



# Calcium diglyceroxide synthesized by mechanochemical treatment, its characterization and application as catalyst for fatty acid methyl esters production



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## HIGHLIGHTS

- Ca-diglyceroxide (CaDG) synthesis by mechanochemical treatment of CaO and glycerol.
- Methanolysis of sunflower oil catalyzed by CaDG.
- Physical interpretation of the role of the CaDG.
- Analysis of different working conditions of methanolysis using kinetic model.

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## ABSTRACT

In the present work, calcium diglyceroxide (CaDG) was synthesized by mechanochemical treatment of CaO dispersed in glycerol, and characterized by X-ray diffraction (XRD), thermal analysis (TGA/DTA), infrared spectroscopy (FTIR), and Hammett indicator method for base strength determination. The obtained CaDG was tested as a catalyst in the methanolysis of sunflower oil under different working conditions: catalyst amount, agitation speed, temperature and methanol to oil molar ratio. The main advantage of CaDG used as a catalyst in methanolysis is related to the initial rate of methanolysis. According to many previously reported data in literature the mass transfer resistance controls the overall rate of methanolysis, but it is not observed with CaDG used as catalyst. Recently developed kinetic model that describes the complex methanolysis process was successfully applied for this system and model parameters were determined, supporting the explanation of the physical effect of the CaDG catalyst on the reduction of mass transfer resistance and increasing the rate of methanolysis. The absence of mass transfer rate at the beginning of process is a consequence of the nature of the CaDG, which is adsorbed at the droplet interfaces between methanol and oil leading to the formation of fine dispersion of these two immiscible liquids.

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## 1. Introduction

Biodiesel, a mixture of fatty acid methyl esters (FAME) is a promising substitute to diesel fuels due to its environmental benefits and the fact that it might be synthesized from renewable resources. It is usually produced by methanolysis of triglycerides in the presence of a catalyst. Although homogeneous base catalyst is most commonly used in biodiesel synthesis, solid catalyst could be a better choice since no neutralization and washing steps are required, it is easily separated from the reaction mixture by

filtration and can be reutilized in the case of slurry system or it can be used as packed-bed in continuous process of methanolysis.

CaO is one of the most thoroughly studied catalysts for heterogeneously catalyzed biodiesel production [1,2]. Nevertheless, Kouzu et al. [3,4] revealed that CaO was the active phase only at the beginning of the methanolysis, but when glycerol is produced as a by-product of the reaction, it reacts with CaO producing calcium diglyceroxide,  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$ . Catalysts obtained from CaO and glycerol, according to some authors named diglyceroxide or glyceroxide and to others glycerolate, have been also studied and reported as very active catalysts in the transesterification of triglycerides as shown in Table 1 [3–14]. León-Reina et al. [5] have given more information about the structure of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  and

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**Table 1**  
Literature review of catalyst obtained from CaO and glycerol for biodiesel production.

