EXPERIMENTAL STUDY ON LOW COST BIODIESEL PRODUCTION ALKALINE BASED CATALYSTS BY USING FRYING OIL

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ABSTRACT

The primary aim of this research is to investigate the best alkaline-based for the used frying oil (UFO) biodiesel production, using the alkaline catalyzed transesterification method. Transesterification reaction of UFO with methanol, in the presence of several alkaline-based catalysts, is carried out under identical typical transesterification process parameters. The effects of catalyst formulation on biodiesel yield are evaluated by using five different alkaline catalysts, sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide ($NaOCH_3$), mixture of NaOH and KOH, and mixture of KOH and $NaOCH_3$ in the UFO biodiesel conversion process. A sample of virgin oil (VO) biodiesel is produced using NaOH catalyst, as the comparison reference for UFO biodiesel. The highest yield for UFO biodiesel production in this research was achieved by $NaOCH_3$ catalyst, which gave 96.2% which shown that the $NaOCH_3$ catalyst had advantages in yields-effective and times-effective for the biodiesel production. However, for commercialize purpose, the cost of $NaOCH_3$ was too high which had made it not practical to use. In order to have a balance between yield-effective, times-effective, and cost effective characteristics, the mixture of KOH and NaOH catalyst was found to be the optimum catalyst in this biodiesel production study.

KEYWORDS*: biodisel, used frying oil, alkaline-based catalyst, transesterification.*

1.0 INTRODUCTION

The most critical challenge encountered by biodiesel industry is its price is still higher than retail petrol-diesel. The cost of biodiesel production varies depending on the base stock, geographic area, variability in crop production from season to season, the price of crude petroleum, and other factors (Demirbas, A., 2008). A huge amount of used frying oil (UFO) generated by the restaurants, fast food outlets, and food processing industries everyday and everywhere around the world. Instead of draining this oil, it could be recycled to be an alternative raw material in biodiesel production. However, large amount of free fatty acids in UFO is undesirable in alkali catalyzed transesterification reaction, and so, the conversion of UFO to biodiesel becomes more complicated. Used frying oils contain higher amount of free fatty acids (FFA), water content, and food particles. Those contents are undesirable in transesterification process as FFA would react with alkali catalyst to form soap, and high water content would drive the triglycerides to form free fatty acids. Consequently, pretreatment of used frying oils is necessary to filter out the solid particles, and reducing the acid values and water contamination in the oil.

Alkali catalyzed transesterification method still hold the most favored approach in biodiesel production because its projected high yield, relative to low temperature, pressure, and simple reactions during the process. The overall biodiesel production process using alkali catalyzed transesterification method can be divided into four major stages: raw materials preparation, transesterification, washing, and drying. For heterogeneous catalysts, Mg-Al hydrotalcite gave the highest biodiesel yield (97%) (Georgogianni, K.G, 2008), but with relatively longer reaction duration (24 hours). For homogeneous catalysts, comparisons were commonly made on potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium methoxide ($KOCH_3$), and sodium methoxide ($NaOCH_3$). Potassium based catalysts (KOH and $KOCH_3$) showed a higher biodiesel yield than sodium based catalysts (NaOH and $NaOCH_3$) for a longer reaction duration like 120 minutes (Encinar, J.M *et.al*., 2007), (Rashid, U. *et.al*., 2007). For shorter reaction duration like 30 minutes and 60 minutes, sodium based catalysts (NaOH and $NaOCH_3$) achieved the better biodiesel yield than potassium based catalysts (KOH and KOCH3) (Dias, J.M *et.al*., 2008), (Meng, X.M . *et.al*., 2008).

Based on several studies on biodiesel production, methanol is the most common alcohol used in transesterification, and the optimum methanol-to-oil molar ratio is 6:1 (Rashid, U. *et.al*., 2007), (Dias, J.M *et.al*., 2008), (Leung, D.Y.C *et.al*., 2006). The optimized reaction temperature for transesterification reaction obtained by several biodiesel studies were similar, which is in the range of 60^oC to 70^oC. Duration for complete reaction is normally depending on the types of biodiesel process and catalyst. In general, conversion of oil to biodiesel has the highest rate at the early stage of the reaction, and will gradually slow down until equilibrium is achieved. Biodiesel that will be blended with diesel fuel or used a substitute for diesel should meet the most commonly used standards, ASTM D6751 and EN 14214 .Testing biodiesel for compliance with ASTM standards can be done by commercial fuel testing laboratories. It is advisable to conduct periodic full tests of the biodiesel produced using small-scale units in the municipal facility.

