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Research Article

Relevance of the Physicochemical Properties of Calcined Quail Eggshell (CaO) as a Catalyst for Biodiesel Production

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The CaO solid derived from natural quail eggshell was calcined and employed as catalyst to produce biodiesel via transesterification of sunflower oil. The natural quail eggshell was calcined at 900°C for 3 h, in order to modify the calcium carbonate present in its structure in CaO, the activity phase of the catalyst. Both precursor and catalyst were characterized using Hammett indicators method, X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TG/DTG), CO_2 temperature-programmed desorption (CO_2-TPD), X-ray photoelectronic spectroscopy (XPS), Fourier infrared spectroscopy (FTIR), scanning electron microscopy (SEM), N_2 adsorption-desorption at −196°C, and distribution particle size. The maximum biodiesel production was of 99.00 ± 0.02 wt.% obtained in the following transesterification reaction conditions: X_{MR} (sunflower oil/methanol molar ratio of 1 : 10.5 mol : mol), X_{CAT} (catalyst loading of 2 wt.%), X_{TIME} (reaction time of 2 h), stirring rate of 1000 rpm, and temperature of 60°C.

1. Introduction

The increase of the world population has led to a depletion of fossil resources and the generation of high residue content. In the last years, both society and governments have become aware of this issue, attempting these wastes without commercial interest in the other one with high added value. The eggshell is an example of these products without interest that could be treated to reuse in several applications. Eggshells are mainly composed of a network of protein fibers, associated with crystals of calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), and calcium phosphate $Ca_3(PO_4)_2$ as well as organic substances and water, calcite ($CaCO_3$) being the main constituent [1].

The major uses for this material are associated with the agriculture as fertilizer, pH correction of the acidic soils. The thermal treatment of the eggshell wastes as raw material can lead to the formation of an inexpensive and environment-friendly basic catalyst. This material is one alternative of the nonrenewable calcium carbonate mineral sources. The use of this new source can minimize the impact on the natural reserves of limestone and synthesis of $CaCO_3$ or dolomite $Ca_xMg_{(1-x)}CO_3$, which have been highly used for research purposes, obtaining excellent results for biodiesel production [2–4].

Biodiesel is obtained by the transesterification reaction of triglycerides, which are derived from vegetable oils or animal fats, with short chain alcohols (methanol, ethanol, and propanol) to obtain a mixture of alkyl esters and glycerol as by-product [5, 6]. Biodiesel is the most potential alternative energy to fossil fuels since it is biodegradable, renewable, and nontoxic [7, 8].

Traditionally, the synthesis of biodiesel has taken place using homogeneous catalysts, such as NaOH [9], KOH [10], and H_2SO_4 [11], obtaining high conversion values; however the use of these catalysts presents several disadvantages such as the inability to reuse the catalyst and the high generation of waste and effluents which can be hazardous and corrosives. For this reason, the use of solid heterogeneous catalysts as alternative to the traditional homogenous catalysts has been proposed. The use of heterogeneous catalysts minimizes environmental damage and improves the effectiveness of the process which reduces the biodiesel cost. In addition, solid catalysts can be easily separated from the reaction medium and regenerated for several reaction cycles [12]; besides that, the use of solid catalysts diminishes the volume of wash water and organic solvent required in the purification step of the biodiesel.

Heterogeneous basic catalysts commonly used in the transesterification reaction are Ca-Al hydrocalumite [13], MgO [14], CaO [14–16], BaO [17], Li-CaO [18], CaO-ZnO [19], CaO/SBA-15 [20], MgO-CaO [20], CaO/Al_2O_3 [21], CaO-La_2O_3 [22] calcium/chitosan spheres [23], and natural calcium [24]. Of these, CaO has been the active phase that has exhibited the highest activity under mild reaction conditions with a long lifetime and a low catalyst cost [25]. A natural source, such as the quail eggshell waste, could emerge as a potential catalytic precursor for biodiesel production due to its low cost and high efficiency of its active phase in the transesterification reaction after a thermal treatment to form the CaO phase, as is reported in

$$CaCO_3 \longrightarrow CaO + CO_2 \tag{1}$$

In this sense, several researches have reported catalytic precursors based on calcium oxide, which were obtained from natural sources such as eggshell [25–28], bivalve clam shell [29], waste mussel shell [30, 31], waste of animal bone [31], snail shell [32], golden apple snail shell [32], crab shell [25, 33], oyster shell [34], waste fish *(Labeo rohita)* [35].

The objective of this research was the use of another natural calcium source not reported in the literature as quail eggshell wastes as raw material to obtain CaO by a thermal treatment (900°C for 3 h). The catalytic behavior of this catalyst was evaluated in the biodiesel production using methanol and sunflower refined oil as reagents. The material was characterized using Hammett indicators method, X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TG/DTG), CO_2-thermoprogrammed desorption (CO_2-TPD), X-ray photoelectronic spectroscopy (XPS), Fourier infrared spectroscopy (FTIR), scanning electron microscopy (SEM), N_2 adsorption-desorption at −196°C, and distribution particle size, to evaluate whether the calcium carbonate was converted into calcium oxide as well as verify its catalytic activity. The biodiesel production was performed using a factorial design studying the variables that influence the catalytic behavior, such as X_{MR} (sunflower oil/methanol to molar ratio), X_{CAT} (catalyst loading), and X_{TIME} (reaction time) in the biodiesel production.

2. Material and Methods

2.1. Materials and Reagents. Commercially edible grade sunflower oil was obtained from a supermarket (Liza, Brazil) and methanol (99.95%) was obtained from Vetec (Rio de Janeiro, Brazil). The physicochemical properties and fatty acid composition of sunflower oil are summarized in Supplementary Material Table S1 (available online at https://doi.org/10.1155/2017/5679512). The gases used in the experiments were He (99.999%, Air Liquide), N_2 (99.999%, Air Liquide), and CO_2 (99.99%; Air Liquide). The quail eggshell was obtained from domestic residences (Fortaleza, Brazil). The fatty acid composition of sunflower oil was determined by promoting the esterification of the fatty acids and quantified by CG/FID. This esterification reaction was carried out according to the procedure described in the EN 14214:2008 [36].

2.2. Preparation and Activation of Basic Catalyst. Natural quail eggshell was thoroughly washed several times with warm water. The residue of quail eggshell was crushed in a household blender, sieved, and stored for characterization of the precursor catalytic. The catalysts were synthesized by a thermal treatment of the precursor in a muffle furnace at 900°C for 3 h with temperature ramp of 30°C min^{-1} (Figure 1). The purpose of the thermal treatment is the decomposition of the organic matter present in the natural quail eggshell and the decarbonation of the calcium carbonate to form the desired calcium oxide, which has catalytic activity for biodiesel production.

