Kinetics of Base-Catalyzed Transesterification of Triglycerides from *Pongamia* Oil

S.K. Karmee[a], D. Chandna[b], R. Ravi[b], and A. Chadha[c,*]

Departments of [a]Chemistry, [b]Chemical Engineering, and [c]Biotechnology, Indian Institute of Technology Madras, Chennai 600 036, India

ABSTRACT: The kinetics of transesterification of *Pongamia* oil using methanol at 60°C were studied. The forward as well as the reverse rate constants of all three steps involved in the transesterification of *Pongamia* oil are reported for the first time. Among the forward rate constants, the one governing the conversion of TG to DG was the highest and the one for DG to MG was the lowest. A distinct feature of the present work is the direct estimation of the equilibrium constants of all three steps by measuring the concentrations of TG, DG, and MG at very long reaction times. This reduced the number of parameters to be determined from the kinetic data by one-half, thereby leading to more accurate estimation of the rate constants. The equilibrium constant of the final step involving the conversion of MG to methyl ester and glycerol was at least an order of magnitude greater than that of the first two reaction steps. A detailed comparison was made with kinetic parameters reported in literature. The trend in the relative magnitudes of the rate constants appears to be unique to *Pongamia* oil.

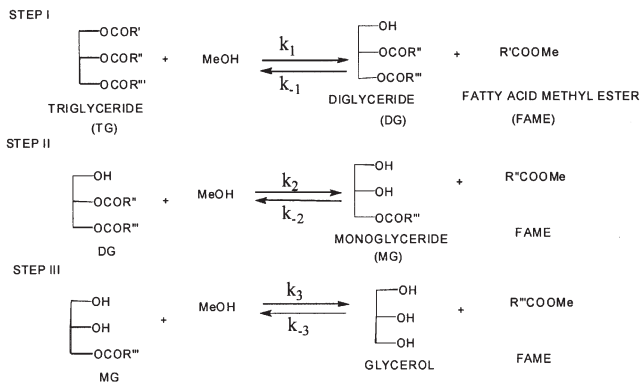
Paper no. J11302 in *JAOCS 83*, 873–877 (October 2006).

KEY WORDS: Biodiesel, DG, kinetics, MG, *Pongamia* oil, TG, transesterification.

The direct use of vegetable oils as fuels is known; however, their esterified products, referred to as biodiesel, which result from a process called transesterification, are preferred because of their superior fuel properties. It is therefore essential to understand the kinetics of transesterification to optimize reactor design for commercial production of biodiesel. Transesterification can be catalyzed by base, acid, or enzymes. Methanol is the most common alcohol used in esterification although ethanol, isopropanol, and butanol (1) have also been reported.

Apart from edible oils, nonedible oils from *Jatropha* (2) and *Pongamia* (3) have been used to prepare biodiesel. *Pongamia pinnata* (Leguminosae; Papilonaceae) is a plant found mainly in the native Western Ghats in India, northern Australia, Fiji, and in some regions of Eastern Asia (4). We have transesterified oil from the seeds of *P. pinnata* with methanol in the presence of base (3). Oil from the seeds of *J. curcas* L., a plant native to tropical America that is also found throughout India and Andaman, also has been used in preparing biodiesel (2).

It is normal to model transesterification as a three-step process (Scheme 1). In the first step, TG are converted to DG and methyl esters, which in turn are converted to MG and methyl esters in the second step. In the third and final step, MG is converted to glycerol and methyl ester. In each step, one molecule of methyl ester is formed for every molecule of glyceride reacted. In addition to these three steps, a shunt reaction involving the direct reaction of TG and methanol to yield methyl ester and glycerol also has been considered (5,6). In the past, kinetic studies of transesterification have focused on soybean oil (5,6) and palm oil (7). In those studies, the oil was regarded as consisting exclusively of TG, however, this is not always the case. Refined oils mainly consist of TG of FA (1). Crude oil, on the other hand, also can contain DG and MG (8). The rate of transesterification of any oil will depend on its initial composition. Karmee *et al.* (9), who undertook the first kinetics study of transesterification of *Pongamia* oil, reported that the oil comprised a mixture of TG, DG, and MG in the ratio 42:26:11, respectively (9). In that study (9), the kinetics of transesterification of MG isolated from *Pongamia* oil was investigated, and rate constants for the third step were reported. In the present work, the rate constants of all three steps are reported. In addition to the initial composition of oil, mass transfer limitations influence the rate of the reaction.



