

Production of biodiesel from acid oil using sulfuric acid as catalyst: kinetics study

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Abstract

Biodiesel production is becoming more relevant due to its environmental advantages together with the global petroleum situation regarding decreases of the reserves, instability of the prices and so on.

The kinetics of the esterification and transesterification reaction of an acid oil (10% of initial free fatty acid) was studied using ethanol and a homogenous acid catalyst. The controlling step method was employed to obtain the kinetic equations, and nonlinear multiparametric routine was implemented to estimate the kinetic parameters. The selected reaction rate represented the experimental data for several operating conditions satisfactorily.

Keywords: biodiesel; esterification; kinetic; sulfuric acid; acid oil

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1 INTRODUCTION

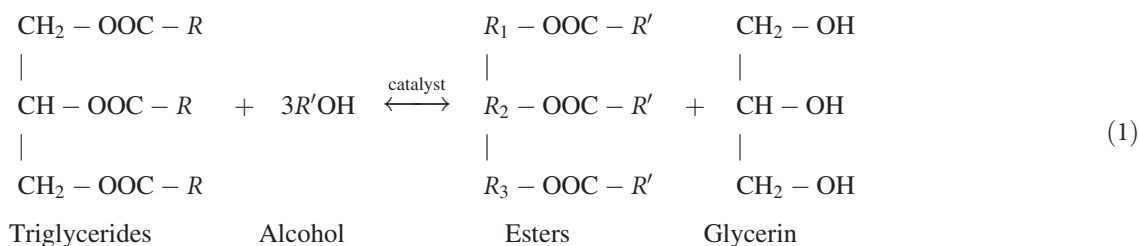
Fuel consumption has considerably increased over the last few years; therefore, great efforts have been made to find other renewable and sustainable alternatives for fossil fuel. Biodiesel is a valuable option because of its environmental benefits such as lower toxicity for humans, i.e. lower CO and sulfur emissions and a minimum amount of particle matter [1–4].

The most common way to produce biodiesel is by transesterification of vegetable oils with an alcohol. The reaction can be catalyzed by alkalis, acids or enzymes or by carried out under supercritical conditions [5–21].

The main disadvantage in biodiesel production is the high cost of the raw materials used, normally refined oils. Therefore, different feedstocks (waste, acid and frying oils) are being evaluated as possible substitutes. These alternative raw materials are less expensive, although being likely to appear more impure.

In acid oils, the amount of free fatty acid (FFA) could vary from 3 to 40%. When 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 the saponification reaction might take place [2–4]. Nevertheless, the FFA could be transformed into ester by means of the direct esterification reaction.

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



where R and R' denotes any hydrocarbon chain.

The kinetics of the esterification reaction has extensively been studied [22–30]. However, in those works, the FFA was considered a pure component. Berrios *et al.* [31] and Tesser *et al.* [32] have considered acid oil with several concentration of FFA. Nevertheless, the amount of triglycerides has not been included in the reaction mechanism proposed. It could be considered constant if its concentration does not change during the reaction. However, this is unlikely to happen because the conditions for the transesterification to take place are appropriate.

In the present work, the kinetics of the direct esterification of the FFA has been studied using acid oils in two different contexts. In the first case, triglycerides have been considered inert. Consequently, only the esterification reaction (2) has been considered. From laboratory results, a second alternative was proposed where the transesterification reaction of triglycerides (1) occurs together with the direct esterification reaction (2). For both cases, the kinetic models were developed and their kinetic parameters have been fitted using experimental data obtained at different operating conditions such as reaction temperature, amount of catalyst, alcohol/oil molar ratio and different initial percentages of FFA in the mixture. These kinetic models were obtained applying the rate-controlling step method to the different reaction mechanisms proposed.

Both alternatives were found to be suitable to reproduce the experimental data for different temperatures and amounts of catalyst. However, when both reactions are taken into account, the kinetic model fits the information more accurately.

2 MATERIALS AND EXPERIMENTAL METHOD

The experimental runs were carried out in a lab scale reactor of 500 ml equipped with a mechanical agitation manipulated by speed control at 200 rpm. The reaction temperature was controlled by thermostatic bath that allowed setting the temperature at the desirable value with an error of $\pm 0.1^\circ\text{C}$.

To carry these experiments, refined sunflower oil from a commercial brand were used. Ethanol anhydrous and sulfuric acid, brand 'Anebra', were utilized as reagent and catalyst, respectively. Ethanol was chosen instead of methanol due to its lower toxicity and the fact that this alcohol could be produced from renewable sources.

