Kinetics of Transesterification of Palm-Based Methyl Esters with Trimethylolpropane

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ABSTRACT: Kinetics of transesterification of palm-based methyl esters (POME) with trimethylolpropane (TMP) to polyol esters was investigated. A kinetic model of reaction was obtained by assuming a series of irreversible elementary reactions at various temperatures. The reaction rate constants were determined under limited conditions. The optimal ratios for k_2/k_1 and k_3/k_1 were 0.70–0.80 and 0.21–0.25, respectively. Both palm oil methyl esters (PPOME) and palm-kernel oil methyl esters (PKOME) were reacted with TMP by using sodium methoxide as catalyst. The POME-to-TMP molar ratio and catalyst weight percentage were held constant at 10:1 and 0.4%, respectively. The effects of temperature (70–110°C) and raw materials (PKOME and PPOME) were investigated and found to have a significant impact on the reaction kinetics. When using a large excess of POME and continual withdrawal of methanol *via* vacuum, the reaction reached completion in less than 20 min at 80°C. After removal of unreacted POME, the final product contained approximately 98 wt% triesters.

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Biodegradable lubricants derived from vegetable oil-based basestocks exhibit better lubricity, an excellent viscosity index, and lower volatility than petroleum-based or synthetic lubricants (1–3). These characteristics should result in lower engine friction, increased fuel economy, and increased engine life. When blended with additives, some vegetable oil formulations perform as well as or better than the commercial standard, 10W-30 SG. Despite these advantages, vegetable oil-based lubricants have been slow in gaining wide acceptance as lubricants owing to their variable quality, higher cost compared with mineral oils, and inherent performance limitations (4). One of the techniques used to improve the lubrication properties of the vegetable oil is to change the structure of the oil by converting it to a new type of ester called polyol esters. It is a synthetic ester because it is no longer in its natural form (vegetable oil). Properties such as viscosity index (VI), pour point, oxidative stability, and thermal stability are affected by the structure of the ester molecule. Hence, the combination of selected FA or esters of the oil with alcohol can produce synthetic esters with an appropriate structure for unique applications. Common fat-based synthetic lubricants are of the following types: branched polyol esters, mono- and dibasic esters, and glycol esters (5). The most important group is the polyol esters derived from branched polyol. Having no hydrogen atom on the β-carbon of its structure provides these esters with a high degree of thermal stability seldom found in vegetable oils (4).

Vegetable oil-based polyol esters have been produced in various ways from FA (6,7) and FAME (8,9). In Malaysia, palm-based methyl esters (POME) are assuming an increasingly important role as starting materials in the oleochemical industry. Methyl esters are reportedly superior to FA for producing a number of FA derivatives. Their production cost is also more competitive owing to lower capital and energy costs. Consequently, POME were chosen as starting materials in the synthesis of polyol esters as lubricants. The polyol selected was trimethylolpropane (TMP), as it is branched and has a relatively low m.p. The transesterification reaction involves cleavage of an ester group, RCOO–, from POME by the –OH group of TMP to produce the new palm-based TMP esters. Since there are three –OH groups in TMP, the process yields intermediate formation of monoesters (ME), diesters (DE), and triesters (TE). Methanol (M = MeOH) is a by-product that is removed to ensure completion of the reaction (Eqs. 1–4):

$$\text{TMP} + \text{POME} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \text{ME} + \text{M} \qquad [1]$$

$$\text{ME} + \text{POME} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \text{DE} + \text{M} \qquad [2]$$

$$\text{DE} + \text{POME} \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \text{TE} + \text{M} \qquad [3]$$

The overall reaction is

$$\text{TMP} + 3\text{POME} \underset{k_0'}{\overset{k_0}{\rightleftharpoons}} \text{TE} + 3\text{M} \qquad [4]$$

Although there are many reports on the transesterification kinetics of vegetable oils to methyl esters including soybean, rapeseed, and palm oils (10–13), there is no published report on the kinetics of transesterification of POME with polyol. Furthermore, most of the work on soybean oil used mathematical simulators to solve multiple rate equations simultaneously for the rate constants that provide the best fit to the experimental data (11,12). However, according to Levenspiel (14), in multiple complex reactions (Eqs. 1–4), the more important performance parameter would be the product distri-

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bution equation relating the rates of change of a certain component with respect to another rather than the rate of an individual reaction. On the basis of the simplicity of this approach in analyzing the kinetics of complex reactions, it will be examined further in this study.

