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Transesterification and Production of Biodiesel from Waste Cooking Oil: Effect of Operation Variables on Fuel Properties

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Abstract: Biodiesel is proved to be the best replacement for diesel because of its unique properties like low toxicity, no sulfur emissions, no particulate matter pollutants, significant reduction in greenhouse gas emissions and biodegradability. Several processes for biodiesel fuel production have been developed, among which transesterification using alkali catalysis gives high levels of conversion of triglycerides to their corresponding methyl esters in short reaction times. It is prepared from waste vegetable oils and animal fats by trans-esterification process. It is alkali catalyzed reaction which involves waste cooking oil, methanol, and potassium hydroxide. The study focus on the physical and chemical properties of waste cooking oil (WCO), transesterification and production of biodiesel from WCO. The operation variables used were methanol/oil molar ratio (5:1-9:1), catalyst concentration (0.5-2.0 wt%), temperature (30-70°C). The evolution of the process was followed by gas chromatography, determining the concentration of the methyl esters at different reaction times. The biodiesel was characterized by its density, viscosity, high heating value, cetane index, cloud and pour points, characteristics of distillation, flash and combustion points, saponification value, and iodine value according to ISO norms. The biodiesel with the best properties was obtained using a methanol/oil molar ratio of 6:1, potassium hydroxide as catalyst (1%), and 60°C temperature. This biodiesel had properties very similar to those of no. 2 diesel.

Keywords: Trans-Esterification, Biodiesel, Alternative Fuel, Fuel Properties, Waste Oil

1. Introduction

Increasing concerns regarding environmental impacts, the soaring price of petroleum products together with the depletion of fossil fuels have prompted considerable research to identify alternative fuel sources. Biofuel has recently attracted huge attention in different countries all over the world because of its renewability, better gas emissions and its biodegradability. It is estimated that biodiesel/bio-ethanol could replace approximately 10% of diesel fuel consumption within Europe and 5% of Southeast Asia's total fuel demand [1]. The alternatives to diesel fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. Many of these requisites are satisfied by vegetable oils or, in general, by triglycerides. Indeed, vegetable oils are widely available from a variety of sources, and they are renewable. Also,

these fuels are easily biodegradable, they have practically null sulfur content, and their transport and storage offer no problems. Consequently, these products can be considered viable alternatives for diesel fuel [2, 3]. Their main drawback is price, which is higher than for oil derived diesels. In consequence, their use must be accompanied by a policy oriented toward their total tax exemption. However, WCO is used as a diesel fuel substitute. Large quantities of WCO are available throughout the world. Estimates of the amount of WCO in the US range from 4.5 billion to 11.3 billion liters a year [4]. WCO is used as additive oil for fodder preparation and in the manufacture of soap. In some other countries, the oil from the better restaurants then goes to poorer ones, or perhaps to individuals for food preparation. In few restaurants, the vegetable oil after the

first use is passed through an oil recycler and then reused for cooking. After the second use, the oil is collected in a common slump and sent to microbiological laboratory for the manufacture of soap. In a few countries, the use of WCO in the production of animal feeding is prohibited and this has resulted in the availability of surplus quantity of WCO. Large portions of WCO are illegally dumped into rivers and wastelands causing environmental pollution [2, 5]. The use of WCO as a fuel for diesel engines would reduce human or animal consumption, the illegal dumping and environmental degradation. Biodiesel can be processed from different mechanisms; transesterification is the most common process, in this process an ester compound is replaced with an alcohol in the alkyl group [5, 6, 7]. Biodiesel can be defined as fatty acid methyl esters (FAME) derived from the transesterification of triglycerides (vegetable oils or animal fats) with alcohol and suitable catalyst [6, 8, 9, 10]. Biodiesel is used as mix constituent of petroleum diesel in proportions for running a diesel engine, since using neat biodiesel has some engine issues [7, 11]. The crops identified for biodiesel are corn, sunflower, palm, olive, canola, soybean, rape and peanut soils, and animal-based lipid [8]. Economic feasibility of biodiesel depends on the availability of low-cost feed stocks [12]. The key issue for large scale application of biodiesel compared to petroleum diesel is the high cost of biodiesel due to the high cost of feedstock oils as both the edible and non-edible oils are limited. Moreover, it has been reported that nearly 70-95% of the total production cost is related to the cost of raw materials. This issue can be overcome by the use of waste cooking oil (WCO) as raw material which can effectively reduce the feedstock cost to 60-70%. Likewise, the cost of catalyst also affects the overall production cost. Several studies have been made to use waste materials for low cost catalyst preparation to develop sustainable biodiesel production process [13, 9]. This paper studies the physical and chemical properties of waste cooking oil, transesterification and production of biodiesel from waste cooking oil. The factors affecting the process parameters reported are studied and the point of interest focuses on their alcohol to oil ratio, reaction temperature, catalyst both qualitative and quantitative scope and the optimum condition.