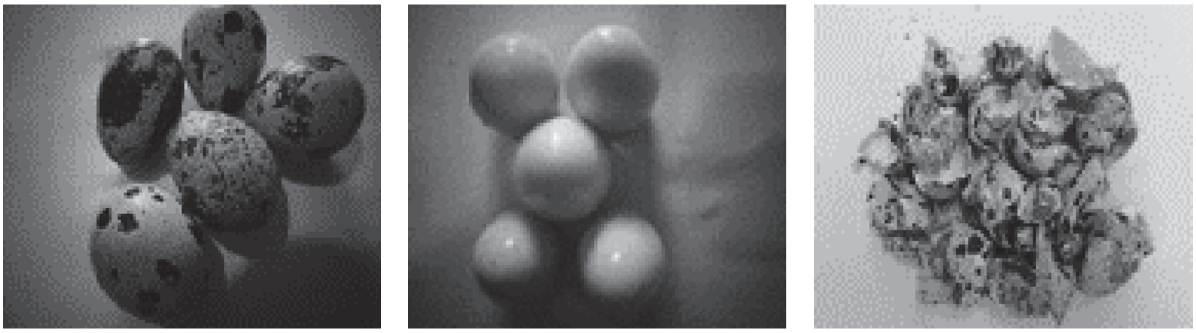
2.3. Material Characterization. Both natural quail eggshell and calcined quail eggshell were characterized by Hammett indicators method, XRD, XRF, TG/DTG, CO_2-TPD, XPS analysis, FTIR, SEM, N_2 adsorption-desorption at −196°C, and distribution particle size analysis. All of these characterization tests were performed to observe the differences after the thermal process modification.

Hammett Indicators Method. 0.1 g of calcined dried material was added to a test tube and stirred with 5 mL of anhydrous methanol. Then, one drop of 0.1% Hammett indicators (phenolphthalein, bromophenol blue, and phenol red) was added and left to equilibrate for 2 h. The changes of color were recorded.

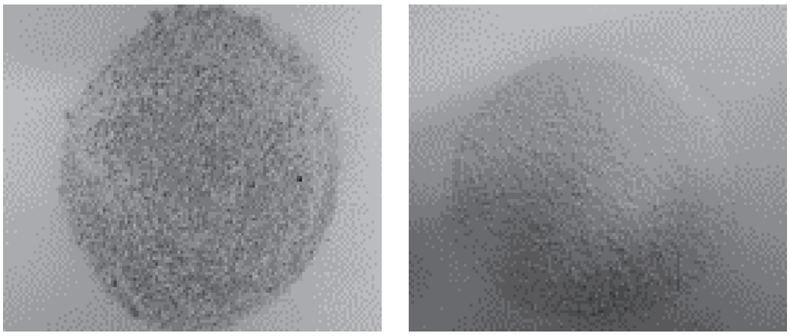
The chemical composition was measured by fluorescence spectrometer X-ray Rigaku brand, model ZSX mini II, operating at a voltage of 40 kV and a current of 1.2 mA in the tube coupled to Pd.

The mineralogical identification was carried out using X-ray diffraction (XRD) on a diffractometer X'Pert Pro MPD in a tube CuKα operating at a voltage of 40 kV and a current 40 mA. To perform the analysis the powders were placed in the cavity of a support used as a sample holder. The spectra obtained swept the range 10–70°. The particle size of precursor and catalyst was estimated by Williamson-Hall method with a fitting of the diffraction profile. The crystallographic composition was obtained from Rietveld method by using the X'Pert HighScore Plus software.

The thermal decomposition of the quail eggshell was analyzed by thermogravimetric analysis/differential thermal analysis (TG/DTG), carried out on a Shimadzu TGA-50 analyzer operating under the following conditions: air flow



(a) Natural quail eggshell (b) Edible part of quail eggshell (c) Waste natural quail eggshell



(d) Waste powder natural quail eggshell (e) Quail eggshell calcined at 900°C for 3 h

Figure 1: Method of obtaining the CaO from natural quail eggshell.

rate atmosphere (50 $cm^3 min^{-1}$); heating rate (10°C min^{-1}); and temperature (25–900°C).

The basicity of the catalyst was studied by temperature-programmed desorption of CO_2. Approximately 100 mg of sample was pretreated with a stream of helium at 800°C for 30 min (10°C min^{-1} and 60 mL min^{-1}). The reaction temperature was then decreased to 100°C, and a flow of pure CO_2 (60 mL min^{-1}) was subsequently introduced into the reactor for 30 min. The CO_2-TPD reaction was carried out between 100 and 800°C under a flow of helium (10°C min^{-1}, 30 mL min^{-1}), and the amount of CO_2 evolved was analyzed using a quadrupole mass spectrometer (Balzer GSB 300 02) equipped with a Faraday detector (0–200 U), which monitors the mass of CO_2 (44 U) during the experiment.

X-ray photoelectron spectra were collected without exposure to the atmosphere using a physical electronics PHI 5700 spectrometer with nonmonochromatic Mg Kα radiation (300 W, 15 kV, and 1253.6 eV) with a multichannel detector. Spectra of each sample were recorded in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were fitted using Gaussian–Lorentzian curves in order to determine the binding energies of the different element core levels more accurately. The calcined quail eggshell was treated at 900°C for 3 h and instantly was introduced into the analysis chamber and analyzed.

The FTIR analyses of catalyst were carried out using an FTIR spectrometer (model 8500; Shimadzu), which was operated in the range of 4000–400 wavenumber/cm^{-1}. A standard KBr technique was used for preparing the samples.

To observe the surface morphology of precursor and catalyst, both samples were initially covered with a thin layer of gold (10 nm) using a sputter coater (SCD 050; Baltec, Liechtenstein) and observed using a JEOL JXA-840A scanning electron microscope (20 kV) under a vacuum of 1.33 $\times 10^{-6}$ mbar (Jeol, Japan).

The textural parameters (S_{BET}, V_P, and d_P) were evaluated from nitrogen adsorption-desorption isotherms at −196°C as determined by an automatic ASAP 2020 system from Micromeritics. Prior to the measurements, samples were outgassed at 200°C and 10^{-4} mbar overnight. Surface areas were determined by using the Brunauer–Emmett–Teller (BET) equation and a nitrogen molecule cross section of 16.2 Å. The pore size distribution was calculated by applying the Barrett–Joyner–Halenda (BJH) method to the desorption branch of the N_2 isotherm. The total pore volume was calculated from the adsorption isotherm at $P/P_0 = 0.996$.

