Biodiesel from an Alkaline Transesterification Reaction of Soybean Oil Using Ultrasonic Mixing

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ABSTRACT: The feasibility of using ultrasonic mixing to obtain biodiesel from soybean oil was established. The alkaline transesterification reaction was studied at three levels of temperature and four alcohol-to-oil ratios. Excellent yields were obtained for all conditions. For example, at 40°C with ultrasonic agitation and a molar ratio of 6:1 methanol/oil, the conversion to FAME was greater than 99.4% after about 15 min. For a 6:1 methanol/oil ratio and a 25 to 60°C temperature range, a pseudo second-order kinetic model was confirmed for the hydrolysis of DG and TG. Reaction rate constants were three to five times higher than those reported in the literature for mechanical agitation. We suspect that the observed mass transfer and kinetic rate enhancements were due to the increase in interfacial area and activity of the microscopic and macroscopic bubbles formed when ultrasonic waves of 20 kHz were applied to a two-phase reaction system.

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Since the oil crisis of the 1970s, research interest in the area of alternative fuels has expanded. Many studies have been conducted on the availability and practicality of an environmentally friendly fuel that could be obtained from domestic sources. Methanol, ethanol, compressed natural gas, liquefied petroleum gas, liquefied natural gas, vegetable oils, reformulated gasoline, and reformulated diesel fuel have been considered as alternative fuels.

In the 1930s and 1940s, vegetable oils were used as emergency fuels (1). These oils contain no sulfur and have about 10% oxygen by weight. This tends to reduce their unburned hydrocarbons, sulfur dioxide, carbon monoxide, and particulate emissions compared with diesel fuel. Therefore, using vegetable oil-based fuel may reduce air pollution (2). Because of the high viscosity and low volatility of vegetable oil as compared with diesel fuel, problems such as engine deposits, injector coking, piston ring sticking, and thickening of the lubricating oil occur frequently (3). However, these effects can be reduced or eliminated through transesterification of the vegetable oil to form alkyl esters (3). The process of transesterification removes glycerol from the TG and replaces it with alkyl groups from the alcohol used for the conversion process (4). This process decreases the viscosity but maintains properties similar to diesel fuel.

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Transesterification consists of a number of consecutive, reversible reactions that decompose the glycerides to esters and glycerol. The TG are converted stepwise to DG, MG, and finally glycerol. The reaction is influenced mainly by the type of catalyst, molar ratio of alcohol to TG, mixing, content of FFA (which are natural degradation products of oils), water content, reaction temperature, and alcohol used as the reagent (5). To complete the reaction stoichiometrically, a 3:1 molar ratio of alcohol to TG is needed. In practice, the ratio of alcohol to TG needs to be higher to drive the equilibrium to a maximum ester yield. The alkaline catalysts include NaOH, KOH, carbonates, and the corresponding sodium and potassium alkoxides. Sulfuric acid, sulfonic acids, and hydrochloric acid are usually used as acid catalysts. The transesterification reaction involves two immiscible phases. The less-dense phase has the catalyst dissolved in the alcohol, whereas the other contains the oil or fat. The reaction between these species can occur only in the interfacial region between the liquids, as alkaline catalysts are essentially insoluble in the oil phase. Vigorous mixing is required to increase the area of contact between the two phases. In the present work we consider the use of ultrasound for this purpose.

Like any sound wave, ultrasound alternately compresses and stretches the molecular spacing of the medium through which it passes, causing a series of compression and rarefaction cycles (6). If a large negative pressure gradient is applied to the liquid so that the distance between the molecules exceeds the critical molecular distance necessary to hold the liquid intact, the liquid will break down and voids (cavities) will be created, i.e., cavitation bubbles will form. At high ultrasonic intensities, a small cavity may grow rapidly through inertial effects. As a result, some bubbles undergo sudden expansion to an unstable size and collapse violently, generating energy for chemical and mechanical effects, and may increase the mass transfer rates by disrupting the interfacial boundary layers (known as the liquid jet effect). Another effect of ultrasound agitation is acoustic streaming mixing, in which a macroscopic flow is induced in the liquid by the absorption of the ultrasonic wave by the reactive medium.

