



Two steps alkaline transesterification of waste cooking oil and quality assessment of produced biodiesel

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Abstract

Biodiesel is an environmentally friendly renewable diesel fuel alternative. In Egypt, millions liters of waste cooking oil (WCO) are discarded annually into sewage systems, pollute water streams and adds to the cost of treating effluents. In an attempt to reduce the cost of biodiesel and pollution caused by WCO, this study aimed to investigate the feasibility of biodiesel production from WCO by applying two steps alkaline transesterification process using methanol, KOH as a catalyst and hot distilled water for purification. The produced biodiesel was physico-chemically characterized. From the results it was clear that the produced biodiesel was within the recommended standards of biodiesel fuel ($r > 0.95$) and met the criteria required to be a diesel substitute compared with the Egyptian petro-diesel fuel standards ($r = 0.999$).

Key words: Biodiesel, waste cooking oil, physico-chemical characterization

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1. Introduction

According to the environmental worries and the consumption of non-renewable fuel, biodiesel is a non-petroleum-based fuel defined as fatty acid methyl or ethyl esters derived from natural energy resources, developing alternative resources of energy as a substitute of traditional fossil fuels have been raised. Biodiesel is produced by chemical reaction of vegetable oil or animal fat with an alcohol such as methanol or mono-alkyl esters of long chain fatty acids derived from a renewable lipid feed stock [1,2]. Biodiesel produced by transesterification reaction can be catalyzed with alkali, acid or enzyme, in which a primary alcohol reacts with the triglycerides of fatty acids (vegetable oils) to form glycerol and esters [3]. Chemical catalyst processes, including alkali or acid are more practical compared with the enzymatic method. The use of acid catalysts has been found to be used for pretreating high free fatty acid feedstock but the reaction rates for converting triglycerides to methyl esters are very slow. Enzymes have

shown good tolerance for the free fatty acid level of the feed stock but the enzymes are expensive and unable to provide the degree of reaction completion required to meet the ASTM fuel specification. Immobilization of the enzyme and use of multiple enzymes in sequence may provide future opportunities in this area [4]. Alkali process can achieve high purity and yield of biodiesel product in a short time [5,6]. A major hurdle towards widespread commercialization of biodiesel is its high price. Biodiesel costs approximately one and a half times that of petroleum-based diesel, depending on feedstock oils [7]. It is reported that approximately 70-95% of the total biodiesel production cost arose from the cost of raw material; that is, vegetable oil or animal fats [8]. A reduced cost option is to produce biodiesel from waste fats and oils. Nevertheless, the price of waste cooking oil (WCO) or used frying oils is 2.5-3.0 times cheaper than virgin vegetable oils [9]. The annual consumption of vegetable oil in Egypt exceeds Million Tones/year [10]. Egyptians eat fava beans as a source of protein in their diet and fried flafel (green fava bean paste) is the most popular food in Egypt served at houses and fast-

food popular restaurants. As in case of French fries, fried flafel requires frying in vegetable oil. In addition, the Egyptian dietary pattern and habits make use of potatoes and fish. Consequently, millions of liters of oil used for frying foods are discarded each year into sewage systems. Thus, it adds to the cost of treating effluent or polluted water streams. From a waste-management standpoint, producing biodiesel from WCO is environmentally beneficial.

The aim of this study is to produce biodiesel from waste cooking oil (WCO) in an attempt to reduce the cost of biodiesel and reduce waste and pollution from waste oil in Egypt.

2. Materials and methods

2.1. Chemicals and reagents

Pure calcium chloride, potassium hydroxide, anhydrous sodium sulfate and methanol were purchased from E.Merck Co. (Germany).

2.2. Waste cooking oil

The sample of waste cooking oil (WCO) of non edible oil grade (frying El-Fakher oil), was collected from a local fast-food popular restaurant (Giza, Egypt).

2.3. Pretreatment

Collected WCO was dried over calcium chloride (CaCl_2) and then filtered to remove any suspended matter, CaCl_2 crystals, and burned food bits, etc.

