



## Hydrated lime as an effective heterogeneous catalyst for the transesterification of castor oil and methanol

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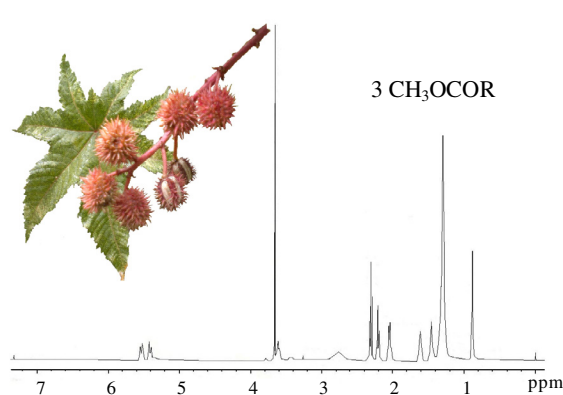
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### HIGHLIGHTS

- ▶ Hydrated lime and CaO were evaluated in the transesterification reaction.
- ▶ The catalyst's changes were analyzed by X-ray powder diffraction.
- ▶ The active phase after the first use was calcium hydroxide.
- ▶ Calcium diglyceroxide was identified as the main crystalline phase after the reuses.
- ▶ A 98% conversion was achieved within 14 h of reaction at room-temperature.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Hydrated lime (HL) and CaO were evaluated as solid base catalysts in the transesterification of castor oil and methanol. Castor oil and the alkyl esters produced after the transesterification reaction were characterized by <sup>1</sup>H NMR and TLC analysis. Since full conversion of the raw materials into biodiesel (BD) was obtained with both HL and CaO, the influence of the catalyst amount, methanol:oil ratio, reaction time, and reaction temperature was studied employing HL due to the economic and process advantages of HL over CaO. The catalyst's changes throughout reaction time and after the catalyst reutilization were analyzed by X-ray analysis of the recovered mixture of HL, raw materials and products. From the X-ray diffraction analysis it was corroborated that the crystalline phases after 10, 30, 60 and 120 min were Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> as the main and secondary phases, respectively. From the results it was clear that the catalyst's active phase after the first use was Ca(OH)<sub>2</sub>. However, when the catalyst was reused, calcium diglyceroxide was identified by X-ray analysis as the main crystalline phase and it remained up to the third reuse. The catalyst stability was determined and the results revealed that although a conversion decrease was observed after the first reuse, the catalyst increased its activity in the second reuse maintaining a conversion up to 84% after the third one. Room-temperature biodiesel production was also investigated. In this sense, 98% conversion was achieved at 14 h of reaction.

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## 1. Introduction

In the last decades, biodiesel (BD) has received much attention worldwide since it is generally recognized as the best substitute of

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petroleum-based diesel fuel as both of them exhibit very similar characteristics such as cetane number, specific gravity, and boiling point [1,2]. Nevertheless, BD has some advantages over petroleum-based diesel fuels: it is biodegradable, possesses low toxicity and sulfur content, reduces most exhaust emissions and it is produced from renewable resources, among others [1]. It is generally obtained by the transesterification of a triglyceride with an alcohol, also called alcoholysis, in which glycerol is generated as a by-product. In this sense, the reaction is commonly carried out by homogeneous bases and/or acids [3,4]. These catalysts are commonly used in the industries due to several reasons: (a) they are able to catalyze the reaction at low reaction temperature and atmospheric pressure; (b) high conversion can be achieved in a minimal time; and (c) they are widely available and economical [5]. Among the advantages of the homogeneous base-catalyzed reaction are that catalysts such as NaOH and KOH are relatively cheap and widely available, produce very fast reaction rates, the reaction can occur under mild reaction conditions and are less energy intensive. In the same way, the advantages of the acid-catalyzed reaction are its insensitivity to free fatty acids and water content in the oil, it is the preferred method if low-grade oil is used and esterification and transesterification occur simultaneously [5].

It is important to stress that at the outset of BD production, refined edible oils such as soybean oil, sunflower oil, olive, cotton, rapeseed, and palm, were employed. In fact, in 2008 about 84% of the world's biodiesel production was covered by rapeseed oil. The remaining portion was from sunflower oil (13%), palm oil (1%), soybean oil and others (2%) [6]. Nonetheless, this caused a severe controversy due to the price increment of these oils and the decision of employing these oils for energy production or human consumption. Based on the aforementioned, biodiesel producers had been encouraged to use non-edible oils such as waste oils, castor, jatropha, and rubber seed [6,7]. Among these inedible oils, castor oil has been recognized as a potential raw material for biodiesel production. For instance, in Brazil, one of the major biodiesel producers, although some vegetables have received attention from the Brazilian government, including peanut, sunflower and palm, the castor bean plant has obtained special attention because of its relative resistance to hydric stress, ability to develop under adverse climate and soil conditions, low production cost and because it is easily grown, even in Brazil's vast semi-arid regions, where frequent droughts severely limit agricultural production. Its seeds show oil contents ranging from 45% to 50%, with a productivity of 470 kg of oil per hectare. Additionally, because castor bean is not suitable for human consumption and its cultivation can be carried out in marginal lands its use as energy source does not compete with food production [8]. From all these characteristics, castor oil has been recognized as a potential source to promote social and economic development in semi-arid regions where poverty is commonly widespread.

