SETTLING BEHAVIOUR OF GLYCEROL DURING BIODIESEL PRODUCTION

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Abstract

The effect of the types of oil such as used oil, waste cooking oil, palm oil and soybean oil and different types of alcohol such as methanol, ethanol and mixture of methanol and ethanol on the settling behaviour of glycerol has been investigated. The experiments were undertaken via transesterification using sodium hydroxide (NaOH) as a catalyst under optimum reaction conditions. The yield of biodiesel produced in each variation was determined and the equal ratio of the product (biodiesel) and the by product (glycerol) obtained from each batch experiment were vigorously re-mixed and subsequently, the settling behaviour of glycerol was investigated. The results revealed that optimum conditions can not be selected from by considering only the settling behaviour of the glycerol. The yield of the biodiesel and prices of the alcohol and oil should be taken in account. This work has been very successful in establishing the link between the yield of biodiesel (the desired product) and the settling behaviour of the glycerol (the by product).

Keywords: Settling behaviour, Glycerol, Biodiesel, Transesterification

I. INTRODUCTION

Diesel fuel plays an important role in the industrial economy of a country. These fuels are important in the transport sector, electricity generation and farming. Demand is increasing steadily, and in order to meet this demand and with respect to increasing awareness for sustainability, alternative fuels whose production is technically feasible, economically competitive, environmentally acceptable are sought [1-2].

Biodiesel is defined as a substitute for or a realistic alternative to diesel fuel because it provides a fuel from renewable resources which has lower environmental impact than petroleum diesel. Befouls are biodegradable, essentially non toxic and produce lower emissions of net greenhouse gases and sulphur to the atmosphere [3−5]. Biodiesel is synthesized by a chemical reaction known as transesterification of vegetable oils or animal fats with an alcohol such as methanol, ethanol and butanol [5]. This process involves the use of different catalysts such as sulphuric and hydrochloric acid [6], alkalis such as sodium hydroxide and potassium hydroxide [4-6] and in some instances even biocatalysts for example the lipase enzyme produced by micro organisms [5, 7−8].

Ethanol is made form agricultural products such as corn, sugar cane, and, in the future, it is expected that cellulosic material like switch grass, wood chips and other agricultural residue will provide additional sources of material. Methanol, which is the cheapest alcohol, can be made from all of the above plus natural gas and coal. Currently, analytical grade ethanol costs $ 30 for 2.5 L and the commercial grade costs $ 40 for 20 L while comparative methanol prices are $ 13 and $ 26 respectively.

Generally, vegetable oils and animal fats are primarily water insoluble and hydrophobic substances that are made up of one mole of glycerol and three moles of fatty acid and are typically referred to as triglyceride (TG) [3, 10]. The transesterification reaction of oils and fats with an alcohol leads to the generation desired fatty acid alkyl esters (FAAE) or biodiesel together with the by-product glycerol (See Fig.1) [9 - 11]. The free glycerol formed must be removed from the biodiesel mixture, since the presence of glycerol can cause damage to diesel engine [12-13].

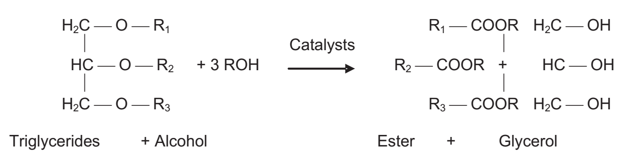

Fig. 1. Stoichiometric transesterification reaction of biodiesel [9 - 11]

The efficient removal the residual TG and glycerol from the FAAE plagues biodiesel required an approach to derive reaction as close to complete conversion of the TG as possible. Since, the transesterification of TG is an equilibrium reaction, therefore limits to this approach [11, 14-15]. Typically, the conventional transesterification results in a two phase reaction as a result, mass transfer limited. More specifically, the vegetable oils and alcohol are not miscible [11, 16-18].

Efficient separation of glycerol from the biodiesel-glycerol mixture is necessary to improve both the yield and quality of the biodiesel. Thus, the aim of this research is to study the settling behaviour of glycerol during base-catalyzed transesterification reactions. Parameters such as type of oil (i.e. waste cooking oil, palm and soya oil), oil-alcohol ratios and type of alcohol (i.e. methanol, ethanol and mixtures of all types) were varied to evaluate the separation efficiencies of glycerol from biodiesel suspension.

