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العدد 13– المجلــد 7

Production of Biodiesel From Waste Cooking Oil

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الملخص

أدى استخدام زيت الطهي المستهلك في عملية تخليق الوقود الحيوي إلى تقليل تكلفة المواد الخام. بعد دراسة الشروط المناسبة لإنتاج الوقود الحيوي من حيث نسبة زيت الطهي المستهلك إلى الميثانول، تأثير درجة حرارة التفاعل، وتأثير زمن التفاعل وذلك بإجراء تفاعل الأسترة بوجود 1.0٪ (وزن / حجم) هيدروكسيد الصوديوم كمحفز. وجد من التحليل أن أفضل نسبة لإنتاج الوقود الحيوي هي نسبة 1: 3 زيت الطهي المستهلك إلى الميثانول ، أفضل درجة حرارة للتفاعل هي 60 درجة مئوية ، وأفضل زمن تحريك لخليط التفاعل هو 40 دقيقة. تم تحضير كمية كبيرة من الوقود الحيوي من خلال تطبيق أفضل الشروط المطلوبة للحصول على أعلى نسبة انتاجية من الوقود الحيوي والتي كانت تساوي 87.19٪ (وزن / وزن) بعد عملية الغسل الرطب خمس مرات بواسطة 30 مل من الماء المقطر. وجد أيضا أن المكافئ الحمضي للوقود الحيوي يساوي 2.53 مجم KOH / جم, وتراوحت كثافة الوقود الحيوي من 0.80 إلى 0.843 جم / مل. أثبتت الدراسة أن عملية إنتاج الوقود الحيوي باستخدام زيت الطهي المستهلك ممكنة تقنيا وغير مكلفة.

Abstract

The use of waste cooking oil for biodiesel synthesis reduces the cost of raw materials.
After studying the appropriate conditions for biodiesel production in terms of the ratio of waste oil to methanol, the effect of reaction temperature, and the effect of reaction time by conducting a transesterification reaction with 1.0 %w/v sodium hydroxide as a catalyst. It was found from the analysis that the best ratio for biodiesel production is 1:3 ratio of waste oil to methanol, the best reaction temperature is at 60ºC, and the best stirring time for the reaction mixture is 40 minutes. A large amount of biodiesel was prepared by applying the best conditions required to obtain the highest yield of the biodiesel, which was equal to 87.19% w/w after a five times wet washing process by 30 mL of distilled water. It was also found that the acid equivalent of biodiesel was 2.53 mg KOH /g, and biodiesel density ranged from 0.80 to 0.843 g / mL. The study proved that the biodiesel production process using waste cooking oil is technically feasible and inexpensive.

Keywords: Biodiesel ; Waste cooking oil ; Transesterification ; Density; Acid equivalent.

Introduction

Biodiesel fuel is defined according to the American Society for Testing and Materials (ASTM) as mono alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as animal fat or vegetable oil, and this type of biodiesel is environmentally less contaminating, nontoxic, and biodegradable compared to diesel fuel [1]. Animal fats

and vegetable oils are the main raw materials for biodiesel. Among the most widely used vegetable oils for biodiesel production are peanut oil, soybean oil, canola oil, and cottonseed oil. But these oils are edible, and due to the high economic cost of using these oils as raw materials for the production of biodiesel, it makes it impossible to produce biodiesel from these oils in many countries[2-6]. For this, reducing biodiesel production costs is the main problem facing biodiesel production processes, especially the cost of raw materials, so the use of waste cooking oil is one of the good ways to reduce production cost, which is sometimes freely available, and can be a promising alternative to edible vegetable oil [7].

