



EFFECT OF ALCOHOL RATIO AND REACTION TEMPERATURE ON THE BIODIESEL PRODUCTION FROM USED COOKING OIL

Dr. Aouf A. Al-Tabbakh¹, *Amer A. Mohammed², Nassir A. M. Habib³

- 1) Lecturer, Mechanical Engineering Department, Al-Mustansiriyah University, Baghdad, Iraq.
- 2) Lecturer, Mechanical Engineering Department, Al-Mustansiriyah University, Baghdad, Iraq.
- 3) Assist Lecturer, Applied science school, University of Technology, Baghdad, Iraq.

Abstract: Biodiesel, or alkyl ester, is an alternative renewable, biodegradable and nontoxic diesel fuel produced by catalytic transesterification of oil. It can be successfully employed in diesel engines and liquid fuel burners. The present work deals with a system for transesterification of vegetable oil using a stirring reactor. Used cooking oil is employed for this purpose due to its availability and cost-effectiveness. The transesterification of oil was carried out using molar ratios (oil:methanol) of (1:9, 1:7, 1:5, 1:3) and reaction temperatures of (45, 55, 60, 70 °C). Sodium Hydroxide NaOH was used as a catalyst by an amount of 1% of oil weight and a stirring speed of 500 rpm was applied for 2 hours. The results showed that the production of biodiesel depends on the molar ratio of (oil:methanol) and on the reaction temperature. The optimal values that gave the highest productivity of biodiesel occurred at the molar ratio of (1:7) (oil:methanol) at a reaction temperature of (60 °C) in the presence of NaOH as a catalyst by an amount of 1% of oil weight.

Key words: Biodiesel, Transesterification, bio-fuel, Methanol, Cooking oil.

تأثير نسبة الكحول ودرجة حرارة التفاعل على انتاج الديزل الحيوي من زيت الطبخ المستعمل

الخلاصة: وقود الديزل الحيوي، أو ألكيل استر هو وقود بديل متجدد قابل للتحلل، وغير سام حيث يتم انتاجه من عملية استرة الزيت المحفزة، ويمكن استعماله بنجاح في محركات الديزل وحراقات الوقود السائل. تم في هذا البحث استخدام مفاعل لاسترة الزيت النباتي بخلطه مع الميثانول واستخدام لهذا الغرض زيت الطبخ المستعمل لتوفره وقلة تكلفته. تم اجراء عملية الاسترة للزيت باستخدام النسب المولية (زيت:ميثانول): (1:9، 1:7، 1:5، 1:3) ولدرجات حرارة تفاعل (45، 55، 60، 70 °C) واستخدام هيدروكسيد الصوديوم NaOH عاملا مساعدا بمقدار 1% من وزن الزيت مع تطبيق خلط بسرعة 500 دورة في الدقيقة لمدة ساعتين. أظهرت النتائج أن إنتاج الوقود الحيوي يعتمد على نسب الخلط للزيت والميثانول كذلك على درجات حرارة التفاعل. كانت القيم المثلى التي تعطي اعلى انتاجية للوقود الحيوي هي عند درجة حرارة (60°C) ونسبة خلط مولية (زيت:كحول): (1:7) باستخدام هيدروكسيد الصوديوم عاملا مساعدا بمقدار 1% من وزن الزيت من وزن الزيت.

1. Introduction

The transesterification of vegetable oil with alcohol produces a type of fuel known as Biodiesel [1]. Biodiesel is a fuel of organic origin consisting of long chain fatty acids.

*Corresponding Author amerhabib732@yahoo.com

The application of this fuel in diesel engine offers environmental benefits when compared with fossil fuels. Food stocks of vegetable oil (Virgin and waste) and animal fats have been explored for production of biodiesel [2]. Other renewable resources from which biodiesel had been produced is algae [3]. Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine with little or no engine modifications. Interest in organic oils for biodiesel production has been motivated by its low polluting nature and renewability compared with fossil diesel fuels [4].

The use of edible vegetable oils and animal fats for biodiesel production raises many concerns as it may threaten the supply of food for human use. Therefore the use of non-edible plant oil sources and waste products of edible oil industry becomes feasible as a feedstock for biodiesel production which may not threaten man food resources [5]. The use of biodiesel has increased in the last decade as a renewable, biodegradable, and nontoxic fuel. It has been produced from vegetable oils in north America, Europe, Japan and Malaysia [6],[7],[8]. Moreover, according to many researches, net energy content of used vegetable oil is higher than fresh oil and petro-diesel. The production of biodiesel from used frying oil can be considered environmentally friendly. The combustion of biodiesel has CO₂ emission that is 40% less than the emission of hydrocarbon diesel. This makes it favorable to solve part of global warming problem [9].

