ORIGINAL ARTICLE

Methyl ester production from high free fatty acid mixed crude palm oil

Gumpon Prateepchaikul[1], Michael L.Allen[2], Theerayut Leevijit[3] and Kittisak Thaveesinsopha[4]

Abstract

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Methyl ester production from high free fatty acid mixed crude palm oil
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Methyl esters were prepared from mixed crude palm oil containing a high free fatty acid content by using a two-stage process. Sulfuric acid was used as the catalyst in an esterification reaction which was then followed by a transesterification reaction using sodium hydroxide as the catalyst. The products of the reaction at various time intervals were sampled to determine the percentage of tri-,di-, and monoacyl glycerides, free fatty acid and methyl ester present. Analysis was performed by a thin layer chromatographic technique. A factorial experiment was carried out using 8, 10 and 12% by volume of methanol and 1, 3 and 5 % w/w of sulfuric acid in the acid catalyzed esterification process. Similarly, 16 , 20 and 24% v/v methanol and 2, 3 and 4 % w/w of sodium hydroxide were used in the alkaline catalyzed transesterification process. Results from the analyses showed that with 3 and 5 % w/w of sulfuric acid, the free fatty acid of the oil could be significantly decreased in less than one hour at 60°C. However, the amount of methanol used had a negligible effect on the reduction of the free fatty acid content. The subsequent transesterification process using sodium hydroxide as catalyst and 20 and 24 % v/v of methanol produced an ester having 99 % w/w methyl ester.

Key words : mixed crude palm oil, 2 stage process, esterification-transesterification process

[1]M.Eng.Sc. (Mechanical Engineering), Assoc Prof., [2]M.Eng. (Chemical Engineering), Prof., [3]M.Eng. (Mechanical Engineering), [4]Postgraduate Student in Mechanical Engineering, Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Thailand 90112.
Corresponding e-mail: gumpon.p@psu.ac.th

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บทคัดย่อ

กำพล ประทีปชัยกูร ไมเคิล แอล อัลเลน ธีระยุทธ หลีวิจิตร และ กิตติศักดิ์ ทวีสินโสภา

การผลิตเมทิลเอสเตอร์จากน้ำมันปาล์มดิบชนิดหีบรวมชนิดกรดไขมันอิสระสูง

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งานวิจัยนี้เป็นการศึกษากระบวนการผลิตเมทิลเอสเตอร์จากน้ำมันปาล์มดิบที่มีค่ากรดไขมันอิสระสูง ด้วยกระบวนการแบบสองขั้นตอน โดยใช้กรดซัลฟูริคเป็นตัวเร่งปฏิกิริยาในปฏิกิริยาเอสเตอร์ริฟิเคชันตามด้วยปฏิกิริยาทรานเอสเตอร์ริฟิเคชันซึ่งใช้โซเดียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยา ในระหว่างการทำปฏิกิริยาจะทำการดึงตัวอย่างของผลผลิตที่ระยะเวลาต่าง ๆ ออกมา เพื่อทำการตรวจวัดค่าร้อยละโดยมวลของ ไตร- ได- และโมโนอัลไคกลีเซอร์ไรด์ กรดไขมันอิสระ และเมทิลเอสเตอร์ที่อยู่ในผลผลิต การวิเคราะห์จะใช้เทคนิคโครมาโตกราฟฟิคแบบฟิล์มบาง ในการทดลองขั้นตอนเอสเตอร์ริฟิเคชันจะใช้ปริมาณเมทิลแอลกอฮอล์ที่อัตราส่วน 8, 10 และ 12% โดยปริมาตรส่วนกรดซัลฟูริคจะใช้อัตราส่วน 1, 3 และ 5% โดยน้ำหนัก ในขณะที่ขั้นตอนทรานเอสเตอร์ติฟิเคชันจะใช้ปริมาณเมทิลแอลกอฮอล์ที่อัตราส่วน 16, 20 และ 24% โดยปริมาตร และใช้โซเดียมไฮดรอกไซด์ 2, 3 และ 4% โดยน้ำหนัก ผลการวิเคราะห์พบว่าเมื่อใช้กรดซัลฟูริค 3 และ 5% โดยน้ำหนัก จะสามารถลดค่ากรดไขมันอิสระที่มีค่าสูงลงได้ในระยะเวลาน้อยกว่าหนึ่งชั่วโมงที่อุณหภูมิปฏิกิริยา 60°C อย่างไรก็ตามปริมาณเมทิลแอลกอฮอล์ไม่ได้มีผลที่เป็นนัยสำคัญมากในการลดปริมาณกรดไขมันอิสระที่มีอยู่ในน้ำมัน กระบวนการทรานเอสเตอร์ริฟิเคชันที่ใช้โซเดียมไฮดรอกไซด์เป็นสารเร่งปฏิกิริยา ซึ่งใช้ปริมาณเมทิลแอลกอฮอล์ 20 และ 24% จะสามารถทำให้เกิดเมทิลเอสเตอร์ที่มีความบริสุทธิ์ 99%

