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Production and Evaluation of Biodiesel from Sheep Fats Waste

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Abstract

Animal fats are a good, promising and ethical alternative source for biodiesel production, but they need more complex treatments than vegetable oils. Iraqi butchery plants waste fats (sheep fat) which are suggested as feedstock to produce biodiesel. This type of fat contains a large quantity of free fatty acids (FFAs) (acid number 49.13 mg KOH/g of fat). The direct transesterification of such fats produce high amount of soap instead of desired biodiesel, so a pre-treatment step (to reduce FFAs) is necessary before transesterification. This step was done by esterification of the free fatty acids in the fat by adding ethanol and using 1% acid catalyst (H_2SO_4) for 30 minutes. The results showed that the acid number of sheep fat after pre-treatment step reduced to 0.97 mg KOH/g of fat at esterification step. Transesterification of treated fats (produce from esterification) used to convert biodiesel. The maximum yield of biodiesel was about 85 vol. % for treated fats obtained with 25/100 ethanol/fat wt. ratio, 70° C reaction temperature and 50 minutes total treatment period (pre-treatment step and transesterification reaction). The suggested model of the production rate kinetic of transesterification reaction, found that the production rate is inversely proportional with the volume of biodiesel produced with activation energy of 25320 J/mole.

Keywords: Biodiesel, sheep fats waste, esterification, alkyl catalyst transesterification

Introduction

The world energy crisis is a result of population growth and increasing consumption of energy in both developed countries and emerging economies. From 1973 to 2007, worldwide primary emerging consumption almost doubled from 256 to 505 million gaga joules (GJ) [1]. This crisis will expand especially with the predicted decline of petroleum reserves that will occur at a rate between 2 and 3% per year starting in 2010 [2].

Therefore, there is a strong need to replace petroleum with other, more sustainable energy sources such as solar energy, biomass, geothermal, wind and water. Biomass is a renewable material such as wood, agriculture crops or animal's wastes, and municipal wastes, especially when used as a source of fuel or energy. Biomass burned directly or processed into biofuels such as methane (biogas), ethanol (bioethanol) and biodiesel.

Historically the first car group in the USA operated on ethanol fuel

(bioethanol). Then the inventor Dr. Rudolf diesel at 1900 used the first diesel engine and operated it by peanut oil [3].

Recently engines don't accept these oils (and animal fats) as a fuel due to their inappropriate physical properties such as longer molecule chains, lower pour points, higher flash points, and chemical composition of unprocessed oils and fats. These features cause poor atomization, bad vapor–air mixing, low pressure, and incomplete combustion and engine deposits. It is possible to reduce the viscosity of oils and fats to improve the physical features through dilution, pyrolysis, micro emulsion and transesterification [4].

Transesterification and esterification produced biodiesel. Biodiesel is one of the most used fuels in diesel engines without any major modification produced from vegetable oils and waste animal fats. Biodiesel has attracted governmental attention and support as an alternative, renewable, and potentially "clean" fuel for diesel engines. Since biodiesel derived largely from renewable biological resources, biodiesel is safer for the environment and produces significantly less air pollution compared to petroleum diesel [5,6].

One popular process for producing biodiesel from the fats/oils is transesterification of triglyceride by methanol or ethanol to make methyl esters or ethyl ester of the straight chain fatty acid. The purpose of this process is to lower the viscosity of the oil [7].

Oil esters (biodiesel) have certain advantages such as lower viscosity, lower flash point, higher vapor pressure and easier processing relative to animal fatty acid esters, but they are noneconomic, non-feasible due to many vegetable oils (about 95%) used in the production of biodiesel are edible oils, and hence are valuable. For the same reason, the use of edible vegetable oils for biodiesel production leads to short ages of the food. Animal fats in human food constitute health hazards; this is one of the reasons for their low-cost [8].

The present work intends to produce ethyl ester from the waste sheep fat by alkyl catalyst transesterification. Animal fats are a good alternative source for biodiesel production but their treatment is more complex than fresh vegetable oils [9].

Animal fats contain a large amount of free fatty acids, so that pretreatment to reduce the FFA is a necessary step. Then the alkali catalyst will react with the free fatty acids to form soaps [10]. This reaction is undesirable and reduces the yield of the biodiesel product. The pretreatments step is done by two ways: the first way is the extraction of the free fatty acids (FFAs) in the fat by adding ethanol; and, the second way is the esterification of free fatty acids (FFAs) in the fat by adding ethanol and used acid catalyst (H_2SO_4). The effects of ethanol /fat wt. ratio, and the reaction temperature are studied for the conversion of sheep fat to optimize the reaction conditions.

