

Synthesis of biodiesel via homogeneous Lewis acid catalyst

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Abstract

Nowadays, most biodiesel (fatty acids methyl esters, FAME) is produced by the transesterification of triglycerides (TG) of refined/edible type oils using methanol and an homogeneous alkaline catalyst. However, production costs are still rather high compared with the ones of petroleum-based diesel fuel. To lower costs and make biodiesel competitive less-expensive feedstocks such as waste fats or non-edible type oils could be used. The use of homogeneous alkaline catalysts in the transesterification of such types of fats and oils poses great difficulties due to the presence of large amounts of free fatty acids (FFA). This paper studies the use of carboxylic salts as a possible alternative, because these catalysts are active also in the presence of high FFA concentrations.

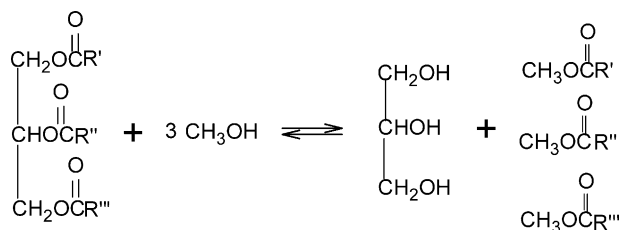
The most active catalyst (Cd, Mn, Pb, Zn carboxylic salts) have been individuated and a correlation of the activities with the cation acidity has been found.

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1. Introduction

Biodiesel (fatty acids methyl esters, FAME) has recently become very attractive, because of its environmental benefits and the fact that it is produced from renewable sources [1]. Nowadays, most biodiesel is produced by the transesterification of triglycerides of refined/edible type oils using methanol and an alkaline catalyst (NaOH, NaOMe) [1–3]:



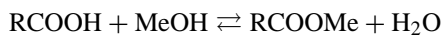
However, production costs are still rather high, compared to petroleum-based diesel fuel production costs [1,2]. To lower costs and make biodiesel competitive with petroleum-based diesel, less-expensive feedstocks such as waste fats or non-edible type oils, could be used [1–3]. Homogeneous alkaline catalysts in the transesterification of such types of fats and oils cannot directly be used due to the presence of large amounts of free fatty acids (FFA) [1–3]; in fact, for the use of these catalyst the FFA concentration should be less than 0.5% (w/w) [4].

Several methods have been proposed to solve these problems:

- alkali refining method [5]: an alkali such as caustic soda is added to transform free fatty acids into fatty acid soaps and these are then removed by washing with water;
- excess addition of catalyst method [5]: in addition to the amount of catalyst sufficient for transesterification, an excess of alkali is added in relation to the FFA amount;
- solvent extraction method [5]: free fatty acids are removed by extraction with a selective solvent;

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- (d) distillation refining method [5]: free fatty acids are distilled away from the oil;
- (e) pre-esterification method [2,5]: FFA are firstly esterified to FAME by using an acid catalyst:



and then the transesterification is performed, as usual, by using an alkaline catalyst;

- (f) use of Bronsted acid catalysts [3,6]: an esterification and transesterification step are both promoted by a Bronsted acid catalyst at high temperature.

All the first four methods (a–d) result in a loss of product (biodiesel). Moreover, methods (a) and (b) give place to problems during phase separation, method (a) before the transesterification, method (b) after it because of the formation of emulsion due to the presence of soaps. Method (c) requires a high solvent/oil weight ratio while methods (d) and (e) require high energy use.

Methods (e) and (f) seems to be more attractive. The acid-catalyzed pre-esterification of FFA – method (e) – is a common practice in decreasing FFA levels in high FFA feedstocks, before performing the base-catalyzed transesterification [3]. Zhang et al. [6] recently showed, by a technological assessment of different continuous processes, that the acid-catalyzed process using waste oil is technically feasible and less complex than two a step process (pre-esterification with homogeneous acid catalyst and alkali catalyzed stages), although no commercial biodiesel plants since the time of their work have been reported to use the acid-catalyzed process.

