Efficient production of biodiesel from low-cost feedstock using zinc oleate as catalyst

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Deborath M. Reinoso *, Daniel E. Damiani, Gabriela M. Tonetto

Planta Piloto de Ingeniería Química PLAPIQUI (UNS–CONICET), Camino "La Carrindanga" Km 7, CC 717, CP 8000, Bahía Blanca, Argentina

ABSTRACT

In this study, the synthesis of fatty acid methyl esters (FAME) by the transesterification of low-cost feedstock containing 10 and 22 wt.% free fatty acid (FFA), using zinc oleate (ZnOl) as catalyst, was investigated. The performance of the ZnOl salt in the reaction medium was evaluated in terms of activity and stability in the presence of free fatty acids. At 140 °C and 2 h of reaction time, triglyceride conversion was 100%, FAME yield was close to 95%, and fatty acid conversion was 75.9% and 82.6% for feedstock with 10 and 22 wt.% FFA, respectively. The zinc carboxylic salt was able to catalyze simultaneously the triglyceride transesterification and the fatty acid esterification reactions with high activity and selectivity under moderate operating conditions and slight FAME and triglycerides hydrolysis.

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1. Introduction

Biodiesel is a renewable, non-toxic and biodegradable fuel. In order to reduce production costs and make it more competitive, the use of inexpensive raw materials with high free fatty acid (FFA) content, such as waste oils and non-edible oils, has been proposed [1–3].

The conventional synthesis of fatty acid methyl esters (FAME) from low-cost acidic raw materials requires a special process combining acid and base catalysis. The first stage involves the esterification of FFA using a strong acid as catalyst [4], usually H_2SO_4, and the second step is conventional alkaline transesterification [5]. This process requires additional steps for the neutralization and separation of the catalysts, which generates additional costs [6,7]. If the FFA content is very high, the overall process is performed using acid catalysis. However, homogeneous acid catalyst systems are not widely used because of their corrosive power, reduced efficiency and the high temperature required in the operation [1].

An alternative method for pretreating acidic feedstocks consists of generating mono- and diglycerides from glycerol and FFA at 200 °C using $ZnCl_2$ as catalyst. This treatment has the disadvantage of requiring high temperatures and that reaction rates are relatively low [8].

Nowadays, catalysts that simultaneously promote the transesterification of triglycerides and the esterification of FFA are the focus of much research. There are few studies related to the production of biodiesel in a single step with unconventional inexpensive raw materials and using non-corrosive acid catalysts [9–13].

The transesterification of non-edible Jatropha oil using heterogeneous catalysts based on mixed oxide of Zn and Mg with different Zn/Mg molar ratios was recently reported [14]. The basic solid catalyst presented a FAME yield of 83% at 120 °C and 3 h of reaction. However, the study of the solid in consecutive uses showed that the activity of the material decreased by leaching of the active ion in the reaction.

In addition, the use of common Lewis acids ($AlCl_3$ and $ZnCl_2$) in the synthesis of biodiesel demonstrated that they are potential alternative catalysts for the transesterification of vegetable oil and the esterification of long-chain fatty acids [15].

Zinc aluminate was proposed as an interesting catalyst in the synthesis of methyl esters from refined and acid raw materials. This heterogeneous catalyst presented FAME yields close to 100% operating at 190–220 °C. However, the water in the reaction medium inhibits the activity of zinc aluminate, and thus the water content must be less than 0.15% [16].

Sreeprasanth et al. [17] studied the use of Fe-Zn double-metal cyanide (DMC) complexes in the production of biodiesel and biolubricants. These hydrophobic compounds with strong Lewis acid sites showed good activity and tolerance to FFA. Yan et al. [18] reported on another zinc compound with acid and base sites, namely $ZnO-La_2O_3$, which showed to be active for the methanolysis of unrefined raw materials (5–20% wt. FFA). It presented a high FAME yield in the 180–200 °C range, without significant activity in the hydrolysis of triglycerides and FAME.

Other catalysts with Lewis acid sites, such as zinc carboxylic salts of the metals Cd, Mn, Pb, and Zn, proved to be active in the transesterification and esterification of acid feedstocks [19,20]. The results demonstrated that the activity of these catalysts was related to the Lewis acid strength of the metals and to the structure of the anion [20]. Jacobson et al. [21] studied the production of FAME from used

* Corresponding author. Fax: +54 291 4861600.
E-mail address: dreinoso@plapiqui.edu.ar (D.M. Reinoso).

edible oils with 15 wt.% FFA using various solid acid catalysts. Their results indicated that zinc stearate immobilized on silica gel is a stable and active catalyst for the simultaneous transesterification and esterification reactions. At 200 °C and 10 h of reaction time, a FAME yield of 81% was obtained, with a concentration of 1.6 wt.% FFA.

In a previous work, Reinoso et al. [22] found that zinc oleate is an active material in the transesterification of refined soybean oil. This compound, with Lewis acid sites, is soluble in the non-polar phase (oil and FAME) at reaction temperature, and re-crystallizes at room temperature. A detailed [25,29] (which included the full distribution of products in the reaction time and a meticulous characterization of the catalyst before and after reaction) determined the behavior of the catalyst system, the stability range, and its possible transformation into zinc glycerolate under certain experimental conditions. This information makes it possible to understand the results obtained by other authors[19,20] and opened up a new research field to operate under mild experimental conditions.