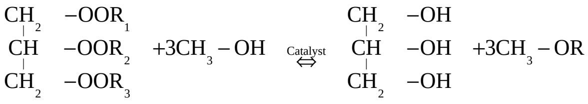
ภาควิชาวิศวกรรมเครื่องกล คณะวิศวกรรมศาสตร์ มหาวิทยาลัยสงขลานครินทร์ อำเภอหาดใหญ่ จังหวัดสงขลา 90112

The continued high demand for energy in the transportation and industrial sectors of the Thai economy means that the importation of crude petroleum oil and finished petroleum products requires the expenditure of valuable overseas exchange which could otherwise be used for the development and modernisation of equipment and infrastructure. Diesel fuel is essential for the transportation and industrial sectors of any modern economy. However, it is derived from a non-renewable, non-sustainable resource. It is therefore highly improbable that its price will be significantly reduced until an alternative energy source is found and utilised commercially. Biodiesel (methyl and ethyl esters of natural oils and fats) is a renewable diesel fuel that is produced from agricultural resources. It can be used to partially or totally replace petroleum-sourced diesel ("petro-diesel") without any engine modifications. In fact, its properties are so similar to conventional diesel that it can be blended in any proportion with "petro-diesel". Biodiesel obtained from energy crops, as well as being a sustainable product, produces beneficial effects on the environment. These include the reduction in acid rain and, indirectly, in the "greenhouse effect" of carbon dioxide caused by fossil fuel combustion.

Not surprisingly, biodiesel is receiving increased attention as an alternative, non-toxic, biodegradable and renewable diesel fuel. Just as with petro-diesel, the properties of biodiesel vary somewhat depending on the oil feedstock and on the alcohol used but, generally, the effects are minor. As a consequence, biodiesels derived from a wide variety of sources can be used as a direct substitute for petro-diesel fuels (Mittelbach *et al.*, 1992).

The chemistry of the reactions

Biodiesel is defined as a fatty acid methyl ester or ethyl ester obtained from vegetable oils or animal fats. Fatty acid methyl esters are conventionally produced by the transesterification of vegetable oils and fats using methanol in the presence of a suitable catalyst. Essentially, transesterification is the chemical reaction between triacyl glycerides and alcohol in the presence of a catalyst to produce mono-esters. Both the straight and branched chain triacyl glyceride molecules are transformed in this process to mono-esters and glycerol. The transesterification process actually consists of a sequence of three consecutive reversible reactions. That is, conversion of triacyl glycerides to diacyl glycerides, then the conversion of the diacyl glycerides to monoacyl glycerides. The monoacyl glycerides are finally converted into glycerol. Each step yields one molecule of the ester and its reaction is reversible. The overall reaction can be represented by the following scheme.



$$\begin{array}{ll} CH_2 & -OOR_1 \\ | & \\ CH & -OOR_2 \\ | & \\ CH_2 & -OOR_3 \end{array} + 3CH_3-OH \overset{\text{Catalyst}}{\Leftrightarrow} \begin{array}{ll} CH_2 & -OH \\ | & \\ CH & -OH \\ | & \\ CH_2 & -OH \end{array} + 3CH_3-OR$$

It can be seen that for each molecule of triacyl glyceride, three molecules of alcohol are required stoichiometrically. In practice, a higher molar ratio is used in order to get higher ester production from this reversible reaction. Transesterification reactions can be catalysed by both homogeneous and heterogeneous catalysts. The homogeneous catalysts include alkalis and acids. The most commonly used alkaline catalysts are the hydroxides and methoxides of sodium and potassium. Sulfuric acid, hydrochloric acid and para-toluene sulfonic acid are the preferred acid catalysts.

To achieve good conversion of vegetable oil to ester, the free fatty acid of the oil should not exceed 1 % w/w for the alkaline-catalyzed transesterification reaction (Canakci and Van Gerpen, 2001). (This corresponds to an acid value of 2 mg KOH/g). Danako and Cheryan (2000a) transesterified refined palm oil and found that by using 1% of potassium hydroxide as the catalyst and a reaction temperature of 50°C with the molar ratio of alcohol to oil 6:1, the reaction was very fast and it reached equilibrium within 60 minutes. The same results were obtained by Danako and Cheryan (2000b) when using a continuous process to produce methyl ester from refined palm oil.

Noureddini and Zhu (1997) studied the transesterification process of soy bean oil by using ethyl alcohol. They found that the degree of mixing between the alcohol and the triglyceride was the major constraint in the transesterification process. Boocock *et al.* (1996) added 1.25 unit volume of tetrahydrofuran per unit volume of methanol in the mixture and found that the mixture quickly became homogeneous. Antolin *et al.* (2002) studied the effect of the amount of catalyst, the amount of alcohol, and temperature on the purity of ester obtained from the transesterification of sunflower oil in a batch stirred tank reactor. They found that when 3 times the stoichiometric amount of ethyl alcohol and 0.28% by weight of KOH were used with a reaction temperature of 60°C, ester could be obtained at a purity of 96% w/w.