SCHEME 1

Owing to this effect, experiments were conducted with THF as cosolvent to ensure the homogeneity of the reaction mixture (3,10). We conducted experiments with TG isolated from *Pongamia* oil. TG, DG, and MG in the reaction mixture were separated using TLC, and their concentrations were measured at various times. A separate set of experiments was carried out at very long times to calculate the equilibrium constant for each step. Using the values of the equilibrium constants, the kinetic data were analyzed to calculate the rate constants. Experiments were also carried out starting with pure MG (isolated from *Pongamia* oil) in order to compare

*To whom correspondence should be addressed. E-mail: anjuc@iitm.ac.in

our results with those obtained in our earlier reported work (9) in which ^{1}H NMR was used as the method of analysis.

EXPERIMENTAL PROCEDURES

Materials. All chemicals and crude *Pongami*a oil were purchased from local sources. Methanol was dried and distilled before use. All ^{1}H NMR spectra were recorded on a Bruker 400 MHz instrument.

Separation of TG, DG, and MG from Pongamia oil. *Pongamia* oil was analyzed by TLC and high-pressure TLC using 80:20:1 hexane/ethyl acetate/acetic acid (by vol). The TG, DG, and MG fractions were in the ratio 42:26:11 (11). This ratio was further confirmed by the actual yields of the three glyceride fractions obtained after separating TG, DG, and MG by column chromatography.

Isolation and characterization of TG, DG, and MG from crude Pongamia oil. The MG fraction separated by column chromatography was characterized by ^{1}H NMR as reported earlier (9). TG and DG separated by column chromatography were characterized using ^{1}H NMR in $CDCl_3$ and tetramethylsilane (TMS). TG are triesters of glycerol. They are symmetrical if (i) all three FA are identical; or (ii) the 1- and 3-positions have identical FA. When the FA in the TG are different, the C_1 and C_3 methylene protons are magnetically nonequivalent, thereby yielding four double doublets in the ^{1}H NMR spectrum (10). The details of the ^{1}H NMR are as follows: δ (ppm): 4.15–4.19 (2 dd, 2H), 4.25–4.30 (2 dd, 2H), and 5.25–5.30 (m, 1H).

DG could be present as 1,2- and/or 1,3-diglycerides. 1,2-DG are chiral and, therefore, the methylene protons at C-1 and C-3 are magnetically nonequivalent. The details of the ^{1}H NMR are as follows: δ (ppm): 3.68–3.70 (dd, 2H), 4.25–4.32 (dd, 2H), and 5.02 (m, 1H) for 1,2-DG, and 4.07 (m, 1H) and 4.17 (m, 4H) for the 1,3-DG, which are symmetric (10).

Analysis of the reaction mixture by preparative TLC. Silica gel was coated on TLC plates (10 × 5 cm), which were then air-dried for 5 h and kept in an oven for 30 min. Samples (0.2 mL) were taken from the reaction mixture at different time intervals. The aliquots were neutralized with two drops of glacial acetic acid and diluted with 2 mL of hexane. The mixture was washed with water (3 mL × 5) to remove soap, unreacted base, and glycerol. The organic layer was separated and concentrated under reduced pressure. The reaction mixture was placed into a vial, and 1 mL of ethyl acetate was added. The sample was then applied to the TLC plate. The plates were developed using 80:20:1 hexane/ethyl acetate/acetic acid (by vol), after which they were kept inside an iodine chamber. TG, DG, and MG were identified by comparing with the standard glycerides. The silica gel was washed with ethyl acetate to remove TG, DG, and MG. The solvent was then evaporated, and the samples were transferred to pre-weighed vials. Residual trace amounts of solvent were evaporated under nitrogen, and vials were reweighed.