Biodiesel production by transesterification reaction of vegetable oil with alcohol in presence alkali, acid, or enzyme as a catalyst. The alkali and acid transesterification reactions require shorter reaction time and lower costs as compared to the enzyme-catalyzed reaction. One limitation to the alkali-catalyzed reaction is its sensitivity to the purity of reactants; the alkali-catalyzed system is very sensitive to both water and free fatty acids [1,8]. Also, the alkali-catalyzed process is not suitable for vegetable oils that are high in free fatty acids, more than 3% [9]. Therefore, the transesterification reaction is first carried out in the presence of acid as a catalyst to remove the high content of free fatty acids, then the reaction is carried out in the presence of alkaline as a catalyst, which improves biodiesel production [10]. Improper disposal of used frying oil may contaminate ground water. In Libya, a large amount of frying oil is consumed daily in homes and restaurants where it is disposed of directly without trying to be recycled in appropriate industries such as soap making. Therefore, frying oil poses a huge environmental and economic burden. In recent years, concern for the environment has begun to increase in Libya, including the reuse of raw materials, including waste cooking oil. The aim of the current work is to study the production of biodiesel using waste cooking oil containing less than 3% free fatty acid, and to study the best conditions for biodiesel production in terms of the proportion of waste oil to methanol, the effect of reaction temperature, and the effect of reaction time.

Materials and Methods

Waste corn oil produced by Al-Wadi Al-Dhahabi Company was collected during three months from Libyan houses. Then the waste oil was purified from food residues by filtration by a filter paper, and the moisture interfering with the waste oil was removed by boiling. The samples were kept in clean and dry glass bottles at room temperature until the start of biodiesel production and chemical analysis. Methanol (HPLC grade), Ethanol (Absolute), and n- Propanol were procured from NTL Nentech, Ltd, Brixworth – Northants, UK. Potassium hydroxide, sodium hydroxide, and sulphuric acid were obtained from Winlab-Laboratory chemicals reagents Fine chemicals-UK. A hot plate with magnetic bar stirrer used for heating the mixture in the round bottom flask, and a round-bottom flask with water - cooled reflux condenser arrangement was used as laboratory-scale reactor for the experimental studies in this work.

Preparation of biodiesel from waste oil

0.50 g of sodium hydroxide was immersed in 25 mL of methanol and the mixture was stirred with slow heated until the alkali was completely dissolved, then the mixture was

cooled and 25 mL of the waste oil was added to it and stirring the mixture well for 40 minutes at a temperature 20 ºC and then left for 24 hours until the process of separating the glycerol from the biodiesel by obtaining two layers that were separated from each other using a separating funnel. Biodiesel product was washed by 25 mL of distilled water and the washing process was repeated several times. The above steps were repeated with different ratios of the waste oil: methanol as (1:3), (1:6), and (1:8), as well as the above steps were repeated by inverting the ratios as follows (3:1), (6:1), and (8:1) with 1.0 % w/v sodium hydroxide as catalyst.

The effect of reaction temperature on biodiesel production

The effect of reaction temperature on the preparation of biodiesel was studied by repeating the steps of esterification reaction of 3:1 ratio of oil to methanol respectively, at the following temperatures (20, 40, 60, and 80 ºC) with 1.0 % w/v sodium hydroxide as catalyst. The reaction mixture was stirred for 40 minutes in a water bath by stabilizing the reaction temperature at one of the above temperatures, then the biodiesel was separated from glycerin and the weight of each was recorded. Finally, the fuel was washed with 25 mL of distilled water.

Effect of reaction stirring time on biodiesel yield

After studying the best waste oil to methanol ratio (3:1), and the best esterification reaction temperature (60 ºC) on the yield percentage of biodiesel. The effect of stirring time (30, 40, 60, 90, and 100 minutes) on the biodiesel yield was studied by repeating the esterification reaction steps in the presence of the 1.0 %w/v sodium hydroxide as a catalyst, where the reaction mixture was stirred in a water bath at 60 ºC for one of the times above, then the biodiesel was separated from the glycerol and the weight of each was recorded, finally the biodiesel was washed with 25 mL of distilled water.

