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

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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.

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

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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.

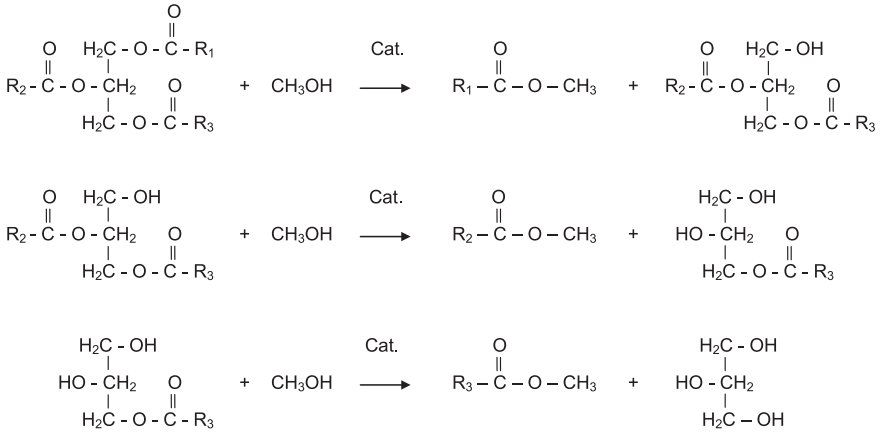
The transesterification of the acid oils was carried out using methanol (Aberkon, chromatographic quality) and models of economical feedstocks with 10 and 22 wt.% FFA, named Oil-10FFA and Oil-22FFA, respectively. The raw materials consisted of refined soybean oil (commercial brand) and oleic acid (OA, 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:

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

$$Y_{FAME} = \frac{\text{mol FAME}/3}{\text{mol TGE}_{it}} 100 \quad (2)$$



Scheme 1. Transesterification of triglycerides with methanol.