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Synthesis, characterization and applications of carbon-based calcium catalysts deriving from avocado seeds for biodiesel production from waste cooking oil

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In this work, avocado seeds were successfully used as precursors to produce carbon-based calcium catalysts for biodiesel production. The catalysts were synthetized *via* precipitation method, by loading different amounts of calcium nitrate on carbonized supports obtained by pyrolysis under nitrogen flow of dried biomass. The effect of Ca loaded on the structure and the activity of the catalysts for biodiesel synthesis from sunflower oil with methanol was investigated. Results showed that supported catalyst loaded with 20%wt of Ca, efficiently promote the trans-esterification process (FAMEs content >80%) with the catalyst that was easily recovered and reused. Reaction conditions were then optimised using the desirability function applied on the response surface methodology analysis of a Box–Behnken factorial design of experiments. Finally, the optimized conditions were adopted on several non-edible oils with Free Fatty Acids content range between 1 and 15 mg KOH/g. In all cases, a FAMEs content >95% was in any case obtained.

Key words: Biodiesel, calcium oxide, heterogenous catalysts, avocado seeds, FFAs

INTRODUCTION

The depletion of petroleum reserves and the growing global energy demand has led to the use of alternative renewable energy respect to petroleum-based fuels [1,2]. In Europe, several countries proposed a ban on the sale of petrol and diesel cars by making the switch to electric-powered vehicles, with many nations that will follow their lead. Biodiesel is a clean renewable fuel, which has chemical and physical properties similar to the fossil fuels [3,4]. In addition, it is biodegradable, oxygenated and free of sulfur with consequently reduced gas emissions in atmosphere compared to petroleum diesel [5,6].

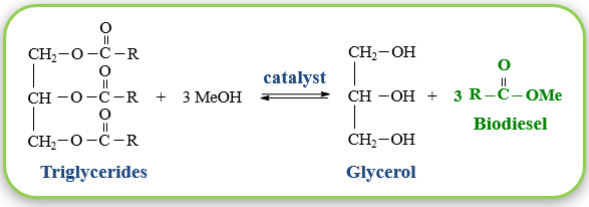

Fig. 1. General equation for the synthesis of Biodiesel from Triglycerides.

Biodiesel is a mixture of Fatty Acid Methyl Esters (FAMEs), typically produced by trans-esterification of glycerides contained into natural resources such as vegetable oil or animal fats with biomethanol produced from natural resources (CO_2, biomass, and waste [7,8]) (Figure 1), in presence of homogeneous basic catalysts (sodium or potassium hydroxide, carbonates or alkoxides [9,10]).

Such catalysts are quite sensitive to the presence of water and Free Fatty Acids (FFAs) which can be contained in small quantities in vegetable oils and animal fats. In particular, the presence of FFAs not only leads to the formation of soaps with difficulty in the separation of biodiesel produced, but also to the production of large amounts of chemical wastes [11,12]. For these reasons, refined oils or highly pure fats must be used with a consequent increase in production costs. On the other hand, homogeneous acid catalysts (hydrochloric, sulphuric and nitric acid) are no-sensible to FFAs and therefore usable for low quality feedstocks such as waste cooking oils, non-edible oils and raw animal fats [13,14]. However, they are slower respect to the basic catalysts and require reactors resistant to the acid corrosion. Thus, research efforts have been switched in the development of heterogenous catalysts [15,16]. These catalysts can be easily recovered and the end of the process and re-used for several cycles of reaction without significantly loss of catalytic activity. Hydrotalcites [17,18], mixed oxides [19,20], heteropolyacids [21], ion exchange resins [22,23] and zeolites [24] were used for the conversion of several feedstocks but for the complex expensive synthesis procedures and the reagents used, they not have still reached the full growth. Consequently, research was focused on the

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production of new "green catalysts", which can be prepared directly from biomass or its derivatives. Ligno-cellulosic biomass [25], animal bones [26] and waste shells [27] were positively used as catalysts for the biodiesel production, by significantly reducing the production costs. In addition, they are biodegradable and re-usable for several cycles of reaction. In this work, carbon-based calcium catalysts deriving from avocado seeds were synthetized and tested in the trans-esterification reaction of sunflower oil with methanol.

Once identified the most active catalyst, Box–Behnken response surface methodology was then applied to maximize FAMEs yield. Finally, the optimized conditions were adopted on several non-edible oils characterized with high FFAs content to verify the applicability of the process.

MATERIALS AND METHODS

Reagents and Instruments

All chemical reagents used in this work were of analytical grade and were used directly without further purification or treatment.

Avocado seeds (Persea Americana) were purchased from a local market of Aguascalientes (Mexico).

Carbolite Eurotherm tubular furnace was used for the synthesis of carbon-based calcium catalysts.

Identification of the different methyl esters were carried out by gas chromatography-mass spectroscopy (GC-MS) using a Perking Elmer Clarus 500 equipped with a Clarus spectrometer. Quantitative determinations were performed using a Varian 3800 GC-FID. Both instruments were configured for cold on-column injections with a HP-5MS capillary column (30 m; Ø 0.32 mm; 0.25 μm film).

Synthesis of carbon-based calcium catalysts

Avocado seeds obtained from the fruit of *Persea Americana* were used as precursors for the synthesis of carbon-based calcium catalysts. Supported material was obtained by pyrolysis of the starting biomass for 2 h at 900 °C under N_2 flow. Carbon-based calcium catalysts were synthetized *via* precipitation method. 10 g of organic support and 11.8 g of calcium nitrate tetrahydrate (weight ratio Ca to support = 20%) were suspended into 100 mL of deionized water. Then, a sodium hydroxide solution 1.5 N was added until to obtain the precipitation of calcium hydroxide. The system was stirred for 1 h at 70 °C. Finally, the precipitate was filtered, washed with deionized water and activated for 2 h at 900 °C under N_2 flow. Using the same procedure, supported catalysts with 10 and 5%wt of calcium loaded were also synthetized.