The particle size analyses were performed using the Mastersizer Particle Analyzer 2000, Hydro 2000 UM, Malvern (United Kingdom).

2.4. Transesterification Reaction. Transesterification reaction was conducted in a three-necked glass reactor with a condenser and magnetic stirrer, 60 mL of sunflower oil with different volumes of methanol, and varied amounts of catalyst

Table 1: Chemical composition (wt.%) of natural quail eggshell and calcined quail eggshell.

Material	Elements (wt.%)								
	Ca	P	S	K	Al	Cl	Si	Sr	Σ
Natural quail eggshell	97.71	1.30	0.31	0.19	0.16	0.15	0.13	0.06	100.00
Calcined quail eggshell	99.20	0.54	—	0.11	0.10	—	—	0.05	100.00

(over the weight of oil). The sunflower oil/methanol molar ratios (X_{MR}) used were 1 : 9, 1 : 10.5, and 1 : 12 and the catalyst loading (X_{CAT}) was 2, 2.5, and 3 wt.%. The temperature was fixed at 60°C and the reaction time (X_{TIME}) was 2, 2.5, and 3 h. After the reaction, the catalyst was separated by centrifuging the mixture at 2250 rpm for 30 min. The catalyst was separated by filtration, and the reaction mixture (biodiesel production and glycerin as coproduct) was placed in a funnel for phase separation. The residual methanol was evaporated using a rotary evaporator at 100°C for 15 min.

2.5. Quantification of the Biodiesel. A suitable experimental design was chosen to optimize the reaction condition based on the catalyst loading (X_{CAT}) and sunflower oil/methanol molar ratios (X_{MR}) as well as evaluate the optimal reaction conditions corresponding to maximum Y_{FAME} yield. Response surface methodology was used to analyze the results from the experiments. STATISTICA (version 7.0, StatSoft, Tulsa, OK) was used for statistical analysis of the experimental data. Analyses were carried out at a 95% confidence level.

The content of biodiesel was determined according to the procedure described in standard EN 14103 [37]. Analyses were done using a Varian CP-3800 gas chromatograph equipped with a CP-WAX 52CB (30 m × 0.25 mm × 0.05 μm) capillary column and a flame ionization detector (FID). For sample preparation, 250 mg of ester phase to be analyzed was added to 5 mL of a solution containing methyl heptadecanoate (at the final concentration of 10 mg L^{-1}, serving as internal standard) in heptane. 1 μL of the mixture was injected in the chromatography. The content of methyl esters of fatty acids was calculated as described in

$$Y_{\mathrm{FAME}}\ (\mathrm{wt.\%}) = \left[\frac{\sum A_t - A_{pi}}{A_{pi}}\right]\frac{C_{pi}\cdot V_{pi}\cdot 100}{W}, \quad (2)$$

where $\sum A_t$ is the total area of the peaks of methyl esters; A_{pi} is the peak area of internal standard (methyl heptadecanoate). C_{pi} is the concentration of internal standard solution (10 mg L^{-1}), V_{pi} is the added volume in 5 mL solution of methyl heptadecanoate, and W is weight in 250 mg of sample (biodiesel).

2.6. Reuse of Catalyst. The calcined quail eggshell (900°C for 3 h) was reused in the transesterification reaction by three cycles. The transesterification reaction conditions were optimized: X_{MR} (1 : 10.5), X_{CAT} (2 wt.%), and X_{TIME} (2 h). Between each cycle the catalyst was separated from reaction medium by centrifuging the mixture at 2250 rpm for 30 min, washed twice with methanol, dried at 100°C during 30 minutes, and stored in a desiccator. Prior to the reuse, the material was recalcinated to remove the recarbonation of the CaO species. This procedure was followed for each reaction cycle.

