

Analysis of Parameters for Fatty Acid Methyl Esters Production from Refined Palm Oil for Use as Biodiesel in the Single- and Two-stage Processes

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Abstract

In the present study, the production of fatty acid methyl esters (FAME) for use as biodiesel from the alkaline transesterification of refined palm oil (RPO) was found to occur optimally using a molar RPO (triglyceride) to methanol ratio of 1:6, in the presence of 1% NaOH (catalyst) in methanol (w/v), at 60°C, in 30 min and with vigorous mixing. Comparing performance of the reaction that was carried out in the single- and two-stage processes showed that the single-stage process was more superior to the latter as it was faster, easier, required less handling procedure and produced higher yield of FAME. Under the optimally derived conditions, the single-stage process proved capable of more than 95% yield of FAME. When analyzed, the RPO FAME produced met the standards for use as biodiesel in five basic properties tested.

Keywords: transesterification; fatty acid methyl esters; refined palm oil, biodiesel

Introduction

The increasing economic potential of biodiesel had switched the role of coconut oil and palm oil commonly used for cooking in Asian countries like Malaysia, Indonesia, Thailand and Phillipines to be used as feedstock in biodiesel production [1]. Biodiesel is defined as the mono alkyl esters of long-chain fatty acids derived by transesterification of renewable feedstock, such as vegetable oil or animal fats, for use in compression-ignition engines [2]. Biodiesel, or fatty acid methyl esters (FAME), is an environmental friendly fuel that may be used in blends with conventional diesel or directly in diesel engines without any modification.

Transesterification is a process in which an ester is transformed into another by interchange of the alkoxy moieties. The transformation could essentially occur by mixing the two components, and may be accelerated by addition of an acidic or alkaline catalyst [3]. The alkaline transesterification of triglycerides, with methanol as reactant, is summarized in Fig. 1. In accordance to the reaction stoichiometry, one mole of triglyceride reacts with three moles of methanol (in the presence of NaOH as catalyst) to produce three moles of FAME and one mole of glycerol. However, as transesterification is reversible and proceeds towards an equilibrium, the glycerol produced may shift the reaction backwards and not in favor of the product, FAME. This would reduce the conversion yield [4].

In the present study, the possibility of reducing the inhibitory effect of glycerol on transesterification was studied by modifying several reaction conditions using the typical one-step [5] and two-step alkaline-catalytic processes [6].

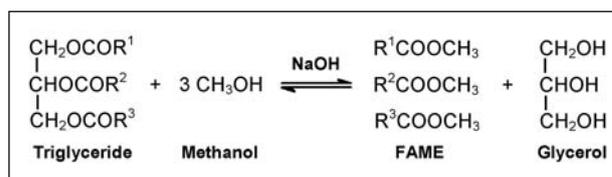


Figure 1: Alkaline-catalytic transesterification of triglyceride

Materials and Methods

Chemicals

All chemicals and reagents used were of analytical grade. The refined palm oil (RPO) used, described hereafter as triglyceride, was subjected to Sulfuric Acid-Methanol Method No. 2.4.1.1 JOCS, 1996, to convert it into its methyl esters before detection of the fatty acid composition by gas chromatography (GC) in accordance to the standard method No. 2.4.2.1 JOCS, 1996 [7] (Table 1). The amount of free fatty acids in the oil was kept at minimum level below 0.05%.

Transesterification

Experiments were performed based on modifications of the procedures described by Dmytryshyn *et al.* [8] and Lang *et al.* [9]. The transesterification experiments were performed in a 250 ml round bottom flask attached with a thermometer immersed in a water bath. The optimal conditions for the alkaline-catalytic transesterification was determined by using different ratios of methanol to

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Table 1: Fatty acid composition of RPO

Fatty acid	Composition	RPO# (%)
Myristic acid	14:0	1.0
Palmitic acid	16:0	31.5
Stearic acid	18:0	3.0
Arachidic acid	20:0	0.3
Behenic acid	22:0	0.1
Palmitoleic acid	16:1	-
Oleic acid	18:1	49.0
Linoleic acid	18:2	14.0
Linolenic acid	18:3	0.3
Ricinoleic acid	18:1-OH	0

#RPO: refined palm oil

triglyceride (0% to 200% excess from the stoichiometric value), different amounts of NaOH (catalyst) in methanol (0.5% to 3.0% (w/v), and observing the effect of mixing at different temperatures (room temperature to 70°C) and reaction time (0 to 70 min). Anhydrous methanol (99%) was used as the reactant. The product obtained after the reaction was then evaporated by rotary evaporator (Büchi Rotavapor R-200, Switzerland) at 70°C for 20 min. It was then separated by gravity settling where the top phase consisted of FAME while glycerol settled at the lower portion as a byproduct. FAME was then washed with water to neutralize the catalyst, and later purified by silica gel treatment and dehydrated through a column filled with anhydrous sodium sulphate.