Trans-esterification reaction of sunflower oil with methanol

In a glass reactor of 15 mL, 2 g of sunflower oil (residual acidity = 0.21 mg KOH/g) were placed with 1.08 g of methanol (molar ratio methanol to oil = 15) and 0.1 g of catalyst (weight ratio catalyst to oil = 5%). The reaction was carried out for 3 h at 100 °C. Then, the system was cooled and the catalyst was recovered by centrifugation. The organic phase was recovered by evaporation of methanol under N_2 flow with the glycerol that decanted on the bottom as separate phase. Upper organic phase was recovered, washed with deionized water and dried under vacuum. Finally, methyl-esters were determined by gas-chromatography using methyl heptadecanoate as internal standard. Optimization of reaction conditions were performed using a three-level and three-factorial Box–Behnken experimental design. Amount of catalyst (2.5, 5 and 7.5%wt, X_1), molar ratio methanol to oil (10, 15 and 20, X_2), reaction time (1, 3 and 5 h, X_3) and temperature (60, 80 and 100 °C, X_4) were selected as independent variables while FAMEs content (%wt) was selected as dependent variable.

Free Fatty Acids determination

FFAs were determined *via* titration using a 0.1 N KOH normalised solution and phenolphthalein as indicator in a 1:1 diethyl-ether: ethanol medium (1 g sample dissolved into 150 mL solvent).

ANALYSIS OF RESULTS

Trans-esterification tests for biodiesel production

Preliminary tests were conducted on sunflower oil to test the efficacy of the synthetized catalysts in the biodiesel production. Increasing the amount of calcium loaded from 5 to 20%wt, an increase of activity in the trans-esterification of glycerides was observed, strictly connected to the basic properties of the catalysts (Fig. 2a). When Ca loaded was 20%wt, a FAMEs content >80%wt was obtained at 100 °C after 3 h in the reaction conditions adopted (5%wt of catalyst, molar ratio methanol to oil = 15). In addition, respect to the use of CaO that was completely dissolved during the process, the catalyst was easily recovered and reused 3 times without loss of the activity. Finally, the optimization of reaction conditions were conducted by response surface methodology of a Box-Behnken factorial design of experiments (Fig. 2b). By carrying out the trans-esterification reaction at 99.5 °C for 5 h

(7.3%wt of catalyst, molar ratio methanol to oil = 15.6), a FAMEs content of >99%wt was obtained.

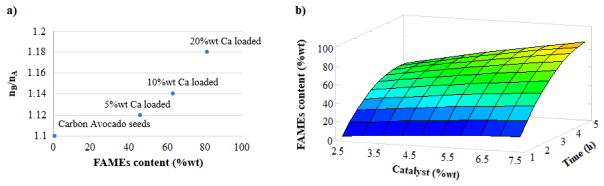

Fig. 2. a) Correlation between FAMEs content (%wt) and basic/acid properties (n_B/n_A) of the catalysts and b) Response surface plot of the effects of catalyst and reaction time at fixed temperature (80 °C) and molar ratio methanol to oil (15).

$$FAMEs = -162.71 + 4.4674X_1 + 4.5032X_2 + 7.6919X_3 + 1.8221X_4 - 0.23094X_1^2 + 0.0055167X_2^2 - 2.9705X_3^2 - 0.0051833X_4^2 - 0.139X_1X_2 + 1.156X_1X_3 + 0.0362X_1X_4 + 0.40475X_2X_3 - 0.03785X_2X_4 + 0.13169X_3X_4$$

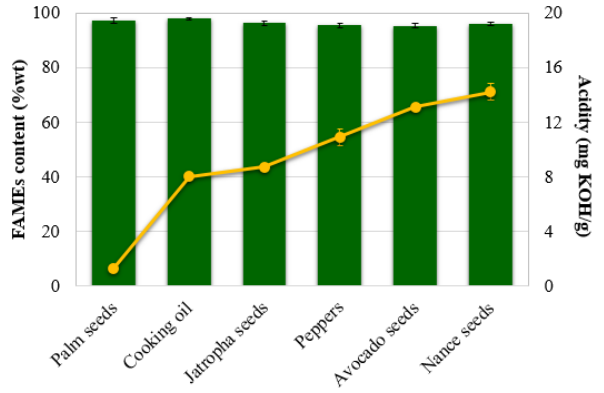

Fig. 3. Biodiesel production from non-edible oils by using supported catalyst with 20%wt of Ca loaded.

Finally, the optimized conditions were adopted on non-edible oils with high FFAs content (1-15 mg KOH/g). In all cases, a FAMEs content >95%wt in the product isolated was obtained, confirming the efficacy of process and the applicability of catalyst in the biodiesel production from several raw oils. However, in order to evaluate the economy of the entire process, it is necessary not only maximize the methyl esters yield but also to consider other factors such as the energy required for the recovery of methanol at the end of the process [28,29]. For this reason, further studies will be developed with the aim to optimize the overall economy of the process.

CONCLUSION

Carbon-based calcium catalysts deriving from carbon avocado seeds were synthetized and tested in the trans-esterification reaction of sunflower oil with methanol. The catalysts were synthesized by precipitation method with calcium oxide which was homogeneously dispersed on the surface of carbonized supports. Among the different catalyst tested, supported catalyst loaded with 20%wt of Ca shows the best catalytic activity in the trans-esterification process, related to its basic properties. Finally, the catalyst was successfully tested on several non-edible oils with high FFAs content, by significantly reducing the costs required for the biodiesel production.

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