Kinetic study of the esterification of free fatty acid and ethanol in the presence of triglycerides using solid resins as catalyst

P. Jasen[1] and J.M. Marchetti[2*]
[1]*Departamento de Física, Instituto de Física del Sur, Universidad Nacional del Sur. (CONICET), Av. Alem 1253, 8000 Bahía Blanca, Argentina;* [2]*Department of Mathematical Science and Technology, Norwegian University of Life Science, Drobakveien 31, 1432 Aas, Norway*

Abstract

Biodiesel production is gaining more and more relevance due to its environmental advantages and because of the world situation of petroleum: decreases of reserves, augmentation of prices etc. Biodiesel is produced by transesterification of triglycerides; however, it can also be generated by the esterification of fatty acid, normally considered as an impurity. The evolution of the reaction when using oleic acid (diluted in triglycerides) and ethanol, in the presence of a heterogeneous catalyst, has been studied. Kinetics expression for the esterification reaction as well as for the esterification and transesterification taking place simultaneously have been developed and fit with the experimental data. It is shown that, when both reactions are being taking into account, the kinetics fits the experimental data better since it does consider the interaction between all the compounds involved. The kinetics expression obtained represented satisfactorily the experimental information for several operations conditions.

*Corresponding author: jorge.mario.marchetti@umb.no

1 INTRODUCTION

Petroleum fuel consumption has increased considerably over the last year due to the increase in the population and therefore, in the energy requirements. Because of this, and due to the fact that petroleum is a non-renewable source of fuel, over the last years, efforts have been directed to finding new sources of alternative energy. In the area of liquid fuels, biodiesel is taking the lead in order to substitute for the regular diesel fuel.

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Some of the major advantages are environmental benefits such as less toxicity for humans, low CO and sulfur emissions and a minimum amount of particle matter [1–4].
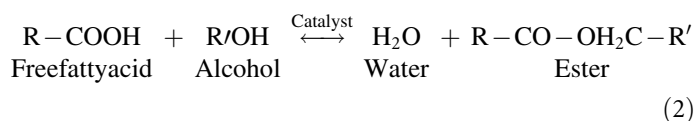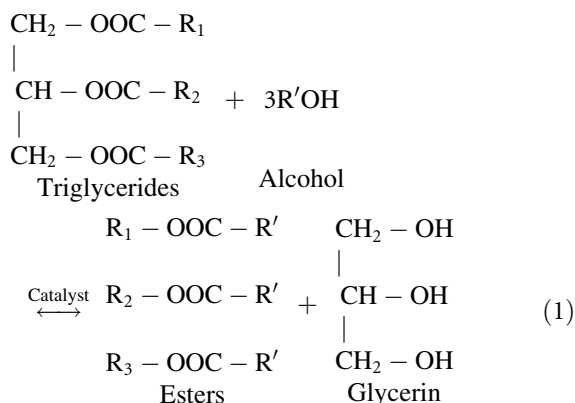
Transesterification reaction is the main way to produce biodiesel from a vegetable oil and an alcohol. The reaction can be alkali-catalyzed, acid-catalyzed or enzyme-catalyzed, or carried out under supercritical conditions [5–21], mainly produced by using refined oils. The main drawback in biodiesel production is the high cost of raw materials. Therefore, different feedstocks (waste, acid and frying oils) are being evaluated as possible substitutes. These alternative raw materials are less expensive; however, they present higher amounts of different impurities.

A very important impurity is the free fatty acids (FFAs). Its concentration varies from 3 to 80% depending on whether it is an acid oil, frying oil or a soapstock, where the amount of FFAs could be close to 100% [22]. For those cases, where the amount of FFAs in the feedstock exceeds 0.5%, the use of the conventional alkali catalyst is not recommended due to the fact that soap will be produced due to the interaction of fatty acids and homogeneous basic catalyst [2–4].