Single-stage process

For the single-stage process, 88.7 ml of triglyceride was reacted with 11.3 ml of methanol (1:3 molar ratio of triglyceride to methanol) in accordance to the stoichiometry of its transesterification. The mixture (100 ml) was then reacted at different temperatures using different ratios of methanol to oil and different catalyst concentrations. Separation was done in a separatory funnel by gravity settling for 1 h followed by evaporation of methanol. In the single-stage process, the product was directly analyzed for conversion to FAME after the purification process.

Two-stage process

In the two-stage process, the optimal conditions obtained for the parameters affecting transesterification were applied in two cascade reactions. The experiment was held in a similar manner as described above but with the amount of methanol and catalyst being divided into 50% for each stage. The total amount of mixture in the reaction was 100 ml. A 1:6 molar ratio of triglyceride to methanol was used in order to utilize 100% stoichiometric excess of methanol (the optimum condition for methanol to oil ratio that was previously determined). The amount of NaOH used was 1.0% (w/v) in methanol.

In the first stage, 0.10 g of NaOH was added to 10.15 ml of anhydrous methanol and stirred until the catalyst

was completely dissolved. Triglyceride was placed in the reaction flask inside the water bath and sodium methoxide solution was added into the oil to start the reaction. The mixture was stirred at 210 rpm by a mounted stirrer at 60°C for 20 min and then poured into a separatory funnel.

After 1 h of separation, glycerol was removed from the separatory funnel as a dark brown coloured liquid from its bottom. Another 0.1 g NaOH was added to 10.15 ml of methanol, and stirred until the NaOH dissolved. This was then added to the top phase obtained from the first stage, and was again reacted for 20 min with consistent stirring. The mixture was later poured into a separatory funnel and allowed to separate. Once glycerol was removed by gravity settling, the methyl esters produced were purified as previously described before being analyzed for its FAME content.

Analysis of FAME

Percentage of conversion to FAME in all experiments was determined by using the gas chromatography mass spectrometry (GCMS; Shimadzu Co., Kyoto). Sample (2 µl) was injected into the capillary column CBPI-M25-05 with diameter of 0.25 mm and length of 25 m. Helium was used as the carrier gas. The column head pressure was regulated at 43.0 kPa, and the flow rate at 1 ml/min. Initial temperature was programmed at 60°C. The temperature was then increased to 230°C at 15°C/min. Injection of samples was performed at the set detector temperature of 230°C.

Chromatograms generated from mass spectra were compared to authentic peaks obtained from standard compounds from the National Biology Society (NBS) & National Institute of Standards and Technology (NIST) Mass Spectra Library, Japan.

Standard characterization of FAME for use as biodiesel

To characterize the physical and chemical properties FAME for use as biodiesel, the following five tests were performed: the Copper Strip Corrosion Test adapted from American Society for Testing and Materials (ASTM

D-130), kinematic viscosity test at 40°C (ASTM D-445), Acid Number Test (ASTM-664), a modified American Oil Chemist's Society (AOCS) version of Soap and Catalyst Test and Total Glycerol Content Test (ASTM D-6584).

Results and Discussion

Optimized conditions for alkaline-catalytic transesterification

According to Freedman *et al.*, the three most important parameters affecting triglyceride transesterification were the molar ratio of methanol to triglyceride, the nature and the amount of catalyst, and the reaction temperature [5]. However, Barnwal and Sharma also stated that the most important variables that influenced transesterification reaction were the reaction temperature, ratio of alcohol to oil, catalyst, the need of mechanical mixing and purity of the reactant [10]. In the present study involving the production of FAME for use as biodiesel via the alkaline-catalytic transesterification reaction, the optimum variables determined were the need of mixing, ratio of methanol to triglyceride, amount of catalyst used, reaction temperature and reaction time.

The need for mixing

Mixing is a physical operation which reduces non-uniformities in fluid by eliminating gradients of concentration and other properties. Mixing is accomplished by interchanging material between different locations to produce mingling of components. A system that is perfectly mixed display random homogenous distribution of system properties [11]. Due to the fact that palm oil was immiscible with sodium methoxide solution and by observing the physical appearance of the reaction mixture with and without mixing, it could be concluded that mixing was crucial in the alkaline transesterification reaction. Without mixing, the reaction mixture formed a two-phase liquid system which inhibited the transesterification reaction.