Considering the catalytic potential of zinc carboxylic salts, in the present work, the transesterification of low-cost feedstocks with FFA concentrations of 10 and 22 wt.% as models of yellow and brown grease, respectively, was studied using zinc oleate as catalyst. The behavior of the Zn carboxylic salt was evaluated in terms of activity, selectivity and stability in the reaction medium.

2. Materials and methods

2.1. Catalyst synthesis

The zinc oleate salt (ZnOl) was prepared by metathesis reaction in an alcoholic solution [23]. First, the sodium oleate salt was synthesized at room temperature from a stoichiometric amount of oleic acid and sodium hydroxide in ethanol solutions with constant stirring. Then a stoichiometric amount of aqueous solution of zinc chloride was added and the resulting precipitate was kept under vigorous agitation at room temperature for 1 h. Finally the salt obtained was washed several times with ethanol, filtered, and stove dried at 50 °C.

2.2. Catalyst characterization

The structures of the catalytic solids (synthesized and used in reaction) were analyzed by X-ray powder diffraction (XRD, Philips PW1710) using Cu Kα1 (1.54060 Å) radiation scanning in the 2θ range of 2–60° in all the cases, operating at 45 Kv and 30 mA. The materials were also evaluated by diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS, Nicolet 6700 FT-IR spectrometer). The amount of Zn in the non-polar phase, after a water-wash treatment, was determined by inductively coupled plasma (ICP, Shimadzu 9000 multitype with high resolution).

2.3. Catalytic tests

The catalyst tests were carried out in a 600 cm^3 Parr reactor equipped with a 4-angled blade stirrer. The catalyst and the reactants were fed into the reactor, and then the system was heated without agitation until reaction temperature was reached. At that moment agitation was started and a zero time sample was taken. The evolution of the reactants and products was estimated by taking reaction samples periodically.

The transesterification of the acid oils was carried out using methanol (Aberkon, chromatographic quality) and models of economical feedstocks with 10 and 22 wt.% FFA, named Oil-10FFA and Oil-22FFA, respectively. The raw materials consisted of refined soybean oil (commercial brand) and oleic acid (OA, Sigma Aldrich, 90%). The reaction conditions involved were temperature 140 °C, catalyst load 3 wt.%, methanol:oil molar ratio 30:1, and agitation rate 500 rpm.

The quantification of the products and reactants was performed by gas chromatography according to UNE-EN norm 14105 with a Perkin Elmer AutoSystem XL chromatograph. The analysis was carried out using a capillary column (ZB-5HT Zebron) with dimethylpolysiloxane stationary phase, 15 m length, 0.32 mm inner diameter and 0.10 μm film thickness. The column was coupled to the injector with a deactivated silica guard column (Zebron) with 0.53 mm inner diameter and 5 m length. A split injector was used with a temperature of 50 °C. The carrier gas was H$_2$ with 12 psi inlet pressure, and air was used as auxiliary gas. The FID detector operated at 350 °C and the total analysis time was 35 min. The specific oven temperature started at 50 °C, then it was increased to 180 °C (15 °C/minute), 230 °C (7 °C/minute), and 370 °C (10 °C/min). The FFA content was determined by acid-base titration (UNE-EN norm 14104).
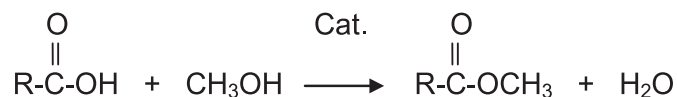
Triglyceride conversion (X_{TG}) and FAME yield (Y_{FAME}) were calculated using the following equations:

$$X_{TG} = \frac{\text{mol TG}_{it} - \text{mol TG}_{ft}}{\text{mol TG}_{it}} 100 \tag{1}$$

$$Y_{FAME} = \frac{\text{mol FAME}/3}{\text{mol TGE}_{it}} 100 \tag{2}$$
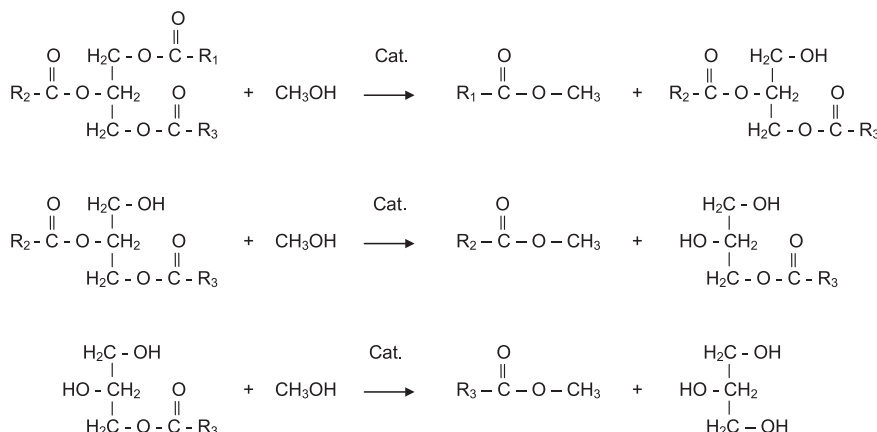
Scheme 1. Transesterification of triglycerides with methanol.