II. MATERIALS AND METHODS

A.1. Solvents and Chemicals

The biodiesel used in this study was produced from five different types of oil using alkaline catalyst, sodium hydroxide (NaOH), and two different alcohols (99.9% containing <0.1% water each) methanol and ethanol. All chemicals were analytical grade (Universal, Malaysia). The five different types of oil comprised: three commercial edible grades namely rice bran oil, palm oil and soybean; vegetable oil obtained from a restaurant after it had been used to fry chicken; and a mixture of used vegetable oil and animal fat oil were obtained from a pilot plant for biodiesel production (600 L day^{1} capacity), (Simedarby, Malaysia).

B.2. Biodiesel Production and Experimental Design

All biodiesel production was carried out in the laboratory according to a methodology previously described [19-21]. The main equipment consisted of a 500 ml round bottom flask equipped with a magnetic stirrer and a water cooled condenser. The alkali-catalyzed transesterification reaction was performed using different alcohol/oil molar ratios and various amounts of catalyst. The mixture was vigorously stirred and refluxed on hot plate and magnetic stirrer (Scientific industries G560 E, USA) for the desired reaction time (15-20 min) and temperature (55-60 °C) until the reaction completed, the mixture of methyl ester (biodiesel) and the by product of glycerol were used for further study. Tables 1-4 show summaries of experimental plans and the optimum conditions used throughout this study. The ratio of methanol (MeOH) and sodium hydroxide (NaOH) in each reaction is the optimum ratio corresponding to the maximum yield of biodiesel achievable.

Table 1. Conditions used for mixture of used vegetable and animal fat oils during biodiesel Production

Type of alcohol	Oil Type	Operating Condition
Methanol	The mixture of used vegetable and animal fat oil (100 ml)	Oil amount: 100 ml Methanol (MeOH): 18% NaOH: 5% Reaction temperature 55-60 °C Reaction time 15-20 min.

Table 2. Conditions used for used vegetable oil during biodiesel production

Type of alcohol	Oil Type	Operating Condition
Methanol	used vegetable oil(100 ml)	Oil amount: 100 ml. Different concentration of (MeOH): 20, 30, 40, and 50% were used and 0.58% of NaOH kept constant. Reaction temperature 55-60 °C Reaction time 15-20 min

Table 3. Conditions used for used vegetable oil during biodiesel production

Type of alcohol	Oil Type	Operating Condition
Methanol	Used vegetable oil (100 ml)	Oil amount: 100 ml Alcohol amount: 30% NaOH: 0.37% Reaction temperature 55-60 °C Reaction time 15-20 min
Ethanol		
Methanol + Ethanol (1: 1 ratio)		

Table 4. Conditions used for various oil types during biodiesel production

Type of alcohol	Oil Type	Operating Condition
Methanol	Rice bran oil (100 ml)	Oil amount: 100 ml Methanol (MeOH): 30% NaOH: 0.37% Reaction temperature 55-60 °C Reaction time 15-20 min
Methanol	Palm oil (100 ml)	
Methanol	Soybean oil (100 ml)	

C.3. Settling behaviour

The biodiesel fuels were produced under different conditions following the experimental methodologies shown in section 2.2. Subsequently, equal ratios of the product (biodiesel) and the by product (glycerol) obtained from each batch experiment were vigorously re-mixed for 5 minutes using a magnetic starrier and thereafter, the prepared suspensions were transferred to 100 ml measuring cylinders (30 mm in diameter). Settling tests were carried out until the equilibrium position of sediment (glycerol)-supernatant (biodiesel) interface was reached. Subsequently the thickness of the interface was recorded with settling time. A fresh sample was used for each trial and at least three replications were made for each sample used.

III. RESULTS AND DISCUSSION

A.1. Biodiesel production and glycerol settling behaviour

A.1.1 Effect of oil sources and type

The position of the interface between sediment (glycerol) and supernatant liquid (biodiesel) for different types of oil is shown in Fig. 1 as a function of time. The glycerol produced from non used oils (palm, rice bran and soya oils) settled faster than the one produced from the mixture of used vegetable and animal fat oil. The highest settling rate for glycerol was recorded when the soybean oil was used.