To obtain an oil acid of a known acidity, an amount measured of oleic acid was added to the vegetable oil. The mixture was prepared and fed to the reactor to be heated up. Once the reaction temperature was reached, the catalyst mixed with the alcohol was fed and the reaction started. In each run, the liquid samples were withdrawn at different specific times by means of a valve placed at the bottom of the reactor.

Once it was removed from their reaction mixture, the sample was washed with water in order to stop the reaction as well as to facilitate the separation. To improve the separation of

phases, a centrifuge was used for 20 min. From the upper phase (oil phase), a small sample was taken for GC analysis and a slightly bigger sample was used for titration.

Titration procedure was done by diluting the oil sample into ethyl ether and ethanol (50% vol), adding phenolphthalein as an indicator. The acidity was then measured by using a KOH solution of concentration and normality known. This was done accordingly to AOCs Standard Methods Ca 5a-40 [33].

The amount of KOH consumed was recorded, and the acidity of the sample could be calculated by means of the following relation:

$$a = \frac{V \ 100 \ PM \ C}{Mg} \quad (3)$$

From to the acidity of the system, the amount of oleic acid (C_{ffa}) is therefore established at each time. Consequently, the conversion of FFA (x_{ffa}) was calculated using this expression:

$$x_{ffa} = \frac{a_{ffa}^{t=0} - a_{ffa}^{t=t}}{a_{ffa}^{t=0}} \quad (4)$$

where $a_{ffa}^{t=0}$ is the initial acidity of the fatty acid mixture and $a_{ffa}^{t=t}$ is the acidity of the same at 't' time.

In this case, that sulfuric acid was used as catalyst, it was taken care that the acid was not present in the oil phase. The experimental data selected by this study showed that sulfuric acid does not appear in the samples within of 1.8% in the acid index.

The concentration of triglycerides, diglycerides, monoglycerides, biodiesel and glycerin were analyzed by capillary gas chromatography (GC). Each sample of the oil phase was diluted in pyridine (50 mg/5 ml), 100 μl from of the solution were mixed with 200 μl *N,O*-bis(trimethylsilyl)-trifluoroacetamide and 100 μl trimethylchlorosilane. This new mixture was heated up for 20 min at 70°C and 1 μl was then injected to a GC Varian 3700. The GC was fitted with 15 m \times 0.32 mm \times 0.1 mm column DB-5HTJ&W Scientific.

The titration and the GC method are complimentary methods due to the fact that different compounds could be analyzed with this technique. However, the FFA was checked with both techniques. This procedure allowed us to verify the results of the GC analysis.

3 KINETIC MODELS

The kinetic expressions were 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:

$$\frac{dx_{ffa}}{dt} = \frac{-r_{ffa}}{C_{ffa}^0} \quad (5)$$

The kinetic parameters from the proposed mechanism were

Table 1. Kinetic parameters.

Parameter	Value	Units
k_{∞}	0.058	l/(kg s)
E	23.137	kJ/mol
K_{∞}	6.42×10^{67}	
ΔH	399.572	kJ/mol
K_1	7.62×10^{-2}	l ² /mol ²
K_2	3.14×10^1	l/mol
K_3	1.00×10^{-11}	l/mol

adjusted with experimental data presented elsewhere [34,35]. To carry out this procedure, a non-linear regression routine based on the Marquard [36] algorithm was used.

The selection of the model was done by comparing statistical criteria such as standard deviation and variance among others.

3.1 Case I: esterification reaction

In this case, only the proposed esterification reaction took place whereas the transesterification reaction did not. Hence, the triglycerides can be considered inert in the reaction.

To obtain the kinetic expression, the mechanism proposed by Straitweiser *et al.* [37] was chosen. From this mechanism and applying the controlling step method, several possible expressions for the kinetic reaction rate were obtained. Upon applying statistical criteria, the following reaction rate (r , mol/l/s) turned out to be the most accurate one.

$$r_{\text{ffa}} = \frac{m_{\text{cat}}^0}{1 + K_1 C_{\text{faec}} C_w + (K_2 C_{\text{faec}} C_w / C_{\text{ffa}}) + K_3 C_{\text{faec}}} k \left(C_{\text{ffa}} - \frac{C_{\text{faec}} C_w}{C_{\text{alc}} K} \right) \quad (6)$$

where m_{cat}^0 is initial concentration of the catalyst (kg/l), faec fatty acid ethyl oleate, C concentration of a compound (mol/l), k kinetic constants in l/(mol h), $k = k_{\infty} \exp(-E/RT)$, where E is activation energy (kJ/mol), R is universal gas constant and T is temperature (K), and $K = K_{\infty} \exp(-\Delta H/RT)$, where K_i is equilibrium constants and ΔH is heat of reaction (kJ/mol).

