

Used Frying Oil for Biodiesel Production Over Kaolinite as Catalyst

Jorge Ramírez-Ortiz, Jorge Medina-Valtierra, and Merced Martínez Rosales

Abstract—Biodiesel production with used frying by transesterification reaction with methanol, using a commercial kaolinite thermally-activated solid acid catalyst was investigated. The surface area, the average pore diameter and pore volume of the kaolinite catalyst were $10 \text{ m}^2/\text{g}$, 13.0 nm and $30 \text{ mm}^3/\text{g}$, respectively. The optimal conditions for the transesterification reaction were determined to be oil/methanol, in a molar ratio 1:31, temperature $160 \text{ }^\circ\text{C}$ and catalyst concentration of 3% (w/w). The yield of fatty acids methyl esters (FAME) was 92.4% after 2 h of reaction. This method of preparation of biodiesel can be a positive alternative for utilizing used frying corn oil for feedstock of biodiesel combined with the inexpensive catalyst.

Keywords—Biodiesel, frying corn oil, kaolinite, transesterification

I. INTRODUCTION

WORLD production figures for biodiesel shows it has emerged as a complementary alternative to petroleum diesel. Compared to petroleum diesel, biodiesel (fatty acids methyl esters or FAMES) reduce emissions of particulate matter and carbon monoxide and such emissions; it does not contain aromatic hydrocarbons nor sulphur. Also biodiesel is non-toxic; highly biodegradable, and it is renewable since it represents an almost closed CO_2 cycle (approximately 78%) when derived from biomass. Biodiesel is a fuel formed by mono-alkyl esters of long-chain fatty acids derived from vegetable or animal oils and fats which meet ASTM D6751 specifications, and it is designated as B100 according to the American Society for Testing and Materials (ASTM) [1]. This fact calls the attention that biodiesel production is, currently, the economically feasible, even when commercial-scale production of biodiesel using refined vegetable oils as raw material whose price makeup 70-95% of the total production cost [2]. The using of oils with a high FFA content leads to a large catalyst consumption and increases the cost of biodiesel purification. This is due to the fact that the FFA are saponified by the homogeneous alkaline catalyst producing insoluble soap-like precipitates.

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To overcome this limitation it is necessary to seek for inexpensive supplies of inedible vegetable oil, such as used frying oil (UFO) in order to ensure the economic viability of biodiesel production. Since UFO is much more inexpensive than refined vegetable oils, its use can reduce biodiesel cost production to half its price [3]. While refined vegetable oil contains less than 0.5% by weight of FFA, UFO contains between 0.5 to 15% FFA by weight. Hence, the possibility of using basic homogeneous catalysts with UFO is not recommended. An alternative is to use solid acid catalysts, since these have several advantages: they are insensitive to the presence of FFA and can simultaneously catalyze the reactions of esterification and transesterification; they can be easily separated from the reaction environment, regenerated and recycled; reduce the problems with corrosion in the reactor. The solid acid catalyst will also produce a more pure glycerol because the production process does not require a washing or neutralization steps.

Kaolinite is a very important clay mineral, with numerous industrial applications; its use includes the production of ceramics, cosmetics, paints and paper, as well as pollutants adsorbent and as a catalyst. Kaolinite is a raw, commercial, low-cost, easily available, non-corrosive and environmentally-benign material among others. The use of kaolinite in transesterification and transthiolsterification of β -cetoesters has been reported [4], acid-activated kaolinite was used as a catalyst in the esterification of carboxylic acids mixed with xylene and various different alcohols [5], and also for the esterification of oleic acid with several short-chain alcohols [6].

In this study we report the production of biodiesel from used frying corn oil using commercial kaolinite, thermally-activated as the solid acid catalyst for the transesterification reaction.

II. EXPERIMENTAL

A. Materials and Method

Used frying corn oil was obtained from domestic frying oil from edible commercial corn oil named "Cristal". The following chemicals were supplied by J.T. Baker (Performance Materials S.A. de C.V. México): methanol anhydrous and isopropyl alcohol; triethanolamine, KNO_3 and methyl oleate (99%) and Kaolinite with formula $\text{Al}_2\text{O}_7\text{Si}_2\cdot 2\text{H}_2\text{O}$ and ignition loss of 12 wt%, buffer concentrate, pH 10.00 and methyl heptadecanoate grade standard for GC obtained from Fluka (Sigma-Aldrich Química, S.A. de C.V. México).