EXPERIMENTAL PROCEDURES

Palm oil methyl esters (PPOME) and palm-kernel oil methyl esters (PKOME) were obtained from Carotech Sdn. Bhd. (Ipoh, Perak, Malaysia) and Cognis Oleochemicals Sdn. Bhd. (Teluk, Panglima Garang, Selangor, Malaysia) respectively. TMP was supplied by Merck-Schuchardt (Hohenbrunn, Germany); sodium methoxide and other chemicals were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). *N*,*O*-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) was purchased from Fluka Chemie AG (Buchs, Switzerland). The FA compositions of these samples were determined according to the standard methods for oils and fats analysis (15): PPOME (wt%): C12:0, 0.9; C14:0, 1.5; C16:0, 41.5; C16:1, 0.3; C17:0, 0.1; C18:0, 2.7; C18:1, 40.6; C18:2, 11.9; C18:3, 0.5; PKOME (wt%): C10:0, 0.1; C12:0, 48.9; C14:0, 18.8; C16:0, 10.2; C18:0, 2.7; C18:1, 17.0; C18:2, 2.2. The calculated mean M.W. of the esters were determined from the FA compositions: PPOME, 287; PKOME, 240.

Transesterification of palm-based TMP esters. Reactions were performed in a 500-mL three-necked flask equipped with a thermometer, a sampling port, and a reflux condenser. The condenser was connected to a vacuum line equipped with a relief valve, accumulator, and a vacuum trap. The reactor was immersed in a temperature-controlled oil bath and stirred with a magnetic stirrer. The reactor was filled with 200 g of POME and heated to the desired temperature. The vacuum was maintained constant throughout the process by using the vacuum controller. A known amount of TMP was then added, and the mixture was heated to the operating temperature before catalyst was added. The vacuum was applied gradually after adding catalyst to avoid spillover of reaction materials.

The highest conversion to TMP triesters was obtained at a molar ratio of POME-to-TMP of 3.9:1. However, the reaction employing a 3.9:1 ratio occurred so spontaneously and rapidly that the isothermal condition could not be maintained. Temperature drops of approximately 30 to 40°C were encountered at this ratio, depending on the reaction temperature. Consequently, a 10:1 ratio was used in all experiments. This ratio provided the necessary heat reservoir to maintain the temperature and drive the forward reaction. In the transesterification of palm oil and soybean oil, the typical molar ratio is 6:1 (10,11) but an earlier report (12) showed that at 30:1 ratio the rate constant for the reverse reaction is decreased by almost 200% and the reactions are generally first order. Sodium methoxide was chosen as the catalyst since the alkaline catalyst esterifies vegetable lipids in an anhydrous methanol better than the acid catalyst (16). Moreover, the use of sodium methoxide minimizes alkaline hydrolysis or the saponification of esters often encountered with sodium hydroxide.

The catalyst amount was fixed at 0.9% w/w based on the total mass at a molar ratio of 3.9:1, or at 0.4% based on the total mass at 10:1 molar ratio. The literature suggests an optimal value of between 0.5 and 1.0 wt% for most transesterification reactions (8). The reactions were carried out at 70, 80, 90, 100, and 110°C to examine the dependency of the rate constants on temperature. Samples were taken at specified time intervals for analysis. Each sample was collected in a small vial, capped, and kept in a refrigerator at 2°C prior to analysis. Samples were analyzed for POME, ME, DE, TE, and TMP by GC (17).

RESULTS AND DISCUSSION

Palm oil produces two different types of oil: Palm-kernel oil is obtained from the nut, whereas palm oil is from the mesocarp. The methyl esters of both oils were used in the synthesis to examine the effect of FA composition on lubricating characteristics. The molar ratio of POME to TMP was fixed at 10:1 to maintain dilute system. The experiments were designed to determine the rate constants and activation energies for reactions shown in Equations 1–3.

Transesterification analysis. Figures 1A and 1B show product distribution curves for the transesterification of PPOME and PKOME with TMP at 80°C, respectively. The curves for DE and TE have zero initial slopes, suggesting that

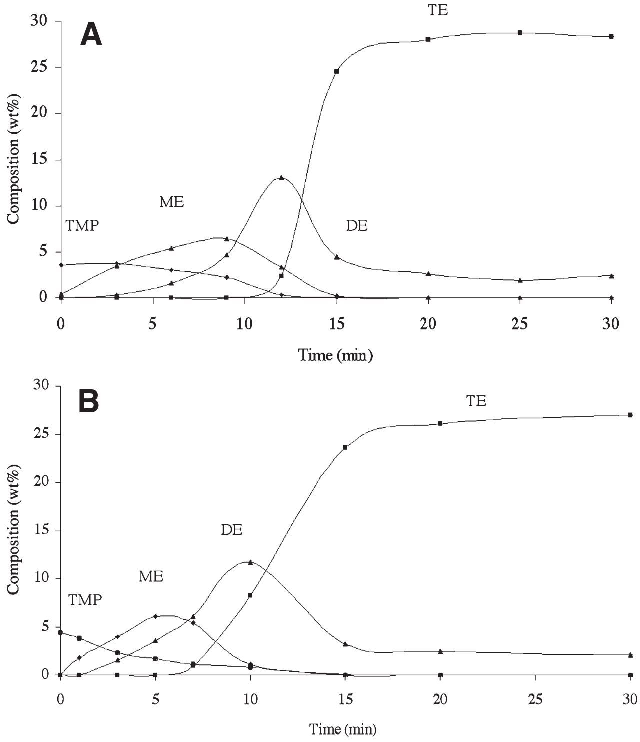

FIG. 1. Product distribution curves for the transesterification of palm-based methyl esters (POME) with trimethylolpropane (TMP) at 80°C. (A) Palm-kernel oil methyl esters, (B) palm oil methyl esters. Monoesters (ME), diesters (DE), triesters (TE). Molar ratio of POME/TMP was 10:1; catalyst, 0.9 wt% sodium methoxide.