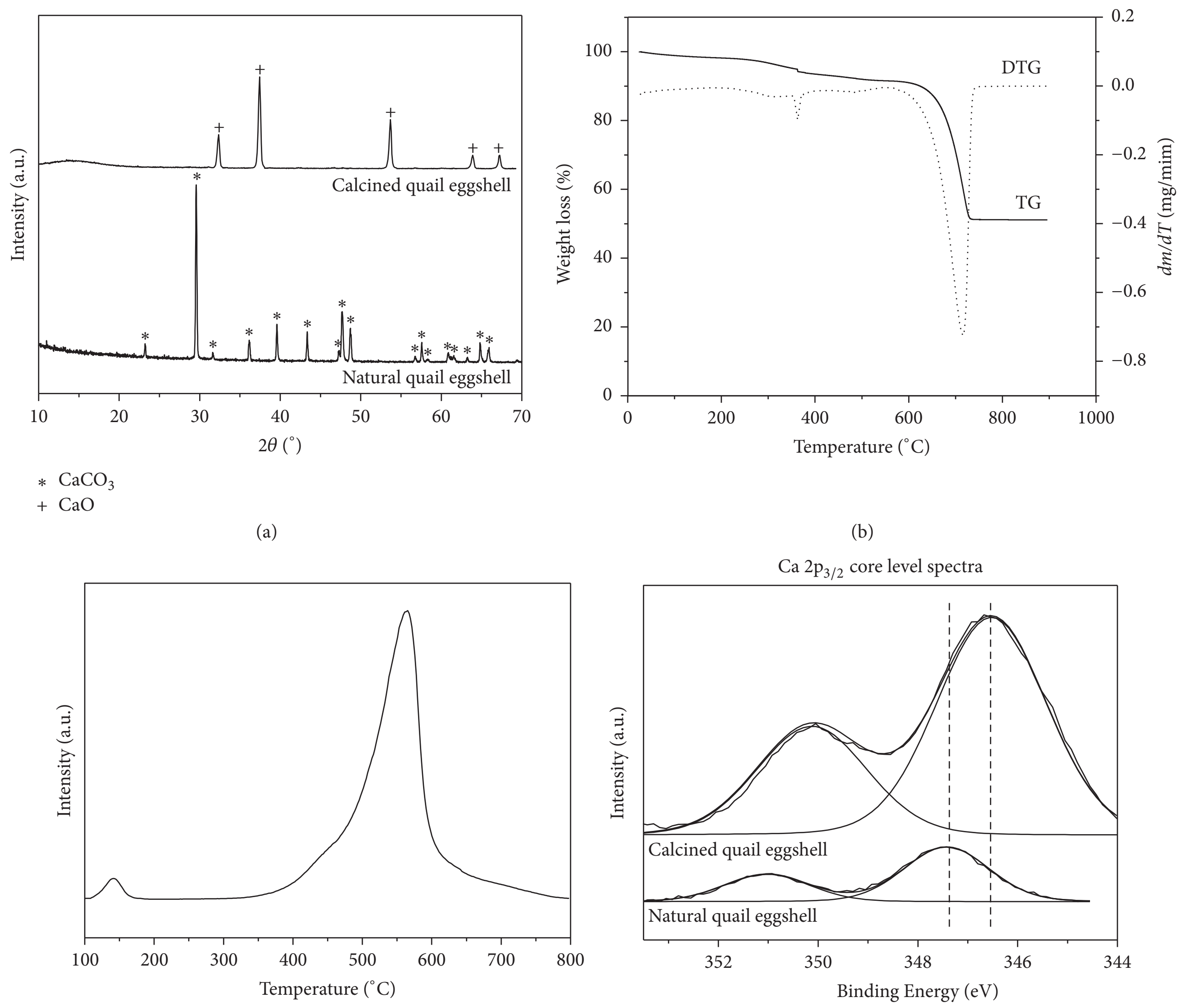
3. Results and Discussion

3.1. Material Characterization

3.1.1. Hammett Indicator Method. The Hammett indicator experiments can provide qualitative information about the strength of the basic sites obtained by thermal treatment of the quail eggshell. The results obtained, compiled in the Supplementary Material Table S2, indicated that the calcined quail eggshell has a basic character, in accordance with the colors observed in acidic and basic medium. From Hammett indicators the changes of color were observed for phenolphthalein from colorless to pink, for bromothymol blue from yellow to blue, and for phenol red from yellow to red. This data reveals that calcined quail eggshell displays basic sites with high strength, which can be employed for the transesterification reaction of sunflower oil with methanol.

3.1.2. X-Ray Fluorescence Analysis (XRF). Table 1 shows the chemical composition of natural quail eggshell and calcined quail eggshell, obtained by X-ray fluorescence analysis. The analysis of the natural quail eggshell reveals a high amount of calcium 97.71 wt.% together with phosphorous and sulfur possibly due to the presence of phospholipid in the membrane of the natural quail eggshell. After the thermal process, the percentage of calcium increases, reaching 99.20 wt.%. Moreover, the presence of lower amounts of other elements (Mg, Fe, P, S, K, Al, Cl, and Si) is noticeable, which will be considered as impurities of the CaO catalyst. The high calcium content of the calcined quail eggshell used in this work suggests that this material could be a promising material to biodiesel production [25].

3.1.3. X-Ray Diffraction Analysis (XRD). Figure 2(a) shows the XRD patterns for natural and calcined quail eggshell used in this research. Natural quail eggshell presents diffraction lines located at 2θ/degree = 23.3, 29.6, 31.6, 36.1, 39.6, 43.4, 47.3, 47.7, 48.7, 56.8, 57.6, 60.9, 61.6, 63.2, 64.8, 65.8, and 66.0, which have been ascribed to the presence of rhombohedra calcite ($CaCO_3$) (01-085-1108 reference code of card ICSD), discarding the presence of other crystallographic phases. After the activation process, the diffraction lines attributed to $CaCO_3$ disappear, with new diffraction lines arising about 2θ/degree = 32.3, 37.4, 53.7, 63.9, and 67.3 corresponding to lime (CaO) (00-044-1481 reference code of card ICSD). The particle sizes of precursor and catalyst were estimated by the Williamson-Hall method through the fitting of the diffraction



(a)

(b)

(c) Calcined quail eggshell

(d)

Figure 2: X-ray diffraction of natural and calcined quail eggshell (a), TG/DTG of natural quail eggshell (b), CO_2-TPD profile of calcined quail eggshell (c), and Ca 2p core level spectra of natural and calcined quail eggshell (d).

profile. The quail eggshell shows a particle size of 315 nm ($CaCO_3$), while the calcined quail eggshell displays a particle size of 240 nm (CaO). The decrease of the crystal size can be attributed to the exothermic conditions of the decarbonation process. The lower intensity peaks for calcined quail eggshell could be related to the reduction in the crystallite size.

3.1.4. Thermogravimetric Analysis (TG/DTG). Figure 2(b) shows the thermal analysis results (TG/DTG) of the natural quail eggshell. The TG/DTG curves present two events of mass losses. The first loss (7.8 wt.%), between 50–525°C, is attributed to the loss of the physisorbed water onto the surface of the material by hydrogen bonds and the decomposition of the organic matter because the membrane of quail eggshell natural is primarily composed of proteins with disulfide groups carbohydrates, phospholipids, and an outer organic layer, which is rich in cysteine. The second mass loss (40.4 wt.%), between 550 and 875°C, is associated with the decomposition of calcium carbonate. In summary, about 51.8 wt.% of catalyst is obtained after the decarbonation process. The data of the natural quail eggshell residue is in the same range compared with X-ray fluorescence data and it is similar to those shown for limestone in previous research [25, 38].

3.1.5. CO_2-TPD Analysis. CO_2-TPD profile was analyzed to evaluate the basicity strength of the calcined quail eggshell (Figure 2(c)). The CO_2-TPD presents two desorption peaks. The first one located between 100 and 190°C is attributed to the presence of small amount of weak basic sites. The second one, more intense, presents a maximum centered at 565°C. The calcined quail eggshell shows an amount of CO_2 adsorbed of 17.43 $mmol{\cdot}g^{-1}$, where 2.15 $mmol{\cdot}g^{-1}$ of CO_2 comes from weak basic sites and 15.27 $mmol{\cdot}g^{-1}$ of CO_2

comes from strong basic sites. These values are close to the theoretical CO_2 adsorption which is equal to 17.82 mmol·g^{-1}, which is in accordance with what was shown in X-ray fluorescence (Table 3) and TG/TGA analysis (Figure 2(b)). The desorption of CO_2 at high temperature confirms the existence of strong basic sites on CaO surface, making it a potential catalyst in the transesterification reaction for the biodiesel production [39].