The objective of this work was to study the biodiesel transesterification reaction using an ultrasonic mixing technique to obtain the highest possible conversion percentages. In this way, a pure fuel can be obtained from the reactor, with fewer requirements for product purification. This will reduce production costs and make biodiesel more competitive in price with diesel fuel.

EXPERIMENTAL PROCEDURES

Reagents. Refined commercial soybean oil (water and FFA contents of 0.11 and 0.03%, respectively) was used. Anhydrous methanol, ethanol, 1-butanol, and 2-propanol (HPLC grade) were purchased from Fisher Scientific (Cayey, Puerto Rico). Potassium hydroxide (pellets, ACS reagent), glycerol (99.5+%), and THF (HPLC grade) were purchased from Aldrich (St. Louis, MO). Analytical standards of MG, DG, and TG were purchased from Aldrich. The standards used for the calibration curves were: (i) triolein (C18:1,9-octadecenoic acid, TG); (ii) tricaprin (C18:[*cis*]-9-octadecenoic acid, TG); (iii) 1,3-diolein (C18:1,9-octadecenoic acid, DG); and (iv) monoolein (C18:1,9-octadecenoic acid, MG). A standard of methyl oleate (C18:1,9-octadecenoic acid, methyl ester) was purchased from Alltech (Santurce, Puerto Rico).

Apparatus. A schematic diagram of the ultrasound reactor is shown in Figure 1. The ultrasound reactor consists of a generator (digital sonifier power supply), which converts a standard 60-Hz line voltage to a high-frequency electrical power of 20 kHz. This high-frequency electrical energy is fed to a piezoelectric transducer, where it is converted to mechanical vibrations of the same frequency. The piezoelectric element is a lead zirconate titanate electrostrictive element, which, when subjected to an alternating voltage, expands and contracts. The transducer vibrates in a longitudinal direction and transmits this motion to the horn tip, which is immersed in the solution, causing cavitation. The 1/2-in. stepped disrupter horn (applicator) is made of titanium and is cylindrical in shape, with a diameter of 1.3 cm and a height of 13 cm. For the titanium alloy horn, the wavelength for 20 kHz of sound is about 26 cm, and this defines the absolute minimum longitudinal dimension of 13 cm, i.e., the half-wavelength. It will give an exact mirror of the vibrational amplitude supplied at one end to the other end. The stepped horn allows magnification of the ultrasonic vibration, i.e., power.

The tip of the horn was submerged in the reaction mixture contained in a glass reactor (250 mL, 5 cm i.d.). The ultrasonic power entering the system was determined to be 14.49 W (i.e., 0.74 W/cm^2) by calorimetric experiments. The reactor was equipped with a jacket, which permitted the recirculation of water from a constant-temperature bath; temperature control of the reaction mixture was generally ±0.5°C. The reactor was also equipped with a thermometer and sampling outlet.

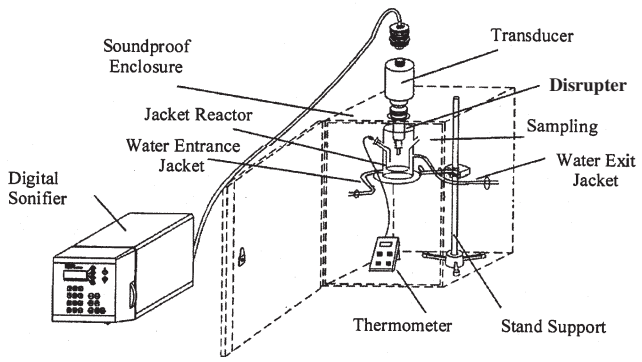

FIG. 1. Schematic diagram of the ultrasound transesterification system.