Homogeneous-phase biodiesel production employing castor oil has been studied by several researchers [9–16], where the effect of distinct reaction parameters has been evaluated. For instance, Meneghetti et al. [16] carried out a comparison of ethanolysis versus methanolysis of castor oil evaluating distinct acid and basic catalyst. They concluded that BD can be obtained by both methods with methanolysis proving much more rapid than ethanolysis. Their best results were: ~85% yield was exhibited with KOCH<sub>3</sub> and methanol at 1 h and 60 °C, 80% yield with NaOCH<sub>3</sub> and methanol at 6 h and 80 °C, 84% yield was calculated with H<sub>2</sub>SO<sub>4</sub> and methanol at 8 h and 60 °C and ~77% yield was determined with HCl at 8 h and 80 °C. On the other hand, Sousa et al. [10] studied the production of methyl esters from castor oil and methanol after neutralization of castor oil with glycerol. They reported a 92.5% yield after 15 min of reaction at atmospheric pressure and ambient temperature in a batch reactor, employing potassium hydroxide as catalyst.

In this context, despite the above-mentioned advantages of homogeneous-phase BD production it must be pointed out that this route gives rise to severe drawbacks such as: the catalyst cannot be reused or regenerated, expensive separation of the homogeneous catalyst from the reaction mixture, generation of large amounts of wastewater during separation of the products, the high consumption of energy, corrosion on reactor and pipelines from the use of high alkaline or acid conditions and long reaction times [5,17]. Additionally, the presence of free fatty acids (FFAs) may cause soap by-product formation if basic catalysts are employed lowering biodiesel yield and hindering the separation of the esters from glycerol [18].

Thus, the use of solid catalysts represents an attractive solution since the catalysts can be easily separated from the products, the products do not contain impurities of the catalyst and the cost of final separation could be reduced, they can be readily regenerated and reused and it is more environmentally benign because there is no need for acid or water treatment in the separation step [3,4,17].

BD production employing solid catalysts has been studied by many authors worldwide. However, their use in the transesterification reaction employing castor oil is rare perhaps for the intrinsic characteristics of castor oil (hygroscopicity and high content of FFA) since some heterogeneous catalysts are water-sensitive [19] and the presence of FFA would require the addition of more catalyst to compensate this acidity and avoid catalyst deactivation [19,20].

Sreeprasanth et al. [21] evaluated double-metal cyanide complexes as solid catalysts in the preparation of fatty acid alkyl esters (biodiesel/biolubricants) from vegetable oils. The reaction conditions were 3 wt.% of catalyst with respect of oil, oil:methanol molar ratio of 1:15, a reaction temperature of 170 °C and a reaction time of 8 h. The conversion achieved with castor oil was 78.3%.

De Almeida et al. [22] carried out the transesterification of soybean and castor oil employing superacid sulfated titania catalyst. All reactions were performed in 1 h at 120 °C using a methanol/oil/catalyst molar ratio of 120/20/1. In the methanolysis of soybean and castor oil their best yields were 40% and 25% in fatty acid methyl esters, respectively.

Albuquerque et al. reported the use of CaO supported on mesoporous silicas as basic catalyst for transesterification reactions [23]. The most active catalyst was tested in the biodiesel production from castor and sunflower oils, by using a methanol:oil molar ratio of 12, a reaction temperature of 60 °C and a catalyst concentration of 1 wt.%. The authors reported conversion values of 65.7% and 95% after 1 and 5 h of reaction time, respectively.

Recently, hydrated lime (HL) was employed as a heterogeneous catalyst in the transesterification of used soybean oil and methanol [24] demonstrating that it did not require an activation process for achieving complete conversion of the raw materials into biodiesel. Also, its reusability was determined revealing that it was highly active up to the second reutilization. Due to its low cost, commercial availability, resistance to atmospheric poisoning, and reusability, HL represents a new alternative for lowering the cost of biodiesel.

Therefore, in this work, HL was employed as a heterogeneous catalyst in the transesterification of castor oil and methanol. The effect of the reaction parameters such as catalyst loading, reaction time, reaction temperature, oil:methanol ratio, and reusability were evaluated. Also, the catalyst active phase was identified throughout the reaction time and after each reuse, respectively.

## 2. Experimental section

### 2.1. Materials

Castor beans were collected from fruiting plants of *Ricinus communis* L. in the "Mixteca Poblana" South of Puebla State, Mexico

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