| Catalyst and oil  | Catalyst preparation  | Reaction conditions    |             |             |                          |                              | Yield, %             | Refs. |
|---|---|------------------------|-------------|-------------|--------------------------|------------------------------|----------------------|-------|
|   |   | T, °C                  | Molar ratio | wt% of cat. | Time, h                  | Agitation, min <sup>-1</sup> |                      |       |
| Ca diglyceroxide<br>Soybean oil   | 500 mg of CaO, 100 mL of MeOH and 35 mL of glycerol, heated at 50 °C (N <sub>2</sub> atmosphere), under agitation overnight, filtrated and washed twice with MeOH   | 60                     | 14:1        | 0.7         | 2                        | 1000                         | >90                  | [5]   |
| Ca diglyceroxide<br>Castor oil  | Hydrated lime and glycerol (molar ratio 0.21), under mechanical stirring, in the 5–180 min range and at 30, 60 and 70 °C (N <sub>2</sub> atmosphere), centrifuged at 5000 rpm for 15 min  | 55                     | 12:1        | 1.6         | 2                        | 1000                         | 100                  | [6]   |
| Ca diglyceroxide<br>Soybean oil   | CaO immersed in glycerol  | 65                     | 12:1        | 1           | 1                        | 500                          | ~65                  | [7]   |
| Ca diglyceroxide<br>Soybean oil   | CaO immersed in glycerol, at 60 °C (N <sub>2</sub> atmosphere)  | 65                     | 12:1        | 1           | 1–2                      | 500                          | 1 h ~65<br>2 h >90   | [3]   |
| Ca diglyceroxide<br>Soybean oil   | CaO immersed in glycerol blending into methanol at the equivalent volumetric ratio, at 60 °C, 2 h. Filtrated, washed with MeOH and dried at 80 °C   | (a)<br>25<br>(b)<br>65 | 12:1        | 0.45<br>0.1 | (a)<br>6 h<br>(b)<br>2 h | 500                          | (a) 24<br>(b) 89     | [8]   |
| Ca diglyceroxide<br>Sunflower oil   | 3 g of CaO mixed with 10 g of glycerol and 44 g of MeOH, heated at 60 °C, and left under mechanical agitation for 3 h. Filtrated, washed twice with THF and dried overnight at 60 °C under vacuum   | 60                     | 12:1        | 2           | 4                        | –                            | >95                  | [9]   |
| Ca diglyceroxide<br>Soybean oil   | 90 mL of MeOH, 30 mL of glycerol and 2 g CaO calcined at 600 °C, vigorously stirred at 60 °C for 8 h. Centrifuged, washed with MeOH and dried at 100 °C for 2 h   | 60                     | 9:1         | 1.3         | 2                        | 850                          | 82.6                 | [10]  |
| Ca diglyceroxide<br>Sunflower oil   | CaO immersed in MeOH in the presence of glycerol (50 vol%) at 65 °C for 2 h   | 65                     | 14:1        | 1           | 2                        | 500                          | ~65                  | [4]   |
| Ca diglyceroxide<br>Waste cooking oil   | 0.053 mol of CaO mixed with 0.0108 mol of glycerol and 1.37 mol of MeOH, agitated 3 h at 60 °C. Filtrated, washed twice with THF and dried overnight at 60 °C under vacuum  | 60                     | 9:1         | 1           | 0.5                      | (a) 850<br>(b)<br>ultrasonic | (a) 65.6<br>(b) 93.5 | [11]  |
| Ca glyceroxide<br>(a) soybean oil<br>(b) waste frying oil                           | CaO, glycerol and MeOH at a mass ratio of 1:1.6:13.4, sonication during 15 min  | 60                     | 7:1         | 0.4         | 2                        | 1000                         | (a) 94<br>(b) 89     | [12]  |
| Ca glyceroxide<br>Sunflower oil   | 0.1 g of CaO mixed with 1.5 g of methanol containing 10 mg, 40 mg or 60 mg of glycerol, 15 min at 50 °C (N <sub>2</sub> atmosphere)   | 50                     | 14:1        |             | 3                        | 1000                         | ~95                  | [13]  |
| Ca monoglycerolate<br>Refined soybean oil   | 3.00 g of commercial CaO with 100 g glycerol mechanically stirred for 15 min in an Erlenmeyer flask, then inserted in a water bath (40 °C) for 24 h. The supernatant was transferred to polyethylene container, inserted into steel reactor and heated in a drying stove for 7 days at 120 °C | 50                     | 50:1        | 2           | 2                        | 500                          | 62.79                | [14]  |
| Ca diglycerolate<br>Refined soybean oil   | 3.00 g of commercial CaO with 100 g glycerol mechanically stirred for 15 min in an Erlenmeyer flask, then inserted in a water bath (40 °C) for 24 h. The supernatant was transferred to polyethylene container, inserted into steel reactor and heated in a drying stove for 7 days at 120 °C | 50                     | 50:1        | 2           | 2                        | 500                          | 98.63                | [14]  |
| Ca diglycerolate<br>Refined soybean oil   | 7.00 g of commercial CaO with 11.5 g of glycerol dissolved in 50 mL of methanol, at methanol reflux for 4 h. Solid was washed, centrifuged 4 times with a 1:1 isopropanol:glycerol mixture, followed by 2 washing/centrifugation steps with ethyl ether and drying at 60 °C for 1 h           | 50                     | 50:1        | 2           | 2                        | 500                          | 99.9                 | [14]  |
| Ca glycerolate [Ca(C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> )]<br>Sunflower oil | Ca(OH) <sub>2</sub> and glycerol (mass ratio of 1:10), at 180 °C for 2 h, washed twice with ethanol, and dried overnight at 60 °C under vacuum  | 60                     | 12:1        | 2           | 4–8                      | –                            | 4 h 55 h<br>~95      | [9]   |

have reported its high activity in the transesterification of triglycerides. Activity of CaDG has been explained assuming that the interaction between glyceroxide and calcium ions exists, which creates a surface with hydrophobic and hydrophilic sites, and a hydrogen bond network favoring the approaching of methanol (MeOH) and triglyceride (TG) [5]. When CaO is used, only methanol can easily approach the catalyst surface, decreasing the accessibility of TG molecules [5].

However, heterogeneously catalyzed methanolysis reaction is very complex process because it occurs in a three-phase system consisting of a solid (catalyst) and two immiscible liquid phases (oil and methanol) [15]. Combination of different chemical and physical processes determines the kinetics of triglycerides methanolysis. The mass transfer of reactants to the catalyst surface

where reaction occurs, have an important role at the beginning of the process, while in the later stage the rate of process is governed by chemical reaction at catalyst surface. The mass transfer resistance is caused mainly by the immiscibility of nonpolar TG phase and the polar methanol phase. Owing to its low solubility the methanol is dispersed throughout the oil and for increase of initial rate of methanolysis methanol drops need to be broken into fine dispersion, either by increasing mixing intensity or by action of some chemical agents. Both actions lead to the formation of a larger surface area between methanol and oil. Namely, during methanolysis of vegetable oil (triglycerides) such process of fine dispersion formation evidently exists under the influence of formed diglycerides (DG), monoglycerides (MG) and fatty methyl esters (FAME) in the reaction of triglycerides and methanol.

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