2.4. Transesterification and biodiesel production

The production methodology followed in this study was according to that of Tomosevic and Siler-Marinkovic [11] with little modification, where the alkali-catalyzed transesterification was applied. Basically, methanol was the alcohol of choice and KOH was used as the catalyst. Potassium methoxide solution (PMS) was prepared freshly by mixing a predetermined amount of methanol (≈ 12 wt % of oil) with KOH (≈ 1.0 wt % of oil) in a container until all the catalyst dissolved. The PMS was then added to 200 g of WCO and stirred vigorously for 30 min at 30 °C. Then, the mixture was carefully transferred to a separating funnel and allowed to stand for 4 h. The lower layer (glycerol, methanol and most of the catalysts) was then drained out. The upper layer (methyl esters MEs, some methanol and traces of the catalyst) was transferred into another flask containing freshly prepared PMS mixed at 60 rpm under reflux at 60°C for 30 min. Afterwards; the mixture was carefully transferred to a separating funnel and allowed to stand over night. The glycerol was removed by gravity settling, whereas the obtained crude esters layer was transferred into water bath to remove excess methanol at 65°C and 20 kPa. The obtained crude methyl esters were then cleaned thoroughly by washing with warm (50 °C) deionized

water, dried over anhydrous Na_2SO_4 , weighted and applied for further analysis.

All the steps and further analysis were in duplicates and the final reported results were the average values.

2.5. Fourier transforms infrared spectroscopy (FTIR) analysis

FTIR analysis was performed using instrument, Perkin Elmer, model spectrum one, for detection of transesterification efficiency of WCO by determination of active groups produced from these process.

2.6. Gas chromatography (GC) analysis

The esterified product was analyzed using GC. The analysis was carried out by using Agilent 6890 plus, equipped with a HP-50 capillary column (0.53 mm x 30 m, 0.5 μm film) and flame ionization detector. Pure nitrogen was used as a carrier gas. The oven temperature of injector was 250 °C and sample size was 1 μL . The identification of the fatty acid esters was established by chromatographic reference mixture of fatty acid esters of known composition.

2.7. Physico-chemical characterization of produced biodiesel

The purified product obtained from oil esterification was tested for estimating their fuel properties using the standard methods of analysis for petroleum product, ASTM Standard Methods [12] and compared with the Egyptian standards for petro-diesel oil and European and American standards of biodiesel (EN14214 and D-6751, respectively).

3. Results and discussion

Chemical properties (acid, iodine and saponification values) of the WCO used as a feedstock were determined and compared with those of produced biodiesel after purification step (Table 1).

The acid value measures the content of free acids in the sample, which have influence on fuel aging. It is measured in terms of the quantity of KOH required to neutralize the sample. The base catalyzed reaction is reported to be very sensitive to the content of free fatty acids, which should not exceed a certain limit, recommended to avoid deactivation of the catalyst, formation of soaps and emulsion [13]. Sharma et al. [14] reviewed that acid value of the feedstock for alkaline transesterification has to be reduced to less than 2 mg KOH/g (i.e. 1%); while only few examples of transesterification with feedstock acid value reached 4.0 mg KOH/g (i.e. 2%) were recorded. They also reported that when waste cooking oil is used as feedstock, the limit of free fatty acids is a bit relaxed and the value a little beyond 1% (i.e. 2 mg KOH/g) which did not have any effect on the methyl ester conversion. The feedstock acid value obtained in this study was ≈ 5 mg KOH/g oil. Thus in the light of the previous discussion on the requirements for the feedstock acid values, it could be

concluded that the used WCO had values above the recommended 2 mg KOH/g. However, this value did not turn out to be limiting for the efficiency of the applied two-steps process, as it will be discussed later along to the obtained product yield and purity.

The acid value of the produced MEs was 0.48 mg KOH/g oil. The average percentage of acid value lowering from the feedstock to the corresponding biodiesel was about 91%. The recorded acid value of the produced biodiesel is higher than that of standard petro-diesel, but it meets the standards limits of EN14215 and D-6751, indicating that the free fatty acid content will not cause operational problems, such as corrosion and pump plugging, caused by corrosion and deposit formation.

