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Biodiesel production from cotton oil using heterogeneous CaO catalysts from eggshells prepared at different calcination temperatures

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Keywords: biodiesel; calcination temperature; cotton oil; eggshell.

Abstract: Biodiesel is a fuel from vegetable oil or animal fat, and is a promising substitute for petroleum-derived diesel. Transesterification is the most widely used method in biodiesel production. Eggshell is rich in calcium carbonate (CaCO_3), and when it is subjected to heat treatment it results in calcium oxide (CaO). CaO from eggshells was prepared at different calcination temperatures, and characterized by X-ray diffraction, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The obtained CaO was used as a catalyst. All catalysts showed good stability and excellent morphology for biodiesel synthesis. Catalytic activity was evaluated by the methyl transesterification reaction of cotton oil for 3 h, 9:1 methanol:oil molar ratio, 3 wt% (catalyst/oil weight ratio) catalyst and 60°C. Biodiesels showed an ester content of 97.83%, 97.23% and 98.08%, obtained from calcined eggshell at 800°C, 900°C and 1000°C, respectively. Biodiesel quality was affected by the acidity of the cation exchange resin. The kinematic viscosity of biodiesel was in accordance with specification, except for the biodiesel obtained from the calcined catalyst at 1000°C. The CaO from eggshells obtained at different calcination temperatures is promising for biodiesel synthesis.

Abbreviations

¹ H NMR	proton nuclear magnetic resonance
ABNT	Brazilian Association for Technical Standards
ASTM	American Society for Testing and Materials
BC800	biodiesel obtained from eggshell calcined at 800°C
BC900	biodiesel obtained from eggshell calcined at 900°C
BC1000	biodiesel obtained from eggshell calcined at 1000°C
C800	eggshell calcined at 800°C
C900	eggshell calcined at 900°C
C1000	eggshell calcined at 1000°C
DTG	differential thermal analysis
NBR	Brazilian norm
SEM	scanning electron microscopy
TGA	thermogravimetric analysis

1 Introduction

Biodiesel has been highlighted as an alternative to fossil fuel due to the global crisis and environmental problems [1]. Biodiesel is usually obtained by the transesterification method, which consists of a reaction between triglyceride and alcohol and a catalyst. Homogeneous catalysts are most commonly used, even though they are toxic, highly flammable and corrosive [2]. In addition, they cause technological problems [3] resulting from the significant generation of effluents and there is difficulty in removing catalyst from biodiesel [4].

Heterogeneous catalysts, such as alkaline earth metal oxides, heteropolyacids and zeolites have been investigated for biodiesel production. Among the alkaline earth metal oxides is calcium oxide (CaO) [5].

CaO is a promising catalyst in transesterification for biodiesel production due to low cost, easy preparation, availability, and non-corrosiveness [6], and because of its high basic resistance, it causes less environmental impact [7]. Therefore, this solid catalyst is frequently used due to

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its long life usage, high catalytic activity and the fact that it requires only moderate conditions for the reaction to occur [8]. CaO can be obtained from a variety of sources such as calcite, crab shells, oyster shells, snail shells, bones, ostrich eggs and chicken eggs [9].

Researchers have recently developed studies on CaO from eggshell, which is considered a green catalyst, and it has been shown to be promising in biodiesel production [10].

The feedstocks used for biodiesel production using heterogeneous catalysts with CaO from eggshell were soybean oil, canola oil, jatropha oil, beef tallow, palm oil, palm olein oil, karanja oil and frying oil [5, 11–22]. All feedstocks obtained an excellent biodiesel yield. It was noted that there are few works about the production of cotton oil biodiesel using CaO as a catalyst [23] which produced biodiesel from used cotton oil.

According to the National Agency of Petroleum, Natural Gas and Biofuels [24], cotton oil is one of the most used feedstocks for biodiesel produced in Brazil. Cotton oil comes from cottonseeds, and is a byproduct from the cotton ginning process to obtain fiber [25]. Therefore, the usage of these feedstocks also generates more income from other byproducts obtained from the oil processing. Besides, according to the National Supply Company [26], cotton is the second largest oleaginous produced in Brazil. In the present work, the production of cotton oil biodiesel using CaO from eggshell prepared at different calcination temperatures was developed.