$$R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH + CH_3OH \xrightarrow{\text{Cat.}} R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OCH_3 + H_2O$$

Scheme 2. Esterification of a fatty acid with methanol.

where TG_{it} and TG_{ft} correspond to the triglyceride concentration (mol) at initial and final time, respectively. TGE represents the equivalent triglycerides moles:

$$\text{mol } TGE_{it} = \text{mol } TG_{it} + \text{mol } FFA_{it}/3 \tag{3}$$

3. Results and discussion

3.1. Non-catalytic transesterification and esterification reactions

Blank tests of the transesterification of the refined and acid raw materials (Oil-10FFA and Oil-22FFA) without catalyst were carried out. When acid raw materials are used in the transesterification of triglycerides (Scheme 1), the esterification of fatty acids occurs simultaneously (Scheme 2).

The results obtained for the non-catalytic transesterification of commercial soybean oil and the Oil-10FFA and Oil-22FFA samples at 140 °C and 120 min of reaction time are presented in Table 1. Low activity was found in the methanolysis of the refined soybean oil, with triglyceride conversions of 6.6% and a FAME yield of 2.6%. Dasari et al. [24] reported that the alcoholysis of triglycerides is kinetically controlled due to the ability of methanol to diffuse in oil. At the same time, the intermediate glycerides and FAME formed during the reaction generate a solvation effect, increasing as a result of the solubility of methanol.

On the other hand, in the blank essays performed with FFA, there was an increase in triglyceride conversion compared with the transesterification of refined soybean oil. At 120 min of reaction time, triglyceride conversion was 17.7% and 17.9% with an overall FAME yield of 6.1% and 7.8% for the Oil-10FFA and Oil-22FFA samples, respectively. This increase in activity is associated with the auto-catalytic effect of the fatty acid present in the reaction medium [20].

The results of the non-catalytic esterification of acid oils present a final OA conversion of 7.9% and 22.3% for Oil-10FFA and Oil-22FFA, respectively. The non-catalytic esterification of pure OA (Fig. 4) presents a final conversion of 22.5%. The decrease in OA conversion for the Oil-10FFA sample could be attributed to its lower content of fatty acid, which exhibits auto-catalytic activity in esterification, and catalyzes the transesterification (as indicated above).

3.2. Catalytic activity of ZnOl in simultaneous transesterification and esterification reactions

The evolution of the products and reactants over time in the methanolysis of Oil-10FFA and Oil-22FFA when the reaction was catalyzed with ZnOl is shown in Fig. 2 and 3. It also presents the reaction

Table 1
Non-catalytic transesterification of refined and acid oil (10–22 wt.% OA) with methanol at 140 °C and 2 h: product distribution, triglyceride and oleic acid conversion, and FAME yield.

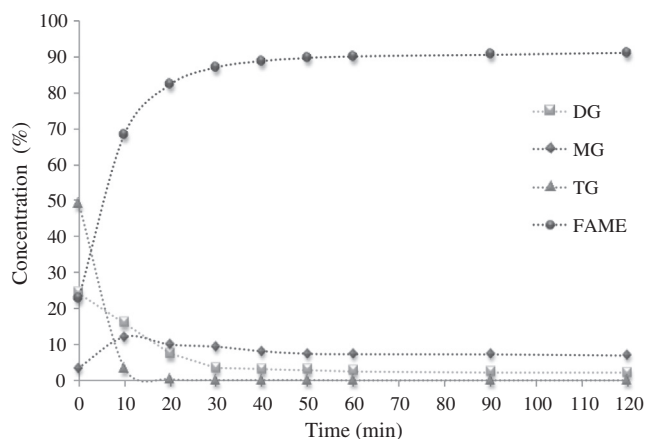| Composition of the non-polar phase (% p/p)	Free fatty acid content		
	0 wt.%	10 wt.%	22 wt.%
Monoglycerides	0.4	1.5	1.0
Diglycerides	3.5	9.8	11.3
Triglycerides	93.4	74.1	64.1
FAME	2.7	6.1	7.8
Oleic acid	–	8.5	15.8
TG conversion (%)	6.6	17.7	17.9
FAME yield (%)	2.6	6.1	7.8
OA conversion (%)	–	7.9	22.3

Fig. 1. Transesterification of refined and acid oil with methanol at 140 °C and 3 wt.% catalyst.

with refined soybean oil for comparison purposes (Fig. 1). The results show clear differences between the tests performed with refined and acid raw materials. In the transesterification of commercial soybean oil without special treatment (Fig. 1), the ZnOl catalyst exhibited high activity at short reaction times. At 40 min of reaction time, the distribution of the products was: FAME = 88.8, MG = 8.1, DG = 3.0 and TG = 0.1 wt.%.