The main drawback of the pre-esterification method (e) consists in the necessity to remove the homogeneous acid catalyst from the oil after pre-esterification. This problem can be solved with the use of an heterogeneous acid catalyst [3,4]. However, the necessity to eliminate the water formed in FFA esterification still remains because the presence of water may favour ester saponification under alkaline conditions [7].

The disadvantage of the acid-catalyzed process – method (f) – is that the reaction, normally, requires a high methanol to oil molar ratio and high acid catalyst concentration. Zang et al. [6] obtained a 97% oil conversion to FAME within 240 min, using a 50:1 molar ratio of methanol to oil and a 0.14:1 weight ratio of sulphuric acid to oil at 80 °C. However, this process gives rise to problems linked with the corrosive action of the liquid acid catalyst and to the high quantity of obtained by-products [2]. Actually, a plant of 10,000 t/y of biodiesel co-produces 2000 t/y of CaSO₄ [5] with the sulphuric acid being neutralized with CaO. A solid acid catalyst could to eliminate these problems but nowadays the proposed catalysts have not yielded satisfactory results, and much greater research efforts are necessary [2].

Basu and Norris proposed, as a possible solution to the production of biodiesel from oil with a high FFA concentration, the use of a mixture of calcium acetate and barium

acetate as catalyst [7]. They showed that this catalyst, operating in a temperature range 200–250 °C and with 5 × 10⁻³:1 weight ratio of catalyst to oil, can be used in the presence of a high FFA concentration, obtaining after purification, a crude ester phase a with very low FFA concentration and high conversion of triglycerides. However, in other transesterification reactions several acetates of bivalent metals have been used as catalysts [8]. Since the activity of the catalysts is a function of both metal acidity and ester and alcohol molecular structures, every ester–alcohol couple will have a specific metal that will give a maximum of activity [9]. Starting from these considerations, this paper reports the results of a catalytic screening of acetates of the following metals: Ca, Ba, Mg, Cd, Mn, Pb, Zn, Co, Ni in the transesterification of the TG with methanol. Moreover, the stearates of all the above metals were synthesized and the influence of the molecular weight of catalyst anion on the reaction have also been investigated. Furthermore, the influence of the presence of water and of FFA respectively on the activity has been studied. Finally, we will show the possibility to perform TG transesterification and FFA esterification in a single step, using a low catalyst concentration. A method for removing the metal catalyst has been suggested.

2. Experimental

2.1. Methods, techniques and reagents

The catalytic screening was performed in small stainless steel vial reactors. The reaction was made by introducing reagents (methanol and soybean oil with an acidity of 0.2%, w/w) and a catalyst in each reactor. All reactor sets (6) were then heated in a ventilated oven. The temperature of the oven was increased from room temperature at a fixed rate (20 °C/min) until reaching the reaction temperature of the runs (150–200 °C). Then, after 55 min the temperature was quickly diminished by putting the vials in a cold bath. Experimental runs were also made with the addition of water and FFA to the reactants.

Acetates and the synthesized stearate of the following metals: Ca, Ba, Mg, Cd, Mn, Pb, Zn, Co, Ni were tested as catalysts.

The syntheses of metal stearates were performed in a magnetically stirred glass reactor. The jacketed reactor was kept isothermal by recirculating a thermostated oil at 180 °C. The reactions were made by introducing a metal acetate and stearic acid in stoichiometric amounts. The acetic acid formed during the reaction (3 h) was stripped by a nitrogen stream with flow rate 2 l/h and collected in a condenser. The conversion obtained in the performed syntheses, reported in Table 1, were calculated by measuring the amount of acetic acid recovered.