To avoid soap formation, the FFA should be either removed from the system or transform into a more valuable product. Conventionally, a physical refining is more suitable to remove the fatty acids; however, due to a chemical reaction, esterification, it is possible to modify them into biodiesel and increase the productivity of the biodiesel plant.

The main reactions involved when acid oil is employed are summarized as follows:

$$
\begin{array}{l}
\mathrm{CH_2 - OOC - R_1} \\
| \\
\mathrm{CH - OOC - R_2} \quad + \quad 3R'OH \\
| \\
\mathrm{CH_2 - OOC - R_3} \\
\text{Triglycerides} \qquad \text{Alcohol}
\end{array}
$$

$$
\xleftrightarrow{\text{Catalyst}}
\begin{array}{l}
\mathrm{R_1 - OOC - R'} \quad \mathrm{CH_2 - OH} \\
\qquad\qquad\qquad\qquad | \\
\mathrm{R_2 - OOC - R'} \quad + \quad \mathrm{CH - OH} \\
\qquad\qquad\qquad\qquad | \\
\mathrm{R_3 - OOC - R'} \quad \mathrm{CH_2 - OH} \\
\text{Esters} \qquad\qquad \text{Glycerin}
\end{array}
\tag{1}
$$

$$
\underset{\text{Freefattyacid}}{\mathrm{R - COOH}} \; + \; \underset{\text{Alcohol}}{\mathrm{R'OH}} \; \xleftrightarrow{\text{Catalyst}} \; \underset{\text{Water}}{\mathrm{H_2O}} \; + \; \underset{\text{Ester}}{\mathrm{R - CO - OH_2C - R'}}
\tag{2}
$$

where R and R′ denote any hydrocarbon chain.

The esterification reaction has been widely studied for several operational conditions and many types of catalysts such as sulfuric acid, sulfonic acid, heterogeneous resins and enzymes [23−38]. Kinetics expression were also obtained for several cases; however, the most common scenario is using the fatty acid as a pure raw material [27−31].

Kinetics expressions for the esterification reaction of oleic acid in the presence of different amounts of triglycerides were obtained by Berrios et al. [32] and Tesser et al. [33]. In the latest, no reference to the influence of the presence of triglycerides neither to the effect of the evolution of the transesterification is presented, considering that the both raw materials are close to a 50% wt. relation.

In the present work, the kinetics of the direct esterification of FFAs has been studied using acid oils in two different contexts. In the first case, triglycerides have been considered as an inert, consequently only the esterification reaction [Equation (2)] has been considered as taking place and the conversion of triglycerides is neglected.

Experimental data have shown that the transesterification takes place to such an extent that triglycerides cannot be considered as an inert. Therefore, the second proposed alternative takes into account that the transesterification reaction of triglycerides [Equation (1)] occurs simultaneously with the direct esterification reaction [Equation (2)].

A kinetic model was developed for both scenarios and compared with experimental data for both reactions. The kinetics models were implemented using the rate-controlling step method to both different proposed reaction mechanisms.

2 EXPERIMENTAL SECTION

The experimental data were obtained in a lab-scale batch reactor at different operating conditions such as reaction temperature, amount of catalyst, alcohol/oil molar ratio and different initial percentages of FFA in the mixture. Ethanol and a basic solid resin were used as reactant and catalysts, respectively. Ethanol was chosen instead of methanol due to its lower toxicity and the fact that this alcohol could be produced from renewable sources.

The reactor is a 500 ml glass reactor. A warmer jacket was used to heat the set up to the selected temperature and kept there with an error of 0.1°C. The oil was heated up before the resin and the alcohol was added and the reactor started.

The catalytic resin used a commercial base resin that was previously washed with water and alcohol and then regenerated as established by the vendor in order to have a fresh catalyst.

