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TRANSESTERIFICATION OF PALM OIL: EFFECT OF REACTION PARAMETERS

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ABSTRACT

*The most practical and suitable method for industrial production of methyl esters of palm oils with negligible free fatty acids (*e.g.* neutralized palm oil and refined, bleached and deodorized palm oil) is methanolysis of the glycerides catalyzed by sodium hydroxide. Several parts including the type of catalyst, oil/alcohol ratio, temperature, stirring speed and free fatty acids content, have been found to influence the transesterification of palm oil. Optimum reaction conditions were obtained with a molar ratio of methanol-to-oil at 10:1 and a reaction time of 7 min at ca. 65½C. The rate of reaction was optimized at a stirring speed of 150 rpm. The minimum amount of methanol required to achieve total conversion was 233% (excess methanol) (a methanol-to-oil molar ratio of 10:1). The catalyst used should not exceed 0.5 mole kg^{-1} oil as otherwise it would cause solidification of the reaction mixture due to soap formation. For a large number of glyceride oils containing <5% free fatty acids, transesterification to methyl esters can be readily effected using additional sodium hydroxide to neutralize the free fatty acids. Glycerol from the transesterification process was purified from 80%-85% to more than 96% with a yield of not less than 75%.*

Keywords: Transesterification, sodium hydroxide, alkaline catalyst, palm oil, methyl esters.

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INTRODUCTION

Transesterification is a general term used to indicate the direct conversion of triacylglycerols lipids by alcohols to alkyl esters without first isolating the free fatty acids (FFA). More specifically in alcoholysis, the triacylglycerols in a fat or oil are reacted with excess alcohol in the presence of a catalyst.

The catalyst may be acidic (*e.g.* sulphuric acid, hydrogen chloride, boron trifluoride, *etc.*) or alkaline (*e.g.* metal alkoxide, alkaline hydroxide, *etc.*), with the alkaline catalysts giving faster reactions. The well-known mechanisms of acid and alkaline alcoholysis are depicted in *Figure 1*.

All the steps in the transesterification process are reversible but the equilibrium can be shifted with excess alcohol so that transesterification proceeds practically to completion. In acid catalyzed transesterification, fatty acids can be formed by the reaction of carbocation II with the water in the reaction mixture. Thus, the preferred conditions for acid catalyzed esterification of triacylglycerols are, therefore, a large excess of an appropriate alcohol and the absence of water.

Methyl esters can be prepared either by esterification of fatty acids or transesterification of fat triglycerides. The predominant process for the manufacture of methyl esters is transesterification of fat and oils with methanol. The ester interchange, *i.e.* replacement of the alcohol component glyceride by methanol, takes place quite easily at a low temperature of 50½C–70½C and atmospheric pressure with excess methanol and an alkaline catalyst (Freedman *et al.*, 1984; Choo *et al.*, 1990; Goh and Choo, 1992).

The alkaline catalyst, sodium hydroxide (NaOH), was used in the methanolysis of palm oil (Ohi *et al.*, 1983). Equal weights of oil and 1 wt% NaOH in methanol were refluxed for 1 hr, with occasional swirling of the reaction mixture while heating. Another method described also involved the use of equal weights of oil and 1 wt% NaOH in methanol solutions but with the reactant mixture shaken for 2 hr at room temperature.

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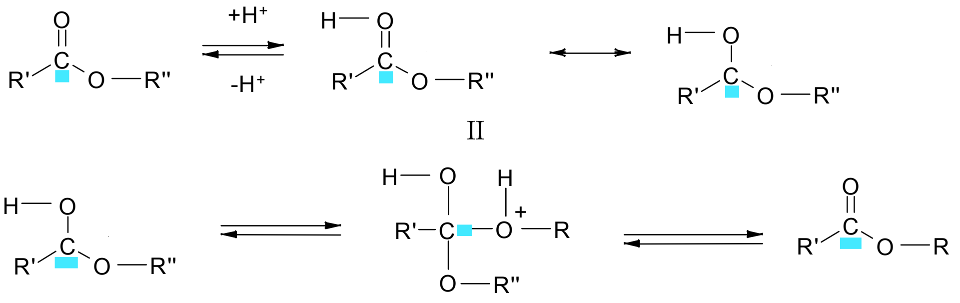
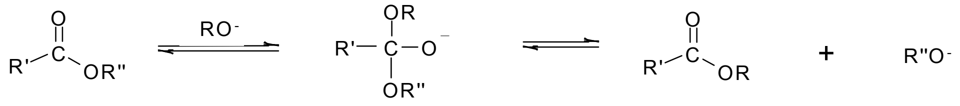


Scheme 1. Mechanism of acid alcoholysis.



Scheme 2. Mechanism of alkali alcoholysis.

Figure 1.

The reaction variables affecting the transesterification need to be investigated to obtain the optimum conditions with the objective of designing a continuous pilot plant for producing methyl esters. In the present study, parameters such as the type of catalyst, oil/alcohol ratio, temperature, stirring speed and FFA content were investigated.

MATERIALS AND METHODS

Materials

All palm oil and palm oil products (crude or refined) used were analysed for their acidity (*i.e.* percent FFA) before reaction. The catalysts used were freshly prepared before the reactions. Alcohols used were either A.R. or anhydrous grade. Petroleum spirit (b.p. 60½C-80½C) and chloroform were redistilled and dried over anhydrous sodium sulphate (Na_2SO_4). Catalysts were commercially available reagent grades. The high perfomance liquid chromatography (HPLC) solvents were all HPLC grade.