Transesterification of TG using KOH. In two separate experiments, 2 g (0.0022 mol) of TG and a known amount of catalyst KOH, either 20 mg (1 wt%) or 40 mg (2 wt%), were dissolved in the required amount of methanol (0.022 mol, 0.89 mL). The temperature was maintained at 60°C. Samples were removed at different times, neutralized using glacial acetic acid, washed with water (5 mL × 3) to remove unreacted base, glycerol, and trace amounts of soap, and extracted with *n*-hexane. The organic layer was separated and concentrated to obtain the soap- and glycerol-free sample, which was analyzed by preparative TLC as explained in the previous paragraph. Reaction was performed at 1:10 molar ratio of TG/methanol at 60°C.

Effect of cosolvent (THF) on transesterification of Pongamia oil. The reaction was performed by taking *Pongamia* oil (10 g, 0.019 mol) and methanol (20.77 mL, 0.513 mol) in a 1:27 molar ratio and 1 wt% KOH (100 mg). To this, THF (18.13 mL, 0.217 mol) was added at 60°C. Samples were taken at fixed time intervals and worked up as for the TG experiment. After purification, each sample was analyzed using ^{1}H NMR using $CDCl_3$ as a solvent and TMS as an internal standard.

Transesterification of MG using KOH. The transesterification procedure was similar to that followed for TG except that 0.056 mol (2.94 mL) of methanol was added to 2 g of MG to ensure an MG/methanol ratio of 1:10. The amount of catalyst used was the same as for TG (20 mg), and the temperature was maintained at 60°C.

RESULTS AND DISCUSSION

Reaction mixtures involved in transesterification could, in general, be biphasic (10) and, hence, transport effects might need to be accounted for in the model for kinetics. The presence of transport effects is indicated by a characteristic initial lag phase (6,9). Noureddini and Zhu (6) have shown that, for soybean oil at sufficiently high temperatures (60°C and above) and high mixing rates, the transesterification reaction takes place almost entirely in the kinetically controlled regime. Furthermore, they observed that the methyl esters act as a solvent for the reactants, thus making the transport effects negligible. It has been argued (10) that the addition of THF as a cosolvent facilitates the formation of a homogeneous reaction mixture and increases the reaction rate. In this study, however, experiments conducted with THF as a cosolvent did not result in any dramatic increase in the reaction rate, thus pointing out that the reaction mixture was homogeneous even without the addition of the THF. Notably, no lag phase was observed (Fig. 1), further confirming the homogeneity of the reaction mixture. From earlier studies (7), it is known that the optimal catalyst amount is 1 wt% for most oils. Confirming the optimal amount of catalyst for the methanolysis of *Pongamia* oil, experiments done with 1 and 2 wt% catalyst did not show any marked difference in the reaction rate.

Outline of method for parameter estimation. The kinetic model adopted in the present work was that all the three steps in Scheme 1 are reversible. Furthermore, each reaction step, forward as well as backward, is elementary as written. Given that transport effects are negligible, the following equations hold for the batch reactor in which the kinetics experiments were carried out:

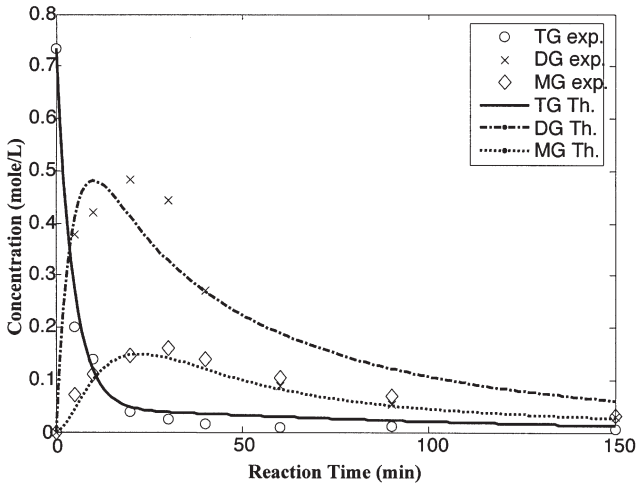


FIG. 1. Plot of experimental data and theoretical predictions when pure TG is used for transesterification. Th., theoretical; exp., experimental.