3.1.6. X-Ray Photoelectronic Spectroscopy (XPS). In order to evaluate the surface composition of the natural quail eggshell and calcined quail eggshell, XPS measurements were carried out. Supplementary Material Table S3 compiles the binding energy values (in eV) and the atomic concentration (in wt.%) of each analyzed element. Both Ca $2p_{3/2}$ and Mg $2p_{3/2}$ core level spectra show a contribution located at 347.4 and 89.3 eV, respectively, ascribed to the presence of Ca^{2+} and Mg^{2+} in the form of carbonate. C 1s core level spectrum of the natural quail eggshell presents three contributions attributed to the adventitious carbon and organic matter (284.8 eV), C=O, C-N, and C-S about 287.3 eV, assigned to proteins residues such as amino acids and disulfide groups, and carbonate species at 290.0 eV, respectively. O 1s core level spectrum shows a unique contribution about 531.7 eV corresponds to the oxygen species in the form of carbonate. N 1s core level spectrum also exhibits a band about 399.2 eV attributed to amine groups, while S 2p core level spectrum presents two contributions located at 168.2 and 162.5 eV, ascribed to sulfate and sulfide species, respectively. Finally, P $2p_{3/2}$ core level spectrum exhibits a contribution about 133.8 and 133.6 eV in the form of phosphate species (Supplementary Material Table S3). The presence of the band located in the N 1s, S $2p_{3/2}$, and P $2p_{3/2}$ core level is attributed to the existence of proteins residues in the form of amino acids and phospholipid species on the surface of the natural quail eggshell.

After the thermal activation, C 1s core level spectrum shows how the signals attributed to the organic matter and carbonate species suffer a significant decrease. In the same way, the contribution of both N 1s and S $2p_{3/2}$ also disappears after calcination step. This fact provokes an increase of the other atomic concentrations. In addition, both Ca $2p_{3/2}$ in Figure 2(d) and Mg $2p_{3/2}$ suffer a shift at lower binding energy that suggests the formation of their respective oxide species.

3.1.7. Fourier Transform Infrared Spectroscopy Analysis (FTIR). Figures 3(a) and 3(b) show the FTIR spectra for natural quail eggshell and calcined quail eggshell. The spectrum of natural quail eggshell in Figure 3(a) shows the presence of the out-of-plane bending, the asymmetric stretching, and the in-plane bending modes of the carbonate groups, characteristic of natural dolomite, located at 869 cm^{-1}, 1426 cm^{-1}, and 714 cm^{-1}, respectively. Besides the internal modes, the combination of the previous bending modes has also been observed at 1801 cm^{-1} and 2522 cm^{-1}. Finally, the band located at 3444 cm^{-1} has been attributed to H-bonded water of the humidity [25, 38, 40]. Moreover, a band about 2900 cm^{-1} appears assigned to alkyl C-H stretch due to the organic matter of the quail eggshell.

After the thermal treatment of quail eggshell in Figure 3(b) a new hydroxyl band appears about 3637 cm^{-1}, which can be assigned to OH groups of calcium [25]. The bands located at 1647 cm^{-1} and 1454 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of O-C-O bonds of unidentate carbonate at the surface of the calcium oxide. The band at 1050 cm^{-1} also arises from these carbonates groups. The band centered at 3454 cm^{-1} is assigned to H-bonded water [25, 41].

3.1.8. Scanning Electron Microscopy Analysis (SEM). Figures 4(a) and 4(b) show the SEM micrographs of natural quail eggshell and calcined quail eggshell. The SEM micrograph displays that natural quail eggshell has structure of irregular and heterogeneous distribution of particle sizes ($CaCO_3$ and organic matter), while the SEM micrograph of calcined quail eggshell exhibits particles with lower particle size and more homogeneous distribution probably due to exothermic process that takes place in the decarbonation step, as was indicated previously in the XRD data (Figure 1(a)).

3.1.9. N_2 Adsorption-Desorption at −196°C and Distribution Particle Size Analysis. The textural properties of both natural quail eggshell and calcined quail eggshell are summarized in Supplementary Material Table S4. The textural properties reveal that both precursor and catalyst lack porosity. Nonetheless, after the activation process, S_{BET} increases slightly due to the porosity generated between particles of a lower size as revealed by the XRD in Figure 2(a) and the SEM micrographs in Figures 4(a) and 4(b).

Figures 3(c) and 3(d) display the grain-size distribution of natural quail eggshell and calcined quail eggshell. The particle size was estimated as statistic average. The natural quail eggshell exhibits a wide range of grain-size distribution with a maximum of 242 μm. After the thermal treatment, the grain-size is narrower and diminishes, displaying a maximum of 9 μm due to the decomposition of the calcium carbonate by the removal of CO_2 is a exothermic process, leading to particles with a lower grain-size, confirming data shown in XRD, SEM micrographs, and the textural properties.

3.2. Experimental Design Analysis. A set of experiments were carried out to determine the influence of the variables (X_{MR}, X_{CAT}, and X_{TIME}) on the transesterification reaction of sunflower oil with methanol for the production of biodiesel production. The factors were preestablished with the intention of obtaining an optimum catalytic activity for catalyst studied. The optimization experiments were performed according to a matrix of the experimental designs $3^{**}(k\text{-}p)$ and Box-Behnken 3^2 with a central point in triplicate (Table 2). The dependent variable, Y_{FAME}, corresponds to the conversion of triglycerides into methyl esters. The parameters evaluated were the sunflower oil/methanol molar ratio (X_{MR}), catalyst loading (X_{CAT}), and reaction time (X_{TIME}). The stirring rate was set at 1000 rpm and the temperature was 60°C for all the experiments. Negative values on the scale correspond to lower values of the variable, while positive values represent higher values of the same, according to the parameters studied.

Table 2: Matrix of the experimental designs 3^{**} (k-p) and Box-Behnken. Data are presented as mean ± standard deviation, $n = 3$.