The kinetic parameters for the selected model are reported in Table 1.

The obtained activation energy ($E = 23.137$ kJ/mol) is of the same magnitude as one obtained by Sendzikiene *et al.* [30] (13.290 kJ/mol).

The experimental and calculated conversion of FFA for three different reaction temperatures (35, 45 and 55°C) are shown in Figure 1. As it can be seen, the model predicts the experimental data satisfactorily. The effect of the amounts of catalyst is displayed in Figure 2.

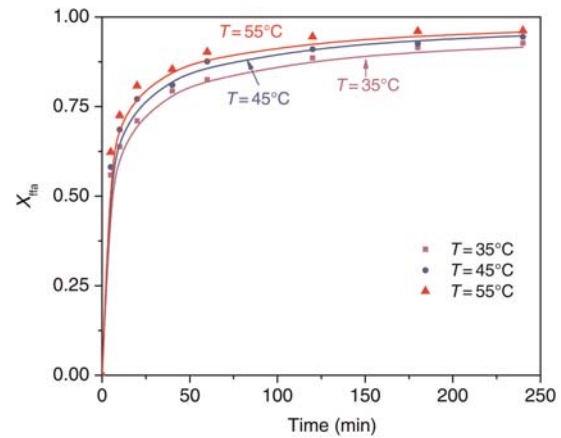


Figure 1. Conversions of FFA for different temperatures. Dashed line area of the curve denotes the simulated values and filled symbols experimental data. Case I: initial FFA = 10.68%; $n = 6.1:1$; $S = 2.1\%$; rpm = 200.

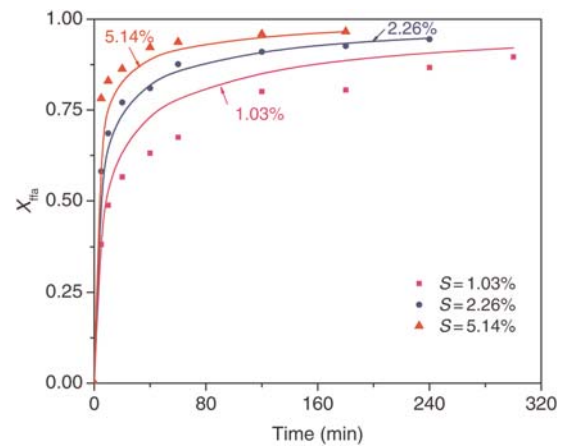


Figure 2. Conversions of FFA for different values of S . Dashed line area of the curve denotes the simulated values and filled symbols denote experimental data. Case I: initial FFA = 10.68%; $n = 6.1:1$; rpm = 200; $T = 45^\circ\text{C}$.

3.2 Case II: esterification and transesterification reactions

Considering experimental laboratory results, the transesterification reaction could take place simultaneously with the esterification reaction. For this reason, a global reaction mechanism should be proposed to obtain the kinetic expression for both the esterification and the transesterification reactions.

The proposed mechanism is as follows:

- (1) $\text{TG} + \text{ALC} \leftrightarrow \text{DG} + \text{FAEE}$
- (2) $\text{DG} + \text{ALC} \leftrightarrow \text{MG} + \text{FAEE}$
- (3) $\text{MG} + \text{ALC} \leftrightarrow \text{G} + \text{FAEE}$
- (4) $\text{FFA} + \text{ALC} \leftrightarrow \text{H}_2\text{O} + \text{FAEE}$

Each step in the above mechanism is an elementary reaction.