The iodine value of the feedstock used in this study, which is a measure of unsaturation degree, was ≈ 62 mg $I_2/100$ g oil. According to JUS EN 14214 [15], MEs used as diesel fuel must have an iodine value less than 120 g I_2 per 100 g of sample. MEs obtained in this study had low iodine value of ≈ 60 mg $I_2/100$ g and this finding is in accordance to the fatty acid composition, i.e. the calculated total unsaturation degree of MEs (Table 2 and Fig. 1). Predojevic [13], reported that, iodine value depends on the feedstock origin and greatly influences fuel oxidation tendency. Consequently, in order to avoid oxidation, special precautions must be taken during the storage of biodiesel produced from WCO, as it is known that, used frying oils have a variety of qualities, and possess properties significantly different from the neat oils. During frying process, oil is continuously or repeatedly subjected to high temperatures in the presence of air and moisture. Under these conditions a variety of degradation reactions can occur, such as auto-oxidation, thermal polymerization, thermal oxidation, isomer cyclization and hydrolysis which increase the iodine value.

Saponification value represents milligrams of potassium hydroxide required to saponify one gram of fat or oil. The obtained results indicated that in general, esters had higher saponification values than the corresponding oils. Saponification values of the feedstock and product ≈ 200 and 207 mg KOH/g oil, respectively. The average percentage of the increase in saponification value was 3.76%. It is known that a triglyceride has 3 fatty acid chains associated and each triglyceride will give 3 methyl esters, stoichiometrically it may be expected that the same amount of fatty acid carbon chain in neat feedstock oil and biodiesel will react with the same amount of KOH giving the soaps, i.e. their saponification values will be the same. But this assumption could be varied in case of using WCO as a feedstock, as its properties differ significantly from neat oils as a consequence of cyclization, polymerization and degradation of triglycerides that occur during the frying process.

The biodiesel yield was estimated after the reaction, before and after the purification step. The produced biodiesel weight relative to the initial used WCO was taken as the biodiesel yield. Crude biodiesel yield of 92 wt% was obtained from transesterification of 200 g WCO and methanol with KOH as catalyst, which was reduced to 85 wt%, after purification step. This reduction is not surprising because it is

known that, the glycerol, alcohol, catalyst and mono- and diglycerides, found in crude MEs besides fatty acid esters would have been removed during the purification step.

The infra red spectrum of the produced biodiesel, (Figure 2), showed the IR bands at 1020, 1169 and 1241, corresponding to the presence of ester C-O-, 1744 for C=O ester, 2854, 2923 for (CH_2 , CH_3), 3008 for (C=C) and 3468 corresponding to the presence of alkynes group. The presence of ester group and absence of hydroxyl peak can be correlated to the transesterification process of WCO. The chemical structure of the product was determined using *gas chromatography* as shown in Table 2 and Figure 1. It is clear that, the carbon number of the ester produced from the transesterification process is in the range ($C_{16} - C_{18}$). The product consists of about 69.4% saturated fatty acid ester (mainly 66.4% stearic acid ester and 3% palmitic acid ester), and about 30.6% unsaturated fatty acid ester, containing one double bond (oleic acid ester).