Acid Equivalent acid and density

Acidity was estimated by titrating the free fatty acids present in the specified weight of waste oil against 0.1N sodium hydroxide. 5g of waste oil was dissolved in 75 mL of n. propanol. The mixture was stirred well and drops of phenolphalein were added to them and it was titrated against 0.1N potassium hydroxide solution to the point where the color of the indicator changed, then the equivalent acid was calculated from the following equation [11]:

$$\text{Acid equivalent.} = 5.6 \times V/W$$

where V (mL) is the volume of potassium hydroxide required to neutralize the acidity of the sample, and W (g) is the weight of the sample.

Density of the produced biodiesel was determined and compared with the recent literature. Density was measured using a density bottle at 20 ºC.

Results and discussion

An attempt was made to prepare biodiesel through the transesterification reaction between methanol and waste cooking oil, as shown in the equation below:

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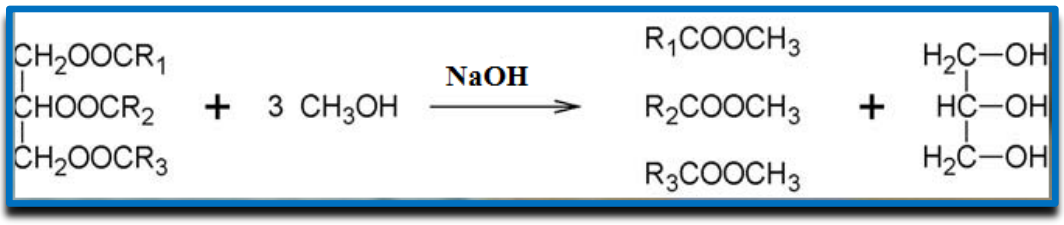

The free fatty acid reacts with sodium hydroxide to produce soap, also some impurities in the waste cooking oil could not be converted to esters and remained in the final product, which contributed to the lower esters concentration and product purity [12].

Waste cooking oil to methanol ratio is one of the most important parameters in determining the percentage of biodiesel production. Experiments of biodiesel production were conducted with molar ratios of waste oil to methanol, and the ratio of methanol to waste oil ranged from 1:1 to 1:8 , respectively. Table 1 shows the effect of the ratio between the waste oil to methanol on the productivity of biodiesel at the constant of temperature 60 °C, and constant time of reaction (40 minutes).

Table 1 Effect of the ratio between the waste oil to methanol on the productivity of biodiesel.

Oil : Methanol ratio	Reaction time/ mints	Reaction temperature / °C	Biodiesel (% w/w)	Density (g / mL)
1:1	40	60	34.27	0.836
3:1	40	60	_	_
6:1	40	60	_	_
8:1	40	60	_	_
1:3	40	60	81.7	0.856
1:6	40	60	suspend	_
1:8	40	60	suspend	_

When the reaction between waste oil and methanol is carried out at a ratio of 1:3, respectively, at a temperature of 60 oC and the reaction time is 40 minutes, we get two clear layers of biodiesel and glycerol that are easy to separate from each other by a regular separating funnel as shown in Fig.1A, and the yield of biodiesel obtained is higher from those obtained when conducting the reaction in a ratio of 1:1. While when the reaction was carried out, when the proportion of the waste oil was less than the proportion of methanol, when the molar ratio of waste oil to methanol was 1: 3, 1: 6, and 1 :8 at constant temperature

60 oC, and the reaction time was 40 minutes two transparent layers were obtained as shown in Fig.1B, so that it is difficult to separate them from each other, which are the biodiesel and glycerol layers, as shown in Fig.1B, and therefore, these percentages are not valid for biodiesel production. Also, when the reaction is carried out by taking a very high percentage of the waste oil, for example, when the reaction is made between the waste oil and methanol at a ratio of 6:1, and 8:1, respectively, we get a suspension mixture so that the biodiesel cannot be separated from the glycerol, which indicates that this ratio is also not valid for biodiesel production.

