ORIGINAL PAPER

Kinetics of Palm Oil Methanolysis

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Abstract   A kinetics study of palm oil methanolysis was conducted at three different temperatures and three different concentrations of catalyst, sodium hydroxide, keeping constant the molar ratio of methanol to oil and the rotational speed of the impeller (6:1 and 400 rpm). The maximum conversion of palm oil and productivity to methyl esters were obtained at 60 °C and 1 wt% of NaOH based on palm oil, and they were 100 and 97.6%, respectively. The statistical analysis of conversions of palm oil and productivities to methyl esters as functions of temperature and concentration of catalyst, after 80 min of reaction, allowed them to fit second order polynomial equations, which adequately describe the experimental behavior. The experimental data appear to be a good fit into a second order kinetic model for the three stepwise reactions, and the reaction rate constants and the activation energies were determined. In this article we present the kinetic constant and activation energies for the experiments with 0.2% wt of NaOH. The effect of molar ratio on the concentration of products was investigated, while the temperature (55 °C), the concentration of catalyst (0.60 wt% of NaOH), and the rotational speed (400 rpm), were held constant. The results showed that the conversion

and the productivity increased due to methanol excess, and were higher for the reactions with a molar ratio of 6:1.

Introduction

The application of fatty acid methyl esters as an alternative fuel for diesel (biodiesel) and as raw material for the production of anionic surfactants that could replace the linear alkyl benzene sulfonates (LABS) in household detergents, has triggered the interest of governments, industries and researchers in these basic oleochemicals, which also have been gradually replacing the fatty acids as the raw material for the production of derivative oleochemicals [1].

The fatty acid methyl esters are produced by methanolysis of fats and oils, using acidic or alkaline catalysts, enzymes and without a catalyst in supercritical conditions for methanol [2–8]. There are three stepwise reactions [9]: partial methanolysis of the triglyceride (TG) to form the diglyceride (DG), partial methanolysis of DG to form the monoglyceride (MG), and partial methanolysis of MG to form glycerol (G). In each one of the three reactions a molecule of methyl ester (EM) is formed.

In the literature, there are some kinetic studies of the methanolysis of fats and oils, of which only a few use palm oil. Freedman et al. [10] studied the butanolysis and the methanolysis of soybean oil. For the methanolysis with a 6:1 molar ratio of methanol to oil, 0.5 wt% of sodium methoxide as catalyst by oil weight and temperatures between 20 and 60 °C, the experimental data fit better to a combination of second order consecutive and fourth order

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shunt reaction kinetic model. Energies of activation determined in the study ranged from 8 to 20 kcal gmol^{-1}. Boocock et al. [11] discussed the results and the analysis done by Freedman [10], and explained the differences between butanolysis and methanolysis as the result of a two phase reaction in which methanolysis occurs only in the methanol phase, where the oil concentration is very low, and the reaction rate is limited by mass transfer.

Noureddini and Zhu [12] studied the methanolysis of soybean oil with sodium hydroxide as catalyst, and, excluding the initial phase where the reaction is diffusion controlled, concluded that a second order model for the three consecutive reactions adequately describes the soybean oil methanolysis and that it is not necessary to incorporate the shunt reaction proposed by Freedman. Energies of activation, estimated by an expression similar to the Arrhenius equation, are in the range of 6.4–20 kcal/gmol. Cheah and Choo [13] established that the global kinetics of the palm oil methanolysis (TG + 3M ↔ 3 EM + G), is appropriately represented by a second order irreversible model. The values of the kinetic constant for the reaction at 64 °C and a molar ratio methanol to oil of 15:1 were 1.9×10^{-2}, 4.5×10^{-2} and 9.9×10^{-2} L gmol^{-1} min^{-1}, for 0.25, 0.50 and 0.75 wt% of NaOH based on the mass of oil, respectively.

Darnoko and Cheryan [14] concluded that the model, which presented a better fit with the experimental data for palm oil methanolysis with 1 wt% of KOH as catalyst and a molar ratio of 6:1, is pseudo second order through the first 30 min of reaction. The values of the energies of activation for the transformation of TG→DG, DG→MG, and MG→G, were 14.7, 14.2 and 6.4 kcal mol^{-1}, respectively.

