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KINETICS STUDY ON TRANSESTERIFICATION OF PALM OIL

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ABSTRACT

The kinetics of base-catalyzed transesterification of palm oil based on parameters such as oil and alcohol ratio, catalyst concentration and temperature were investigated to optimize the conversion rate. Our findings showed that both sodium hydroxide and sodium methoxide had high kinetic constants depicting fast formation of palm oil methyl esters with conversions above 99%. Fast formation of palm oil methyl esters with a rate constant of 0.163 litre mole min^{-1} was obtained when the reaction parameters were: molar ratio of oil to methanol, 1:10; catalyst concentration, 0.125 mole kg^{-1} oil; and temperature, 60½C.

Keywords: transesterification, kinetics, sodium hydroxide, sodium methoxide, crude palm oil.

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INTRODUCTION

Transesterification of vegetable oils and fats to methyl and ethyl esters using different reactants, reaction conditions and catalysts have been reported (Freedman *et al.*, 1984; Choo *et al.*, 1990; Goh *et al.*, 1992). The typical conditions in the transesterification of vegetable oils are generally mild - a temperature of 50½C to 70½C with 0.5% to 1% alkaline catalyst. With the current trend towards the environment-friendly biofuel (Pryde *et al.*, 1982; Ong *et al.*, 1984; Knothe *et al.*, 2001), coupled with financial incentives, producers are encouraged to build not only new plants but to improve the existing production plants to produce high quality methyl esters of biodiesel grade (Boocock *et al.*, 1998).

In the present study, the optimum conditions to produce palm oil methyl esters by transesterification of crude palm oil (CPO) with methanol using alkaline catalysts, namely, sodium methoxide (NaOMe) and sodium hydroxide (NaOH) were investigated. With the new trend and depth in the development in the biofuel industry, it is hoped to establish the optimum reaction conditions for good yields in the minimum reaction time and material consumption. In this context, experiments with varying reaction parameters were conducted to study the kinetics of the formation of palm oil methyl esters.

MATERIALS AND METHODS

Materials

CPO was from the Malaysian Palm Oil Board's Experimental Palm Oil Mill in Labu, Selangor, Malaysia. Methanol, NaOMe and anhydrous sodium sulphate (Na_2SO_4) were of A.R. grade (Merck). The catalyst, NaOMe (30%), was obtained from Degussa GmbH (Germany).

Methods

Transesterification of CPO and methanol was catalyzed by either NaOH and NaOMe in a batch system. The reaction set-up included a round bottom flask equipped with a condenser and thermometer. The flask was immersed in a water bath on a magnetic stirrer with heating plate. For the NaOH catalyzed reactions, the catalyst was dissolved in methanol and the mixture added to the reaction mixture at the reaction temperature. For the NaOMe catalyzed reactions, the methanolic solution at 30% concentration was added, also at the elevated reaction temperature.

On completion of the reaction, the glycerol layer was decanted and the esters purified and dried. The esters were washed with warm distilled water in excess methanol using a separating funnel until a

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neutral decanted aqueous layer was obtained. Finally, the esters were subjected to a vacuum pump to ensure that no traces of distilled water and methanol remained in the product.

Aliquots of the sample were taken at reaction times, t = 1, 3, 5, 7, 9, 12, 15, 18, 21, 25 min, and thence, after every 5 min to study the kinetics of the transesterification. The samples were also purified immediately as mentioned above to remove the catalyst and stop the reaction. However, instead of subjecting the samples to a vacuum pump, the neutral aliquots were dried with anhydrous Na_2SO_4 because of their small volumes. The degree of transesterification during and at completion of the reaction was ascertained by gas chromatography (GC) (Lau *et al.,* 2002).

Experiments with varying reaction parameters such as catalyst concentration, reaction temperature and ratio of oil to methanol were conducted to study their effects on the transesterification process.

RESULTS AND DISCUSSION

Catalyst Concentration

The effect of catalyst concentration was studied using molar ratios of oil to methanol at 1:10, a reaction temperature of 60½C and stirring rate at 350 rpm. The reactions were carried out with NaOMe or NaOH at 0.125, 0.1875 and 0.25 mole kg^{-1} oil.

All the reactions using NaOMe achieved ester conversion above 99% after 5 min. The effect of the catalyst was obvious within the initial 5 min. A dosage of 0.125 mole kg^{-1} of oil produced ester conversion of 99.5% after 5 min, while it took only 3 min using 0.1875 mole kg^{-1} oil. This result indicates that faster ester conversion was obtained with a higher dosage of catalyst. However, there was no further improvement with the catalyst concentration increased from 0.1875 mole kg^{-1} oil to 0.25 mole kg^{-1} oil. Thus, it can be concluded that 0.125 mole kg^{-1} oil sufficed for NaOMe to achieve ester conversion above 99.5% in 5 min. A longer reaction time had no significant effect on the ester conversion. The effect of concentration of NaOMe is illustrated in *Figure 1.*

