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Sustainable hydrocarbon fuels via “one-pot” catalytic deoxygenation of waste cooking oil using inexpensive, unsupported metal oxide catalysts

Ağah Yıldız[a], Jillian L. Goldfarb[b], Selim Ceylan[a,*]

[a] Ondokuz Mayıs University, Faculty of Engineering, Chemical Engineering Department, 55139 Kurupelit, Samsun, Turkey
[b] Cornell University, Department of Biological & Environmental Engineering, Ithaca, NY 14853, USA

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ABSTRACT

The present work explores the potential to upgrade waste cooking oil (WCO) via deoxygenation using inexpensive, unsupported metal oxide catalysts (CaO, TiO_2, Mn(IV)O, and ZnO) in the absence of a hydrogen feedstock. WCO was mixed with 5 wt% catalyst material in a stainless steel reactor and heated to 300 °C for 60 min. The relative concentration of fatty acids increased upon heating in the absence of any catalyst, from ~15% of the total identifiable compounds for WCO to 64% for the Organic Liquid Products as a result of the nearly complete conversion of aldehyde and ester groups to organic acids, alkanes and aromatics. The inorganic catalysts shifted the product distributions significantly. CaO and ZnO slightly increased the concentration of acidic groups (versus WCO) but produced less acids than OLP alone, while Mn(IV)O and TiO_2 resulted in overall decreases of free fatty acids. Mn(IV)O showed a slight preference for alkene formation, whereas TiO_2 was selective toward alkanes. All catalysts – and uncatalyzed heating – showed significant deoxygenation in terms of ridding the WCO of C-O groups. Thermal treatment of WCO (with and without catalysts) resulted in a 25% increase in higher heating values, in line with those of commercial jet fuels. While the “one-pot” catalytic upgrading of WCO would not result in a direct substitute for aviation fuel, this work demonstrated the potential to significantly upgrade WCO using an inexpensive catalyst without relying on copious amounts of hydrogen gas to affect a hydrodeoxygenation reaction.

1. Introduction

Reversing climate change requires a global shift to a bio-based economy in which sustainable, renewable fuels play a key role in both the transportation and energy generation sectors [1]. A critical bottleneck in renewable fuels development is the poor quality and need for significant upgrading of as-produced fuels [2]. Studies across the literature propose new methods to produce biomass and carbonaceous waste-based renewable liquid hydrocarbons with comparable properties to their petroleum-based counterparts [3]. Many of these studies examine model compounds and surrogate reactions to identify potential reaction pathways, but lack validation with “real-world” systems. While such work is key to identifying possible catalysts, an integrated biorefinery will need to process a range of heterogeneous feedstocks depending on seasonal and regional availability [4].

Lipids such as vegetable oils, animal fats, waste cooking oils, etc. are constantly available, and often as a discarded waste. Consumption of edible oils is expected to increase threefold by 2050, with ever-increasing amounts of waste cooking oil (WCO) generated alongside this rise in consumption [5]. Considerable research has been done on the transesterification of food waste lipids to fatty acid methyl ester (FAME)-based biodiesel [6]. However, the automotive sector is unwilling to embrace this form of biodiesel writ large, citing concerns of poor cold flow properties, oxidative instability, and engine corrosion [7]. These poor properties are a result of the high number of oxygen moieties present [8]. The copious amount of glycerol generated during transesterification (up to 10% of products) further hampers biodiesel deployment on a meaningful scale to reduce climate change [9]. Yet WCO represents a potentially valuable biofuel feedstock given its high energy content and otherwise costly disposal. To overcome issues associated with high oxygen fuel contents, the oxygen atoms in the fatty acids – extant on most of the saturated and unsaturated molecules even after cooking – must be removed.

The conversion of biomass-based oxygenated compounds to

Abbreviations: DCO, decarbonylation; DCO_2, decarboxylation; DO, deoxygenation; FTIR, Fourier Transform Infrared Spectroscopy; GC–MS, Gas Chromatography-Mass Spectrometry; HDO, hydrodeoxygenation; HHV, higher heating value; OLP, organic liquid products; WCO, waste cooking oil (feedstock

* Corresponding author.

E-mail address: selim.ceylan@omu.edu.tr (S. Ceylan).

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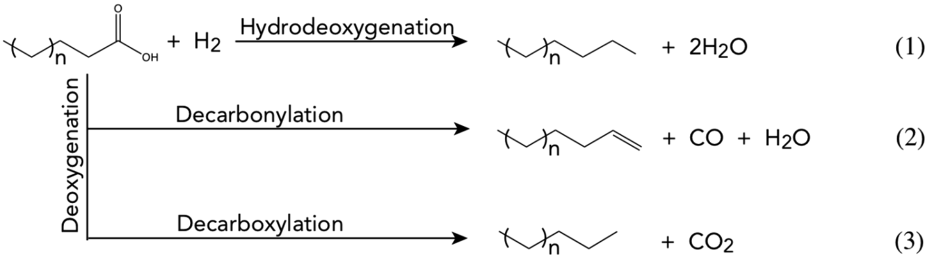

Fig. 1. Hydrodeoxygenation and deoxygenation pathways for WCO to hydrocarbons.

hydrocarbons happens via two main pathways: hydrodeoxygenation (HDO) and deoxygenation (DO), the latter of which may occur through mechanisms including decarboxylation (carbon dioxide elimination, DCO_2) and decarbonylation (carbon monoxide elimination, DCO)[10]. HDO is a cracking process that requires high pressure and an abundant supply of hydrogen gas, converting molecules with oxygen-containing moieties to straight-chain hydrocarbons (usually alkanes) and water, as shown in Eq. (1) (Fig. 1). When used for the deoxygenation of fatty acids, often both decarboxylation and hydrodeoxygenation reactions occur on the same catalyst, but at different rates [11]. DCO_2 and DCO will sequentially generate hydrocarbons with one carbon fewer than the initial fatty acid, as well as CO and H_2O, (byproducts of $DCO_{2)}$ and CO_2 from DCO (Eqs. (2) and (3)).

