

Kinetics of Transesterification of Soybean Oil

H. Nouredдини* and D. Zhu

Department of Chemical Engineering, University of Nebraska, Lincoln, Nebraska 68588-0126

ABSTRACT: Transesterification of soybean oil with methanol was investigated. Three stepwise and reversible reactions are believed to occur. The effect of variations in mixing intensity (Reynolds number = 3,100 to 12,400) and temperature (30 to 70°C) on the rate of reaction were studied while the molar ratio of alcohol to triglycerol (6:1) and the concentration of catalyst (0.20 wt% based on soybean oil) were held constant. The variations in mixing intensity appear to effect the reaction parallel to the variations in temperature. A reaction mechanism consisting of an initial mass transfer-controlled region followed by a kinetically controlled region is proposed. The experimental data for the latter region appear to be a good fit into a second-order kinetic mechanism. The reaction rate constants and the activation energies were determined for all the forward and reverse reactions.

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KEY WORDS: Biodiesel, kinetics, methyl esters, mixing, renewable fuels, soybean oil, transesterification, triglycerides.

Over the last few years, fatty acid methyl esters have assumed importance as research has intensified on the utilization of vegetable oils and animal fats derivatives for liquid fuels, known as biodiesel. Fatty acid methyl esters are products of the transesterification of fats and oils with alcohols in the presence of an acid or an alkaline catalyst. Three consecutive and reversible reactions are believed to occur (1). Mono- (MG) and diglycerides (DG) are the intermediates formed in these reactions.

The variables affecting the transesterification process (also called alcoholysis) have been intensively investigated as widening industrial uses were found for esters (2–6). Molar ratio of alcohol to vegetable oil, type of catalyst, temperature, and presence of impurities such as free fatty acids and moisture are among the variables that have been studied.

There are a number of kinetic studies in the literature on the transesterification of esters with alcohol. However, only a few of these studies deal with vegetable oils and fatty esters. The studies on the transesterification kinetics for nonfatty esters include: the determination of the reaction rate constants, the equilibrium constant, and the activation energy for the acid-catalyzed reaction of butanol with ethyl acetate (7) and ethanol with butyl acetate (8). A review by Sridharan and Mathai (9) on the transesterification reactions involving alco-

holysis, acidolysis, vinyl interchange, and ester-ester interchange contains many of the reported studies.

The transesterification kinetics for vegetable oils and fatty esters has been reported in a few studies. Dufek and coworkers (10) studied the acid-catalyzed esterification and transesterification of 9(10)-carboxystearic acid and its mono- and dimethyl esters and reported unequal chemical reactivity for different carboxyl and carboxymethyl groups. Freedman and coworkers (1) investigated both acid- and alkaline-catalyzed transesterification of soybean oil with butanol and methanol. They determined the reaction rate constants as reaction parameters such as temperature, molar ratio of alcohol to soybean oil, and catalyst type and concentration were varied. Generally, a second-order reaction for all three reversible reactions provided a satisfactory mechanism. At a molar ratio of methanol to soybean oil of 6:1, a second-order mechanism with a fourth-order shunt mechanism best described the kinetics. Other kinetic studies include transesterification of C₁₈ unsaturated fatty acids contained in tall oil with methanol (11), acidolysis of castor oil with oleic acid (12), esterification of oleic acid with 1-octanol using an immobilized enzyme on polymeric support (13), and the idealized kinetic model for the lipase-catalyzed interesterification of fats and oils (14). This model, which was based on an idealized system of two fatty acids, provided a base to quantitatively study the role of minor components in these reactions.

A factor of particular importance in the transesterification process is the degree of mixing between the alcohol and triglyceride (TG) phases. TG and alcohol phases are not miscible and form two liquid layers upon their initial introduction into the reactor. Mechanical mixing is normally applied to increase the contact between the reactants, resulting in an increase in mass transfer rate. Therefore, variations in mixing intensity are expected to alter the kinetics of the transesterification reaction.

Although some type of mixing, mostly in the form of a mechanical stirrer, has been applied in all kinetic studies, the effect of mixing intensity on the kinetics of the reaction has not been fully addressed. Better understanding of the mixing effects on the kinetics of the transesterification process will be a valuable tool in process scale-up and design.