This study is conducted to utilize a process for producing and purifying ethyl esters (biodiesel) from the waste of animal fats to use locally in electrical-generators of animals butchery plant. Operating conditions such as temperature, ethanol/fat wt. ratio and reaction time were studied. The produced biodiesel evaluated by measuring its properties.

Experimental Work

Materials

1. Sheep fats used in the present study were collected from main slaughterhouses in Iraq. At the laboratory, they were melted by

slow heating to 60 °C and filtered in order to obtain the fat and remove gums, protein residues, and suspended particles. Thus, the obtained fats which were homogenous in nature were stored in tight opaque plastic jars to prevent oxidation. The specific gravity of the sheep fat was 0.8772.

2. Ethyl alcohol was obtained from local markets with a purity of 88 to 90% and a specific gravity 0.7692.
3. Sodium hydroxide as a base catalyst (RIEDEL_DEHAEN AG SEELZE_HANNOVER Chem. rian, plozchen, DAB7, B.P.1968 M.Wt. 40).
4. Sulfuric acid was obtained from local market. The purity of this acid was 98% (Sp.Gr. was 1.84) AR.
5. Glycerol (etwa 87%) Zur Analysis $C_3H_8O_3$.
6. Phenolphthalein (as an indicator).

Equipment

The equipment used in this study for the pretreatment step (esterification) and transesterification steps is shown schematically in Figure 1.

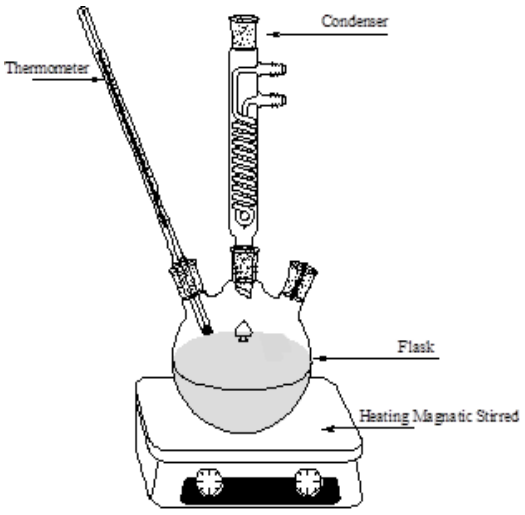

Fig. 1, Schematic diagram of the equipment

The main parts of the equipment are:

1. Heat flat magnetic stirrer.
2. Reflux Condenser.
3. Centrifuge.
4. Mercury thermometer from zero to 250 °C.
5. 3 Necks flask (500 ml).
6. Sensitive balance.
7. Chiller.

Esterification of Sheep Fat

The esterification reaction was carried out between acid and free fatty acid (FFA) to produce ester (biodiesel) and water. The FFA reduced in the fat to less than 2 mg KOH/g of fat, which to be suitable to produce biodiesel in transesterification reaction [1].

The system was maintained at atmospheric pressure and the experiments were carried out at constant temperature. The agitation was kept constant at 300-rpm. This method was studied at different percentages of ethanol/fat wt. ratio from 20/100 to 40/100, and used 1% of sulfuric acid as a catalyst at a constant time of about 30 minutes, and at different temperatures (40 to 70 °C).

The reactor was loaded with about 50g of sheep fat, preheated to the desired temperature and the agitation started. The reaction started when ethyl alcohol was added to the sheep fat in the reactor. After 10 minutes from the reaction, one percent of sulfuric acid was added and the reaction continued to 30 minutes. Then, the mixture was transferred to the separating funnel to separate treated fat from alcohol. The top layer was alcohol acid, and part from FFA in the fat and the bottom layer was a treated fat. The separating time was about 30 minutes and it was instant to start the transesterification method.

Production of Biodiesel by Alkyl Catalyst Transesterification

The ethyl alcohol and base catalyst (sodium hydroxide) are used to produce biodiesel, but in this way the fat is not used directly. Fat contains a

high number of FFA; this leads to a chemical reaction between FFA in the fat and the base catalyst to form soaps. After the pre-treatment method of the FFA in the fat, this reaction is desirable to yield biodiesel.

The system was maintained at atmospheric pressure and experiments were carried out at constant temperature. The agitation was kept constant at 300-rpm. This method was studied at different percentages of ethanol/fat wt. ratio from 20/100 to 40/100; the temperatures of the reaction ranged from 40 to 70 °C and 1% of sodium hydroxide at different times (10, 15, 20, 25, 30, 45, 60 minutes).