The experimental data used in this work have been previously published in Marchetti et al. [34] for the esterification reaction and in Marchetti and Errazu [35] for the transesterification reaction. Therefore, it will not be presented here; however, Table 1 presents the mayor operational conditions and final conversions obtained and used. To the best of our knowledge, these data are fitted for the first time in the present research.

3 KINETICS DEVELOPMENT

The kinetics expression has been obtained using the controlling step reaction method applied to several possible reaction mechanisms. The FFA conversion as a function of time was calculated using the batch reaction equation:

$$
\frac{dx_{FFA}}{dt} = \frac{-r_{FFA}}{C_{FFA}^0}
\tag{3}
$$

The kinetics parameter in the proposed mechanism has been fitted with experimental data presented elsewhere [34−36] using a non-linear regression routine based on the Marquardt algorithm [29, 39] was used.

The selection of the model has followed several criteria, statistical parameter such as the standard deviation, variance as well as visualization criteria in fitted plots.

Table 1. Experimental data used.

Temperature (°C)	% catalyst	% initial FFA	Molar ratio	Conversion (%)
45	2.27	10.68	6.13	82.57
45	5.1	10.68	6.13	83.84
45	7.05	10.68	6.13	85.85
45	2.27	10.68	4.12	18.58
45	2.27	10.68	5	27.87
45	2.27	2.812	6.13	85.02
45	2.27	27.22	6.13	85.14
30	2.27	10.68	6.13	26.38
55	2.27	10.68	6.13	88.68

3.1 Case I: esterification reaction

For the first scenario, we obtained the kinetic expression for the esterification alone, while considering the triglycerides as inert material of the system but that does provide volume to the liquid phase. In order to obtain the kinetic expression, we tested a total of 32 mechanisms and fitted them against experimental data.

The 32 mechanisms that were proposed are based on different adsorption, reaction or desorption controlling steps. It has been proposed that all compounds get adsorbed over the resin. It has been studied when only polar compounds or only non-polar compounds are adsorbed. The reaction has also been considered as the controlling step and in some scenarios, the desorption of the products has been considered as the step that requires the higher energy. All possibilities were tested and the result was compared and analyzed.

We have selected, from all the possibilities, the mechanism that satisfied better the selection criteria as presented in Equations (4–6). This mechanism considers the adsorption of polar compounds (ethanol and water) on the solid catalytic resin, while biodiesel and fatty acids are not being adsorbed because they are non-polar compounds.

$$FFA + s \rightarrow ALCs \tag{4}$$

$$FFA + ALCs \rightarrow FAEE + H_2Os \tag{5}$$

$$H_2Os \rightarrow H_2O + s \tag{6}$$

Considering the controlling step as the adsorption of the alcohol over the solid catalyst [Equation (4)], the final kinetics expression is as follows:

$$r_{FFA} = m_{cat}k\left(C_{alc} - \frac{C_{faee}C_w}{C_{FFA}K}\right) \tag{7}$$

$$m_{cat} = \frac{m_{cat}^0}{1 + K_1C_w + (K_2C_{faee}C_w/C_{FFA})} \tag{8}$$

where $k = k_\infty e^{(-E/RT)}$ and $K = K_\infty e^{(-\Delta H/RT)}$. m_{cat}^0 is the initial concentration of the catalyst (kg/l).

The kinetics constants can be obtained from Equations (7) and (8) after fitting the experimental data. The values for the constants are presented in Table 2. It can be seen that the value of K_∞ is to the power of 64. This number shows that the reverse reaction is not taking place and the system is

