

Kinetic Study of the Base-Catalyzed Transesterification of Monoglycerides from *Pongamia* Oil

Sanjib Kumar Karmee^a, P. Mahesh^b, R. Ravi^b, and Anju Chadha^{a,*}

Departments of ^aChemistry and ^bChemical Engineering, Indian Institute of Technology Madras, Chennai-600 036, India

ABSTRACT: The kinetics of the transesterification of vegetable oil is known to follow a three-step reaction mechanism. The third step involves the transesterification of MG. In this study, the transesterification of MG obtained from crude *Pongamia* oil was achieved with methanol in the presence of KOH as the catalyst. A MG/methanol ratio of 1:10 was used at different temperatures (30, 45, 55, and 60°C). ¹H NMR was used to monitor the progress of transesterification. The study revealed that the kinetics of this reaction followed a reversible second-order model, with a good fit obtained for all temperatures except 30°C. This result is explained as arising out of the importance of transport effects at low temperatures. The forward rate constant increased with an increase in temperature, whereas the reverse rate constant showed a decreasing trend, suggesting that the proposed reverse reaction was not an elementary step.

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Vegetable oils (edible or nonedible) and their derivatives are fast gaining recognition as fuels that have the potential to replace conventional fuels (1,2). Vegetable oils may be used directly as fuels, in which case they are referred to as straight vegetable oils, but it is their derivatives such as esterified oils, commonly called biodiesel, that are much sought-after owing to their superior fuel properties (3). Among others, some of the oils already in use as biodiesel are soybean, palm, and rapeseed (4–8). In India, a wide variety of nonedible oils are produced in addition to the edible oils. One of the nonedible oils being used as a diesel substitute is the oil from the seeds of *Pongamia pinnata*, commonly called Honge in the southern state of Karnataka (9). It is found in the native Western Ghats throughout India, northern Australia, Fiji, and in some regions of eastern Asia. In India, owing to its low cost, *Pongamia* oil is popular with farmers, who use it to run pumps that irrigate their fields (10). However, like other oils, there are limitations in the use of this nonedible oil as fuel. Its high viscosity and poor combustion characteristics cause poor atomization, fuel injector blockage, excessive engine deposits, and engine oil contamination (11). To improve the fuel quality of *Pongamia* oil, it must be esterified. This can be done by reacting it with an alcohol

(methanol is commonly used) in the presence of either a base or an acid catalyst to give FAME. Base catalysts are generally preferred over acid catalysts because they lead to faster reactions (12). The base catalysts generally used for transesterification reactions are NaOH, KOH, or their alkoxides. Potassium hydroxide is preferred over other bases because, at the end of the reaction, the reaction mixture can be neutralized with phosphoric acid. This produces potassium phosphate, which is a well-known fertilizer (13).

A kinetic study of the transesterification reaction of oils can provide parameters that can be used to predict the extent of reaction at any given time under particular reaction conditions (7). Oil is a complex mixture of glycerides with different chain lengths of FFA. The composition of an oil depends on the plant from which it is obtained. The FA profile of *Pongamia* oil, as reported in the literature (9), is presented in Table 1. As widely reported, oils contain mainly TG. However, the crude *Pongamia* oil used in this study contained ~35% DG and MG. The processing of oil also affects its properties (14). In addition to this, oils also differ in their FA profile, indicating the importance of having a kinetic model available for the transesterification of each oil that has the potential to be used as a biodiesel. The kinetics of the transesterification of vegetable oils (4,5) is usually modeled as a three-step process, as shown in Figure 1. In addition to the above set of elementary reactions, a shunt reaction also has been proposed (4), in which a TG molecule reacts directly with three molecules of methanol to yield three molecules of the methyl ester. However, Nouredini and Zhu (5), in their kinetic study of the transesterification of soybean oil, observed no improvement in the fit of their proposed model with the experimental results by adding a shunt reaction. The transesterification of soybean oil with methanol or 1-butanol proceeded according to pseudo first-order or second-order kinetics, depending on the molar ratio of alcohol to soybean oil (4), whereas the reverse reaction was second order (5). In the case of the transesterification of palm oil by methanol with KOH as a catalyst (6,7), again a three-step reaction sequence

TABLE 1
FA in *Pongamia* Oil^a

FA	Percentage	FA	Percentage
Palmitic	3.7–7.9	Lignoceric	1.1–3.5
Stearic	2.4–8.9	Eicosenoic	9.5–12.4
Oleic	44.5–71.3	Arachidic	2.2–4.7
Linoleic	10.8–18.3	Behenic	4.2–5.3

