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CHARACTERIZATION OF BIODIESEL PREPARED FROM WASTE COOKING OIL

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ABSTRACT: Increased energy consumption and the depletion of petroleum reserves have pushed up oil prices globally. Diminishing the petroleum reserve is another global risk factor. Producing Biodiesel vegetable oils and animal fat by transesterification can be a considerable energy alternative. In this study, biodiesel is produced from waste cooking oil by transesterification method with methanol in the presence of HCl as a catalyst. Biodiesel production begins with mixing raw the collected used cooking oil into one pool. The mixture is then settled for 8 hours at room temperature before initiating the transesterification process 90°C by mixing HCl (1% of oil weight) with methanol, while the methanol: oil ratio is 1:4. The process lasts for 9 h under a condenser. Biodiesel purification is carried out by washing the product twice with hot water (temperature 70°C) to remove excess reactants and byproducts such as alcohol, catalysts, soap and glycerine, and fatty acid methyl ester (FAME). The resulting diesel density of 3.72 kg/m³ (at 15°C), a kinematic viscosity of 8.93 mm²/sec., at 40°C, calorific value was 41299 kJ/kg, Total acid number of 0.111 was for waste cooking oil, Cetane number of 48.95, acid value (AV) was 1.135 mg/koh was and Ester value (EV) was 178.42 mg/koh. The Saponification value (SV) was 179.56 mg/koh, pH was 5.7, and Glycerol Weight was 97.53 (Gw).

Key words: Biodiesel, preparation, fuel properties, transesterification, GLC

INTRODUCTION

Biodiesel, an alternative fuel adequate for internal combustion engines, is produced by transesterification of vegetable oil (sunflower oil, rapeseed oil, soybean oil, palm oil, oil from exotic plant species) or animal fat into fatty acid methyl esters (FAME). Biodiesel is clear, flammable liquid free of impurities. It is water-insoluble with yellow color (Malovcov, 2013). Biodiesel is reported, non-toxic, biodegradable and environmentally safe (Eevera, 2009). According to current standards, transesterification of vegetable oils with alcohol into methyl esters is the most accepted method to meet the requirements of EN 14214 standard for biodiesel production (Talebian-Kiakalaieh, 2013). The biodiesel transesterification process separates the

fatty acids from the glycerol base, producing free esters, either with or without using a catalyst (Eevera, 2009; Malovcova, 2013). The utilization of different types of catalysts improves the rate and yield of biodiesel. Many different alcohols can be used in this reaction, including methanol, ethanol, propanol, and butanol. The methanol application is more feasible because of its low-cost and physical, besides its chemical advantages, such as high polarity and the shortest alcohol chain. According to Fig. 1, R1, R2 and R3 are long chains of hydrocarbons called fatty acid chains. In this reaction on one mole of triglyceride reacting reacts with three moles of methanol to produce three moles methyl ester (biodiesel) and one-mole glycerol (Malovcova, 2013; Talebian-Kiakalaieh, 2013).

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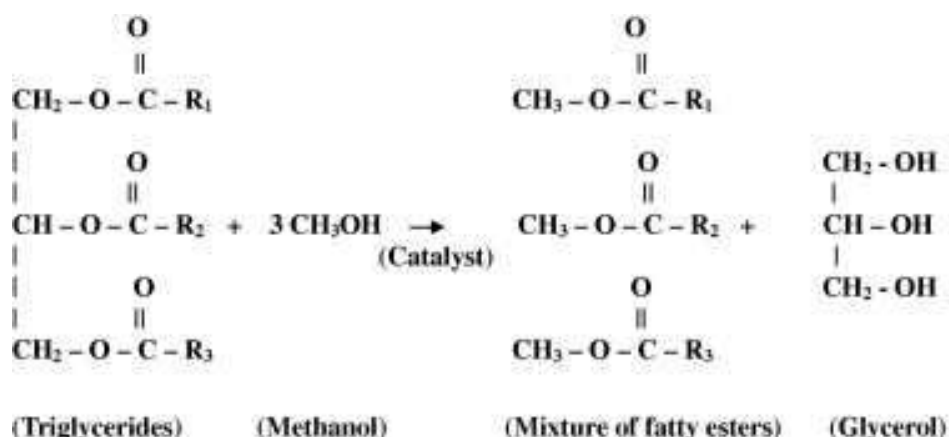


