Kinetics of Palm Oil Transesterification in a Batch Reactor

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ABSTRACT: Methyl esters were produced by transesterification of palm oil with methanol in the presence of a catalyst (KOH). The rate of transesterification in a batch reactor increased with temperature up to 60°C. Higher temperatures did not reduce the time to reach maximal conversion. The conversion of triglycerides (TG), diglycerides (DG), and monoglycerides (MG) appeared to be second order up to 30 min of reaction time. Reaction rate constants for TG, DG, and MG hydrolysis reactions were 0.018–0.191 $(\text{wt\%}\cdot\text{min})^{-1}$, and were higher at higher temperatures and higher for the MG reaction than for TG hydrolysis. Activation energies were 14.7, 14.2, and 6.4 kcal/mol for the TG, DG, and MG hydrolysis reactions, respectively. The optimal catalyst concentration was 1% KOH.

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Methyl esters derived from vegetable oil (biodiesel) have good potential as an alternative diesel fuel. The cetane number, energy content, viscosity, and phase changes of biodiesel are similar to those of petroleum-based diesel fuel (1). Biodiesel is produced by transesterification of large, branched triglycerides (TG) into smaller, straight-chain molecules of methyl esters, using an alkali or acid as catalyst (2). There are three stepwise reactions with intermediate formation of diglycerides (DG) and monoglycerides (MG) resulting in the production of 3 mol of methyl esters (ME) and 1 mol of glycerol (GL) as follows (3,4).

The overall reaction is:

$$\mathrm{TG} + 3\,\mathrm{ROH} \xrightarrow{\text{Catalyst}} 3\mathrm{R'CO_2R} + \mathrm{GL} \qquad [1]$$

The stepwise reactions are:

$$\mathrm{TG} + \mathrm{ROH} \underset{k_4}{\overset{k_1}{\leftrightarrows}} \mathrm{DG} + \mathrm{R'CO_2R} \qquad [2]$$

$$\mathrm{DG} + \mathrm{ROH} \underset{k_5}{\overset{k_2}{\leftrightarrows}} \mathrm{MG} + \mathrm{R'CO_2R} \qquad [3]$$

$$\mathrm{MG} + \mathrm{ROH} \underset{k_6}{\overset{k_3}{\leftrightarrows}} \mathrm{GL} + \mathrm{R'CO_2R} \qquad [4]$$

Transesterification reactions have been studied for many vegetable oils such as soybean, rapeseed, sunflower, and safflower seed (5,6). Common catalysts for transesterification are NaOH, KOH, or sodium methoxide. However, sodium methoxide causes formation of several by-products, mainly sodium salts, which have to be treated as waste (7). In addition, a high-quality oil is required with this catalyst. Potassium hydroxide has an advantage in that, at the end of the reaction, the reaction mixture can be neutralized with phosphoric acid, resulting in potassium phosphate, which can be used as fertilizer. Isigigur *et al.* (6) reported that potassium hydroxide was superior to sodium hydroxide as a catalyst for the transesterification of safflower seed oil.

A study of the kinetics of transesterification will provide parameters that can be used to predict the extent of the reaction at any time under particular conditions. Among several kinetic studies published on transesterification of simple esters, only a few were concerned with the transesterification of vegetable oil fatty esters, such as those by Freedman *et al.* (3) and Noureddini and Zhu (4). Although methyl esters from palm oil have been produced on a pilot scale in Malaysia, there are no published reports on its kinetics.

EXPERIMENTAL PROCEDURES

Refined, bleached, and deodorized palm oil was obtained from Archer, Daniels Midland (Decatur, IL). Reference standards such as tripalmitin, triolein, diolein, monoolein, methyl oleate, methyl palmitate, methyl heptanoate, and glycerol of >99% purity were purchased from Nu-Chek-Prep, Inc. (Elysian, MN) and Sigma Chemical Co. (St. Louis, MO). Methanol and potassium hydroxide were of analytical grade obtained from Fisher Scientific Co. (Pittsburgh, PA).