Procedure. The reaction mixture was prepared by mixing 120 g of soybean oil, 1.5% (kg/L oil) potassium hydroxide, and the amount of alcohol required for the desired molar ratio. Molar ratios were calculated by taking the M.W. for the soybean oil (calculated from the FA percentages; see Ref. 7) as 862.74. The vegetable oil was introduced into the reactor and heated to the reaction temperature. KOH (1.8 g) was dissolved in the prescribed amount of alcohol and heated to the desired temperature. This solution was then added to the reactor and ultrasonic mixing was started immediately.

A sterile syringe was used to withdraw samples (0.1 cm^3) from the middle of the reaction vessel for analysis. Approximately 400 mg of the sample mixture was placed in a vial and diluted with 10 mL of THF. One drop of 0.6 N hydrochloric acid was added to neutralize the catalyst and stop the reaction. Separate studies had determined that this dilution and neutralization stopped the reaction immediately (8). The samples were kept at 20°C until required for further analysis.

HPLC was used to evaluate the conversion efficiencies of the various transesterification reactions. Analyses were performed using size-exclusion chromatography with a Hewlett-Packard Series 1100 chromatograph equipped with a refractive index detector and a SPHER-Cyano 60A column (length 250 mm, i.d. 4.6 mm; Princeton Chromatography, Cranbury, NJ).

The column temperature was 25°C, and THF was used as the mobile phase, held at a flow rate of 0.35 mL/min. A Waters Model 740 recorder registered the detector signal and performed peak integration. The run time was 20 min. Approximately 40 μL of sample was injected manually into a 20-μL injector loop.

The detector response for glycerides was used to analyze the production of biodiesel esters quantitatively. The response was defined as the area of each HPLC component peak.

RESULTS AND DISCUSSION

The variables of reaction temperature, molar ratio of alcohol to TG, type of alcohol that affected the equilibrium, and reaction time of the alkaline-catalyzed transesterification using ultrasonic mixing were studied.

Effects of reaction temperature. The results obtained from the transesterification of soybean oil (3:1 methanol/oil ratio) at different temperatures are shown in Figure 2A. Increasing the temperature slightly decreased the equilibrium conversion percentage of FAME (e.g., after 2 h the conversions were 89.78 ± 0.04, 89.40 ± 0.09, and 89.29 ± 0.06% at 25, 40, and 60°C, respectively). The conversion percentages were defined as the number of moles of glycerides that had reacted per mole of oil fed to the system. The results suggest that lower temperatures did not have a significant effect on the maximal conversion percentage of FAME or on the equilibrium displacement to the products. Also, from Figures 2B and 2C, one can observe that a decrease in temperature did not necessarily increase the equilibrium displacement to products when a 6:1 or 4.5:1 molar