Fig. 1. Methanolysis of triglyceride

Generally, the transesterification reaction involves some critical parameters, significantly influencing the final conversion rate and yield. The essential variables are reaction temperature and time, the oil free fatty acid content and water content, type and amount of catalyst, the molar ratio of alcohol to oil, the type of chemical stream of alcohol, and the use of co-solvent and mixing intensity (Talebian-Kiakalaieh, 2013). The majority of the world's energy needs are supplied through petrochemical sources, coal and natural gases, apart from hydroelectricity and nuclear energy. All these sources are finite will be consumed shortly at the current usage rates (Srivastava and Prasad, 2000). Diesel fuels have an essential function in a developed country's industrial economy and are currently being used in transports, industrial and agricultural goods. The world demand for diesel fuels increases to compensate for the shortage in petroleum products and commensurate the increasing demands in national and international transport. This trend has stimulated the recent interest in alternative sources for petroleum-based fuels. An alternative fuel should be easily available, environment friendly and techno-economically competitive. One starting material of such fuels is triglycerides and their derivatives. Being renewable, widely available from a variety of sources and having low sulphur contents close to zero, and hence causing least environmental damage, vegetable oils are a good choice for biodiesel production. Chemically the oils consist of triglyceride molecules of three

long-chain fatty acids, that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of the carbon chain, orientation and position of double bonds in these chain. Thus biodiesel refers to lower alkyl esters of long-chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids. This work aims to test the feasibility of producing biodiesel from waste vegetable oils by transesterification with methanol in the presence of an alkaline catalyst (KOH) and evaluate the produced physicochemical characteristics methyl esters fuel.

MATERIALS AND METHODS

Materials

The waste cooking oil obtained from restaurants in Zagazig city, Sharkia Governorate, Egypt n-Hexane, methanol, sodium methoxide, sodium hydroxide, potassium hydroxide, potassium methoxide and anhydrous sodium sulfate were purchased from Merck chemical co.. Pure fatty acid esters, used as standards, were procured from Sigma chemical co. All the chemicals used were of analytical grade.

Transesterification of Waste Cooking Oil

In a one liter 3-neck round bottom flask, 100 ml of Egyptian linseed and waste cooking oil (50g) were heated and stirred in a water bath equipped with magnetic stirrer (1000 rpm) adjusted at 20-65°C. KOH was added to

methanol at a dry weight ratio of 0.3 -2% by weight of oil and molecular ratio of 3:1-10:1). in a separate flask and carefully shake till KOH became completely soluble in methanol (methoxide is formed). Methoxide was added to the heated oil (90 °C). The product was left in a separating funnel for 12 hours and then the ester layer was collected after complete separation by washing with hot water for 56 times, using anhydrous Na₂SO₄ according to (Abdel Fatah *et al.*, 2012).

Fatty Ester Profile by Gas Chromatography (GC)

Fatty acid methyl esters (FAME) were separated using a Varian (Walnut Creek, CA, USA) 8400 gas chromatograph (GC) equipped with a flame ionization (FID) detector and SP2380 (Supelco, Bellefonte, PA, USA) column (30 m 40.25 mm i.d., 0.20µm film thickness). Carrier gas was heat 1 mL/min. The oven temperature was held at 150°C for 15 min, increased to 210°C at 2°C/min, followed by an increase to 220°C at 50°C/min. The injector and detector temperatures were 240°C and 270°C, respectively. FAME peaks were identified by comparison with the retention times of known reference standards. Each FAME determination was run in triplicate and average values were calculated.

Physical and Chemical Properties of Investigated Oils

Determination of density

Density was measured using the standard method according to AOAC method (1995).

Determination of kinematic viscosity

Kinematic viscosity (ν , in square millimeters per second) was determined with Cannon-Fenske viscometers CT-1000 (Cannon Instrument, State College, PA, USA) at 40°C according to Knothe and Steidler (2005). All experiments were run in triplicate and the mean values were calculated.

Determination of flash point

The flash point of sample was measured using the standard method according to AOAC (1995).

Determination of cloud point

The cloud point was determined as the temperature at which the sample begins to haze following AOAC (1995).

Determination of pour point

The pour point was determined according to ASTM D.97 method (Kywe and Oo, 2009).

Determination of acid value

Acid value of the oil was determined according to AOAC (1995).

Determination of iodine value

The iodine value was determined using the Hanus method as described in AOAC (1995).

RESULTS AND DISCUSSION

Fatty Acid Composition

Data in Table 1 show the main fatty acid (FA) found in waste cooking oil. Linoleic acid (C18:2, 26.1%) was the major FA followed by oleic (C18:1, 20.5%). Other minor fatty acid included palmitic acid (C16:0, 12.8%), and stearic acid (C18:0, 2.2%). This result is in agreement with previously reported data (Savita *et al.*, 2012).