B. Catalyst Preparation

The kaolinite obtained from Fluka was used as received, and without any prior treatment, was thermally activated. Calcination was carried out under static air in a programmable furnace, for 10 h at 800°C, with a heating rate of 10 °C min⁻¹ from room temperature to the calcination temperature.

C. Catalyst Characterization and Evaluation of Fatty Acid Methyl Esters content

A Fourier transformed infrared FTIR Varian 640-IR spectrometer was used to identify the surface functional groups of kaolinite and calcined kaolinite. The spectra were recorded in a range of 4000-500 cm⁻¹. The N₂ adsorption-desorption isotherms were obtained at liquid nitrogen temperature using the ASAP 2010 from Micrometrics Instrument. Before each measurement, the samples were outgassed at 130 °C for 2 h. The specific surface area, the porous area, the porous volume and the pore size distribution were obtained, respectively, using Brunauer-Emmett-Teller (BET), t-plot and Barrett-Joyner-Halenda (BJH) methods. The acidity of kaolinite was determined through a titration acid-base using an AR25 Research Accumet potentiometer. Density and viscosity of used frying corn oil and biodiesel samples were determined using the picnometer method at room temperature and using an Ostwald viscometer at 40 °C respectively. Free fatty acids (FFA) of used frying oil were measured carrying this out by pH-metric method. Complete extraction of FFA from an oil test sample into the reagent: 0.2M triethanolamine + 0.02 M KNO₃ in 50% H₂O + 50% i-PrOH (%V). 50 mL of the reagent and 5 mL of test sample was added. The pH value was measured after approximately 3 min, and the %FFA were found using a table reported there [7]. An Agilent 6890N equipped with a hydrogen flame ionization detector and a polar capillary column (50m x 0.32 mm, 1.00 μm film; DB-WAX) was used for sample analysis. Helium was used as the carried gas. The column temperature was programmed from 210 °C holding 10 min, with a heating rate of 10 °C min⁻¹, to 250 °C holding 10 min. The injector temperature was set at 250 °C and detector set at 300 °C. The split ratio was 80:1 and 1 μL of the sample was injected. The analysis of fatty acid methyl ester (FAME) percentage yield for each sample was done using European Standard EN14103 and was calculated by using (1). Free fatty esters in the samples were determined using stock solution methyl heptadecanoate which was used as internal standard and n-heptane. Methyl esters were identified by comparing their relative and absolute retention times with standards.

$$\%ME = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{C_{EI} V_{EI}}{m} \times 100 \quad (1)$$

ΣA= the total peak area from the methyl ester C14 to C24:1

A_{EI}= the peak area of methylheptadecanoate

C_{EI} = the concentration, in mg/mL of the methyl heptadecanoate solution

V_{EI} = the volume, in mL of the methylheptadecanoate solution

m = the mass, in mg, of the sample

D. Transesterification of Used Frying Oil with Methanol

The used frying corn oil did not undergo any previous treatment; it was only left to dry on a hot plate with stirring at 140 °C for 3h to evaporate the water and then was vacuum filtered to extract solids such as pieces of solid food and sediment. The content of FFA in used frying corn oil was 0.45%. Before the experiment, the catalyst was dried at 120 °C in an oven until used. The catalyst test was performed using a stainless steel batch reactor Parr 4522 equipped with a stirring, thermocouple and a manometer, surrounded by a heating mantle, controlled by a proportional integral derivative temperature controller.

Exact quantities of the used frying corn oil and methanol were then put into the reactor containing the kaolinite thermally activated. In a typical experiment, UFO was mixed with methanol and 3 wt. % of the solid catalyst (related to oil weight). The reaction mixture was kept under constant stirring (627 rpm) at 160 °C for 2 h. After the reaction was complete, the reactor and its content were allowed to cool and placed in a 600 mL beaker. After settling, two distinct layers were formed. The bottom layer contained some of unreacted oil without reaction, glycerin and a small quantity of catalyst, while the top layer was biodiesel diluted with methanol and a small quantity of glycerin. A rotavapor was used to recover the excess methanol and obtain biodiesel which was analyzed by gas chromatography. The percentage of yield of used frying corn oil as its methyl esters was calculated by (2). A blank reaction without catalyst was also performed as a control experiment.

$$Yield = \frac{\text{weight of methyl esters produced, } W1}{\text{weight of oil used in reaction, } W2} \times 100 \quad (2)$$

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

The surface area, the average pore diameter and volume of pore of kaolinite catalyst were 10 m²/g, 13.0 nm and 30 mm³/g, respectively. A requirement of catalyst for production of FAME is large interconnected pores that would minimize diffusional limitations of molecules having a long alkyl chain [8].