Table 2. *Values of kinetics parameters for esterification.*

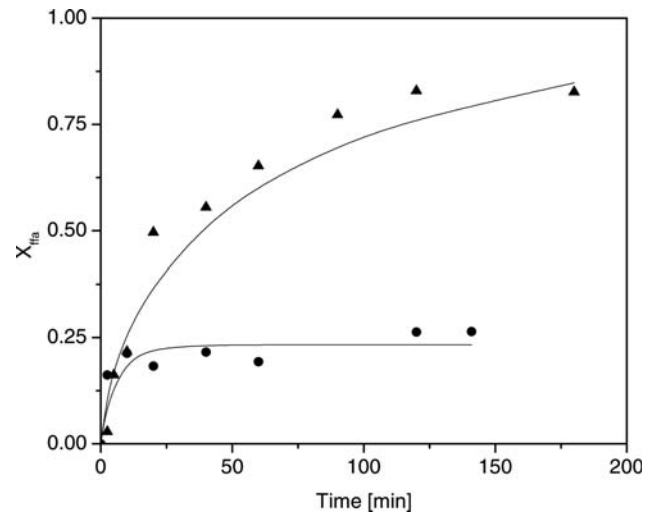| Parameter	Value	Units
k_∞	2.22×10^{-2}	l/(kg h)
E	1.00×10^3	cal/mol
k_∞	3.07×10^{66}	
H	9.56×10^4	cal/mol
K_1	6.16×10^{-1}	l^2/mol^2
K_2	1.71×10^2	l/mol

Figure 1. *FFA conversion. Initial FFA concentration = 9.94%, N (molar ratio of alcohol/oil) = 6.1:1, S = 2.1%. RPM = 200, T = 30°C. Filled circle, experimental; continuous line, model, T = 45°C. Filled triangle, experimental; continuous line, model.*

behaving close to an irreversible one. The esterification reaction, when considered that is taking place alone, it is completely shifted toward the desire product. However, it is suggested that the transesterification reaction might be taking place simultaneously.

Figure 1 shows a good agreement between the experimental data and the model for two selected temperatures. The experiments were done with a mixture of 90% of sunflower oil and 10% of oleic acid mix with a molar ratio of 6:1 of ethanol and in the presence of 2%wt of solid resin. It can be seen that the model predicts quite satisfactorily the result from the experiments, showing a dispersion at higher temperatures.

Figure 2 shows changes in conversion for FFA as a function of time for two loads of catalyst. It could be seen that for the smallest amount, the model has good agreement with the experimental data while for higher values of catalyst load, the model over-predicts the data.

3.2 Case II: esterification and transesterification reaction

As presented by the results from the experiments [34, 35], and the indication from the previous model, the transesterification reaction takes place simultaneously with the esterification reaction. Because of this, a complete reaction mechanism (considering both reactions) must be obtained and compared with the experimental data.

