Synthesis of Fatty Acid Methyl Esters from Pomace Oil Catalyzed by Zinc Stearate: A Kinetic Study of the Transesterification and Esterification Reactions

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Abstract: In this work, the simultaneous transesterification and esterification reactions of olive pomace oil with methanol catalyzed by zinc stearate were studied. This catalyst is a crystalline solid at room temperature, but it is soluble in the reaction medium at reaction temperature. Zinc stearate has surfactant properties that cause the formation of an emulsion in the reaction system. The stability of the emulsion formed in the oil–methanol–catalyst system was compared to that in the FAME (fatty acid methyl esters)–methanol–catalyst system. It was observed that the emulsion formed in the presence of high amounts of FAME is much more unstable, which makes the catalyst easy to separate from the reaction products. The kinetics of esterification and transesterification were also studied. All the kinetic and equilibrium constants were determined with a complete model, considering the three stepwise reactions corresponding to the transesterification of triglycerides and the esterification of free fatty acids. The parameters obtained were used to model the operating conditions that would allow obtaining biodiesel that meets the quality standards.

Keywords: fatty acid methyl esters; zinc stearate; pomace oil; kinetic model; transesterification; esterification

1. Introduction

Biodiesel (FAME) is an alternative fuel that can be used to replace diesel fuel completely or partially in auto-ignition engines without requiring any modification [1]. The industrial process most commonly used for biodiesel production is the transesterification of triglycerides (TG) with a low-molecular-weight alcohol in the presence of acid or base catalysts, depending on the quality of the raw material. To date, vegetable oils have been the preferred raw material, especially due to their high energy content and easy processing for large-scale production. Other advantages include immediate availability as liquids and being renewable and biodegradable [2].

Biofuels obtained from edible oils are the so-called first-generation fuels. However, competition with the food market causes social, economic, and environmental issues, since there is competition for agricultural land and water with food crops, which could cause food shortages and affect the price of these raw materials [3]. In addition, the loss of biodiversity associated with deforestation is another problem associated with these first-generation biofuels. Presently, these oils continue to be used for biodiesel production, although the development of second-generation biodiesel is being encouraged, using alternative raw materials such as waste from the food industry, animal fats, and low-quality or used oils.

In this work, raw pomace oil was used as raw material to produce biodiesel. This is a low-cost oil [4,5] obtained by solvent extraction from "alperujo", a residue of the olive oil industry that is not suitable for human consumption due to its high acidity, its color, and its odor, among other qualities [6,7]. In a previous work in our research group [8], raw pomace oil was studied as raw material in biodiesel production using zinc stearate as catalyst. At 140 °C, with 3% catalyst loading and a methanol/oil molar ratio of 30, 98% and 67% of triglyceride and free fatty acids (FFA) conversions and 84% of FAME yield were achieved.

There are studies on the production of biodiesel from pomace oil using different catalysts. Yüsel [9] reported the use of Thermomyces lanuginosus lipase on olive pomace powder as a catalyst for biodiesel production. The maximum FAME yield obtained was 93% at 25 °C in 24 h. Bonet-Ragel et al. [10] also used an immobilized lipase as catalyst to obtain biodiesel from alperujo oil with a high degree of acidity. They obtained a FAME yield of 29% after 6 h of reaction at 30 °C. Both studies added methanol in three stages to avoid the inhibition of lipase.

As for homogeneous catalysis, Hernández et al. [11] studied the transesterification of pomace oil catalyzed by KOH. They achieved a FAME yield of 95% at 60 °C in 1 h of reaction time. On the other hand, Lama-Muños et al. [6] studied a two-stage process that included acid esterification with H_2SO_4 followed by base transesterification using NaOH, obtaining a maximum FAME yield of 95% at 60 °C after 80 min of reaction.

In the process of biodiesel production with acid raw materials, it is desirable to have an active catalyst in both the transesterification and esterification reactions, as well as an easy separation of the catalyst from the reaction medium.

In a previous work carried out by our research group [12], the use of zinc carboxylate salts in the esterification of oleic acid and in the transesterification of refined soybean oil with methanol was studied. Specifically, zinc laureate (LaZn), zinc palmitate (PaZn), zinc stearate (StZn) and zinc oleate (OlZn) were studied. LaZn, PaZn, and StZn are crystalline solids, but soluble in the reaction medium at temperatures above 100 °C.

In these salts, the Zn^{+2} cation is tetrahedrally coordinated to the oxygen atoms of the carboxylic groups, giving a layer based on a simple tetragonal network [13]. All the studied carboxylic salts exhibited thermal stability under nitrogen atmosphere up to 200 °C [14]. In the transesterification of soybean oil at 100 °C and 120 min, TG conversions of between 90–94% were obtained with FAME yields of between 71–74% [12]. The catalysts remained unchanged after three consecutive reactions. On the other hand, at 140 °C and 120 min reaction time, TG conversion was greater than 99% with FAME yields above 84%. It was found that StZn was partially transformed into zinc glycerolate. Finally, the authors also analyzed the esterification of oleic acid with methanol at 140 °C in the presence of carboxylic Zn salts. The salts showed good catalytic activity, with final conversions of FFA greater than 60% at 120 min of reaction time.

On the other hand, in a previous study [15] it was found that the catalyst is part of a self-organized system in the reaction medium (macroemulsion). Furthermore, in that work, the kinetic parameters of the transesterification reaction of soybean oil were obtained considering second-order mechanism for the three consecutive reactions, obtaining FAME and glycerol as products and mono and diglycerides as intermediates [15]. There are some reports in the literature that study kinetic models for the transesterification or esterification reactions, most of them correspond to analysis of the global reactions [16–18]. Regarding the simultaneous transesterification and esterification reactions, very few reports of all consecutive reactions were found. Konwar et al. [19] studied the individual reaction kinetics of the simultaneous esterification and transesterification of acidic oils over a mesoporous sulfonated carbon catalyst. A second-order pseudo-homogeneous kinetic model was proposed and explained the experimental results. Shu et al. [20] also studied the reaction kinetics of simultaneous transesterification and esterification using two carbon-based solid acid catalysts, considering a second-order kinetics and a pseudo-homogeneous system.