2.0 METHODOLOGY

In the conversion of biodiesel, replicated experiments are carried out with five different types of catalysts i.e. sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide ($NaOCH_3$), mixture of NaOH and KOH, and mixture of KOH and $NaOCH_3$, under the typical optimized reaction conditions. Virgin oil (VO) biodiesel is catalyzed by sodium hydroxide (NaOH), as a comparison reference for biodiesel. The amount of UFO that used in every batch of biodiesel production was 1kg with the molecular weight at 267g/mol.

2.1 Used Frying Oil (UFO) & Virgin Oil (VO)

The oil feedstock was supplied by Kian Seng Food Industries Sdn. Bhd. The UFO was actually the product of 1-time frying process. A sample of used frying oil is mixed with isopropyl alcohol, and the mixture is titrated with alkali substance (KOH, NaOH, $NaOCH_3$) in the presence of few drops of phenolphthalein indicator to obtain the acid values. The same titration method is applied to obtain its acid values.

2.2 Premixing of Methanol-Catalyst Solution

Premixing of methanol with molar ratio 4:1 to the oil and predefined amount of catalyst solution was done in a 1 litre beaker, with stirring effect at around 150 rpm, and slightly heating effect to accelerate the mixing process. Five different types of catalysts were used on the conversion of UFO biodiesel.

2.3 Transesterification

Transesterification experiments were performed in the batch reactor. The 1kg of UFO was measured and filled into the reactor for each batch of the biodiesel production. The mixture was agitated vigorously by using the magnetic stirrer of hotplate stirrer, at the speed control at 600rpm. The reaction temperature in the reactor was monitored in the range of 60±2°C throughout the experiment. The completion of the reaction was determined by taking the mixture sample for thin layer chromatography (TLC) test at the first 20 minutes and subsequence of 5 minutes interval. Once the transesterification reaction is completed, agitation and heating was stop, and the mixture was leaved for about 5 minutes for the phase separation process. Two layers would be formed in the reactor, with the glycerol phase settled at the bottom and mixture of methyl ester phase at the top. The glycerol is drained out from the reactor through a nozzle at the bottom of the reactor. A 1-liter separation funnel was also used to run the fine separation process for biodiesel and remaining glycerol.

2.4 Washing

The mass of the biodiesel was measured before the washing process was carried out. In the washing stage, hot distilled water (about 70^{o}C) was used to wash the biodiesel. 500ml of hot distilled water was introduced into biodiesel manually, along with the magnetic stirring speed at 150rpm. The mixture of biodiesel and water was stirred for 3 minutes, and then the stirrer was switched off for allow the phase separation between biodiesel and water could be carried out. Biodiesel, which has the lower density, would form a yellowish layer on the top, while the distilled water would form a cloudy layer at the bottom. The distilled water layer was drained out from the reactor and completion of the washing process is determined by using the pH paper to measure the pH of the methyl ester or biodiesel. The accepted pH of biodiesel is 7, which is neutral. Separation funnel was used to run the fine separation process for biodiesel and remaining distilled water.

2.5 Drying

Drying is the process to remove the remaining water content in the biodiesel by vaporizes the water content with heat supply. The washed biodiesel in the reactor was being stirred at 150rpm and gradually heated until the temperature of biodiesel reached 100^{o}C. The biodiesel was maintained at 105^{o}C for 10 minutes, in order to ensure all the water content in biodiesel was eliminated. The dried biodiesel would appear in clear and deep golden color. The biodiesel would be sent to the Malaysian Palm Oil Board (MPOB) for undergo certain chemical testing to get its characteristics.