In this study, the effect of mixing on the kinetics of the transesterification of soybean oil with methanol was investigated. The molar ratio of alcohol to TG and the concentration of catalyst (sodium hydroxide) were kept constant while tem-

*To whom correspondence should be addressed. E-mail: hnouredдини@unl.edu.

perature and mixing intensity were varied. Kinetic data were collected at three mixing intensities and five temperature levels. The temperature dependency of the reaction rate constants and the activation energies were determined for all the forward and reverse reactions. The dependency of the reaction rate constants on mixing intensity was also investigated.

EXPERIMENTAL PROCEDURES

Materials. Refined and bleached soybean oils were obtained from Archer Daniels Midland Company (Lincoln, NE). Free acid content of the oil was determined according to AOCS method #Ca 5a-40 (15) to be 0.09%. Certified methyl alcohol of 99.9% purity was purchased from Baxter Diagnostics Inc. (McGraw Park, IL). Sodium hydroxide pellets of 98.2% purity were purchased from Fisher Scientific Company (Pittsburgh, PA). The high-performance liquid chromatograph (HPLC) standards for methyl esters were obtained from Sigma Chemical Company (St. Louis, MO).

A 0.907 wt% stock solution of sodium hydroxide in methanol was prepared and used in all of the reactions. A 6:1 molar ratio of this stock solution with soybean oil amounted to about 0.20 wt% sodium hydroxide in soybean oil.

Reaction conditions. Experiments were designed to determine the reaction rate constants. A 6:1 molar ratio of alcohol to soybean oil, which is a typical ratio for transesterification of vegetable oils, was used in all experiments. To examine the temperature dependency of the reaction rate constants, reactions at 30, 40, 50, 60, and 70°C were studied. All reactions were carried out at atmospheric pressure.

Three different mixing intensities were used to investigate the effect of mixing on the kinetic behavior. The rotational speed of the impeller was set at 150, 300, and 600 rpm. The mixing intensity may also be presented by Reynolds number (N_{Re}). The impeller rotational speed and the N_{Re} are related in Equation 1.

$$N_{Re} = \frac{nD_a^2\rho}{\mu} \quad [1]$$

where n is the rotational speed of the impeller, D_a is the impeller diameter, and ρ and μ are the fluid density and viscosity, respectively. The numerical values for N_{Re} at the beginning of the reactions were determined to be 3100, 6200, and 12,400 for rotational speed of 150, 300, and 600, respectively. There is a significant increase in N_{Re} values as the reaction progresses, which is primarily due to lower viscosity of the products. In the following sections when the mixing intensity is presented by N_{Re} , it is referring to the start of the reaction.

Apparatus. A 1500-mL glass cylindrical reactor equipped with a mechanical stirrer, thermometer, built-in condensing coil, and sample port was used in all kinetic experiments. The reactor was immersed in a constant-temperature circulating bath, Model 1157 VWR Scientific (Philadelphia, PA) which was capable of controlling the temperature to within $\pm 0.01^\circ\text{C}$ of the set point. A mechanical stirrer Model SL 1200, Fisher Scientific (Fairlawn, NJ) fitted with a stainless steel folding

propeller provided the mixing requirements. During the course of the experiment, samples were withdrawn with a 2-mL disposable pipette through an opening on top of the reactor.

Procedures. The reactor was initially charged with 200 g of soybean oil. The reactor assembly was then placed in the circulating constant-temperature bath and heated to the desired temperature. Measured amount of the methanol/sodium hydroxide stock solution (44.3 g), which was heated separately to the reaction temperature, was added to the reactor and the mechanical stirrer was started. The reaction was timed as soon as the mechanical stirrer was turned on.

Sampling and analysis. Samples were drawn at pre-specified time intervals. Approximately 15 samples were collected during the course of each reaction (90 min). The frequency of sample collection varied and was dictated by the reaction conditions. Reactions at higher temperatures and mixing intensities required more frequent sampling at the beginning of the reaction. As the reaction temperature and mixing intensity were decreased, an initial delay in the reaction was experienced, and sample collection was delayed accordingly. This phenomenon is explained in later sections. Samples were taken at 1- and 2-min intervals, early in the reaction, and at 10- to 15-min intervals, later in the reaction.