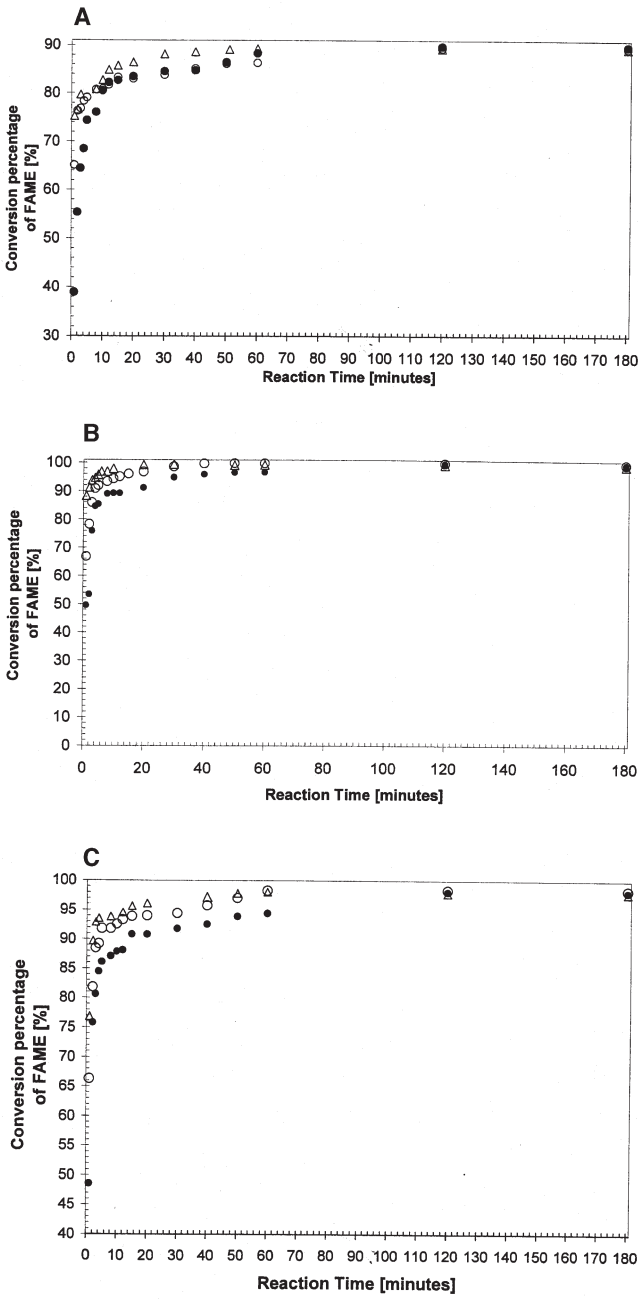

FIG. 2. (A) Effect of reaction temperature on FAME conversion of soybean oil at a 3:1 molar ratio with methanol by alkaline transesterification using ultrasonic mixing. (●) 25°C, (○) 40°C, (△) 60°C. (B) Effect of reaction temperature on FAME conversion at a 4.5:1 molar ratio. Alkaline transesterification using ultrasonic mixing and methanol. (●) 25°C, (○) 40°C, (△) 60°C. (C) Effect of reaction temperature on FAME conversion at a 6:1 molar ratio. Alkaline transesterification using ultrasonic mixing and methanol. (●) 25°C, (○) 40°C, (△) 60°C.

ratio of methanol/oil was used. After 2 h of reaction, the conversion percentages for a 4.5:1 molar ratio were 98.04 ± 0.01, 98.30 ± 0.01, and 97.79 ± 0.07% for 25, 40, and 60°C, respectively. For a 6:1 molar ratio, the FAME conversion percentages in the first minute were 99.72 ± 0.01, 99.78 ± 0.02, and 99.28 ± 0.06% for 25, 40, and 60°C, respectively. The maximum

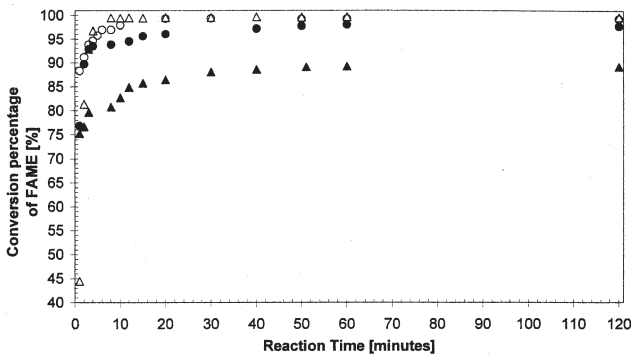

FIG. 3. Effect of molar ratio in a 60°C transesterification reaction. Alkaline transesterification using ultrasonic mixing and methanol. (▲) 3:1, (●) 4.5:1, (○) 6:1, (△) 9:1.

FAME conversion percentages were observed when a temperature of 40°C was used.