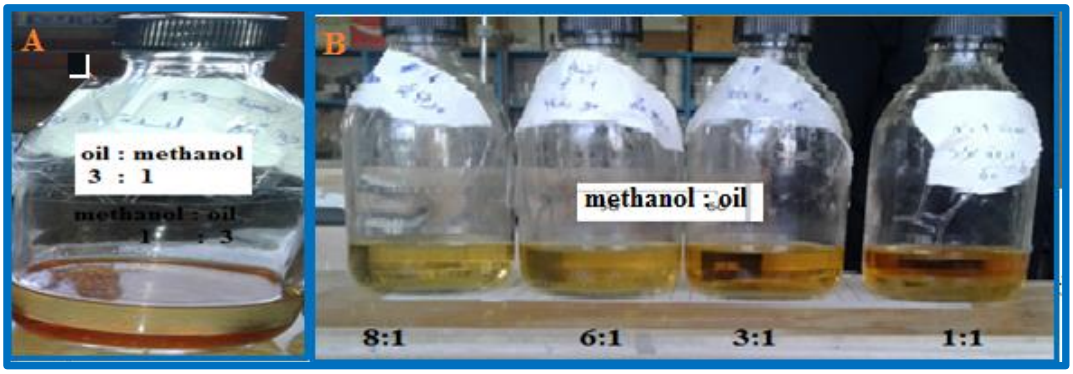

Fig. 1 Effect of molar ratio of methanol to waste cooking oil at 1% w/v sodium hydroxide catalyst, temperature of 60 ºC, and time of reaction 40 minutes.

Effect of chemical reaction temperature

The effect of the reaction temperature of the mixture of waste oil and methanol at a ratio of 1:3 and the reaction time of 40 minutes on the yield and density of biodiesel was studied, and the results were as shown in Table 2.

Table 2 The effect of reaction temperature on biodiesel productivity and density.

Reaction temperature / ºC	Biodiesel percentage (% w/w)	Biodiesel density (g /mL)
20	73.5	0.851
40	79.1	0.824
60	81.7	0.856
80	81.0	0.840

In order to study the effect of transesterification reaction temperature, the chemical reaction was performed in the presence of 1% w/v sodium hydroxide at different temperatures (20, 40, 60, and 80 ºC) for the constant ratio 3:1 of methanol to the waste oil, respectively. The effect of reaction temperature on the conversion has been presented in Table 2 and Fig.2. From the study, it was found that with the increase in the reaction temperature, the productivity of biodiesel increases to a temperature of 60 °C and then the

productivity percentage stabilizes. This result is in agreement with that obtained by Shishir et al.,[13], also Gronroos et al., have reported similar effects of temperature in the ultrasound assisted esterification reactions [14]. From the study, it was found that the production biodiesel density is not affected by the reaction temperature. Table 2 shows that biodiesel density ranged from 8.24 to 8.56 g / mL.

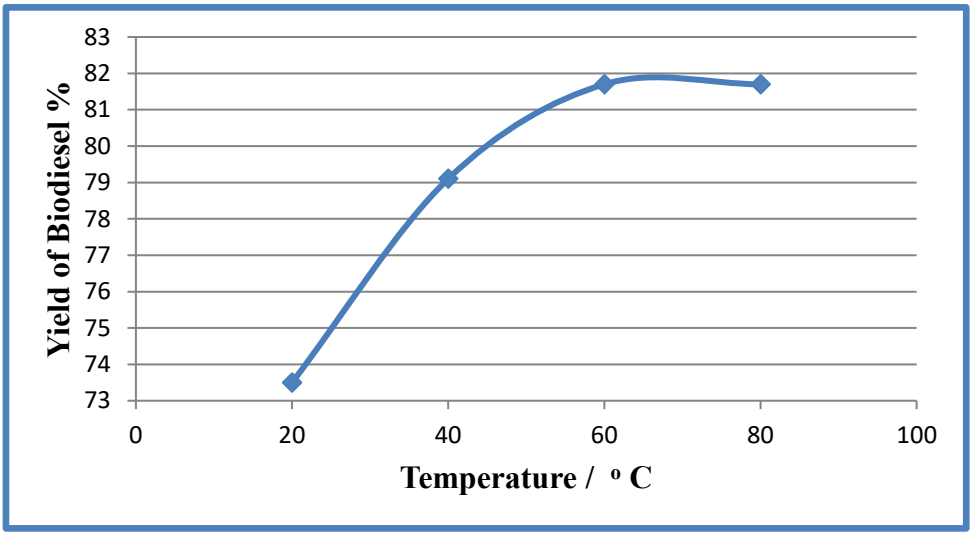

Fig. 2 The relationship between temperature and biodiesel productivity.