In this work, the stability of zinc stearate during the synthesis of FAME from pomace oil was studied. The behavior of the methanol-FAME-catalyst mixtures was also analyzed to evaluate the degree of difficulty of separating the catalyst from the reaction products.

A mathematical model for the methanolysis of pomace oil considering the simultaneous transesterification and esterification reactions was also proposed. The kinetic parameters were estimated, and the results were compared with experimental values.

2. Results and Discussion

2.1. Hydrolysis of Pomace Oil and FAME

Before proposing a mathematical model that describes the methanolysis of pomace oil catalyzed by zinc stearate, all the reactions that take place in the reactor must be identified.

By esterifying the fatty acids from the pomace oil, water is formed. The water could react with the TG or with FAME, hydrolyzing them according to the following equations:

$$TG + 3\,H_2O \rightarrow Gly + 3\,FFA \tag{1}$$

$$FAME + H_2O \rightarrow MOH + FFA \tag{2}$$

Catalytic tests were performed to verify if the hydrolysis reactions took place with the chosen catalyst and under the selected operating conditions. To this end, the initial acidity of the soybean oil and FAME was measured. Taking into account the concentration of oleic acid in the pomace oil, the amount of water formed was calculated considering that the oleic acid was completely esterified.

For the analysis of TG hydrolysis, refined soybean oil, the amount of water calculated as indicated above and a catalyst loading of 3% (with respect to the oil) were used in the catalytic test. The reaction temperature was 140 °C for 30 min.

In the case of the hydrolysis of FAME, the same amount of water and catalyst was considered to be in the previous test, and FAME mass was determined considering that all the TG was consumed giving FAME (conservative results). Temperature and reaction time were the same as in the previous case.

The reaction products were quantified by acid-base titration as described above.

Figure 1 shows the results for the concentration of oleic acid present at the end of the reaction. It can be observed that the change in acidity of the samples after 30 min can be disregarded. Therefore, the hydrolysis reactions were not considered for the subsequent modelling of the system.
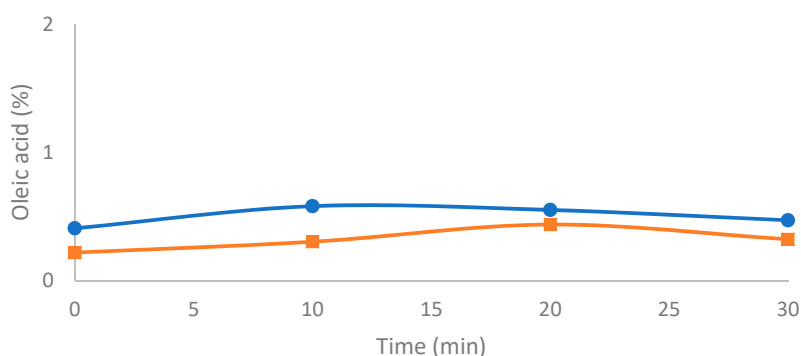

Figure 1. Concentration of oleic acid for the hydrolysis of TG (●) and FAME (■) using zinc stearate as catalyst at 140 °C.

2.2. Catalyst Stability

As mentioned above, StZn remained unchanged after being used in the transesterification of a refined oil for 2 h at 100 °C, but not so when the reaction is carried out at 140 °C for the same time period. In the latter case, the catalyst is partially transformed into Zn glycerolate.

It is very important to ensure the catalyst stability for developing a mathematical model that describes the reactor.

StZn was used in the methanolysis of pomace oil for 30 min at 100 and 140 °C, with 3% of catalyst loading and a methanol/oil molar ratio of 30. The catalyst recovered at the end of the reaction was analyzed by X-ray diffraction (XRD), confirming that its crystalline structure did not undergo any change. This result is due to the shorter time (compared to that used in [12]) and the presence of fatty acid [21].

2.3. Emulsion Stability

Zinc stearate forms part of an organized system in the reaction medium. To evaluate the degree of difficulty of separating the catalyst from the reaction product, two experiments were carried out under the following operating conditions: 2% catalyst loading, initial methanol/oil molar ratio of 25, temperature 100 °C, and reaction times of 60 and 120 min. After the reactions, the resulting mixtures were cooled and transferred to a separating funnel. After a while, the catalyst appeared as an emulsion in the 60 min reaction, located between the polar and non-polar phases (Figure 2a). The upper phase corresponded to methanol and the lower phase to a mixture of glycerides and FAME. As for the 120 min reaction, the catalyst was observed as a white solid at the bottom of the separating funnel (Figure 2b), which makes it easy and simple to recover.
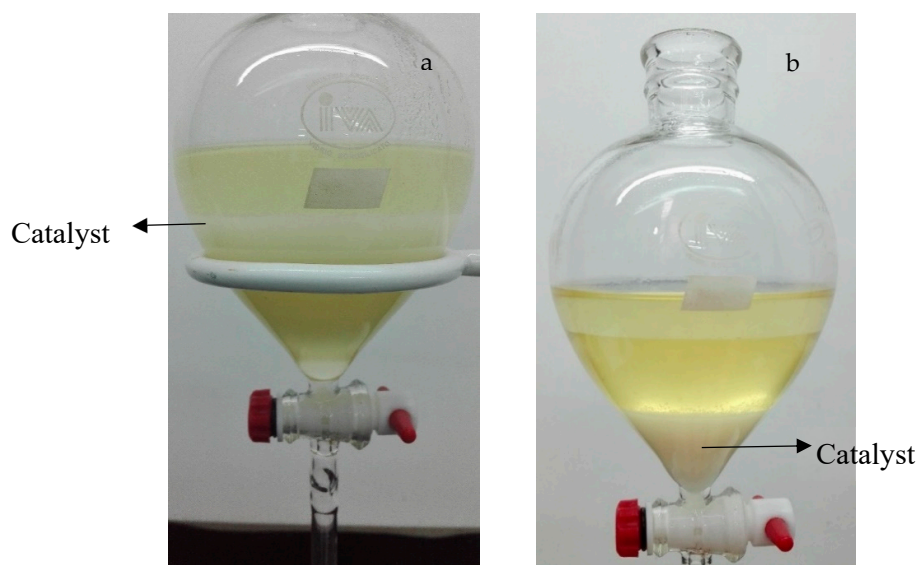

Figure 2. Resulting mixture of the reaction performed at 100 °C, with a methanol/oil molar ratio of 25, 2% catalyst loading, for a reaction time of 60 min (**a**) and 120 min (**b**).