The same conclusions were drawn from the NaOH catalyzed reactions. Catalyst concentration was important for short reactions as the ester conversion increased with more catalyst. It took 7 min to achieve 99% conversion with 0.125 mole NaOH kg^{-1} oil but only 5 min to achieve the same conversion with 0.1875 mole NaOH kg^{-1} oil. Only 3 min were required with the catalyst concentration increased to 0.25 mole kg^{-1} oil. Therefore, for reactions above 10 min, it sufficed to use 0.125 mole NaOH kg^{-1} oil. The detailed results are presented in *Figure 2.*

Ratio of Oil to Methanol

Although stoichiometrically, transesterification of 1 mole of oil requires 3 moles of alcohol, excess of alcohol improves the conversion (Freedman *et al.,* 1984). A molar ratio oil to alcohol of at least 1:6 was used for the transesterification of sunflower oil, soyabean oil, peanut oil and cottonseed oil. The effect of molar ratio of CPO to methanol in the transesterification of palm oil was studied using NaOMe and NaOH as catalysts (0.125 mole kg^{-1} oil) at 60½C and a stirring rate of 350 rpm. The molar ratios of oil to methanol of 1:6, 1:8 and 1:10 were investigated.

Under the reaction parameters mentioned, the molar ratio of oil to methanol had no significant effect on the ester conversion in the NaOMe catalyzed reactions. In all the experiments, an ester conversion of above 99% was achieved after 5 min. Thus, it sufficed sufficient to employ a molar ratio of 1:6 when 0.125 mole NaOMe kg^{-1} oil is used as the higher ratios produced a comparable ester conversion. A higher ratio would therefore be wasteful. The detailed results are presented in *Figure 3.*

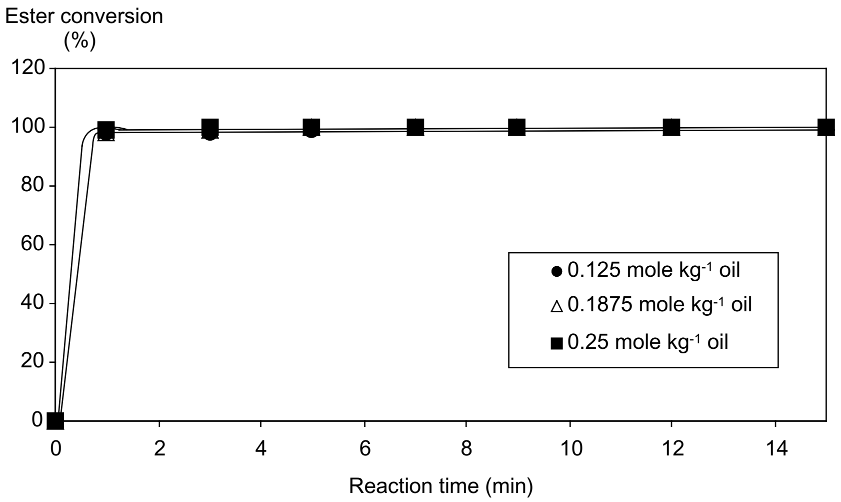
For the reactions using 0.125 mole NaOH kg^{-1} oil as catalyst, the molar ratio was important in determining the ester conversion. The ester conversion improved significantly when the molar ratio of oil to methanol was increased. The detailed results are presented in *Figure 4.* After 5 min reaction, the ester conversion using molar ratios of 1:6, 1:8 and 1:10 were 93%, 95% and 99%, respectively. Ester conversion of 99% was not obtained even when the reaction time was extended. The highest ester conversion achieved using molar ratios of 1:6 and 1:8 was 97% (21 min) and 98% (9 min), respectively. Thus, more excess methanol was needed to push the reaction towards the product for the NaOH catalyzed reactions.

A higher molar ratio of oil to methanol of 1:15 produced only a marginal improvement. Such high excess methanol without significant improvement in the ester conversion is clearly a waste of the raw material. Furthermore, poor phase separation between the palm oil methyl esters and glycerol was observed when a molar ratio of 1:15 was used.