Effect of reaction stirring time on biofuel yield

The effect of changing the reaction time of the waste oil mixture to methanol in a ratio of 3 :1, respectively, at the constant reaction temperature (60 °C), then the yield and density of biodiesel was studied, and the results were shown in Table 2 and Fig.3.

Table 3 Effect of the reaction time on biodiesel productivity and density.

Reaction time / minutes	Biodiesel percentage (% w/w)	Biodiesel density (g /mL)
30	0.81	0.840
40	87.19	0.803
60	87.19	0.800
90	76.29	0.824
100	79.01	0.848

From the study, it was found that the best reaction time for biodiesel production was at a reaction time ranging from 40 to 60 minutes, and it was found that with the increase in time, the amount of biodiesel production decreased, as observed in a reaction time of 90 to

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100 minutes to the breakdown of the ester and have more glycerol. Daniyan et al. reported the same effects of reaction time on biodiesel yield [15].

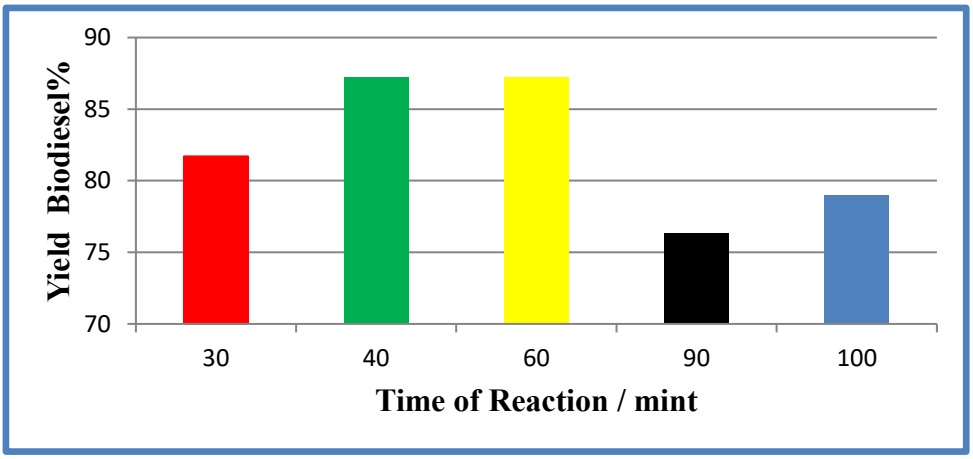

Fig. 3 The relationship between biodiesel yield and reaction time.

Biodiesel density generally depends on the of methyl esters and the residual amount of methanol, for this the characteristic of biodiesel is mainly influenced by the choice of vegetable oil and to some extent by the applied purification steps. Tables 2 and 3 showed that the density of biodiesel before washing ranged from 0.800 to 0.856 g / mL, and after the wet washing it was 0.8947 g / mL. Fig. 4 shows the density of the biodiesel resulting from the esterification reaction at ratio 3:1 of methanol to waste oil at a temperature of 60 ^{o}C with a change in reaction time ranging from 30 to 100 minutes. It was found that the density of biodiesel ranged from 0.800 to 0.848 g / mL, and an average of 0.824 g / mL, where no appreciable difference in density is observed with changing the reaction time or changing the reaction temperature. This result is in agreement with that reported by Shishir et. al.,[13] which was 0.89 g / mL after washing. Also, Harabi et al., reported a similar result for the density of biodiesel at 15 °C, which was 0.889g/mL [16].