Methods

Effect of catalysts and acidity (FFA). The transesterification was conducted in a two-necked 500 ml flask with a reflux condenser and a magnetic stirrer. Typically, 200 g oil were used with molar ratio of methanol-to-oil of 15.6:1. The reaction mixture was stirred and heated to reflux, and samples (0.05 – 0.1 ml) withdrawn at 1, 2, 4, 8, 16, 32, 64 and 90 min after adding the catalyst and thereafter at every 30 min. Sulphuric acid was used to neutralize the base catalyst.

After the reaction was completed, the ester layer was separated from the glycerol layer and washed with distilled water until the washings were neutral. The glycerol layer was extracted three times with petroleum ether (60½C–80½C) and, subsequently, the extract washed with H_2O. Petroleum ether was then removed by a rotary evaporator. The combined ester products were dried over anhydrous Na_2SO_4 overnight, filtered and the residual Na_2SO_4 rinsed with petroleum ether. Removal of the solvents under reduced pressure gave the product.

Effect of stirring speed, concentration of catalyst, temperature and excess methanol on product formation. The transesterification was conducted in a 1-litre glass bottle (6.5 cm diameter and 17.5 cm height) without a condenser. Instead, two holes were drilled through the cover for insertion of a mechanical stirrer and thermometer. The desired temperature was maintained using a water bath. Experiments were carried out with different stirring speeds, varying ratios of methanol-to-oil and at different temperatures.

The effect of stirring speed on the rate of transesterification of palm oil was studied using a molar ratio of methanol-to-refined, bleached and deodorized (RBD) palm oil of 15.6:1 at a temperature of 60 ± 3½C, catalyzed by NaOH (0.75 wt% based on the oil used).

The effect of concentration of catalyst (NaOH) on the transesterification of palm oil was studied using a molar ratio of methanol-to-RBD palm oil of 15.6:1 at a temperature of 60 ± 3½C and a stirring speed of 600 rpm.

The effect of excess methanol on product formation of transesterification of palm oil was studied using NaOH as catalyst (0.75 wt% based on the oil used) at a temperature of 60 ± 3½C and a stirring rate of 350 rpm.

The effect of temperature on transesterification of palm oil was studied using a molar ratio of methanol-to-RBD palm oil of 15.6:1, catalyzed by NaOH (0.75 wt% based on the oil used) and a stirring speed of 600 rpm.

Effect of water in transesterification of palm oil. Transesterification was carried out on RBD palm oil (200 g) with methanol (95 ml) catalyzed by NaOH (0.75 wt% based on the oil used) at 60 ± 3½C with a stirring speed of 350 rpm to study the effect of water content.

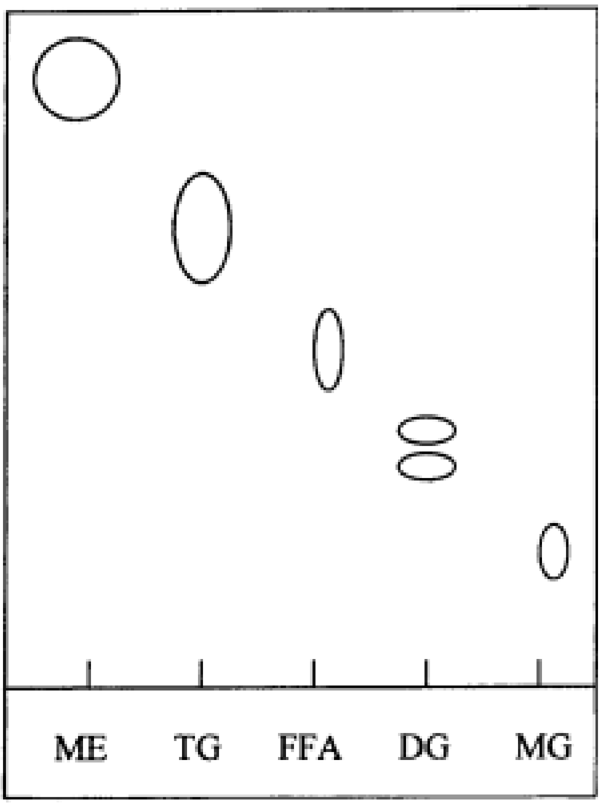
Transesterification of neutralized palm oil. Experiments were carried out using palm oil (200 g), methanol (150 ml) and NaOH as catalyst. The oil used varied from RBD palm oil to crude palm oil (CPO) with 17% and 3.9% FFA. The oil was first neutralized with an appropriate quantity of NaOH. A study was carried out to determine the effect of different quantities of catalyst on the rate of transesterification, which was measured in terms of the time required for the disappearance of triacylglycerols as determined by TLC.

Further, the yield of esters was determined quantitatively as follows. The ester layer was separated from the glycerol layer and washed with distilled water till the washing was neutral. Ester A was obtained. The glycerol layer was extracted three times with petroleum ether, b.p. 60½C–80½C, the extracted petroleum ether was washed with water and petroleum ether removed under rotary evaporation. Ester B was obtained. Esters A and B were combined and dried over anhydrous Na_2SO_4 overnight and filtered. The residue after filtration was rinsed with petroleum ether to obtain the residual ester.