Reaction Temperature

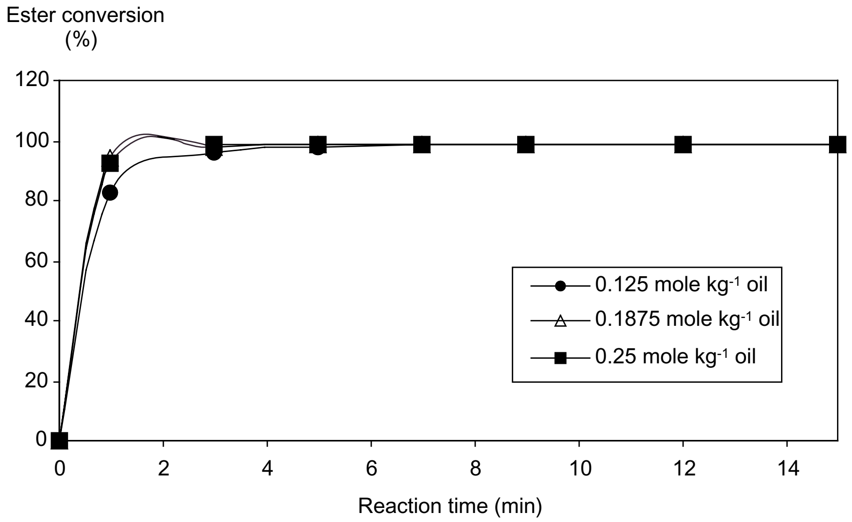
The effect of temperature on the transesterification of palm oil was studied using a molar ratio of CPO to methanol of 1:10, catalyzed by NaOMe and NaOH (0.125 mole kg^{-1} of oil) and at a stirring rate of 350 rpm. The temperatures studied were 50½C, 60½C and 70½C.

For the reactions using NaOMe, ester conversion of 99% was obtained for 50½C, 60½C and 70½C after 5, 3 and 1 min, respectively. Below 5 min reaction time, the ester conversion was increased with the reaction



Note: Reaction conditions: Molar ratio of oil to methanol at 1:10.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 1. Kinetics of the transesterification of palm oil to methyl esters using sodium methoxide as catalyst at various catalyst concentrations.



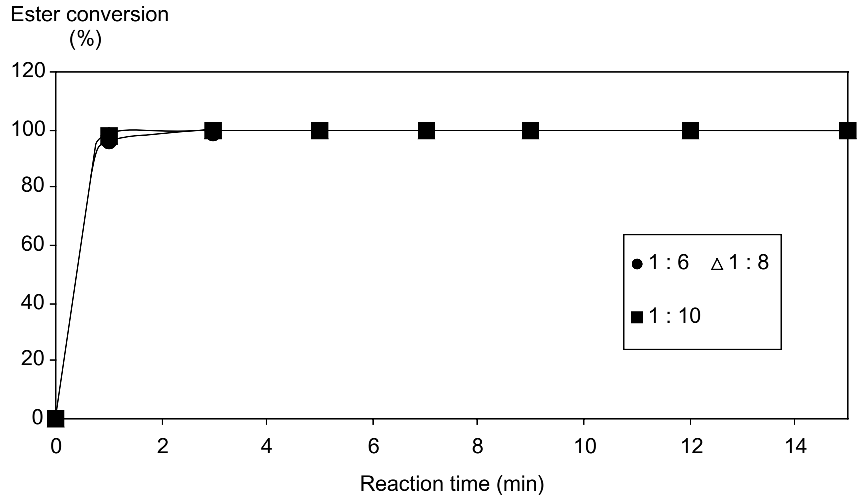
Note: Reaction conditions: Molar ratio of oil to methanol at 1:10.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 2. Kinetics of the transesterification of palm oil to methyl esters using sodium hydroxide as catalyst at various catalyst concentrations.

temperature increased from 50½C to 60½C and 70½C. There was not much effect when the temperature was raised from 60½C to 70½C. Thus, there is no need to raise the reaction temperature to 70½C as the ester conversion is comparable to that obtained at 60½C. A temperature of 50½C can also be used to achieve 99% ester conversion if the reaction time is over 7 min. The detailed results are illustrated in *Figure 5*.

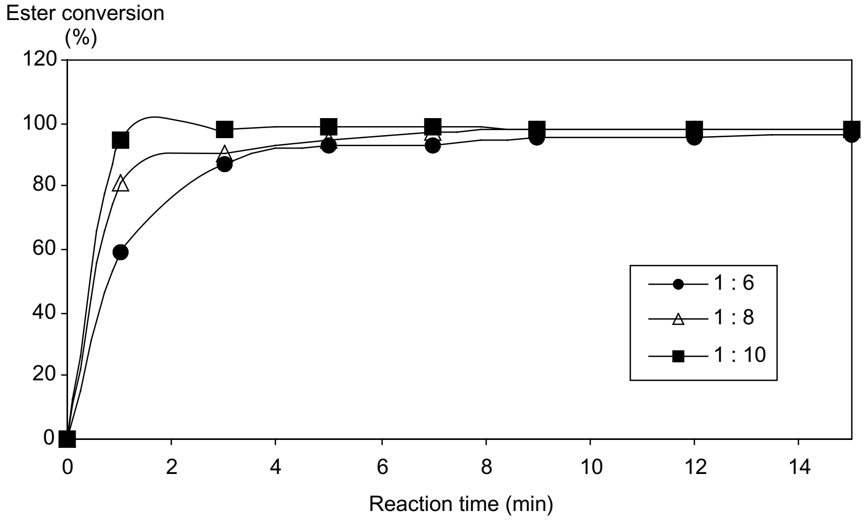
For reactions using NaOH, the effect of temperature was more significant. There were great increments in ester conversion with the reaction temperature raised from 50½C to 60½C and 70½C. An ester conversion of 99% was only obtained at 70½C after 5 min. The same ester conversion was not obtained from the reactions at 50½C and 60½C even up to 60 min. The highest esters conversion (98%) for the reactions at 50½C and 60½C was achieved after 21 min and 7 min, respectively. Thus, for the NaOH catalyzed reactions, it is best to carry them out at 60½C. The detailed results are illustrated in *Figure 6*.