This difference in behavior can be explained by taking into account the FAME concentration obtained at the end of each reaction. Since at 120 min there is a higher FAME concentration in the reaction medium, after a short time the catalyst can be found at the bottom of the container due to the emulsion breakdown.

2.4. Kinetic Modelling

Table 1 shows the estimated parameters obtained with Gproms. The selected variance model was "constant variance".

Table 1. Estimated kinetic parameters for the transesterification and esterification reactions in the methanolysis of pomace oil catalyzed by Zn stearate.

Parameter	Value
R^2	0.91
k_{04} ($L^2 mol^{-1} min^{-1} g^{-1}$)	$1.34 \times 10^{-4} \pm 1.20 \times 10^{-5}$
k_{0-4} ($L^2 mol^{-1} min^{-1} g^{-1}$)	$1.66 \times 10^{-4} \pm 1.19 \times 10^{-4}$

E_{a1} (kJ mol^{-1})	71.0 ± 1.90
E_{a2} (kJ mol^{-1})	80.4 ± 5.49
E_{a3} (kJ mol^{-1})	49.1 ± 2.49
E_{a4} (kJ mol^{-1})	34.1 ± 3.98
E_{a-1} (kJ mol^{-1})	107 ± 5.21
E_{a-2} (kJ mol^{-1})	101 ± 3.78
E_{a-3} (kJ mol^{-1})	62.0 ± 3.09
E_{a-4} (kJ mol^{-1})	83.3 ± 24.2

Table 2 shows the kinetic and equilibrium constants obtained for the estimated parameters at 100 and 140 °C. It can be observed that within the studied temperature range, the equilibrium constants do not vary with temperature. For the same reaction, Pugnet et al. [22] found that the equilibrium constants were independent of temperature for the 180–210 °C range.

Table 2. Forward and reverse kinetic constants and equilibrium constants for the transesterification and esterification reactions in the methanolysis of pomace oil catalyzed by zinc stearate.

| Parameter	100 °C	140 °C
k_1 (L^{2}mol^{-1}min^{-1}g^{-1})	1.08×10^{-4}	1.10×10^{-4}
k_2 (L^{2}mol^{-1}min^{-1}g^{-1})	1.25×10^{-4}	1.27×10^{-4}
k_3 (L^{2}mol^{-1}min^{-1}g^{-1})	1.63×10^{-4}	1.65×10^{-4}
k_4 (L^{2}mol^{-1}min^{-1}g^{-1})	1.34×10^{-4}	1.35×10^{-4}
k_{-1} (L^{2}mol^{-1}min^{-1}g^{-1})	6.41×10^{-4}	6.59×10^{-4}
k_{-2} (L^{2}mol^{-1}min^{-1}g^{-1})	1.67×10^{-4}	1.71×10^{-4}
k_{-3} (L^{2}mol^{-1}min^{-1}g^{-1})	5.30×10^{-4}	5.39×10^{-4}
k_{-4} (L^{2}mol^{-1}min^{-1}g^{-1})	1.66×10^{-4}	1.69×10^{-4}
K_{eq1}	0.169	0.167
K_{eq2}	0.748	0.745
K_{eq3}	0.307	0.307
K_{eq4}	0.808	0.798

It was not easy to compare these results with the literature due to the chemical nature of StZn and the variety of mathematical expressions reported. Most of the studies found in the literature use global reaction models. Only a few kinetic reports of simultaneous esterification and transesterification reactions were found, with a great diversity of results.

The activation energies of the equilibrium constants were 82, 103 and 88 kJ/mol for the three consecutive reactions in the transesterification of rapeseed oil with methanol catalyzed by zinc aluminate [22].

Konwar et al. [19] determined the activation energies for the simultaneous esterification and transesterification reactions using sulfonated mesoporous carbon as catalyst. The activation energies for the direct transesterification reactions were 66.4, 67.9 and 109 kJ/mol, and that corresponding to esterification was 71.5 kJ/mol.