The proposed mechanism follows the same criteria as before, and the alcohol is adsorbed on the resin site [s on Equations (9 to 13)] due to its polarity. The water, however, is not adsorbed and in this case, it is believed that it is rapidly desorbed. In the previous scenario, water took considerable relevance due to the non-consideration of the triglycerides as
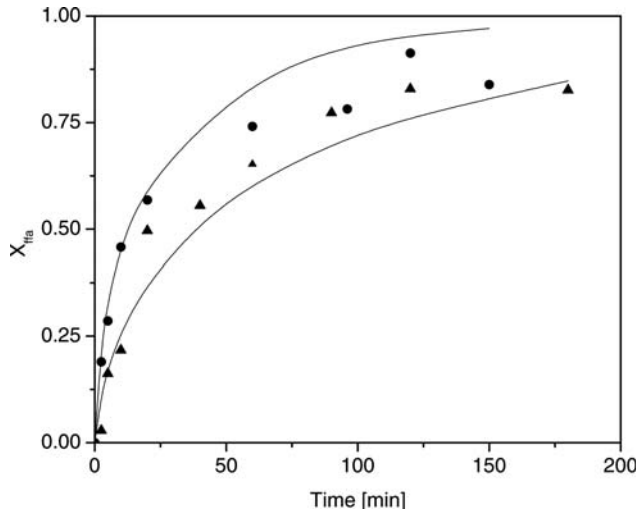
Figure 2. *FFA conversion. T = 45°C, N = 6.1:1, initial FFA concentration = 9.94% and RPM = 200. S = 5.14%. Filled triangle, experimental; continuous line, model. S = 7.05%. Filled circle, experimental; continuous line, model.*
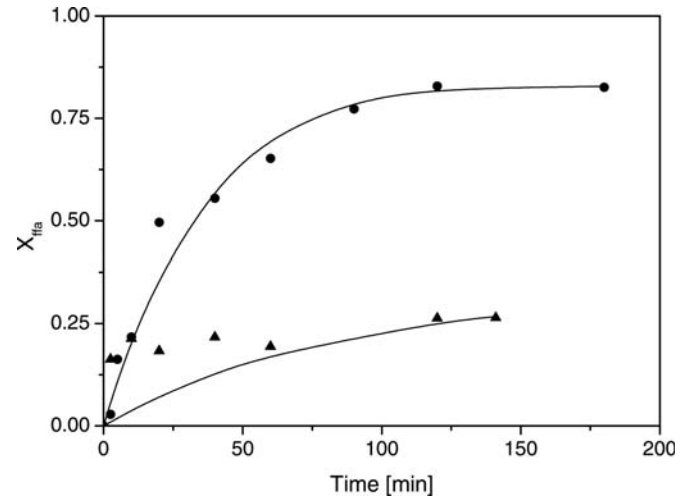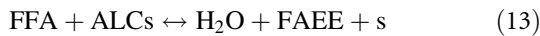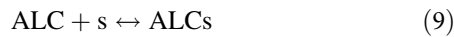

Figure 3. *Conversion of FFA. N = 6.1:1, initial FFA concentration = 9.94%, S = 2.67% and RPM = 200. T = 30°C. Filled triangle, experimental; continuous line, model, T = 45°C. Filled circle, experimental; continuous line, model.*

taking part in the reaction.

$$ALC + s \leftrightarrow ALCs \tag{9}$$

$$TG + ALCs \leftrightarrow DG + FAEE + s \tag{10}$$

$$DG + ALCs \leftrightarrow MG + FAEE + s \tag{11}$$

$$MG + ALCs \leftrightarrow G + FAEE + s \tag{12}$$

$$FFA + ALCs \leftrightarrow H_2O + FAEE + s \tag{13}$$

It was assumed that all the steps are elementary and that the alcohol adsorption is fast enough so that the superficial kinetic expression is the controlling step. The new kinetics expressions are:

$$r_1 = (k_1 C_{tg} C_{alc} K_1 - k_2 C_{dg} C_{faee}) \frac{m_{cat}^0}{1 + K_1 C_{alc}} \tag{14}$$

$$r_2 = (k_3 C_{dg} C_{alc} K_1 - k_4 C_{mg} C_{faee}) \frac{m_{cat}^0}{1 + K_1 C_{alc}} \tag{15}$$

$$r_3 = (k_5 C_{mg} C_{alc} K_1 - k_6 C_g C_{faee}) \frac{m_{cat}^0}{1 + K_1 C_{alc}} \tag{16}$$

$$r_4 = (k_7 C_{ffa} C_{alc} K_1 - k_2 C_w C_{faee}) \frac{m_{cat}^0}{1 + K_1 C_{alc}} \tag{17}$$

where $k_i = k_{i_\infty} \exp^{(-E/RT)}$, $i = 1, 8$.

In order to evaluate the concentration changes over time, the expressions presented in Equations (14–17) were replaced within the expressions in Equation (18). The differential equation system was solved and the concentration profile of

compounds over time was obtained.

$$\frac{dC_{tg}}{dt} = -r_1, \quad \frac{dC_{dg}}{dt} = r_1 - r_2, \quad \frac{dC_{mg}}{dt} = r_2 - r_3, \quad \frac{dC_g}{dt} = r_3,$$
$$\frac{dC_{faee}}{dt} = r_1 + r_2 + r_3 + r_4, \quad \frac{dC_{alc}}{dt} = -\frac{dC_{faee}}{dt}, \quad \frac{dC_{ffa}}{dt} = -r_4 \tag{18}$$

Figure 3 presents the changes with reaction time of the conversion of FFAs, where it can be seen the mathematical kinetics as well as the experimental data. It can be seen that the low temperatures fit is not that good for short reactions times; however, for higher temperatures, the kinetics fits the experimental data with a much better representation than the model from Case I kinetics (Figure 1).

