

Production of Biodiesel from Roasted Chicken Fat and Methanol: Free Catalyst

Jorge Ramírez-Ortiz, Merced Martínez Rosales, Horacio Flores Zúñiga

Abstract—Transesterification reactions free of catalyst between roasted chicken fat with methanol were carried out in a batch reactor in order to produce biodiesel to temperatures from 120°C to 140°C. Parameters related to the transesterification reactions, including temperature, time and the molar ratio of chicken fat to methanol also investigated. The maximum yield of the reaction was of 98% under conditions of 140°C, 4 h of reaction time and a molar ratio of chicken fat to methanol of 1:31. The biodiesel thus obtained exhibited a viscosity of 6.3 mm²/s and a density of 895.9 kg/m³. The results showed this process can be right choice to produce biodiesel since this process does not use any catalyst. Therefore, the steps of neutralization and washing are avoided, indispensables in the case of the alkaline catalysis.

Keywords—Biodiesel, non-catalyst, roasted chicken fat, transesterification.

I. INTRODUCTION

ROASTED Chicken Fat (RCF) is a kind of animal fat that is extracted from all chicken body by heating it with firewood in roasted device. According to Mexican Service of Information, Food, Agriculture, and Fishery (SIAP), in its 2012 report [1] the production of chicken meat was 2.8x10⁶ t and according with Mexican office Financiera Rural [2] 24 % of chicken marketed roasted in México, which mean 6.7x10⁵ t. Based on an estimation of 11% of the total body fat, translate to 7.4x10³ t of fat produced. This large amount of chicken fat is not all exploited, and much of it is poured down the drain producing the pipes from clogging and water pollution.

The biodiesel compared to diesel fuel, reduces emissions of particulate matter and carbon monoxide; it contains neither aromatic hydrocarbons nor sulfur. Biodiesel has minimal toxicity, and it is highly biodegradable.

In present time, an important issue in the production of biodiesel is the cost of production because; more than 95% of the world biodiesel is produced from edible oils such as rapeseed (84%), sunflower oil (13%), palm oil (1%), soybean oil and other (2%), and this represents nearly 75-90% of the overall biodiesel production cost [3]. Nowadays, tendency is to replace these high-cost edibles oils by others feedstock for

to decrease the cost and make biodiesel production profitable in comparison with the price of diesel fuel. These feedstocks are non-edible oils such as *Jatropha curcas*, castor, rubber seed, *sea mango*, waste vegetable oils and animal fats. Now, these feedstocks have become a crucial research topic [4].

Chicken fat is relatively inexpensive source of triglycerides, is a by-product of the processed meat, and has been used as an additive of animal feed, but recent studies showed that this practice facilitates the transmission of potential infectious diseases from one animal species to another [5]. This reason is one for their low cost. Therefore, chicken fat has become a very important potential feedstock for biodiesel production, and, on the other hand, its utilization indirectly serves as an environmental cleaner. Kreutzer [6] claimed that the removal of free fatty acid (FFA) not required if the transesterification is carried out under pressure and temperature (90 bar, 240°C). Under these conditions, even inferior grades of fats and oils with a high FFA content can be converted into methyl esters. Saka and Kusdiana [7] argued that it was possible react the oil and methanol without a catalyst to temperatures of 300-350°C and molar ratio methanol to oil of 42 to 1. So eliminates the need use acid for neutralization and large flows of water to wash.

In this study, we report the transesterification reaction of RCF with methanol without a catalyst for the production of biodiesel. Parameters related to the transesterification reactions, including temperature, time and the molar ratio of RCF to methanol also analyzed.

II. EXPERIMENTAL

A. Chemicals and Materials

RCF was collected as a mixture of solid and liquid phases at room temperature from a roasted chicken store called "DIPORI" in Zacatecas city, México. Anhydrous methanol, ethanol, isopropyl alcohol and n-heptane were purchased from J.T. Baker (Performance Materials S.A. de C.V. México). Methyl heptadecanoate, triethanolamine, potassium hydroxide, Wijs solution, potassium iodide, potassium iodate, sodium thiosulfate, were obtained from Sigma-Aldrich (México).

B. Equipment

The transesterification reaction was carried out in a pressure reactor with a vessel of 2000 mL total capacity (4522-Parr Instrument, Moline, IL, USA) and it was used in the batch mode in identical way to that previously employed in other studies [8].