Regarding the esterification reaction of FFA, Zubir et al. [23] studied the kinetics of the esterification of FFA with ethanol catalyzed heterogeneously with zirconia doped with tungsten with a reversible second-order model in the 30–50 °C temperature range. They obtained 51.9 kJ/mol for the direct activation energy and 87.6 kJ/mol for the equilibrium constant. Lower activation energy values were again found for this reaction than for transesterification.
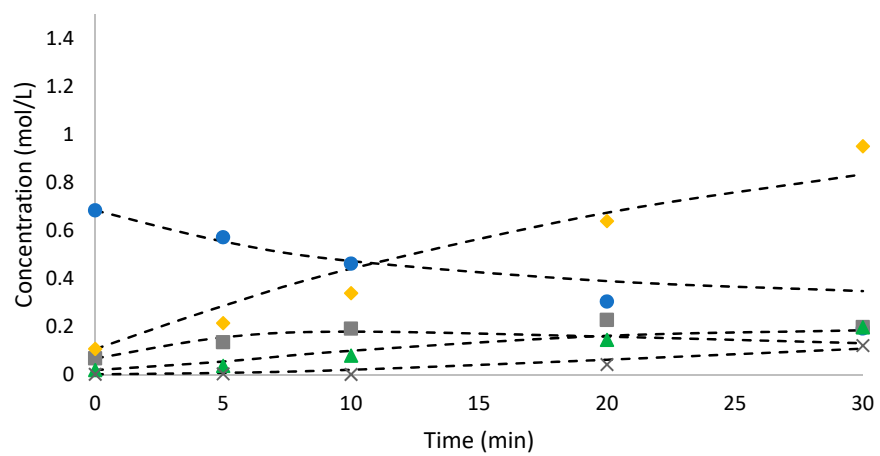
Figure 3 shows the results obtained with the proposed model for the methanolysis of pomace oil catalyzed by StZn under different experimental conditions. The dotted lines correspond to the calculated values, while the dots represent the experimental data.
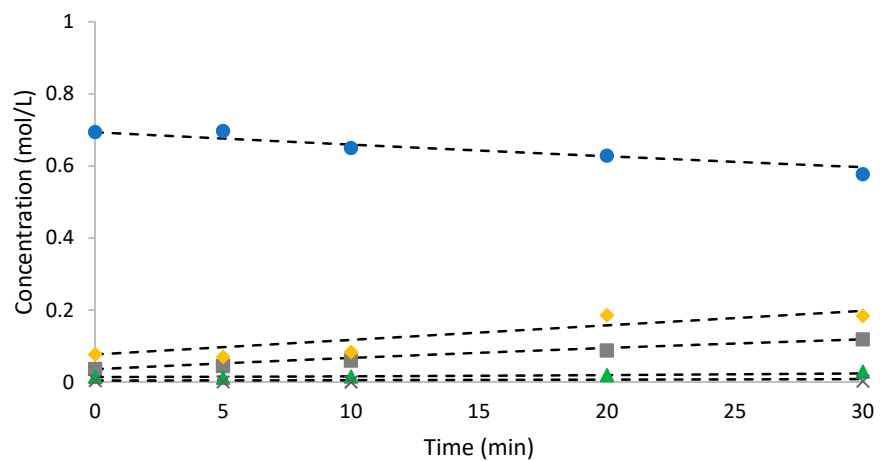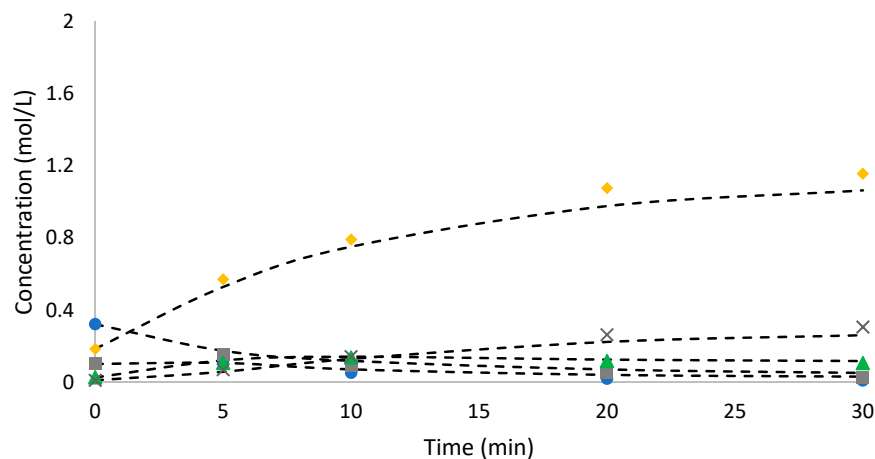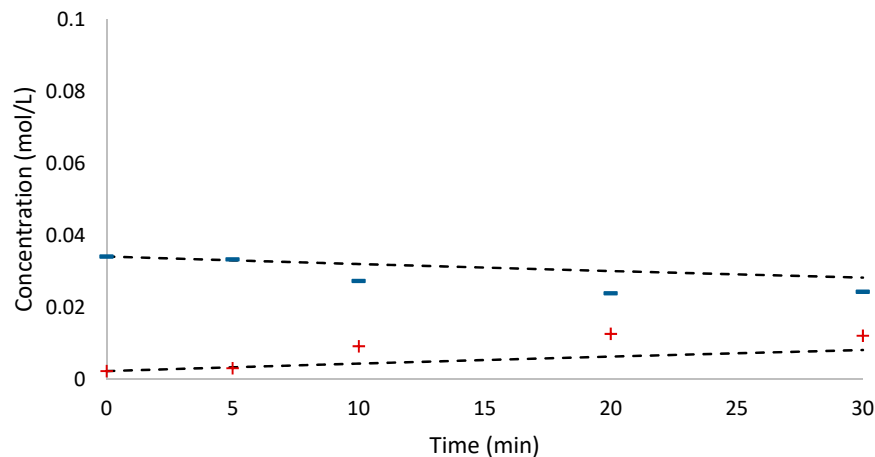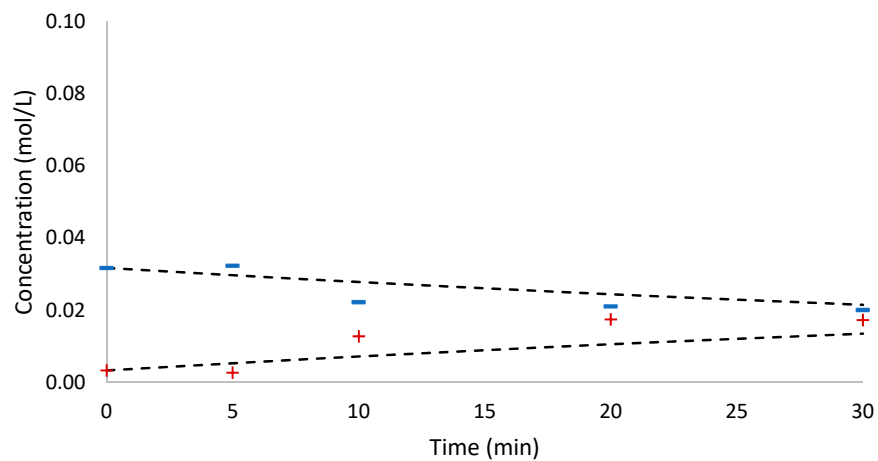
(**a**)
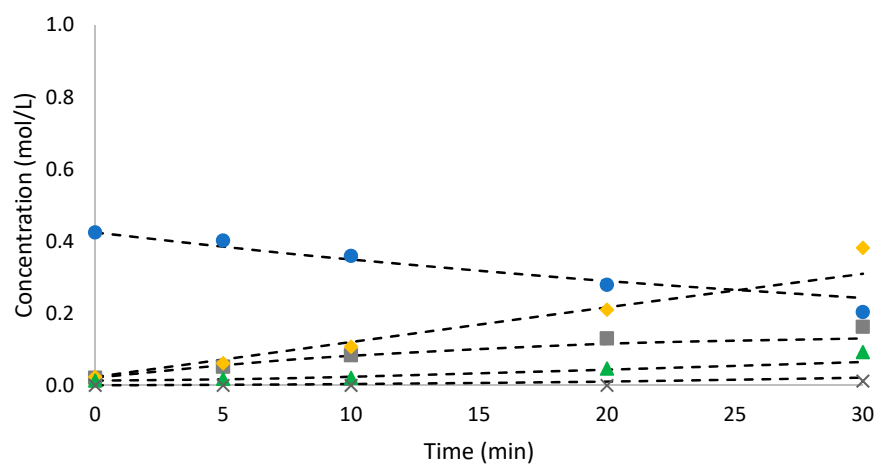
(**b**)