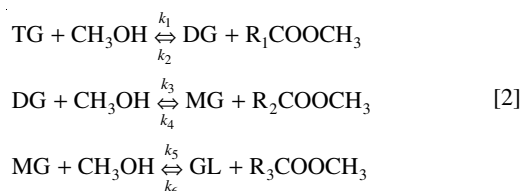
Samples were collected in 10-mL test tubes filled with 4 mL of distilled water. The test tubes were kept in an ice bath at about 5°C prior to use. Samples (2 mL) were quenched in the test tubes by placing them in the ice bath immediately after removal from the reactor. The test tubes were then shaken to stop the reaction. Upon washing, glycerol (GL) and sodium hydroxide are transferred to the water phase, and esters and unreacted GL form a separate liquid layer. The layers were then centrifuged at 1600 rpm for about 15 min to ensure a thorough separation.

An HPLC (ISCO, Lincoln, NE), equipped with a model 2350 pump and a refractive index detector, Refracto Monitor IV (Thermal Separation Products, Riviera Beach, FL), was used for the analysis. Temperature for the column was controlled with a circulating constant-temperature bath. Data collection and analysis were performed with Hewlett-Packard (Wilmington, DE) Chemstation Software. A Spherisorb OSD 2 column (Phase Separation Inc., Norwalk, CT) (250 \times 4.6 mm with 80 Å pore size and 5 μm particle size) was used for the separation. The HPLC mobile phase consisted of a 50:50 volumetric mixture of acetone and acetonitrile. The mobile system was degassed for 15 min in an ultrasonic bath before use in the HPLC system. The HPLC pump operated at 0.70 mL/min, and the column temperature was set at 35°C. Standards for methyl esters, MG, DG, and TG were used to establish the calibration charts. Using these calibration charts, all the integration results were corrected for the weight percentage of the individual components.

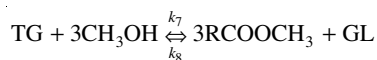
Kinetic modeling. An MLAB computer program (Civilized Software Inc., Washington, DC), which is a general, interactive system for mathematical and statistical modeling, was used. MLAB can simultaneously fit multiple nonlinear

functions, some or all of which may be implicit functions, or may even be defined by a system of differential equations. One of the central components of this system is a curve-fitting program which will adjust the parameters of a model function to minimize the weighted sum of the errors raised to a specific power.

Transesterification of TG with methanol, in the presence of an alkaline catalyst, yields esters of fatty acids and GL. MG and DG are the intermediates. The reaction steps are in Equation 2 where k_{1-8} are rate constants.



Overall reaction:



The general form of the governing set of differential equations characterizing the stepwise reactions involved in the transesterification TG is in Equation 3.

$$\begin{aligned} \frac{d[\text{TG}]}{dt} &= -k_1[\text{TG}][\text{A}] + k_2[\text{DG}][\text{A}] - k_7[\text{TG}][\text{A}]^3 + k_8[\text{A}][\text{GL}]^3 \\ \frac{d[\text{DG}]}{dt} &= k_1[\text{TG}][\text{A}] - k_2[\text{DG}][\text{E}] - k_3[\text{DG}][\text{A}] + k_4[\text{MG}][\text{E}] \\ \frac{d[\text{MG}]}{dt} &= k_3[\text{DG}][\text{A}] - k_4[\text{MG}][\text{E}] - k_5[\text{MG}][\text{A}] + k_6[\text{GL}][\text{E}] \\ \frac{d[\text{E}]}{dt} &= k_1[\text{TG}][\text{A}] - k_2[\text{DG}][\text{E}] + k_3[\text{DG}][\text{A}] - k_4[\text{MG}][\text{E}] \\ &\quad + k_5[\text{MG}][\text{A}] - k_6[\text{GL}][\text{E}] + k_7[\text{TG}][\text{A}]^3 - k_8[\text{GL}][\text{E}]^3 \\ \frac{d[\text{A}]}{dt} &= \frac{-d[\text{E}]}{dt} \\ \frac{d[\text{GL}]}{dt} &= k_5[\text{MG}][\text{A}] - k_6[\text{GL}][\text{E}] + k_7[\text{TG}][\text{A}]^3 - k_8[\text{GL}][\text{E}]^3 \end{aligned} \quad [3]$$

where A and E denote the alcohol and ester concentrations, respectively. In Equation 3, for the case without the shunt-reaction scheme, k_7 and k_8 are set equal to zero. In our kinetic

studies, MLAB was used for simultaneously fitting the system of differential equations, Equation 3, into the experimental data.

One of the difficulties in the curve fitting of nonlinear problems is that the solution may be nonunique and separated. The surface which reflects the sum of squares may not look like a bowl, as it does in linear systems, but more like a series of craters and gullies. Moreover, finding the bottom of one depression is no guarantee that it is the deepest depression. In nonlinear curve fitting, the sum of squares value is usually a local minimum rather than a global minimum. However, it is still a good measure of the goodness-of-fit, provided reciprocals of variances have been entered as weights.

