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Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation

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ABSTRACT

Conversion of canola oil to normal alkane hydrocarbons was investigated using sequential reactions: continuous thermal hydrolysis and fed-batch thermo-catalytic decarboxylation. The free fatty acid (FFA) intermediate product from hydrolysis was quantified using GC–FID, which showed 99.7% conversion and the following components: palmitic, oleic, linoleic, linolenic, stearic, arachidic and behenic acids. The FFA was saturated then decarboxylated at an average rate of 15.5 mmoles/min using a 5% Pd/C catalyst at 300 °C. Approximately 90% decarboxylation conversion to *n*-alkanes was achieved within 5 h of the reaction. The resulting mixture of *n*-alkanes can be readily converted into renewable diesel using isomerization to improve the cold flow properties of the fuel.

1. Introduction

Increasing prices of petroleum, its finite reserves, and environmental effects are leading to greater interest in bio-renewable resources. In particular, biofuels will have a significant role in meeting our liquid transportation fuel needs. There are many biofuel production technologies that are capable of producing liquid transportation fuels, *e.g.*, fermentation, transesterification, pyrolysis, gasification with the Fisher–Tropsch synthesis, and hydrogenation. Many of these processes, specifically “first generation” biofuels, are tied to a single feedstock at the commercial scale. This leads to relying on a single agricultural commodity, where price fluctuations can have a significant impact on the economic feasibility of these processes. In addition the fuel characteristics, *i.e.*, the chemical and physical properties of first generation biofuels (biodiesel and ethanol), differ markedly from the petroleum-derived fuel they are meant to replace. These differences raise challenges in the storage, distribution, and use of first generation biofuels. An ideal biofuel production process would be able to accommodate the following: be able to use a wide variety of feedstocks; be scalable and cost effective; produce a true ‘drop-in’ replacement fuel, minimize infrastructure incompatibilities; have high thermal efficiency and mass yield; a process with a low environmental impact.

Traditional diesel fuel is composed of hydrocarbons in the 10–15 carbon number range [1]. Biodiesel [rigorously defined as a fatty acid methyl ester (FAME)] is typically blended with diesel fuel and obtained through the transesterification of vegetable oils and animal fats, which contain mostly triglycerides [1]. Compared to traditional diesel fuel, biodiesel has the advantages of: reducing particulate exhaust emissions, improved biodegradability, higher flash point and can be produced domestically [1]. However, FAME has a number of shortcomings, namely: low energy density resulting from the carboxyl group, poor cold flow properties, relatively high production costs due to required alcohol and catalyst, higher NO_x exhaust emissions, biologically active, and generally limited to relatively high quality (*e.g.*, low FFA content) feedstocks. With these difficulties, efforts are underway to develop alternative production processes to produce hydrocarbon fuels that are ‘drop-in’ replacements for traditional petroleum-derived fuels. One such process is described here. To date, a wide range of feedstocks including vegetable oils, animal fats, and algal-based oils have been converted into high energy density fuels with physical, chemical and combustion characteristics identical to petroleum-derived fuels via a proprietary thermo-catalytic process [2]. In this process, triglycerides (TGs) from crude lipids are thermally hydrolyzed with subcritical water to form saturated and unsaturated FFA and glycerol (Gly). The FFA intermediate products are then thermo-catalytically decarboxylated to normal alkanes, with the resulting carbon chain length distribution very similar to a petroleum-derived diesel fuel.

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1.1. Hydrolysis

Hydrolysis of TG to form FFA has been used in industry for many years for soap production and other products [3]. With three moles of subcritical water, one mole of triglyceride is split into three moles of FFA and one mole of Gly. The reaction steps are described as follows [4]:

$$C_3H_5(COOR)_3 + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_3H_5(COOR)_2(OH) + RCOOH \quad (R1)$$

$$C_3H_5(COOR)_2(OH) + H_2O \underset{k_4}{\overset{k_3}{\rightleftarrows}} C_3H_5(COOR)(OH)_2 + RCOOH \quad (R2)$$

$$C_3H_5(COOR)(OH)_2 + H_2O \underset{k_8}{\overset{k_7}{\rightleftarrows}} C_3H_5(OH)_3 + RCOOH \quad (R3)$$

$$C_3H_5(COOR)_3 + C_3H_5(COOR)(OH)_2 \underset{k_6}{\overset{k_5}{\rightleftarrows}} 2C_3H_5(COOR)_2(OH) \quad (R4)$$

where triglycerides (TG; $C_3H_5(COOR)_3$) are converted to diglycerides (DG; $C_3H_5(COOR)_2(OH)$) and free fatty acids (FFA; RCOOH), then to monoglycerides (MG; $C_3H_5(COOR)(OH)_2$) and FFA, and finally to FFA and glycerol (Gly; $C_3H_5(OH)_3$). The primary FFA product has many uses, *e.g.*, soap production, synthetic detergents, greases, cosmetics and several other products [3]. Since the FFAs are Lewis acids at high temperatures, they behave as a catalyst to promote the two-step supercritical methanol process [5]. Glycerol is the by-product of the hydrolysis reaction and is also widely used in many industrial applications [6]. Another potential use is its conversion to combined heat and power through direct combustion; glycerol contains approximately 16 MJ of heat per kilogram [7].