DE and TE were not formed directly from TMP. However, ME was formed directly from TMP because of its nonzero initial slope. Furthermore, there was only a small concentration of DE and a zero concentration of ME in the product, thus confirming the postulated reaction mechanism represented by Equations 1–4. The formation of TE began only after 5–10 min of reaction. The rate was slow at the beginning, followed by a sudden increase in rate, and finally reached equilibrium in 20 min. During the first few reactions, DE had to compete with both TMP and ME for POME to form TE and hence slowed down the rate of TE production. With the formation of ME from TMP followed by the decomposition of ME to form DE, there was a progressive buildup of DE and depletion of TMP and ME. The process was repeated until the concentration of DE reached a maximum, decreased, and finally reached equilibrium. The sudden surge in rate of TE formation coincided with the point when the concentration of diesters was at a maximum. This maximum concentration formed by the intermediate is typical of an irreversible series reaction and thus substantiates the assumption of a negligible reversible reaction made earlier (14). The concentrations of intermediates in reversible series reactions usually do not pass through a maximum.

Under the operating conditions employed in this study, the reaction reached completion in less than 20 min at 80°C. After removal of unreacted POME, the final product contained approximately 98 wt% TE. Earlier, Uosukainen *et al.* (8) reported up to 99% total conversion to TMP rapeseed esters in 10 h at 120°C. However, the polyol esters were a mixture of ME, DE, and TE. The improvement in conversion and reaction time is attributed to efficient vacuum and higher excess percentage of methyl ester used in this work.

Effect of temperature. Figures 2A and 2B illustrate the influence of temperature on palm-kernel oil and palm oil TMP ester synthesis at 70–110°C. The selected temperature range was chosen to be high enough to melt TMP (m.p., 60°C) and to allow for homogeneous mixing between reactants. The maximal temperature was constrained by the b.p. of the methyl esters. At high vacuum (10 mbar), methyl ester boils at a considerably lower temperature and can be pulled off by a vacuum should the temperature go too high. Figure 2A shows that the reaction was relatively slow at 70°C, where palm oil TMP TE appeared only after 40 min of reaction. However, when the temperature was increased to 80°C, it took only 10 min for TE to form and another 10 min to complete the reaction. The reaction was further improved as the temperature was raised to 90 and 100°C. However, the effect was reduced when it reached 110°C. Although the rate of reaction at 110°C was much faster than at 80°C, the equilibrium value of TE was very much lower. Similar time courses at various temperatures are also shown in the transesterification of PKOME (Fig. 2B). This reaction exhibited similar behavior at temperatures above 90°C as encountered by POME synthesis at 110°C. The occurrence of the reverse reaction of TE to DE was significant at higher temperatures, hence reducing the overall yield of TE. In addition, the reaction also exhibited stabilization of DE concentration at extended times. After a certain period of time, the rate of the reverse reaction gradually increased until it attained an equilibrium condition, where the rate of the reverse reaction equaled the rate of the forward reaction, i.e., net $r_{\mathrm{DE,net}} = 0$. Consequently, the results indicate that the assumption of irreversible reaction is only applicable for short reaction times and moderate temperatures, explicitly, below 110 and 90°C for palm oil and palm-kernel oil, respectively.