A Fourier transformed infrared FTIR Varian 640-IR (Agilent Technologies, Santa Clara, CA, USA) spectrometer

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was used to identify the functional groups of roasted chicken fat and biodiesel. The spectra were recorded in a range of 4000-600 cm^{-1} . All spectra were accumulated over 32 scans with a resolution of 1.6 cm^{-1} .

A modified method for the determination of fatty acid methyl esters (FAME) on biodiesel based on EN14103 was followed for evaluation of FAME contents [9]. The process includes natural contents of heptadecanoic acid methyl ester, which are found in animal fats and interfere with the internal standard, into the calculation of methyl ester content values. FAME was determined by gas chromatography model HP 6890 coupled with a mass spectrometer, model HP 5973 Mass Selective Detector operating in the electron-ionization (EI) mode. Electron energy was 70 eV, source temperature 200 °C and transfer line 250°C. Spectra data were acquired over a mass range of 30-500 amu at a scan rate of 1 s/scan. Separation was performed on a capillary column HP-5MS column (30 m x 0.25 mm i.d., 0.25 μm film thickness). The carrier gas was helium with flow rate of 1.5 L/min. The temperature of both injector and detector was set to 250 °C. A sample volume of 1 μL biodiesel in n-heptane was injected using a split mode, with the split ratio of 1:20.

C. RCF Characterization

Before using the RCF as feedstock for biodiesel production, was allowed to dry on a hot plate with stirring at 140°C for 3 h to evaporate the water. It was subsequently vacuum filtered to remove solids, such as very little meat pieces and sediment. Density and viscosity of RCF and biodiesel samples were determined using the pycnometer method at room temperature and using a Cannon-Fenske viscometer at 40°C, respectively.

D. Free Fatty Acid Determination

The acid value (AV) was determined using the method reported by Tur'yan and Kardash [10] to prepare the titration reagent by mixing 500 mL deionized water, 500 mL isopropyl alcohol and 7 mL triethanolamine. Place 100 mL of reagent into a conical flask on a magnetic mixer, add 0.5 mL of phenolphthalein solution to obtain pink color of the reagent. Add an oil test portion according to the range of FFA content to the reagent. Mix the reagent on the stirrer until colorless and then, keeping on stirring, begin titration with 0.1 mol/L KOH aqueous solution. The titration was finished at the appearance of the first permanent pink color, which is supposed to persist for 10 s. The amount of KOH consumed was registered, and the AV was calculated by using (1) and by using (2) the percent of free fatty acid (%FFA).

$$AV = \frac{\text{mL of KOH} \times N \times 56.1}{\text{weight of sample}} \quad (1)$$

$$\% \text{ Free Fatty Acid} = AV \times 0.503 \quad (2)$$

where N = normality of KOH

The iodine value (IV) was determined following the AOAC (Wijs method) [11]; saponification value (SV) [12] and molecular weight (M) of the RCF was calculated according to

reported by Zhu et al. [13], by using (3).

$$M = 56.1 \times 1000 \times \frac{3}{SV - AV} \quad (3)$$

E. Transesterification

In a typical experiment, RCF was mixed with methanol in a molar ratio of 1:31 or 1:23 (RCF: methanol). The stirred speed was kept constant at 627 rpm for all runs at 120°C, 130°C or 140°C and 2, 3 or 4 h respectively. After the reaction was complete, the reactor was allowed to cool to room temperature and the mixture of biodiesel, glycerin and methanol was then allowed to rest at room temperature in a decanter funnel until to ensure separation of the phases. The bottom phase consisted of glycerol, and the top phase contained the biodiesel dissolved in methanol. A rotary evaporator was used to recover the excess of methanol and the obtained biodiesel.

III. RESULTS AND DISCUSSION

A. Raw Materials Properties

The FFA level of RCF was found to be 3.3% corresponds to an acid value of 6.6 mg KOH/g and 0.47% moisture content. In general, these two parameters were crucial to obtaining a good yield of biodiesel. Other parameters of RCF are shown in Table I.