The reactor was loaded with the treated fat, which was produced from the separating funnel by the pre-treatment method (esterification), preheated to the desired temperature and the agitation started. The sodium hydroxide dissolved in ethanol and the reaction started when the alcoholic solution was added to the fat.

Washing

Excess alcohol and residual catalyst were washed from the biodiesel with water. Water sprayed in to the top of the separating funnel at low velocity. The excess alcohol and catalyst were removed by the water as it percolated through the separating funnel.

Results and Disscutions

Pre-treatment of FFAs in the Fat

From the experimental works of the esterification step, the acid value was reduced from 49.13 mg KOH/g of fat to 0.97 mg KOH/g of fat and the optimum conversion of FFAs was 98% at 25/100 of ethanol/ fat wt. ratio after 30 minutes. The best temperature was 70 °C for this type of pre-treatment. The pretreatment reactions act as the limiting step of the production. After reducing the FFAs in the fat, the transesterification reaction converts esters from long chain fatty acids into mono alkyl esters.

Effect of operating temperature and time on the biodiesel yield

Operating temperature and reaction time that affect the biodiesel yield from animal fat (sheep fat) was studied in the temperature range from 40 to 70 °C and in the reaction time of up to 60 minutes.

Figures 2 to 5 show the biodiesel yield with reaction time and temperature by esterification method (animal fat treated with H_2SO_4) of the transesterfication. The yield of biodiesel after transesterfication reaction was 61.7 vol. % at 70 °C after 30 minutes, and reached 55.2 vol. % at 40 °C after 30 minutes with 20/100 ethanol/fat wt. ratio (as shown in Fig.2). At 25/100 ethanol/fat wt. ratio (as shown in Fig. 3) the yield of biodiesel was 85.3 vol. % at 70 °C after 20 minutes, and reached 73.4 vol. % at the temperature of 40 °C after 30 minutes. The yield of biodiesel at 30/100 ethanol/fat wt. ratio (as shown in Fig.4) was 72.1 vol. % at 70 °C after 30 minutes, and reached 57.5 vol. % at 40 °C after 30 minutes. While at 40/100 ethanol/fat wt. ratio (as shown in Fig.5), the yield of biodiesel was 76.5 vol. % at reaction temperature of 70 °C after 30 minutes and reached 58.4 vol. % at 40° C after 60 minutes. From these results, the best yield of biodiesel by this method was 85.3 vol. % at 25/100 ethanol/ fat ratio at 70° C after 20 minutes.

Increasing the temperature causes an increase in molecule activity. This means that more molecules have more energy; thus, the possibility of molecule to react is increased, and this causes the removing of water formed during the reaction. Then consequently, higher conversion values

that cause more yield of product material are obtained.

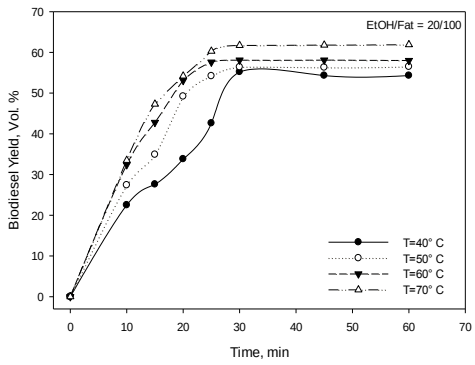

Fig.2, Effect of the reaction temperature on biodiesel yield, 20/100 ethanol/fat wt. ratio

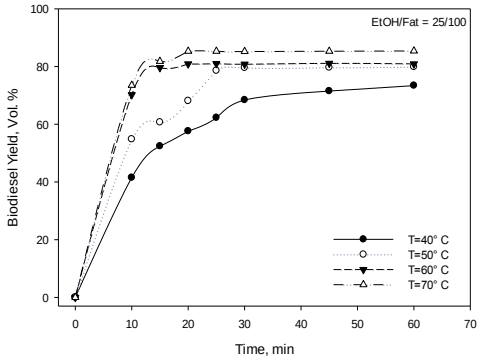

Fig.3, Effect of the reaction temperature on biodiesel yield, 25% ethanol/fat wt. ratio