*To whom correspondence should be addressed at Department of Chemistry, IIT-Madras, Chennai-600 036, India. E-mail: anjuc@iit.ac.in

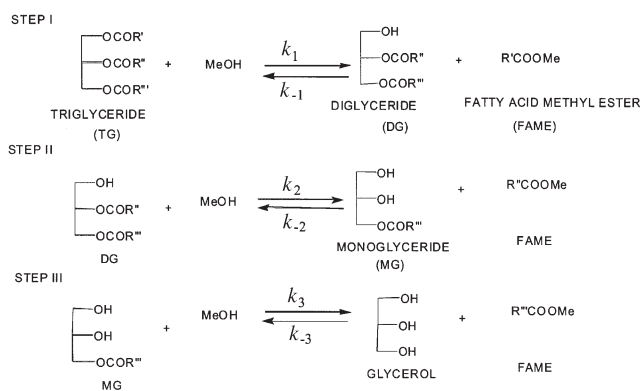


FIG. 1. Transesterification of oils: a three-step process.

was proposed. However, only data up to a reaction time of 30 min were considered, and each step was modeled as an irreversible second-order reaction in the concentration of the corresponding glyceride. Kusdiana and Saka (8) studied the transesterification of rapeseed oil using supercritical methanol without any catalyst. Temperatures as high as 500°C were used, and the rate of transesterification was modeled as first order in the oil concentration.

Two of the methods used to monitor the conversion of oil to its methyl esters are ^1H NMR (15,16) and ^{13}C NMR spectroscopy (17). The results obtained for the transesterification of soybean oil using ^1H NMR techniques are known to be in good agreement with the results obtained by NIR spectroscopy (18); hence, we used the NMR technique in this work.

In our approach to studying the kinetics of the transesterification of *Pongamia* oil, we studied the transesterification of MG, from which the rate constants of reaction step III were determined directly. On the other hand, in an experiment starting with TG (4), these rate parameters had to be determined along with at least four other rate constants (or more if a shunt reaction was assumed). As pointed out by earlier authors (19), this may lead to unreasonable values for the rate constant in steps II and III. This work is the first to study the kinetics of the transesterification of *Pongamia* oil; we report the kinetics of the transesterification of MG of *Pongamia* oil as a first step. Work is in progress to determine the kinetics of the transesterification of DG and TG as well.

EXPERIMENTAL PROCEDURES

Crude *Pongamia* oil was a gift from Dr. Udipi Srinivasa, Department of Mechanical Engineering, Indian Institute of Science, Bangalore, India. Methanol, potassium hydroxide, and acetic acid were purchased locally. Standard triolein, diolein, and monoolein were prepared as reported earlier (20). Stearic acid methyl ester was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). All solvents were used after distillation. Analysis of each sample was done using a 400-MHz ^1H NMR instrument (Bruker, Karlsruhe, Germany). The TG, DG, and MG used for the kinetic study of transesterification reactions were separated by column chromatography from crude *Pongamia* oil.

Separation of TG, DG, and MG from Pongamia oil. *Pongamia* oil (3 g) was analyzed by TLC and high-performance TLC using the solvent system *n*-hexane/ethyl acetate/glacial acetic acid (80:20:1, by vol). The TG, DG, and MG fractions were isolated and found to be in the ratio of 42:26:11. This ratio was further confirmed by the actual yields of the three glyceride fractions obtained after separation by column chromatography. The fractions obtained were characterized as TG, DG, and MG without further characterizing the FA in each of them. ^1H NMR was used to confirm the absence of DG and TG in the fraction of MG separated from *Pongamia* oil.

Typical procedure for the transesterification of MG of Pongamia oil with methanol. Transesterification reactions were performed in a 50-mL three-necked round-bottomed flask equipped with a reflux condenser and thermometer and placed in an oil bath with a temperature controller and magnetic stirrer. MG (4 g) were initially heated to 100°C for 10 min to remove trace amounts of water. The catalyst used was KOH (0.04 g, 1 wt%) (4,6) dissolved in the required amount of methanol. This solution was injected into the reaction chamber through a septum after the MG were cooled to the required temperature. Samples were removed at regular intervals with a syringe. Each sample (0.3 mL) was neutralized using glacial acetic acid and washed with water (10 mL \times 3) to remove unreacted base, glycerol, and trace amounts of soap. It was then extracted with *n*-hexane, and the organic layer was separated and concentrated to obtain a soaps and glycerol-free sample, which was analyzed using ^1H NMR with CDCl_3 -tetramethylsilane (TMS) as solvent.