Run	Coded variables			Real variables			Response
	X_{MR}	X_{CAT}	X_{TIME}	X_{MR}	X_{CAT}	X_{TIME}	Y_{FAME}
1	−1	−1	0	1 : 9	2.0	2.5	87.88 ± 0.01
2	1	−1	0	1 : 12	2.0	2.5	88.16 ± 0.07
3	−1	1	0	1 : 9	3.0	2.5	91.18 ± 0.30
4	1	1	0	1 : 12	3.0	2.5	89.39 ± 0.02
5	−1	0	−1	1 : 9	2.5	2.0	88.61 ± 0.04
6	1	0	−1	1 : 12	2.5	2.0	86.72 ± 0.13
7	−1	0	1	1 : 9	2.5	3.0	91.67 ± 0.02
8	1	0	1	1 : 12	2.5	3.0	98.35 ± 0.02
9	0	−1	−1	1 : 10.5	2.0	2.0	99.00 ± 0.20
10	0	1	−1	1 : 10.5	3.0	2.0	72.53 ± 0.40
11	0	−1	1	1 : 10.5	2.0	3.0	87.17 ± 0.03
12	0	1	1	1 : 10.5	3.0	3.0	88.29 ± 0.01
13	0	0	0	1 : 10.5	2.5	2.5	76.74 ± 0.09
14	0	0	0	1 : 10.5	2.5	2.5	76.80 ± 0.14
15	0	0	0	1 : 10.5	2.5	2.5	75.56 ± 0.90

The investigation of the model was performed by analysis of variance (ANOVA; Table 3). The calculated F-value (35.02) was higher than that shown for F tabulated (4.77). Equations (3) represented the linear model and quadratic model for the studied variables (X_{MR}, X_{CAT}, and X_{TIME}), considering all the regression coefficients for 95% confidence.

$$\begin{aligned} Y_{FAME} &= 91.62 + 0.41 * X_{MR} - 0.29 * X_{MR}^{2} - 3.65 \\ &\quad * X_{CAT} - 2.18 * X_{CAT}^{2} - 0.74 \\ &= 91.62 + 0.41 * X_{MR} - 0.29 * X_{MR}^{2} + 3.68 \\ &\quad * X_{TIME} \\ &= 91.62 - 3.65 * X_{CAT} - 2.18 * X_{CAT}^{2} + 3.68 \\ &\quad * X_{TIME}. \end{aligned} \tag{3}$$

A response surface shown in Figures 5(a), 5(b), and 5(c) for a calcined quail eggshell model shows that, for low concentrations of catalyst, the conversion of biodiesel decreased. In addition, Figure 5 also indicates that the significant factor is X_{MR}, X_{CAT}, and X_{TIME}, which has a positive effect on transesterification reaction at a confidence level of 95%, as noted in the response surface plot. This fact is attributed to the fact that an increase of the catalyst concentration leads to higher amount of available basic sites, which are the active phase in the transesterification reaction, leading to higher conversions to biodiesel. Another key factor is the alcohol : acid ratio. Thus, an excess of methanol leads to the chemical equilibrium shifted toward the products favoring the formation of higher proportions of methyl esters and subsequently increasing the conversion values. Nonetheless the use of higher proportion of methanol also has an adverse effect in the separation process due to the existence of gravity between the phases formed and glycerin ester, increasing their miscibility and promoting the displacement of the balance in the opposite direction toward the formation of mono-, di-, and triglycerides, thereby decreasing the production of methyl esters.

The maximum Y_{FAME} value was 99.99 ± 0.20 wt.%, which was obtained in the central point of the factorial design, namely, the following reaction conditions: X_{MR} (1 : 10.5), X_{CAT} (2 wt.%), temperature (60°C), and X_{TIME} (2 h). Considering the best experimental transesterification reaction conditions, it can be concluded that 1 kg of quail eggshell leads to the obtaining of 82.5 kg of biodiesel production.

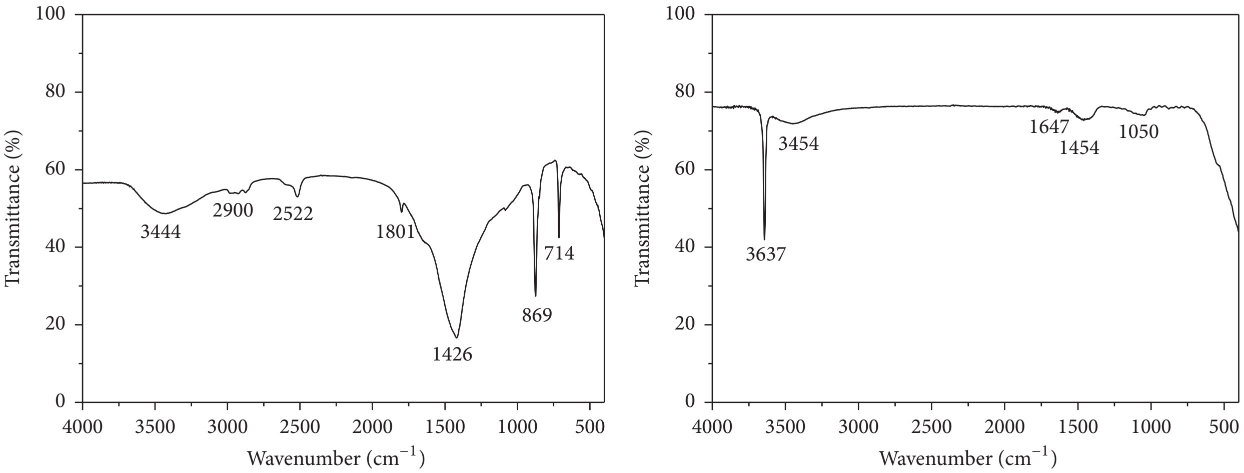
The mechanism of interaction between heterogeneous catalysts based on calcium oxide was described by [42]. In the 1st stage of the transesterification reaction, methyl alcohol reacts with calcium oxide to form the methoxide anion, and then the 2nd stage is the anion methoxide attacking the carbon of the carbonyl group present in triglycerides (refined vegetable oil sunflower) for formation of an intermediate carbonyl group.

Therefore, in the 3rd stage alkoxides groups present in the intermediate carbonyl formed by $CaO\text{-}H^{+}$ produced CaO and another carbonyl intermediate group and in the 4th step the intermediate group is reorganized and form methyl esters (organic phase/biodiesel) and diglycerides. Other authors have pointed out that calcium diglyceroxide $Ca(C_3H_7O_3)_2$ is the active site in the transesterification reaction to obtain biodiesel when CaO is used as solid basic catalyst. This species is formed by the interaction between Ca^{2+} cations and glycerol obtained as by-product. The oxygen anion of the diglyceroxide can abstract H atoms from the OH in methanol for hydrogen bond, yielding a surface methoxide anion. Later, nucleophilic MeO^{-} species attack the carbonyl groups of the triglyceride to form the diglyceride molecule. This process takes place sequentially to form the monoglyceride and glycerol species [43].

The interesting catalytic behavior of the CaO catalyst obtained from a natural calcium source, such as quail eggshell, by a thermal treatment can be attributed to the decrease of both particle and crystal size in the calcination step which supposes an increase of the available basic sites, as indicated in the CO_2-TPD profile TPD (Figure 2(b)), which are necessary for the transesterification reaction. In this sense, previous researches have established that the choosing of the calcium source is a key parameter in the catalytic behavior in the transesterification reaction of triglycerides with short chain alcohols, such as methanol or ethanol [16]. Thus, the decomposition of carbonate precursors has shown the highest conversion values, while the use of calcium nitrate as precursor leads to lower dispersion of the basic sites and subsequent lower conversion values.