The choice of the initial estimates for the parameters also plays an important role in the curve-fitting path to a local minimum. Therefore, in our fitting procedures many different combinations for the first estimates were chosen, and the final results for the reaction rate constants are presented in terms of ranges rather than a single number. For some of the rate constants, this dependency is not significant and the range is fairly narrow, whereas for some, the dependency is significant. The final outputs from the curve-fit which determine the goodness-of-fit, such as the final sum of squares, the root-mean-square, and the determination coefficient (R^2), were practically identical for the given ranges. In other words, all the values in the reported ranges are equally applicable to the reaction kinetics.

Activation energy. Activation energies were estimated by an expression similar to the Arrhenius equation (Equation 4).

$$k(T) = AT^n e^{-E/RT} \quad [4]$$

This expression, derived from the transition state theory, shows the temperature dependency of the reaction rate constant. For $n = 0$, this relationship reduces to the Arrhenius equation. Equation 4 results in different activation energies when the value of n is varied.

Experimental values of the reaction rate constants and temperature were curve-fitted into Equation 4 for $n = 0$ and 1 at $N_{\text{Re}} = 6200$ and 12,400. Table 1 shows that activation energies at both mixing intensities were consistent for a given value of n . This was expected owing to the kinetically con-

TABLE 1
Energy of Activation (cal/mol) at Different Mixing Intensities

Reaction	$N_{\text{Re}} = 6200$		$N_{\text{Re}} = 12400$	
	Arrhenius ^a	Modified Arrhenius ^b	Arrhenius	Modified Arrhenius
TG→DG	13,145	11,707	13,600	12,130
DG→TG	9,932	8,482	9,783	8,313
DG→MG	19,860	18,439	18,769	16,767
MG→DG	14,639	13,433	11,177	9,710
MG→GL	6,421	7,937	5,182	8,036
GL→MG	9,588	10,992	9,873	11,365

^aArrhenius equation, $k = Ae^{-E/RT}$.

^bModified Arrhenius equation, $k = ATe^{-E/RT}$. TG, triglyceride; DG, diglyceride; MG, monoglyceride; GL, glycerol; N_{Re} , Reynolds number.

trolled mechanism. The activation energies ranged from about 6400 to 20,000 cal/mol for the Arrhenius model. This range was narrowed to about 8000 to 18,500 cal/mol when the modified model with $n = 1$ was used.

The results obtained in this study are consistent with the experimental values of the activation energies reported in the literature for other transesterification reactions (7–10). Freedman and coworkers (1) reported activation energies for the reactions involved in the transesterification of soybean oil to be in the range of 8000 to 20,000 cal/mol based on the Arrhenius equation.

RESULTS AND DISCUSSION

Alkaline-catalyzed transesterification of soybean oil at three mixing intensities and five temperatures were studied. The molar ratio of methanol to soybean oil was constant at 6:1, and sodium hydroxide amounted to 0.2 wt% based on the mass of the soybean oil.

Transesterification reaction analysis. A typical concentration curve for the transesterification of soybean oil at 50°C is presented in Figure 1. This figure shows the rate of consumption of TG and formation of methyl esters and GL as well as the intermediate compounds.

Examination of Figure 1 reveals a sigmoidal curve for the production of methyl esters and GL. This indicates a slow reaction rate or delay at the beginning which is followed by a sudden surge and finally a lower rate as the reaction approaches completion. This is a typical behavior for autocatalytic reactions or reactions with changing mechanisms. Since the transesterification reaction of TG is not known to be an autocatalytic reaction, the second possibility was hypothesized as a mass transfer controlled region (slow) followed by a kinetically controlled region (fast) and a final slow region as equilibrium is approached. This hypothesis will be discussed in more detail and will be supported with experimental data in the following sections.

Effect of mixing. In the transesterification reaction, the re-

actants initially form a two-phase liquid system. The reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single phase system is formed. This was substantiated experimentally by taking samples in the slow rate region and subjecting them to gravity settling. Results revealed that samples taken very early into the reaction separated into two phases. However, as sampling was continued, a single phase was observed at a time corresponding to the beginning of the sudden surge in the time-concentration diagram. Figure 2 summarizes this delay or slow rate region as a function of mixing intensity at a constant reaction temperature of 50°C. As expected, this lag time decreased as the mixing intensity was increased and reached a constant value of about 1 to 2 min for N_{Re} greater than 10,000. This result supports the mass transfer controlled theory during the initial stage of the reaction.