The hydrolysis reaction has been studied in both batch [8,9] and continuous [10–12] systems. In a continuous hydrolysis process, water and oil are fed simultaneously, continuously and counter-currently into a high temperature and pressure reactor. High temperatures overcome the activation energy of the reaction as well as increase the water solubility in the lipid phase [13]. This shortened induction time, termed the emulsive hydrolysis period [13], achieves equilibrium quicker. Sufficient pressure is maintained for water, and therefore the entire reaction, in the liquid phase. The counter-flow process was first operated by Ittner [10] at 200 °C which provided satisfactory yields. Mills then studied hydrolysis at a variety of temperatures (185–315 °C) and pressures (10.3–110.3 bar), where a higher yield and more rapid rate of splitting were obtained [11]. The Colgate–Emery [12] and Foster-Wheeler [14] processes are the most well-known industrial fat splitting methods. In the Colgate–Emery process [12], fat and water react in a counter-flow column at about 260 °C and 50 bars. Mass and momentum transfer as well as heat exchange take place along the reactor. This process is non-catalytic and can be operated with high throughput and produce high quality FFA product.

Reaction temperatures and water-to-oil feed ratios are two of the primary variables that offer potential for optimizing the continuous hydrolysis process [15]. Increasing the reaction temperature not only increases the diffusion rate of water and glycerol in and out of TG by the higher electrolytic dissociation of water [13,16–18], but also enhances the rate of reaction and pushes the reaction toward equilibrium [18]. Mills and McClain [19] observed that the water content in coconut oil was about 10% when operating at normal condition but at 293 °C, water and oil form a single phase. King et al. [8] also found that complete miscibility of soybean oil and water occurred at a temperature of 339 °C. As the reaction steps R1–R4 show above, as more water dissolves in the lipid phase, the faster the reaction moves toward completion. Using results from a batch hydrolysis process, Sturzenegger and Sturm [17] found that hydrolysis reaches equilibrium five times faster as temperature is increased from 225 °C to 280 °C. In addition, a study by Lascaray [18] indicated that a temperature increase of 10 °C produces an increase in the rate of reaction by a factor of 1.2–1.5. For non-catalytic hydrolysis, these results provide evidence that reaction temperature has a considerable influence on accelerating the reaction.

Higher ratios of water to oil shift the equilibrium balance in favor of product and affects the degree of hydrolysis [18]. Mass transfer dictates that equilibrium is determined by the concentration of glycerol in the oil phase [13]. To obtain a high degree of hydrolysis, the glycerol concentration in sweet-water (the mixture of glycerol and water) must to be kept low [18]. King et al. [8] showed that lower water-to-oil ratios produced incomplete hydrolysis. As long as the sweet-water is continuously being replaced by fresh water when hydrolysis reaction starts declining, a high degree of hydrolysis was obtained [15]. Thus, the ratio of water-to-oil flow rate affects the rate of reaction and the yield of FFA [15].

1.2. Catalytic decarboxylation

Once all the glycerides from crude lipid are converted to FFA, the next step is to convert these FFA into straight-chain alkanes. A deoxygenation reaction is used to accomplish this. FFA can be deoxygenated via two pathways: decarboxylation, which produces paraffinic hydrocarbon via the removal of the carboxyl group with release of carbon dioxide [20]:

$$C_{17}H_{35}COOH \rightarrow n - C_{17}H_{35} + CO_2 \quad (R5)$$

or decarbonylation, which produces olefinic hydrocarbon by the removal of the carboxyl group and the release of carbon monoxide [20].

$$C_{17}H_{35}COOH \rightarrow C_{17}H_{34} + CO + H_2O \quad (R6)$$

Deoxygenation was first demonstrated in liquid phase with the conversion stearic acid over a metal catalyst supported by carbon [21]. These reactions were carried out over a range of temperatures (300–360 °C) and pressures sufficient to maintain the reactants in liquid phase at the corresponding temperature (*e.g.*, 17–40 bars). Unsaturated FFAs such as oleic acid and linoleic acid were converted to saturated diesel fuel range hydrocarbons via decarboxylation reactions under similar conditions and catalyst [22]. The expected main liquid product, *n*-heptadecane, was formed with high selectivity. *N*-pentadecane was produced from palmitic acid using a similar reaction [23]. The composition in the resulting effluent gas was analyzed and carbon dioxide, carbon monoxide, methane and propane were observed [23]. The concentrations of CO_2 and CO indicate the two deoxygenation pathways described above [24].

Among various catalysts, Pd/C has been shown to have the optimum catalyst performance for decarboxylation [20]. The highest initial reaction rate was obtained from the 5% Pd with carbon support [20]. The catalyst began deactivating after a certain period of time due to the formation of coke and the reduced pore size in the catalyst, mainly from the decarbonylation switchover mechanism, which depends on FFA feed rates, H_2 partial pressure and CO concentration [25]. The catalyst deactivation was investigated in a fed-batch process [25] or continuous [26,27] system with both downward and upward flow because it is challenging to separate the reaction kinetics and deactivation mechanism in batch systems [26]. Using a fed-batch process, Immer and Lamb [25] suggested that reducing H_2 and CO partial pressure as well as ceasing the FFA feed prevents the catalyst from deactivating. Under continuous operation, the effects of residence time, FFA feed rates and reaction temperatures were studied [26,27]. Reduced residence times due to the high feed rates resulted in extensive catalyst deactivation