The effect of reaction temperature on the transesterification palm oil is obvious from these



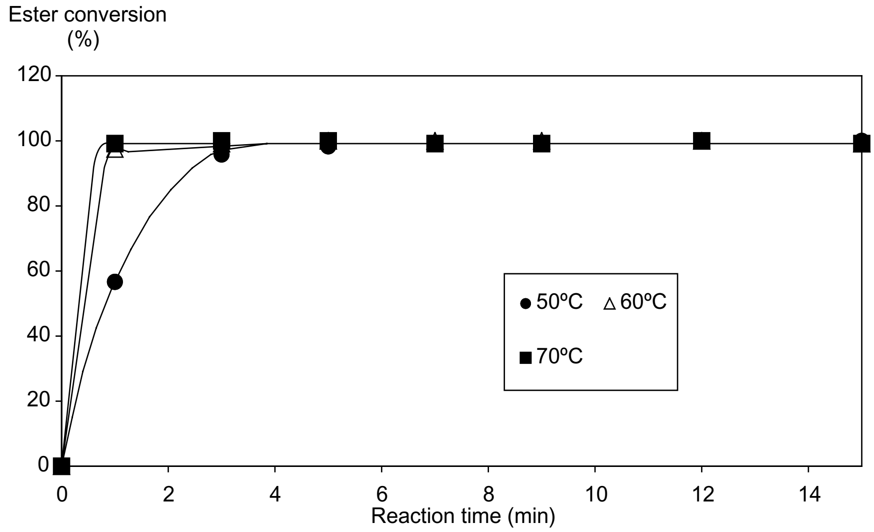
Note: Reaction conditions: Catalyst concentration at 0.125 mole kg^{-1} oil.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 3. Kinetics of the transesterification of palm oil to methyl esters using sodium methoxide as catalyst at various molar ratios.



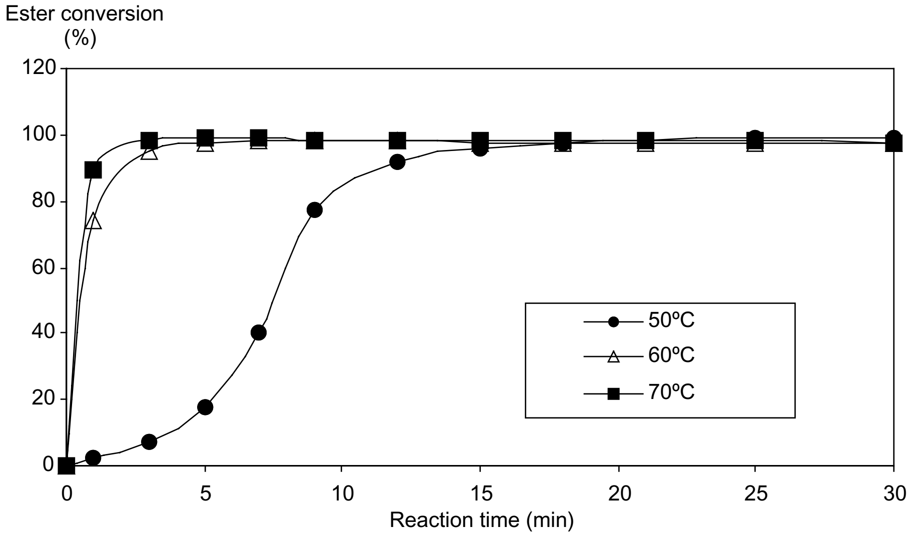
Note: Reaction conditions: Catalyst concentration at 0.125 mole kg^{-1} oil.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 4. Kinetics of the transesterification of palm oil to methyl esters using sodium hydroxide as catalyst at various molar ratios.



Note: Reaction conditions: Catalyst concentration at 0.125 mole kg^{-1} oil.
Molar ratio of oil to methanol at 1:10.
Stirring rate at 350 rpm.

Figure 5. Kinetics of the transesterification of palm oil to methyl esters using sodium methoxide as catalyst at various temperatures.



Note: Reaction conditions: Catalyst concentration at 0.125 mole kg^{-1} oil.
Molar ratio of oil to methanol at 1:10.
Stirring rate at 350 rpm.