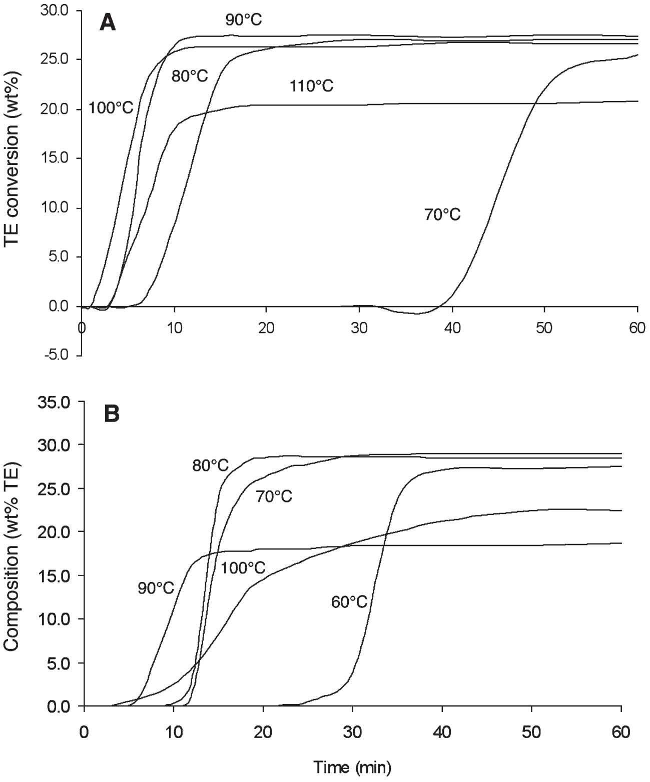

FIG. 2. The effect of temperature and time on the composition of TE in synthesis of palm-based TMP esters at 70–110°C. (A) Palm-kernel oil methyl esters, (B) palm oil methyl esters. See Figure 1 for abbreviations.

Reaction kinetics. The curves in Figures 1A and 1B suggest that the transesterification of POME with TMP follows a multiple series–parallel reaction mechanism (15). For TMP to decompose to form ME, the second-order kinetics would be as follows:

$$-r_{\mathrm{TMP}} = -d[\mathrm{TMP}]/dt = k_1\{[\mathrm{TMP}][\mathrm{POME}] - (1/K_1)[\mathrm{ME}][\mathrm{M}]\} \quad [5]$$

where $K_1 = k_1/k_1'$. To suppress the reverse reaction so that $k_1 >> k_1'$ and $1/K_1 \approx 0.0$, we applied excess POME as well as continuous withdrawal of methanol *via* vacuum.

With that assumption, Equation 5 is reduced to

$$-d[\mathrm{TMP}]/dt = k_1[\mathrm{TMP}][\mathrm{POME}] \quad [6]$$

If we assume that all reactions are irreversible, second order and of constant density, the rates of formation of ME and DE are given by

$$-d[\mathrm{ME}]/dt = k_2[\mathrm{ME}][\mathrm{POME}] - k_1[\mathrm{TMP}][\mathrm{POME}] \qquad [7]$$

$$-d[\mathrm{DE}]/dt = k_3[\mathrm{DE}][\mathrm{POME}] - k_2[\mathrm{ME}][\mathrm{POME}] \qquad [8]$$

Since these rate equations are interrelated, integrating with respect to time to establish the expression for the concentration of components would be complicated. A more convenient way is to eliminate the time variable by dividing one rate equation by another as recommended by Smith (18). Equations 7 and 8 are divided by Equation 6 to yield

$$\frac{d[\mathrm{ME}]}{d[\mathrm{TMP}]} = \frac{k_2[\mathrm{ME}]}{k_1[\mathrm{TMP}]} - 1 \qquad [9]$$

$$\frac{d[\mathrm{DE}]}{d[\mathrm{TMP}]} = \frac{k_3[\mathrm{DE}]}{k_1[\mathrm{TMP}]} - \frac{k_2[\mathrm{ME}]}{k_1[\mathrm{TMP}]} \qquad [10]$$

The process of dividing one rate equation by another would directly yield an equation that relates the distribution of certain products with respect to other components present in the system. Performance parameters for multiple reactions, such as selectivity and fractional yield, can advantageously be based on this product distribution. These parameters are more important in complex multiple reactions than the rates themselves.

In this study, the approach was to derive an expression for product distribution relating the rate of change of the intermediates with respect to the concentration of the limiting reactant, [TMP], by solving Equations 9 and 10. Since the distribution curve for the intermediates, ME and DE, have maxima, the locations of these maxima were used to determine the rate constants. The rate constants that provided the best fit to the experimental data were then applied in the rate equations. Since we did not use mathematical simulators in our study, the derivation of the expression relied heavily on process assumptions such as an irreversible process. The integral form of Equation 6 was derived as

$$\ln\left\{\frac{[\mathrm{TMP}_o][\mathrm{POME}]}{[\mathrm{TMP}][\mathrm{POME}_o]}\right\} = \frac{k_1}{A}t \qquad [11]$$

where $A = 1/([\mathrm{TMP}_o] - [\mathrm{POME}_o])$. The straight-line plot shown in Figure 3 strongly supports our hypothesis that TMP transesterification follows second-order irreversible kinetics. The R^2 values at 70–110°C are generally high, at 0.9903, 0.9972, 0.9923, 0.9938, and 0.9936, respectively. Rearranging Equation 11 and using a mass balance, we get

$$[\mathrm{TMP}]/[\mathrm{TMP}_o] = \frac{[\mathrm{POME}_o] - [\mathrm{TMP}_0]}{[\mathrm{POME}_o]e^{(k_1/A)t} - [\mathrm{TMP}_o]} \qquad [12]$$

On assuming a negligible reverse reaction, the product distribution for monoesters, [ME], in terms of [TMP] was solved from Equations 6 and 9 as