Morgenstern et al. [15] studied the methanolysis of soybean oil between 10 and 45 °C, with a molar ratio of 3:1, with sodium and potassium hydroxide as catalysts. The concentration of products was determined using proton nuclear magnetic resonance spectroscopy (^{1}H NMR). The concentration data revealed that the reaction conducted at 10 °C gets close to the equilibrium after only 120 s, and that the energy of activation is 6.5 kcal mol^{-1}. The initial rate at 45 °C, molar ratio 3:1 and 2.50 mmol of NaOH, was 0.023 M s^{-1}.

In this study, the effect of temperature and the concentration of catalyst on the palm oil methanolysis were evaluated, keeping the molar ratio and the rotational speed of the impeller constant. The forward and reverse kinetic constants and the energies of activation were calculated for second order kinetics for the three consecutive reactions. In addition, the effect of the molar ratio on conversion and productivity at temperature, concentration of catalyst and rational speed constants, were studied.

Experimental Procedure

Materials

Refined, bleached and deodorized edible grade palm oil was obtained from INTERGRASAS S.A. (Bogota, D.C. Colombia). The acid value of palm oil, which was determined according to ASTM D-664, was 0.22 mg KOH/g, and the water content, determined according to ASTM D-1744, was less than 0.01 wt%. Methanol was of CHOR-MASOLV Grade from Riedel-de Haen (Germany). Sodium hydroxide was of analytical grade from MERCK (Darmstadt, Germany). Reference standards such as methyl palmitate, methyl oleate, DL-α palmitin, dipalmitin (mixture of isomers), tripalmitin and glyceryl trioleate, and the silylating agent N,O -bis(trimethylsilyl) trifluoroacetamide (BSTFA) of >99% purity were purchased from Sigma Aldrich Chemical Company (St Louis, MO). Internal standard, tricaprine was obtained from Fluka (Buchs, Switzerland). Pyridine, isopropanol and toluene of Baker ACS grade were obtained from Mallinckrodt Baker Inc. (Phillipsburg, NJ, USA).

Reaction Conditions

For the kinetic study a molar ratio of methanol to oil of 6:1, 400 rpm rotational speed, and sodium hydroxide as catalyst, were used. In order to study the influence of temperature and concentration of catalyst, a multilevel factorial experiment was designed for two variables with three levels, for a total of nine sets of experimental data, which were each conducted twice. Keeping in mind that the final temperature of the melting range of palm oil is 48 °C and the boiling point of methanol at the atmospheric pressure where the trials took place, reactions at 50, 55 and 60 °C were studied. For the concentration of catalyst the levels were 0.2, 0.6 and 1 wt% based on the mass of palm oil.

Rotational speed was defined based on preliminary tests carried out to set a value in which the initial phase controlled by the diffusion was not present, and where there was no effect of this variable over the methyl esters concentration.

In order to study the effect of molar ratio, and according to the results of the kinetic study, reactions were conducted with two additional molar ratios: 3:1 and 4.5:1. For these, the temperature was 55 °C, the concentration of catalyst was 0.6 wt% and the rotational speed was 400 rpm. Together with the reaction conducted with a molar ratio of 6:1, the total number of tests performed to study this variable were three, which were each conducted twice.

The values presented for all the experiments are the average of the duplicate tests.

Equipment

Methanolysis reactions were performed in a 100-ml glass round-bottomed reactor equipped with a reflux condenser, a thermometer and a sampling port. The reactor was immersed in a constant-temperature mineral oil bath equipped with an IKA ETS D-4 temperature controller that was capable of maintaining the temperature within ± 0.1 °C (IKA Works Inc., Wilmington, NC, USA). Agitation was provided with a magnetically stirred IKS RET basic system (IKA Works Inc., Wilmington, NC, USA).

Procedures

The reactor was initially charged with 50 g of palm oil. The reactor assembly was immersed in a constant temperature mineral oil bath and heated to the reaction temperature. A known amount of sodium hydroxide was dissolved in the required amount of methanol and heated separately to the reaction temperature. This solution was added to the reactor and the mechanical stirring was started. The reaction was timed as soon as the addition of the solution was finished.