2. Experiments

2.1. Materials

The waste cooking oil three samples have been collected from three different units and have been named as sample I, II & III. Sample I was taken after being used once for big restaurants, Sample II was collected from the Yarmouk University campus cafeteria and was taken after being used mostly twice, and sample III was collected from small shops in Irbed city, Jordan, which is mostly the kind of used cooking oil produced after repeated cooking or deep-frying several time. The WCO with 5–10 l each, was filtered to remove bits of food particles, and heated to about 110°C for 10-15 minutes to remove any traces of water. The free fatty acid (FFA) value of the used oil was tested and found to be less than 2%; therefore, a one-step transesterification process was used for biodiesel production from the samples of used cooking oils. The characteristics of the WCO samples are illustrated in Tables 1 and 2. Acid values of the samples varied from 0.67 to 1.43 mg KOH/g. The acid value was relatively low in sample I, which was used once. The low level of free fatty acid content in the WCO samples could be an advantageous for an alkali catalyzed trans-esterification process. The samples had saponification values ranging from 252 to 270 mg KOH/g oil. Considering the composition of the samples, the WCO molecular weights can be calculated to be between 678.1 and 704.3 g/mol. This value was much lower than WCO found in other research, which had molecular weight ranging from 866 to 873.4 g/mol [1, 14, 15]. These WCO samples had 10 times higher viscosity than diesel oil. They are composed mainly of saturated short length fatty acid alkyl chains, which was 40–47 wt% of C12:0, 16 wt% C14:0, 10 wt% C16:0 and less than 10 wt% of unsaturated compounds (Table 2). The methanol used (99% pure) is of analytical grade with boiling point of 78°C; the, KOH and anhydrous calcium chloride were of analytical grade and purchased from Loba Chemie Pvt. Ltd. Diesel was taken from commercial diesel (No. 2) with their characteristics listed in Table 1. The WCO samples were mixed together prior to the transesterification.

Table 1. Physical properties of WCO Samples & Diesel.

Property	Unit	Sample I	Sample II	Sample III	Mixed sample	diesel
Flash point	oC	272	249	267	264	86
Could point	oC	26,00	18.50	20.00	20.4	0
Density	g/cm^3	0.92	0.92	0.92	0.92	0.83
Viscosity	mm^2/s	32.08	37.8	33.74	36.5	3.43
Acid number	mg KOH/g	0.76	1.13	1.63	1.43	0.13
Saponification number	mg KOH/g	252.24	270.32	268.68	260.16	-
Iodine number	mg KOH/g	9.84	8.78	12.02	10.67	-

Table 2. Quantitative of fatty acids in WCO samples.

Component	Sample 1	Sample II	Sample III	Mixed sample
C12:0	42 22	46.23	44,37	43.21
C14:0	16.64	17.26	16.31	16.84
C16:0	8.88	7.26	10.58	9.82
C16:1	0.00	0.01	0.22	0.12
C18:0	2.54	2.02	1.82	2.20
C18:1	6.02	4,36	8.04	5.96
C18:2	1.35	1.41	1.68	1.51
C18:3	0.00	0.00	0.02	0.00
C20:0	0.00	0.11	0.04	0.02