(**c**)

(**d**)

Figure 3. Distribution of products and reagents in the transesterification of pomace oil catalyzed by zinc stearate. Operating conditions: (**a**) Temperature = 100 °C; catalyst loading = 1%, methanol/oil molar ratio = 10; (**b**) Temperature = 120 °C; catalyst loading = 1%, methanol/oil molar ratio = 30; (**c**) Temperature = 140 °C; catalyst loading = 1%, methanol/oil molar ratio = 10; (**d**) Temperature = 140 °C; catalyst loading = 3%, methanol/oil molar ratio = 30. References: dotted lines: simulation; dots: experimental data, ● TG; ■ DG; ♦ FAME; ▲ MG; × Gly.

A good fit of the estimated values with the experimental data was observed.

Figure 4 presents the results obtained with the proposed model for the esterification reaction of FFA in pomace oil under the same operating conditions as those selected for the previous figure. The dotted lines correspond to the values obtained with the model, while the dots represent the experimental data. A good fit of the model data with the experimental values was also observed.
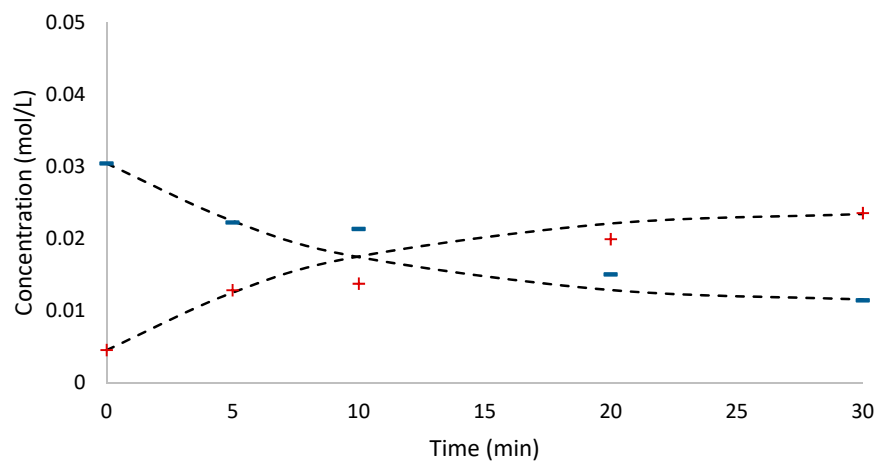

(**a**)

(**b**)
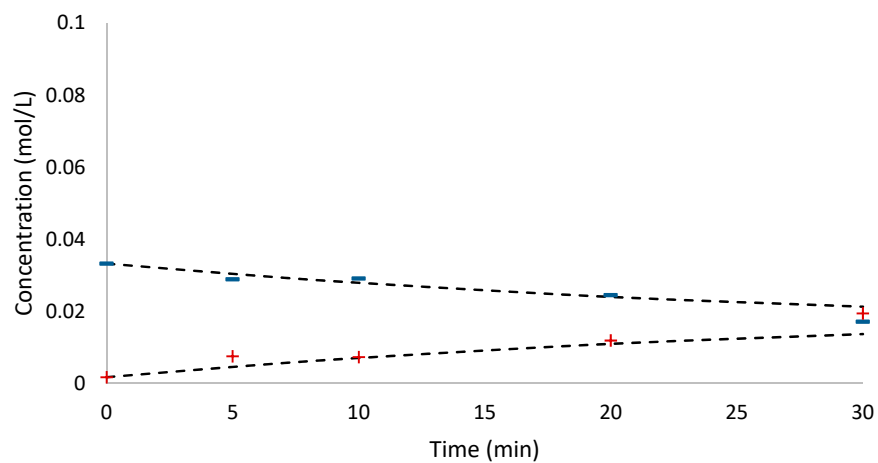
(**c**)

(**d**)

Figure 4. Distribution of products and reagents in the esterification of pomace oil catalyzed by zinc stearate. Operating conditions: (**a**) Temperature = 100 °C; catalyst loading = 1%, methanol/oil molar

ratio = 10; (**b**) Temperature = 120 °C; catalyst loading = 1%, methanol/oil molar ratio = 30; (**c**) Temperature = 140 °C; catalyst loading = 1%, methanol/oil molar ratio = 10; (**d**) Temperature = 140 °C; catalyst loading = 3%, methanol/oil molar ratio = 30. References: dotted lines: simulation; dots: experimental data, − FFA; + H_2O.