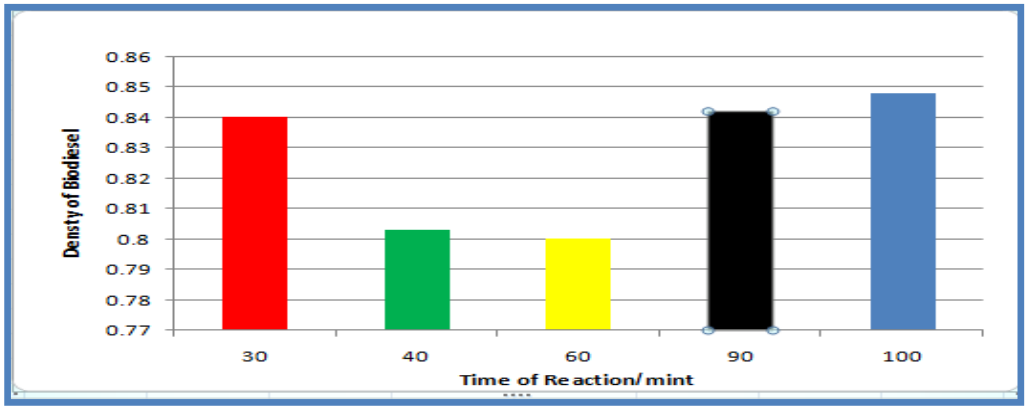

Fig. 4 Effect of change in time of reaction on density of biodiesel

After studying the appropriate conditions for biodiesel production in terms of the ratio of waste oil to methanol, the effect of the reaction temperature, and the effect of the time of reaction, by conducting the reaction in the presence of 1% w/v sodium hydroxide as

a catalyst. It was found that the best ratio of waste oil to methanol is 1:3 respectively, and the best reaction temperature is 60ºC, while the best stirring time ranges from 40 to 60 minutes. The last experiment was conducted by applying all the appropriate conditions for the production of biodiesel, where we took 360 g of waste oil and 1080 g of methanol, and a reaction was performed in the presence of 1% w/v sodium hydroxide as catalyst at the conditions described above. After the wet washing process five times, and in each washing process, the percentage of distilled water is five times the biodiesel as shown in Fig.5, it was found that the yield percentage is 87.19 % w/w, and the acid equivalent value is 2.53 mEq. KOH/g, while the density of biodiesel before and after washing with distilled water was found to be 0.813 and 0.8947 g / mL, respectively.

Fig. 5 Biodiesel product (A) before washing and (B) after washing with distilled water.

Table 4 Acid equivalent of oil before and after use and for a biodiesel product.

Experiment	Oil before use	Waste oil	Biodiesel
Acid equivalent (meq. KOH / g)	2.330	2.280	2.530

Table 4 shows that the acid equivalent of cooking oil before consumption is considered relatively high, so it is preferable when conducting an esterification reaction that the reaction be carried out in the presence of a mineral acid such as sulfuric acid as a catalyst and not an alkali, in order to increase the efficiency of biodiesel production. Also, no appreciable change in the acid equivalent value of biodiesel is observed from that of the cooking oil before and after use.

Conclusion

The study is very important in the current context because it focused on one of the cheaper synthesis methods based on the use of waste cooking oil, which often poses significant environmental risks. From the study, the presence of a sufficient amount of methanol (3:1) during the transesterification reaction is essential to break the glycerol fatty acid linkages. But large amounts of methanol should be avoided. Increasing the reaction ratio of methanol to oil , i.e. 6:1 or 8:1, neither increases the product yield nor the ester content,

but rather makes the ester recovery process complicated and raised its cost. The same result was observed when using a large amount of waste oil in a relative ratio beyond 1:1, as it is difficult to separate the biodiesel from the reaction environment. Also, a study exhibited that the best transesterification reaction conditions are methanol to waste oil ratio 3:1, at reaction temperature 60 ^{o}C, and time of reaction 40 minutes. The percent conversion of biodiesel was found 87 % w/w, density ranged from 0.80 to 0.843 g / mL, and the acid equivalent value is 2.53 mEq. KOH /g.

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