Transesterification of MG at different temperatures. At a MG/MeOH molar ratio of 1:10 (M.W. of MG = 353; average M.W. of FFA = 278 + M.W. of glycerol backbone = 75), the reaction was performed at four different temperatures, i.e., 30, 45, 55, and 60°C.

RESULTS AND DISCUSSION

^1H NMR of MG. The MG fraction separated by column chromatography was characterized by ^1H NMR in CDCl_3 and TMS. The characteristic regions (Fig. 2) for MG observed by ^1H NMR were as follows.

MG. These could be 1- or 2-MG and were positional isomers. Consequently, the methylene protons at C-1 and C-3 were magnetically nonequivalent, due to which four double doublets were observed in the ^1H NMR spectra. The details of the ^1H NMR analysis are as follows: δ (ppm): 3.64–3.80 (2H, 2dd), 3.92 (1H, m), 4.0–4.4 (2H, 2dd), 3.82 (4H, m), and 4.93 (1H, m). The 2-MG, on the other hand, were symmetrical and the C-1 and C-3 methylene protons were magnetically equivalent and appeared as a multiplet, δ 3.82. The methine proton at C-2 also appeared as a multiplet, δ 4.93.

Effect of temperature. Figure 3 shows the conversion of MG to FAME at four different temperatures for a 1:10 molar ratio of MG to methanol. At 30°C, the transesterification reaction proceeded slowly. An optimal conversion of 64.11% was observed at 120 min. Further experiments revealed a limiting equilibrium conversion of 67.5% after 24–48 hours. The reaction was not only faster at 45 and 55°C but also yielded progressively

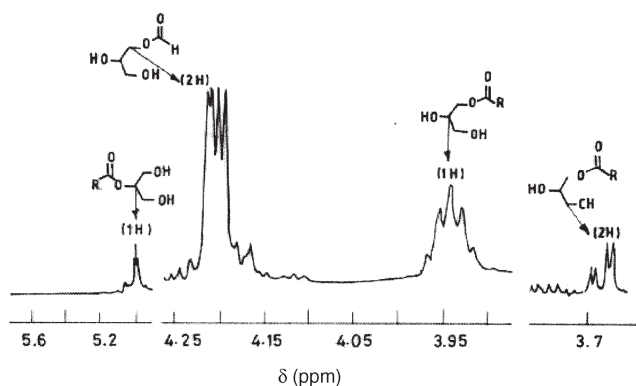


FIG. 2. Characteristic ^1H NMR signals of 1- and 2-MG.

higher equilibrium conversions (96.2 and 98.8%, respectively). At 60°C , conversions up to 30 min were higher than those at 55°C , after which there was no significant difference in conversion between the two temperatures.

Other qualitative features of the conversion vs. time plot are also worth noting. At the higher temperatures (45, 55, and 60°C), a sudden jump in conversion was evident after a short lag time of up to 10 min. This feature also has been reported elsewhere (4,5). The initial lag phase is usually attributed to the transport effects required to transfer the methanol into the oil phase. This initial surge was followed by a slowing down as the reaction approached completion. At 30°C , however, there was a relatively steady increase in conversion after the initial lag period. The conversion levels were also distinctly lower. These results are consistent with the expected domination of transport effects at lower temperatures (17).

A kinetic model for the transesterification of MG. The conversion of MG at any given time is defined as the number of moles of MG reacted per unit mole of MG in the initial reaction mixture. If we neglect volume changes due to the reaction, then the conversion, X , is given by

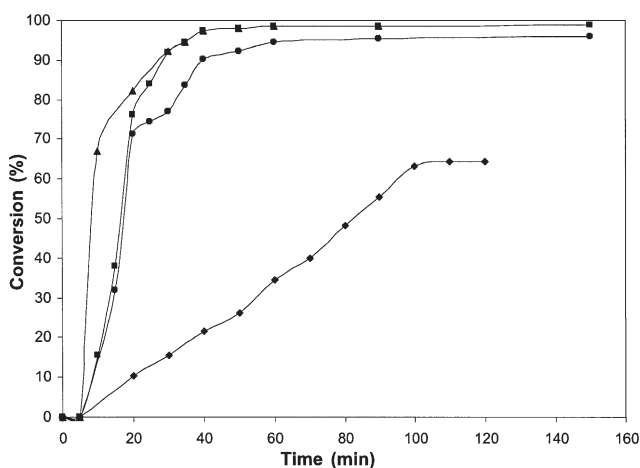


FIG. 3. The conversion of MG to FAME at four different temperatures for a 1:10 molar ratio of MG to methanol: (\blacktriangle) 60°C ; (\blacksquare) 55°C ; (\bullet) 45°C ; (\blacklozenge) 30°C .