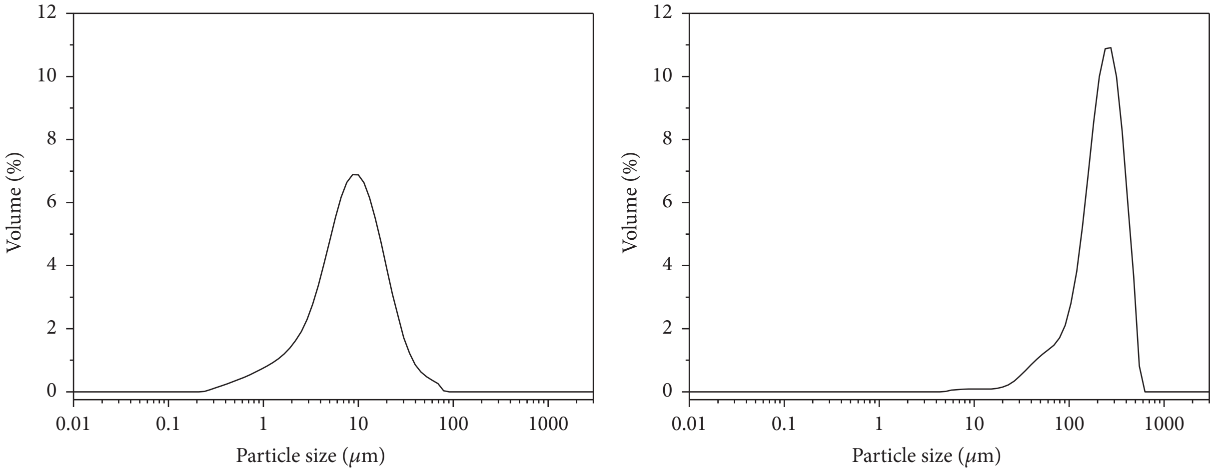
Table 4 compares the Y_{FAME} obtained in this study with the other ones from the literature. Data reported by other authors show that it was not necessary to use extreme transesterification reaction conditions (X_{MR} and X_{CAT}) to obtain Y_{FAME} reported in the literature.

3.3. Characterization of Biodiesel Sunflower. Biodiesel from sunflower oil was analyzed according to the requirements for the standard EN 14214 [35] (acid value, density at 20°C,



(a) Natural quail eggshell

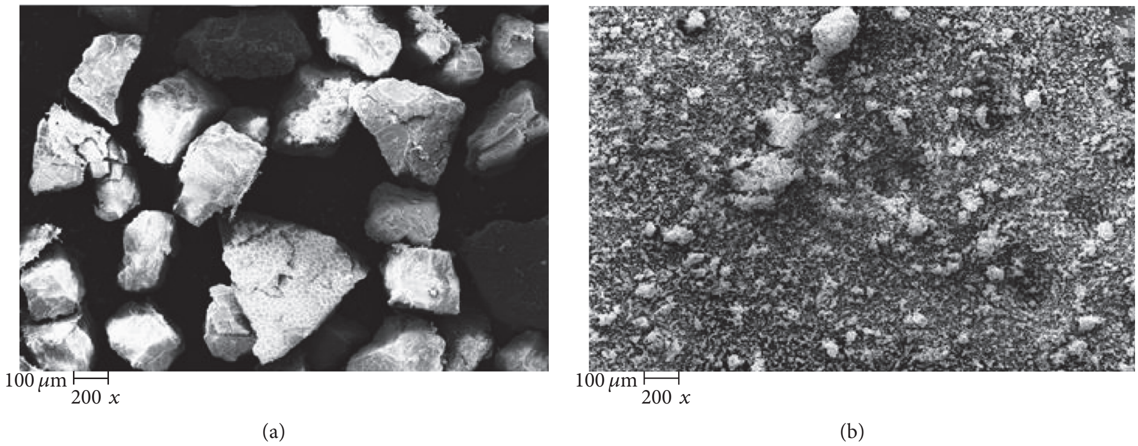
(b) Calcined quail eggshell



(c) Natural quail eggshell

(d) Calcined quail eggshell

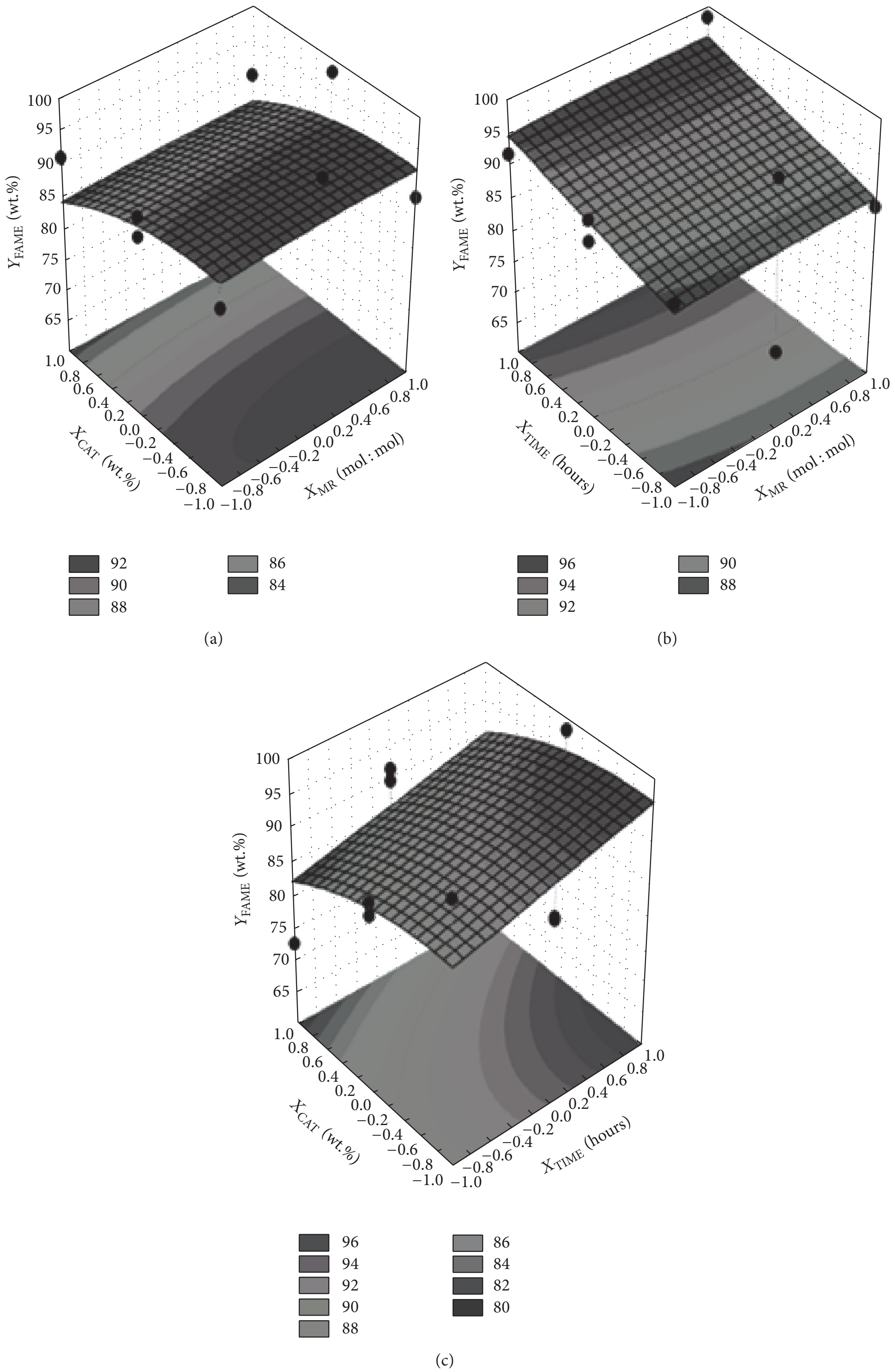
Figure 3: FTIR spectra ((a) and (b)) and distribution particle sizes analysis ((c) and (d)) of natural and calcined quail eggshell.