TABLE I
CHARACTERIZATION OF ROASTED CHICKEN FAT

PARAMETER	UNIT	RCF
Density _{22°C}	Kg/L	907.4
Viscosity _{40°C}	mm ² /s	42.9
Iodine Value	gI ₂ /100g	65.9
Acid Value	mg KOH/g	6.6
Moisture	%	0.47
Molecular Weight	g/mol	856.9
Saponification Value	Mg KOH/g	203

B. Biodiesel

As evident from the Fig. 1 (B), the maximum yield obtained for the conversion of RCF into biodiesel was 98%, which was obtained after 4 h of reaction time at an RCF: methanol molar ratio of 1:31 a temperature of 140°C. This biodiesel there was 78% of fatty acid methyl esters content.

The experimental temperatures utilized were 120°C, 130°C and 140°C, which were outcomes of preliminary investigations reported elsewhere [8]. Transesterification reaction of triglycerides with methanol is well known to be reversible. Therefore, an excess of methanol is required to force the reaction toward the formation of biodiesel.

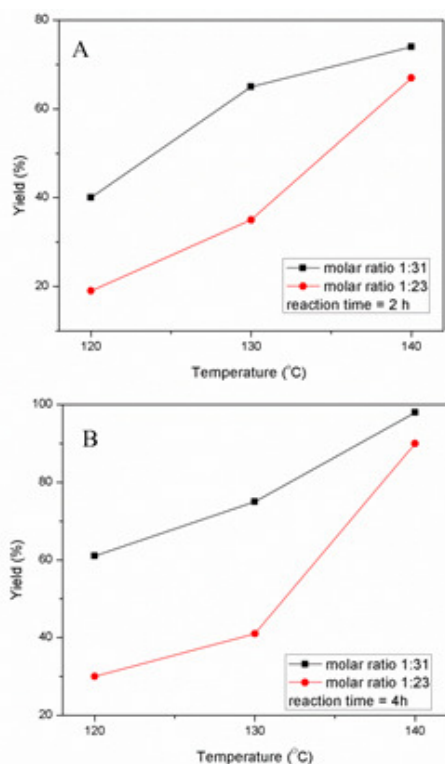


Fig. 1 Variation of yield in connection with a change in molar ratio RCF to methanol, reaction time (A) 2h and (B) 4h respectively versus temperature

In Figs. 1 (A) and (B) shown the effect of the RCF/methanol molar ratios at 1:21 and 1:31 with reaction time at 2h and 4h, at 120°C, 130°C and 140°C, respectively. The results indicate that the molar ratio RCF: methanol of 1:31 produced major yield of biodiesel than molar ratio RCF: methanol 1:21 for all temperatures and reaction times studied. In addition, in Figs. 1 (A) and (B) also show the effect of the temperature for reaction times of 2h and 4h, and the same RCF: methanol molar ratios, 1:21 and 1:31 respectively. The results suggest that to temperature of 140 °C occurred to major yield of biodiesel. Simultaneously, 4h of reaction time produced a yield of 98%.

C. Fourier Transform Infrared Spectrometry (FT-IR)

The FTIR spectra of the RCF and biodiesel are shown in Figs. 2 (A), and (B) and its band assignments, respectively. It is evident from Figs. 2 (A) and (B) that there was not much difference in the spectra of RCF and its biodiesel, but the relative intensity in some signals change from RCF to biodiesel. As can be seen from Figs. 2 (A) and (B) the C-O stretching vibrations produced a band at 1162 cm^{-1} in RCF and two bands at 1168 cm^{-1} and 1194 cm^{-1} in biodiesel. The signal at 1194 cm^{-1} was assigned to the methyl groups near the carbonyl groups. The band at 1238 cm^{-1} assigned to C-O-C asymmetrical stretching vibration in RCF was shifted to 1244 cm^{-1} in biodiesel. Bands located at 1376 cm^{-1} in RCF and 1436 cm^{-1} and 1462 cm^{-1} in biodiesel, which correspond to CH_2 and

CH_3 bending vibrations [14]. All of these shifts showed the conversion of triglycerides of RCF to biodiesel in this process.