The changes of the concentration of triglycerides as well as the concentration of the biodiesel produced are also presented (Figures 4 and 5, respectively). From Figure 4, an accurate fitting of the experimental data with the model proposed for both considered temperatures can be seen. It can also be seen that the higher the temperature, the faster the triglyceride is consumed. Figure 5 presents a similar effect, the higher the reaction temperature, the faster the production of biodiesel. Even though the kinetic expression correlates the experimental values, a bigger difference between the model and the data for lower temperatures can be observed. Similar results can be seen in Figure 3 for the conversion of fatty acids. Table 3 presents the kinetics parameter obtained from the fitting of the experimental data with this more complete model.

As this new kinetics approximation considers both reactions taking place simultaneously, a comparison over the conversion of FFA for both models has been done for one reaction conditions to show the differences between the models. Figure 6
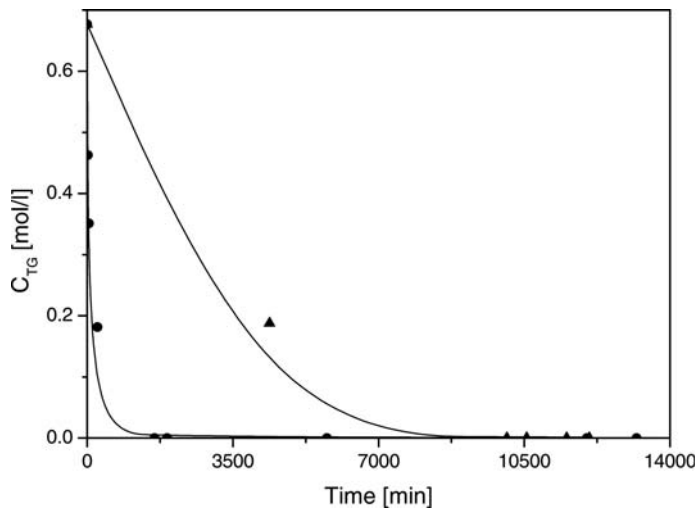
Figure 4. *Concentration of triglycerides. N = 6.1:1, initial FFA concentration = 9.94%, S = 2.67% and RPM = 200. T = 30°C. Filled triangle, experimental; continuous line, Model. T = 45°C. Filled circle, experimental; continuous line, model.*

Table 3. *Kinetic parameters for esterification and transesterification reaction.*

Parameter	Value	Units
$k_{\infty 1}$	1.95×10^{-2}	l/(kg h)
E_1	1.49×10^3	cal/mol
$k_{\infty 2}$	9.03×10^1	l/(kg h)
E_2	2.03×10^3	cal/mol
$k_{\infty 3}$	1.49×10^4	l/(kg h)
E_3	9.85×10^3	cal/mol
$k_{\infty 4}$	8.74×10^1	l/(kg h)
E_4	1.95×10^3	cal/mol
$k_{\infty 5}$	1.01×10^2	l/(kg h)
E_5	9.20×10^3	cal/mol
$k_{\infty 6}$	3.83×10^3	l/(kg h)
E_6	9.41×10^3	cal/mol
$k_{\infty 7}$	2.79×10^{13}	l/(kg h)
E_7	2.35×10^4	cal/mol
$k_{\infty 8}$	1.58×10^1	l/(kg h)
E_8	1.42×10^3	cal/mol
K_1	8.56×10^3	l/mol