Qualitative and Quantitative Analysis

Thin layer chromatography (TLC) on silica gel 60 glass plates was used to monitor the progress of the reactions. The solvent used for developing the plate was n-hexane/diethyl ether/acetic acid, 7:3:1 (v/v/v) and the spray for staining 2, 7 – dichlorofluorinescein or 50% sulphuric acid. For all reactions, 0.5 ml aliquots of the reaction mixture were withdrawn at timed intervals and quenched with dilute sulphuric acid (0.5 ml, 5 N) to neutralize the alkaline catalyst used. The reactants/products were extracted by petroleum spirit for TLC analysis. Completion of the reaction was judged by disappearance of the triacylglycerols and the formation of esters (*Figure 2*).

A useful analytical procedure for determining the composition of a mixture of methyl esters, triacyglycerols and fatty acids was developed using ^{13}C-NMR. *Figure 3* presents the ^{13}C-NMR spectrum of a mixture consisting of methyl esters, triacylglycerols and fatty acids.



Notes: ME - methyl esters; TG - triacylglycerols; FFA - free fatty acids; DG - diacylglycerols; MG - monoacylglycerols.

Figure 2. Analysis of reaction products by thin layer chromatography.

Two modified HPLC analyses were also developed to determine the product composition. The sample after quenching with sulphuric acid (5 N) was extracted and the extract dried over magnesium sulphate. The sample was then passed through a small silica gel column and eluted with petroleum spirit (b.p. 60½C–80½C) and chloroform. Analysis was carried out on 0.83 cm x 20 cm u-Porosil HPLC column with n-hexane/ethyl acetate mixture (98:2 v/v) as solvent and using a refractive index detector. For quantitative analysis of methyl esters, mono-, di- and triacylglycerols, a C18 reverse phase HPLC was found suitable. The conditions used were typically as described. Analysis was carried out on a 300 x 80 mm MCH-10 C18 reverse column with methanol/chloroform mixture (90:10 v/v) as solvent and using a refractive index detector. Typical chromatograms based on these two methods are shown in *Figures 4* and *5*, respectively.

Quantitative analysis of the reaction mixture was also conducted using gas chromatography (GC). The following temperature programming was used: oven temperature: 100½C, initial temperature: 100½C, final temperature: 350½C, injector temperature: 254½C, detector temperature: 360½C, rate: 10½C min^{-1}, carrier gas: Helium at 2.0 ml min^{-1}. A BPX 5 (15 m x 0.32

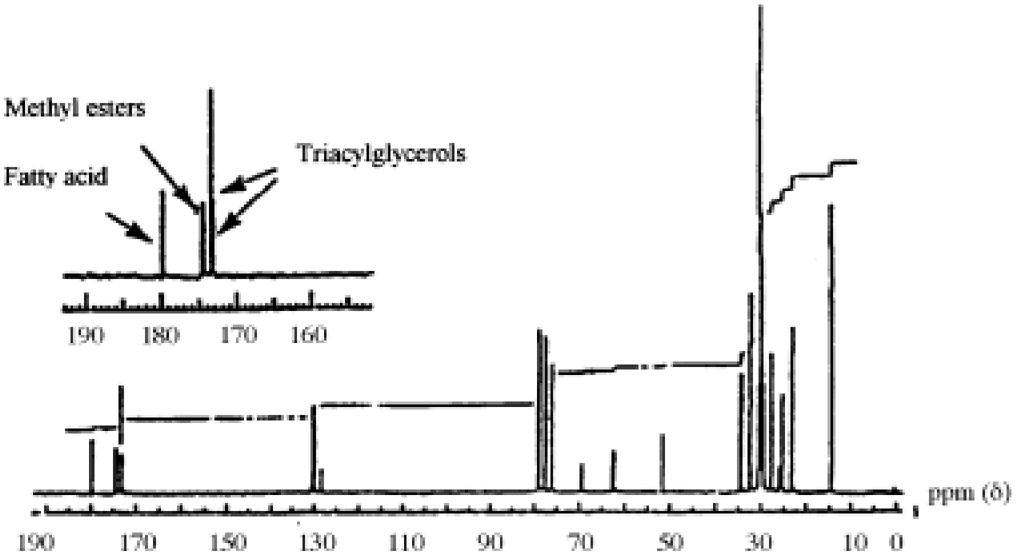


Figure 3. The ^{13}C NMR of methly esters, triacylglycerols and fatty acid mixture.

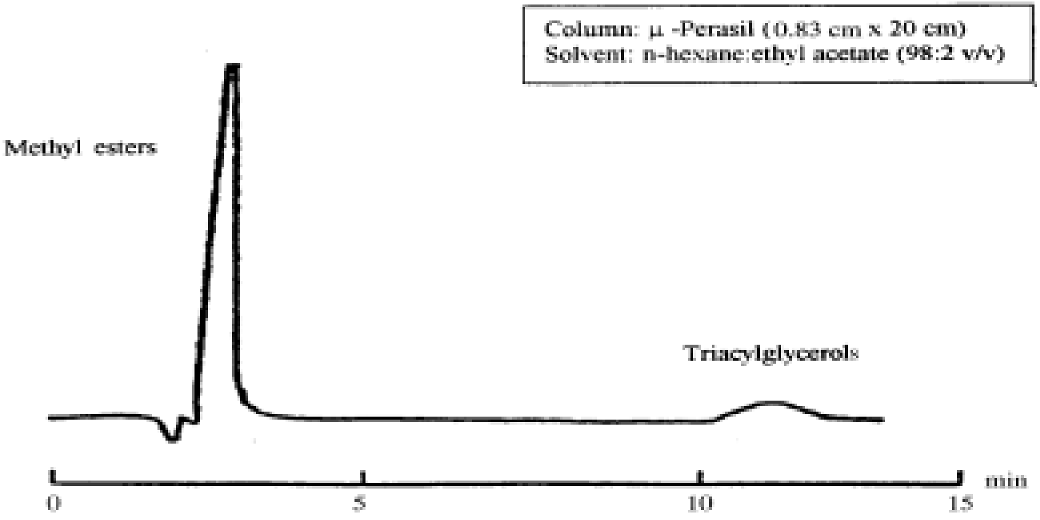


Figure 4. High perfomance liquid chromatography of methly esters and triacylglycerols.