3.0 RESULTS AND DISCUSSION

Titration was the first process in raw material preparation and it is important to determine the acid value of biodiesel respected to different alkaline catalyst that has been used in this study. The result of this titration is shown in Table 1. In order to find the acid value of biodiesel respected to each alkaline catalyst, Equation (1) was being used for the calculation:

$$V_{Acid} = \frac{\left[\frac{(V_{Titration})(C_{Alkaline})}{1000} \times M_{Alkaline}\right]}{m_{Oil}} \quad (1)$$

where

$V_{Titration}$ = volume of alkaline using titration (ml)

$C_{Alkaline}$ = concentration of alkaline solution (mol/liter)

$M_{Alkaline}$ = molecular weight for alkaline (mg/mol)

m_{Oil} = mass of oil used in titration (g)

Acid value (mg alkaline/g oil) can be written as V_{acid} and the total equation is shown in Equation (1). For biodiesel result, it has shown in Table 2 and the graph of yield (%) versus biodiesel samples shown in Figure 1, respectively. If KOH is used for titration, then the unit for acid value could be mg KOH/g oil; while the unit for acid value would be mg NaOH/g oil if the NaOH is used. Table 3 has shown an acid value for each titration result.

Table 1 Result of Titrations

Oil			Isopropyl Alcohol (ml)	Alkaline		
Type	Volume (ml)	Mass (g)		Type	Concentration (mol/liter)	Volume required for titration (ml)
UFO	1	0.96	10	KOH	0.035714	0.8
UFO	1	0.96	10	NaOH	0.050000	0.5
UFO	1	0.96	10	$NaOCH_3$	0.037037	0.7
UFO	1	0.96	10	KOH + NaOH	0.085714	0.3
UFO	1	0.96	10	KOH + $NaOCH_3$	0.072751	0.4
UFO	1	0.96	10	NaOH	0.050000	0.1

Based on Table 3, there are six different types of alkaline are used. KOH and the acid value is approximately to 1.67 mg alkaline/ g oil while NaOH and the acid value been used for titration is approximate to 1.04 mg alkaline/ g oil. For $NaOCH_3$ the acid value is around 1.46 mg alkaline/ g oil. In compound type, which is KOH + NaOH and KOH + $NaOCH_3$, the acid value are 1.29 mg alkaline/ g oil and 1.66 mg alkaline/ g oil for the both compound, respectively and for NaOH, the acid value for titration is 0.23 mg alkaline/ g oil.

Table 2 Results of Biodiesel Production

Oil Feedstock (g)	Methanol (g)	Catalyst (g)			Reaction Temperature (°C)	Reaction Time (minute)	Unwashed Biodiesel (g)	Washed & Dried Biodiesel (g)	Biodiesel Yield (%)
1000(UFO)	480	KOH	6.67		60±2	25	1128	959	95.9
1000(UFO)	480	NaOH	6.04		60±2	25	1096	952	95.2
1000(UFO)	480	$NaOCH_3$	6.46		60±2	25	1158	962	96.2
1000(UFO)	480	KOH NaOH	3.67 2.62	6.29	60±2	25	1104	958	95.8
1000(UFO)	480	KOH $NaOCH_3$	3.39 3.27	6.66	60±2	25	1118	960	96.0
1000 (VO)	480	NaOH	5.23		60±2	25	1152	966	96.6

Table 3 Acid Value for Each Titration Result

Oil	Alkaline	Acid Value (mg alkaline/g oil)
UFO	KOH	1.67
UFO	NaOH	1.04
UFO	$NaOCH_3$	1.46
UFO	KOH + NaOH	1.29
UFO	KOH + $NaOCH_3$	1.66
VO	NaOH	0.23

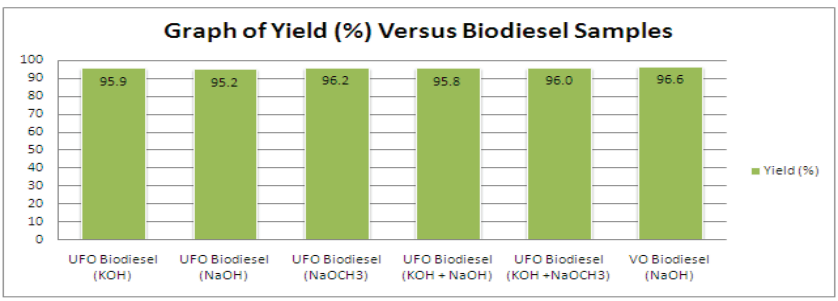

Figure 1 Graph of Yield (%) versus Biodiesel Samples

According to the results of biodiesel production shown in Table 2, there were two types of oil feedstock that used in this biodiesel production study. The yield of VO biodiesel was predicted to be higher than the UFO biodiesel due to VO had better physical properties as well as chemical properties, and the experimental results had also proved the yield of VO biodiesel (96.6%) was higher than other UFO biodiesel samples. The oil feedstock for every batch of biodiesel production was set at 1kg or equals to 1050ml. Although the reactor of the biodiesel production model has the capacity up to 10 liters, but it was found that the magnetic stirrer was unable to provide good stirring effect when the oil feedstock was too much. After considering the volume of methanol-catalyst solution, cost of raw materials, reaction time, and problems probabilities, the mass of oil feedstock for every batch production was decided to be 1kg, which was sufficient for this study.