The FTIR spectra region at 3800-3400 cm⁻¹ of kaolinite shown in Fig. 1(a) showed that the four OH bands represent stretching vibration frequencies at 3686, 3668, 3649 and 3617 cm⁻¹. At 800 °C, all of the OH bands disappear in Fig. 1(b) due to dehydroxylation via by calcination thereby producing thermally activated kaolinite. This transformation occurs with the loss of structural water, consequently only a small part of AlO₆ octahedral is maintained. The rest of the kaolinite was transformed into much more reactive tetra and pentacoordinated units [9].

The value of acid sites was 0.0105 meq/g. Dry kaolinite will promote or catalyze many chemical reactions, and where acid-base interactions are involved, the presence of even small amounts of water usually retards or inhibits the reaction. In

fact, water functions as a base and neutralizes preferentially at the strongest acid sites.

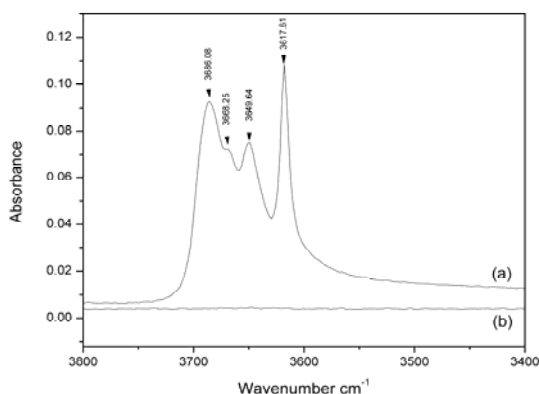


Fig. 1 FTIR spectra of the (a) parent kaolinite before to calcination and (b) kaolinite thermally activated.

B. Effect of Oil to Methanol Molar Ratio on the Yield

It is well known that transesterification of triglycerides with methanol using a solid acid catalyst is reversible and characterized by a slow reaction rate. An excess of methanol is required to force the reaction toward the formation of FAMES.

As it can be observed in Fig. 2, the maximum yield from used corn oil triglycerides to methyl esters was 92.5%, obtained after 2 h of reaction, at a molar ratio oil/methanol 1:31, using 3% catalyst and a temperature of 160 °C. An hour later, the yield dropped to 85% and continued almost unchanged (87%) for another hour [curve (■)]. The decrease in the yield may be due to the fact that the increase in the molar ratio oil/methanol accelerates the transesterification reaction as well as the production of more water molecules which neutralize the acid sites on the surface of metakaolinite. The strength of acidity of these acid sites makes them effected by the moisture content of the reaction media. In the case corresponding to 3% of catalyst and temperature of 160 °C, using a molar ratio oil/methanol of 1:23, 2 hour reaction time and yielded of 67% FAMES. Adding an extra hour of reaction time, the yielded 77% FAMES and up to a maximum value of 94.5% FAMES could be achieved in 4 h, and after this time, there is a drop in yield, to 68%. This reduction in yield can be explained by the degradation of the FAMES and isomerization of triglycerides, due to the long reaction time [curve (▲)- Fig. 2].

When the transesterification was made under the same conditions as displayed in the curve (▲) in Fig. 2, but now with the addition of 5% of kaolinite catalyst, the yield in was 45% in 2 hours. At 3 h the yield increased to 75% to reach a maximum of 95% at a time of 4 h, showing after, a drop in yield to 70% as in the previous case [curve (►) – Fig. 2]. Finally, when the reaction of transesterification in the molar ratio oil/methanol 1:23, without catalyst, at a temperature of 160 °C, the yield was 22% for 2 h and fell to 16% in a 4 h reaction and with the same reaction conditions, but with a molar ratio oil/methanol of 1:31, the yield was 29% in 4 h.