Analysis

Samples were drawn at specified time intervals, predetermined according to how the experiment was developing. Approximately ten samples were collected over 80 min. Samples, 20 mg in size, were derivatized at room temperature as soon as they were drawn of the reactor for 60 min by adding BSTFA as the silylant agent and pirydine as the catalyst. After derivatization and before the GC analysis samples were stored at –2 °C. The derivatized samples were analyzed for methyl esters, monoglycerides, diglycerides, and palm oil by gas chromatography. A Hewlett Packard 5890 Series II GC (Hewlett Packard Co., Germany) equipped with a flame ionization detector, a fused silica (0.3 m × 0.53 mm) precolumn and an aluminum-clad capillary column SUPELCO SGE HT-5, 12 m × 0.53 mm × 0.15 mm (SGE International Pty. Ltd., Victoria, Australia). The samples of 0.4 μL were manually injected. After 1 min of stabilization at 140 °C, the oven temperature was programmed to increase from 140 to 380 °C at 20 °C/min and then was held at 380 °C for 10 min. The injector temperature was 350 °C and that of the detector was 390 °C. Each run was 23 min long. The

carrier gas was nitrogen with a flow of 8 mL/min, and 50:1 split ratio. The acquisition and processing of data were achieved with the program Chemstation (Hewlett Packard Co., Germany). The concentrations of glycerol and methanol were determined through material balance.

Statistical Analysis

The values of conversion and productivity after 80 min of reaction were analyzed by response surface regression procedure to fit second order polynomial equations.

Results and Discussion

Figures 1 and 2 show the typical curve of concentration of raw material and products during palm oil methanolysis. The production of methyl esters and the consumption of palm oil were high during the first 8 min, but decreased through the 20 min where the reaction gets close to the equilibrium. The highest concentrations of monoglycerides and diglycerides, about 10 wt%, were observed during the first 2 min of reaction; after that, their values decreased and were approximately constant as equilibrium was approached. Using the conditions shown in Fig. 1 and after 80 min of reaction, the palm oil concentration was 6.6 wt%. However, the presence of the oil was not detected when the concentration of catalyst was at least 0.6 wt% at any of the temperatures studied. Similarly shaped curves were observed in the other reactions.

Effect of Temperature

Figure 3 shows the effect of temperature on the concentration of methyl esters and monoglycerides at 0.2 wt% of
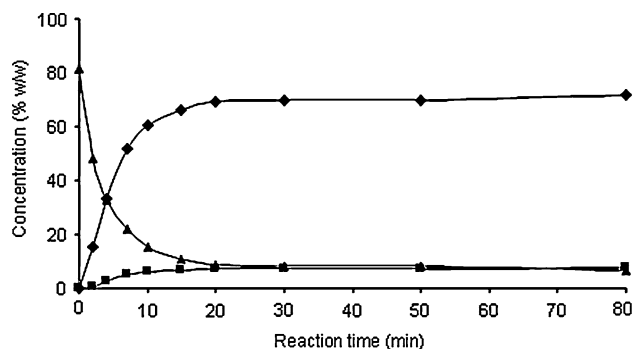

Fig. 1 Composition of methyl esters, glycerol and palm oil during palm oil methanolysis, temperature 50 °C, molar ratio 6:1, 0.2% of NaOH as catalyst, (*filled diamonds*) methyl ester (*filled squares*) glycerol (*filled triangles*) palm oil
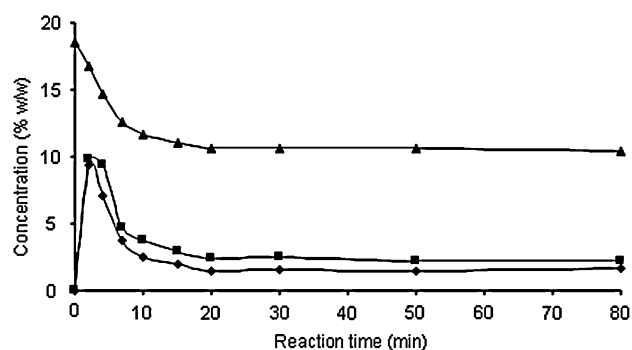
Fig. 2 Composition of monoglycerides, diglycerides and methanol during palm oil methanolysis, temperature 50 °C, molar ratio 6:1, 0.2% of NaOH as catalyst, (*filled diamonds*) monoglycerides (*filled squares*) diglycerides (*filled triangles*) methanol
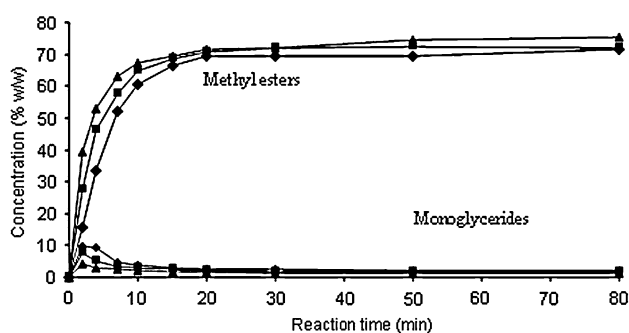