For oil with high free fatty acid content, methyl or ethyl esters cannot be economically produced with an alkaline catalysed transesterification process. This is because fatty acids react with alkalis to produce soap. Not only does this process deplete the catalyst, it also makes subsequent separation and washing difficult. Acid catalysis can be used with this kind of oil but requires a very high molar ratio of alcohol to oil to produce the maximum yield of ester. Crabbe *et al.* (2001) found that by using 3% of sulfuric acid and 23:1 molar ratio of methanol to crude palm oil, 78 % w/w methyl ester could be produced. But to complete the reaction a molar ratio of 35:1 - 45:1 was required.

Canakci and Van Gerpen (1999) studied the acid catalysed transesterification of soy bean oil containing high levels of free fatty acid. One, 3 and 5% by weight of sulfuric acid were used in the study with a molar ratio of methanol to oil set at 3.3:1, 3.9:1, 6:1, 20:1 and 30:1 and with reaction temperatures of 25°C, 45°C, and 60°C. They found that when the reaction temperature was controlled at 60°C and with a 6:1 molar ratio of methanol to oil, the required reaction time was 48 hours. And when the amounts of catalyst were varied from 1% to 5%, the ester formation increased from 72.7% to 95 % w/w.

Ramadhas *et al.* (2005) studied the production of biodiesel from high FFA rubber-seed oil by a two-step esterification (acid-alkaline catalysis) process. Their objective was primarily to reduce the free fatty acid content in the first reaction to a level that did not interfere with the alkali-catalysed second reaction. They found that for the esterification process, with the molar ratio of methanol to oil at 6:1 and with 0.5 % v/v of sulfuric acid, the maximum conversion efficiency was achieved. In a subsequent transesterification reaction, the maximum ester yield could be achieved with 9:1 molar ratio of methanol to oil and 0.5% w/w of NaOH.

Raw material constraints

Palm oil, like other edible oils, is an organic compound which is called a glyceryl ester because each molecule is comprised of a glycerol molecule bonded to a maximum of three fatty acid (carboxylic acid) residues. Each of the three fatty acid groups in palm oil are long chains comprising several carbon atoms (normally 11-19 atoms in length).

In the production of palm-oil, there are two crude oil products extracted: one is crude oil from palm fruit fibre and the other is oil from palm fruit kernel. Free fatty acids from these two kinds of oil are normally controlled at 5 % w/w but for small palm oil extracting industries, palm oil from the whole fruit is extracted (kernel and fibre). Because palm fruit in this process has to be toasted before extraction takes place, the free fatty acid of the oil produced is usually quite high (typically greater than 10 %w/w).

It is difficult to utilise this kind of crude palm oil (which may be called mixed crude palm oil [MCPO]) for making biodiesel by the alkaline transesterification process because the free fatty acid content is too high. In countries where there are large numbers of small scale oil palm plantations, especially where commercial fuel (petroleum products) is imported, it is essential that farmers should be able to produce their own energy from their own product. For economic reasons, they would prefer to extract palm oil for themselves using the processes generally used in small oil-producing industries. As a consequence, the oil produced by farmers always contains high levels of free fatty acid. There are other potential sources of biodiesel that contain high concentrations of free fatty acids which make them unsuitable for a one-stage transesterification process. These sources include badly stored vegetable oils and waste cooking oils. It follows that there is a need for a simple process for the production of biodiesel from high free fatty acid mixed crude palm oil by a two-stage esterification-transesterification process. The subject of this paper is the use of an esterification process to reduce the free fatty acid content to a level where subsequent transesterificaton will be successful. In conjunction with this process development, the properties of the biodiesel produced have also been investigated.

Materials and Methods

Materials

High free fatty acid degummed mixed crude palm oil from small scale palm oil extracting industry was used as raw material. Commercial grades of sulfuric acid, sodium hydroxide and methanol were used in this study. Thin layer chromatograph, TLC: IATROSCAN MK-65, Mishubishi Kagahu Iatron Inc, Japan, was used for analysing the purity of methyl ester from the experiment. Six standard samples: Tripalmitin, Palmitic acid and Methyl Palmitate (obtained from Nacala Tesque, Inc, Kyoto, Japan,); 1,3, - Distearin, DL, Palmitin (mono palmitin) (obtained from Sigma Aldrich Co, USA) and 1,2- Distearin 99%, (from Research Plus, Inc, USA) were used to calibrate the instrument.

Methods

A laboratory scale reactor consisting of a 2000 mL glass flask was used. The flask was heated in a temperature-controlled hot water bath in which the temperature of the water and the oil were constantly controlled at 60°C. The oil in the flask was agitated with a stirrer coupled to an electric motor. The speed of the stirrer was kept constant at 140 rpm.

Acid esterification: 500 mL. of degummed mixed crude palm oil was put in the flash and heated in the hot water bath to 60°C while the stirrer was operating. One, 3 and 5 % w/w of oil of sulfuric acid and 8, 10 and 12 % v/v of methanol were used in the acid esterification process. Methanol was mixed into the oil before the sulfuric acid was added. The reaction time was kept at 90 minutes for all the experiments. After 45 minutes of reaction, the first sample was extracted and washed immediately with water: successive samples were taken every 15 minutes. The stirrer was stopped when the reaction time was reached. The water-bath heater was turned off and the reaction products were left in the flask for 8 hours during which time the flask and its contents cooled to the ambient temperature (approximately 30°C).