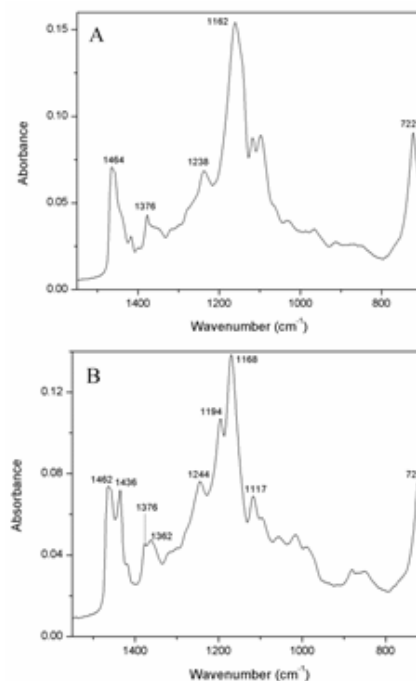


Fig. 2 Fourier transform infrared spectra of RCF (A) and Biodiesel (B)

D. GC-MS Analysis

Fig. 3 shows the following major compounds were found in the biodiesel sample (weight %): myristic acid (C14:0-6.1), palmitic acid (C16:0-29.6), margaric acid (C17:0-0.4), stearic acid (C18:0-4.6), oleic acid (C18:1-42.1), linoleic acid (C18:2-15.9) and linolenic acid (C18:3-1.3) and the fatty acid profile of the RCF is given in Table I. These values were in agreement with those reported by Ahmad et al. [15]. The biodiesel sample gives an ester content of 78% due the biodiesel produce of the RCF contains methyl heptadecanoate, an odd carbon atom number methyl ester which is used as an internal standard in this determination. As tabulated in Table I. oleic acid methyl ester was the predominant in RCF biodiesel. The viscosity, density and, acid value of biodiesel were 6.3 mm^2/s , 895.9 kg/m^3 and, 3.64 mgKOH/g respectively. These values were not near with requirements of ASTM D6751 biodiesel standard, which gave the value range of viscosity between 1.9 to 6.0 mm^2/s , density 870 to 900 kg/m^3 and, 0.80 mgKOH/g respectively.

An integrated process of catalytic composite membranes and sodium methoxide to produce biodiesel from waste chicken fat was developed by Shi et al. [16]. They claimed that chicken oil would be an attractive alternative feedstock for biodiesel production, and the conversion of the transesterification of 98% at the amount of sodium methoxide 1.0 wt% oil weight. Moreover, after the biodiesel was purified gave it 82.5% of FAME content. This value is in agreement with our results of 78% with advantage that we were not used

a catalyst.

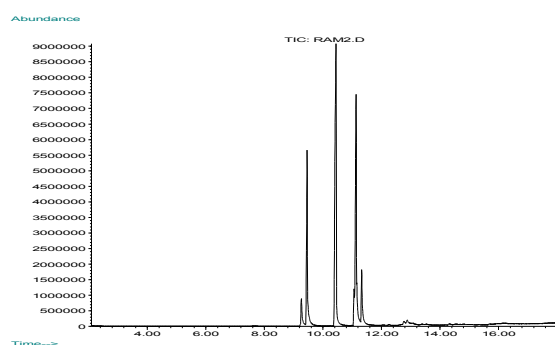


Fig. 3 Gas Chromatography-Mass Spectroscopy (GC-MS) chromatogram of the sample of biodiesel to 140 °C and 4h of reaction time, molar ratio RCF: methanol 1:31

TABLE II
COMPOSITION IN FATTY ACID OF ROASTED CHICKEN FAT

FATTY ACIDS	COMPOSITION (%)
C14:0	6.1
C16:0	29.6
C17:0	0.4
C18:0	4.6
C18:1	42.1
C18:2	15.9
C18:3	1.3

Boey et al. [17] synthesized biodiesel from waste chicken fat and methanol. In addition, it was used the crab and cockle shells as a catalyst and 3h of reaction time. One of the conclusions is that waste chicken fat is a cheap raw material and its low operation cost in biodiesel production makes their process a promising one for possible technological applications. Unfortunately, they do not mention the FAME content percentage. Its results of yield were in accord with ours.

Alptekin and Canakci [18] produced biodiesel from chicken fat with high free fatty acid content (13.45%) and methanol in a two steps process. They used several acids for pretreatment in first step and potassium hydroxide as a catalyst for a second step. They obtained a yield of 87.4% for 4 h of reaction time at 60 °C of temperature. It is a minor yield than ours of 98% although their values of viscosity and acid value were in ASTM range. However, it need use acid for neutralization and large flows of water to wash.

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