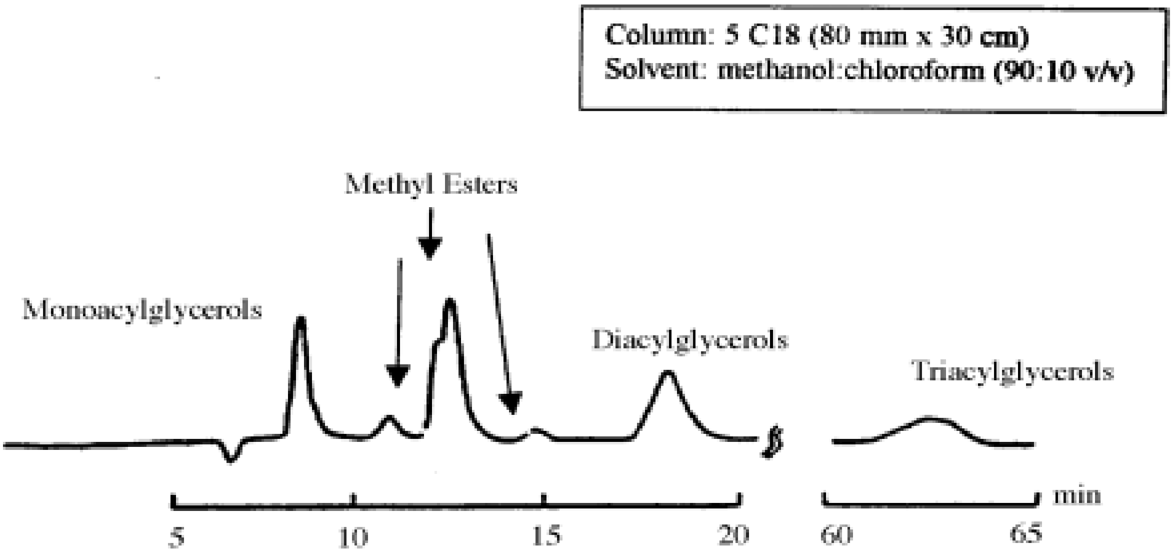
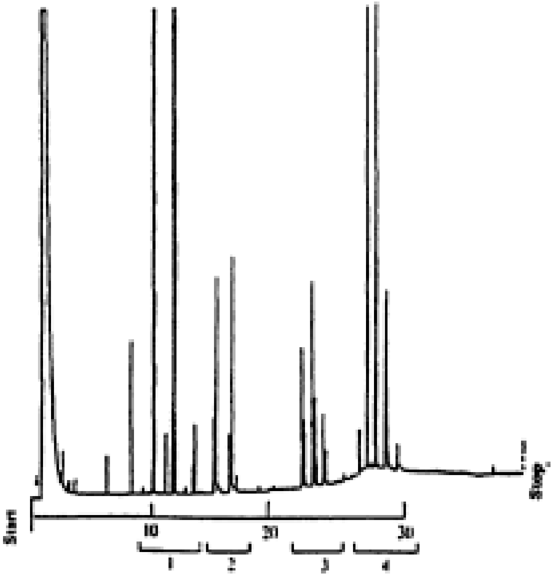


Figure 5. High perfomance liquid chromatography of methly esters, mono-, di- and triacylglycerols.

mm) capillary column was used. *Figure 6* depicts the typical chromatogram of a reaction mixture containing methyl esters, monoacylglycerols, diacylglycerols and triacylglycerols.



Notes: 1 - methyl esters, 2 - monoacylglycerols
3 - diacyglycerols, 4 - triacyglycerols.

Figure 6. Analysis of reaction products by gas chromatography.

Recovery of Glycerol

Methanol was removed from the glycerol layer after transesterification of palm oil. The methanol-free glycerol was then distilled under vacuum, b.p. 120½C– 40½C/0.5 mm Hg. The concentration of crude and distilled glycerol was checked by titration using the AOCS test method.