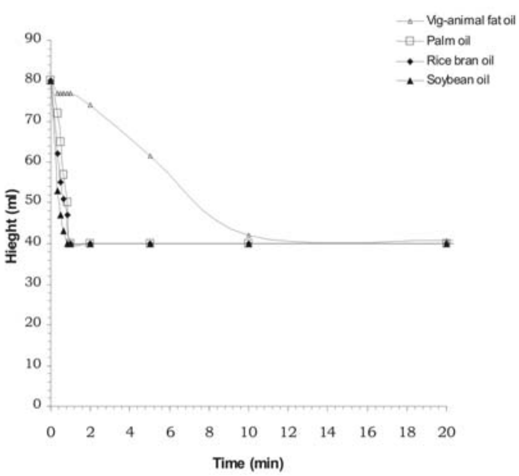

Fig 1. Sedimentation characteristic of glycerol in biodiesel suspension produced from different sources of oil.

The results also show that the final or equilibrium heights of settled glycerol from the pure oils (palm, rice bran and soya oils) are achieved after about 1 minute, while the settled glycerol from the mixture of used vegetable and animal fats reaches the equilibrium condition after about 10 minutes. Fig. 2 is shown here to demonstrate the clear differences in the initial settling rates (i.e. settling times 1-60 seconds) for these oils.

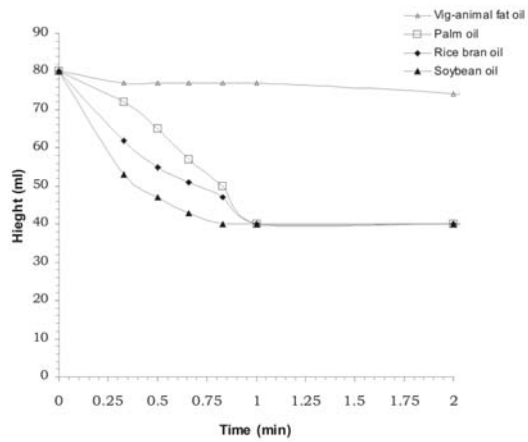

Fig. 2. Initial settling behaviour of glycerol in biodiesel suspension produced from different sources of oil.

The impurities in the mixture of used vegetable oil and animal fat oil and the amount of methanol used could produce small flocs of glycerol (this is optically observed) which reduce the settling rate of glycerol. However, the amount of the methanol can be varied to improve the settling rate of glycerol. It was found that the flocs sizes of glycerol and it is settling efficiency for the mixture of the used vegetable and animal fats oil biodiesel increased if the amount of methanol (MeOH) is increased. But any increase or decrease of the optimum MeOH concentration could seriously reduces the yield (volume of extracted biodiesel / total volume of oil-alcohol mixture used). The yield corresponding to the optimum amount of methanol used for the all different oils are summarized in Table 5. Under these conditions, soybean oil appears to be the best oil for producing biodiesel fuel having a high yield together with efficient settling of the by products.

Table 5. Percentage yield versus optimum concentration of methanol for different types of oil.

Type of oil	% Optimum MeOH amount in 100 ml of oil	% Yield
The mixture of used vegetable and animal fat oil(see Table 1)	18	85
Palm oil (see Table 4)	30	86
Rice bran oil (see Table 4)	30	90
Soybean oil (see Table 4)	30	95

A.2. Effect of oil: alcohol ratio

All the reaction parameters such as reaction time, temperature, type of oil and the amount of catalyst were kept constant and four different concentrations of MeOH (20, 30, 40, and 50% in oil) were used to produce biodiesel fuels from the used vegetable oil. The position of the interface between sediment (glycerol) and supernatant liquid (biodiesel) for different oil-alcohol ratios is shown in Fig. 3 as a function of time. The results show that the settling rate of glycerol is increased as the MeOH concentration is increased from 20 to 40% and remained almost constant when the MeOH concentration is increased from 40 to 50%. The results also confirm that for a similar source of oil, the structure, density, viscosity and appearance of by product (glycerol) can be altered by only changing the alcohol amount and thereby the settling rate can be increased or decreased following this change.