Effect of the amount of alkaline catalyst. The effect of the initial concentration of KOH in methanol was studied for a molar ratio of 9:1 methanol/TG and two different concentrations of the alcohol (1.5 and 2.2% kg/L oil). These experiments showed that changing the amount of KOH used did not affect the equilibrium yield of methyl esters (99.7 ± 0.02% conversion for both catalyst concentrations).

Effect of the molar ratio of methanol to oil. The most important variable affecting the conversion of TG (oil) to biodiesel esters is known to be the molar ratio of alcohol to vegetable oil used (1,9,10). The effects of the molar ratio (3:1 to 9:1) on the transesterification kinetics of soybean oil are shown in Figure 3. The molar ratio had a major effect on the percentage conversion at 2 h when the temperature ranged between 25 and 60°C and the molar ratio varied between 3:1 and 6:1. The methyl ester conversion percentages obtained at molar ratios of 9:1 and 6:1 were 99.67 ± 0.07 and 99.28 ± 0.06%, respectively, at 2 h. As the molar ratio decreased to the stochiometric ratio of 3:1, the FAME conversion percentage decreased to 89.29 ± 0.06%. After 3 min, the conversion percentages were 82.48 ± 0.67, 90.26 ± 0.76, 93.96 ± 0.63, and 92.45 ± 0.65% for 3:1, 4.5:1, 6:1, and 9:1, respectively. We observed that at higher molar ratios, the time required to achieve the maximal conversion decreased.

The results confirmed that to maximize the conversion to esters, an excess of alcohol over the stoichiometric ratio was required. Even under the most suitable conditions for the formation of methyl esters, traces of glycerides remained because of the equilibrium between products and reactants. The weight percentages of DG and TG remained less than 1% at equilibrium when a molar ratio of 6:1 methanol/oil was used.

Furthermore, ratios greater than 6:1 did not have a major effect on the equilibrium conversion percentage; however, they complicated ester and glycerol recovery and would increase the cost of alcohol recovery during the process. A 6:1 molar ratio should be a nearly optimal ratio for this process.

Effects of alcohol type. To investigate the effects of different alcohol types on transesterification, 2-propanol, 1-butanol,

TABLE 1
Effect of Alcohol Type on the Transesterification of Soybean Oil

Alcohol (volume, mL)	TG (% weight)	DG (% weight)	FAME conversion (%)	pK_a
Methanol (33.5)	0.00	0.54 ± 0.02	99.33 ± 0.02	15.5
Ethanol (49)	0.00	0.67 ± 0.02	99.11 ± 0.04	15.9
1-Butanol (77)	1.90 ± 0.02	3.27 ± 0.03	92.02 ± 0.03	19.2
2-Propanol (64)	49.39 ± 0.02	0.00	29.21 ± 0.04	18.0

ethanol, and methanol were compared over a 2-h reaction period with 1.5% KOH as the catalyst and a 6:1 molar ratio of alcohol/oil at 60°C. Table 1 shows the FAME equilibrium conversion percentage for methanol, ethanol, 1-butanol, and 2-propanol. The results obtained showed that the type of alcohol used affected the reaction progress, probably due to the dissociation of these alcohols, similar to the concept of acid dissociation of alcohols in water. The more acidic alcohols reacted rapidly with potassium to form potassium alkoxides, whereas the secondary and tertiary alcohols reacted more slowly. The acidity decreased as the substitution on the alkyl group increased, because a more highly substituted alkyl inhibited solvation of the alkoxide ions and inhibited their dissociation. A similar conversion percentage was observed for methanol and ethanol, since they have approximately the same pK_a value (~15). The lowest conversion percentage was observed when 1-butanol was used in the transesterification reaction because it had the highest pK_a value. If the alkoxide is sufficiently strong to attack the unactivated carboxyl group nucleophilically and form a tetrahedral intermediate, then the progress of the transesterification reaction will be limited by the formation of the alkoxide (9).