There are many previous studies concerning the production of biodiesel. Wright et al. (1944) [10] found that the starting materials used for alkali-catalyzed transesterification must meet real specifications. The glyceride should have an acid value less than unity, and all materials should be completely anhydrous. If the acid value is greater than one, extra amount of NaOH is required to equalize the free fatty acids. Also water causes soap formation, which cleans out the catalyst and reduces catalyst effects. The resulting soaps caused an increase in viscosity formation of gels and makes the separation of glycerol more difficult. Bradshaw and Meuly (1944),[11] noted that the practical range of molar ratios was (1:3.3) to (1:5.25) oil:methanol ratios. The ratio of (1:4.8) was used in some examples, with a yield of 98%, depending upon the kind of the vegetable oils.

Catalysts are divided as alkali, acid, or enzyme. Alkali-catalyzed transesterification is faster than acid-catalyzed (Freedman et al., 1984)[12]. If a glyceride has a higher free fatty acid content and extra water, acid-catalyzed transesterification is suitable (Sprules and Price, 1950; Freedman et al., 1984),[13,12].

Sodium hydroxide was also chosen to catalyze the transesterification due to its lower cost. Ester conversions at the 6:1 ratio for 1% NaOH and 0.5% NaOCH₃ were almost the same after 60 min (Freedman et al.,1984)[12]. Sodium hydroxide is therefore widely used in large-scale processing. Ma et al. (1998),[14] studied the effect of reaction time on transesterification of beef tallow with methanol.

The reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow.

From one to five min, the reaction proceeded very fast with a significant increase in yield.

Then the production of biodiesel slowed down and reached the maximum value at about 15 minutes. The objective of this study is to investigate the biodiesel production

from used cooking oil with different oil:methanol molar ratios and reaction temperatures to find the optimum values of transesterification parameters that give the highest productivity of fuel.

2. Experimental Procedure

The used cooking oil intended for experiments must be clear of any food leftovers. So, it should be filtered via a suitable filtering paper. The reaction of the filtered oil with alcohol (methanol) is performed in a hot plate stirrer fig.(1). The amounts of oil, methanol and catalyst are carefully measured and poured inside the reaction container.

Before starting the transesterification reaction, the oil must be free of any water content in the form of suspended drops. The oil is heated alone (before adding methanol) to 80 °C to evaporate any possible drop of water. After that the oil is cooled to the reaction temperature between 45 – 70 °C. Methanol can now be added to the oil in the container along with the catalyst (NaOH) to embark the reaction. The stirrer is switched on during the reaction at a speed of 500 rpm. The reaction lasts up to 2 hours, after that the stirrer is stopped and the mixture is poured into another plastic container open to air to let any remaining methanol to evaporate. After another one hour the mixture stratifies to two layers: a bottom layer composed of glycerol, and a top layer of liquid fatty acids (biodiesel) ready to be collected from the top of the plastic container.

The collected biodiesel contains some residues of: methanol, NaOH, soap and glycerin. These residues can be removed by mixing the biodiesel with distilled water and shaking the mixture well for about one minute. After that the mixture is let to re-separate into 2 layers of biodiesel and water. The washing process is repeated several times using fresh water each time to ensure the highest purity of the fuel. The amount of water necessary for washing is about 30% of fuel volume.

Fig. (2) illustrates the stoichiometric transesterification process of the cooking oil which is considered as triglyceride. The reaction requires that one mole of triglyceride is mixed with three moles of methanol to produce three moles of fatty acid methanol ester (biodiesel) and one mole of glycerin.