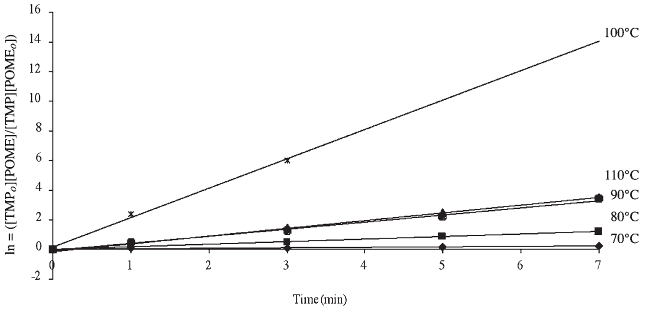

FIG. 3. Second-order reaction model of palm oil TMP ester synthesis at various temperatures. ▲,110°C, $r^2 = 0.9936$; *,100°C, $r^2 = 0.9938$; ●, 90°C, $r^2 = 0.9923$; ■, 80°C, $r^2 = 0.9972$; ◆, 70°C, $r^2 = 0.9903$. See Figure 1 for abbreviations.

$$[\mathrm{ME}] = [\mathrm{TMP}_o]\left(\frac{k_1}{k_1 - k_2}\right)\left\{\left(\frac{[\mathrm{TMP}]}{[\mathrm{TMP}_o]}\right)^{k_2/k_1} - \left(\frac{[\mathrm{TMP}]}{[\mathrm{TMP}_o]}\right)\right\} \qquad [13]$$

Substituting Equation 12 into Equation 13, we obtained an approximate expression of [ME] = *f*(*t*). By setting the derivative of [ME] with respect to time equal to zero, we solved for time when the concentration of ME reaches the maximum,

$$t_{\mathrm{max,ME}} = \frac{1}{k_1C_1}\ln\left(\frac{[\mathrm{TMP}_o] + C_1/C_2^{\,C_3}}{[\mathrm{POME}_o]}\right) \qquad [14]$$

where $C_1 = [\mathrm{POME}_o] - [\mathrm{TMP}_o]$ and $C_2 = k_1/k_2$ and $C_3 = k_1/(k_2 - k_1)$. Since k_2 depends on $t_{\mathrm{max,ME}}$, the values of k_2 that satisfy $d[\mathrm{ME}]/dt = 0$ were found at various $t_{\mathrm{max,ME}}$ and predetermined k_1 as shown in Table 1. The k_2 values were then applied in Equation 13 to determine $[\mathrm{ME}]_{\mathrm{calc}}$, and the results were plotted and compared with experimental data. Good agreement between the calculated and experimental data indicated that the proposed kinetic model was correct. The effect of k_2 on $[\mathrm{ME}]_{\mathrm{calc}}$ was also assessed to determine the sensitivity of k_2 on [ME]. However, only a small range of k_2 values was considered because outside this range the values of $t_{\mathrm{max,ME}}$ would not be consistent with the experimental $t_{\mathrm{max,ME}}$ (30 min). Lines with a close fit to experimental data were obtained at $k_2/k_1 < 1.0$, specifically at a ratio between 0.70 to 0.80. The final k_2 was determined based on the average value along with its corresponding level of certainty. In the synthesis of palm oil TMP ester at 70°C, the optimal k_2 was 0.0294 ± 0.002. A similar effect was also observed in the synthesis of palm oil TMP ester at other temperatures.

TABLE 1
Effects of $t_{\mathrm{max,ME}}$ on k_2 in Palm Oil TMP Ester Synthesis[a] at 70°C

$t_{\mathrm{max,ME}}$	k_2	$t_{\mathrm{max,ME}}$	k_2
20	0.0734	34	0.0265
30	0.0342	35	0.0250
31	0.0321	40	0.0187
32	0.0301		

[a] $t_{\mathrm{max,ME}}$, time (min) of maximal synthesis of monoester; TMP, trimethylolpropane; k_2 is expressed as $(\mathrm{wt\%} \cdot \mathrm{min})^{-1}$.

For Equation 3, the derivation of the rate equation was rather intricate since it involved three reactions simultaneously. However, by dividing rate Equation 8 by Equation 6, we obtained Equation 10, and on substitution of the initial concentration of [DE] = 0 at $t = 0$, the final expression for the changing concentration of DE with time yields

$$[\mathrm{DE}] = R_1\left\{R_2\left(\frac{[\mathrm{TMP}]}{[\mathrm{TMP}_o]}\right) - R_3\left(\frac{[\mathrm{TMP}]}{[\mathrm{TMP}_o]}\right)^{k_2/k_1} + R_4\left(\frac{[\mathrm{TMP}]}{[\mathrm{TMP}_o]}\right)^{k_3/k_1}\right\} \quad [15]$$