About 0.8 g of the sample was transferred by a Lunge pipette into a 500 ml conical flask. The 50 ml distilled water, six to eight drops of phenol red indicator and 1 ml N-sulphuric acid were added and the mixture boiled for 2 to 3 min to expel carbon dioxide. The flask was closed with a stopper carrying a soda-lime tube and cooled to 20½C. The excess acid was carefully neutralized using 0.1N NaOH (to Chinese tea colour). The 100 ml of a 5% solution of sodium metaperiodate were added. The sides of the flask were washed down with distilled water; it was closed with a soda-lime tube; the flask was allowed to stand in the dark (temperature 20½C) for 30 min. Ethylene glycol (5 ml) were added; the flask was swirled and allowed to stand for a further 20 min. Finally, the solution was titrated against 0.125 N NaOH solution. The calculation was done as follows:

$$\text{Percent of glycerol} = \frac{V \times F \times 100}{W}$$

where W = weight of sample
V = volume of NaOH used
F = factor of NaOH
(weight of glycerol/volume)

RESULTS AND DISCUSSION

Effect of Different Catalysts

Several catalysts were applied to the methanolysis of RBD palm oil and the results are shown in *Table 1*. RBD palm oil was selected for these systematic studies as it contained less impurities with a low FFA content of <0.1%. From *Table 1*, it can be seen that Na, NaOH and KOH are effective catalysts. Owing to the fact that KOH is more expensive, the use of NaOH was favoured in the present work. The low efficiency of acid catalysts like H_2SO_4 and HCl could be attributed to their different mechanistic pathway – Fischer type esterification.

TABLE 1. EFFECT OF DIFFERENT CATALYSTS ON TRANSESTERIFICATION OF PALM OIL*

Catalyst	Amount (wt % based on oil)	Reaction time (min)	Remarks
Na	0.1	16 – 32	99 % yield
NaOH	0.2	16 – 32	98 % yield
KOH	1	16 – 32	98 % yield
H_2SO_4 (conc.)	1	> 300	50 % yield
HCl (conc.)	1	> 300	30 % yield
Ion exchange resin (H^+)	2	> 300	Too slow
Dowex 50 (Na^+)	1	> 300	Too slow
Acid treated florisil	2	> 300	Too slow
Activated silica gel	1	> 300	Not suitable

Note: *The following conditions were used: type of oil = RBD palm oil (FFA = 0.05%); ratio of oil-to-solvent (methanol) = 1:15.6; temperature = reflux temperature.

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Effect of Acidity (FFA)

It was noted that the amount of catalyst used depended very much on the acidity or percentage of FFA in the palm oil itself. However, for palm oil with >5% acidity, the basic catalysts became ineffective partly because they were consumed by neutralization. This point was illustrated by the experiments using 8.5% FFA and 16.75% FFA palm oil and 76% FFA sludge oil as tabulated in *Table 2*. For oils containing 8.5% and 16.75% FFA, the reactions proceeded as usual during reflux, although some solids (probably soap formed) were observed when CH_3OH / NaOH was added to the melted oil. This was not observed from oil with < 5% FFA. However, the solids dissolved on reflux. Due to the high content of soap, two layers (ester and glycerol) were not observed when the reaction was complete. During the course of reaction, crystals formed. Therefore, the products were warmed up and washed with hot distilled water but no clear ester layer could be separated out. Instead, washing led to the formation of a soapy emulsion, which could not be broken up by centrifugation at low speed. Aqueous HCl was added and a clear layer consisting of RCOOH and RCOOMe obtained. Dilute NaOH was then added to this layer to neutralize the FFA and a little ethanol to clear it. With this treatment, very clear ester solutions were obtained.

In the case of sludge oil containing 76% FFA, only a trace of ester formed after 7 hr reaction as monitored by TLC. The yield of esters remained the same after 10 hr with triacylglycerols still present. Adding a base to neutralize all the excess FFA did not increase the yield.

Using NaOH catalysed transesterification, methyl esters can generally be prepared in high yields for low FFA oils, being nearly quantitative for the palm oils containing < 1% FFA. For example, the yield of methyl esters from RBD palm oil with about 0.05% FFA was 98%.

Effect of Stirring Speed

The reacting mixture (oil and catalyst/methanol) formed two immiscible layers with oil at the bottom and catalyst/methanol at the top layer. Thorough mixing of the two layers was therefore necessary for the reaction to proceed. Either a mechanical or a magnetic stirrer could be used. By keeping all the reaction parameters constant except the mechanical stirring, the rate of reaction was optimized at 150 rpm beyond which the rate remained unchanged (*Figure 7*). The time for completion of the reaction increased with a decrease in the stirring speed, being 50 min for 80 rpm, 21 min for 100 rpm and 14 min for 125 rpm, indicating the importance of effective mixing.

Effect of Catalyst Concentration

The rate of transesterification was very much dependent on the concentration of catalyst used. In the case of NaOH, the rate increased with increasing catalyst as in *Figure 8*. However, if the catalyst used exceeded 0.5 mole kg^{-1} oil, the reaction mixture solidified from the formation of soap.

Effect of Methanol Concentration

The molar ratio of alcohol-to-vegetable oil is one of the most important variables that affects the ester yield. The stoichiometry of this reaction requires three moles of alcohol per mole of vegetable oil to yield three moles of fatty ester and one mole of glycerol. Pryde (1981; 1982) reported the effect of the mole percent of methanol on soyabean and sunflower methyl ester formation. To obtain 90% or 97% ester conversion, respective molar ratios of 4:1 (33% excess) and 6:1 (100% excess methanol) were required. The present study confirmed the importance of using excess methanol but the amount used must be optimized in view of the phase

TABLE 2. EFFECT OF ACIDITY ON TRANSESTERIFIACTION OF PALM OIL AND YIELD*

% FFA of palm oil	Time of completion (min)	Yield (%)
(1) 6.75	8 – 16	67
(2) 8.5	8 – 16	72
(3) 3.9	8 – 16	92
(4) 76 (sludge oil)	> 420	trace

Notes: * The following conditions were used: weight of oil = 200 g; methanol = 150 ml; reaction temperature = reflux temperature; catalyst = NaOH. The catalyst used for (1), (2) and (3) was NaOH (in excess over the neutralization equivalent for FFA), while that for sludge oil was Na (1 wt % on oil used).