Physical and Chemical properties of Investigated Oils

Density

Bio-diesel fuels are, in general, characterized by higher density than conventional petroleum diesel, which means that volumetrically-operating fuel pumps will inject greater mass of biodiesel than conventional diesel fuel. This in turn will affect the air-fuel ratio hence the local gas temperatures and NO_x emissions, as long as the engine retains its diesel-fuel calibration. Actually, it has been argued that lower diesel densities favor lower NO_x (McCormick *et al.*, 2001), although other researchers have not confirmed such an unequivocal trend. As shown in Table 2. The (average) densities of the waste cooking oil was 3.72 kg/m³, with the overall average value being 880.2 kg/m³. In the United States, there is no specification for biodiesel density. In European countries on the other hand, the acceptable range is quite wide (860-900 kg/m³), and this is met by all examined methyl esters acceptable.

Table 1. Levels of fatty acid percentage in waste cooking oil methyl ester

Fatty acid	Structure	Percentage
Capric acid	C10:0	3.9
Lauric acid	C12:0	11.8
Myristic acid	C14:0	9
Palmitic acid	C16:0	12.8
Palmitoleic acid	C16:1	0.10
Stearic acid	C18:0	2.2
Oleic acid	C18:1	20.5
Linoleic acid	C18:2	26.1
Linolenic acid	C18:3	0.88
Arachidic acid	C20:0	0.09
Behenic acid	C22:0	0.10

Table 2. Physical and Chemical Properties of Biodiesel Waste Cooking Oil

Properties	Waste cooking oil	Biodiesel
Calorific value, kJ/kg	3024	41299
Total Acid number	1.135	0.111
Cetane Number	22.54	48.95
Density (kg/m ³)	3.72	880
Viscosity (mm ² /sec)	8.93	3.8
Saponification value	179.56	190
Ester value	178.42	180
pH	5.7	5.3
The percentage of acidity	5.70	0.45
Glycerol Weight	97.53	0.0
Cloud point (°C)	310	-13
pour point (°C)		-24
Acid value	0.11	1.37
Iodine value	120	2.21

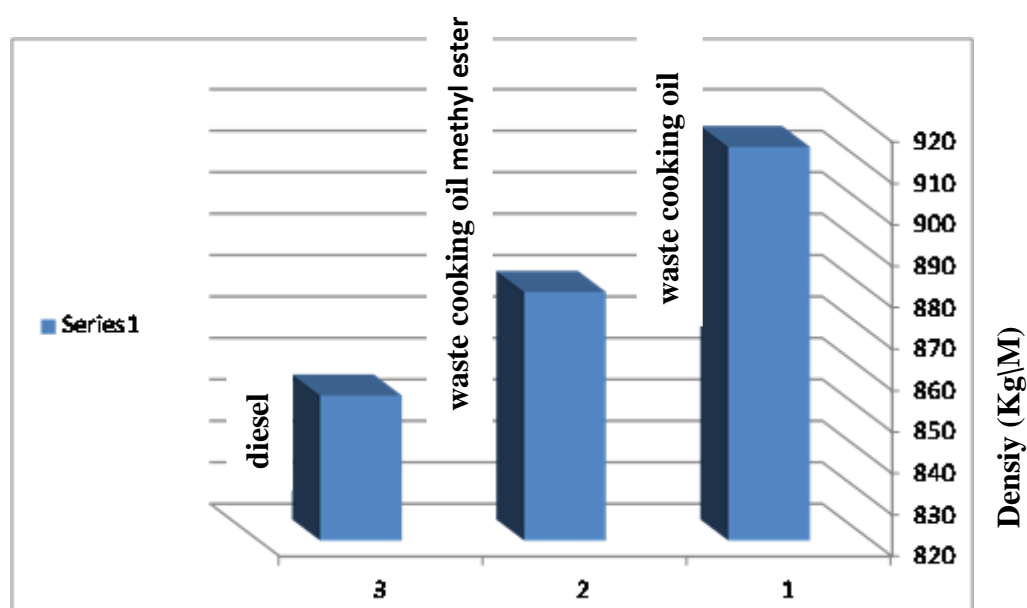


Fig. 2. Density (kg/m^3) of investigated oils

Kinematic viscosity

Viscosity is a measure of the resistance of a fluid which is deformed by either shear or tensile stress. In the case of liquid fuels, the less viscous the fluid is, the greater its ease of movement (fluidity) (Rakopoulos *et al.*, 2006). Vegetable oils have higher viscosities than the acceptable diesel fuel values. Thus, they cannot be used safely as fuels in a compression ignition engine, at least without prior heating to decrease viscosity. On the other hand, the transesterification process reduces the FAME's viscosity to levels comparable to but still slightly higher than that of petrodiesel. As shown in Table 2 the viscosity values of the waste cooking oil was $8.93 \text{ (mm}^2/\text{sec.)}$, and was reduced to 3.8 after the transesterification.