Fig. 3 Effect of temperature on composition of methyl esters and monoglycerides during palm oil methanolysis, molar ratio 6:1, 0.2% of NaOH as catalyst. (*filled diamonds*) 50 °C (*filled squares*) 55 °C (*filled triangles*) 60 °C

NaOH and a molar ratio of 6:1. After 4 min of reaction using the conditions in Fig. 1, the concentration of methyl esters at 50 °C was 34 wt% as compared to 46 wt% at 55 °C and 53 wt% at 60 °C. At the same time, the concentrations of monoglycerides was 9.3, 5.2, and 3.1 wt%, respectively. Nevertheless, after 80 min, the concentration of methyl esters increased only from 72 to 75 wt% when the temperature changed from 50 to 60 °C.

A similar behavior was observed under the other conditions studied. For instance, when the molar ratio was 6:1

and the concentration of NaOH was 1 wt%, after 4 min, concentration of methyl esters in the 50, 55 and 60 °C reactions were 67, 72, and 73 wt%.

Table 1 shows the conversion of palm oil and the productivity

$$\text{Productivity} = \frac{100[\text{EM}]}{3[\text{TG}_\text{O}]}$$

to methyl esters at different temperatures and concentrations of catalyst, after 80 min of reaction. Examination of this table reveals that, although there is a clear effect of temperature on conversion and productivity at 0.2 wt% of NaOH as catalyst, it is less important when concentration of catalyst is increased.

These results show that, within the range studied, the influence of temperature over the palm oil methanolysis is low but perceptible, particularly noticeable during the first min of the reaction, and it is greater when the concentration of catalyst is 0.2 wt% of NaOH. These results agree with those presented by Freedman et al. [2], Noureddini and Zhu [12], and Darnoko and Cheryan [14] who reported that the influence of temperature on the concentration is low around the boiling point of the alcohol.

Effect of Concentration of Catalyst

Figure 4 shows the effect of concentration of the catalyst on palm oil methanolysis at 50 °C and a molar ratio of 6:1. No larger differences were observed on concentration of methyl esters and monoglycerides between 0.6 and 1 wt% of NaOH as catalyst, even though differences were important between 0.2 and 0.6 wt%. For example, after 4 min of reaction, the concentration of methyl esters was 34 wt% at 0.2 wt%, compared to 68 and 72 wt%, at 0.6 and 1 wt%, respectively. After 80 min, the concentration of methyl esters was the same for the 0.6 and 1 wt% reactions, 79 wt%, and only 72 wt% at 0.2 wt% of NaOH. When the temperature was higher, 55 and 60 °C, the behavior was similar but the differences observed were smaller.

Table 1 Conversion of palm oil and productivity to methyl esters at different temperatures and concentrations of catalyst after 80 min of reaction

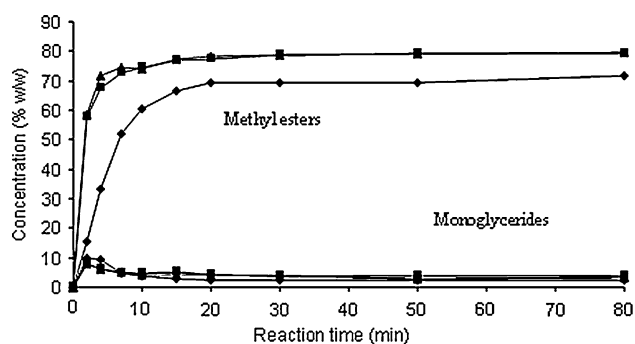| Temperature (°C)	NaOH (wt % based on palm oil weight)					
	0.2		0.6		1	
	Conversion (%)	Productivity (%)	Conversion (%)	Productivity (%)	Conversion (%)	Productivity (%)
50	90.6	87.5	100	95.3	100	96.5
55	91.9	87.9	100	96.0	100	96.9
60	94.3	91.9	100	97.0	100	97.6