(a)

(b)

Figure 4: SEM images for natural quail eggshell ((a) and (b)) and calcined quail eggshell, with an increase of 200x.



(a)

(b)

(c)

Figure 5: Response surface for model of quail eggshell calcined.

Table 3: ANOVA, analysis of variance, for the conversion of sunflower oil to biodiesel by empirical model of quail eggshell calcined at 900°C for 3 h.

Source of variation	Sum of squares	Degrees of freedom	Mean square	F-value
Regression	273.85223	4	68.46305	35.02
Residual	9.77317	5	1.954634	
Total	283.6254	9		$F_{9,5} = 4.77$

Table 4: Comparison of biodiesel production using different wastes eggshell catalysts in transesterification reaction.

Oil/alcohol	Material	X_{MR}	X_{CAT}	Y_{FAME}	Reference
Sunflower oil/methanol	Quail eggshell	1 : 10.5	2	99.00	This work
Sunflower oil/methanol	Eggshell	1 : 9	3	97.75	[25]
Soybean oil/methanol	Eggshell	1 : 9	3	95.00	[40]
Palm kernel oil/methanol	Eggshell	1 : 18	15	96.7	[26]
Palm olein oil/methanol	Eggshell	1 : 12	10	>90.00	[38]
Soybean oil/methanol	Fly ash and eggshell	1 : 6.9	1	96.97	[27]
Waste frying oil	Eggshell	1 : 12	5	94.52	[28]

Table 5: Properties of sunflower biodiesel. Data are presented as mean ± standard deviation, $n = 3$.

Property	Biodiesel from sunflower	EN 14214 standard
Acid value (mg KOH/g)	0.40 ± 0.09	0.5
Density (20°C, kg·m^{-3})	882 ± 1.30	860–900
Kinematic viscosity (40°C, mm^2/s)	4.49 ± 0.04	3.50–5.00
Water content (kg·m^{-3})	101 ± 8	500
Y_{FAME} (wt.%)	99.00 ± 0.20	96.50

kinematic viscosity at 40°C, water, magnesium and calcium content, and conversion of sunflower oils to biodiesel) which are shown in Table 5.

3.4. Reuse and Leaching of Catalyst. The reuse and stability of solid catalysts have an important role in determining the economic application for biodiesel production on a large industrial scale. The reuse of the catalyst was evaluated considering the optimized reaction conditions X_{MR} (1 : 10.5), X_{CAT} (2 wt.%), X_{TIME} (2 h), and temperature (60°C).

The decrease of Y_{FAME} with reuse of the catalyst in the transesterification reaction was demonstrated for 3 cycles. The calcined quail eggshell as heterogeneous catalyst showed only a slight decrease in the catalytic activity after each reuse which can be attributed to the washing and sample handling between each cycle. Thus, it is observed that the conversion of Y_{FAME} decreases to 99.00 ± 0.02 wt.% (1st run), 86.14 ± 0.02 wt.% (2nd run), and 78.26 ± 0.04 wt.% (3rd run) of Y_{FAME}. In this study the decrease in the biodiesel production was similar to the results described by [23] for calcined dolomite. As was previously indicated, CaO species can be solubilized in the glycerol obtained as by-product to form calcium diglyceroxide species, which is the active phase in the biodiesel production. This phase is more soluble than CaO under the reaction conditions used in the transesterification reaction with solid basic catalysts. In any case, Ca^{2+} concentration is significantly lower than that observed for homogenous catalysis [44]. In addition, the solid CaO can be reutilized for several runs, so it seems clearly that CaO obtained from quail eggshell is a robust catalyst in the transesterification reaction.

4. Conclusion

The calcined quail eggshell used as a material promise biodiesel production by transesterification reaction using sunflower oil refined with methanol. The material process thermal treatment (900°C for 3 h) produces small CaO particles which show high basicity and they are responsible for the catalytic activity in the transesterification reaction. The optimization of the reaction parameters led to a maximum biodiesel production of 99.00 ± 0.02 wt.% obtained under the next conditions: X_{MR} (1 : 10.5), X_{CAT} (2 wt.%), X_{TIME} (2 h), magnetic stirring (1000 rpm), and temperature (60°C). Considering the best experimental conditions, it can be concluded that 1 kg of quail eggshell leads to obtaining of 82.5 kg of biodiesel. The reuse of the CaO catalyst under the best reaction parameters revealed a small, but progressive, loss of the biodiesel production from 99.00% to 78.26% after the third cycle by the loss of active sites by formation of carbonaceous deposits and/or the loss of sample in the washing or recalcination step between each cycle.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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