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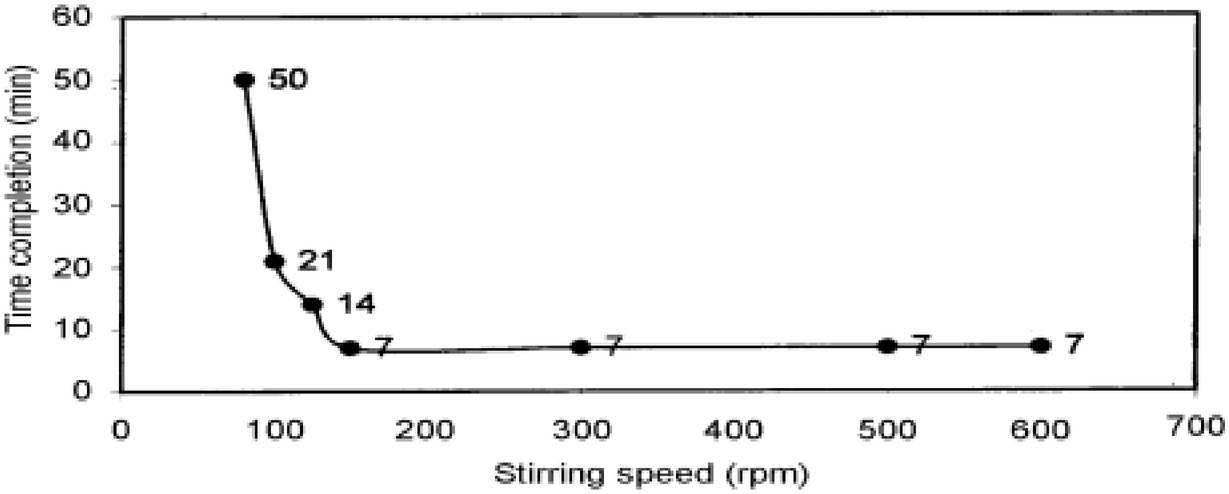
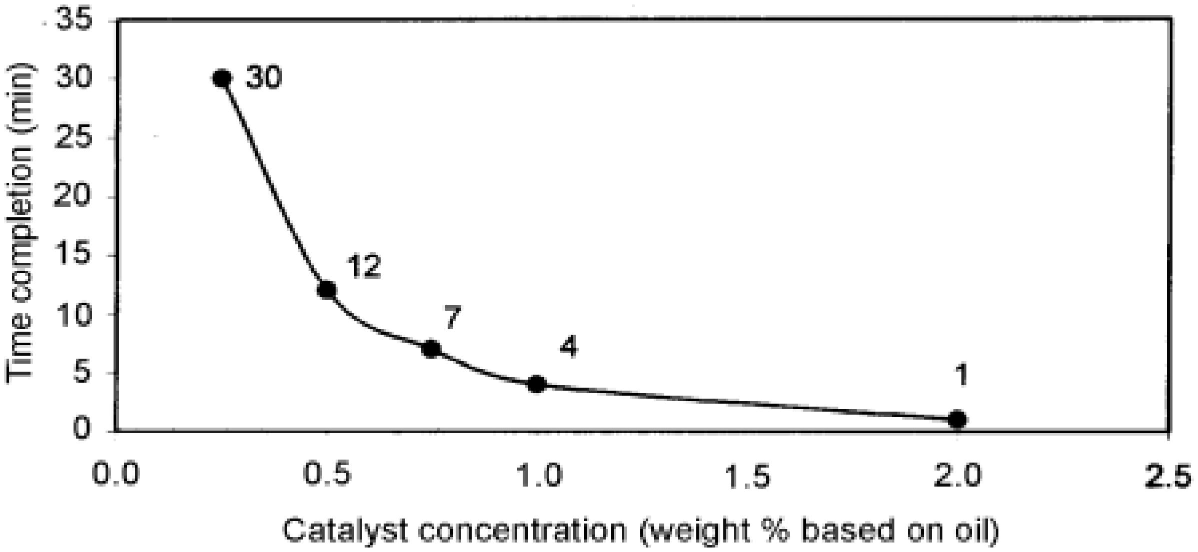


Note: *The following conditions were used: RBD palm oil:methanol = 1:15.6; temperature = 60 ±3½C; amount of NaOH = 0.75 wt % on oil used = 0.1875 mole kg^{-1} oil.

Figure 7. Effect of stirring on rate of methanolyis of palm oil.*



Note: *The following conditions were used: RBD palm oil:methanol = 1:15.6; temperature = 60 ±3½C; mechanical stirring speed = 600 rpm.

Figure 8. Effect of concentration of catalyst (NaOH) on transesterification of palm oil.*

separation. As mentioned earlier, when excess methanol is used (15:1 molar ratio), natural separation of the ester and glycerol layers after the reaction is possible. However, at the theoretical ratio of 3:1, the two layers were not observed but the reaction mixture/product remained semi-solid throughout the reaction and after 6 hr apparently reached equilibrium with significant amounts still of mono-, di- and triacylglycerols remaining. In the 4:1 molar ratio of reactants, natural separation of ester and glycerol was observed with a solid glycerol layer and a semi-solid reaction mixture during the reaction. The glycerol layer from the reaction with 6:1 molar ratio also solidified on overnight storage. A molar ratio of 8:1 or more gave good separation of ester and glycerol which, on overnight storage, remained liquid and clear. The minimum amount of methanol required to achieve total conversion was an excess of 233%, *i.e.* a 10:1 molar ratio. A further increase in the molar ratio beyond this did not significantly increase the rate of product formation (*Table 3*).