Alkaline transesterification: The products from the esterification were stirred and heated to 60°C. 2 % w/w (by weight of oil) of sodium hydroxide was dissolved with 16, 20 and 24 % v/v (of the original oil) of methanol. The sodium hydroxide solution (sodium methoxide/methanol) was added to the heated oil and the reaction was continued for 90 minutes. The first sample was extracted after 45 minutes and then, thereafter, at 15 minute intervals. (Note that no attempt was made to separate the small amount of water that formed in the esterification reaction or the sulphuric acid that it contained)

Analysis: The washed samples were analysed by thin layer chromatograph/flame ionization detector (TLC/FID) (Mishubishi Kagahu Iatron Inc., Japan) with "Chromarod SIII" quartz rods. One to 3 µL of hexane (as extracting solvent) was applied to the rods, followed by development in hexane/diethyl ether/formic acid (50:20:0.3 v/v/v) for 80 mm and hexane/benzene (1:1 v/v) for 100 mm. The rods were dried and scanned under the following conditions: hydrogen flame rate 160 mL/min, air flow rate 2 L/min, speed 30 sec/scan. The methyl esters (ME), triacyl glycerides (TG), diacyl glycerides (DG) and monoacyl glycerides (MG) were effectively separated by this method. Peak areas were calculated with a "Chromstar" chromatography data analysis system. The results were expressed as weight percentages (w/w) of

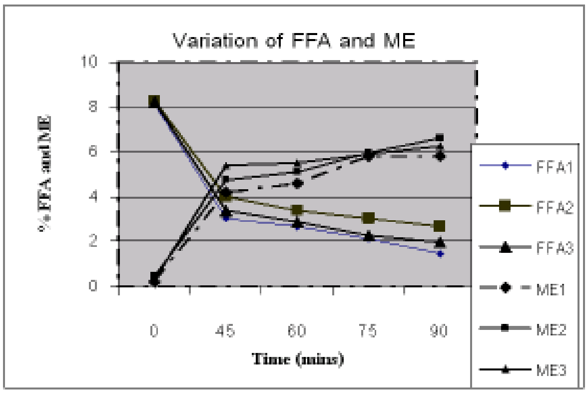


Figure 1. Variation of free fatty acid and methyl ester during acid esterification process by using 1% by weight of sulfuric acid and 8, 10 and 12% by volume of methanol. (FFA1, FFA2, FFA3, ME1, ME2, ME3 stand for free fatty acid and methyl ester variation using 8, 10 and 12 % v/v respectively)

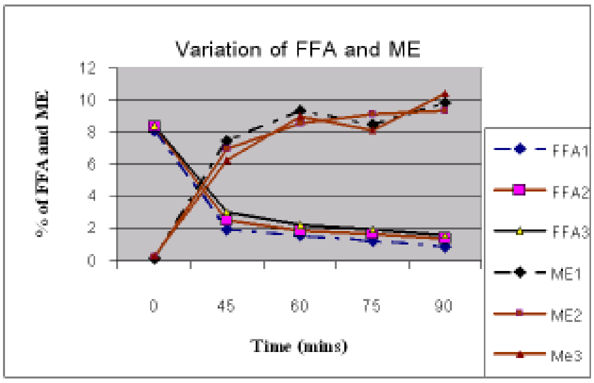


Figure 2. Variation of free fatty acid and methyl ester during acid esterification process by using 3% by weight of sulfuric acid and 8, 10 and 12% by volume of methanol. (FFA1, FFA2, FFA3, ME1, ME2, ME3 stand for free fatty acid and methyl ester variation using 8, 10 and 12 % v/v respectively)

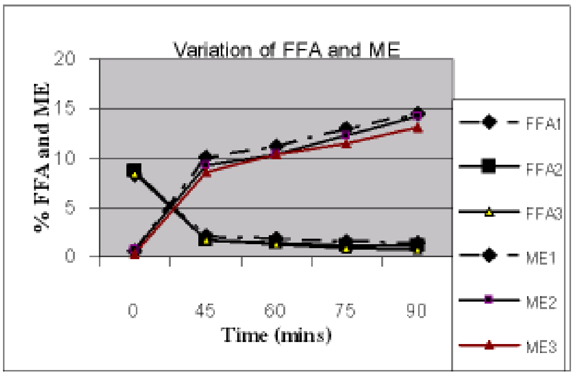


Figure 3. **Variation of free fatty acid and methyl ester during acid esterification process by using 5% by weight of sulfuric acid and 8, 10 and 12% by volume of methanol. (FFA1, FFA2, FFA3, ME1, ME2, ME3 stand for free fatty acid and methyl ester variation using 8, 10 and 12 % v/v respectively)**