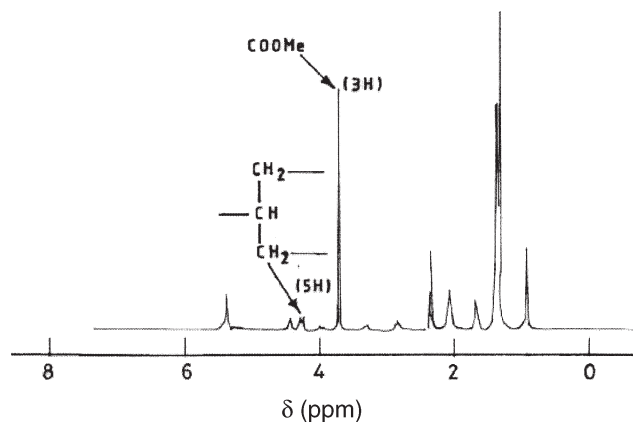


FIG. 4. A typical ^1H NMR spectrum showing the progress of transesterification of MG.

$$X = 1 - \frac{[\text{MG}]_t}{[\text{MG}]_0} \quad [1]$$

where $[\text{MG}]_t$ and $[\text{MG}]_0$ are the concentrations of MG in moles per liter at time t and at time $t = 0$, respectively. In this study, the progress of the transesterification reaction was monitored through ^1H NMR (Fig. 4). A formula for the conversion of TG to methyl esters is given in Reference 15. This formula, modified for the case of MG, leads to

$$X = \frac{5I_{\text{ME}}}{5I_{\text{ME}} + 3I_{\text{MG}}} \quad [2]$$

where I_{ME} and I_{MG} are the integration values of the signals associated with the esters and glycerides, respectively. In obtaining Equation 2, we note that since one mole of ME results from every mole of MG reacted, we may write

$$I_{\text{ME}} \propto 3X \quad [3]$$

The factor 3 accounts for the three protons in a methyl of the methyl ester molecule. Similarly,

$$I_{\text{MG}} \propto 5(1 - X) \quad [4]$$

as there are five protons (four methylene and one methine) in the glyceryl backbone of an MG molecule. Previous kinetic studies of the transesterification of oils (4,5) indicate that a general model for the kinetics of step III (Fig. 1) is that both the forward and reverse reactions are first order in each of the species involved. Thus, the progress of the reaction in a batch reactor is represented by

$$-\frac{d[\text{MG}]}{dt} = k_3[\text{MG}][\text{MeOH}] - k_{-3}[\text{G}][\text{ME}] \quad [5]$$

where k_3 and k_{-3} are the rate constants of the forward and reverse reactions, respectively; $[\text{G}]$ and $[\text{ME}]$ refer to the concentrations of glycerol and methyl ester, respectively (in mol/L). In terms of the conversion (X) defined earlier, Equation 5 may be written as

$$\frac{dX}{dt} = [\text{MG}]_0 [k_3(1-X)(M-X) - k_{-3}X^2] \quad [6]$$

where M is the initial ratio of the concentration of methanol to MG. It would be convenient to write Equation 6 in terms of the equilibrium constant, K_e ($\equiv k_3/k_{-3}$), which in turn can be expressed in terms of the experimentally observable equilibrium conversion, X_e , as

$$K_e \equiv \frac{k_3}{k_{-3}} = \frac{X_e^2}{(1-X_e)(M-X_e)} \quad [7]$$

Integration of Equation 6 leads to

$$\frac{1}{(K_e^{-1}-1)(X_e-q)} \ln \left| \frac{X_e(X-q)}{q(X_e-X)} \right| \equiv f(X) = k_3 t \quad [8]$$

where q is given by

$$q = \frac{M+1 + \sqrt{(M+1)^2 - 4M(1-K_e)}}{2(1-K_e^{-1})} \quad [9]$$

Thus, we may plot $f(X)$ vs. time (Fig. 5), and if our assumed model is correct, a straight line would result and the forward rate constant, k_3 , would be the slope of the straight line. The reverse rate constant may then be obtained from Equation 7.