2.2. Transesterification

The transesterification was carried out in a 250 ml three-neck glass flask equiped with a thermocouple and conneced with a reflux condenser using tap water to condense methanol vapor. The mixture was agitated by using a stainless steel stirrer. A 100 ml sample of oil was introduced and heated to a temperature selected from 30°C, 40°C, 50°C, 60°C, and 70°C. The amount of KOH catalyst used was ranging from 0.5 wt% to 2.0 wt% of the WCO and was dissolved into designed amount of methanol and poured into the flask. The transesterification reaction performed at different molar ratio of oil to methanol, varying from 1:4, 1:5, 1:6, 1:7 and 1:9. The mixture was maintained under stirring at the reaction temperature for designed period of time (30, 60, 90 and 120 minutes). At the completion of the reaction, the flask content was transferred to a separating funnel for glycerol and biodiesel separation for 12 h. The lower darker layer containing glycerol has been removed. The upper layer containing biodiesel was washed several times with a small amount of hot water (to remove traces of glycerol), until the washing were neutral and dried on anhydrous calcium chloride ($CaCl_2$) to remove residual water. The percent yield of biodiesel was calculated using the following equation: Yield % = weight of produced biodiesel / weight of WCO * 100

2.3. Analysis

Different physic-chemical propertied of WCO and biodiesel were measured by using ASTM standard methods, including density (D1298), kinematic viscosity at40°C (D445), flash point (D93), cloud point (D2500), pour point (D97), cetane index (D976) and acid value (D664). The average molecular weight was calculated by MW = 56.1 × 1000 × 3/(SV–AV), where AV (mgKOH/goil) and SV is the saponification value (mgKOH/goil) [16, 17, 18]. Fatty acid quantitative was determined by using a Hitachi G-5000A GC (gas chromatography), analysis is performed for identifying the hydrocarbon compounds such as fatty acids and methyl esters. The separation is carried out by using capillary column Rtx-5MS 30 m × 0.25 mm ID, 0.25 μm with helium at 137.7 ml/min as a carrier gas and 1:100 of split ratio [19].

3. Results and Discussion

3.1. Effect of Temperature

Reaction temperature is the important factor that will affect the yield of biodiesel. For example, higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. However, the increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides and causes methanol to vaporize resulting in decreasing the yield [20, 21, 22]. Usually the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. Therefore, the reaction temperature near the boiling point of the alcohol is recommended for faster conversion by various literatures. Figure 1 shows the effect of temperature on the conversion at the methanol/oil ratio of 6:1 in the presence of 1 wt. % KOH. For the same final reaction time, the percentage of esters increased with temperature. After 5 min, the esters present in the 60, 50, and 30°C runs were 84.4, 63.6, and 51.3%, respectively, showing the influence of temperature on ester conversion. At 90 min, the percentages were 95.1, 80.6 and 70.5, respectively. Hence, there was an initial period during which the reaction was very fast, and then a second period, much longer than the first, in which the composition evolved slowly toward equilibrium. Therefore, the rate of reaction was strongly influenced by the reaction temperature. However, if the temperature increased up to 70°C, there was a slight reduction in the conversion. This is because high temperature enhances both transesterification and saponification reactions [24, 23].

3.2. Methanol to Oil Molar Ratio

One of the most important parameters affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Stoichiometrically 3 moles of alcohol and 1 mole of triglyceride are required for transesterification to yield 3 moles of fatty acid methyl/ethyl esters and 1 mole of glycerol is used. As can be observed in Figure 2, with a stoichiometric