Figure 2 also reveals that the mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant and the reaction rate is primarily influenced by the reaction temperature. This is clearly evident from the slope of the curves in Figure 2. One could easily overlap the kinetically controlled regions of all three curves. Depletion of the reactants and formation of the products result in a more dominant reverse reaction later in the reaction. The final slow region is formed and eventually equilibrium is reached. Figure 2 reveals that this region may also be overlapped at various mixing intensities and therefore is believed to be controlled by chemical reaction. This also suggests that inhibition is not a factor, since GL will have a tendency to phase-separate at low N_{Re} .

Effect of temperature. Temperature dependency of the overall reaction rate is presented in Figures 3 and 4 at two different mixing intensities. This dependency is similar to the effect of mixing intensity and will be analyzed separately for the previously hypothesized mass transfer and kinetically controlled regions. The time for the mass transfer region is shortened as temperature is increased (Figs. 3 and 4) which may be due to

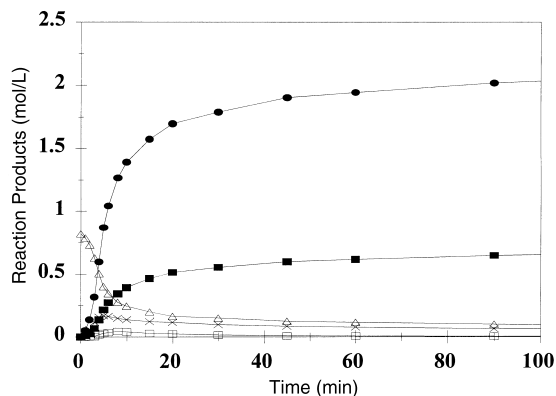


FIG. 1. The composition of the reaction mixture during the transesterification of soybean oil at 50°C and Reynolds number (N_{Re}) = 6200. (Δ) triglycerides; (\bullet) methyl esters; (\times) diglycerides; (\square) monoglycerides; (\blacksquare) glycerol.

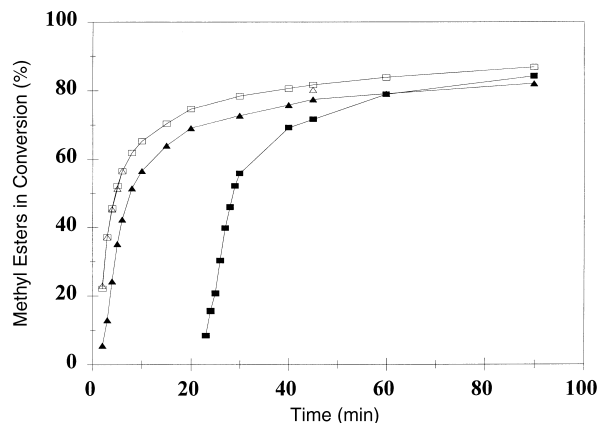


FIG. 2. The effect of mixing intensity and time on the overall conversion to methyl esters at 50°C. (\blacksquare) $N_{Re} = 3100$; (\blacktriangle) $N_{Re} = 6200$; (\square) $N_{Re} = 12400$; (\triangle) $N_{Re} = 18600$. See Figure 1 for abbreviation.

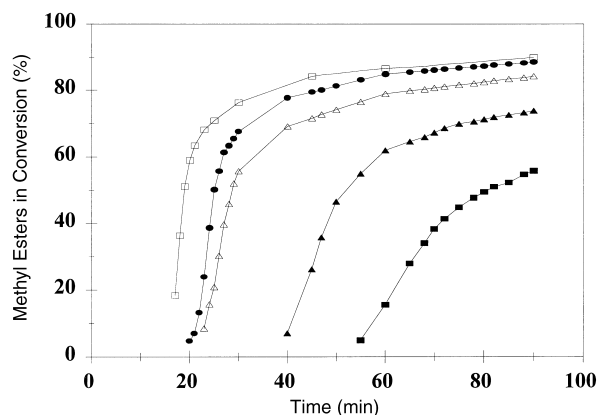


FIG. 3. The effect of temperature and time on the overall conversion to methyl esters at $N_{Re} = 3100$. (■) 30°C; (▲) 40°C; (△) 50°C; (●) 60°C; (□) 70°C. See Figure 1 for abbreviation.