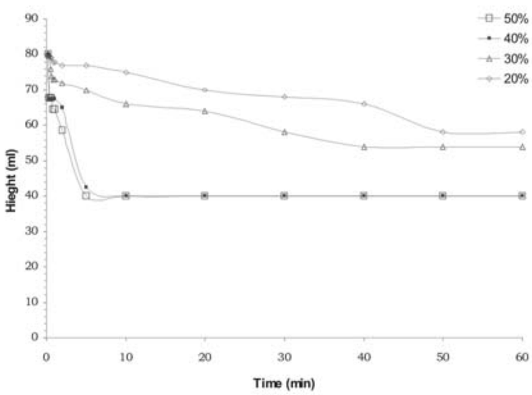

Fig. 3. Sedimentation characteristic of glycerol in biodiesel suspension produced under different concentration of methanol.

On the other hand, the optimum MeOH concentration can not be selected from by considering only the settling behaviour of the glycerol. Optimisation of the by product settling rate and yield of biodiesel is required to define the optimum MeOH concentration. The yields corresponding to the amount methanol used to produce biodiesel from used vegetable oil are summarized in Table 6.

Table 6. Percentage yield versus methanol concentration for used vegetable oil.

% Amount of MeOH in 100 ml of used oil	% Yield
20	72
30	91
40	64
50	60

Table 6 shows that the yield increased from 72% to 91% by increasing the MeOH concentration from 20 to 30%. Further increase of MeOH concentration from 30 to 50 produces an extreme reduction in the yield from 91% to 60%. One can conclude that, the optimum concentration of MeOH for this particularly case seems to be in region of 30%, which produces a high % yield (91%) of biodiesel having reasonable glycerol settling rate.

A.3. Effect of alcohol type

Pure alcohol of methanol, ethanol and mixture of 1:1 ratio of methanol + ethanol are used to investigate the effect of alcohol type on the % yield of the biodiesel and the settling behaviour of the by product. All the reaction parameters such as reaction time, temperature, type of oil and the ratio of alcohol and the catalyst were kept constant. The position of the interface between sediment (glycerol) and supernatant liquid (biodiesel) for different alcohol is shown in Fig. 4 as a function of time. Also the yields corresponding to the 30% of each alcohol and mixture of alcohols used to produce biodiesel from used vegetable oil are summarized in Table 7.

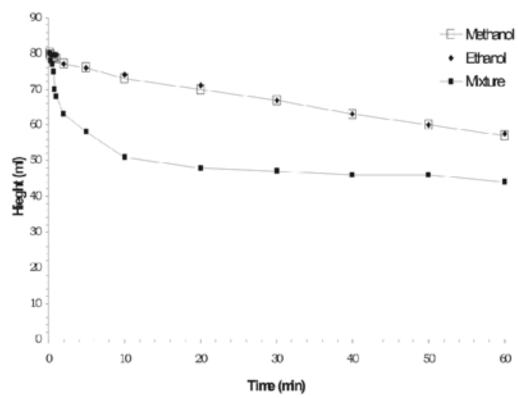

Fig. 4. Sedimentation characteristic of glycerol in biodiesel suspension produced under different types of alcohol.

The results show that, keeping all the parameters constant, there are no differences in settling behaviour of glycerol when pure methanol and ethanol are used. But the yield is increased from 85% to 90% if ethanol is used instead of methanol. On the other hand, the price of litre of ethanol is almost double the price of methanol in the market, then using pure ethanol instead of pure methanol, to improve the yield, required some analysis to find out whether replacing is feasible or not.

Table 7. Percentage yield of different types of alcohol for used vegetable oil.

Type of alcohol	% Yield
Methanol	85
Ethanol	90
Methanol + Ethanol	88

Table 7 also shows that both the settling rate of glycerol and the yield biodiesel produced from methanol-oil mixtures can be increased if some ethanol is added to the mixture. One can conclude that using a mixture of equal ratio of methanol and ethanol alcohols to produce biodiesel is better than using pure ethanol or methanol in term of production cost, yield and settling rate of the glycerol.

IV. CONCLUSIONS

The effect of oil and alcohol type on the yield of the produced biodiesel and settling behaviour for glycerol during the biodiesel production has been investigated. It was found that, the settlement characteristics of the glycerol during the biodiesel production change significantly with oil type and alcohol type and concentration. The results also show that the settling efficiency of glycerol can be improved if the amount of methanol is increased or if ethanol is used instead of methanol or a mixture of both is used instead of pure alcohol. However any increase or decrease of the optimum concentration of alcohol or changing the alcohol type or using mixtures of alcohols instead of pure could seriously varied the yield of the produced biodiesel and increased the production cost. Additional analysis should be considered to find out whether changing above parameters is feasible or not.

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