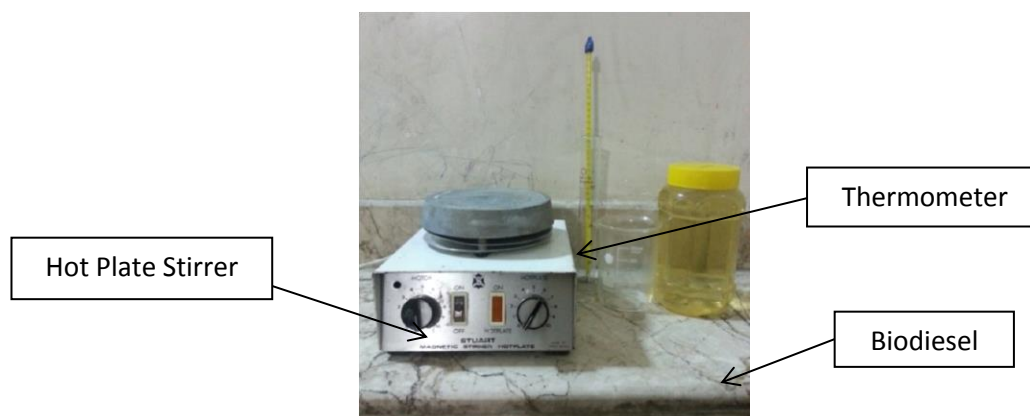


Fig. (1): The stirrer used for biodiesel production

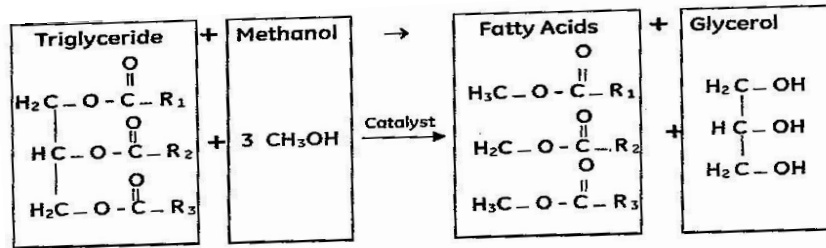


Fig. (2): Stoichiometric transesterification of triglyceride into a fatty acid and glycerol utilizing methanol [16].

Several experiments were carried out to study specific parameters that affect the biodiesel production, including methanol to oil molar ratio and reaction temperature. In each experiment, some parameters being studied were changed while other parameters were fixed. The experiments are summarized in table (1).

Table (1): Parameters used in this investigation

<i>Oil:Methanol Molar Ratios</i>	<i>Reaction Temperature</i>	<i>Fixed Parameters</i>
1:3	45 °C	Alcohol: Methanol Catalyst: NaOH 1% wt Reaction Time: 2 hours Mixing Speed: 500 rpm
1:5		
1:7		
1:9		
1:3	55 °C	
1:5		
1:7		
1:9		
1:3	60 °C	
1:5		
1:7		
1:9		
1:3	70 °C	
1:5		
1:7		
1:9		

3. Results and Discussion

Experiments were carried out for several values of oil:methanol molar ratios and reaction temperatures. The productivity of the reaction is measured by the (fuel yield) which is the molar ratio of biodiesel to glycerol according to the molar ratio of biodiesel to glycerol in Stoichiometric transesterification.

It can be noticed from all results (Figs. 3-6) that the stoichiometric molar ratio (1:3) did not produce the highest fuel yield as it may be expected. Rather, the fuel yield increases with molar ratio reaching its maximum value (98%) at molar ratio (1:7). This can be attributed to the limited contact between the reactants (oil and methanol) at the

stoichiometric ratio (1:3) despite the mixing process accompanying it. The difference in viscosity between the oil and methanol plays important role in restricting the contact between them which is necessary to fulfill the reaction. The chance of full contact between the reactants increases with the increase in molar ratio [17]. However, increasing molar ratio further to (1:9) led to a slight decrease in fuel yield because the extra glycerol remained would drive the reaction back to the left and decrease the yield.

The fuel yield also increases with reaction temperature for all molar ratios but the increase is limited by methanol boiling point (65 °C). When a reaction temperature of (70 °C) is used a decrease in fuel yield is noticed. Applying a reaction temperature above methanol boiling point accelerated the saponification of glycerin before the decomposition of methanol which decreased the fuel yield.

Table (2) illustrates some thermophysical properties of the gained biodiesel compared with the recommended values of standard diesel. The properties were measured at Fuel laboratory and the laboratory of Petroleum Engineering Department, both at the University of Technology in Baghdad. It can be noticed that the values of the properties fall within the recommended limits which favors biodiesel as a future alternative to ordinary diesel.

Table (2): Biodiesel Properties (produced from sunflower)

<i>Property (unit)</i>	<i>Test method</i>	<i>Measured value</i>	<i>Recommended Value Limit</i>
Viscosity cSt at (40 °C)	ASTM D445	4.9	3.5-5.0
Cloud point (°C)	ASTM D2500	0	-
Pour point (°C)	ASTM D97	-2	-
Flash point (°C)	ASTM D93	176	Min. 120
Density at (15 °C)(kg/m ³)	ASTM D1298	870	860-900
Cetane umber	ASTM D613	66	48-67