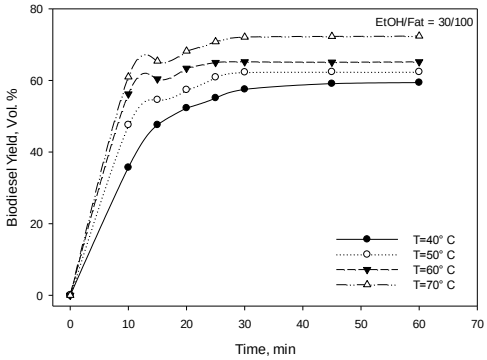

Fig.4, Effect of the reaction temperature on biodiesel yield, 30% ethanol/fat wt. ratio

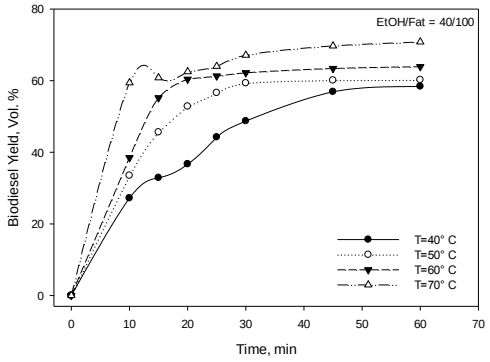

Fig.5, Effect of the reaction temperature on biodiesel yield, 40% ethanol/fat wt. ratio

The Effect Ethyl alcohol/Fat wt. Ratio on the Biodiesel Yield

The experiments of transesterification by esterification step were carried out by varying the ethanol/oil wt. ratio from 20/100 to 40/100. Figures 6 to 9 show the effect of the ethyl alcohol/ fat ratio and time on the biodiesel yield by esterification step of the transesterfication. As can be observed, with 20/100 ethanol/fat wt. ratio, the yield of biodiesel was near 61.7 vol. % after 30 minutes. The biodiesel yield increased as the weight ratio increased, with the best results (about 85%) being for an ethanol/fat wt. ratio 25/100 after 20 minutes. At 30/100 ethanol/fat wt. ratio the yield of biodiesel was 72.1 vol. % after 30 minutes. Nevertheless, a later increase of ethanol/fat wt. ratio to 40/100 did not result in an increase in the yield, since a lower value was obtained, 76.5 vol. %.

Increasing in ethanol/fat wt. ratio causes decreasing the biodiesel yield, due to the higher weight ratio of ethanol/fat leads to complications in the separation of glycerol because the ethanol excess hinders the decantation by gravity so that the apparent yield of esters decreases since part of the glycerol remains in the biodiesel phase.

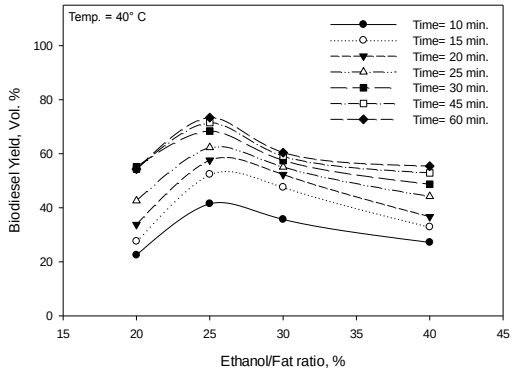

Fig.6, Effect of the ethyl alcohol/ fat wt. ratio and time on the reaction on biodiesel yield, at the temperature 40° C

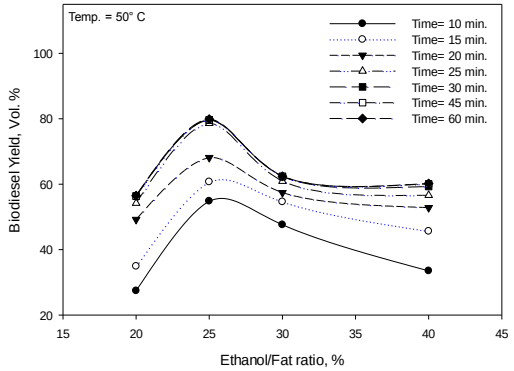

Fig.7, Effect of the ethyl alcohol/ fat wt. ratio and time on the reaction on biodiesel at the temperature 50° C

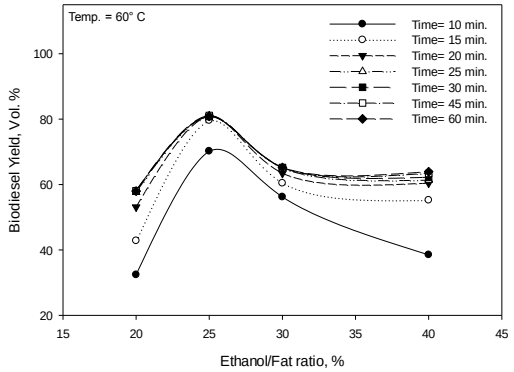

Fig.8, Effect of the ethyl alcohol/ fat wt. ratio and time on the reaction on biodiesel yield, at the temperature 60 °C