where $R_2 = (k_2 - k_3)$; $R_3 = (k_1 - k_3)$; $R_4 = (k_1 - k_2)$; and $R_1 = \{[\mathrm{TMP}_o]k_1k_2\}/R_2R_3R_4$. The rate constant k_3 is a function of both k_1 and k_2. Adopting a similar approach as in k_2, k_3 was obtained from trial-and-error calculations by differentiating Equation 15 with respect to time and setting $d[\mathrm{DE}]/dt = 0$. Using various $t_{\mathrm{max,DE}}$, we obtained k_3 values at constant k_1 and k_2 and analyzed the effects of $t_{\mathrm{max,DE}}$ on [DE] calculated from Equation 15 as shown in Figure 4. In the synthesis of palm oil TMP esters at 90°C, $[\mathrm{DE}]_{\mathrm{max}}$ occurred after 7 min of reaction. At $k_1 = 0.5417$, $k_2 = 0.3939$, this would correspond to a k_3 of 0.0942. Variation of k_3 (or $t_{\mathrm{max,DE}}$) had a marginal effect on $[\mathrm{DE}]_{\mathrm{calc}}$ as long as $t_{\mathrm{max,DE}}$ was kept close to the experimental value (Fig. 4).

Rate constants. Rate constant k_1 was fixed by second-order kinetics obtained from the slope of the plot shown in Figure 2. Using k_1, k_2 values were calculated at various $t_{\mathrm{max,ME}}$ as explained earlier. A close fit of the lines to the experimental points suggests that the kinetic scheme employed is adequate, and from this the rate constants may be proposed. Excellent fits to experimental [ME] data at 70–110°C were obtained at k_2/k_1 ratios of 0.79, 0.76, 0.80, 0.76, and 0.70. These results suggest that the optimal ratio would be between 0.7 and 0.8. The ratio of k_2/k_1 affects the values of $[\mathrm{ME}]_{\mathrm{calc}}$ and $[\mathrm{DE}]_{\mathrm{calc}}$ in opposite manners. $[\mathrm{DE}]_{\mathrm{calc}}$ decreased rapidly as we reduced the k_2/k_1 ratio to improve the values of $[\mathrm{ME}]_{\mathrm{calc}}$. To maintain good estimates of $[\mathrm{DE}]_{\mathrm{calc}}$, very small k_3 and large $t_{\mathrm{max,DE}}$ were required. However, several $t_{\mathrm{max,DE}}$ values are actually possible because $d[\mathrm{DE}]/dt = 0$ could occur at the maximum concentration ($[\mathrm{DE}]_{\mathrm{max}}$) or at equilibrium ($[\mathrm{DE}]_{\mathrm{eq}}$). Again, the best k_3 would be the value that generates the best model for [DE] at predetermined k_1 and k_2 values regardless of the $t_{\mathrm{max,DE}}$. The optimal ratio of k_3/k_1 at different reaction temperatures ranged from 0.18 to 0.21, whereas the ratio of k_3/k_2 ranged from 0.24 to 0.25.

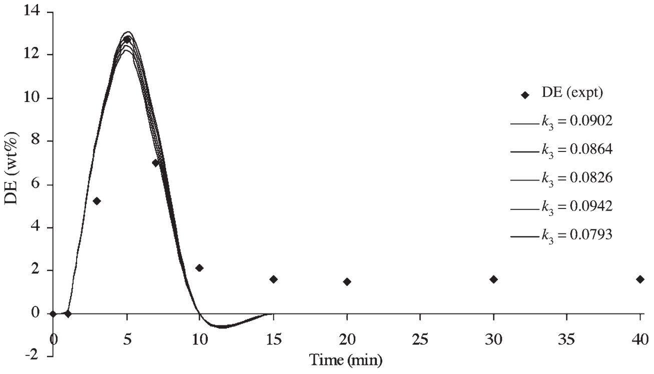

FIG. 4. Effects of k_3 on calculated DE (wt%) in palm oil-based TMP ester synthesis at 90°C. $k_1 = 0.5417$; $k_2 = 0.3939$. See Figure 1 for abbreviations.

The optimal reaction rate constants for each of the three reactions involved in the transesterification of POME with TMP, namely, k_1, k_2, and k_3, are shown in Table 2. The level of uncertainty is approximately 3% of the average value of each of the rate constants. For instance, the level of uncertainty of the k_2 value at 100°C is 0.05, with an average value of 1.6525. The ratios of rate constants k_2/k_1 and k_3/k_1 were calculated to be 0.7–0.8 and 0.18–0.21, respectively. More than one combination of k_1, k_2, and k_3 was actually possible at each reaction temperature. Thus, the solutions were non-unique and posed a tremendous challenge to us in establishing the optimal rate constants for these reactions. The key parameter would be the value of k_1, which depends primarily on the experimental data of [TMP]. In our experience, both first- and second-order kinetics could be used to determine k_1 as long as the ratio of POME/TMP was not less than 10:1. Once k_1 was established, both k_2 and k_3 could be estimated using the ratios. To date, there is no published report on the kinetics of POME transesterification with TMP.