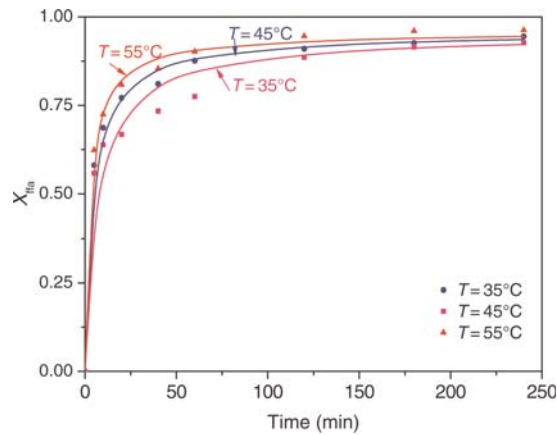


Figure 3. Conversions of FFA for different temperatures. Dashed line area of the curve denotes the simulated values and filled symbols denote experimental data. Case II: initial FFA = 10.68%; $n = 6.1:1$; $S = 2.1\%$; rpm = 200.

The variations in the concentration of each compound is defined as follows

$$\frac{dC_{tg}}{dt} = -r_1 \quad (7)$$

$$\frac{dC_{dg}}{dt} = r_1 - r_2 \quad (8)$$

$$\frac{dC_{mg}}{dt} = r_2 - r_3 \quad (9)$$

$$\frac{dC_g}{dt} = r_3 \quad (10)$$

$$\frac{dC_{faee}}{dt} = r_1 + r_2 + r_3 + r_4 \quad (11)$$

$$\frac{dC_{alc}}{dt} = -\frac{dC_{faee}}{dt} \quad (12)$$

$$\frac{dC_{ffa}}{dt} = -r_4 \quad (13)$$

For the esterification reaction, the same model from Case I was proposed. For the transesterification reaction, a new kinetic expression was obtained, assuming that all steps were elementary. The following resulting expressions were attained:

$$r_1 = k_1 C_{tg} C_{alc} - k_2 C_{dg} C_{est} \quad (14)$$

$$r_2 = k_3 C_{dg} C_{alc} - k_4 C_{mg} C_{est} \quad (15)$$

$$r_3 = k_5 C_{mg} C_{alc} - k_6 C_g C_{est} \quad (16)$$

$$r_4 = \frac{m_{cat}^0}{1 + K_1 C_{faee} C_w + (K_2 C_{faee} C_w / C_{agl}) + K_3 C_{est}} \left(k_7 C_{ffa} - \frac{k_8 C_{faee} C_w}{C_{alc}} \right) \quad (17)$$

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

The experimental conversion of FFA and those from the kinetic model can be observed in Figure 3 for the same

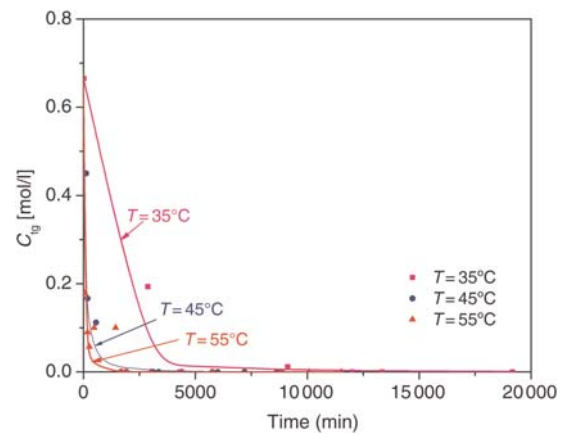


Figure 4. Concentrations of TG for different temperatures. Dashed line area of the curve denotes the simulated values and filled symbols denote experimental data. Case II: initial FFA = 10.68%; $n = 6.1:1$; $S = 2.1\%$; rpm = 200.

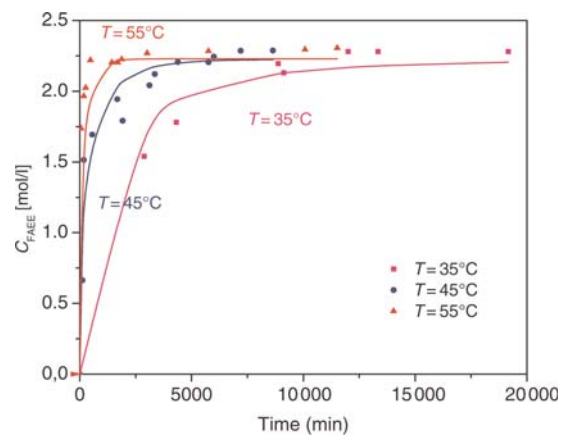


Figure 5. Experimental and calculated FAEE concentrations. Dashed line area of the curve denotes the simulated values and filled symbols denote experimental data. Case II: initial FFA = 10.68%; $n = 6.1:1$; $S = 2.1\%$; rpm = 200.

temperatures of Case I. Once again, a very good representation of the experimental data is achieved.

