2$, H_3PO_4, KOH, K_2CO_3, NaOH etc. [21,22]. There is a growing interest for using alkali hydroxides as activation agents due to their low cost and high activity, with KOH being found to be very promising [23–27]. The KOH regenerated AC was characterized and compared to both fresh and spent non-regenerated AC catalyst by using BET surface area analysis and BJH pore size distribution, X-ray diffraction analysis (XRD), thermogravimetric-differential thermal analysis (TG-DTA), Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Scanning electron microscopy (SEM) analysis.

2. Experimental section

2.1. Materials

Oleic acid (90%), powder activated carbon (AC-DARCO G-60, 100–325 mesh particle size) and hexanes (ACS Grade) were purchased from Sigma-Aldrich, Oakville, ON, Canada. Potassium hydroxide (97%) and nitric acid (68–70%) were purchased from Caledon Laboratories Ltd., Gerogetown, ON, Canada. All the chemicals were 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. Regeneration procedure

Spent AC catalyst was removed from the reactor after each run, then washed with hexanes multiple times to extract the products. The spent AC was placed in a vacuum oven at 80 °C overnight prior to a second catalytic run and regeneration. Regeneration of the spent catalyst was performed by mixing with KOH (300% on wt. basis). KOH pellets were first crushed into powder and uniformly mixed with spent catalyst using a mortar and pestle. The mixture was transferred into a quartz cell and heated in a tubular furnace (Barnstead Thermolyne, Dubuque, IA) at 750 °C @ 0.5 °C/min under Ar atmosphere. The holding time at 750 °C was 3 h. When the temperature reached RT after regeneration, the sample was removed from the furnace and transferred into a beaker. A dilute solution of HNO_3 was added to the beaker to neutralize the KOH and the mixture was centrifuged to separate the solid from liquid. An excess amount of water was added to the solid AC to wash out any remaining KOH or HNO_3, with the washing continued until the pH reached ~7.0. The wet solid was placed in a vacuum oven at 80 °C for 12 h with the dried sample called *regenerated AC*. If the *regenerated AC* formed solid chunks during drying, these chunks were ground into powder before loading to the reactor. After the decarboxylation experiments, the used regenerated catalyst is called *spent regenerated AC*. This procedure was repeated to regenerate the spent catalyst obtained after the 1st regeneration which is named as *regenerated AC-2* and the used catalyst after 2nd regeneration is named *spent regenerated AC-2*.

2.3. Activity tests

Hydrothermal decarboxylation of OA using fresh, spent and regenerated AC was conducted using a bench top continuous flow through reactor (BTRS-JR, Autoclave Engineers, Erie, PA) with a maximum operating pressure of 2900 psi at 650 °C. Decarboxylation experiments using fresh, spent and regenerated AC were performed only at maximized reaction conditions (400 °C, water-to-OA ratio of 4:1, and space time of 2 h) determined from our previous study [20]. 4 g of catalyst was used for each experiment and the flow rates of reactants (OA and water) were calculated from the packed density of catalyst and reactor space–time at ambient conditions. The maximized reaction condition is defined as the conditions to achieve the maximum degree of decarboxylation (91%) and higher selectivity (89.3%) of heptadecane. All the experiments were a repeated minimum of two times to replicate the accuracy of the data.

2.4. Catalyst characterizations

A Tristar II 3020 (Micromeritics Instrument Corporation) was used to measure the specific surface area, pore diameter and pore volume of fresh, spent and regenerated AC using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods. A minimum of 80 mg of sample was degassed at 150 °C for 12 h before measurements to remove any moisture and other adsorbed gases from the catalyst surface. The analysis was performed at −193 °C using 99.995% pure N_2 gas obtained from Praxair (Oakville, Canada). A Bruker D2 Phaser powder diffractometer was used to study the crystal structure of the fresh, spent and regenerated AC using Cu K_α radiation (λ for K_α is equal to 1.54059 Å) over $2\theta = 10–80$ using a scan rate 0.2°/min. ATR-FTIR spectroscopy (Nicolet 6700 FTIR, Thermo Scientific OMNIC^{TM} software) was used to obtain infrared spectra of the fresh, spent and regenerated AC. A Kratos Axis Ultra spectrometer using a monochromatic AlK (alpha) source (15 mA, 14 kV) was used to perform the X-ray photoelectron spectroscopy (XPS) analysis. A Kaiser Optical System RXNI-785 with an excitation wavelength of 785 nm was used to conduct Raman spectroscopy measurements of all AC samples. Crystallite domain size of the AC catalysts were measured using a Renishaw InVia Reflex Raman spectrometer with two additional wavelength lasers (633 nm and 514 nm). A TGA/SDT A851 model gravimetric analyzer