In addition to the above model, we considered another model in which the forward step is treated as pseudo first order in the MG concentration; the reverse reaction is the same as that just described. This amounts to assuming that the methanol concentration essentially remains the same during the course of the reaction. It is a good approximation if methanol is used sufficiently in excess of the MG. One of the objectives of this study was to determine the values of M (defined below Eq. 6) for which this is a good approximation. Analogous to Equation 6, we may write

$$\frac{dX}{dt} = [k'_3(1-X) - k_{-3}[\text{MG}]_0 X^2] \quad [10]$$

$$k'_3 \equiv k_3 [\text{MeOH}]_0 \quad [11]$$

Integration of Equation 10 may be done to arrive at

$$\frac{1}{[\text{MG}]_0(X_e - q')} \ln \left| \frac{(X - X_e)q'}{(X - q')X_e} \right| \equiv g(X) = k_{-3} t \quad [12]$$

where

$$q' = \frac{-K'_e - \sqrt{K'_e{}^2 + 4K'_e[\text{MG}]_0}}{2[\text{MG}]_0}$$

and

$$K'_e = \frac{k'_3}{k_{-3}} = \frac{X_e^2 [\text{MG}]_0}{(1-X_e)} \quad [13]$$

A plot of $g(X)$ vs. time (Fig. 6) would be linear if the assumed model is correct, in which case the slope of the line would give k_{-3} directly. The forward rate constant may then be found from Equation 13.

The results of our analysis are summarized in Table 2 for

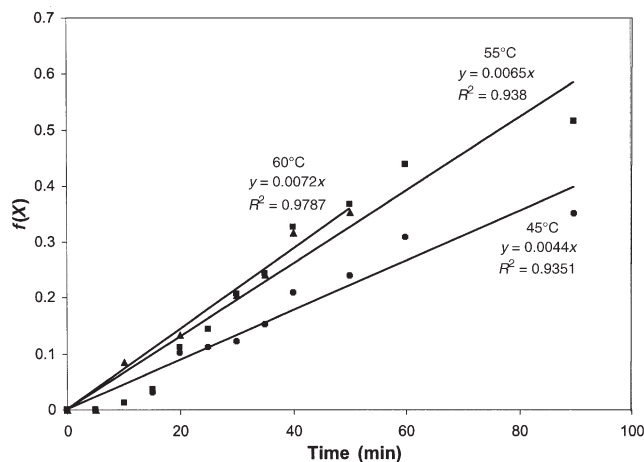


FIG. 5. The second-order forward and second-order backward reaction model for different temperatures: [where $f(X)$ is given in the Results and Discussion section by Eq. 8]: (▲) 60; (■) 55; (●) 45°C.

the four temperatures, namely, 30, 45, 55, and 60°C. In all cases, an M value of 9.64 was used. The table includes the rate constants involved in the two models as well as the R^2 values, indicating the goodness of the straight line fit.

One can see that the reversible reaction model works best at the higher temperatures, 45, 55, and 60°C. The relatively poor fit obtained at 30°C may be attributed to transport limitations that become increasingly important at lower temperatures, owing to the mixing of a highly viscous biphasic liquid mixture. This is also consistent with the qualitatively different conversion vs. time behavior (Fig. 3) observed at 30°C. Furthermore, at all temperatures, the pseudo first-order model is as good as the second-order model, thus pointing out that the M value of about 10 is high enough for the pseudo first-order model to be valid. In addition to the two models just described, we also considered the forward reaction to be second order in

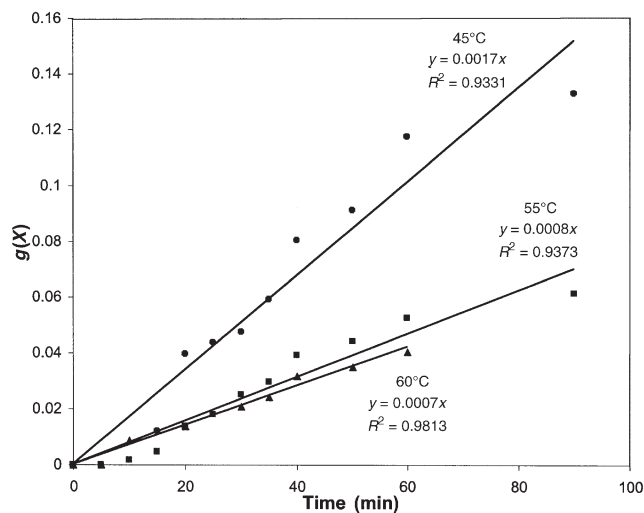


FIG. 6. The pseudo first-order forward and second-order backward reaction model [where $g(X)$ is given in the Results and Discussion section by Eq. 11]: (▲) 60; (■) 55; (●) 45°C.