Batch reaction. Transesterification reactions were performed in a 1-L three-necked flask equipped with a reflux condenser, a thermometer, and a sampling port. The reactor was immersed in a constant-temperature water bath equipped

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with a temperature controller, that was capable of maintaining the temperature within ±0.2°C. Agitation was provided with a magnetic stirrer, which was set at a constant speed throughout the experiment. Initially, the reactor was filled with 500 g palm oil and heated to the desired temperature. A known amount of potassium hydroxide (the catalyst) was dissolved in the required amount of methanol and heated separately to the desired temperature. This methanolic KOH was then added to the base of the reactor (to prevent evaporation of methanol) at which point the reaction was assumed to have started. The molar ratio of methanol/oil was fixed at 6:1 since the literature suggests that this is the optimal ratio for vegetable oil transesterification. The weight of 1 mol oil was determined from the calculated average molecular weight of palm oil based on the known fatty acid composition of the oil.

At various times, a sample was withdrawn quickly from the reactor with a Pasteur pipet. About 300 mg of the sample mixture was placed in a vial and diluted with 5 mL high-performance liquid chromatography grade tetrahydrofuran, and then one drop of 0.6 N hydrochloric acid was added to neutralize the catalyst. Separate studies had determined that this dilution and neutralization stopped the reaction immediately. The sample was then filtered through 0.2 μm polytetrafluoroethylene syringe filter and kept at –20°C until further analysis.

Analysis. The samples were analyzed for TG, DG, MG, total methyl esters, and glycerol content by gel permeation chromatography (8). The composition of the methyl esters was analyzed by gas chromatography (9,10) using an HP 6890 Series Gas Chromatograph System equipped with a split/splitless injection system, a flame-ionization detector, and an HP ChemStation software (Hewlett-Packard, Wilmington, DE). The column was a 30 m × 0.25 mm, 0.25 μm DB-Wax capillary column (J & W Scientific, Folsom, CA) with He at 25 cm/s as the carrier gas and a split ratio of 50:1. Injector and detector temperatures were 250°C, oven temperature started at 120°C for 2 min, increased to 230°C at a rate of 5°C/min, and held at this temperature for 5 min. Methyl heptanoate was used as the internal standard.

RESULTS AND DISCUSSION

Figure 1 shows the progress of the transesterification reaction for palm oil in the first 90 min of reaction time. The temperature was 50°C, the catalyst was 1% potassium hydroxide, and the methanol/oil molar ratio was 6:1. In the initial stages of the reaction, production of ME was rapid. The rate then diminished and finally reached equilibrium in about 60 min. The increase in ME concentration was followed by an increase in glycerol concentration as it was liberated from TG molecules. However, the relative proportion of GL produced was not always the same as that of the esters produced. This is due to intermediate products such as DG and MG. TG concentration decreased as the reaction proceeded; after 60 min, TG concentration was only 0.54%. The highest concentrations of DG and MG were observed in the first minute; their levels then decreased and reached equilibrium after 60 min. Data at other temperatures followed a similar pattern (11).

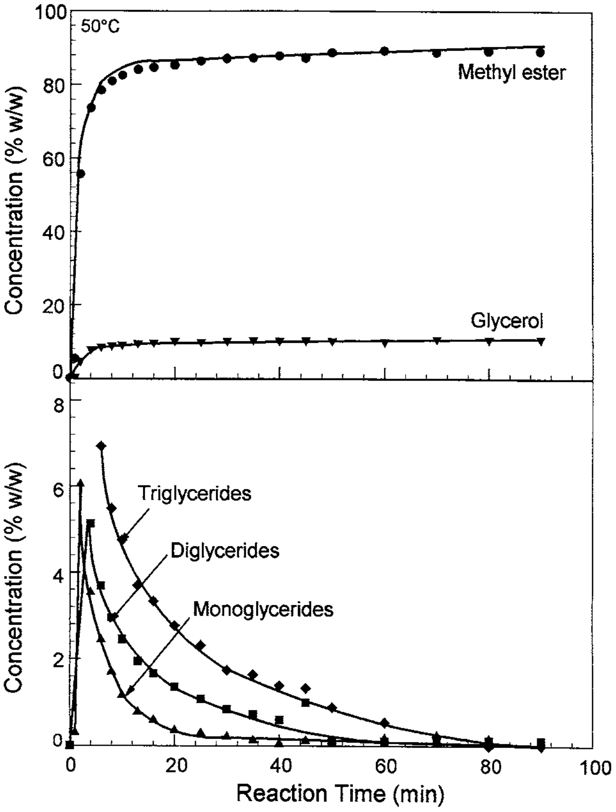

FIG. 1. Composition of reaction products during palm oil transesterification at 50°C. Molar ratio of oil/methanol was 6, catalyst was 1% KOH.