The excess methanol used in the reaction can be recovered for reuse. The recovery of excess methanol is necessary to reduce the material cost. The amounts of methanol recovered from both the ester and glycerol layers separately are shown in *Table 4*. On average, about 25% and 34% of the methanol were recovered from the ester and glycerol layers, respectively.

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TABLE 3. EFFECT OF EXCESS METHANOL ON PRODUCT FORMATION OF TRANSESTERIFICATION OF PALM OIL*

Molar ratio (oil:methanol)	Time of completion (min)
1:3	> 360**
1:4	360
1:6	23
1:8	12
1:10	7
1:11	7
1:15.6	7

Notes: * The following conditions were used: NaOH = 0.75 wt % on oil used = 0.19 mole kg^{-1} oil; temperature = 60 ±3 ½C; stirring speed = 350 rpm.

** For molar ratio = 1:3, the reaction was still not complete after 6 hr reaction.

TABLE 4. RECOVERY OF EXCESS METHANOL FROM TRANSESTERIFICATION OF RBD PALM OIL*

Amount of methanol recovered	
Ester layer	**Glycerol layer**
(1) 26 ml (26% 2.7 moles)	35 ml (35%, 3.65 moles)
(2) 24.4 ml (24.4%, 2.5 moles)	32.5 ml (32.5%, 3.4 moles)

Note: * The following conditions were used: amount of oil = 200 g; methanol = 100 ml; molar ratio of methanol:oil = 1:10.5.

Effect of Temperature

Feuge and Gros (1949) concluded that transesterification can occur at a moderate temperature of 50½C in their work on the effect of temperature (at 70½C, 50½C and 30½C) on the ethanolysis of peanut oil (6:1 molar ratio) with 0.2% NaOH. Pryde (1981) worked on methanolysis of soyabean oil (6:1 molar ratio, 1% sodium hydroxide) at 60½C, 45½C and 32½C. It was concluded that the transesterification proceeded satisfactorily at 32½C over several hours. Therefore, it was useful to investigate how the methanolysis of RBD palm oil (15.6:1 molar ratio, 0.75% sodium hydroxide) is influenced by temperature, *i.e.* at 60½C, 50½C, 40½C and 28½C (ambient). The results of these experiments showed that at 60½C the time for completion of the reaction was 7 min, at 50½C, 13 min, at 40½C, 32 min and at ambient temperature, 2 hr. These results (*Table 5*) compare favourably with the reported rates for other vegetable oils at comparable temperatures.

The results of methanolysis of CPO with 3.9% FFA are quite consistent with those of RBD palm oil (*Table 6*). As expected, the rate of reaction increased with increasing temperatures – for every 10% rise in temperature in the range 40½C-60½C, the rate almost doubled.

Effect of Water Content in Methanol

The effect of water content in the methanol on the transesterification reaction was tested (*Table 7*) and it was found that with moisture up to 4%, the reaction could still proceed satisfactorily. The confirmation of this point is important as this means extensive purification/drying of the recovered methanol is not necessary, hence cutting down the process cost.

The FFA of esters formed from reactions with 5% and 10% H_2O in methanol were determined and found to be only 0.16% and 0.11%, respectively. This shows that the H_2O in methanol did not promote the hydrolysis or saponification reactions.

Transesterification of Neutralized Palm Oil

It was noted that the amount of catalyst used depended very much on the acidity of the palm oil itself. *Table 8* shows that RBD palm oil with very low acidity (0.05% FFA) required very little catalyst (0.019 mole NaOH kg^{-1} of oil) for transesterification. In the case of 1.7% FFA CPO, the amounts of alkaline catalysts required were more (0.065 mole Na kg^{-1} of oil and 0.065 mole NaOH kg^{-1} g of oil) because the FFA must first be neutralized before the reaction can

TABLE 5. EFFECT OF TEMPERATURE OF TRANSESTERIFICATION OF REFINED BLEACHED DEODORIZED PALM OIL*

Temperature, T ± 3 °C	Time of completion (min)
60	7
50	13
40	32
27 – 28 (ambient)	120

Note: * The following conditions were used: RBD palm oil:methanol = 1:15.6; stirring speed = 350 rpm; NaOH = 0.75 wt % based on oil = 0.1875 mole kg^{-1} oil.

TABLE 6. EFFECT OF TEMPERATURE OF TRANSESTERIFICATION OF CRUDE PALM OIL WITH 3.9% FREE FATTY ACID*

Temperature, T ± 3 °C	Time of completion (min)
60	6
50	14
40	20
30	120

Note: * The following conditions were used: amount of oil = 200 g; methanol = 100 ml; stirring speed = 350 rpm.

TABLE 7. EFFECT OF WATER CONTENT IN METHANOL FOR TRANSESTERIFICATION OF REFINED BLEACHED DEODORIZED PALM OIL*

Amount of water (%) (with respect to oil used)	Triglyceride (%) unreacted after 7 min of reaction**	Completion time (min)
0	Trace	7
1	Trace	7
2	5	10
3	5	10
4	5	10
5	10	20
10	30	150

Notes: * The following conditions were used: oil = 200 g (RBD palm oil); methanol = 95 ml (anhydrous methanol); NaOH = 0.75 wt % on palm oil used = 0.1875 mole kg^{-1} oil; temperature = 60 ± 3 ½C; stirring speed = 350 rpm.