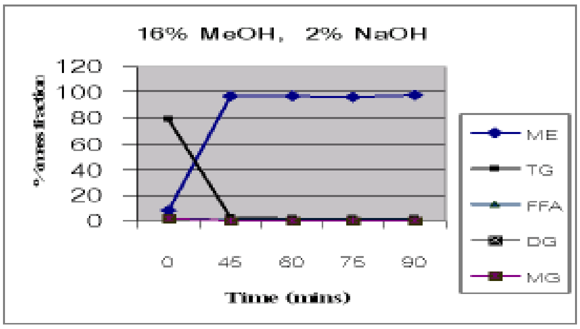


Figure 4. **Changes of the component s of oil from time zero to 90 minutes using 1% by weight of sulfuric acid and 8% by volume methanol in acid esterification and 16% MeOH by volume 2% NaOH by weight in alkaline transesterification process.**

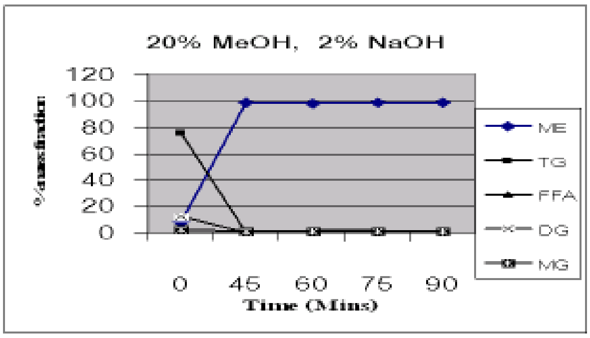


Figure 5. **Changes of the component s of oil from time zero to 90 minutes using 1% by weight of sulfuric acid and 10% by volume methanol in acid esterification and 20% MeOH by volume 2% NaOH by weight in alkaline transesterification process.**

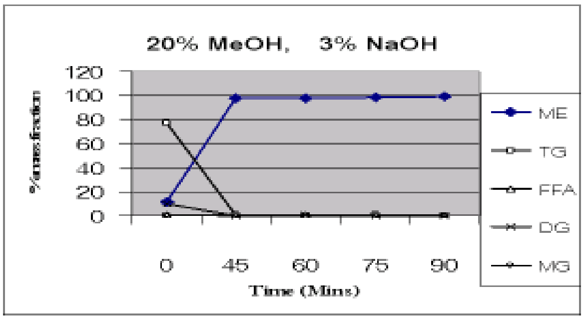


Figure 6. **Changes of the component s of oil from time zero to 90 minutes using 1% by weight of sulfuric acid and 10% by volume methanol in acid esterification and 20% MeOH by volume 3% NaOH by weight in alkaline transesterification process.**

the reaction product on a water- and glycerol-free basis.

Results and Discussion

Acid Esterification

Figures 1-3 show the changing of mass fraction of free fatty acid and methyl ester during acid esterification process by using 1, 3 and 5% by weight of sulfuric acid and 8, 10 and 12% by volume of methanol. Triglyceride slightly dropped and diglyceride slightly increased while monoglyceride was almost constant for 1 % w/w sulphuric acid. For 3 and 5 %w/w of sulphuric acid, triglyceride and diglyceride were significantly changed. This is because strong acid catalyst caused the conversion of some triglyceride to diglyceride and methyl ester. It can also be seen that in all

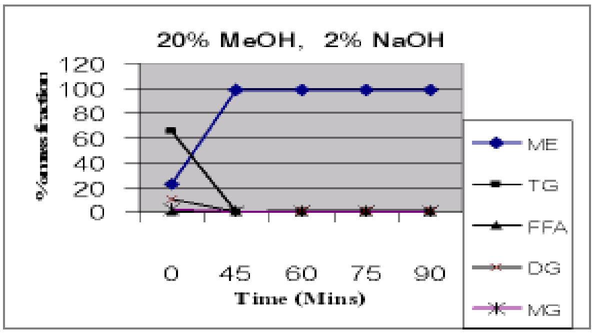


Figure 7. **Changes of the component s of oil from time zero to 90 minutes using 3% by weight of sulfuric acid and 10% by volume methanol in acid esterification and 20% MeOH by volume 2% NaOH by weight in alkaline transesterification process.**

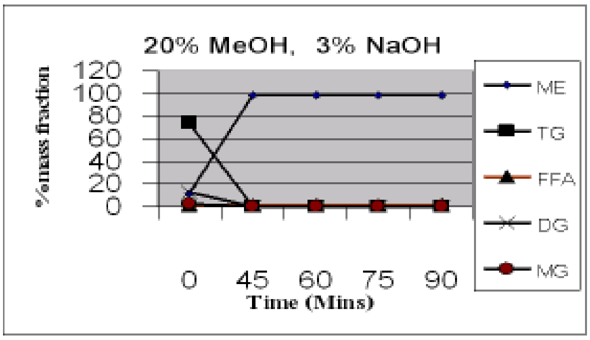


Figure 8. **Changes of the component s of oil from time zero to 90 minutes using 3% by weight of sulfuric acid and 10% by volume methanol in acid esterification and 20% MeOH by volume 3% NaOH by weight in alkaline transesterification process.**

cases, the free fatty acid content (FFA) dropped with respect to time while the mass fraction of ester (ME) increased. As shown in Figures 1-3, for the same amount of sulfuric acid used, the free fatty acid content was not apparently related to the amount of methanol added. This implies that 8 % v/v of methanol provided sufficient excess methanol for the free fatty acid present.