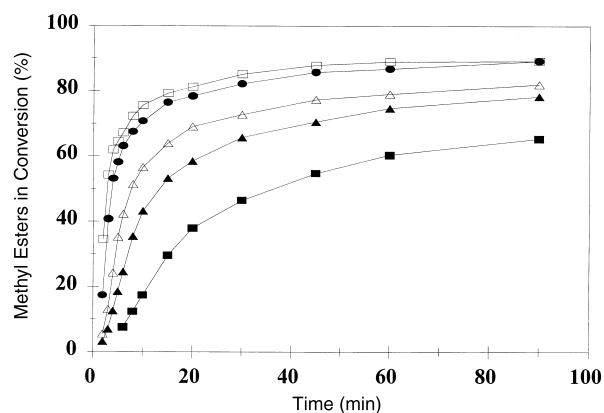


FIG. 4. The effect of temperature and time on the overall conversion to methyl esters at $N_{Re} = 6200$. (■) 30°C; (▲) 40°C; (△) 50°C; (●) 60°C; (□) 70°C. See Figure 1 for abbreviation.

the higher energy state of the molecules resulting in more fruitful collisions. Higher solubility of the reactants at elevated temperatures may also be partially responsible for this behavior. Mass transfer region is reduced from 55 to about 20 min as temperature is increased from 30 to 60°C at $N_{Re} = 3100$ (Fig. 3). At higher mixing intensities, the mass transfer region is short and this effect is not significant (Fig. 4).

In general, with multiple reactions, a high temperature favors the reaction of higher activation energy, and a low temperature favors the reaction of lower activation energy. Table 1 lists the calculated activation energies for the three reversible reactions involved in the transesterification reactions. In the first two reactions (TG \leftrightarrow DG and DG \leftrightarrow MG) the energy of activation is higher for the forward reactions. Thus, higher temperatures should favor these reactions, and higher concentrations of MG are expected. However, for the third reaction (MG \leftrightarrow GL), the forward reaction has a lower activation energy than the reverse reaction. Theoretically, this implies a more favorable reverse reaction at higher temperatures but, apparently, higher concentrations of MG offset this effect and the kinetic-controlled region for the combined trans-

esterification reactions is more favorable at higher temperatures (Figs. 3 and 4). This effect becomes minimal as temperature is increased and the overall conversion reaches an asymptotic value at about the boiling temperature of the alcohol (Fig. 4).

Mechanism of transesterification reaction. Freedman and coworkers (1) studied the kinetics of the acid- and alkaline-catalyzed transesterification of soybean oil with 1-butanol and methanol at 30:1 and 6:1 molar ratios of alcohol to soybean oil. They proposed pseudo first-order kinetics at large molar excess of alcohol and second-order kinetics combined with a shunt-reaction scheme at the lower alcohol excess level. In this study, a second-order reaction mechanism with and without the shunt reaction was evaluated by mathematical modeling. In our kinetic modeling, the initial stage of the reaction was not included since it is short and is minimized at realistic temperatures and mixing intensities. For example, at 70°C and a high mixing speed of 600 rpm, time for the mass transfer-controlled region was practically nil.

A total of 15 sets of experimental data were evaluated with both kinetic schemes. Figure 5 shows a typical fitting of the experimental results excluding the shunt mechanism. Reaction rate constants resulting from this curve fitting are tabulated in Table 2 together with the rate constants including the shunt mechanism. Examination of the curve-fitting results showed good fit of the lines to the experimental points in all cases. Inclusion of the shunt reaction did not improve the fit and the indicators which determine the goodness of the fit such as the final sum of squares, the root-mean-square, and R^2 were unchanged or less favorable. Furthermore, the values for the rate constants, k_1 to k_6 , did not change significantly when the shunt mechanism was included, and the values for k_7 and k_8 were several orders of magnitude smaller than k_1 to k_6 . This was also true when their significance in the rate equations was weighted against other terms resulting from k_1 to k_6 . Therefore, inclusion of a shunt mechanism to describe the transesterification kinetics is not necessary.