The physico-chemical properties of the produced biodiesel as compared to Egyptian standards of petro-diesel oil and European and American standards for biodiesel are illustrated in Table 3. The initial boiling point (IBP) of the produced biodiesel is 229°C. The higher distillation temperature may shorten the ignition delay of the fuel and it decreases the probability of the occurrence of knocking in the diesel engine [13, 16-18]. It is clear that the produced biodiesel has a density of 0.9055 g/cm³, which is higher than that of diesel fuel (0.82-0.07 g/cm³). Carbon residue is an important indicator for the measure of the tendency to form carbonaceous deposits in an engine; which causes a blockage in the nozzles, corrosion, and cracking of the components. It is clear that, the produced biodiesel has carbon residue of 0.63% and ash content 0.002%. The low ash content is another advantage, where if left upon the engine parts it cause their abrasion. The flow properties, including cloud point and pour point, are 3°C and 0°C, respectively. This indicates that the produced biodiesel would be more suitable in cold conditions as compared to petro-diesel. The produced biodiesel is characterized by low sulfur content (0.12%). This is considered to be an advantage of the prepared biodiesel, as the presence of sulfur in the fuel leads to formation of acidic sulfur oxides; SO₂ and SO₃, which are corrosive gases that might corrode the engine parts and lead to the environmental pollution. The flash point of the produced biodiesel is 202 °C. This is considered to be higher than that of standard Egyptian petro-diesel oil (55 °C). Liquid fuel with high flash point can prevent auto ignition and fire hazard at high temperature during transportation and storage periods. Hence, such produced biodiesel can be stored and handled safely. Viscosity is a significant fuel property that affects the flow and atomization characteristics of a liquid fuel. This parameter is also useful for evaluating the methyl ester contents of biodiesel samples, since there is a correlation between the content of esters and the viscosity; the higher the viscosity, the lower the ester content [16-18]. The kinematic viscosity of the produced biodiesel is 8.38 cSt at 40 °C. It is found to be larger than that of the standard petro-diesel (1.6-7 cSt). This inferred that the produced biodiesel will have inferior injection and

Table 1. Some chemical properties of waste cooking oil (WCO) used as feedstock for methyl esters preparation and produced biodiesel

Parameters	Feedstock	Produced biodiesel
Acid value mg KOH/g	5.1	0.48
Iodine value mg I ₂ /g	62.0	60.0
Saponification value mg KOH/g	199.5	207.0

Table 2. Composition of biodiesel obtained by transesterification of WCO using GC

Fatty acid ester	Carbon number chain	Wt%	Molecular formula
Palmetic	16	3.00	C ₁₆ H ₃₂ O ₂
Stearic	18	66.40	C ₁₈ H ₃₆ O ₂
Oleic	18	30.60	C ₁₈ H ₃₄ O ₂

Table 3. Physicochemical properties of produced biodiesel compared to the Egyptian standards of petro-diesel fuel and two international biodiesel standards

Test	Produced Biodiesel	Egyptian Diesel oil	Biodiesel (EN14214)	Biodiesel D-6751
Flash point °C	202	> 55	> 101	> 130
Density g/cm ³ @ 15.56 °C	0.9055	0.82-0.87	0.86-0.9	----
Kinematic Viscosity cSt @ 40 °C	8.38	1.6-7	3.5-5	1.9-6
Kinematic Viscosity cSt @ 100 °C	4.34	---	----	----
Total acid number (mg KOH/g)	0.48	Nil	< 0.5	< 0.8
Cloud point °C	3	---	- 4	----
Pour point °C	0	4.5-15	----	----
Initial boiling point IBP °C	229	----	----	----
Cetane number	63.8	Min. 55	> 51	> 47
Calorific value MJ/Kg	38.54	Min. 44.3	32.9	----
Total S wt%	0.12	Max. 1.2	< 0.01	< 0.05
Ash content wt%	0.002	Max. 0.01	0.02	< 0.02
Carbon residue wt%	0.63	Max.0.1	< 0.03	< 0.05
Copper strip corrosion @ 100°C	1a	1a	Class 1	No. 3 Max.
Water content wt%	0.08	Max. 0.15	< 0.05	0.05
Iodine number mg I ₂ /100 g	60	---	120	---

Table 4. Correlation coefficient between produced biodiesel, Egyptian petro-diesel, European and American biodiesel standards

Diesel Source	Produced Biodiesel	Egyptian Diesel oil	Biodiesel (EN14214)	Biodiesel (D-6751)
Produced Biodiesel		0.999	0.969	0.958
Egyptian Diesel oil			0.97	0.968
Biodiesel (EN14214)				0.999
Biodiesel (D-6751)				