Figure 5 shows all the result data of the catalytic tests. A good fit between the calculated and experimental data for all the tests performed under different operational conditions can be observed.
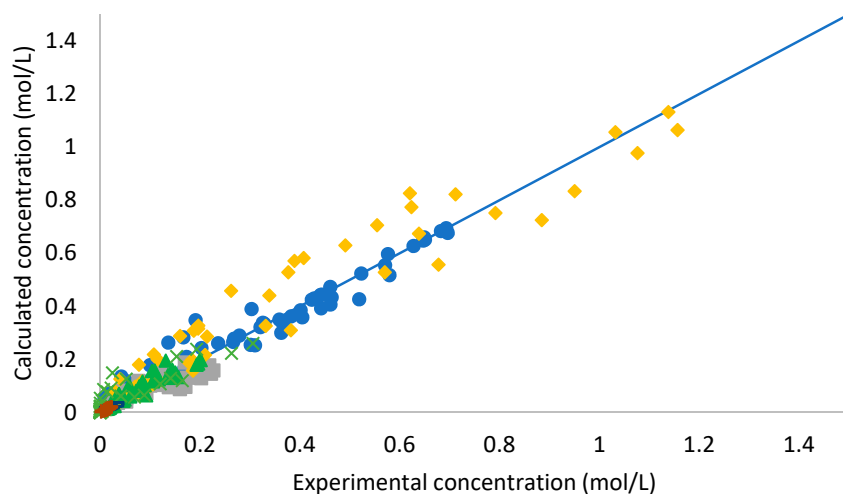

Figure 5. Parity plot of calculated vs. experimental concentrations. References: ●TG; ■ DG; ♦ FAME; ▲ MG; × Gli; − FFA; + H_2O.

2.5. Validation of the Mathematical Model

A reaction conducted at 120 °C, with 2% catalyst loading and a molar ratio of 30 (which was not used for the kinetic model) was simulated using the parameters obtained with the mathematical model. The experimental TG conversion obtained at 30 min of reaction was 62%, FFA conversion was 58% and FAME yield was 38%. The calculated values obtained with the model were: X_{TG} = 64%, X_{FFA} = 53%, Y_{FAME} = 39%. The corresponding errors for this case were of 8% for the conversions and of 2% for FAME yield, showing the good fit of the model to the experimental data.

Figure 6 shows the results of the concentrations of all the calculated species vs the experimental values for a reaction time of 30 min.
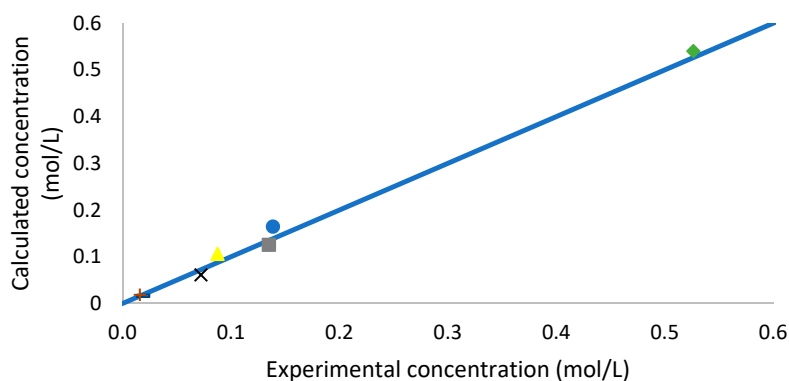

Figure 6. Calculated values vs. experimental concentrations for the validation reaction of the model. References: ● TG; ■ DG; ♦ FAME; ▲ MG; × Gli; − FFA; + H_2O.

2.6. Simulation

The mathematical model could be useful to generate operating strategies for the reaction process that allow obtaining biodiesel within the quality standards in terms of product composition.

Various operational strategies were simulated for a different number of steps of batch reactions performed at 140 °C with 3% of catalyst loading and a methanol/oil molar ratio of 30 (optimal conditions in the studied range).

Table 3 shows the selected simulations (I to VI) with their corresponding stages consisting of reaction cycles with different reaction times, with separation of glycerol and water between them. The results of TG and FFA conversion, concentrations of FAME, MG, and DG and acid value obtained in each case at the end of the process are also presented, as well as the quality specifications of biodiesel according to Argentine standard IRAM 6515-1.

Table 3. Operating strategies for the methanolysis of pomace oil at 140 °C, with a methanol/oil molar ratio of 30 and 3% catalyst loading.

| | Simulation | | | | | | IRAM 6515-1 standard |
	I	II	III	IV	V	VI	
Total operating time (min)	90	120	180	120	180	135	
Stage 1 (min)	30	60	60	30	60	45	
Stage 2 (min)	30	30	60	30	60	30	
Stage 3 (min)	30	30	60	30	30	30	
Stage 4 (min)	-	-	-	30	30	30	
X_{TG}	0.97	0.97	0.98	0.98	0.99	0.99	
X_{FFA}	0.94	0.95	0.96	0.97	0.98	0.97	
FAME concentration (% p/p)	95	95	96	98	98	98	96.5
MG concentration (% p/p)	1.03	0.90	0.84	0.50	0.47	0.45	0.8
DG concentration (% p/p)	0.51	0.44	0.37	0.26	0.25	0.23	0.2
Acid value (mg KOH/g)	0.11	0.11	0.09	0.04	0.04	0.04	0.5

It can be observed that the number of steps for the water and glycerol removal is determinant for the reactor performance, as expected in reversible reactions. The concentrations of FAME and byproducts of Simulation VI were within the quality standard. In this case, the reaction took place in short times (135 min) in 4 stages. The time of the stages was selected taking into account the catalyst stability.