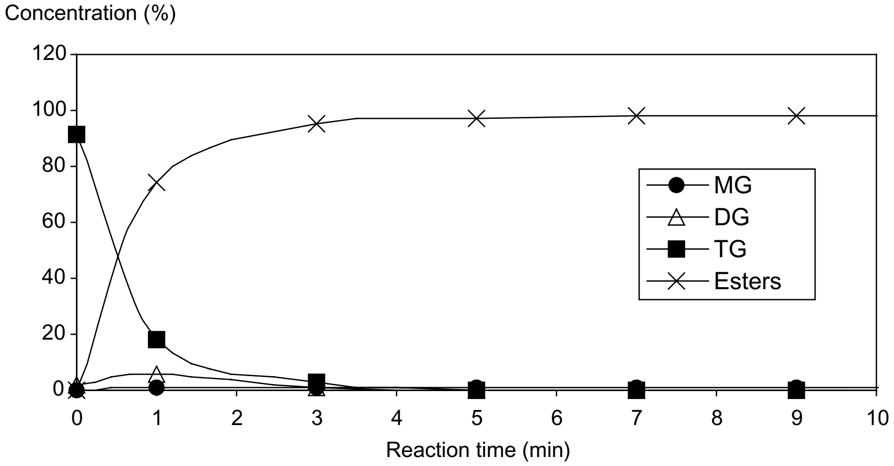
Figure 6. Kinetics of the transesterification of palm oil to methyl esters using sodium hydroxide as catalyst at various temperatures.

results. A reaction temperature at 60½C is suitable for both catalysts as it is very near the boiling point of methanol (64.6½C) and melting point of CPO (55½C). Thus, at the temperature, the reaction mixture is thoroughly homogenized and the reactants in good contact with one another.

Conversion of Glycerides to Methyl Esters

The concentrations of glycerides, namely, monoglycerides, diglycerides and triglycerides, were monitored throughout the reactions. *Figure 7* illustrates the typical trend in the glyceride concentrations during the transesterification. Triglycerides decreased tremendously and rapidly over the reaction, while the methyl esters increased rapidly indicating fast formation of the aforementioned product. Diglycerides increased, then decreased. The monoglycerides, however, did not show any significant fluctuation. This indicates that the conversion of triglycerides to intermediates (diglycerides and monoglycerides) and product (methyl esters) proceeded at the same time, while the intermediates, such as diglycerides and monoglycerides, were converted to monoglycerides and then methyl esters subsequently (*Figure 8*). This explains the trends in the glyceride compositions observed.

The traces of diglycerides and monoglycerides in the end product even with high ester conversion indicated an equilibrium between the reactants and products since transesterification is a reversible reaction.



Notes: (i) Reaction conditions: Catalyst concentration at 0.125 mole kg^{-1} oil.
Molar ratio of oil to methanol at 1:10.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

(ii) MG – monoglycerides, DG – diglycerides and TG – triglycerides.

Figure 7. Glyceride composition during transesterification of palm oil using sodium hydroxide.

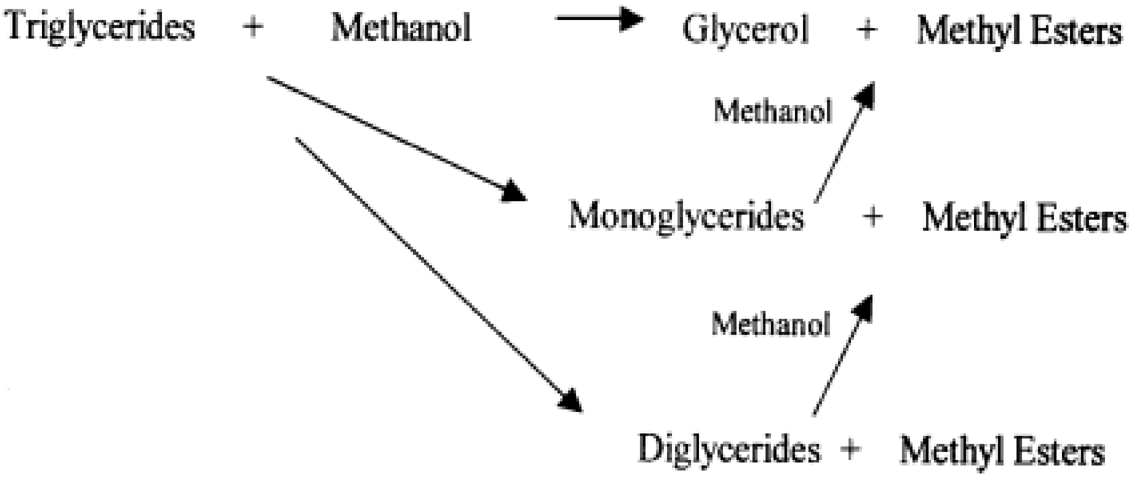
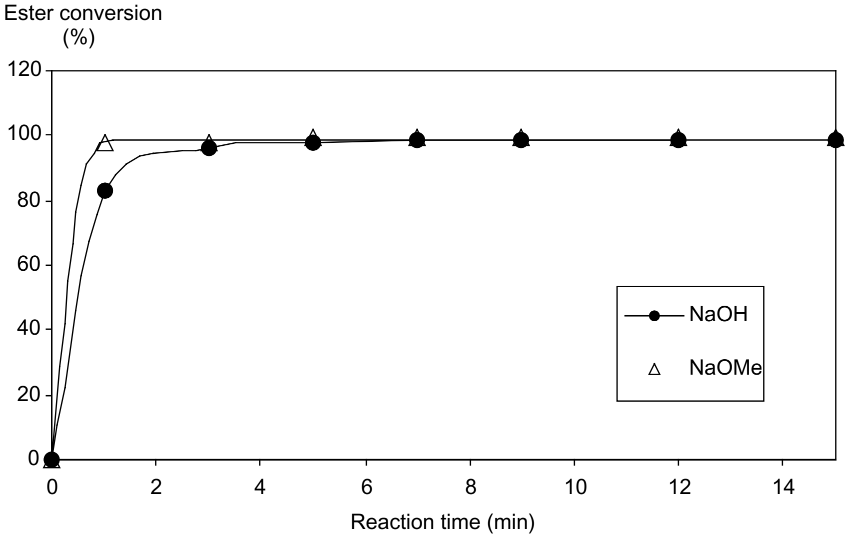