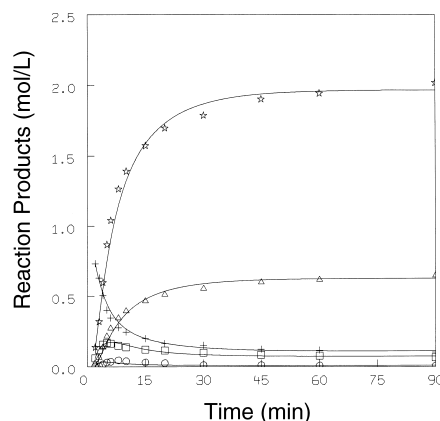


FIG. 5. Kinetic modeling curves and experimental points for the composition of the reaction mixture during the transesterification of soybean oil at 50°C and $N_{Re} = 6200$. (+) Triglycerol; (☆) methyl esters; (□) diglycerides; (○) monoglycerides; (△) glycerol. See Figure 1 for abbreviation.

TABLE 2
Average Reaction Rate Constants at 50°C and $N_{Re} = 6200^a$

Rate constant	Without shunt reaction	With shunt reaction
k_1	0.050	0.049
k_2	0.110	0.102
k_3	0.215	0.218
k_4	1.228	1.280
k_5	0.242	0.239
k_6	0.007	0.007
k_7	—	7.84×10^{-5}
k_8	—	1.58×10^{-5}

^aSee Table 1 for abbreviation.

Reaction rate constants. Reaction rates almost always increase with temperature for elementary irreversible reactions. Multiple and reversible reactions do occasionally exhibit an optimal temperature with respect to the yield of a desired product. The optimal temperature is observed by a maximum on a rate constant vs. temperature plot, or it may simply be the highest temperature under investigation. Our objective was to explore the temperature dependency of the reaction rate constant for the transesterification reactions.

The kinetic modeling procedures using MLAB programs were presented earlier. The representative modeling results for the rate constants at $N_{Re} = 12,400$ are presented in Figure 6 as a function of temperature where the rate constants are presented as a range indicated by vertical lines and the legend marks denote the average values. Rate constants for the first two reactions in Equation 2 increase with temperature for both the forward and reverse reactions (Fig. 6). The rate of increase was much faster for the forward reaction than the reverse reaction. For example, for the reaction of $TG \leftrightarrow DG$, forward reaction rate was increased by a factor of about 14 while the reverse reaction was increased only by a factor of about 7 when the temperature was raised from 30 to 70°C. For the reaction of $DG \leftrightarrow MG$, there was a 37-fold increase in the forward reaction with only an 11-fold increase in the reverse reaction. Therefore, in reactions one and two, both forward reactions are favored at higher temperatures. In the third reaction, $MG \leftrightarrow GL$, Figure 6 shows an apparent decrease in the reaction rate constants as the reaction temperature is in-

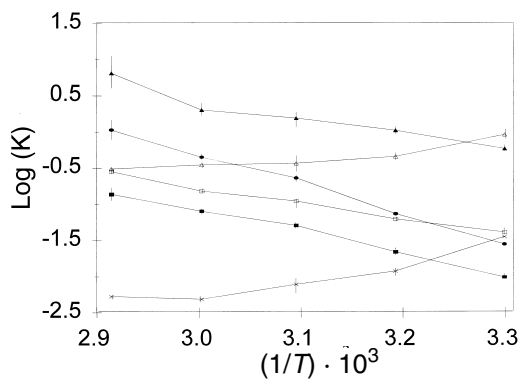


FIG. 6. The temperature dependency of the reaction rate constants at $N_{Re} = 12400$. (■) k_1 ; (□) k_2 ; (●) k_3 ; (▲) k_4 ; (△) k_5 ; (X) k_6 .

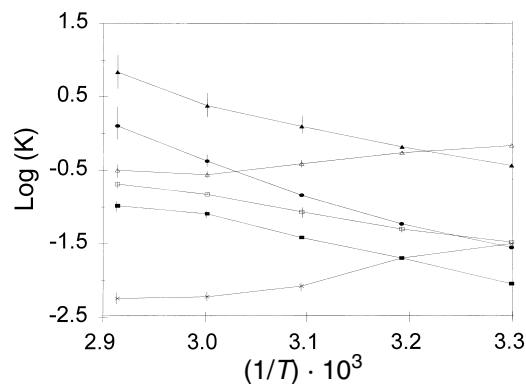


FIG. 7. The temperature dependency of the reaction rate constants at $N_{Re} = 6200$. (■) k_1 ; (□) k_2 ; (●) k_3 ; (▲) k_4 ; (△) k_5 ; (X) k_6 .

creased. This was discussed earlier in terms of the energy of activation. In terms of the reaction rate constants, the forward reaction rate constant in the third reaction is reduced by only a factor of 2, whereas the reverse reaction is reduced by a factor of 10 as temperature is increased. This means a more favorable forward reaction than the reverse reaction in the third reaction at high temperatures. The overall formation rate of the desired product (methyl esters) is also more favorable at higher reaction temperatures (Fig. 4). No optimal temperature was detected for the reaction, and the highest temperature, 70°C, was the most favorable in the temperature range under investigation.