In the methanolysis of the acid raw materials Oil-10FFA and Oil-22FFA (Fig. 2 and 3), a decrease in the overall activity is observed. For the test performed with Oil-10FFA (Fig. 2), TG concentration decreases to values below 1 wt.% at 60 min of reaction. The maximum concentration of the intermediate products DG and MG was found at 20 and 40 min of reaction time, respectively. FAME formation presented a maximum level of 93.9% at 120 min of reaction time.

In the catalytic test performed with the Oil-22FFA sample (Fig. 3), the TG content dropped to values below 1 wt.% after 90 min of reaction time. DG and MG reached a maximum concentration at 30 and 60 min, respectively. FAME final concentration for this test was 92.9 wt.%.

The evolution over time of the methylic esterification reaction catalyzed with ZnOl for the different initial concentrations of OA is shown in Fig. 4. In these catalytic tests, a marked difference is observed between the different FFA contents present in the raw material. The esterification of the Oil-10FFA and Oil-22FFA samples presented higher conversion of OA, reaching 75.9% and 82.5% at 120 min of reaction time, whereas in the esterification of pure OA (90% wt) conversion was lower with a value of 41.8% at final time (t = 120 min).
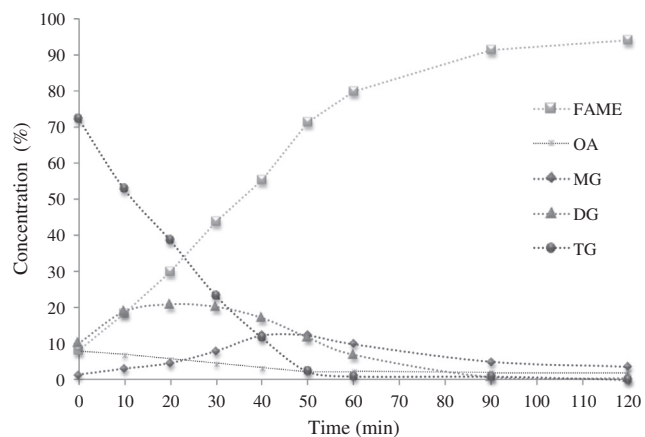

Fig. 2. Transesterification of acid oil (10 wt.% OA) with methanol at 140 °C and 3 wt.% catalyst (with respect to total feedstock).
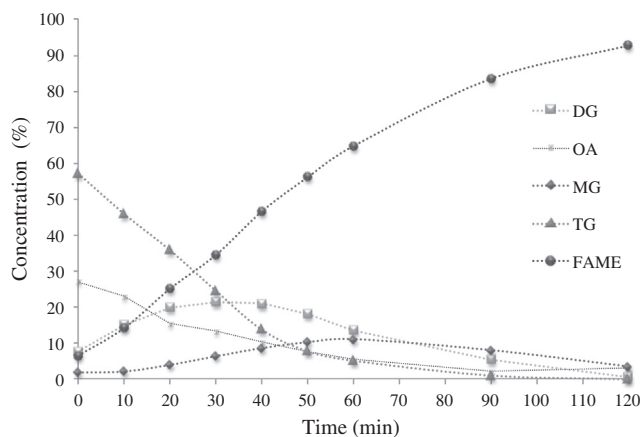
Fig. 3. Transesterification of acid oil (22 wt.% OA) with methanol at 140 °C and 3 wt.% catalyst (with respect to total feedstock).

Fig. 5. XRD patterns of ZnOl synthesized (a) and used in acid oil transesterification with 10 (b) and 22 wt.% OA (c).

3.3. Characterization of the spent catalyst

The correct synthesis of the Zn carboxylic salt was evaluated by XRD (Fig. 5a) and FTIR (Fig. 6a). The XRD results determined crystalline structures of chains arranged as slanted bilayer with a basal distance of 41.057 Å [23] In addition, Zn oleate is formed by a weakly crystallized region, constituted during the precipitation process [22]. The FTIR spectra present the absorption bands corresponding to the Zn carboxylic salt [22].

The catalytic solid recovered after reaction was characterized by XRD (Fig. 5b and c), and the results were confirmed by FTIR (Fig. 6b and c). The diffraction pattern of the catalytic material used in the transesterification of Oil-10FFA (Fig. 5b) shows the characteristic peaks corresponding to the crystalline phase of the zinc glycerolate salt (ZnGly, JCPDS No. 00-23-1975). The signals of maximum intensities are located at $2\theta = 10.9°$ (100), 20.67° (111), 17.12° (001), and 27.57° (211) [25]. This was confirmed by FTIR (Fig. 6b), the main characteristic signals correspond to ZnGly salt [25–27].