HDO is often carried out using transition and noble metal catalysts supported on inert substrates such as Al_2O_3, whereby hydrocarbon yields of over 80% can be achieved at moderate temperatures in the presence of hydrogen [12]. The hydrogenation of unsaturated fatty acids such as oleic acid leads to the production of fatty alcohols, which in the presence of transition metal catalysts such as Ni subsequently undergo esterification to produce alkanes such as heptadecane and octadecane [13]. While HDO is effective at removing oxygen from biofuels, its high H_2 requirement – upwards of 300–400 m^3 H_2 per m^3 of oil – limits the economic and environmental advantages of this catalytic pathway [14–16]. Further still, many proposed so-titled “deoxygenation” processes are actually hydrodecarbonylation and hydrodecarboxylation – requiring H_2 as a feedstock [17,18]. This, combined with catalyst deactivation via coking, hampers large-scale sustainable biofuel production across both feedstocks and thermochemical conversion methods [19–22].

A more economically viable option for the conversion of WCO to hydrocarbons may be via deoxygenation. Both homogeneous and heterogeneous catalysts have proven effective in decarboxylation reactions, but are often comprised of precious metals such as Pd and Pt [14,23–26], though a limited number of studies have used metal oxides based on Ca, Co, La and [27–29]. Liu et al. reported that for Ni_xP/HZSM-22 catalyzed conversion of palmitic acid, decarbonylation and decarboxylation are attributed to the Ni_xP, whereas the zeolite support was responsible for isomerization reactions (due to the Brønsted acid sites) and cracking reactions (from Lewis acid sites)[30]. Likewise, increasing the amount of ZnO on supported catalysts such as Al_2O_3-ZnO is known to increase catalyst acidity [31]. One well-explored DO pathway that does not require an H_2 feedstock is the catalytic oxidative decarboxylation of FAMEs in the presence of persulfate ions, $S_2O_8{}^{-2}$. This leads to alkene, alcohol and ester compounds as a result of the oxidation of alkyl groups; the yield of alkenes can be enhanced by the presence of silver and copper [32,33]. The mechanism for such reactions is thought to be the formation of a silver-carboxylate complex, followed by radical initiation, forming an unstable carboxyl radical which degrades to an alkyl group [11]. Conversely, Henkel decarboxylation of carboxyl groups on aromatic molecules likely occurs because of a two-electron abstraction of CO_2, and often results in the production of benzene and 1,4-terephthalate [34,35]. While reducing H_2 input, the stoichiometric peroxydisulfate consumption (and corresponding production of sulfate), coupled with the need for a solvent with available hydrogen to produce an alkane, limits the widescale biorefinery implementation of this pathway. Furthermore, producing alkenes from these alkanes would require a second metal catalyst, additional reagents and further separation of co-products.

Foglia and Barr showed that homogeneous catalysis via chlorinated rhodium could selectively decarbonylate stearic acid into hetpadecenes without hydrogen input and secondary catalytic processing [36]. Murray et al. demonstrated that unsaturated fatty acids could be converted to alkenes via a tandem isomerization-decarboxylation pathway using a ruthenium carbonyl catalyst [37]. Such promising dual-function catalysts could lead to hydrocarbon production for liquid biofuels, without high hydrogen or energy requirements, though the use of limited materials such as Ru potentially limits economic and environmental feasibility. Less expensive, more abundant catalysts such as activated alumina have been suggested for pyrolytic conversions of carboxylic acid-laden feedstocks, with transformation to hydrocarbons often occurring through ketones via γ-hydrogen transfer and/or reduction to alcohol followed by dehydration [38]. During such pyrolytic (cracking) processes, there is often a significant loss of carbon which results in a lower energy content of the resulting fuel. Furthermore, because the reaction must happen at high temperatures (above 450 °C), the energy penalty for extracting such fuels is therefore higher.

The present study investigates a “one-pot” catalytic reaction of fatty acids and esters from WCO under pressure and elevated temperature using inexpensive, unsupported (as-received) metal oxide catalysts without the addition of hydrogen. The catalysts chosen have negligible solubility in WCO, and as such all reactions are heterogeneous. The goal was to explore the viability of using low-cost, widely available catalysts such as CaO, TiO_2, Mn(IV)O, ZnO for deoxygenation of WCO in terms of product composition, heating value and thermal stability of the resulting fuel.

2. Materials and method

2.1. Raw material

WCO was obtained after domestic use from sunflower oil. It was first gravity separated to remove large particulates via settling, and then filtered to remove suspended solid particles. Catalysts (CaO, TiO_2, Mn(IV)O, ZnO) of high purity grade were purchased from Sigma Aldrich.

2.2. Experimental apparatus

Deoxygenation of WCO was conducted in a stirred stainless steel batch reactor with a total volume of 250 mL. The reactor has a maximum working temperature of 500 °C and pressure of 250 bar. Prior to each experiment, the reactor was cleaned with acetone and dichloromethane. It was charged with approximately 20 mL WCO (sample weight recorded) and 5 wt% catalyst. The reactor was sealed and purged with N_2 gas. The reactor was heated to 300 °C (over the course of two hours) and then maintained at 300 °C for 60 min under constant stirring. The experiments were repeated three times to ensure reproducibility.