$$-\frac{d[\mathrm{TG}]}{dt} = k_1[\mathrm{TG}][\mathrm{MeOH}] - k_{-1}[\mathrm{DG}][\mathrm{ME}] \quad [1]$$

$$-\frac{d[\mathrm{DG}]}{dt} = k_2[\mathrm{DG}][\mathrm{MeOH}] - k_{-2}[\mathrm{MG}][\mathrm{ME}] - k_1[\mathrm{TG}][\mathrm{MeOH}] + k_{-1}[\mathrm{DG}][\mathrm{ME}] \quad [2]$$

$$-\frac{d[MG]}{dt} = k_3[\mathrm{MG}][\mathrm{MeOH}] - k_{-3}[\mathrm{Gl}][\mathrm{ME}] - k_2[\mathrm{DG}][\mathrm{MeOH}] + k_{-2}[\mathrm{MG}][\mathrm{ME}] \quad [3]$$

where [ ] refers to the concentration of the corresponding species and Gl, ME, and MeOH refer to glycerol, methyl ester, and methanol, respectively. Data from two different experimental runs were analyzed for parameter estimation: one starting with pure TG and another starting with pure MG. A program was developed to implement the quasi-linearization algorithm (12). The program was validated using the example of the two-step reaction involving the pyrolytic dehydrogenation of benzene to diphenyl and triphenyl (12). For comparison purposes, the Matlab optimization function *Lsqnonlin* was also used to estimate the parameters. The two methods adopted, i.e., the quasi-linearization scheme and the Matlab function *Lsqnonlin*, will henceforth be referred to as methods 1 and 2, respectively. In all, six kinetic parameters, k_1, k_{-1}, k_2, k_{-2}, k_3, k_{-3}, must be estimated. The number of parameters can be reduced to three if the equilibrium constants K_1, K_2, and K_3, defined as

$$K_1 = \frac{k_1}{k_{-1}},\ K_2 = \frac{k_2}{k_{-2}},\ K_3 = \frac{k_3}{k_{-3}} \quad [4]$$

are available from experimental data. The equilibrium constants were calculated by using the concentrations of the various species at sufficiently long reaction times after ensuring that all reactions reached equilibrium. Table 1 shows that the calculated values of the equilibrium constants at a reaction time of 800 min were close to those at 500 min, and the values calculated at 800 min were used to calculate the forward rate constants from the parameter estimation programs. Clearly, this approach can be expected to result in more accurate estimation of the rate constants than if all six rate constants were directly determined from kinetic data, which is commonly done (5,6) because only three parameters need to be determined from the given data set as opposed to six when the equilibrium constants are not known.

TABLE 1
Equilibrium Constants Estimated from Experimental Data at Various Reaction Times

t (min)	K_1	K_2	K_3
210	1.24	0.36	10.43
240	1.17	0.34	14.13
280	1.7	0.31	16.54
300	1.7	0.29	18.67
350	1.65	0.29	19.18
400	1.7	0.28	19.7
450	1.84	0.28	20.85
500	2.01	0.27	22.06
800	1.99	0.27	21.74

Initial guess estimates. One of the key inputs to any parameter estimation scheme involving nonlinear equations is suitable initial guesses for each of the parameters to be estimated. For this purpose, a separate program was developed, which used as input the experimentally measured concentration vs. time data for TG, DG, and MG, and fitted a polynomial to each of them. The rates of change of these concentrations were evaluated from the time derivatives of these polynomials. Then, using Equations 1–3, initial estimates of k_1, k_2, and k_3 were obtained. These initial estimates were then fed into the parameter estimation programs.