The FAME yields, in the catalytic tests, were determined using the H-NMR technique (Bruker 200 MHz) [10], i.e., measuring the area of H-NMR signal related to methoxylic

Table 1
Conversion obtained in the synthesis of stearates

Run	Stearates	Conversion (%)
1.1	Ba(OOC(CH ₂) ₁₆ CH ₃) ₂	73
2.1	Ca(OOC(CH ₂) ₁₆ CH ₃) ₂	73
3.1	Mg(OOC(CH ₂) ₁₆ CH ₃) ₂	72
4.1	Cd(OOC(CH ₂) ₁₆ CH ₃) ₂	89
5.1	Mn(OOC(CH ₂) ₁₆ CH ₃) ₂	62
6.1	Pb(OOC(CH ₂) ₁₆ CH ₃) ₂	58
7.1	Zn(OOC(CH ₂) ₁₆ CH ₃) ₂	64
8.1	Co(OOC(CH ₂) ₁₆ CH ₃) ₂	81
9.1	Ni(OOC(CH ₂) ₁₆ CH ₃) ₂	66

(A₁) and methylenic groups (A₂), respectively:

$$Y_{\text{FAME}} = \frac{A_1/3}{A_2/2}$$

In the case of non-acid oil, the FAME yield corresponds also to the conversion of glyceride groups (λ_{Gly}):

$$\lambda_{\text{Gly}} = Y_{\text{FAME}}$$

To have the conversion of glyceride groups, when the reaction is performed on acid oil, the initial FFA weight fraction (w_{FAME}) and FFA conversion (λ_{FAME}) must be considered, because FAME are also produced in the FFA esterification. In this case, we have:

$$\lambda_{\text{Gly}} = Y_{\text{FAME}} \left(1 + \frac{\text{PM}_{\text{oil}}}{3\text{PM}_{\text{OA}}} \frac{w_{\text{FAME}}}{1 - w_{\text{FAME}}} \right) - \lambda_{\text{FAME}} \frac{\text{PM}_{\text{oil}}}{3\text{PM}_{\text{OA}}} \frac{w_{\text{FAME}}}{1 - w_{\text{FAME}}}$$

FFA conversion is determined by measuring the residual FFA concentration by titration [11].

In order to confirm the results obtained in the vials, different runs were performed in a 1 dm³ autoclave reactor at 210–220 °C. These runs were performed by introducing reactants and catalyst into the autoclave and heating until the fixed reaction temperature was achieved. The temperature profiles of heating were roughly linear: the reaction temperature was achieved in about 80 min. Samples of the reaction mixture were withdrawn at different times and analyzed by both H-NMR spectroscopy and titration.

3. Results and discussion

First of all, a catalytic screening of different metal acetates in the transesterification of a “neutral” soybean oil (FFA concentration = 0.2%, w/w) in the temperature range adopted by Basu and Norris [7] (200 °C) was performed. Table 2 reports both the other related operative conditions and the results.

Since at high temperatures the stainless steel internal surface of the vials can catalyze the transesterification reaction [12], also a run without catalyst was performed. The obtained value for the conversion of glyceride groups at 200 °C in the absence of catalyst was about 8%.

Table 2
List of runs performed with acetates as catalyst at 200 °C

Run	Catalyst	M ²⁺ (mmol)	λ_{Gly}
1.2	Ba(OOCCH ₃) ₂	0.0571	0.11
2.2	Ca(OOCCH ₃) ₂	0.0577	0.31
3.2	Mg(OOCCH ₃) ₂ ·4H ₂ O	0.0573	0.39
4.2	Cd(OOCCH ₃) ₂	0.0578	0.85
5.2	Mn(OOCCH ₃) ₂	0.0575	0.67
6.2	Pb(OOCCH ₃) ₂	0.0580	0.81
7.2	Zn(OOCCH ₃) ₂ ·2H ₂ O	0.0583	0.67
8.2	Co(OOCCH ₃) ₂ ·4H ₂ O	0.0577	0.20
9.2	Ni(OOCCH ₃) ₂ ·4H ₂ O	0.0574	0.07
10.2	Ca(OOCCH ₃) ₂ , Ba(OOCCH ₃) ₂ (Ca/Ba = 3/1, w/w)	0.0587	0.38

Soybean oil 2.0 g (FFA 0.2% w/w), methanol 0.88 g.

As can be seen, all the considered acetates except nickel acetate have shown catalytic activity. In particular, the activity of barium acetate is lower than the activity of all the other considered metal acetates, while calcium acetate is higher only than barium and cobalt acetate. The catalyst mixture (Ca(OOCH₃)₂/Ba(OOCH₃)₂ = 3/1, w/w) proposed by Basu and Norris [7] shows a little cooperative effect giving place to a slight increase in the obtained conversions, compared to the performance of the single acetates.