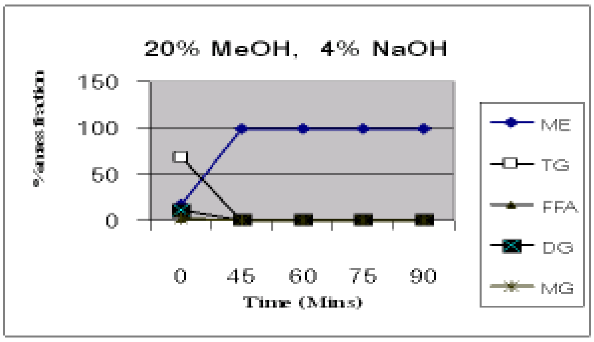


Figure 9. **Changes of the component s of oil from time zero to 90 minutes using 3% by weight of sulfuric acid and 10% by volume methanol in acid esterification and 20% MeOH by volume 4% NaOH by weight in alkaline transesterification process.**

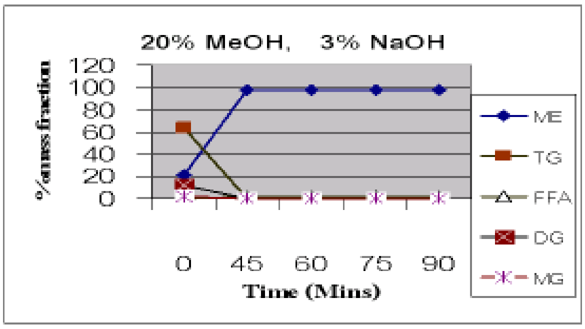


Figure 10. **Changes of the component s of oil from time zero to 90 minutes using 5% by weight of sulfuric acid and 10% by volume methanol in acid esterification and 20% MeOH by volume 3% NaOH by weight in alkaline transesterification process.**

Alkaline Transesterification

After 90 minutes of stirring in acid esterification process, the mixture was left to cool to the ambient temperature over a period of 8 hours. Most of the water that was formed in the reaction had dropped to the bottom of the glass flask but it was not removed before the subsequent transesterification. Thus the total product was stirred

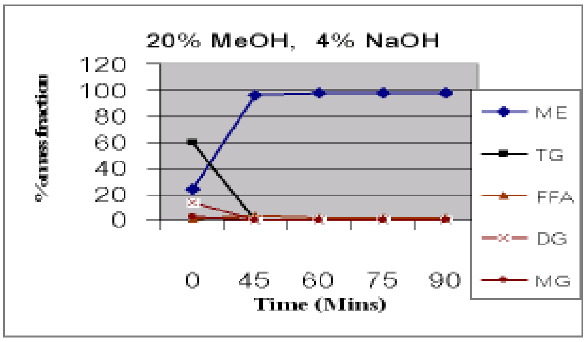


Figure 11. **Changes of the component s of oil from time zero to 90 minutes using 5% by weight of sulfuric acid and 10% by volume methanol in acid esterification and 20% MeOH by volume 4% NaOH by weight in alkaline transesterification process.**

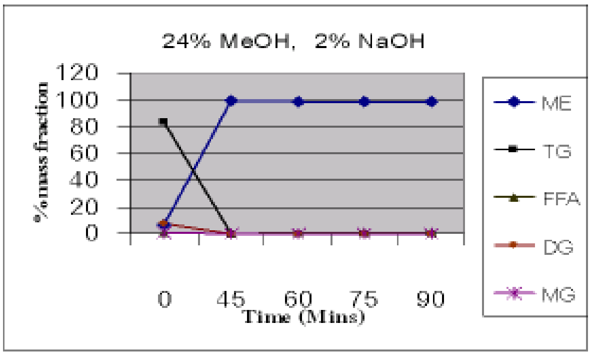


Figure 12. **Changes of the component s of oil from time zero to 90 minutes using 1% by weight of sulfuric acid and 12% by volume methanol in acid esterification and 24% MeOH by volume 2% NaOH by weight in alkaline transesterification process.**

and heated to 60°C before the methanol/methoxide solution was added. 16%, 20% and 24% methanol was used as a volume percentage of the original oil used. In this methanol 2%, 3% and 4% w/w of sodium hydroxide was dissolved to form the methoxide. Samples at various time intervals were extracted and analysed for percentage of mass fraction of ester, fatty acid, and the acyl glycerides.

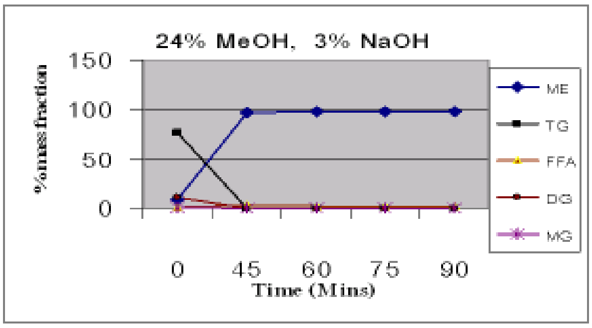


Figure 13. **Changes of the component s of oil from time zero to 90 minutes using 1% by weight of sulfuric acid and 12% by volume methanol in acid esterification and 24% MeOH by volume 3% NaOH by weight in alkaline transesterification process.**

