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

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Introduction

In this work, avocado seeds were successfully used as precursors to produce carbon-based calcium catalysts for biodiesel production. The catalysts were synthetized *via* impregnation 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 similar results to those obtained with pure calcium oxide. In addition, the catalyst was easily recovered and reused for several cycles of reaction without loss of catalytic activity. Reaction conditions were then optimised using the desirability function applied on the response surface methodology analysis of a Box–Behnken factorial design of experiments. By carrying out the reaction at 99.5 °C for 5 h with 7.3%wt of catalyst (respect to the oil) and a molar ratio oil to methanol of 15.6, almost a FAMEs content of 100% was obtained. Finally, the optimized conditions were adopted on several oils with Free Fatty Acids content in the range 1-15 mg KOH/g. In all cases, a FAMEs content >95% was in any case obtained.

Materials and Methods

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* impregnation method. 10 g of organic support and 11.78 g of calcium nitrate tetrahydrate (weight ratio Ca to support = 20%) were suspended into 100 mL of deionized water. Then, 66.5 mL of sodium hydroxide solution 1.5 N were added dropwise 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. Molar ratio methanol to oil (10, 15 and 20), amount of catalyst (2.5, 5 and 7.5%wt), temperature (60, 80 and 100 °C) and reaction time (1, 3 and 5 h) were selected as independent variables while FAMEs content (%wt) was selected as dependent variable.

Analysis of results

Characterization of carbon-based calcium catalysts

XRD analysis of carbon-based calcium catalysts obtained from avocado seeds after activation for 2 h at 900 °C under N_2 flow were reported in Fig. 1a. After the thermal treatment, crystallized of calcium oxide were formed on the surface of the catalysts, identified by the presence of diffraction peaks 2θ at: 32.18°, 37.32°, 53.82°, 64.11°, 67.32°, 79.61° and 88.46° with the intensity proportional to the amount of calcium loading. In addition, some peaks with low intensity of calcium hydroxide were detected at 2θ of: 17.87°, 28.51°, 34.10° and 47.48°. FT-IR spectra of the heterogenous catalysts show the presence of broad band at 1420 cm^{-1}, typically assigned to asymmetric stretch of CO_3^{2-} group, which can be attributed to the formation of new structure characterized by the presence of C-O-Ca bond.

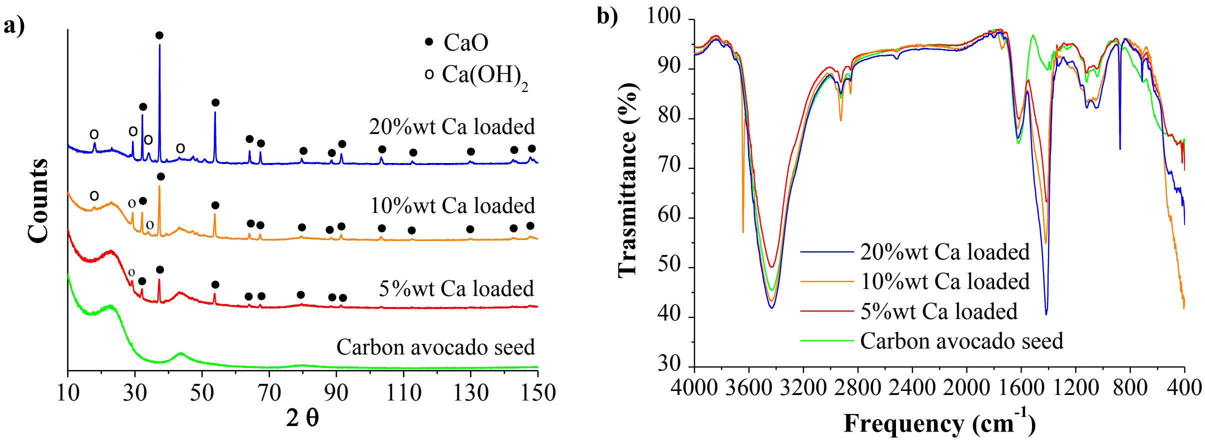

Fig 1. a) XRD and b) FT-IR spectra of carbon-based calcium catalysts.

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 of 82.7%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 99.5 ± 0.3%wt was obtained.

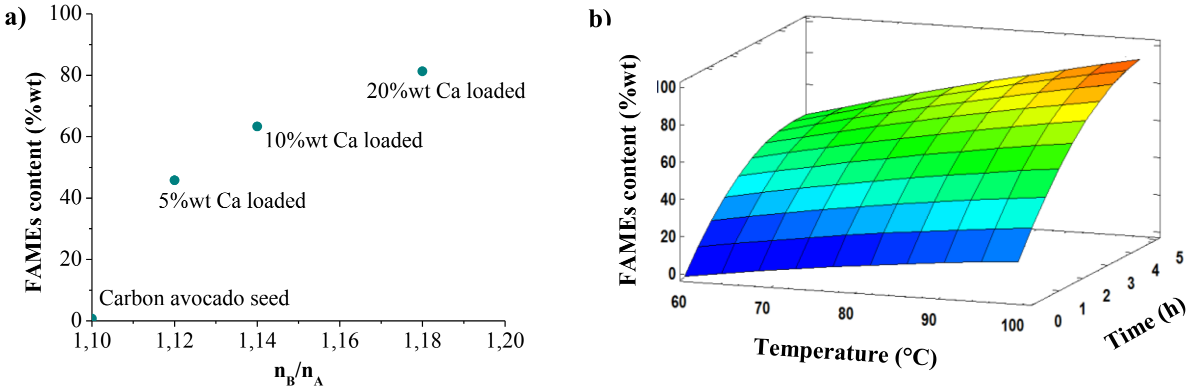

Fig 2. a) Correlation between FAMEs content (%wt) and basic/acid properties of catalysts and b) Response surface plot of the effects of temperature and reaction time at fixed catalyst (5%wt) and molar ratio methanol to oil (15).

Finally, the optimized conditions were adopted on bio-oils with high FFAs content (1-15 mg KOH/g) deriving from different biomasses. In all cases, a FAMEs content after reaction >95%wt was obtained.

Table 1. Biodiesel production from different bio-oils using supported catalyst with 20%wt of Ca loaded.

Bio-oils	Acidity (mg KOH/g)	FAMEs content after reaction (%wt)
Palm seeds	1.3 ± 0.4	97.2 ± 1.1
Peppers	10.9 ± 0.6	95.4 ± 0.7
Jatropha seeds	8.7 ± 0.1	96.2 ± 0.8
Avocado seeds	13.1 ± 0.1	95.3 ± 0.9
Nance seeds	14.2 ± 0.6	96.1 ± 0.6

Conclusion

Carbon-based calcium catalysts deriving from avocado seeds are active to convert bio-oils deriving from different biomasses. They are easily recovered at the end of the reaction cycle and can be used several times reducing the environmental impact of the catalysts disposal.

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