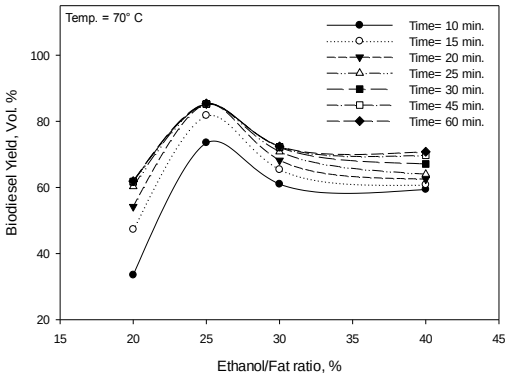

Fig.9, Effect of the ethyl alcohol/ fat wt. ratio and time on the reaction on biodiesel yield, at the temperature 70°C

Kinetics of Production Rate

Kinetics studies for data obtained from laboratory unit usually play an important role in modeling and scale up designs for new biodiesel production units.

In order to find the rate of a product that describes the effects of temperature, and the time of the reaction on production rate, kinetic model of production was suggested and a chosen model fits the data with a higher correlation coefficient. This model is given by Equation (1) below:

$$ry = \frac{k_{\circ} \exp(-E / RT)}{(a + bT) + (c + dT) y^{n}} \quad \ldots(1)$$

Where:

$ry = \frac{dy}{dt}$ Production rate of biodiesel (vol. % / min).

y = vol. % of biodiesel.

t = reaction time (min).

$k_{\circ}$ = frequency constant ((vol. %)$^{1-n}$/ time).

E = activation energy (J/mole).

n = reaction order.

a, c = arbitrary constant.

b, d = arbitrary constant (K^{-1})

The yield of the product (y) was fitted by the fourth order polynomial degree formula according to the time (for certain temperature). Then *dy* over *dt* has been calculated by the differentiation of the polynomial equations. This step was repeated for other temperatures.

After that, the obtained data of dy/dt was regarded with the suggested models (Eq. 1). The correlated coefficient of the suggested model shows excellent presentation (> 0.9) of data by the suggested model of Eq. 1. Constant values of the suggested model (Eq.1) are summarized in Table 1.

Table 1, Constant values of the suggested model (Eq.1)

Constant value	Transesterification by esterification pre-treatment
$k_\circ$ (vol. $\%^{1-n}$/ time)	$1.18*10^8$
E (J/mole).	25320
a	1
b (K^{-1})	3.85
c	0.022
d (K^{-1})	0.003
N	2.0

Statistical calculation of the suggested model for experimental data shows that the solution of the model (eq.1) is proportionally correlated with the experimental data. The distribution of the experimental data around the model solution (regression coefficient (R)) is about 0.9618, standard deviation (S) is 1.056, and average relative error is -0.1256 in 95 % confidence level, as summarized in Table 2.

Predicted values calculated from empirical model (Eq. 1) and experimental data are shown in Figure 10.

Table 2, Statistical analysis of the model

Statistical analysis	Esterification method
Regression coefficient (R)	0.9618
Standard deviation (S)	1.056
Average relative error	-0.1256
Confidence level	95%

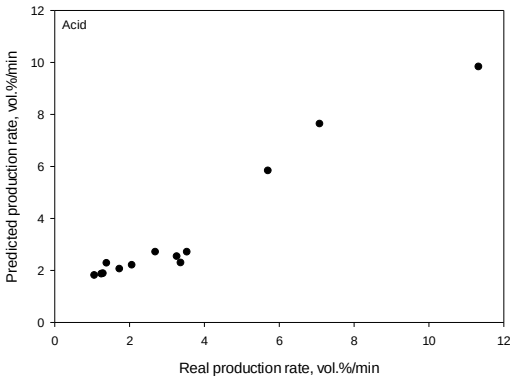

Fig.10, Experimental and predicted values of apparent rate constant by using suggested model of esterification method

Conclusion

According to the results obtained from this study, the following conclusions were obtained:

1. The FFAs pre-treatment of sheep fat by esterification method is more efficient. The acid value of fat was lowered from 49.14 mg KOH/g of fat to 0.97 mg KOH/g of fat at a conversion of 98%.
2. The maximum yield of biodiesel produced by this process was about 85 vol. % at the conditions ethanol/fat wt. ratio 25/100, reaction temperature 70° C and 20 minutes.

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