Figure 8. Pathway of glyceride conversion to methyl esters.

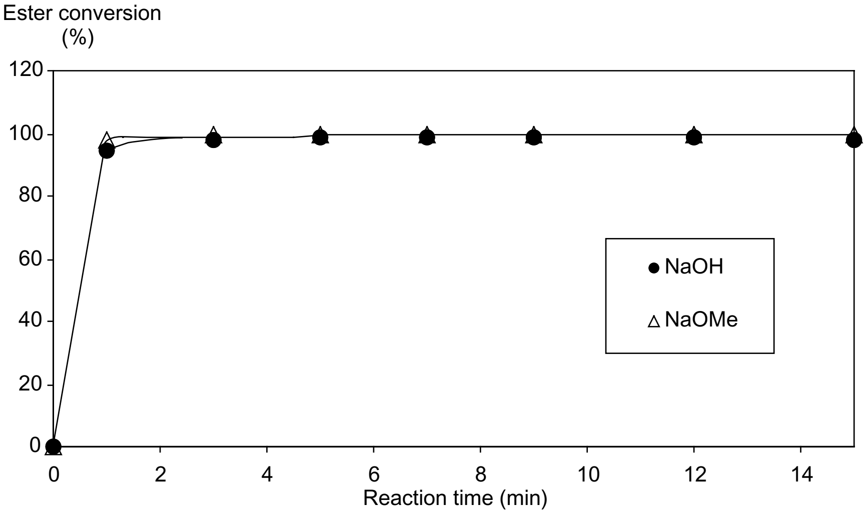
Comparison of Sodium Methoxide with Sodium Hydroxide as Catalysts

NaOMe has been cited as the most effective alcoholysis catalyst (Freedman *et al.*, 1984). The results from this study also showed NaOMe to be more superior to NaOH although both catalysts exhibited good catalytic performance. NaOMe offered a faster and higher ester conversion than NaOH at the same concentration (*Figures 9, 10* and *11*). For example, when 0.125 mole NaOH kg^{-1} oil was used, an ester conversion of above 99% was achieved in 5 min. For the same result, 0.1875 mole NaOH kg^{-1} oil was needed. However, if the reaction was carried out longer, 0.125 mole NaOH kg^{-1} oil sufficed.



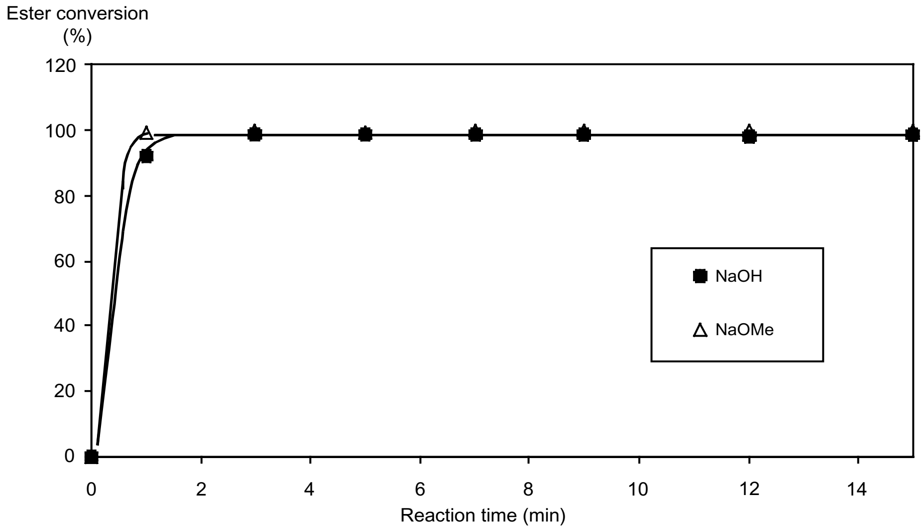
Note: Reaction conditions: Molar ratio of oil to methanol at 1:10.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 9. Transesterification of palm oil using a catalyst concentration of 0.125 mole kg^{-1} oil.