Accuracy of parameter estimates. A measure of the accuracy of parameter estimates was obtained through the quantity *S*, referred to as the residual norm and given by:

$$S = \sum_i ([\mathrm{TG}]^{\mathrm{exp}} - [\mathrm{TG}]^{\mathrm{pred}})^2 + ([\mathrm{DG}]^{\mathrm{exp}} - [\mathrm{DG}]^{\mathrm{pred}})^2 + ([\mathrm{MG}]^{\mathrm{exp}} - [\mathrm{MG}]^{\mathrm{pred}})^2 \quad [5]$$

where the index *i* runs over all experimental data points and the superscripts "exp" and "pred" refer to the experimental and the predicted values, respectively. Clearly, the lower the residual norm, the better are the parameter estimates. In both methods 1 and 2, the parameters were obtained through minimizing the quantity *S*.

Parameter estimation from data using pure TG. The results are summarized in Tables 2 and 3 and Figure 1. It was clear that among the forward rate constants, k_2 had the lowest value and k_1 the highest (Sr. nos. 1 and 2 in Table 2). These results were consistent with the initial rapid rise in DG concentration as well as with continued presence of DG at longer times. The results from methods 1 and 2 were similar, differing by about 20–35%. The *S* value obtained from the latter was about 60% of that obtained using method 1 and, hence, may be regarded as the more accurate estimate. The appropriate plot (Fig. 1) showed a good fit of the theoretical predictions to the experimental data. Among the reverse rate constants, that of step 2 (formation of MG from DG and vice versa) was the highest, followed by that of step 1 (Sr. nos. 1 and 2 in Table 3).

TABLE 2
Forward Rate Constants for Transesterification of *Pongamia* Oil

Sr. no.	Data	k_1 L mol^{-1} min^{-1}	k_2 L mol^{-1} min^{-1}	k_3 L mol^{-1} min^{-1}	Method	Residual norm (S)
1	TG	0.0286	0.0058	0.0111	Method 2	0.0478
2	TG	0.0252	0.0083	0.0168	Method 1	0.0796
3	MG	—	—	0.0114	Method 2	2.25×10^{-5}
4	MG	—	—	0.0116	Integral analysis	0.9993(R^2)

TABLE 3
Reverse Rate Constants for Transesterification of *Pongamia* Oil

Sr. no.	Glyceride	k_{-1} L·(mol min)	k_{-2} L·(mol min)	$k_{-3} \times 10^4$ L·(mol min)	Method
1	TG	0.0144	0.0213	5.11	Method 2
2	TG	0.0127	0.0305	7.73	Method 1
3	MG	—	—	5.24	Method 2
4	MG	—	—	5.34	Integral analysis

Parameter estimation from data using pure MG. In this case, the concentrations of both TG and DG were very small. Consequently, only the third step (i.e., the formation of methyl ester and glycerol from MG) was considered. The value of k_3 was almost identical to that obtained using the data starting with pure TG (Sr. no. 3 in Table 2). The fit was extremely good with a very low value of S (Fig. 2). Moreover, the integral method of analysis adopted in Reference 9 was also used to estimate k_3. The value obtained (Sr. no. 4 for k_3 in Table 2) was almost identical to the one obtained using method 2. The R^2 value (0.993) was very close to unity and, hence, indicated excellent fit.

Robustness of parameter estimates. To address the question of robustness of the parameter estimates, the window of convergence (Table 4) was determined. This gave the range of initial guesses for which the program converged to values reported in Table 2. It is clear that method 2 resulted in a wider window of convergence compared with that obtained from method 1. In general, the estimates of the forward rate constants were quite robust with respect to the initial guesses.