The activity of the tested metal acetates in the transesterification reaction is probably related to the Lewis acidity of the metal [8], and there is, in general, an optimal value of this acidity for every ester–alcohol couple employed in the reaction [9]. In Fig. 1, the conversion of the glyceride groups obtained with the different metal acetates is reported as a function of the logarithm of their stability constants in the formation of the corresponding complex with dibenzoilmethane ($\log \beta_{\text{DBM}}$) [9,13]. The values of these constants can be considered as a relative measure of metal acidity [9,13–15]. As can be seen, in the oil transesterification with methanol as for other transesterification reactions [9,13], the activity rises to

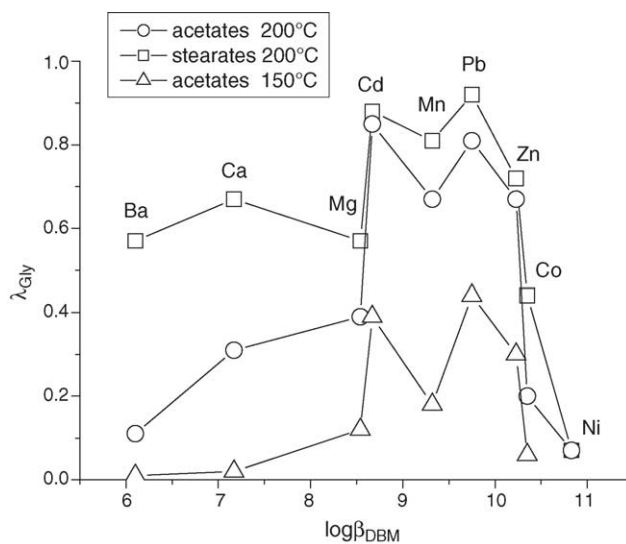
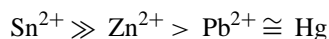


Fig. 1. Conversion of glyceride groups vs. $\log \beta_{\text{DBM}}$. Oil (FFA 0.2%, w/w) = 2.0 g, methanol = 0.88 g, $M^{2+} = 0.057 \pm 0.002$ mmol.

reach a maximum range with the increase in metal acidity and then falls. In our case, the maximum is in the range of the $\log \beta_{\text{DBM}}$ between 8.60 (corresponding to cadmium) and 10.23 (corresponding to zinc).

However, in the transesterification reactions of TG with methanol other factors must also be considered. For example, the reaction mixture giving rise to a multiphase reaction system leads to the partition of the catalytic species between the two phases. In order to investigate the influence of this aspect, as the catalyst phase partition can be related to the molecular weight of the catalyst anion, runs were also performed by using metal stearates instead of acetates in the same condition. In Fig. 1, the obtained conversions of glyceride groups are reported. The results of Fig. 1 clearly show the influence of the used anion. In all cases we observed an increase in the catalytic activity for stearate metals with respect to acetates, with the exclusion of Ni that remained inactive in both cases. In particular, barium increases the conversion of glyceride groups by nearly four times, while calcium and cobalt by nearly two times.

The nature of the anion, when it gives place to a strong interaction with the cation, as in the case of the catalysts reported by Abreu et al. [16], can also change the order of metal activity. In fact, by using metal complexes of 3-hydroxy-2-methyl-4-pyrone, Abreu et al. found the following activity order:



i.e., in this case the catalyst activities followed their metal acid strength monotonically.

Runs where then performed at a lower temperature (150 °C) using acetates, to study the influence of this parameter. As can be seen in Fig. 1, temperature has a strong influence on catalytic activity. As a matter of fact, at 150 °C barium and calcium acetates show no activity while the yields obtained with the metal having $\log \beta_{\text{DBM}}$ in the range 8.60–10.23 are in the range 18–44%. It is important to point out that the influence of temperature is linked not only to the values of the activation energy of the reaction in the presence of the different metals, but also with the influence of temperature on catalyst phase distribution.