Effect of temperature. The effect of temperature on palm oil transesterification was studied at a catalyst (KOH) concentration of 1% and a methanol/oil molar ratio of 6:1. Owing to the semisolid nature of palm oil at room temperature, the minimum temperature used in this work was 50°C. Below 50°C, the high viscosity of the oil caused problems in pumping and stirring. Storage temperatures for palm oil were about 55°C to maintain its liquidity. The maximum temperature studied was 65°C because the boiling point of methanol is 68°C. Temperature had a small but noticeable effect on the transesterification reaction, as shown in Figure 2.

Figure 3 shows a typical distribution of products and intermediates at 4 min of reaction time. At 50°C, conversion of TG to ME was 73% as compared to 82% conversion at 65°C. Freedman *et al.* (5) also reported rapid formation of ME during transesterification of soybean oil and sunflower oil: after 1 min, 80% of TG were converted to ME and after 1 h, ME concentration was 93–98% of the reaction mixture.

Reaction kinetics. The best kinetic model for our data appears to be a pseudo second-order model for the initial stages of the reaction, followed by first-order or zero-order kinetics. To test this hypothesis, a model was developed based on the kinetics of TG hydrolysis (12). The second-order reaction rate for TG in Equation 2 would be as follows (13):

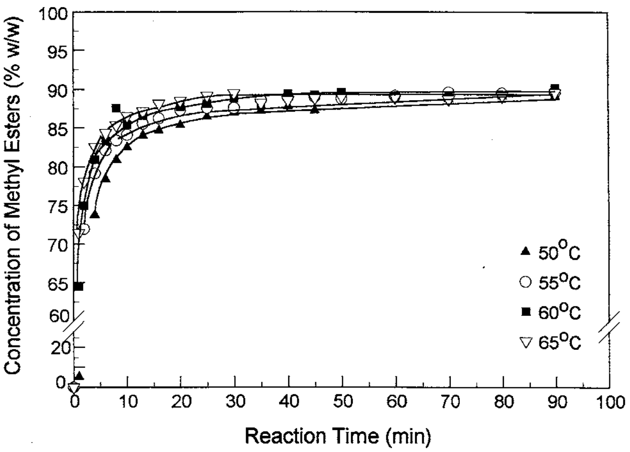

FIG. 2. Effect of reaction temperature on the transesterification reaction. Molar ratio of oil/methanol was 6, catalyst was 1% KOH.

$$-d[\mathrm{TG}]/dt = k[\mathrm{TG}]^2 \qquad [5]$$

Integration of Equation 5 yields:

$$k_{\mathrm{TG}} \cdot t = 1/[\mathrm{TG}] - 1/[\mathrm{TG}_0] \qquad [6]$$

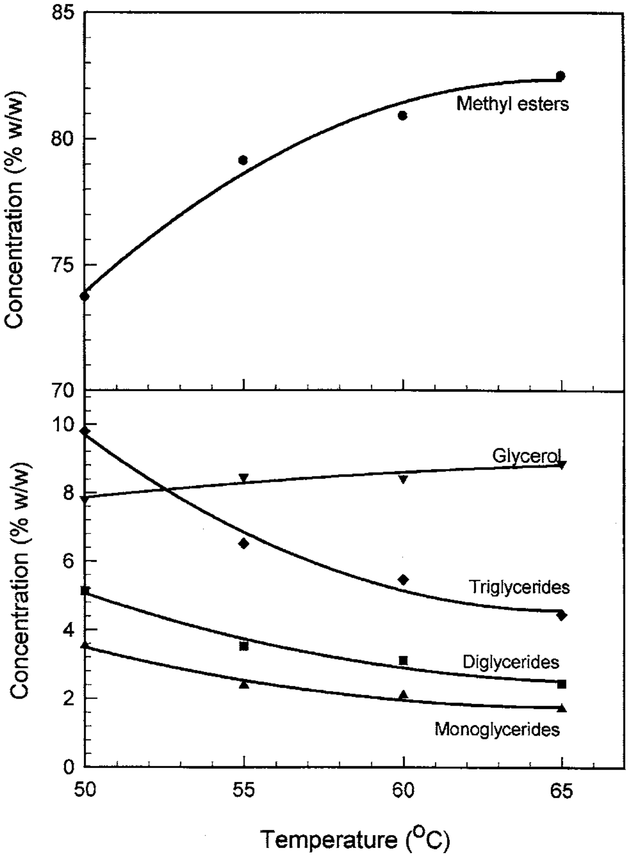

FIG. 3. Effect of temperature on composition of products and intermediates at 4 min of the transesterification reaction of palm oil. Molar ratio of oil/methanol = 6, catalyst was 1% KOH.