amount of methanol, the conversion to esters was near 70% after 1 h. The ester yields increased as the percentage of methanol increased, with the best results being for a molar ratio of 6:1, and temperature of 60°C in the presence of 1 wt% KOH. The conversion reached a value of above 50% in just 30 min. increasing the ratio from 5:1 to 6:1 increased the conversion. It rose from 50% for the ratio of 5:1 to 66% for the ratio of 6:1. The difference in the conversion between the ratios of 5:1 and 6:1 was about 26% in the first 90 min and slightly decreased to 14–15% for the last 30 min.
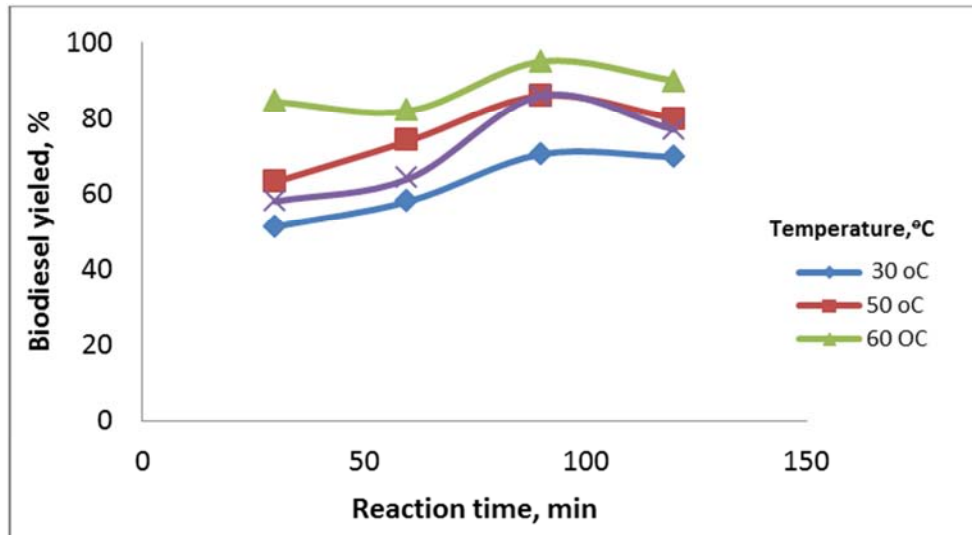

Figure 1. Effect of Temperature 60°C with reaction time (molar ratio 1:6 and KOH 1.0 wt %).

The difference in the conversion was less than 5% when the methanol/WCO ratio increased from 6:1 to 7:1. A further increase in the methanol/WCO ratio above 7:1 caused a reduction in the conversion. It was 84% for the ratio of 9:1 compared to 88% for the ratio of 7:1 after 90 min. For methanol/oil molar ratio less than 6:1 the reaction was incomplete, and at 9:1 methanol/oil molar ratio the separation of glycerol was difficult, since the excess methanol hindered the decantation by gravity so that the apparent yield of esters decreased because part of the glycerol remained in the biodiesel phase. Hence, the best results were obtained for an intermediate methanol/oil molar ratio of 6:1. These results are similar to those found in the literature [23, 25,].
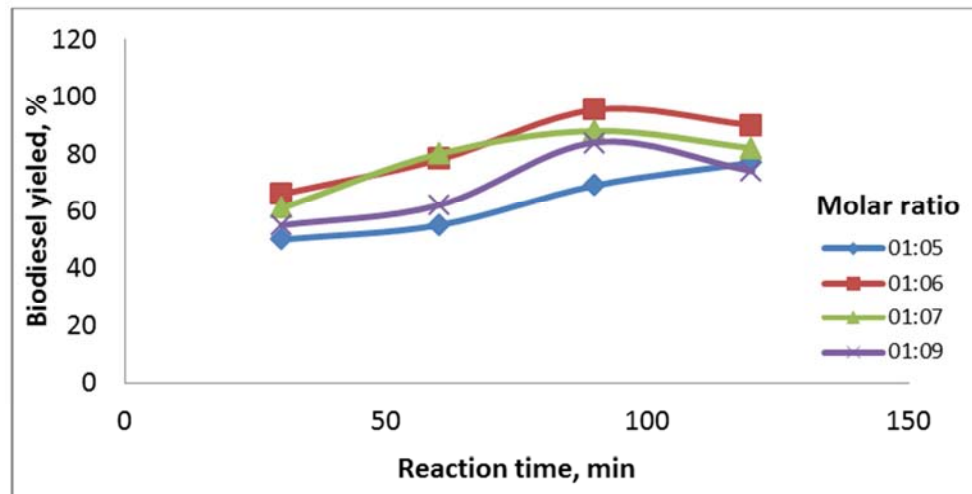

Figure 2. Effect of molar ratio with reaction time (Temperature 60 °C and KOH 1.0 wt %).