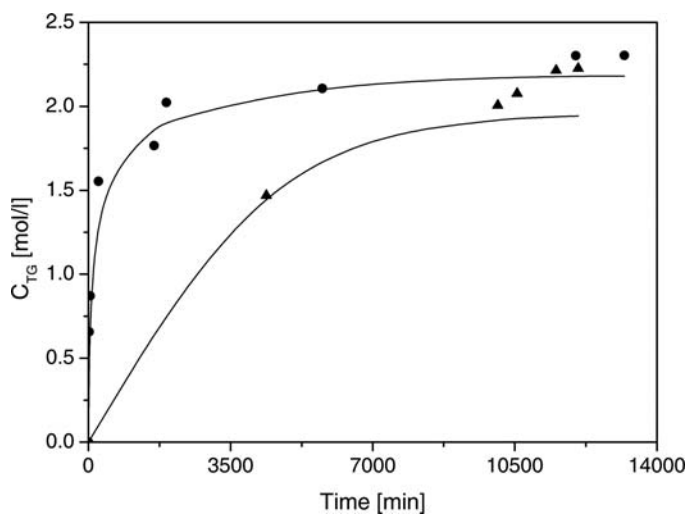**Figure 5.** *FAEE concentration. Initial FFA concentration = 10.68%, N = 6.1:1, S = 2.1%. RPM = 200. T = 30°C. Filled triangle, experimental; continuous line, model, T = 45°C. Filled circle, experimental; continuous line, model.*
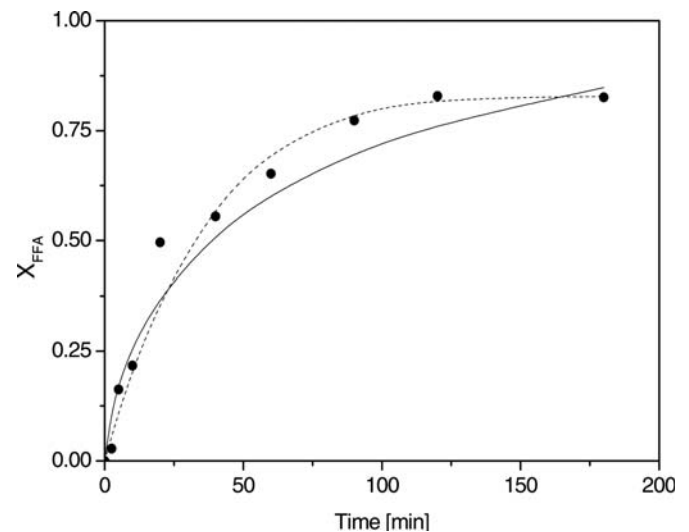

Figure 6. *Comparison of the two different mechanisms. Continuous line, case TG as inert; dashed line, case TG involved in the mechanism; filled circle, experimental information.*

shows the experimental information as well as both proposed kinetics models. It can be seen that when both reactions take place simultaneously, the fitting is more accurate.

4 CONCLUSIONS

The reaction kinetics of the direct esterification has been studied in the presence of triglycerides and ethanol for a heterogeneous solid catalyst (basic resin).

As a first step, we studied the esterification reaction while the transesterification was considered to have no influence. A mechanism was established and the experimental data were fitted using a multiparametric non lineal routine. The results are satisfactory when changes in the reaction temperature and in the amount of catalyst were considered (Figures 1 and 2).

As it was previously seen from the experimental data, the transesterification reaction took place within some grade of advance and therefore must be considered. A more complete mechanism involving both reactions was established. With this new alternative, the experimental information for both reactions was fitted against the kinetics models, obtaining accurate results.

In order to establish the benefits of using a more complex model, a comparison of both kinetics expression on the conversion of the FFA was considered (Figure 6), and these results show that the complete model provided a more adequate fitting, considering all the relevant aspects.

ACKNOWLEDGEMENTS

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