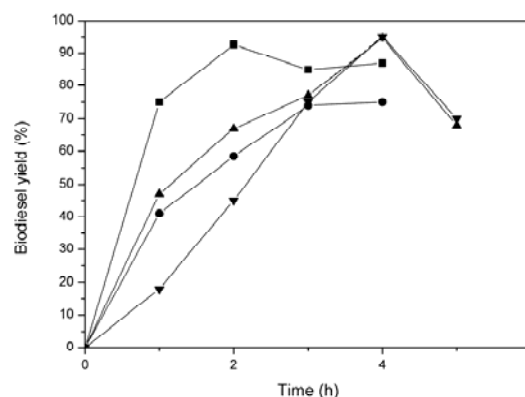


Fig. 2 Biodiesel yield (%) vs Time (h) for (■) molar ratio 1:31 (oil/methanol) to 160 °C and 3% catalyst, (▲) molar ratio 1:23 (oil/methanol) to 160 °C and 3% catalyst, (●) molar ratio 1:31 (oil/methanol) to 140 °C and 3% catalyst, (►) molar ratio 1:23 (oil/methanol) to 160 °C and 5% catalyst.

C. Effect of Reaction Temperature

The experimental temperatures utilized were 140 °C and 160 °C. The normal behavior for the catalyzed reactions is that the yield rate increases with temperature; the higher the reaction temperature, the shorter the time to reach the maximum yield, thus concluding that transesterification is an endothermic reaction. As Fig. 2 shows in curve (■), the sample of FAMES obtained at 2 h reaction time and at a temperature of 160 °C reached a yield value of 92.5%, while the sample at 2 h reaction and a temperature of 140 °C for the same molar ratio oil/methanol 1:31 gave a value of 58.5%, shown in curve (●). This suggests a high effect of the temperature on the transformation of fatty acids with a rapid increase in transesterification products.

D. Resultant Biodiesel Composition

A typical chromatogram obtained for a sample of the fatty ester profile of used frying corn oil as determined by gas chromatography FAME analysis is shown in Fig. 3. In the GC chromatogram as performed by using a standardized method (EN 14103), the large peaks observed in the chromatogram are the C 16-C18 fatty acid methyl esters. Also shown in the chromatogram, based on retention times, are different FAMES found in corn oil. Used frying corn oil is composed of six fatty acids: myristic, palmitic, stearic, oleic, linoleic and linolenic. Of all fatty acids, linoleic acid is the dominant FAME having a typical value of 51.12% (w/w). The total saturated and unsaturated fatty acid content of the used frying corn oil was 13.9% and 84.3% (w/w), respectively. Palmitic acid 11.69% (w/w) was the predominant saturated fatty acid. The fatty acid profile of vegetable oil is a primary factor influencing oxidation since the rate of oxidation depends on the number and position of double bonds up to 2 h of reaction with a maximum yield of 92.5% for 1:31 molar ratio and 160 °C and 3% of catalyst.

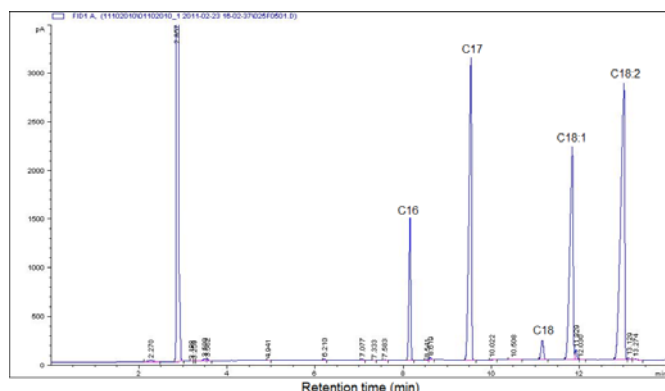


Fig. 3 Chromatogram of biodiesel shown retention time of FAMES

A. Properties of the Resultant Methyl Ester Mixtures

The properties of the methyl ester mixtures obtained from transesterification of used frying corn oil with methanol are: the viscosity of FAME is 5.44 mm²/s, this is in agreement with the requirements of ASTM D6751 biodiesel standard, which gave the value range of viscosity between 1.9 and 6.0 mm²/s. The density of FAME is 900.15 Kg m⁻³ based on the same standard; the density specification is given in the range between 870 and 900 Kg m⁻³.

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