Kinetic parameters. The kinetics of conversion under ultrasonic mixing was determined for the 6:1 methanol/oil molar ratio (previously determined to be optimal). Since a stable emulsion was observed throughout the liquid mixture when ultrasonic mixing was applied to the transesterification reaction, the ultrasound reactor may be modeled as a perfect mixed-batch reactor. For an irreversible reaction, it is possible to determine the reaction order and the specific rate constant by numerically differentiating concentration vs. time data. This method is applicable when reaction conditions are such that the rate is essentially a function of the concentration of only one reactant (8). However, by utilizing the method of excess reactants, it is also possible to determine the relationship between the reaction rate and the concentration of other reactants. The kinetic parameters were calculated as a pseudo-order (MeOH-excess) model for the initial stages of the reaction. The concentration of methanol remained essentially unchanged during the course of the reaction. The model applied only to the first minutes of the reaction, where it could be assumed that the equilibrium did not affect the kinetics of the reaction. A differential method was used to estimate the reaction rate constants for both TG to DG and the subsequent reaction to MG.

The differential method of analysis consists of the linearization of the equation obtained by combining the mole balance for a constant-volume batch reactor with the rate law. The rate-law expressions for TG and DG hydrolysis are given by Equations 1 and 2, respectively.

$$r_1 = -k_{TG}'[TG]^{\beta_A} \quad [1]$$

$$r_2 = -k_{TG}'[TG]^{\beta_A} - k_{DG}'[DG]^{\beta_C} \quad [2]$$

where r_1 is the rate of TG hydrolysis, r_2 is the rate of DG hydrolysis, [TG] is the concentration of TG, [DG] is the concentration of DG, β_A is the order of TG, β_C is the order of DG, k_{TG}' is the specific rate of pseudo-order TG hydrolysis, and k_{DG}' is the specific rate of pseudo-order DG hydrolysis. These pseudo-order rate laws did not consider the reversibility of the reaction. For this reason, they apply to the initial stage of the reaction (8). The slope of the plot of $\ln(-dC_A/dt)$ as a function of $\ln(C_A)$ is equal to the reaction order, where C_A is the concentration. The specific reaction rate could be estimated from the intercept. The linear rate-law expressions for DG and TG hydrolysis are given in Equations 3 and 4, respectively:

$$\ln\left(-\frac{d[TG]}{dt}\right) = \ln k_{TG}' + \beta_A \ln[TG] \quad [3]$$

$$\ln\left(-\frac{d[DG]}{dt} + k_{TG}'[TG]^{\beta_A}\right) = \ln k_{DG}' + \beta_C \ln[DG] \quad [4]$$

where $d[TG]/dt$ is the derivative of TG concentration with respect to time and $d[DG]/dt$ is the derivative of DG concentration with respect to time. An integral method was used to validate the kinetic parameters obtained from the differential analysis. The reaction order determined from the differential method was used to integrate the differential equation used to model the batch system. If the order is correct, the appropriate plot determined from the integration of the concentration–time data should be linear. This method could be applied only to linear differential equations. Specific rate constants were used to determine the Arrhenius activation energy from a plot of the specific pseudo-order rate constant vs. the reciprocal of absolute temperature.

TG hydrolysis kinetic parameters. Figure 4 shows the graphs that were obtained to determine the order for the TG hydrolysis reaction. At the three temperatures studied, the reaction order (β_A), with a 90% confidence interval, was between 1.64 (± 0.31) and 1.99 (± 0.20) (Table 2). This is consistent with reported literature values of approximately 2 (7,10).