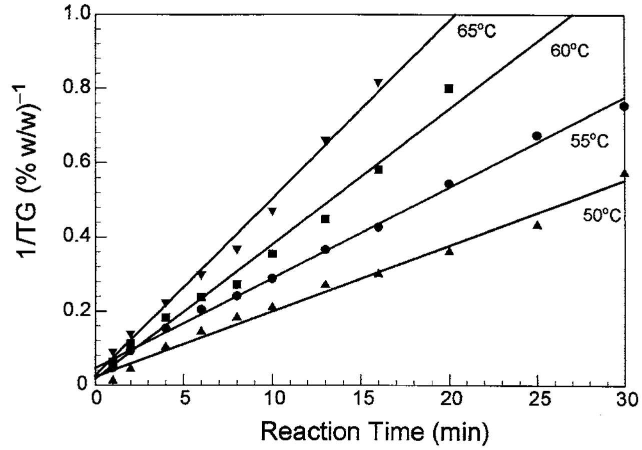

FIG. 4. Pseudo second-order reaction model of triglyceride hydrolysis (Eq. 6) at various temperatures. Molar ratio of oil/methanol was 6, catalyst was 1% KOH.

Similarly, the same procedure applied to Equations 3 and 4 would result in:

$$k_{\mathrm{DG}} \cdot t = 1/[\mathrm{DG}] - 1/[\mathrm{DG}_0] \qquad [7]$$

$$k_{\mathrm{MG}} \cdot t = 1/[\mathrm{MG}] - 1/[\mathrm{MG}_0] \qquad [8]$$

where k is the overall pseudo rate constant, t is the reaction time, TG_0 is the initial triglyceride concentration, DG_0 is the initial highest diglyceride concentration, and MG_0 is the initial highest monoglyceride concentration.

For the hydrolysis of TG, a plot of reaction time (t) vs. 1/[TG] will be a straight line if the model (Equation 6) is valid. Figure 4 shows such plots at the four temperatures in the early stages of the reaction (up to 30 min of reaction time). The slope is k_{TG} with the units of $(\mathrm{wt\%{\cdot}min})^{-1}$. Similar straight lines were obtained for DG and MG hydrolysis (11). The values of k and its corresponding correlation coefficient are shown in Table 1. There is an increase in k at higher temperatures, and the order

TABLE 1
Reaction Rate Constant k (wt% min)$^{-1}$ for Triglyceride (TG), Diglyceride (DG), and Monoglyceride (MG) Hydrolysis at Different Temperatures

Glyceride	Temperature (°C)	Reaction rate constant, k (wt%·min)$^{-1}$	R^2
TG → DG	50	0.018	0.9865
	55	0.024	0.9966
	60	0.036	0.9822
	65	0.048	0.9903
DG → MG	50	0.036	0.9940
	55	0.051	0.9974
	60	0.070	0.9860
	65	0.098	0.9678
MG → GL[a]	50	0.112	0.9733
	55	0.158	0.9619
	60	0.141	0.9862
	65	0.191	0.9843

[a] GL, glycerol.

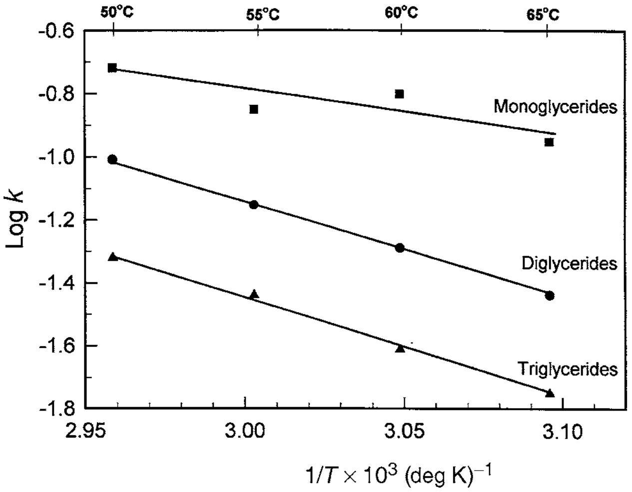

FIG. 5. Arrhenius plot of reaction rate vs. temperature for esterification reactions (Eq. 9).