3.1 Alcohol Feedstock

Methanol was selected as the alcohol feedstock for the transesterification process. The hazard level of methanol is lower than ethanol, which made it easier in handling and storage. In transesterification reaction, 3 mol of methanol is required to react with 1 mol of triglyceride in order to produce 3 mol of methyl ester and 1 mol of glycerol at the end of the process. However, instead of using 3 mol of methanol, the biodiesel researchers like Meng X.M *et.al.* (2008), and Umer R. & Farooq A. (2007) had proved that 6 mol of methanol was preferable as it gave the highest biodiesel yield. The advantages of using 6:1 methanol-to-oil molar ratio were the reaction time was reduced and provided very high yield, but the cost of production would also increased apparently. The retail price of methanol that provided by Polyscientific Enterprise Sdn. Bhd. was RM55 per 18 liters. The density of methanol is 0.7918 g/cm^3. By applying some calculations and conversion method, the price of methanol in 1 gram could be determined.

Equivalent cost and mass of methanol that related to different methanol-to-oil molar ratio was constructed, based on the molecular weight of UFO in this study as given in Table 4. This could give a clearer comparison on methanol's cost. High production cost and long reaction time are definitely not practical for commercialize the biodiesel. Thus, 4:1 methanol-to-oil molar ratio was selected to be used in this study, after considered the retail price of methanol and the biodiesel production yield. In other words, 480g of methanol was required to react with 1000g of oil to have 4:1 methanol-to-oil molar ratio in this study. Based on the results, the biodiesel production yield among the six samples was considered high as the range of percentage was from 95.2% to 96.6%. This had proved that 4:1 methanol-to-oil molar ratio was sufficient for the transesterification reaction.

Table 4 Equivalent Mass and Cost of Methanol With Different Methanol-To-Oil Molar Ratio

Methanol-to-oil Molar Ratio	Equivalent Mass of Methanol (g)	Equivalent Cost of Methanol (RM)
3:1	359.55	1.44
4:1	479.40	1.92
5:1	599.25	2.40
6:1	719.10	2.88

3.2 Alkaline Catalysts

The purpose of adding up alkaline catalyst into transesterification reaction is to reduce the reaction time for complete the whole process. The alkaline catalyst would not be consumed throughout the entire transesterification process. In order to study the effects of the mixture catalysts to the biodiesel production yield, the mixture of KOH and NaOH was mixed in the equal molar ratio, which is 1:1, and the same molar ratio was also applied in the mixture of KOH and $NaOCH_3$. The general amount of alkaline catalyst that required in transesterification reaction is 0.5% of the mass of oil feedstock for each production batch. However, since the UFO and VO are normally in acidic, it would consume certain amount of alkaline catalyst in the transesterification process. This would cause insufficient catalyst amount for optimum state, and the reaction time as well as the yield would be affected. Thus, an addition amount of alkaline catalyst is required for the acidic consumption, and this addition amount could be indicated by the acid value through the titration process.

Based on the acid value results in Table 3, the acid value of UFO which titrated by KOH was 1.67mg KOH/g oil. It meant that the addition amount of KOH for acidic consumption was 1.67g if 1000g of UFO was used as the feedstock for biodiesel production. Consequently, the total mass of KOH required for the transesterification in this study would be 6.67g, after sum up the addition amount and general amount of KOH catalyst for 1000g of UFO feedstock.