Comparison with literature results. Comparison was first made with the results of our earlier work (9), which was the first study of the kinetics of transesterification of *Pongamia* oil. There, the transesterification of MG isolated from the oil was studied by monitoring the formation of methyl esters by ^{1}H NMR. Hence, only the rate constants of the third step were determined. The values of k_3 reported here were larger by about a factor of 1.5. Given that the experimental techniques and methods of analysis in the two cases were vastly different, this agreement was quite reasonable. Moreover, the equilibrium constant obtained from experiment in the earlier case was roughly one-half of that reported here. This was attributed to the fact that the earlier value was obtained at a relatively shorter reaction time (150 min). The net result was that the reverse rate constant for the third step obtained earlier was larger by about a factor of 1.25. Among the forward rate constants, k_1 was the largest and k_2 the smallest. From Tables 2 and 3, the following relations existed among the rate constants of the three steps involved in transesterification: $k_1 > k_3 > k_2$ and $k_{-2} > k_{-1} > k_{-3}$.

These trends were compared with the results reported in the literature. For transesterification of soybean oil with methanol at 50°C using NaOH as catalyst, Noureddini and Zhu (6) observed that $k_3 > k_2 > k_1$ and $k_{-2} > k_{-1} > k_{-3}$. The authors used HPLC for quantitative analysis. The trends in equilibrium constants reported by the authors were similar to those found in the present work: The third reaction had a much higher equilibrium constant than the other two, with that of step 2 being the lowest. This similarity, however, did not carry over to the forward rate constants. For transesterification of soybean oil with butanol using NaOBu as catalyst and GC for composition analysis, Freedman *et al.* (5) found that $k_1 > k_2 > k_3$ and $k_{-1} >> k_{-3} > k_{-2}$. Although they performed experiments with methanol as

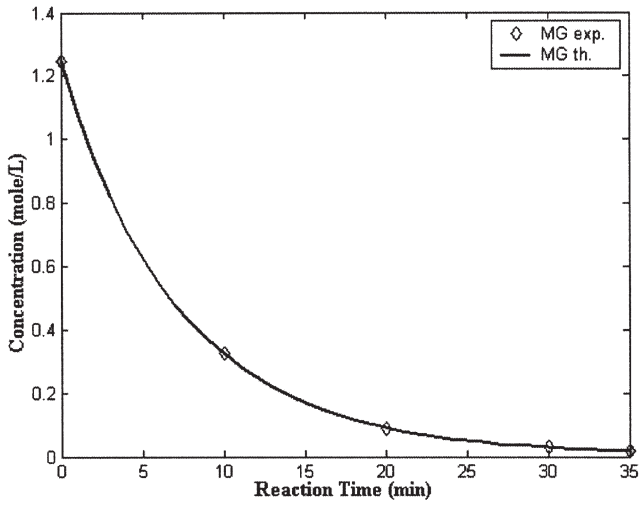


FIG. 2. Plot of experimental data and theoretical predictions when pure MG is used for transesterification. For abbreviations see Figure 1.

TABLE 4
Robustness of Rate Constant Estimates: Window of Convergence Tests

Sr. no.	Glyceride	Window of convergence for	Lower limit L/(mol min)	Upper limit L/(mol min)	Method
1	TG	k_1	1.0×10^{-13}	0.15	Method 2
2	TG	k_2	4.2×10^{-9}	38	Method 2
3	TG	k_3	5.0×10^{-7}	243.6	Method 2
4	TG	k_1	3.2×10^{-4}	0.04	Method 1
5	TG	k_2	5.0×10^{-5}	0.02	Method 1
6	TG	k_3	7.2×10^{-10}	0.036	Method 1
7	MG	k_3	1.5×10^{-10}	0.151	Method 2