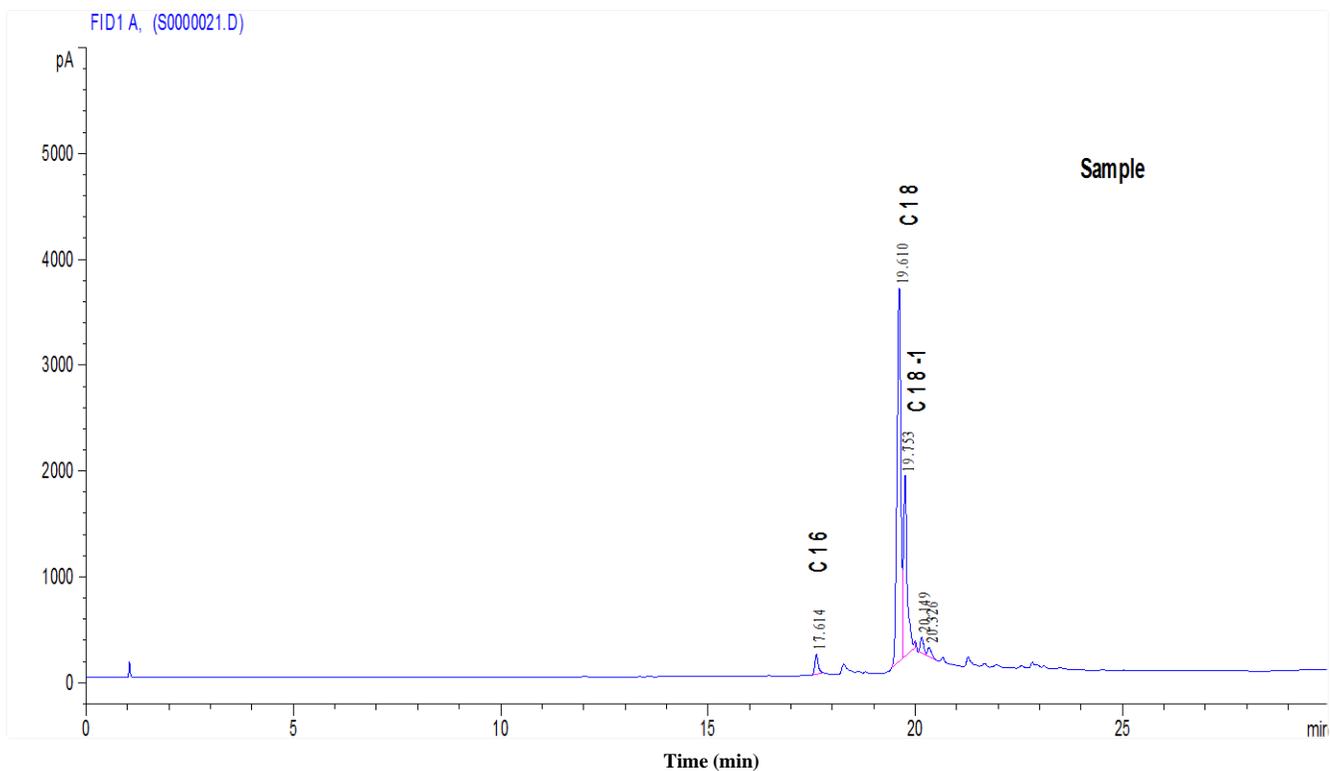


Figure 1: Fatty acid profile of methyl ester product of the waste cooking oil

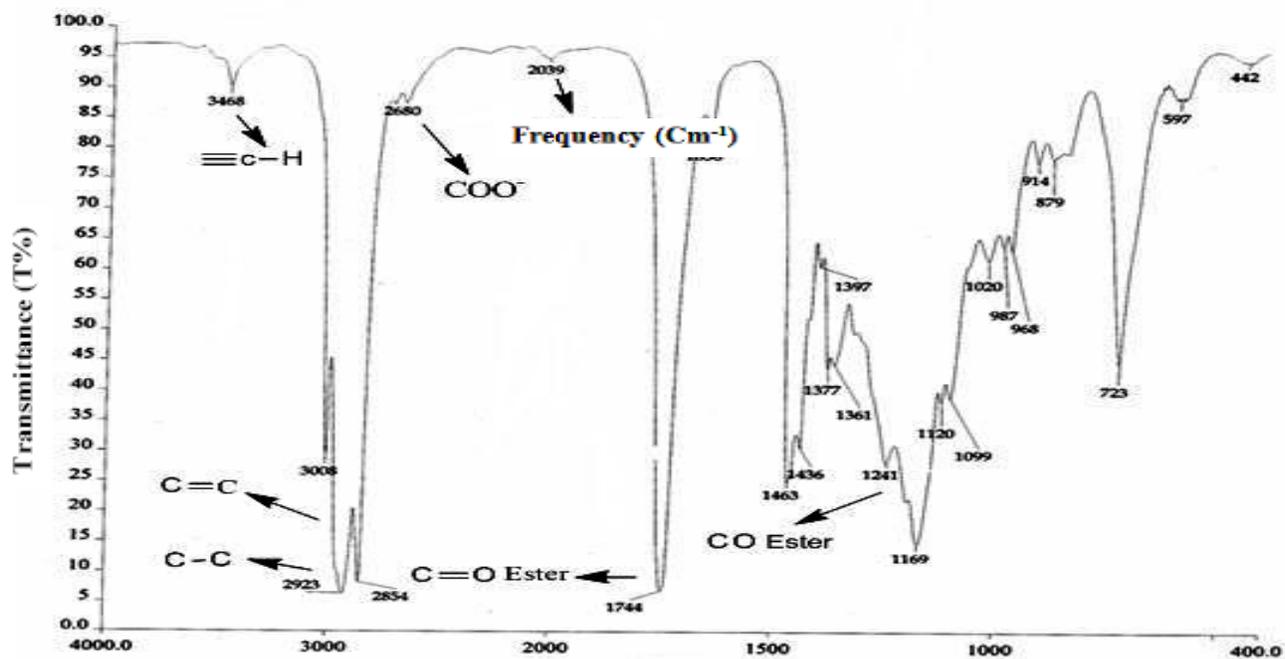


Figure 2. Infra-red structure of methyl ester of waste cooking oil

atomization performance, but offer lubrication and protection for moving parts of an engine. The calorific value of the obtained biodiesel; 38.54 MJ/Kg is an acceptable value. Although it is lower than the Egyptian standards for petro- diesel (44.3 MJ/Kg), it is higher than that of European standard for biodiesel (32.9 MJ/Kg). The cetane number of the diesel fuel is the indicator of the ignition quality; a high cetane number for a diesel fuel leading to a higher performance, shorter ignition delay and duration of the combustion period resulting in lower emission of all pollutants other than oxides of nitrogen (NO_x), besides less occurrence of knocking noise. The obtained data revealed higher cetane number; 63.8 compared to petro-diesel; 55. Usually, the Cetane number increases, with the increase of saturated fatty acid content in biodiesel fuel [3].

From the above results, it can be concluded that, there are positive correlation (Table 4) between the produced biodiesel, Egyptian petro-diesel, European biodiesel (EN14214) and American biodiesel (D-6751) standards with correlation coefficient ($r > 0.95$).

Conclusion

There are differences in physicochemical properties of the produced biodiesel compared with the Egyptian standards of petro-diesel oil, but the properties of the biodiesel are completely acceptable with positive correlation coefficient ($r = 0.999$). The higher flash point of the produced biodiesel is beneficial from a safety aspect, and the low sulfur content is the reason for the extremely low SO_x emissions associated with its use as a fuel. The considerable high cetane number leads to a smoother running of the engine with less noise. The produced biodiesel is within the recommended standards of biodiesel fuel ($r > 0.95$), good in quality and its yield is satisfactory. Biodiesel obtained from waste cooking vegetable oils can be considered a promising option in Egypt. Waste cooking oil is available and relatively cheap price for biodiesel production in comparison with fresh vegetable oil costs.

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