Fig. 4 Effect of the concentration of catalyst on composition of methyl esters and monoglycerides during palm oil methanolysis, temperature 50 °C, molar ratio 6:1, (*filled diamonds*) 0.20% (*filled squares*) 0.60% (*filled triangles*) 1%

Examination of Table 1 reveals that at the three temperatures studied, there were no differences on the conversion between 0.6 and 1wt%, although the productivity increased 1.2, 0.9, and 0.6% for the reactions at 50, 55 and 60 °C. In conclusion, the effect of the concentration of catalyst on palm oil methanolysis conversion and productivity is important, although it is most noticeable when the concentration of the catalyst increases from 0.2 to 0.6 wt%, and when the temperature is 50 °C.

Srivastava and Prasad [16] established that the maximum level of activity of alkaline catalysts occurs in the range of 0.5–1 wt% based on oil, with oil conversions from 94 to 99%. On the other hand, Ma et al. [17] reported that the maximum catalyst activity in tallow methanolysis was obtained with 0.3 wt%. Darkono and Cheryan [14] reported that for reactions at 60 °C and 0.5 wt% of KOH as catalyst, the concentration of methyl esters showed an initial phase controlled by the diffusion. In this study that behavior was not observed even for reactions at 50 °C and 0.2 wt% of NaOH, probably because the mixture regime was turbulent enough to reduce the problems of mass transfer that were presented at the beginning of the reaction due to inmiscibility of the raw materials [12].

Statistical Analysis

Equations 1 and 2 show second order polynomials for conversion and productivity, where T is temperature (°C) and C is the catalyst percentage (wt% of NaOH), obtained from the statistical analysis. The analysis of variance (ANOVA) showed that the second order polynomials were adequate to represent the relationship between the response and the studied variables, with satisfactory coefficients of determination. For the case of the statistical model of the conversion, C and C^2 were significant, and for the productivity C, C^2 and T, which confirm the qualitative analysis made before for these variables.

$$\text{Conversion} = -426.297 + 18.064T + 25.604C - 0.155T^2 \\ - 0.463TC + 1.146C^2 \ (R^2 = 0.973) \quad (1)$$

$$\text{Productivity} = -330.704 + 14.458T + 20.437C - 0.122T^2 \\ - 0.4125TC + 4.375C^2 \ (R^2 = 0.967) \quad (2)$$

Reaction Kinetics

Based on the observed behavior for the composition of raw materials and products during the reaction, and the kinetics models presented by Freedman [10] and Noureddini and Zhu [12], the kinetic model presented in Eq. 3 was evaluated. The model is a system of six differential equations where each one of the rate constants corresponds to a parameter that must be found. In this model, besides the three consecutive reactions, a shunt reaction in which three methanol molecules react simultaneously with a triglyceride molecule, was included.

$$\frac{d[\text{TG}]}{dt} = -k_1[\text{TG}] \cdot [\text{M}] + k_{-1}[\text{DG}] \cdot [\text{EM}] - k_4[\text{TG}] \cdot [\text{M}]^3 + k_{-4}[\text{G}] \cdot [\text{EM}]^3$$

$$\frac{d[\text{DG}]}{dt} = k_1[\text{TG}] \cdot [\text{M}] - k_{-1}[\text{DG}] \cdot [\text{EM}] - k_2[\text{DG}] \cdot [\text{M}] + k_{-2}[\text{MG}] \cdot [\text{EM}]$$

$$\frac{d[\text{MG}]}{dt} = k_2[\text{DG}] \cdot [\text{M}] - k_{-2}[\text{MG}] \cdot [\text{EM}] - k_3[\text{MG}] \cdot [\text{M}] + k_{-3}[\text{G}] \cdot [\text{EM}]$$