Flash point

The flash point (FP) is a measure of the temperature to which a fuel must be heated such that the mixture of vapor and air above the fuel gets ignited; FP varies inversely with the fuel's volatility. As documented in Table 2, storage of neat bio-diesel is thus much safer than diesel in this regard (Tsegay, 2017). Specifically, the (average) values of flash point for waste cooking oil methyl ester was 65°C . European specifications require bio-diesel fuels to have at least 101°C

flash point, whereas in the US the minimum required level is lower (93°C); Although flash point depends, in general, on the originating oil, it is not directly linked to the fatty acid composition (Berman *et al.*, 2011).

Cloud point and pour point

Biodiesel has higher cloud and pour points than conventional diesel fuel (Fernando *et al.*, 2007; Sanford *et al.*, 2011). Table 2 illustrates that waste cooking oil has relatively a high cloud point -13°C , while the derived biodiesel has a highly reduced point (-24°C).

Acid value (AV)

The AV of waste cooking oil and its prepared methyl esters was higher, (Table 2) most of the FFA had been removed. In the case of waste cooking oil, the AV was 0.111, while in the case of waste cooking oil methyl esters, it was 1.37. These data agreed with Shailesh *et al.* (2010), who stated that the acid value of waste cooking oil methyl ester was in the same range.

Iodine value

The iodine value is a parameter used to determine the degree of unsaturation in a vegetable oil or animal fat. This number indicates the mass of iodine (I_2) in grams that is necessary to completely saturate, by means of a

stoichiometric reaction, the molecules of 100 g of a given oil (Lapuerta *et al.*, 2009). Table 2 illustrates the iodine values of the examined bio-diesels oils. It was 108 for the waste cooking oil methyl ester. There is no specification in the US for the Iodine value, whereas European specifications require that bio-diesels used in compression ignition engines have a (rather low) maximum value of Iodine value of the order of 120. The idea behind this specification is that, high fuel iodine values indicate propensity for polymerization resulting in deposit formation (Graboski and McCormick, 1998). This means that investigated on the other hand waste cooking oil methyl ester is accepted.

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خواص البيوديزال المحضر من الزيوت المستعملة

مي عبدالله إبراهيم كردي - محمود زكي سطوحى - حفناوي طه حفناوي - أيمن محمد السيد جمعه

قسم الكيمياء الحيوية الزراعية - كلية الزراعة - جامعة الزقازيق - مصر

أدى استهلاك الطاقة المتزايدة الي نضوب الاحتياطيات النفطية الي ارتفاع اسعار النفط في العالم ويعد تناقص احتياطي البترول الي مشكلات متصلة بالنسبة لطاقة الاحفورية لذلك يتم تطوير طاقة بديلة واحدة في العالم و هي وقود الديزل الحيوى، وهو منتج من استرة الكحولات مع الزيوت النباتية و الدهون الحيوانية و هو بديل اكثر مرعاة للبيئة من الديزل البترولي، وفي هذه الدراسة يتم انتاج وقود الديزل الحيوي من نفايات زيوت الطهى (زيت عباد الشمس) والاسترة مع الميثانول وحمض الهيدروكلريك، حيث يتم اجراء عملية الاسترة علي درجة حرارة 90 درجة مئوية لمدة 8 ساعات ويتم الخلط بنسبة 1 من الزيت إلى 4 من الميثانول، ثم بعد ذلك يتم الغسيل بالماء والفصل وذلك للحصول علي الديزل بافضل جودة و ذلك بازالة الشوائب والمواد الثانوية المتبقية مثل الكحول الزائد والمواد الحفازة الزائدة والصابون والجلسرين حيث كان هذا الجراء غني باستر ميثل الاحماض الدهنية، وكانت الكثافة 3.72 كجم/م لنفايات زيت الطهى عند درجة حرارة 15 درجة مئوية، وكانت اللزوجة الحركية عند درجة حرارة 40 مئوية 8.93 مم/الثانية لنفايات زيت الطهى، وكانت القيمة الحامضية (AV) 1.135 لنفايات زيت الطهى، وكانت مجمل القيمة الحامضية لزيت البيوديزل 0.111، وكان رقم استان 48.95 لزيت البيوديزل، وكان رقم التصبن (SV) 179.56 لنفايات زيت الطهى وكان رقم الاستر (EV) 178.42 لنفايات زيت الطهى، وكان رقم pH 5.7 لنفايات زيت الطهى، وكان وزن الجلسرول (GW) 97.53 لنفايات زيت الطهى .

المحكمون:

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