TABLE 5
Comparison of Rate Constants Obtained in this Study with Literature Values

k_1	k_2	k_3	k_{-1}	k_{-2}	k_{-3}	Units	Temp. °C	Reference
—	—	7.2×10^{-3}	—	—	6.35×10^{-4}	$L \cdot mol^{-1} \cdot min^{-1}$	60	9
3,822	1,215	792	—	—	—	min^{-1}	60	5
—	—	—	121	7	11	$L \cdot mol^{-1} \cdot min^{-1}$	60	5
0.050	0.215	0.242	0.110	1.228	0.007	$L \cdot mol^{-1} \cdot min^{-1}$	50	6
0.036	0.070	0.141	—	—	—	$(wt\% \cdot min)^{-1}$	60	7
0.0286	0.0058	0.0111	0.0144	0.0213	5.11×10^{-4}	$L \cdot mol^{-1} \cdot min^{-1}$	60	Present study

well, they did not report the corresponding rate constant values. In addition to the three steps in Scheme 1, a fourth-order shunt reaction involving TG and methanol was also considered (5,6). No significant change in the rate constants of the three steps, however, was observed (6).

Darnoko and Cheryan (7) modeled the transesterification of palm oil as a series of irreversible second-order reactions in TG, DG, and MG. They used the initial time data obtained by gel permeation chromatography and reported that $k_3 > k_2 > k_1$. This trend was the same as that obtained by Noureddini and Zhu (6) and opposite to that of Freedman *et al*. (5). The results reported in this work were partly similar to that reported by Freedman *et al*. in that the forward rate constant of the first step (the transesterification of TG) had the largest value. The second step, however, was the slowest step in the present study, whereas in their work, the third step was the slowest. The results summarized in Table 5 indicate that the oil as well as the alcohol and catalyst could qualitatively alter the kinetics of transesterification. More work is required to identify clearly the role played by each.

REFERENCES

1. Ma, F., and M.A. Hanna, Biodiesel Production: A Review, *Bioresource Technol. 70*:1–15 (1999).
2. Foidl, N., G. Foidl, M. Sanchez, and M. Mittelbach, *Jatropha curcas* L. as a Source for the Production of Biofuel in Nicaragua, *Ibid. 58*:77–82 (1996).
3. Karmee, S.K., and A. Chadha, Preparation of Biodiesel from Crude Oil of *Pongamia pinnata*, *Ibid. 96*:1425–1429 (2005).
4. Lakshmikanthan, V., *Tree Borne Oil Seeds*, Directorate of Nonedible Oils and Soap Industry, Khadi and Village Industries Commission, Mumbai, India, 1978, 10 pp.
5. Freedman, B., R.O. Butterfield, and E.H. Pryde, Transesterification Kinetics of Soybean Oil, *J. Am. Oil Chem. Soc. 63:*1375–1380 (1986).
6. Noureddini, H., and D. Zhu, Kinetics of Transesterification of Soybean Oil, *Ibid. 74*:1457–1463 (1997).
7. Darnoko, D., and M. Cheryan, Kinetics of Palm Oil Transesterification in a Batch Reactor, *Ibid. 77*:1263–1267 (2000).
8. Min, D.B., and B.S. Mistry, Isolation and Identification of Minor Components and Their Effects on Flavor Stability of Soybean Oil, *Devel. Food Sci. 17:*499–519 (1988).
9. Karmee, S.K., P. Mahesh, R. Ravi, and A. Chadha, Kinetic Study of Base-Catalyzed Transesterification of Monoglycerides from *Pongamia* Oil, *J. Am. Oil Chem. Soc. 81*:425–430 (2004).
10. Boocock, D.G.B., S.K. Konar, V. Mao, C. Lee, and S. Buligan, Fast Formation of High-Purity Methyl Esters from Vegetable Oils, *Ibid. 75*:1167–1172 (1998).
11. Karmee, S.K., Preparation of Biodiesel from Oil of *Pongamia* and Value Added Products from Renewable Resources: A Green Approach, Ph.D. Thesis, Indian Institute of Technology Madras, India, 2005.
12. Seinfeld, J.H., and L. Lapidus, *Mathematical Methods in Chemical Engineering, Volume 3: Process Modeling, Estimation, and Identification*, Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1974.

[Received January 2, 2006; accepted July 8, 2006]