In the present study, mechanical mixing was performed by a 4 cm in diameter marine propeller-type impeller attached to a HEIDOLPH RZR 2020 mounted stirrer at 400 rpm to enhance mass transfer. A low stirring rate at 180 rpm resulted in incomplete reaction [12], while mixing at 400 rpm was reported to produce an optimum yield [13]. A flask with rounded edges base was used as the reaction vessel to discourage the formation of stagnant regions. In the alkaline transesterification, a high degree of conversion to FAME was achieved when the oil and reactant phases were well mixed and this could be done only with aided mixing.

Ratio of methanol to triglyceride

As transesterification is an equilibrium reaction, it requires a large excess of alcohol to drive the reaction so that it will favor the formation of products. By utilizing RPO as triglyceride, a molar ratio of 1:6 (triglyceride to

methanol) involving 100% excess of methanol from the stoichiometric balance showed the highest yield of FAME at 95.51% (Fig. 2). The reaction was incomplete for molar ratios of less than 1:6, yielding lower production of FAME. Increasing the molar ratio to 1:7.5 and 1:9 did not result in further increase in the yield of the methyl esters. In alkaline transesterification, the use of molar ratio of more than 1:6 resulted in higher production cost and may create complexity in the separation of glycerol [5]. However, this is also dependent on the type of oil used as a molar ratio of 1:9 was found to be optimal for the *Cynara cardunculus L.* oil [14].

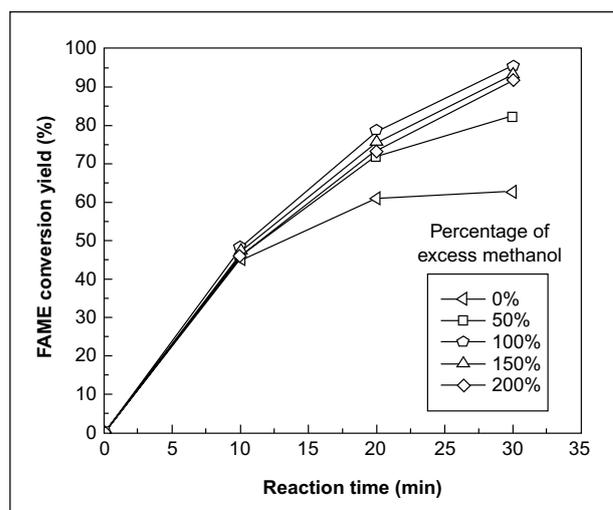


Figure 2: Yield of FAME with various percentage of excess methanol used.

Amount of catalyst

In the present study, a 1% NaOH in methanol (w/v) was found to yield the highest amount of FAME (Fig. 3). Further increase in the catalyst concentrations did not increase the production of FAME but resulted in difficulties to separate FAME that were formed from glycerol. The yield of methyl esters at higher amounts of catalyst, i.e., 2.0%, 2.5% and 3.0% (w/v) in methanol, was lower due to the formation of saponified products during the washing process.

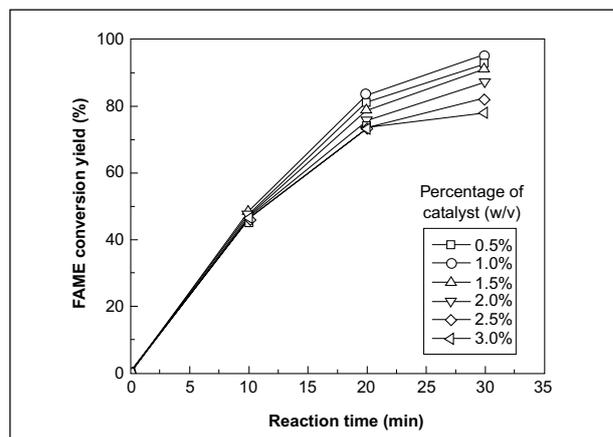


Figure 3: Yield of FAME in the presence of different percentage of NaOH (catalyst) in methanol (w/v).

Reaction time and temperature

The rate of conversion to FAME appeared to increase with reaction time in the first 30 min of the reaction (Fig. 4). The reaction was very slow during the first few minutes possibly due to the mixing and dispersion of methanol into triglycerides, which were just started. After 30 min, there was a slight decline in the percentage of FAME conversion yield. This was probably due to the formation of glycerol in the reaction mixture which slowly drove the backward equilibrium reaction, which is not a common characteristic of the dissolution and kinetics effects as described by Marchetti and Errazu [15]. For the reaction that was conducted at 70°C, the yield was low because methanol had started to evaporate, and thus, hamper progress of the reaction.