The evolutions of the concentration of TG and biodiesel as a function of time are shown in Figures 4 and 5. As shown, when the temperature increases, the TG concentrations decrease and the biodiesel production increases.

The accuracy of the kinetic model for three different amounts of catalyst is presented in Figure 6, considering the variations of the FFA conversions.

The kinetic parameters obtained from the fitting of the experimental data with the Case II are stated in Table 2.

A comparison of the conversion of FFA obtained with both models (Cases I and II) was done. Figure 7 shows the experimental information and the result of both kinetic fittings.

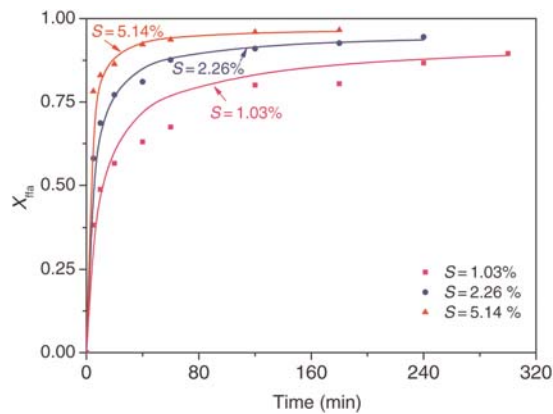


Figure 6. Experimental and calculated conversions of FFA. Dashed line area of the curve denotes the simulated values and filled symbols denote experimental data. Case II: initial FFA = 10.68%; $n = 6.1:1$; rpm = 200; $T = 45^{\circ}\text{C}$.

Table 2. Kinetic parameters.

Parameter	Value	Units
$k_{\infty 1}$	1.59	l/(mol s)
E_1	38.70	kJ/mol
$k_{\infty 2}$	0.33	l/(mol s)
E_2	38.70	kJ/mol
$k_{\infty 3}$	3.194	l/(mol s)
E_3	38.70	kJ/mol
$k_{\infty 4}$	5.97	l/(mol s)
E_4	38.70	kJ/mol
$k_{\infty 5}$	1.01×10^{11}	l/(mol s)
E_5	107.11	kJ/mol
$k_{\infty 6}$	4.03×10^{-4}	l/(mol s)
E_6	38.74	kJ/mol
$k_{\infty 7}$	9.50	l/(kg s)
E_7	37.99	kJ/mol
$k_{\infty 8}$	1.67×10^{-5}	l/(kg s)
E_8	12.76	kJ/mol
K_1	1.17	l ² /mol ²
K_2	1.10	l ² /mol ²
K_3	2.00	l/mol

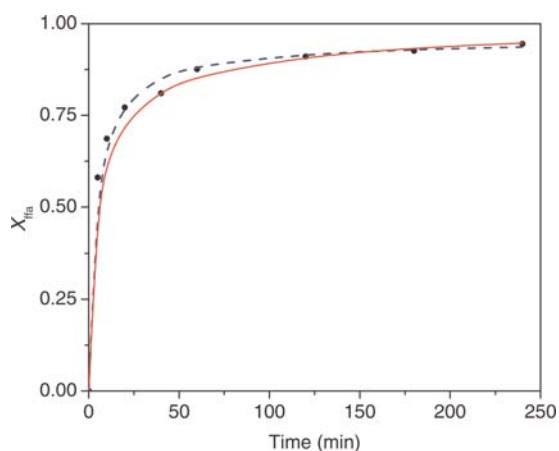


Figure 7. Comparison of the two models: continuous line, Case I; dashed line, Case II; bullets, experimental data.

4 CONCLUSIONS

The kinetic reaction of the direct esterification was studied in the presence of triglycerides with a homogenous acid catalyst (sulfuric acid), obtaining good results.

As a first step, the esterification reaction was studied, considering the triglycerides as inert because the transesterification reaction did not take place. A mechanism was established and the experimental data were fitted using a multiparametric non-linear routine. Satisfactory results were obtained for different reaction temperatures and amounts of catalyst (Figures 1 and 2).

The laboratory experience showed that the transesterification reaction took place at the same time the esterification was studied. For this reason, a more complete mechanism was proposed involving both reactions. This model fitted the experimental data more accurately.

This kinetic study is an important tool to study the reaction rate of the esterification and the transesterification reactions of an oil with high amount of FFAs. This kinetics is suitable for reactor design.

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