3.3 Yields-Effective

The biodiesel production yield in this study was referred to the percentage ratio of the mass of washed and dried biodiesel to the mass of initial oil feedstock. Among the biodiesel samples that converted from UFO, sodium methoxide ($NaOCH_3$) had given the highest production yield which is 96.2% after 25 minutes of reaction time. Another two basic alkaline catalysts which were KOH and NaOH had achieved 95.9% and 95.2% yield respectively after the same reaction time. On another hand, the mixture of KOH+$NaOCH_3$ catalyst had given the yield of 96.0%, which was stayed between the yields of KOH and $NaOCH_3$ catalyst; while the mixture of KOH+NaOH catalyst also given the yield of 95.8% that stayed in the range of KOH's and NaOH's yields. The result had proved that the mixture catalysts would have part of the effects and characteristics of their original pure substance, and their yields would not exceed the highest yield among their original pure substances. The biodiesel production yield for virgin oil feedstock had given higher yield than used frying oil feedstock, which was 96.6%.

3.4 Times-Effective

For the times-effective considerations, all the alkaline catalysts had shown a similar capability in accelerated the transesterification reaction, as all the biodiesel products were complete reacted in the time between 20 to 25 minutes. However, if the premixing of methanol-catalyst solution is taken into time considerations, then $NaOCH_3$ had achieved the shortest time for dissolving in the methanol. This was due to the $NaOCH_3$ was appeared in powder form while other catalysts were appeared in pellets form. The NaOH catalyst was required the longest time for completely dissolved in the distilled water, as it was appeared in pellet form and its pellets was larger than KOH. Thus, $NaOCH_3$ should have advantage in the total biodiesel production time.

3.5 Cost-Effective

Production cost is one of the major concerns in the biodiesel industry as the high production cost always is a challenge for the biodiesel supplier. In order to develop biodiesel industry and make it could compete with diesel, the retail price of biodiesel has to be set at least approach the retail price of diesel. Thus, the raw materials cost which including UFO, methanol, and different alkaline catalysts are also put into considerations when selecting the most suitable method in producing the biodiesel. As mentioned in the previous section, the used frying oil in this study was bought from the Kian Seng Food Industries Sdn. Bhd. The selling price of the UFO was RM130 per 180 liters of UFO, and 180 liters of UFO was equals to about 172.8kg. That means the price of 1kg of UFO is RM0.75. The retail price for methanol was RM55 per 18 liters. Based on the calculation stated before, the methanol consumption in 1 batch of biodiesel production was approximately 480g, which was equals to RM1.92. There were five different types of alkaline catalysts used to accelerate the transesterfication reaction in this study, but they were basically only consisting of three different chemical substances. The cost of alkaline catalyst per batch production is given in Table 5 while Table 6 shown the total materials cost calculated by sum up the cost of UFO, methanol, and different alkaline catalyst in each batch of biodiesel production.

Table 5 Cost of Alkaline Catalyst per Batch Production

Alkaline Catalyst	Consumption per Batch Production (kg)	Retail Price (RM)/kg	Cost of Alkaline Catalyst per Batch Production (RM)
KOH	0.00667	190	1.27
NaOH	0.00604	130	0.79
$NaOCH_3$	0.00646	670	4.33
KOH + NaOH	0.00629	-	1.04
KOH + $NaOCH_3$	0.00666	-	2.84

Table 6 Total Materials Cost for Each Batch Production

Biodiesel	Cost of UFO per Batch Production (RM)	Cost of Methanol per Batch Production (RM)	Cost of catalyst per Batch Production (RM)	Total Materials Cost (RM)
Biodiesel (KOH)	0.75	1.92	1.27	3.94
Biodiesel (NaOH)	0.75	1.92	0.79	3.46
Biodiesel ($NaOCH_3$)	0.75	1.92	4.33	7.00
Biodiesel (KOH+NaOH)	0.75	1.92	1.04	3.71
Biodiesel (KOH+$NaOCH_3$)	0.75	1.92	2.84	5.51

4.0 CONCLUSION

The primary goal of this study was to find out the best alkaline-based catalyst for biodiesel production, in terms of yields-effective and times-effective. This paper had covered the study of biodiesel production processes, basic equipments, and critical process parameters. In order to study the effects of catalyst formulation on biodiesel yield was transesterified with methanol, in the presence of five different catalysts e.g. sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide ($NaOCH_3$), mixture of NaOH and KOH, and mixture of KOH and $NaOCH_3$.

The experimental results had shown that different alkaline catalyst would give different production yield at the end of the process. As for the yields-effective considerations, the sodium methoxide ($NaOCH_3$) catalyst had given the highest biodiesel production yield among the other catalysts.

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