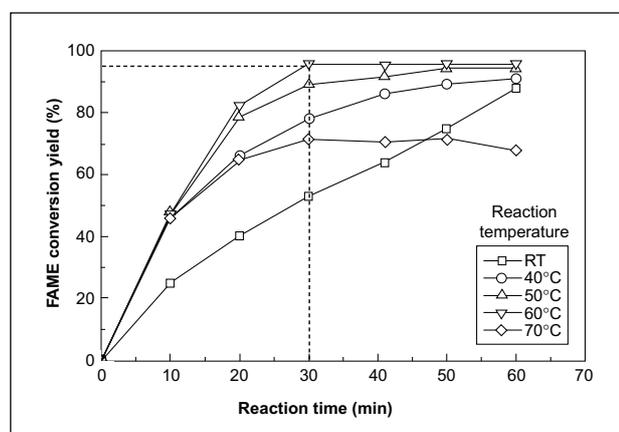


Figure 4: Yield of FAME at different reaction temperature and time.

The alkaline transesterification performed under the optimally derived conditions of 1:6 triglyceride to methanol ratio, 1% NaOH in methanol (w/v), at 60°C and 30 min of reaction time was enough to yield more than 95% of methyl esters (biodiesel). This optimum reaction time differed according to the type of oil used as longer reaction time was reported for peanut, cottonseed, sunflower and soybean oil but less reaction time was reported for beef tallow [5,16].

Single- and two-stage processes

Comparison between the yields of FAME conversion using the single- and two-stage processes was done by applying the above optimal conditions obtained. The two-stage process was initially assumed to be more efficient as glycerol produced in the first stage could be removed to prevent inhibition of the transesterification reaction; and the remaining tri-, di- and monoglycerides could further react to produce FAME in the second stage. In the present study, however, the single-stage process was found to produce 95.53% yield of FAME while the yield of FAME from the two-stage process was 90.13%. This was probably due to the nature of the two-stage process that only utilized half the amount of catalyst and methanol to triglyceride ratio in each stage. This ratio was not enough to push the equilibrium to favor the product formation. There were also extra transferring processes in the two-stage process which decreased the reaction efficiency. The types of FAME produced under the optimized conditions are listed in Table 2.

Table 2: Types of FAME produced under the optimized conditions

FAME*	Composition	% FAME* in RPO [#]
Methyl myristate	14:0	1.0
Methyl palmitate	16:0	30.4
Methyl stearate	18:0	2.6
Methyl oleate	18:1	48.3
Methyl linoleate	18:2	13.2
Methyl linolenate	18:3	0

*Fatty acid methyl esters [#]RPO: refined palm oil

Table 3: Properties of RPO FAME in accordance to the various standards for biodiesel as automotive fuel

Property	Unit	RPO FAME	EU	US	Japan
			(EN14214)	(ASTM)	(JASO M360)
Kinematic viscosity (40°C)	mm ² /s	3.52	3.50 ~ 5.00	1.9 ~ 6.0	3.50 ~ 5.00
Corrosion (Cu) 3h at 50°C	-	No. 1	No.1	No.3	No.1
Acid value	mg KOH/g	0.47	<0.50	<0.50	<0.50
Soap Amount	g Sodium oleate/g	1.95 x 10 ⁻²	-	-	-
Catalyst amount	g NaOH/g	4.56 x 10 ⁻³	-	-	-
Total glycerol content	wt%	0.22	<0.25	<0.24	<0.25

Characterization of FAME for use as biodiesel

In order to qualify as a diesel substitute for automotive fuel use, FAME had to display several key properties that met the specifications as stated in the biodiesel standard. The RPO FAME produced in this study showed good quality biodiesel fuel in compliance with the listed standards (Table 3). However, several other concerns are yet to be determined. From a practical point of view, fuel should have good fluidity at low temperature to survive winterization. Besides, the fuel should also be stable against oxidation during storage for the assurance of quality and prevention of denaturation. In order for the RPO FAME to be fully accepted for use as a high

quality biodiesel fuel, further standard analyses of the flash point, cold filter plugging point and cetane number need to be performed.

Conclusion

The results presented in the present study demonstrated that the single-stage process was more superior to the two-stage process for the production of FAME under optimally characterized conditions. In addition, the RPO FAME produced met the standards for use as biodiesel in five key properties tested.

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