The activation energies (E_a) were estimated from the Arrhenius equation [$\log_{10} k = (-E_a/2.303R)/T + C)$]. From a plot of log k vs. $1/T$, the slope, which equals $-E_a/2.303R$, can be determined. An example is shown in Figure 5 for palm oil TMP ester synthesis at 70–100°C. Since the model is only valid for temperatures below 110°C, the data at 110°C were not included in the plot. The activation energies for the three reactions were similar, ranging from 33.3 to 33.9 kcal/mol (Table 3). The only reports of E_a values for k_1, k_2, and k_3 are for transesterification reactions of vegetable oils with methanol to form methyl esters (10–12). Darnoko and Cheryan (10) reported activation energies for the reactions involved in the transesterification of palm oil with methanol in the range of 6.4 to 14.7 kcal/mol under atmospheric pressure and at 50–65°C. Although direct comparison could not be made between these data, the activation energies for transesterification of POME with TMP are higher than

TABLE 2
Average Reaction Rate Constants at Different Temperatures in the Synthesis of Palm Oil and Palm-Kernel Oil TMP Esters[a]

	Rate constants (wt%·min)$^{-1}$		
Temperature (°C)	k_1	k_2	k_3
Palm oil methyl ester			
70	0.0368	0.0294	0.0074
80	0.1877	0.1425	0.0410
90	0.5417	0.3939	0.0942
100	2.1812	1.6525	0.4600
110	0.5134	0.3820	0.0953
Palm-kernel oil methyl ester			
70	0.0977	0.0606	0.0132
80	0.1538	0.0978	0.0218
90	0.3939	0.2521	0.0552
100	0.4013	0.1364	0.0044

[a]For abbreviation see Table 1.

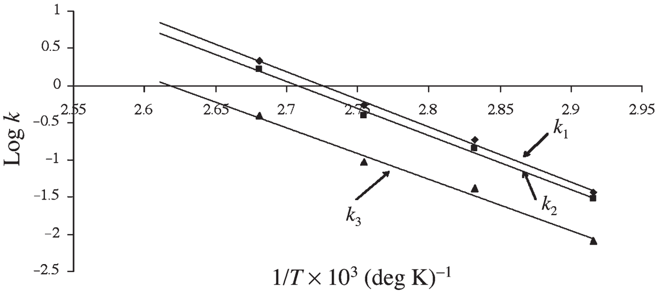

FIG. 5. Arrhenius plot showing the temperature dependency of the reaction rate constants. ◆, k_1, ■, k_2, and ▲, k_3. Molar ratio of POME/TMP was 10:1, catalyst 0.9 wt% sodium methoxide. See Figure 1 for abbreviations.

TABLE 3
Activation Energy for Transesterification of TMP, Monoesters (ME), and Diesters (DE) with Palm Oil and Palm-Kernel Oil Methyl Esters[a]

Reaction	Rate constant	E_a (kcal/mol)	R^2
Palm oil methyl ester			
TMP ↔ ME	k_1	33.9	0.9953
ME ↔ DE	k_2	33.3	0.9945
DE ↔ TE	k_3	33.6	0.9851
Palm kernel oil methyl ester			
TMP ↔ ME	k_1	17.2	0.9544
ME ↔ DE	k_2	17.6	0.9590
DE ↔ TE	k_3	17.6	0.9654

[a]For other abbreviation see Table 1.

of palm oil with methanol. Since the synthesis of palm-based TMP esters took place under vacuum, the reactions were more sensitive to temperature variation and resulted in higher activation energies.

The activation energies for k_1, k_2, and k_3 in palm kernel TMP ester synthesis were 17.2, 17.6, and 17.6 kcal/mol, respectively. Although this implies that the temperature affects these intermediate reactions in a similar manner, it also indicates that the reactions involving PKOME are less sensitive to temperature than PPOME. This is due to smaller activation energies resulting from palm-kernel oil TMP ester synthesis compared with those from palm oil TMP ester synthesis. However, since we carried out the experiments for PKOME only at limited temperatures, the results might not be reliable.

To verify the kinetic parameters obtained in this work, 13 sets of experimental data from the transesterification of PPOME with TMP at 80°C were compared with the values calculated from the model equations. By using the rate constants tabulated in Table 3, the product distribution model proposed for [DE] (Eq. 14) was fitted to the experimental data, as shown in Figure 6A. The close fits of lines to points at this temperature and the other three temperatures studied in the region away from the equilibrium strongly support the validity of the proposed models and the rate constants resulting from the curve fitting. The sum of squared errors for calculated [DE] using k_1, k_3, and k_3 in Table 3, as compared with experimental data at different temperatures at 70, 80, 90, and 100°C, were 10.1, 12.1, 23.7, and 43.4 for a total of 89.3. The higher the temperature, the greater the errors encountered by the model. Other supportive evidence for the proposed model is the correlation coefficients obtained by linear plots to determine energies of activation (Fig. 4). The coefficients were generally high, at 0.9953, 0.9945, and 0.9851 for k_1, k_2, and k_3, respectively.