3.3. Effect of Catalyst

Fig 3, KOH is frequently soluble in solvent and easily promotes the reaction. Generally, catalyst concentration can affect the rate of biodiesel reaction and beyond the limitation of catalyst additions it̓s represented in Fig. 3. So, KOH catalyst used with 0.5, 1.0, 1.5 and 2.0 wt. % concentration for WCO, 0.5 wt% showed only 79.2% biodiesel yield and also 1.5 wt.% showed only 86% biodiesel yield. For 2.0 wt% catalyst showed biodiesel yield of 78.3% the decreases is due to the higher concentration of catalyst addition which gives a negative effect on the biodiesel production. On the other hand, using 1.0 wt. % of catalyst showed 95.4% biodiesel yield for WCO which is higher biodiesel yield than the other

concentrations. In general, as the catalyst concentration increased, the conversion of triglycerides also increased during 90 min time period. The conversion did not vary significantly above 90 min time period and slightly reduced in the last 30 min. This could be explained by the fact that the formation of soap hindered the separation of the methyl ester phase during the washing step. The soap particles formed emulsions with water, which resulted in an increase in the viscosity. This phenomenon did not occur at low KOH concentrations. As a consequence, the yields of biodiesel were low for the cases of 1.5 wt% and 2 wt% KOH. This is because the addition of excess alkaline catalysts caused more triglycerides participation in the saponification reaction, resulting in increased production of soap and mentioned and a reduction of the esters yield [1, 23, 26].
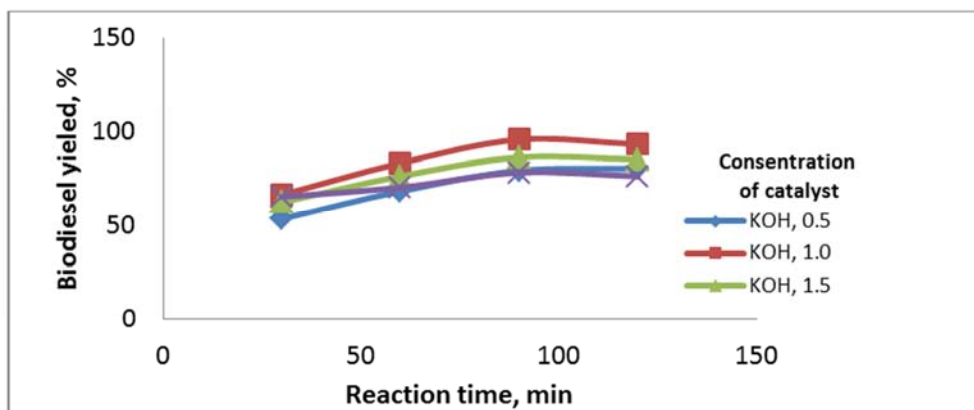

Figure 3. *Effect of concentration of catalyst (KOH) with reaction time (Temperature 60 °C and molar ratio 1:6).*

3.4. Effect of Reaction Time

The increase in fatty acid esters conversion was observed when there was an increase in the reaction time. The reaction was slow at the beginning due to mixing and dispersion of alcohol and oil. after that the reaction proceeded very fast. According to many researchers, the biodiesel yields are directly proportional to the reaction times used. This experiment was conducted at reaction time of 30, 60, 90 and 120 min with the constant parameters: 60°C of reaction temperature and 1wt% of KOH catalyst used in 6:1 molar ratio of WCO. Figure 4 shows that effect longer mixing gives higher yield than using shorter time. So biodiesel yields increases with increasing the reaction time. However, based on the results, it shows 90 min reaction time gave a better result than other reaction times used here. In other words, 1t shows that the biodiesel yields were lower when reaction time of 120 min was used. This undesirable result may be due to the higher soap formation when longer reaction time was used. Thus, the rate of soap formation was also increased [22, 27].
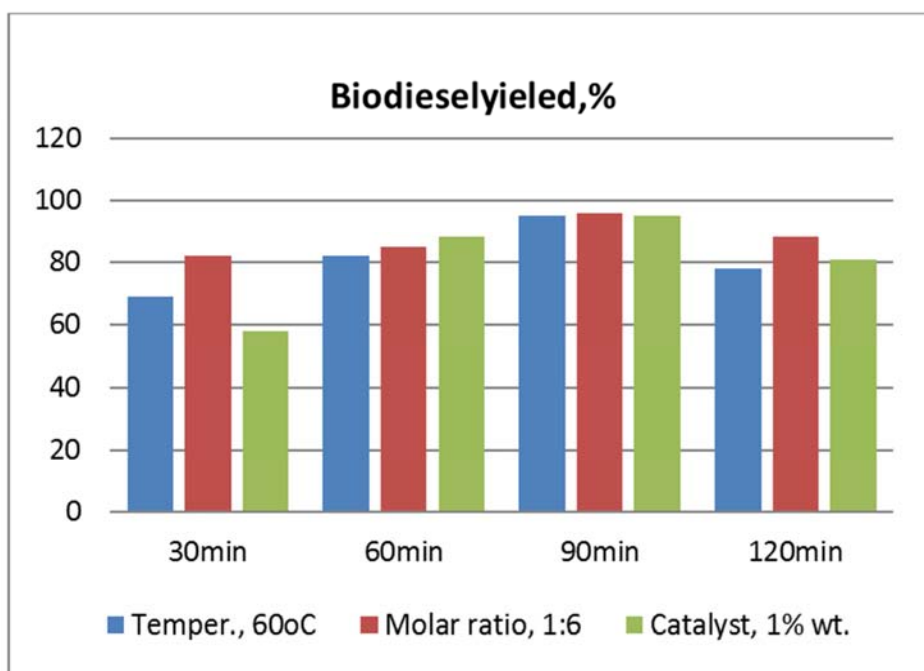