TABLE 2
Rate Constants for the Transesterification of MG at 30, 45, 55, and 60°C

T^a (°C)	X_e^b	Reversible second-order model (second-order forward and second-order backward reactions)			Reversible pseudo first-order model (pseudo first-order forward and second-order backward reactions)		
		$k_f[\text{MG}][\text{MeOH}] - k_b[\text{ME}][\text{GI}]$			$k_f[\text{MG}][\text{MeOH}]_0 - k_b[\text{ME}][\text{GI}]$		
		k_3^c ($\times 10^3$)	k_{-3}^d ($\times 10^3$)	R^{2e}	k_3 ($\times 10^3$)	k_{-3} ($\times 10^3$)	R^2
30	0.675	1.3	8.31	0.84	0.99	6.8	0.846
45	0.963	4.4	1.5	0.935	4.42	1.7	0.933
55	0.988	6.5	0.76	0.938	6.75	0.8	0.937
60	0.99	7.2	0.635	0.98	7.12	0.7	0.981

^aTemperature.^bEquilibrium conversion.^cForward reaction rate constant, units: L/(mol·min)^dBackward reaction rate constant, units: L/(mol·min)^e R^2 (or r^2) is known as the square of the Pearson product, or the coefficient of determination. The Pearson product is defined as $r = [n(\Sigma XY) - (\Sigma X)(\Sigma Y)] / \sqrt{[n\Sigma X^2 - (\Sigma X)^2][n\Sigma Y^2 - (\Sigma Y)^2]}$

MG as reported previously (7), but this model consistently yielded poorer results at all temperatures. It may be mentioned here that in earlier reports where the oil itself was used to study the kinetics of transesterification, wide variations in the ratios of oil/alcohols were used (2). Based on a thorough search of SciFinder, no reports are on a kinetic study of the transesterification of MG alone. Based on the rate constant values reported in Table 2, the values of the equilibrium conversion at 45°C for MG/MeOH ratios of 1:6 and 1:3 were 94 and 87, respectively. The corresponding values at 55°C were 95 and 98%, respectively. Thus, we predicted a high conversion at 55°C even for a ratio of 1:3 (MG/MeOH), unlike for oils, where a 1:6 ratio is required for a comparable conversion (2). Experiments to verify the above predictions are underway in our laboratory. These experiments also would enable us to test the accuracy of the pseudo first-order model for the forward reaction as well as the importance of transport effects for the ratios 1:3 and 1:6.

The values of the rate constants reported in Table 2 were calculated by assuming that the reaction was initiated as soon as the methanol and catalysts were added to the MG. However, as explained earlier, transport effects involved in bringing the methanol into the oil phase would dominate in the early phase of any experimental run. This is reflected in the initial lag time of 5 to 10 min observed in the conversion vs. time plot (Fig. 3). An effective value of the lag time was estimated by evaluating the value of R^2 as a function of the lag time and choosing that value for which R^2 was maximum. In the above procedure, the range in lag time was restricted to the time interval between the time when the first positive value of conversion was measured and the preceding time instant when a conversion measurement was made. The results are summarized in Table 3. It may be noted that the rate constants reported in Table 3 are within 20% of the corresponding values in Table 2, with the agreement improving as expected with an increase in temperature.

Although an increasing trend was obtained for the forward rate constant from 30 to 60°C, it must be noted that the data at 30°C were representative of kinetic as well as transport effects. This result could also be responsible for the unusually high value of the reverse rate constant obtained at 30°C compared

TABLE 3
Effective Lag Time and the Rate Constant of the Forward Reactions

	Temperature (°C)			
	30	45	55	60
Effective lag time (min)	10	6	2	0
Forward rate constant (L/mol·min) $\times 10^3$	1.2	5.8	7.4	7.2

with the values at the higher temperatures studied. The negative activation energy obtained for the backward reaction also pointed out that it was not strictly an elementary reaction. It may be pointed out here that negative activation energies were reported previously for both the forward and the backward reaction steps in a study involving the transesterification of soybean oil (5).

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