Note: Reaction conditions: Molar ratio of oil to methanol at 1:10.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 10. Transesterification of palm oil using a catalyst concentration of 0.1875 mole kg^{-1} oil.



Note: Reaction conditions: Molar ratio of oil to methanol at 1:10.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 11. Transesterification of palm oil using a catalyst concentration of 0.25 mole kg^{-1} oil.

However, during purification (washing with water) of the esters to remove the catalyst used, less emulsion was formed with NaOH than NaOMe. The formation of emulsion may cause losses in the end product if no special care is taken, lowering the product yield.

Another advantage of NaOMe is easy handling as it is available in methanolic 30% solution. NaOH on the other hand, is available as pellets and needs to be dissolved in methanol before adding to the reaction mixture.

Determination of the Reaction Rate Constant, k

Kinetics data were obtained from the different sets of transesterification reactions. The data could be described reasonably by a second order rate expression:

$$\text{Triglycerides [TG]} + 3 \text{ methanol [ML]} \longrightarrow 3 \text{ methyl esters [ME]} + \text{Glycerol}$$

$$r = \frac{-d[TG]}{dt} = k[TG][ML]$$

where r = rate of reaction
k = rate constant
[TG] = concentration of oil
[ML] = concentration of methanol

Integration yields (Smith, 1981):

$$kt = \frac{1}{[ML]_o - 3\,[TG]_o} \ln \frac{[ML]}{[TG]} - \ln\left\{\frac{[ML]_o}{[TG]_o}\right\}$$

$$t = \frac{1}{k[TG]_o\,\{[ML]_o/[TG]_o - 3\}} \ln \frac{\{[ML]_o/[TG]_o\} - 3x_{TG}}{\{[ML]_o/[TG]_o\}\,(1 - x_{TG})}$$

$$= \frac{1}{k} f(x_{TG}) \qquad \text{where } x_{TG} = \frac{[TG]_o - [TG]}{[TG]_o}$$

The rate constant, k, for each of the reaction was determined from the slope of the plot of $f(x_{TG})$ versus reaction time (t) (*Figures 12, 13* and *14*). Each transesterification reaction had its own k value which varied from one reaction to another depending on the reaction parameters. The k values for the various transesterification reactions are tabulated in *Table 1*. These kinetics data would be useful for designing a reactor system for the transesterification of palm oil to its methyl esters.

CONCLUSION

Both NaOH and NaOMe offered good catalytic activity for the transesterification of CPO with the latter being superior to the former. At a catalyst concentration of 0.125 mole kg^{-1} oil, an ester conversion of above 99% can be achieved by conducting the reaction at 60½C and a molar ratio of oil to methanol of 1:10. The NaOMe catalyzed reaction, however, could yield the same ester conversion even when the molar ratio of oil to methanol was reduced to 1:6.

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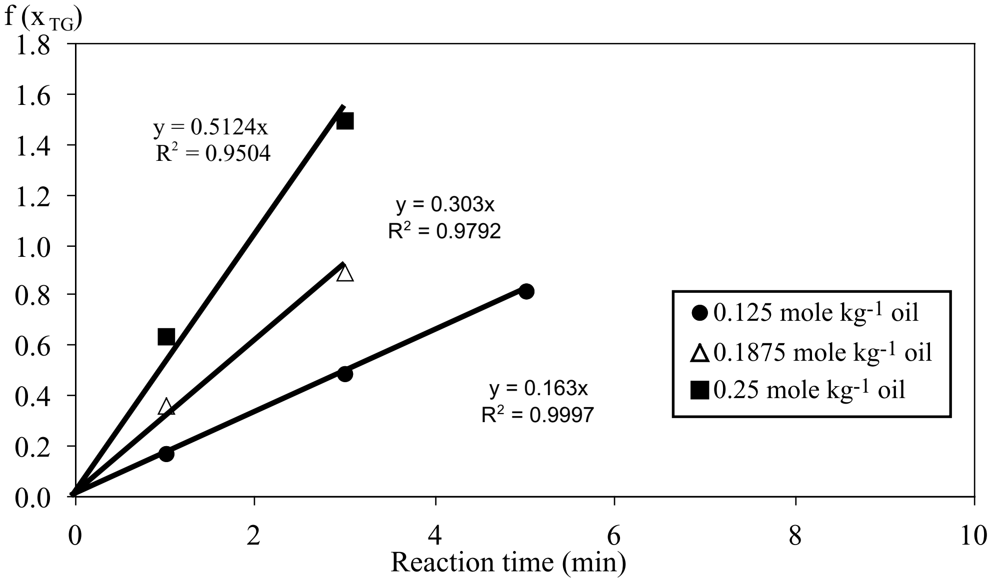
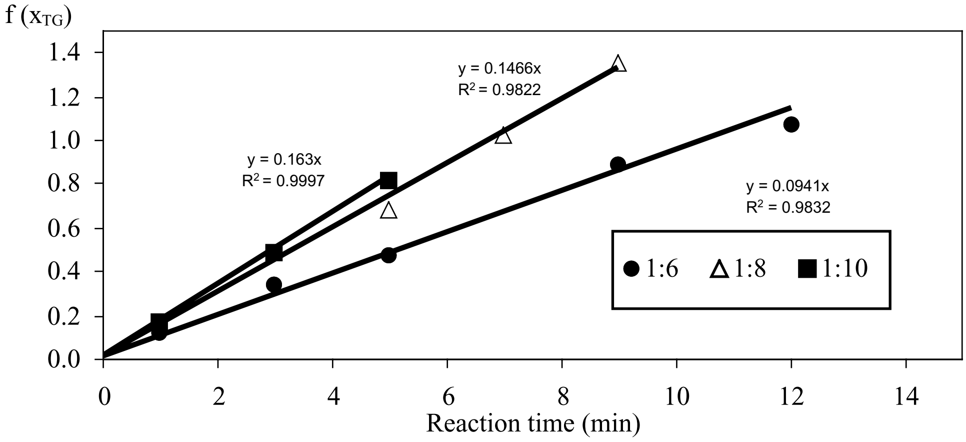