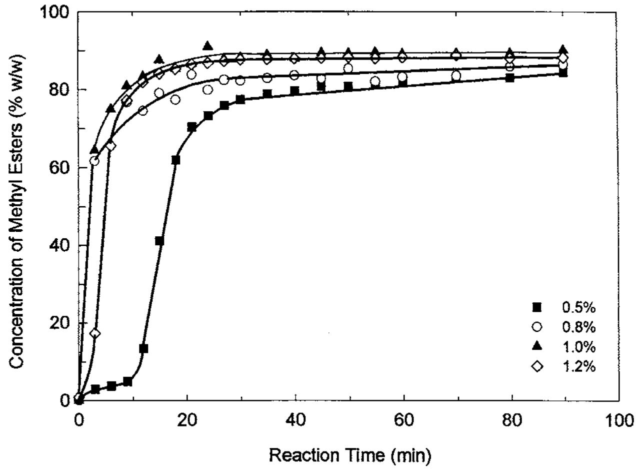

FIG. 6. Effect of catalyst concentration (%) on production of palm oil methyl esters. Molar ratio of oil/methanol was 6 , temperature = 60°C.

of magnitude of k is $k_{MG} > k_{DG} > k_{TG}$. These data were used to determine the Arrhenius energy of activation from a plot of the reaction rate constant (k) vs. the reciprocal of absolute temperature (T), according to the equation:

$$\log_{10} k = (-E_a/2.303R)/T + C \qquad [9]$$

where E_a is the energy of activation, R is the gas constant, and C is a constant. The plot is shown in Figure 5, and activation energies are shown in Table 2. Our values of E_a are in the same range as other work (3) for the TG-DG and DG-MG reactions, but our value for the MG-GL reaction is smaller.

Effect of catalyst concentration. Figure 6 shows the effect of concentration of the KOH catalyst, expressed as a weight percentage of the oil. At the lowest catalyst concentration (0.5%), there was a lag in ME production, followed by a rapid increase in rate after 6 min. The rate then decreased after 30 min. Noureddini and Zhu (4) also observed a sigmoidal pattern for the production of ME from soybean oil. Boocock *et al.* (14) suggested the lag is because this is a two-phase reaction mixture. The oil concentration in the methanol phase is low at the start of the reaction, leading to mass transfer limitations. As the reaction proceeds, the concentration of oil in the methanol phase increases, leading to higher rates. No large differences were observed in TG conversion to ME between 1% and 1.2% KOH. Others have also observed 1% KOH to be optimum for transesterification of safflower seed oil (6) and rapeseed oil (15) although Vicente *et al.* (16) suggested higher levels of alkali were better for the transesterification reaction.

TABLE 2
Activation Energy for Hydrolysis of TG, DG, and MG During Transesterification of Palm Oil[a]

Reaction	E_a (kcal/mol)	R^2
TG → DG	14.7	0.9959
DG → MG	14.2	0.9998
MG → GL	6.4	0.7457

[a] For abbreviations see Table 1.

TABLE 3
Distribution of Methyl Esters Derived from Palm Oil (expressed as concentration in weight %)

Methyl ester	This work	Maycock (17)
Methyl laurate (12:0)	0.35	0.2
Methyl myristate (14:0)	1.08	1.1
Methyl palmitate (16:0)	43.79	44.0
Methyl palmitoleate (16:1)	0.15	0.1
Methyl stearate (18:0)	4.42	4.5
Methyl oleate (18:1)	39.90	39.2
Methyl linoleate (18:2)	9.59	10.1
Methyl linolenate (18:3)	0.17	0.4
Methyl arachidate (20:0)	0.38	0.4

Composition of ME. There were no significant changes in the concentration of nine major ME during the entire 90 min of reaction, as analyzed by gas chromatography (11). The distribution of ME is shown in Table 3.

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