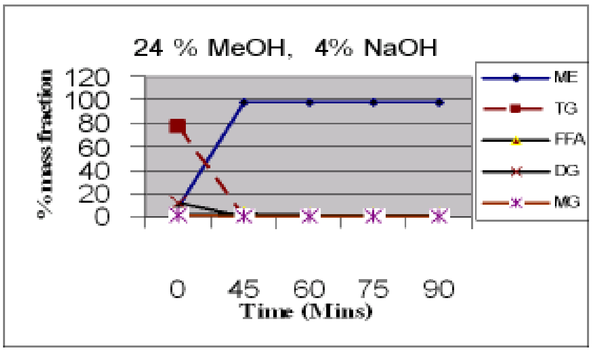


Figure 14. **Changes of the component s of oil from time zero to 90 minutes using 1% by weight of sulfuric acid and 12% by volume methanol in acid esterification and 24% MeOH by volume 4% NaOH by weight in alkaline transesterification process.**

Some results of the processes are shown in Figure 4 to Figure 18. Triglyceride was converted to methylester at the first 45 minutes and equilibrium condition was achieved in the next 45 minutes. Fixing 1% sulfuric acid and 2% sodium hydroxide constant in the reaction while varying the amount of methanol by 24%, 30% and 36% made the purity of methyl ester higher from 97.5% to 98.6%

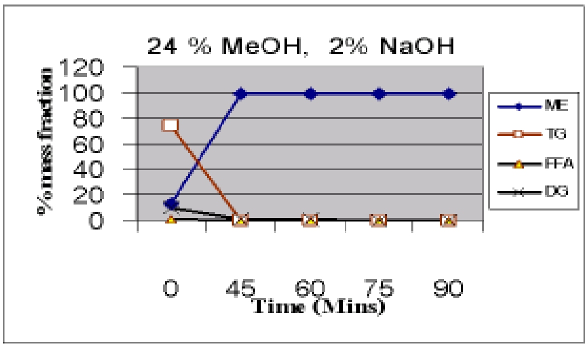


Figure 15. **Changes of the component s of oil from time zero to 90 minutes using 3% by weight of sulfuric acid and 12% by volume methanol in acid esterification and 24% MeOH by volume 2% NaOH by weight in alkaline transesterification process.**

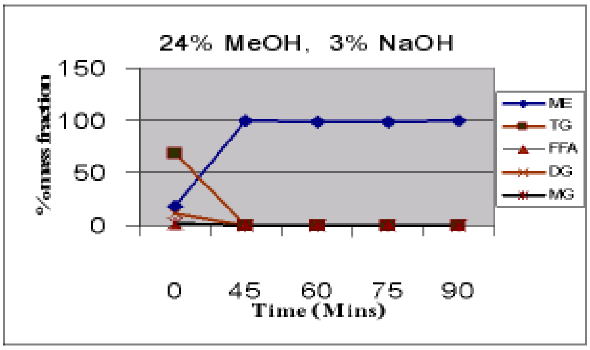


Figure 16. **Changes of the component s of oil from time zero to 90 minutes using 3% by weight of sulfuric acid and 12% by volume methanol in acid esterification and 24% MeOH by volume 3% NaOH by weight in alkaline transesterification process.**

and 99.12% respectively as seen from Figures 4, 5 and 12. Increasing the sodium hydroxide concentration in the transesterification process from 2%, 3% and 4% by weight tended to decrease the conversion of the methyl ester as the viscosity increased and gel formed.

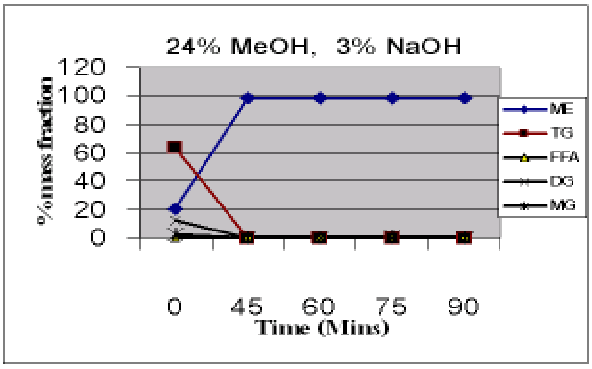


Figure 17. **Changes of the component s of oil from time zero to 90 minutes using 5% by weight of sulfuric acid and 12% by volume methanol in acid esterification and 24% MeOH by volume 3% NaOH by weight in alkaline transesterification process.**

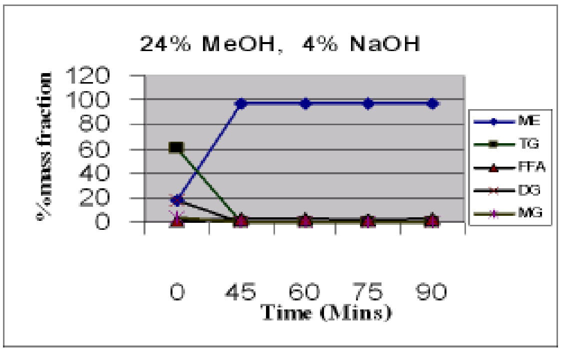


Figure 18. **Changes of the component s of oil from time zero to 90 minutes using 5% by weight of sulfuric acid and 12% by volume methanol in acid esterification and 24% MeOH by volume 4% NaOH by weight in alkaline transesterification process.**