The results obtained for the characterization of the catalyst used in the transesterification of Oil-10FFA demonstrated the transformation of ZnOl into ZnGly by the interaction between zinc carboxylate and the glycerol formed in the reaction medium. Additional tests showed that the formation of ZnGly from ZnOl and glycerol requires both temperature and pressure conditions. The formation of the glycerol salt at 140 °C and atmospheric pressure is much slower, and the process was
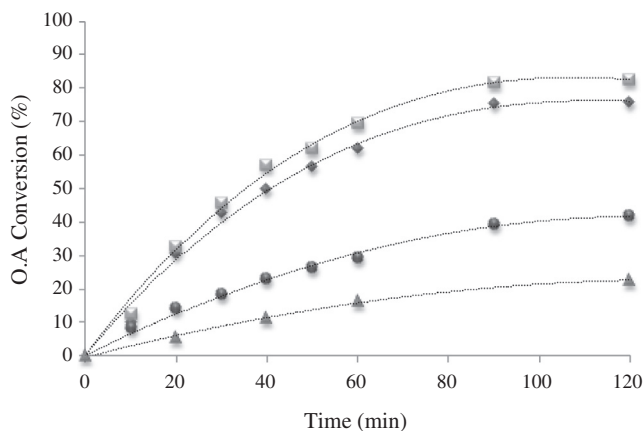
accelerated by pressurizing the system with N_2 (~160 psi, corresponding to the methanol vapor pressure). This behavior was similar to that found for the methyl transesterification of refined soybean oil at 140 °C [22].

The solid recovered from the reaction performed with the Oil-22FFA sample (Fig. 5c) presented the characteristic signals of Zn oleate at 2θ values = 2.07°, 4.13°, 6.21°, and 10.36° (FCPDS No. 00-055-1619). The FTIR spectrum (Fig. 6c) exhibited the typical vibration bands of Zn carboxylic salts. [22,28].

Different solids were recovered when using OIL-10FFA or OIL-22FFA due the different degrees of reaction progress, which generated a different composition of the reaction medium. This resulted in a singular interaction between glycerol and $Zn+2$ or AO and Zn^{+2}. When Oil-10FFA was used as raw material, the higher reaction progress and the lower FFA concentration allowed for better interaction of glycerol with Zn^{+2} ions. This resulted in ZnGly formation. When Oil-22FFA was used, the higher concentration of oleic acid promoted its interaction with Zn^{+2}, allowing for ZnOl salt formation.

The Zn content was analyzed by inductively coupled plasma (ICP) in the oil phase, after a water-wash, determining Zn concentrations of 10 and 433 mg L^{-1} for the Oil-10FFA and Oil-22FFA samples, respectively. These results show that the transformation of ZnOl in the reaction medium when Oil-10FFA is used as raw material generates a solid material (ZnGly) that can be easily recovered. When Oil-22FFA was used, the ZnOl solid crystallized partially in the reaction medium at room temperature, because the remainder of FFA content enables more easily the ZnOl crystal formation. The rest of the carboxylic salt was crystallized

Fig. 4. Esterification of OA pure and FFA in acid oil with methanol at 140 °C. ■ 22, ◆10, ● 100 wt.% OA. Experiments without catalyst, reference ▲ 100 wt.% OA.
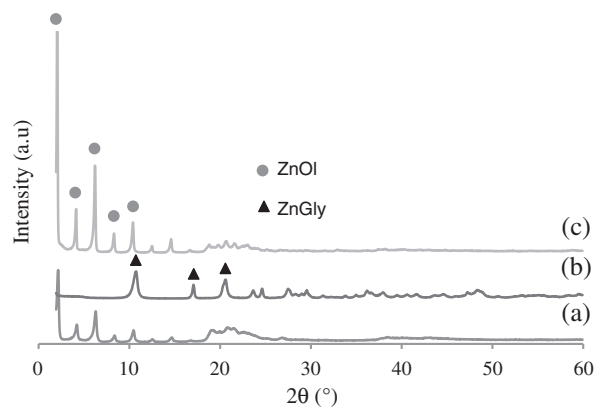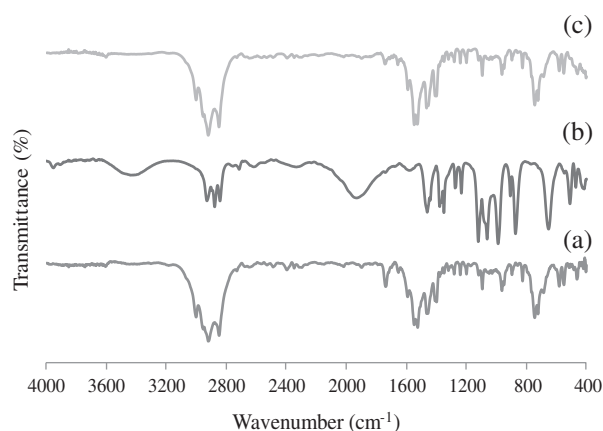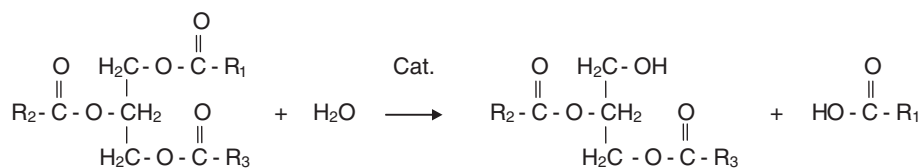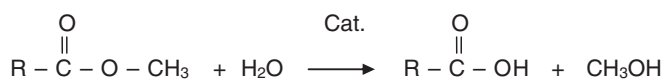

Fig. 6. FTIR spectrum of ZnOl synthesized (a) and used in the transesterification of acid oil with 10 (b) and 22 wt.% (c) FFA.