Figure 4. *Effect of reaction time on production of Biodiesel yield (Concentration of catalyst (KOH) 1%wt., Temperature 60°C and molar ratio 1:6).*

Table 3. *Characteristics of produced biodiesels in contrast with standard value.*

Property	Unit	Standard method (ASTM)	Value according standard method	Biodiesel (WCO)	Diesel
Viscosity	mm^2/s	D6751	1.9–6.0	7.8	3.43
Acid number	Mg KOH/g oil	D664	0.8 max	0.42	0.13
Density (15°C)	g/cm^3	D1298	0.86 – 0.90	0.86	0.83
Flash point	°C	D 93	130 (min)	135	86
Cloud point	°C	D2500	-	5	3
Pour point	°C	D97	-	1	-7
Cetane index	-	D 976	47 (min)	49	-

3.5. Characterization of Biodiesel

Different physical properties of biodiesel including the kinematic viscosity, the density, the acid value, the flash point, the cloud point and the pour point, were measured to ensure they meet the international standards (ASTM D6751). Table 3 lists the results and also compares them with those of petroleum diesel fuel. It can be seen from this table that the biodiesel produced in this research has the required properties to be used in diesel engines. Chemical conversion of WCO into biodiesel resulted in significant reduction of the viscosity from 36.5 mm^2/s for WCO to 7.8 mm^2/s for biodiesel. This fact shows that biodiesel viscosity is well consistent with the required value in ASTM standard. Therefore, by transesterification, engine problems associated with high viscosity of waste cooking oils such as incomplete combustion and ignition delay will be eliminated [24, 25]. The density of biodiesel, which influences the quality of atomization process, and the acid value of biodiesel, which is a measure of free fatty acid content, also matched ASTM standards, as shown in table 3. The flash point (135°C) was much higher than that of diesel (86°C), and hence, shows that there is no alcohol residue in biodiesel structure. Consequently, transportation, storage and handling of this biodiesel are better than the conventional diesel in terms of safety. The cloud point and pour point are greater than those obtained by other researchers [18, 27], making this biodiesel less suitable for performance in cold conditions if used in pure form. However, biodiesel is frequently blended at different ratios with petroleum diesel to overcome these problems of the pure form.

4. Conclusion

Used frying oil has suitable characteristics for transesterification. The process produced biodiesel with properties similar to those of diesel. Consequently, the use of waste frying oil is an effective way to reduce the raw material cost. Besides, the pollution problems were reduced. The optimum conditions for biodiesel production from WSCO have been studied. Result shows optimal condition of biodiesel productions are 1:6 volumetric oil-to-methanol molar ratio, 1 wt. %KOH at 60°C reaction temperature. This study has provided evidence that waste cooking oil may be employed as a substantial source of biodiesel as fuel in diesel engines. Because, the produced biodiesel is of good quality within the array of standard method specifications and the production yield is apt. up to approximately 99% under optimum conditions. Biodiesel from used cooking oil could be used as a diesel fuel which considered as renewable energy and environmental recycling process from waste oil after frying. Nevertheless, the transesterification progressed satisfactorily even at room temperature, which could be very interesting for industrial-scale production due to the energy savings that it would imply.

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