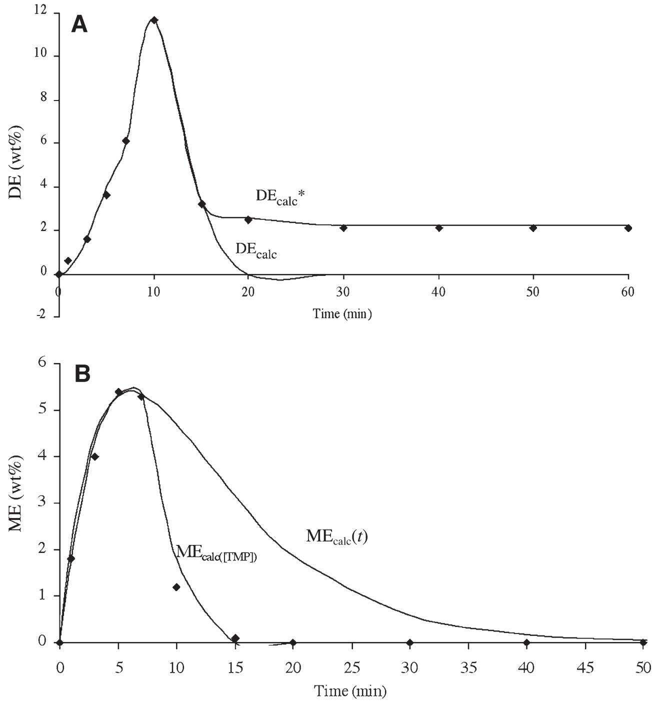

FIG. 6. Comparison between the calculated and experimental values of (A) [DE] and (B) [ME] during the transesterification of palm-kernel oil methyl esters with TMP at 80°C. See Figure 1 for abbreviations.

However, the model failed to predict [DE] at equilibrium. Since it correlated [DE] in terms of the limiting reactant [TMP], the value of [DE] was zero when TMP diminished from the reaction media (completely reacted) at equilibrium. (TMP is completely reacted and no longer exists in the reaction media.) During the course of the reaction, more DE was accumulated in the system due to the lower rate of DE decomposition to TE than was attributed to the rate of DE formation from ME ($k_3 < k_2$). At this point, the rate of reverse reaction had gradually increased as more ME formed and less POME remained in the system. When the reaction finally reached equilibrium, the rate of forward reaction would be equal to the rate of the reverse reaction, and the stabilization of [DE] would prevail. This proves that the irreversible model is not valid at the later stages of reaction. However, when we substituted the [TMP] after 15 min with low values, i.e., 6×10^{-4}, 2×10^{-4}, 1×10^{-5} wt%, we obtained the curve $\mathrm{DE_{calc}}$* shown in Figure 6A with a total sum of squared error of 0.22, compared with 12.1 produced by the $\mathrm{DE_{calc}}$ curve. Since the GC analysis ignored small concentrations, the TMP concentrations at later stages of reaction were assumed to be zero. The assumption of zero TMP concentrations contributed significantly to the inconsistencies between the proposed model and the experimental data.

The [ME] values calculated from Equation 13 were also compared against the experimental values at 80°C (Fig. 6B). Examination of the results showed a close fit of the lines to the experimental data. This indicates that the proposed kinetic scheme was valid for ME distribution at all stages of reaction. When [ME] reached the maximum, it competed favorably with TMP for POME to form DE, thus producing more DE, and quickly disappeared from the system together with TMP. Moreover, the rate of ME decomposition to DE was much higher than the rate of DE decomposition to TE ($k_2 > k_3$). Since the model correlates [ME] with [TMP], good agreement between calculated and experimental data was obtained for [ME]. The indictors used to determine the goodness of fit include the total sum of squared errors and R^2. The R^2 was 0.9918, and the total sum of squared errors was 0.12, largely due to errors incurred at the later stages of reaction. The [ME] were also correlated with respect to time by substituting the ratio [TMP]/[TMP_o] in Equation 13 with Equation 12. The results are shown in Figure 6B as [$\text{ME}_{\text{calc}}(t)$] with a total sum of squared errors of 16.89. Hence, the best model for [ME] would be Equation 13, which correlates [ME] with experimental [TMP].

Finally, since the concentration is expressed in terms of weight percentage, the concentration of triesters [TE] can be determined by the difference,

$$[\text{TE}] = 100 - [\text{POME}] - [\text{TMP}] - [\text{ME}] - [\text{DE}] \qquad [16]$$

The product distribution models given by Equations 10, 11, and 13 allow us to estimate directly the concentrations of intermediates at certain periods of time. However, as shown earlier, the models are only applicable for initial reactions and moderate temperatures. Outside these limits, the assumption of irreversible reactions applied in the models is no longer valid. In addition the models rely heavily on the accuracy of the experimental [TMP].

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