Scheme 3. Triglyceride hydrolysis.

Scheme 4. FAME hydrolysis.

by lowering the temperature ($-18\ °C$). In this case, it would be advisable to evaluate the optimum conditions under which the complete transformation of ZnOl into ZnGly can be achieved in order to simplify the recovery of the catalyst from the reaction medium.

3.4. Catalytic activity of ZnOl in the hydrolysis of FAME and triglycerides

The activity of the ZnOl catalyst in the hydrolysis of TG (Scheme 3) and FAME (Scheme 4) was studied at 140 °C and 120 min of reaction time. The tests were carried out considering 6 wt.% water content with respect to FAME and TG, and 3 wt.% of ZnOl. The amount of water fed into the reactor was selected taking into account the amount of water generated in the esterification of the Oil-22FFA sample for an OA conversion of ~80%.

The results obtained for the catalytic hydrolysis tests are shown in Fig. 7. In the presence of water, the Zn carboxylic salt presented a slight activity in the hydrolysis of FAME and TG. At 120 min of reaction time, 10.3% and 6.1% of fatty acid were generated from FAME and TG, respectively.

3.5. Analysis of the results

The Zn carboxylic salt showed good activity in the transesterification of low-cost feedstocks in the presence of free fatty acids (Table 2). At 140 °C and 2 h of reaction time, TG conversion was close to 100% with a FAME yield of ~93% for initial FFA contents of 10 and 22 wt.%. Regarding esterification, OA conversion at final time was of 75.9% and 82.6% for Oil-10FFA and Oil-22FFA, respectively.
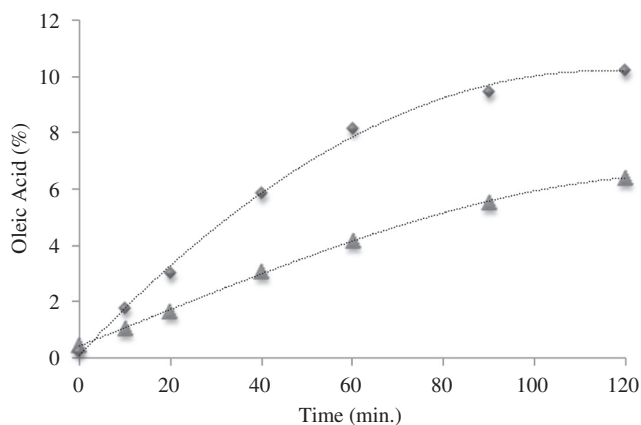

Fig. 7. Hydrolysis of triglycerides ◆ and FAME ▲ catalyzed by ZnOl at 140 °C and 3 wt.% catalyst (with respect to feedstock).

The final concentration of the intermediates MG and DG was lower for Oil-10FFA and Oil-22FFA than for the refined oil (MG was 3.4, 3.5 and 6.9 wt.%, respectively). This occurs with a higher FAME yield for the acid raw materials than for the refined soybean oil (~93% vs. 84%). These results indicate that Zn oleate is an active material able to catalyze simultaneously the transesterification of triglycerides and the esterification of fatty acids achieving good results, operating in a single stage, under moderate reaction conditions and with mild hydrolysis.

The reaction system under study is very complex because four different reactions take place simultaneously in the same reaction medium: transesterification, esterification, hydrolysis, and the "transformation of the catalyst" into Zn glycerolate. Nevertheless, this complex system applied to acid raw materials is very efficient, giving high FAME yields under moderate reaction conditions.

A decrease in the transesterification activity of the acid raw materials compared with the refined soybean oil can be observed in Figs. 1, 2, and 3. And in the case of esterification (Fig. 4), there is a notable increase in activity for the Oil-10FFA and Oil-22FFA samples compared with the pure oleic acid.

Table 3 shows how triglyceride conversion decreases as the initial concentration of FFA in the raw material increases at 1 h of reaction time. TG conversion was of ~100%, 99%, and 94% for the refined oil and the Oil-10FFA and Oil-22FFA samples, respectively. On the other hand, OA conversion (60 min) increases for the acid raw materials (~62% and 69% for Oil-10FFA and Oil-22FFA) compared with that for pure OA (29%).

In order to understand the phenomenon taking place, the initial reaction rates (when the catalyst has not yet transformed into ZnGly) were analyzed. The initial reaction rates for OA and TG in the esterification and transesterification reactions for the four catalytic tests (pure OA, Oil-10FFA, Oil-22FFA, and refined soybean oil) are presented in Table 4. The reaction rate is expressed as RATE [$mmol_{reactant}/s$].