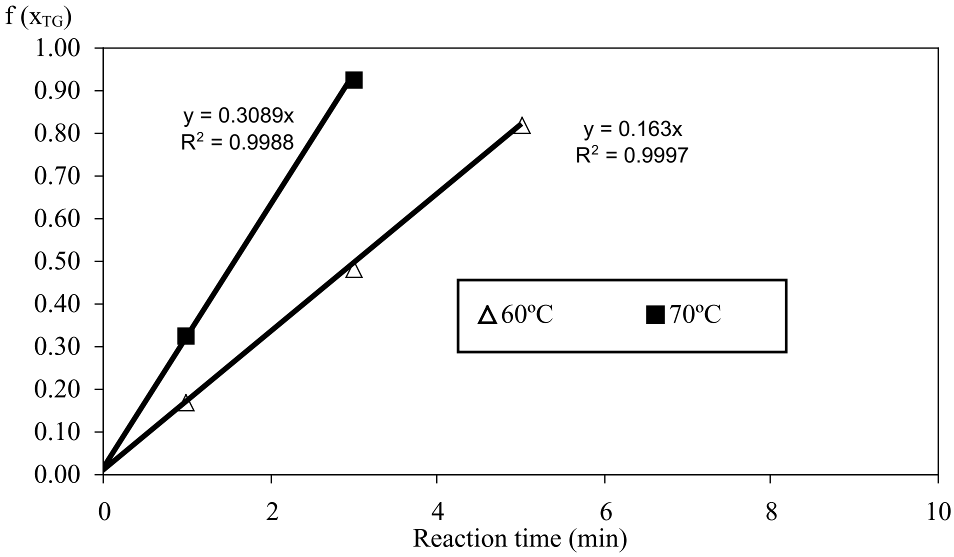
Note: Reaction conditions: Molar ratio of oil to methanol at 1:10.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 12. Graph of the integration method results for the transesterification reaction using sodium hydroxide as catalyst at various concentrations.



Note: Reaction conditions: Catalyst concentration at 0.125 mole kg^{-1} oil.
Reaction temperature at 60½C.
Stirring rate at 350 rpm.

Figure 13. Graph of integration method results for transesterification reaction using sodium hydroxide as catalyst at the various molar ratios of oil to methanol.



Note: Reaction conditions: Catalyst concentration at 0.125 mole kg^{-1} oil.
Molar ratio of oil to methanol at 1:10.
Stirring rate at 350 rpm.

Figure 14. Graph of integration method results for transesterification reaction using sodium hydroxide as catalyst at various reaction temperatures.

TABLE 1. REACTION PARAMETERS AND THE RESPECTIVE RATE CONSTANT FOR TRANSESTERIFICATION OF PALM OIL TO METHYL ESTERS USING SODIUM HYDROXIDE AS CATALYST

Molar ratio oil:methanol	Stirring rate (rpm)	Temperature (½C)	Catalyst concentration (mole kg^{-1} oil)	Rate constant, k (litre mole^{-1} min)
1:10	350	60	0.1250	0.163
1:10	350	60	0.1875	0.313
1:10	350	60	0.2500	0.526
1:6	350	60	0.1250	0.097
1:8	350	60	0.1250	0.147
1:10	350	70	0.1250	0.309

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