Figure 5 shows the results from the integral approach, assuming a second-order reaction. Note the excellent correlations that were obtained supporting our analytical approach. From

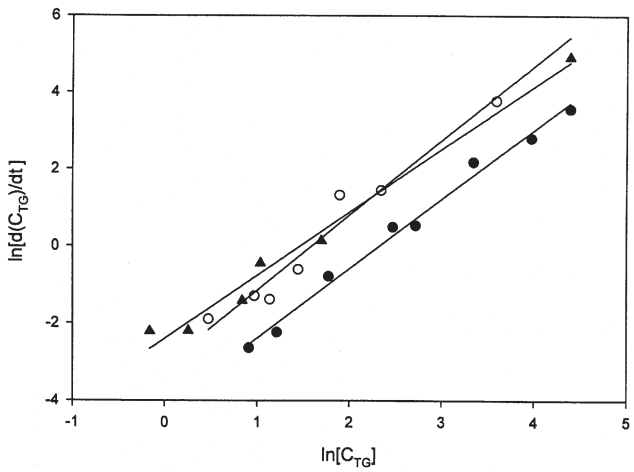

FIG. 4. Differential method for determination of the order of the conversion of TG to DG. Alkaline transesterification using ultrasonic mixing and methanol. (●) 25°C, (○) 40°C, (▲) 60°C.

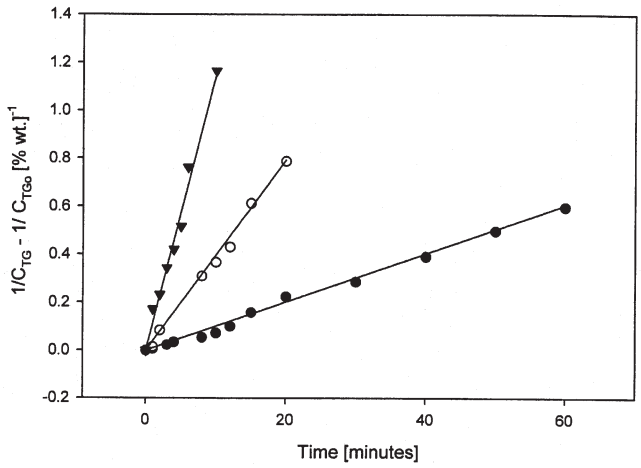

FIG. 5. Pseudo-order reaction model of TG hydrolysis at various temperatures. Alkaline transesterification using ultrasonic mixing and methanol. (●) 25°C, (○) 40°C, (▲) 60°C.

these graphs, we estimated the specific rate of pseudo-order TG hydrolysis (K_{TG}') (Table 2). It is notable that the calculated values for K_{TG}' using ultrasonic mixing were three times higher than those reported in the literature using mechanical agitation. This increase is expressed in terms of an enhancement factor (E_{US}). These data were used to determine the Arrhenius activation energy from a plot of the reaction rate constant (K_{TG}') vs. the reciprocal of absolute temperature. For TG hydrolysis, an activation energy of 53.13 kJ/mol was estimated, in comparation with a value of 67.25 kJ/mol reported in the literature (7).

DG hydrolysis kinetic parameters. Figure 6 shows the graphs that were obtained to determine the reaction order (β_C) using the derivative method for the DG hydrolysis reaction. At the three temperatures studied, the order (at a 90% confidence value) ranged from 1.98 (± 0.15) to 2.33 (± 0.21), again consistent with reported literature values of approximately 2 (7,10). From these graphs, the specific rates of pseudo-order DG hydrolysis (K_{DG}') were estimated, and again a good fit was obtained. Table 3 shows the average values for the reaction order and rate constant. Also, note in Table 3 that the calculated values using ultrasonic mixing were 4.5 times higher than those reported in the literature using mechanical agitation. These data were used to determine the Arrhenius activation energy (Fig. 7), and the estimated activation energy (57.52 kJ/mol) was compared with that reported in the literature (72.21 kJ/mol) (7). A lower activation energy was reported since the reaction rate constant obtained in this work was greater than that obtained in the literature (7,10). The reaction rate constant we determined contained a lower mass transfer component than that reported in the literature. In our case, the apparent activation energy value was not representative of the minimal energy that must be possessed by reacting molecules before the reaction will