A similar behavior of the RATE in Table 4 can be observed for the conversions at 60 min of reaction time. In the case of TG, the reaction rates are higher for the reaction of the refined oil than for the acid mixtures (0.1 vs. 0.05 and 0.04 $mmol_{TG}/s$). For OA, the rate is lower for the esterification of the pure fatty acid (1.2×10^{-4} vs. 2.5×10^{-4} and 2.7×10^{-4} mmolAO/s).

In a previous work [20], it was reported that a ligand exchange occurs during the esterification reaction catalyzed with Zn carboxylate. The carboxylate anion of the catalyst salt is exchanged for the fatty acid anion to be esterified. In addition, the mechanisms for the transesterification of triglycerides catalyzed by Zn carboxylates were analyzed [29]. It was found that the preferred mechanism included

Table 2
Transesterification of acid oil (10–22 wt.% OA) with methanol using ZnOl as catalyst at 140 °C and 2 h: triglyceride and oleic acid conversion, and FAME yield.

Composition of the non-polar phase (% p/p)	Free fatty acid content	
	10 wt.%	22 wt.%
TG conversion (%)	100	100
FAME yield (%)	93.9	92.9
AO conversion (%)	75.9	82.6

Table 3
Transesterification of refined and acid oil (10–22 wt.% OA) with methanol using ZnOl as catalyst at 140°C and 1 h: product distribution, triglyceride and oleic acid conversion, and FAME yield.

Composition of the non-polar phase (% p/p)	Free fatty acid content		
	0 wt.%	10 wt.%	22 wt.%
Monoglycerides	7.3	9.9	11.0
Diglycerides	2.6	7.1	13.6
Triglycerides	0.0	0.9	5.2
FAME	90.1	79.8	64.8
Oleic acid	–	2.3	5.4
TG conversion (%)	100	98.9	93.4
FAME yield (%)	82.9	79.3	64.3
OA conversion (%)	–	61.7	69.6

the initial coordination of methanol, carboxylate shift and the co-coordination of the triglyceride with an alkoxide-like moiety.

Taking into account that Zn^{+2} presents a flexible coordination geometry that allows for an easy ligand exchange [30], it could be considered that the decrease in the transesterification rate in the presence of FFA is a result of the interaction of the oleic acid with Zn^{+2}, which would compete with the larger TG molecule and the rest of the glycerides.

Regarding the increase in the esterification rate for the Oil-10FFA and Oil-22FFA samples compared with the pure OA, two factors associated with the increase in the methanol:oleic acid (a) and catalyst:oleic acid (b) molar ratios were considered.

In order to evaluate the influence of the larger amount of methanol with respect to OA, an esterification test with the same initial reactant concentrations as those present in the transesterification of Oil-10FFA (methanol:oil molar ratio of 90:1) was carried out. The OA conversion observed was similar to that of the esterification performed with a methanol:oil molar ratio of 30:1, indicating that the larger amount of methanol was not the cause of the difference observed.

The effect of the catalyst loading was studied by comparing the results with those obtained for the esterification test performed with 6% catalyst [22], where an OA conversion of 62.5% was reached for a reaction time of 120 min. Based on these results, the increase in the esterification activity observed for the Oil-10FFA and Oil-22FFA samples (compared with pure OA) can be associated with the increase in the catalyst:oleic acid molar ratio.

4. Conclusion

Zinc oleate was able to catalyze simultaneously the triglyceride transesterification and fatty acid esterification reactions with high activity and selectivity under moderate operations conditions. At 140°C and 2 h of reaction time, triglyceride conversion was 100%, FAME yield was close to 93% and fatty acid conversion was 75.9% and 82.6% for an initial 10% and 22% FFA concentration in the feedstock, respectively. The Zn carboxylic salt exhibited low activity in the hydrolysis reaction. At 140 °C, Zn oleate can be easily transformed into Zn glycerolate, which can be easily separated from the reaction medium.