For Simulation VI, the concentration profile of the species when glycerol and water were removed at the end of each stage is shown in Figure 7a, while Figure 7b shows the profile concentration of MG, DG, and FFA in particular.
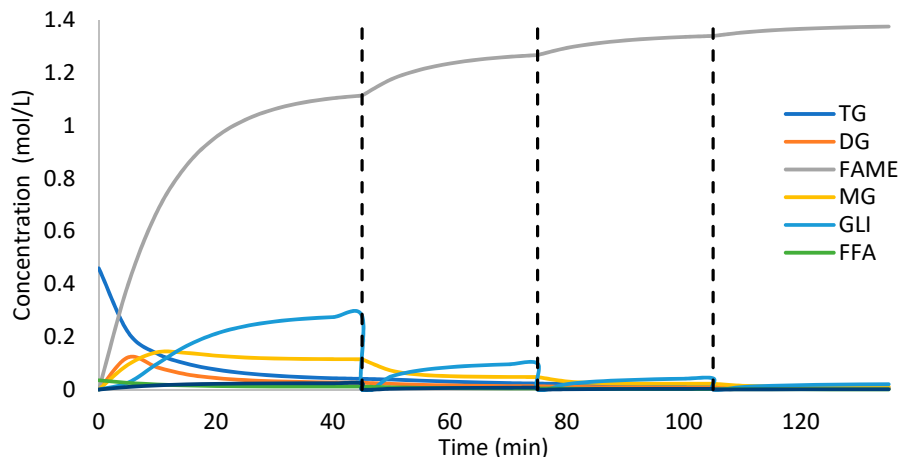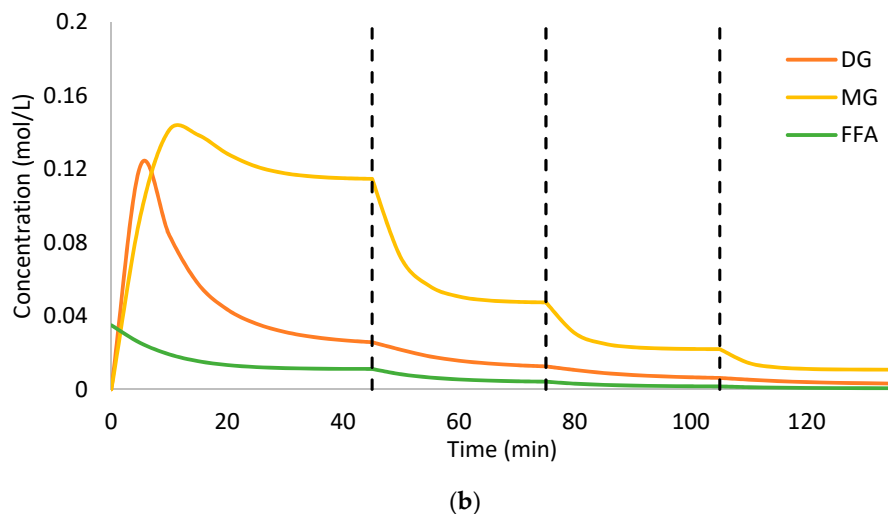

(**a**)

Figure 7. Concentration profile of the simulation of the methanolysis of pomace oil catalyzed by zinc stearate in 4 stages with glycerol and water removal between stages. Temperature: 140 °C, catalyst load: 3%, methanol/oil molar ratio: 30.

3. Materials and Methods

3.1. Catalyst Syntheshis

The zinc stearate was prepared by metathesis in an alcoholic solution [13,24]. First, 0.035 mol of NaOH (Dorwil, 99%) was dissolved in 150 mL of ethanol (Dorwil 99.5%), and 0.035 moles of stearic acid (Sigma-Aldrich, 99%) in 100 mL of ethanol. The sodium salt was obtained by mixing together the solutions. This precipitate was dissolved in water, and a stoichiometric amount (0.0175 mol) of $ZnCl_2$ (Biopack, 99%) dissolved in 100 mL of water was added, stirring it for 1 h. The resulting mixture was filtered, washed with ethanol and water repeatedly, and finally dried at 50 °C for 24 h.

The characterization of the crystalline structures of the synthesized catalyst was determined by XRD using a Philips PW1710 equipment with Cu Kα radiation scan in the 2–60° 2θ range. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique was applied using a Nicolet 6700 Thermo scientific multiplex spectrophotometer.

3.2. Catalytic Tests

The methanolysis reactions of pomace oil were carried out in a 600 mL Parr reactor operating in batch mode. For all the reaction tests, the reagents and the catalyst were added first, then the reactor was sealed and, once the reaction temperature was reached, the stirring was started. At this point, the reaction has begun, and a small concentration of FAME is observed at initial time.

Methanol (UVE HPLC) and pomace oil characterized previously were used as reagents. In a recent work [8], it was reported that the acid value of pomace oil is 2.3 mg KOH/g oil and the aqueous content corresponds to 0.07%.

The reaction samples were analyzed by gas chromatography following European standard UNE-EN-14105 using a Perkin Elmer AutoSystem XL (sourced: USA) chromatograph equipped with a capillary column (ZB-5HT Zebron) and a flame ionization detector (FID). The fatty acid content was determined by acid-base titration following European standard UNE-EN 14104.