** The completion time of reaction with 0% H_2O was taken as 7 min and this was taken as reference and used for comparison.

TABLE 8. TRANSESTERIFICATION OF NEUTRALIZED REFINED BLEACHED DEODORIZED PALM OIL*

Weight % of NaOH used (mole kg^{-1} oil)	Time completed (min)	Yield (%)
0.2 (0.05)	16 – 32	98
0.1 (0.025)	32 – 64	97

Note: * The following conditions were used: weight of oil = 200 g; methanol = 150 ml; reaction temperature = reflux temperature; FFA = 0.05% (weight % of base catalyst required to neutralize the oil: NaOH = 0.0074 wt % = 0.0019 mole kg^{-1} oil).

proceed (*Table 9*). Reactions with less alkaline catalyst than the amount to neutralize the oil did not work as may be expected. For example, when 0.05 mole NaOH kg^{-1} was added to the 1.7% FFA oil (ca. 0.06 mole H^+ kg^{-1}) *in situ*, only a trace of esters was formed. Further addition of catalyst allowed the transeserification to proceed. Hence, the amount of alkaline catalyst used should be sufficient to neutralize the acid present in the oil, plus a slight excess to act as catalyst. This point was further substantiated by the CPO containing higher FFA (3.9%; ca. 0.153 mole H^+ kg^{-1}) as shown in *Table 10*. With 0.155 mole NaOH kg^{-1} of oil to neutralize the oil and an excess of 0.053 mole NaOH kg^{-1} of oil as catalyst, the reaction proceeded to completion within 8-16 min. As in the previous case, the addition of NaOH in amounts insufficient to neutralize the FFA did not cause transesterification. The addition of excess base over the neutralization equivalent, *e.g.* 0.057 mole Na kg^{-1} of oil, to this 3.9% FFA CPO allowed the rapid catalytic reaction to be completed within 8-16 min.

Removal of Soap by Centrifugation

The preparation of palm oil methyl esters invariably gave rise to soap formation from the FFA, water and NaOH. When the NaOH catalyst was used for transesterification of palm oil with 2%-5% FFA, the yield was low as the soap formed during the reaction caused emulsion formation. When more NaOH was used for even higher FFA palm oil (*Table* 2: 8.5%, 16.75% FFA), the yield was even lower as the whole ester product was completely emulsified and dilute acid had to be introduced to break the emulsion. The separation problem could be overcome by high speed centrifugation. The ester layer, after removal of methanol (distillation), was centrifuged immediately, without any washing to remove the soap and excess alkali. After centrifugation, the ester was clear and neutral with the soap settled as a lump at the bottom. This method was successfully demonstrated for the reaction using CPO (5% FFA) and crude palm stearin (3.6% FFA) catalyzed by NaOH.

TABLE 9. TRANSESTERIFICATION OF NEUTRALIZED CRUDE PALM OIL WITH 1.7% FREE FATTY ACID[a]

Weight % of NaOH used (mole kg^{-1} oil)	Time completed (min)	Yield (%)
0.5 (0.125)	8 – 16	91
0.4 (0.10)	16 – 32	91
0.35 (0.0875)	32 – 64	91
0.32 (0.08)	32 – 64	90
0.2[b] (0.05)	overnight[c]	trace

Notes: [a] The following conditions were used: weight of oil = 200 g; methanol = 150 ml; reaction temperature = reflux temperature; FFA = 1.7% (ca. 0.06 mole H^+ kg^{-1}).
[b] Weight % of base catalyst required to neutralize the oil: NaOH = 0.26 wt % = 0.065 mole kg^{-1} oil.
[c] After 7.5 hr of reflux and 12 hr of standing.

TABLE 10. TRANSESTERIFICATION OF NEUTRALIZED CRUDE PALM OIL WITH 3.9% FREE FATTY ACID*

Weight % of NaOH used (mole kg^{-1} oil)	Time completed (min)	Yield (%)
0.83 (0.2075)	8 – 16	92
0.55 (0.1375)	> 360	trace

Notes: * The following conditions were used: weight of oil = 200 g; methanol = 150 ml; reaction temperature = reflux temperature; type of oil used = CPO with 3.9 % FFA (ca. 0.152 mole H^+ kg^{-1}).
0.61 wt % of NaOH (0.153 mole kg^{-1} oil) was required to neutralize the oil + 0.2 wt % (0.05 mole kg^{-1} oil) as catalyst.

Recovery of Glycerol

The glycerol layer from the transesterification of CPO was analysed as 80%-85% pure after the excess methanol was removed. The purity was checked by direct titration and further confirmed when the crude glycerol was distilled under vacuum. Allowing for some losses of glycerol in the condenser and residue, the yield of distilled glycerol of > 96% purity was found to be not less than 75%. The impurities in the crude glycerol were probably soap and some esters. This was shown by the fact that when the soap and esters were removed by acidification followed by extraction with hexane, the remaining glycerol had a slightly higher purity of 97.4%.

CONCLUSION

Optimum reaction conditions were obtained with a molar ratio of methanol-to-oil of 10:1 and a reaction time of 7 min at ca. 65½C. For oils containing <5% FFA, this transesterification to methyl esters was readily effected using additional NaOH to neutralize the FFA.

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