2 Materials and methods

2.1 Materials

Refined cotton oil (Saúde, Barueri, São Paulo, Brazil) was obtained from a local supermarket. Methanol (99.8%, Neon, São Paulo, São Paulo, Brazil) and white eggshells were collected from domestic residences (Sooretama, Espírito Santo, Brazil).

2.2 Catalysts preparation

The eggshells were washed in distilled water to remove impurities and all organic matter eventually adhered to them. After washing, the eggshells were dried in an oven (Quimis, Diadema, São Paulo, Brazil) at 105°C for 2 h. Then, the eggshells were crushed with a mortar and pestle, and a grinder (Cadence, Caxias do Sul, Santa Catarina, Brazil) was used to turn them into a fine powder. The crushed material was dry sifted (Bertel, Laranjeiras, Caieiras, São Paulo, Brazil)

and subjected to vibration for 5 min in a set of sieves with apertures of 16, 20, 28, and 35 mesh. The sieved samples were placed in a rectangular alumina (Jomon, Viamão, Rio Grande do Sul, Brazil) tray and calcined in an oven (Vulcan, 3-550PD model, Dentsply, Distrito Industrial, Pirassununga, São Paulo, Brazil) for 2 h (rate of 5°C/min). The catalysts were eggshell calcined at 800°C (C800), 900°C (C900) and 1000°C (C1000).

After calcination, the catalysts were stored in flasks and placed on a desiccator to avoid a reaction with moisture and the atmospheric air.

2.3 Catalyst characterization

X-ray diffraction was used to identify the crystalline compounds. The samples were analyzed in a Shimadzu diffractometer XRD LabX 6000 (Shimadzu, Nakagyo-Ku, Kyoto, Japan), using Cu-K α radiation ($\lambda = 1.5406$ Å), operating at 30 kV and 40 mA, and with scanning steps at 3° min⁻¹.

The crystallite size D of CaO was estimated from the Scherrer equation, by Eq. (1) [27]:

$$D = \frac{k\lambda}{\beta_{hkl} \cos\theta} \quad (1)$$

where D is the crystallite size, β_{hkl} is the broadening of the hkl diffraction peak measured at half of its maximum intensity (in radians), θ is the Bragg's angle (°), k is the shape factor ($k = 0.9$), and λ is the wavelength of Cu-K α radiation.

Evaluation of the thermal stability was performed by thermogravimetry. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA 50 thermobalance (Shimadzu, Nakagyo-Ku, Kyoto, Japan), at a heating rate of 10°C/min up to 1000°C under an argon flow rate of 50 ml/min.

Morphology was verified scanning electron microscopy (SEM). The samples were covered with a thin layer of gold using a cathodic sputtering coater and the images of microstructured samples on the surface were visualized through an electronic scan from a Shimadzu microscope (Shimadzu, Nakagyo-Ku, Kyoto, Japan).

2.4 Biodiesel synthesis

The transesterification reaction was performed using a 500 ml jacketed reactor (Marconi, MA 502/D model, Algodoal, Piracicaba, São Paulo, Brazil), equipped with a mechanical stirrer, with a condensation system and a thermostat water circulator to keep the temperature constant. CaO and methanol were mechanically stirred for 1.5 h at room temperature. The resulting calcium methoxide was added to the reactor containing cotton oil heated at 60°C. The reactor was operated under constant stirring for 3 h, using a methanol:oil molar ratio of 9:1 and 3 wt% (catalyst/oil weight ratio). After the reaction, the catalyst was separated by centrifugation for 30 min at 3200 rpm. The reaction mixture was allowed to settle in by a separation funnel for 18 h. The desired product from the upper phase was purified with cation exchange resin and then placed in a rotary evaporator to remove methanol.

2.5 Biodiesel characterization

The composition of biodiesel was determined by gas chromatography coupled to mass spectrometry, using a selective mass detector, (Shimadzu, QP-PLUS-2010 model, Nakagyo-Ku, Kyoto, Japan). The chromatographic column used was the Rtx-5MS silica capillary type with stationary phase (30 m × 0.25 mm × 0.25 μm), using helium as the carrier gas. The optimized conditions were described by Pardo et al. [28]. The injector temperature was 250°C, the helium flow was 1 ml/min, the source temperature was 200°C, and the interface temperature was 250°C. The determination of the methyl esters was performed by comparison with the mass spectra of the Wiley 7 equipment library.