$$\frac{d[\text{EM}]}{dt} = k_1[\text{TG}] \cdot [\text{M}] + -k_{-1}[\text{DG}] \cdot [\text{EM}] + k_2[\text{DG}] \cdot [\text{M}] - k_{-2}[\text{MG}] \cdot [\text{EM}]$$
$$+ k_3[\text{MG}] \cdot [\text{M}] - k_{-3}[\text{G}] \cdot [\text{EM}] + k_4[\text{TG}] \cdot [\text{M}]^3 - k_{-4}[\text{G}] \cdot [\text{EM}]^3$$

$$\frac{d[\text{G}]}{dt} = k_3[\text{MG}] \cdot [\text{M}] - k_{-3}[\text{G}] \cdot [\text{EM}] + k_4[\text{TG}] \cdot [\text{M}]^3 - k_{-4}[\text{G}] \cdot [\text{EM}]^3$$

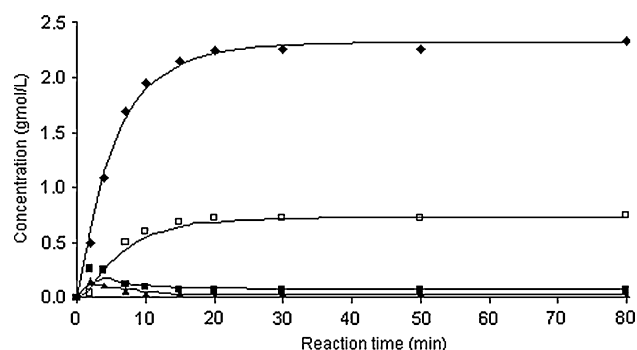$$\frac{d[\text{M}]}{dt} = -\frac{d[\text{EM}]}{dt}$$

(3)

Fig. 5 Experimental points and kinetic modeling curves for the composition of the reaction mixture during palm oil methanolysis, temperature 50 °C, 0.2% of NaOH as catalyst, molar ratio 6:1, (*filled diamonds*) methyl ester (*filled squares*) monoglycerides (*filled triangles*) diglycerides (*open squares*) glycerol

The differential equations system was solved utilizing Runge Kutta's method of the fourth order. The rate constants were obtained after a minimizing process of the summed squared error. Two scenarios were taken into account: the first one without including associated terms to the shunt reaction, k_4 and k_{-4} with which the parameter number that must be adjusted is six, and the model is reduced to one of second order for the consecutive reactions. In the second scenario, which exactly belongs to the one that shows Eq. 3, the two equilibrium constants of the shunt reaction were included, and therefore eight parameters must be calculated.

Figure 5 shows experimental and calculated data from the kinetics model of second order for the three consecutive reactions at 50 °C, 0.2 wt% of NaOH and molar ratio 6:1. The rate constants for the two proposed scenarios are presented on Table 2. For the nine reactions carried out rate constants that allow a good curve fitting were found. In the reactions at 55 and 60 °C and concentrations of NaOH 0.6 and 1 wt%, the presence of palm oil and diglycerides after 20 min were not detected. Based on the previous results and

assuming that after this time the reaction gets closer to equilibrium and therefore the reaction rate is zero, it was concluded that the kinetics constants for the reactions DG→TG and MG→DG, k_{-1} and k_{-2}, are equal to zero.

Inclusion of the shunt reaction in the kinetics model was considered unnecessary, because values of the rate constants k_1–k_{-3} did not change significantly when the shunt reaction was included and because the values of the constants k_4 and k_{-4} are at least two orders of magnitude smaller than k_1–k_{-3}. Additionally the summed squared error was slightly reduced and the coefficients of determination (R^2) either changed little or did not change.

Noureddini and Zhu [12], also considered it unnecessary to include of the shunt reaction, while Freedman [10] who proposed the inclusion of the shunt reaction into the model, justified it based on the diminishing of the summed squared errors, and also on the increase of the correlation coefficients obtained by linear regression from the Arrhenius plot.

Figure 6 shows the Arrhenius plot of the reaction rate constants at 0.2 wt% of NaOH. For TG↔DG and DG↔MG reactions, the values of energies of activation for the forward reaction (13.5 and 17.4 kcal gmol^{-1}, respectively) are greater than the ones for reverse reactions (10.3 and 16.2 kcal gmol^{-1}, respectively), while for the reaction MG↔G the opposite occurs (6.2 kcal gmol^{-1} for the forward reaction and 11.9 kcal gmol^{-1} for the inverse reaction). Thus, higher temperatures favor the formation of DG and MG, but also favor the consumption of G for the reaction G→MG. For the global reaction TG + 3M ↔ EM + G, with 0.2 wt% of NaOH as catalyst and molar ratio 6:1, the energy of activation for the forward reaction (16.4 kcal gmol^{-1}), is higher than the energy of activation of the inverse reaction (13.6 kcal gmol^{-1}) and therefore EM formation is favored at greater temperatures. These results suggest that kinetics for the forward reactions dominates over the reverse.