References

[1] E. Lotero, Y. Liu, D. Lopez, K. Suwannakarn, D. Bruce, J. Goodwin Jr., Synthesis of biodiesel via acid catalysis, Ind. Eng. Chem. Res. 44 (2005) 5353–5363.
[2] M. Gui, K. Lee, S. Bhatia, Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock, Energy 33 (2006) 1646–1653.
[3] J. Kansedo, K. Teong, S. Bhatia, Cerbera odollam (sea mango) oil as a promising non-edible feedstock for biodiesel production, Fuel 88 (2009) 1148–1150.
[4] H. Farag, A. El-Maghraby, N. Taha, Optimization of factors affecting esterification of mixed oil with high percentage of free fatty acid, Fuel Process. Technol. 92 (2011) 507–510.
[5] Y. Zhang, M. Dube, D. McLean, M. Kates, Biodiesel production from waste cooking oil: 1. Process design and technological assessment, Bioresour. Technol. 89 (2003) 1–16.
[6] J. Marchetti, V. Miguel, A. Errazu, Techno-economic study of different alternatives for biodiesel production, Fuel Process. Technol. 89 (2007) 740–748.
[7] P. Felizardo, J. Machado, D. Vergueiro, M. Joana, N. Correia, J. Pereira Gomes, J. Moura Bordado, Study on the glycerolysis reaction of high free fatty acid oils for use as biodiesel feedstock, Fuel Process. Technol. 92 (2011) 1225–1229.
[8] J. Van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe, PBD: related information: work performed by Iowa State University, Renewable Products Development Laboratory, and USDA/NCAUR2004.
[9] C. Baroi, A. Dalai, Simultaneous esterification, transesterification and chlorophyll removal from green seed canola oil using solid acid catalysts, Catal. Today 207 (2013) 74–85.
[10] F. Dawodu, O. Ayodele, J. Xin, S. Zhang, D. Yan, Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst, Appl. Energy 114 (2014) 819–826.
[11] B. Peng, Q. Shu, J. Wang, G. Wang, D. Wang, M. Han, Biodiesel production from waste oil feedstocks by solid acid catalysis, Process Saf. Environ. Prot. 86 (2008) 441–447.
[12] Y. Zhang, W. Wonga, K. Yung, One-step production of biodiesel from rice bran oil catalyzed by chlorosulfonic acid modified zirconia via simultaneous esterification and transesterification, Bioresour. Technol. 147 (2013) 59–64.
[13] W. Omar, N. Amin, Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst, Fuel Process. Technol. 92 (2011) 2397–2405.
[14] H. Lee, Y. Taufiq-Yap, M. Hussein, R. Yunus, Transesterification of jatropha oil with methanol over Mg-Zn mixed metal oxide catalysts, Energy 49 (2013) 12–18.
[15] N. Soriano, R. Venditti, D. Argyropoulos, Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification, Fuel 88 (2009) 560–565.
[16] L. Bournay, G. Hillion, P. Boucot, A. Chodorge, C. Bronner, A. Forestiere, Eur. Pat. Appl. EP 1352893A1 (2003).
[17] P. Sreeprasanth, R. Srivastava, D. Srinivas, P. Ratnasamy, Hydrophobic, solid acid catalysts for production of biofuels and lubricants, Appl. Catal. A Gen. 314 (2006) 148–159.
[18] S. Yan, S. Salley, K. Simon Ng, Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La₂O₃ catalysts, Appl. Catal. A Gen. 353 (2009) 203–212.
[19] X. Hou, Y. Qi, X. Qiao, G. Wang, Z. Qin, J. Wang, Lewis acid-catalyzed transesterification and esterification of high free fatty acid oil in subcritical methanol, Korean J. Chem. Eng. 24 (2007) 311–313.
[20] M. Di Serio, R. Tesser, M. Dimiccoli, F. Cammarota, M. Nastasi, E. Santacesaria, Synthesis of biodiesel via homogeneous Lewis acid catalyst, J. Mol. Catal. A Chem. 239 (2005) 111–115.
[21] K. Jacobson, R. Gopinath, L. Meher, A. Dalai, Solid acid catalyzed biodiesel production from waste cooking oil, Appl. Catal. B Environ. 85 (2008) 86–91.
[22] D. Reinoso, D. Damiani, G. Tonetto, Zinc carboxylic salts used as catalyst in the biodiesel synthesis by esterification and transesterificaction: study of the stability in the reaction medium, Appl. Catal. A Gen. 449 (2012) 88–95.
[23] S. Barman, S. Vasudevan, Melting of saturated fatty acid zinc soaps, J. Phys. Chem. B 110 (2006) 22407–22414.
[24] M. Dasari, M. Goff, G. Suppes, Noncatalytic alcoholysis kinetics of soybean oil, J. Am. Oil Chem. Soc. 80 (2003) 189–192.
[25] D. Reinoso, D. Damiani, G. Tonetto, Zinc glycerolate as a novel heterogeneous catalyst for the synthesis of fatty acid methyl esters, Appl. Catal. B Environ. 144 (2014) 308–316.
[26] J. Das, I. Evans, D. Khushalani, Zinc glycolate: a precursor to ZnO, Inorg. Chem. 48 (2009) 3508–3510.
[27] J. Das, D. Khushalani, Nonhydrolytic route for synthesis of ZnO and its use as a recyclable photocatalyst, J. Phys. Chem. C 114 (2010) 2544–2550.
[28] D. Atek, N. Belhaneche-Bensemra, Eur. Polym. J. 41 (2005) 707–714.
[29] D. Reinoso, M. Ferreira, G. Tonetto, Study of the reaction mechanism of the transesterification of triglycerides catalyzed by zinc carboxylates, J. Mol. Catal. A Chem. 377 (2013) 29–41.
[30] S. Sousa, P. Fernandes, M. Ramos, The carboxylate shift in zinc enzymes: a computational study, J. Am. Chem. Soc. 129 (2007) 1378–1385.

Table 4
Reaction rate for the transesterification of soybean oil and acid oil (10 and 22 wt.% OA) and the esterification of FFA and OA with methanol using ZnOl as catalyst at 140 °C.

Reaction rate	SB oil	Oil-10FFA	Oil-22FFA	OA
OA rate [mmol$_{AO}$/s]	–	2.5×10^{-4}	2.7×10^{-4}	1.2×10^{-4}
TG rate [mmol$_{TG}$/s]	0.107	0.051	0.038	–