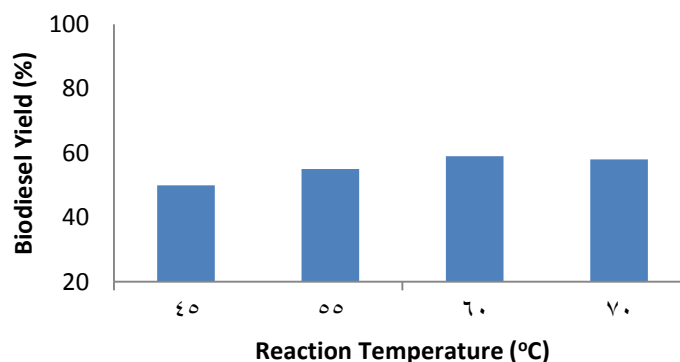


Fig. (3): Effect of reaction temperature on biodiesel yield at 1:3 molar ratio

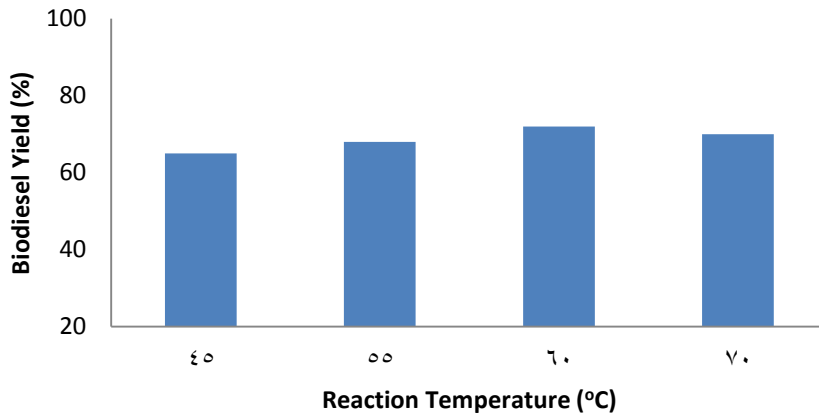


Fig. (4): Effect of reaction temperature on biodiesel yield at 1:5 molar ratio

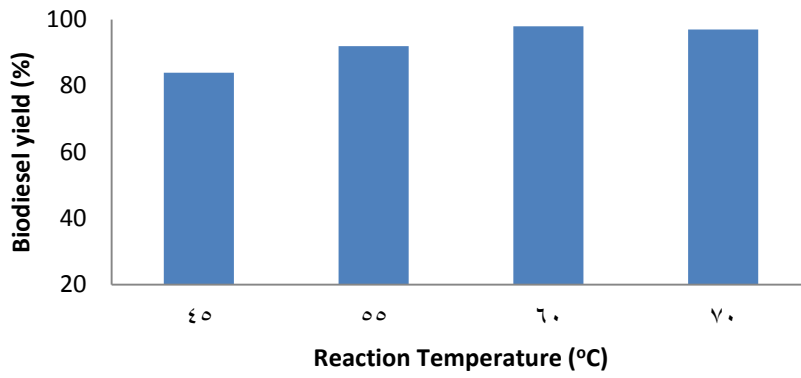


Fig. (5): Effect of reaction temperature on biodiesel yield at 1:7 molar ratio

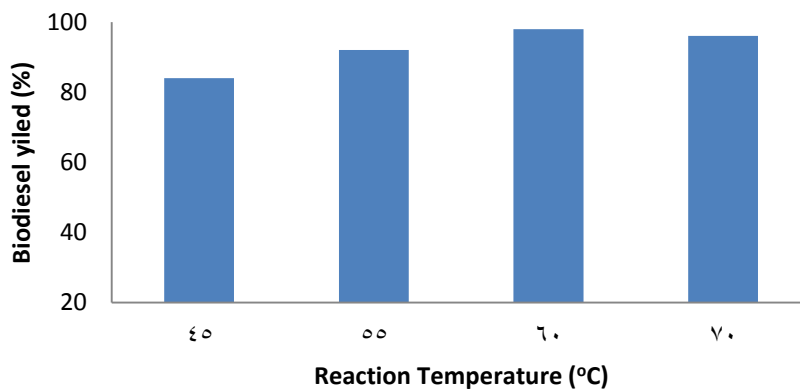


Fig. (6): Effect of reaction temperature on biodiesel yield at 1:9 molar ratio

4. Conclusions

This study dealt with the production of a new fuel (biodiesel) from the transesterification of used cooking oil with methanol. The reaction was accelerated by NaOH as a catalyst. Stirring the mixture was necessary during the period of reaction which lasted 2 hours. The highest fuel yield achieved was 98% at oil: methanol molar ratio of 1:7 and reaction temperature of 60 °C.

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