TABLE 2
Kinetic Parameters for the TG Hydrolysis Reaction

	Experimental		Literature (7)		
Reaction temperature (°C)	β_A	K_{TG}' (wt%·min)$^{-1}$	β_A	K_{TG}' (wt%·min)$^{-1}$	Ultrasound factor E_{US}
25	1.99 ± 0.26	0.0110 ± 0.0012	2.00	—	—
40	1.90 ± 0.06	0.0402 ± 0.0007	2.00	—	—
60	1.64 ± 0.01	0.1056 ± 0.0134	2.00	0.036	2.93

TABLE 3
Kinetic Parameters for the DG Hydrolysis Reaction

	Experimental		Literature (7)		
Reaction temperature (°C)	β_A	K_{DG}' (wt%·min)$^{-1}$	β_A	K_{DG}' (wt%·min)$^{-1}$	Ultrasound factor E_{US}
25	2.33 ± 0.15	0.0276 ± 0.0035	2.00	—	—
40	1.98 ± 0.22	0.1060 ± 0.0380	2.00	—	—
60	2.16 ± 0.06	0.3200 ± 0.0146	2.00	0.070	4.57

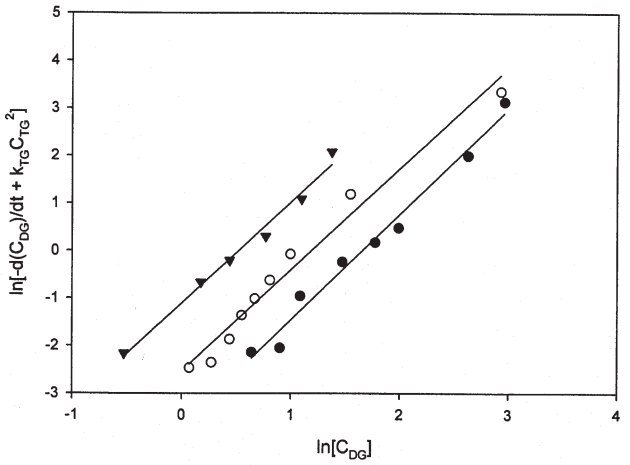

FIG. 6. Pseudo-order reaction model of DG hydrolysis at various temperatures. Alkaline transesterification using ultrasonic mixing and methanol. (●) 25°C, (○) 40°C, (▲) 60°C.

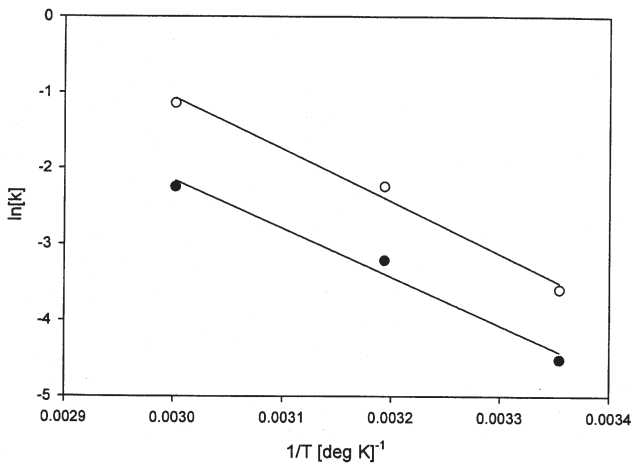

FIG. 7. Arrhenius plot of the reaction rate vs. temperature for the transesterification reaction. Alkaline transesterification using ultrasonic mixing and methanol. (●) TG, (○) DG.

occur, since the measurements of kinetic parameters were taken under the diffusion limitation regime.

These results show that ultrasonic mixing could result in commercial processing advantages, especially by increasing the conversion during shorter time periods or by using smaller equipment than with conventional agitation systems. It should be mentioned that ultrasonic mixing results in the formation of very small emulsion droplets that allow excellent contact between the reactants and catalyst. This is very important, not only during bulk synthesis but also during the polishing period (<1% limiting reactants).

ACKNOWLEDGMENTS

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