Discussion

The objective of the experiment was to provide a simple technique for making biodiesel from mixed crude palm oils. In particular, the elimination of the titration method to estimate the

Table 1. Properties of methyl esters of mixed crude palm oil in comparison with other ester and biodiesel standard

Property	Test method	Mixed crude palm oil methyl ester	Biodiesel standard					Diesel standard
			Austria	Germany	Italy	Frence	Thailand	
Cetane number	ASTM D613	na	≥ 48	≥ 49	-	-	≥ 51	≥ 47
Distillation 90% recovery (°C)	ASTM D86	331.6	-	-	-	-	-	≤ 357
Specific gravity at 15.6°C	ASTM D4052	na	0.87-0.89	0.875-0.90	0.86-0.90	-	0.86-0.90	0.81-0.87
Heating value (J/g)	ASTM D240	39810	-	-	-	-	-	-
Flash point (°C)	ASTM D93	162	≥ 100	≥ 100	≥ 100	-	≥ 120	≥ 52
Viscosity at 40°C (cSt)	ASTM D445	3.21	6.5-8.0[8]	3.5-5.0	3.5-5.0	-	3.5-5.0	1.8-4.1
Water and sediment (%wt)	ASTM D2709	0.03	-	≤ 0.03	≤ 0.07	≤ 0.02	≤ 0.05	≤ 0.05
Copper-strip corrosion	ASTM D130	na	-	1	-	-	≤ 1	≤ 1
Pour point (°C)	ASTM D97	9	-	-	-	-	-	≤ 10
Cloud point (°C)	ASTM D2500	12	-	-	-	-	-	-
Carbon residue (%wt)	ASTM D4530	0.2	-	≤ 0.30	≤ 0.50	-	≤ 0.30	≤ 0.05
Ash (%wt)	ASTM D482	0.02	-	≤ 0.01	-	-	≤ 0.02	≤ 0.01
Sulphur (% wt)	ASTM D4294	na	≤ 0.02	≤ 0.01	≤ 0.01	-	≤ 0.001	≤ 0.035

amount of sodium hydroxide was considered most desirable. However, because the total reaction products from the esterification are used in the transesterification, it was known that some of the sodium hydroxide would be neutralised by the sulfuric acid present. Thus 80 g of sodium hydroxide will be neutralised by 98 g of sulfuric acid. For this reason, there must always be a higher weight percentage of sodium hydroxide added for transesterification than the weight percentage of sulfuric acid added for esterification. As a consequence, no reliable results from transesterification were produced when 5 % w/w sulfuric acid had been used.

Triglyceride was converted to methylester at the first 45 minutes and equilibrium condition was achieved in the next 45 minutes. Fixing 1% sulfuric acid and 2% sodium hydroxide constant in the reaction while varying the amount of methanol by 24%, 30% and 36% made the purity of methyl ester higher from 97.5% to 98.6% and 99.12% respectively as seen from Figures 4, 5 and 12. Increasing the sodium hydroxide concentration in the transesterification process from 2%, 3% and 4% by weight tended to decrease the conversion of the methyl ester as the viscosity increased and gel formed.

Properties of Mixed Crude Palm Oil Methyl Ester

Table 1 shows the properties of methyl ester from mixed crude palm oil produced from the experiment in comparison with diesel and other biodiesel standards. Due to the high expense of the analysis, only some properties were analysed. It can be seen that all of the fuel properties of mixed crude palm oil methyl ester that was produced from the experiment are comparable to those other biodiesel standards and diesel.

Conclusion

The objective of this project was to investigate the acid-alkaline catalyzed methyl ester production process from mixed crude palm oil which is the palm oil produced from small scale palm oil industries or the farmer community and normally the free fatty acid of the oil is high due to the oil extracting process. The variables affecting the ester formation including the amount of methanol, amount of both acid and alkaline catalysts and reaction time were investigated to determine the best purity of methyl ester produced. Thin layer liquid chromatograph was used to determine the purity of the ester. Some properties of ester produced were measured. It can be seen that fixing the acid catalyst at 1% by weight and 2% of sodium hydroxide while varying the amount of methanol at 24%, 30% and 36 % by volume can achieve the purity of methyl ester at 97.5%, 98.6% and 99.12%. It can also be seen that the free fatty acid of the oil can be decreased below 2% within 90 minutes by using the acid catalyst in the first stage. According to result of the methyl ester properties that had been analysed, all of them passed the Thai biodiesel standard for fatty acid methyl ester. Due to the expense of the analysis, only some properties were analysed. However the optimal condition for producing methyl ester from high free fatty acid mixed crude palm oil is 1 % w/w sulfuric acid and 8 % methanol for the first stage and 2 % w/w sodium hydroxide and 16 % methanol for the second stage in which 97.5 % purity of methyl ester can be achieved.

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