3.3. Kinetic modelling

The transesterification of TG with methanol consists of three consecutive reversible reactions, obtaining diglycerides (DG) and monoglycerides (MG) as intermediates and glycerol (Gly) and methyl esters of fatty acids as products. The reactions involved are the following:

$$TG + MOH \leftrightarrow DG + FAME \tag{3}$$

$$DG + MOH \leftrightarrow MG + FAME \tag{4}$$

$$MG + MOH \leftrightarrow Gly + FAME \tag{5}$$
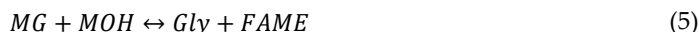
The esterification of fatty acids with methanol is a reversible reaction where the products are FAME and water:

$$FFA + MOH \leftrightarrow FAME + H_2O \tag{6}$$
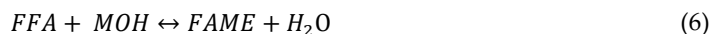
The proposed model assumes first order kinetics for each compound involved in the reaction. The reaction rate expressions are:

$$v_1 = k_1 C_{TG} C_{MOH} - k_{-1} C_{DG} C_{FAME} \tag{7}$$

$$v_2 = k_2 C_{DG} C_{MOH} - k_{-2} C_{MG} C_{FAME} \tag{8}$$

$$v_3 = k_3 C_{MG} C_{MOH} - k_{-3} C_{Gly} C_{FAME} \tag{9}$$

$$v_4 = k_4 C_{FFA} C_{MOH} - k_{-4} C_{H_2O} C_{FAME} \tag{10}$$

where C_i is the concentration of the corresponding compound (mol L^{-1}), v_i is the reaction rate (mol g^{-1} min^{-1}), and k_i and k_{-i} are the kinetic constants for the forward and reverse reactions (L^{2}mol^{-1} min^{-1}g^{-1}). The kinetic constants depend on temperature assuming the following Arrhenius equations:

$$k_i = k_{0i}\, e^{\left(-\frac{E_{ai}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)} \tag{11}$$

$$k_{-i} = k_{0-i}\, e^{\left(-\frac{E_{a-i}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)} \tag{12}$$

where i = 1,2,3,4; k_{0i} and k_{0-i} are the pre-exponential factors of the forward and reverse reactions (L^{2}mol^{-1} min^{-1}g^{-1}), E_{ai} and E_{a-i} are the activation energies of the forward and reverse reactions (KJ mol^{-1}), T is temperature in K, and R is the ideal gas constant (0.0083 KJ mol^{-1} K^{-1}).

The kinetic constants of the transesterification of soybean oil at 100 °C obtained in a previous work [15] were used; thus, the reference temperature chosen was 373 K. The activation energies of all the reactions and the kinetic parameters of the esterification reaction of FFA were estimated. The resulting equations are the following:

$$k_1 = 1.08\ 10^{-4}\, e^{\left(-\frac{E_{a1}}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)} \tag{13}$$

$$k_2 = 1.25\ 10^{-4}\, e^{\left(-\frac{E_{a2}}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)} \tag{14}$$

$$k_3 = 1.63\ 10^{-4}\, e^{\left(-\frac{E_{a3}}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)} \tag{15}$$

$$k_4 = k_{04}\, e^{\left(-\frac{E_{a4}}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)} \tag{16}$$

$$k_{-1} = 6.41\ 10^{-4}\, e^{\left(-\frac{E_{a-1}}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)} \tag{17}$$

$$k_{-2} = 1.67\ 10^{-4}\, e^{\left(-\frac{E_{a-2}}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)} \tag{18}$$

$$k_{-3} = 5.30\ 10^{-4}\, e^{\left(-\frac{E_{a-3}}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)} \tag{19}$$

$$k_{-4} = k_{0-4}\, e^{\left(-\frac{E_{a-4}}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)} \tag{20}$$

The hypotheses considered for the reactor model were as follows [15]:

1. Perfect mixing of reagents and products.
2. The reaction system can be considered pseudo-homogeneous and isothermal.

3. The catalyst is dissolved and perfectly mixed in the reactor. There is no mass transfer limitation.
4. The methanol concentration is constant during the reaction.

Therefore, the mass balances of the species are shown below:

$$\frac{dC_{TG}}{dt} = -v_1 \frac{m}{V} \tag{21}$$

$$\frac{dC_{MOH}}{dt} = 0 \tag{22}$$

$$\frac{dC_{DG}}{dt} = (v_1 - v_2) \frac{m}{V} \tag{23}$$

$$\frac{dC_{FAME}}{dt} = (v_1 + v_2 + v_3 + v_4) \frac{m}{V} \tag{24}$$

$$\frac{dC_{MG}}{dt} = (v_2 - v_3) \frac{m}{V} \tag{25}$$

$$\frac{dC_{Gl}}{dt} = v_3 \frac{m}{V} \tag{26}$$

$$\frac{dC_{FFA}}{dt} = -v_4 \frac{m}{V} \tag{27}$$

$$\frac{dC_{H_2O}}{dt} = v_4 \frac{m}{V} \tag{28}$$

where m is the catalyst mass (g), V is the reactor volume (L), and t is the reaction time (min).

Gproms software was used to solve the set of both algebraic and differential equations, and to adjust the experimental data.

The goodness of fit was measured using the coefficient of determination (R^2), calculated with the following equation:

$$R^2 = \frac{\sum_{i=1}^{n}\left(C_i^{calc} - \bar{C}\right)^2}{\sum_{i=1}^{n}(C_i - \bar{C})^2} \tag{29}$$

4. Conclusions

The aim of this work was to obtain a better understanding of the behavior of zinc stearate as an environmentally friendly catalyst in the transesterification of triglycerides and the esterification of the FFA present in olive pomace oil with methanol. The stability of the emulsions formed with oil and methanol in the presence of the catalyst and with FAME and methanol with StZn was compared. It was found that the FAME–methanol–catalyst emulsion was much more unstable than that corresponding to the oil, which makes the catalyst easier to recover from the reaction medium at final time, when there are high concentrations of FAME.

All the kinetic parameters were determined with a complete model, considering three stepwise reactions corresponding to the transesterification of TG and the esterification of FFA (all reversible). The goodness of fit was corroborated by simulating the results of a reaction obtained using other operating conditions. The parameters obtained could be used to select operating conditions that allow producing biodiesel within the quality standards.

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