To investigate the effect of water on catalytic activity, three runs were carried out with the presence of an excess of water (water/methanol = 0.07, w/w) under the same conditions of the runs performed at 200 °C ($T=200$ °C, $M^{2+} = 0.057 \pm 0.002$ mmol, oil (FFA = 0.2%, w/w) = 2.0 g, methanol = 0.88 g) using calcium acetate and lead acetate as the catalyst, respectively. Water has a strong depressive effect on the activity of all the investigated metals, as can be seen in Fig. 2, where the obtained conversions of glyceride groups are reported. This effect can be attributed to the interaction of water with the cation of the catalysts which decreases their acid strength.

The activities of these catalysts in the presence of water were tested also in the presence of high FFA concentrations. The runs were performed under the same conditions changing

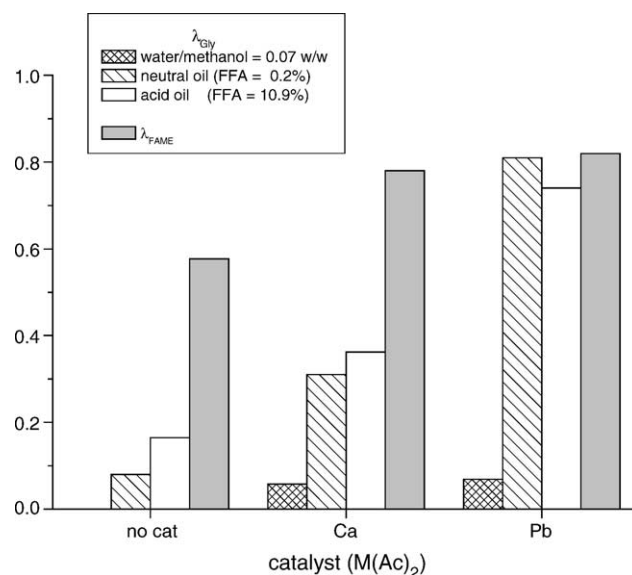


Fig. 2. Influence of water and FFA on glyceride groups and FFA conversions for different acetates used ($T=200$ °C, oil = 2.0 g, methanol = 0.88 g, $M^{2+} = 0.057 \pm 0.002$ mmol).

only the oil acidity ($T=200$ °C, $M^{2+} = 0.057 \pm 0.002$ mmol, oil (FFA = 10.88%, w/w) = 2.0 g, methanol = 0.88 g). The acid oil was prepared by adding oleic acid to the soybean oil. A run without catalyst in the presence of high FFA concentration was done, to measure the conversion of glyceride groups and FFA under these reaction conditions (see Fig. 2).

It must be pointed out that the conversion of glyceride groups in the run without catalyst increases a little in the case of transesterification of acid oil with respect to the transesterification of neutral oil. This increase is probably due to the catalytic effect exerted by the presence of FFA in the reaction medium (see Fig. 2). Together with transesterification, also a non-catalytic esterification reaction occurs. In fact, at the end of the reaction an FFA conversion of nearly 0.6 is reached (see Fig. 2).

The effect of water on the catalytic activity of tested metals is related to its concentration. As matter of fact, the conversion of glyceride groups is poorly affected by FFA presence, notwithstanding the presence of water formed by the esterification reaction at the same time (see Fig. 2).

The above-mentioned catalysts also showed a catalytic activity in the esterification reaction. In fact, the FFA conversion is higher than that obtained without catalyst (see Fig. 2).

The results described were confirmed with runs performed in a 1 dm³ autoclave reactor. The runs were performed at a temperature of 210–220 °C with acid oil – oil (FFA = 7.5%, w/w) = 250 g, methanol = 114 g – in the absence of catalyst, in the presence of 1 g of lead acetate and of the Basu and Norris catalytic mixture (Ca/Ba acetate) [7], respectively. The obtained results are reported in Fig. 3. As can be seen, the activity of lead acetate is higher than that of the Basu and Norris catalytic mixture, in the transesterification reaction.