Table 2 Reaction rate constants for palm oil methanolysis, temperature 50 °C, 0.2% of NaOH as catalyst, molar ratio 6:1

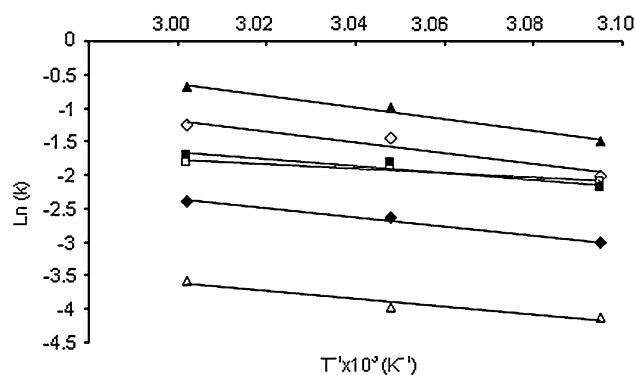| Rate constant	Without shunt reaction	With shunt reaction
k_1 (L gmol^{-1} min^{-1})	0.049	0.049
k_{-1} (L gmol^{-1} min^{-1})	0.112	0.098
k_2 (L gmol^{-1} min^{-1})	0.226	0.222
k_{-2} (L gmol^{-1} min^{-1})	0.133	0.111
k_3 (L gmol^{-1} min^{-1})	0.122	0.117
k_{-3} (L gmol^{-1} min^{-1})	0.016	0.015
k_4 (L^3 gmol^{-3} min^{-1})	–	7.67×10^{-6}
k_{-4} (L^3 gmol^{-3} min^{-1})	–	0

Fig. 6 Arrhenius plot of palm oil methanolysis, 0.2% of NaOH as catalyst and molar ratio 6:1. (*filled diamonds*) k_1 (*filled squares*) k_{-1} (*filled triangles*) k_2 (*open squares*) k_{-2} (*open diamonds*) k_3 (*open triangles*) k_{-3}

Effect of Molar Ratio

The effect of the molar ratio was studied at 55 °C and 0.6 wt% of NaOH, because from these values of temperature and concentration of catalyst there were not great differences in concentrations of raw materials and products during palm oil methanolysis, conversion is maximum (100%) and productivity is only 1.4% smaller to the higher obtained in this study. Concentration of methyl esters increased when the molar ratio changed from the stoichiometry to 6:1, while monoglycerides concentration diminished. As a consequence, the conversion of palm oil and the productivity to methyl esters increased with the excess of methanol. For instance, at 4 min of reaction, methyl ester concentration increased from 54 to 69 wt% when the molar ratio changed from the stoichiometry to 4.5:1, and to 73% when changed to 6:1. After 15 min, concentration of methyl esters and monoglycerides were essentially identically for the 4.5:1 and 6:1 reactions. Conversions of palm oil were 94.3, 98.0, and 100% for the reactions with molar ratios 3:1, 4.5:1 and 6:1, after 80 min. Productivities to methyl esters were 81.8, 92.0, and 96.0%, respectively.

These results reveals a considerable effect of the molar ratio on the conversion and productivity, more significant, in the first 10 min of the reaction and when this variable changes from 3:1 to 4.5:1. The positive effect of the excess of methanol on palm oil methanolysis is a consequence of the reversible character of the reaction and the displacement of the reaction towards products when excess of one of the raw materials is used.

Bradshaw and Meuly [9] stated that the practical range of molar ratio for methanolysis of fatty compounds is from 3.3:1 to 5.25:1. Freedman et al. [2] reported that the maximum conversion to methyl esters is obtained when the molar ratio is 6:1 and that greater molar ratios do not increase the productivity, makes glycerol recovery difficult and increases the cost of alcohol recovery.

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