Variations in rate constants with temperature at $N_{Re} = 6200$ were practically identical (Fig. 7). This finding further confirms the hypotheses of kinetically controlled mechanism for the transesterification reactions after the formation of the single phase.

In conclusion, the concentration curve for the product methyl esters and GL was sigmoidal. Based on a stepwise and reversible reaction mechanism, the experimental results clearly demonstrated an initial mass transfer-controlled region which was followed by a kinetic-controlled region. The inclusion of the shunt reaction mechanism did not appear to be necessary. The results also suggest that the inhibition effect of GL is not a factor even in the later stages of the reaction. Results on the activation energies suggest that, over the range investigated, Arrhenius kinetics for the forward reactions dominates.

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REFERENCES

1. Freedman, B., R.O. Butterfield, and E.H. Pryde, Transesterification Kinetics of Soybean Oil, *J. Am. Oil Chem. Soc.* 63:1375-1380 (1986).
2. Freedman, B., E.H. Pryde, and T.L. Mounts, Variables Affect-

- ing the Yield of Fatty Esters from Transesterified Vegetable Oils, *Ibid.* 61:1638–1643 (1984).
- Ahn, E., E. Koncar, M. Mittelbach, and R. Marr, A Low-Waste Process for the Production of Biodiesel, *Sep. Sci. Tech.* 30:2021–2033 (1995).
 - Kusy, P.F., Transesterification of Vegetable Oils for Fuels, *Proceedings of the International Conference on Plant and Vegetable Oils as Fuels*, ASAE, St. Joseph, MI, 1982, pp. 127–137.
 - Tanaka, Y., A. Okabe, and S. Ando, Method for the Preparation of a Lower Alkyl Ester or Fatty Acid, U.S. Patent 4,303,590 (1981).
 - Sankaran, V., Transesterification of Triglycerides, U.S. Patent 4,966,876 (1990).
 - Farkas, L., O. Schachter, and B.H. Vromen, On the Rate of Acid-Catalyzed Transesterification of Butyl Alcohol and Ethyl Acetate, *J. Am. Chem. Soc.* 71:1991–1994 (1949).
 - Davies, B., and G.V. Jeffreys, Continuous Transesterification of Ethyl Alcohol and Butyl Acetate in a Sieve Plate Column. II. Batch Reaction Kinetics Studies, *Trans. Inst. Chem. Eng.* 51:271–274 (1973).
 - Sridharan, R., and I.M. Mathai, Transesterification Reactions, *J. Sci. Ind. Res.* 33:178–187 (1974).
 - Dufek, E.J., R.O. Butterfield, and E.N. Frankel, Esterification and Transesterification of 9(10)-Carboxystearic Acid and Its Methyl Esters. Kinetic Studies, *J. Am. Oil Chem. Soc.* 49:302–306 (1972).
 - Solov'ev, V.V., B.N. Bychkov, G.N. Koshel, and L.A. Rodivilova, Kinetics of Esterification of C₁₈ Unsaturated Fatty Acids by Methyl Alcohol, *Zhurnal Prikladnoi Khimii* 62:2128–2131 (1989).
 - Erciyes, A.T., L. Dandik, and O.S. Kabasakal, The Kinetics of the Esterification Reaction Between Castor Oil and Oleic Acid, *J. Am. Oil Chem. Soc.* 68:639–641 (1991).
 - Yong, Y.P., W.R. Murphy, and E. Robinson, Esterification Using an Immobilized Enzyme on Porous Polymeric Supports, *ChemE Res. Event*:474–476 (1994).
 - Moore, S.R., and J. Davies, The Kinetics of Lipase-Catalyzed Interesterification of Fats and Oils, *Ibid.*:526–528 (1994).
 - Method Ca 5a-40. Sampling and Analysis of Commercial Fats and Oils for Free Fatty Acids, in *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th edn., edited by W.E. Link, Champaign, American Oil Chemists' Society, 1989.

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