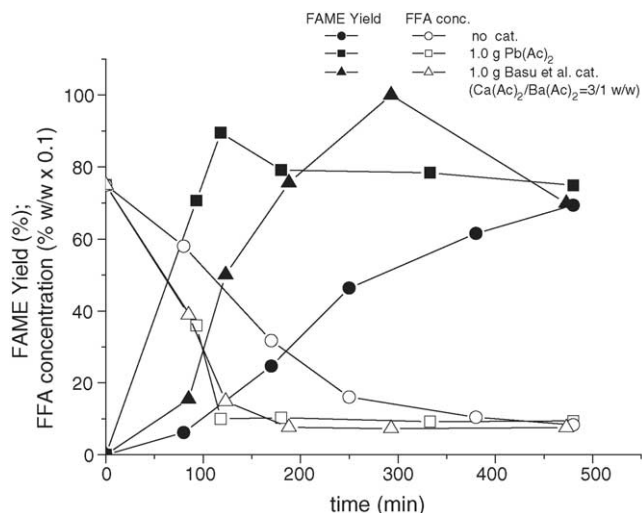


Fig. 3. Yields of FAME (%) and FFA concentration over the time ($T=210\text{--}220\text{ }^{\circ}\text{C}$, oil = 250.0 g, methanol = 114 g).

Over time the glycerides conversion reaches a maximum value then decreases, in the case of catalyzed runs. This behaviour was also observed by Abreu et al. [16] who explained the observed decrease over time as the intervention of a reverse reaction favoured by the formation of a two-phase system, with its consequent different catalyst partition. However, much greater research efforts will be done to explain this behaviour, in the future.

An other run was conducted in autoclave to verify the performance of the best catalyst (Pb stearate) founded in the screening. The runs was performed at a temperature of $210\text{--}220\text{ }^{\circ}\text{C}$ with acid oil – oil (FFA = 7.4%, w/w) = 250 g, methanol = 114 g – in the presence of only 0.1 g of lead stearate. The autoclave was kept at $210\text{--}220\text{ }^{\circ}\text{C}$ for 200 min and then cooled at room temperature. The FAME phase was separated by glycerine phase by means of a separator funnel. After methanol distillation, we obtained 0.96 glyceride conversion and 0.74% FFA final concentration. The comparison of these results with those reported in Fig. 3, taking also into account that lead stearate concentration is 10 times less than lead acetate, confirms that Pb stearate is the best catalyst in the transesterification of acid oils.

4. Conclusions

As has been seen, bivalent cations are catalysts for both transesterification and esterification reactions. Catalytic activities are related to the Lewis acid strength of the metals (which must have an optimal intermediate value) and to the molecular structure of the anion. The best catalytic performances were obtained with cation metals having a complex stability constant with dibenzolmetane ($\log \beta_{\text{DBM}}$) [9,13] in the range between 8.60 (corresponding to cadmium) and 10.23 (corresponding to zinc). Then the stearates have better performances than acetates because their higher solubility in the oil phase where the reaction occurs.

Notwithstanding the fact that the activity of the best catalyst $\text{Pb}(\text{Ac})_2$ is lowered by the water formed during esterification of FFA, by using a low catalyst concentration (4×10^{-4} :1 weight ratio of catalyst to oil) it is possible to obtain high FAME yields (96%) and a low final FFA concentration (<1%), in a relatively short reaction time (200 min). We can conclude, therefore, that this class of catalyst could be used for a single stage process [17], in which the final ester phase could be purified by FAME distillation, as suggested by Basu and Norris [7] and by Zhang et al. [6]. The residual (triglycerides, diglycerides, monoglycerides, catalyst) can be re-circulated to the esterification–transesterification reactor, while the glycerol is obtained, after treatment with exchanges resin to eliminate metal traces. Glycerol obtained is clearer than the one obtained with the classical technology based on the use of alkaline catalysts giving place to soaps forming emulsion difficult to remove. The proposed catalyst have greater activity than that proposed by Basu and Norris [7]. Moreover, with respect to the process suggested by Zhang et al. [6] using sulphuric acid for promoting both esterification and transesterification this process has the advantages of using a lower molar methanol/oil ratio (12/1 instead 50/1) and not necessitate an heavy neutralization process of the acid catalyst.

Acknowledgement

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