The chemical composition of biodiesel was performed by analysis in gas equipped with a flame ionization detector using GC-2010 Plus (Shimadzu, Nakagyo-Ku, Kyoto, Japan). The methodology was adapted from [28].

Cotton oil and biodiesels, 20 mg of each sample, were analyzed by proton nuclear magnetic resonance (¹H NMR) (using a Varian® spectrometer, VNMRs 400 model, Santa Clara, CA, USA), operating with a magnetic field of 9.4 T, using a 5 mm probe Broad-Band 1H/19F/X at 25°C. The solvent used in the analyses was deuterated chloroform (CDCl₃) (Sigma-Aldrich, Jurubatuba, São Paulo, Brazil).

Viscosity [Brazilian Association for Technical Standards (ABNT) method NBR 10441], acidity index (ABNT method NBR 11115), moisture content (Shimadzu, MOC – 63U model, Nakagyo-Ku, Kyoto, Japan), specific mass (Anton Paar digital densimeter,

DMA 4500M model, Vila Mariana, São Paulo, Brazil) and calcium content (complexometric titration), adapted from [29], were also determined.

3 Results and discussion

3.1 Characterization of the catalyst

Eggshells *in natura* and calcinated were analyzed by X-ray diffractograms from 20° to 80° according to Figure 1.

A diffractogram obtained from *in natura* eggshells (Figure 1A) showed the predominance of calcium carbonate (CaCO₃) in calcite form. Diffraction peaks of CaCO₃ present in *in natura* eggshells were identified at 2θ = 23.22°, 29.6°, 36.16°, 39.62°, 43.36°, 47.72°, 48.72°, 48.72°, 56.76° and 57.62°, in accordance to the Joint Committee on Powder Diffraction Standards files. It was observed that the highest intensity peak of diffraction occurred in 2θ = 29.6°.

After calcination, the CaCO₃ present in the eggshell was transformed in CaO as shown in Figures 1B–D. The diffraction peak of CaO was identified at 2θ (C800) = 32.3°,

Figure 1: X-ray diffractogram of (A) *in natura* eggshell, (B) eggshell calcined at 800°C, (C) eggshell calcined at 900°C and (D) eggshell calcined at 1000°C.

37.44°, 53.94°, 64.24°, 67.46° and 79.82°; 2θ (C900) = 32.24°, 37.4°, 53.9°, 64.2°, 67.42° and 79.82°; and 2θ (C1000) = 32.22°, 37.38°, 53.88°, 64.18°, 67.4° and 79.68°. The highest intensity diffraction peak was found at 2θ = 37.44°, 37.4° and 37.4°, respectively, for C800, C900 and C1000. These results were similar to those reported by Wei et al. [11].

The presence of weak peaks between 30° and 40° (Figures 1B and C) corresponds to calcium hydroxide [Ca(OH)₂], which indicates that CaO absorbed some moisture from the air and this can be confirmed by the low mass loss verified by TGA (Figures 4B and C), which was already seen in [11, 30].

The increase of calcination temperature originates more intense and sharp peaks, which signifies an increase in the crystallinity of the material and elimination of CaCO₃ [31]. The crystallite size of the CaO was not significantly affected at a calcination temperature of 800–900°C. An increase in the crystallite size was observed at a calcination temperature of 1000°C, as shown in Figure 2. This was observed by Mguni et al. [32] who reported that this could be due to sintering at this high temperature.

The morphology of *in natura* and calcined eggshells was investigated by SEM using a magnification of 500× and 2000× as illustrated in Figure 3. *In natura* eggshells showed an irregular surface with heterogeneous particle distribution and no porous structure defined, as observed in Figure 3A. This morphology is similar to the one described by [11]. After heat treatment, eggshells showed irregular changes in the crystal structure to the interconnected skeleton, as reported by [33]. It was still possible to observe that particle distribution is more homogeneous and the presence of larger porosities was found in calcined eggshells as shown in Figures 3D, F and G. CaO obtained from the eggshell calcined at 800°C was rod-shaped. With

the increase in temperature to 900°C, it was observed that the particles become spherical in shape. The CaO obtained at 1000°C also showed a spherical shape. It is still possible to observe the reduction of CaO particles with increasing temperature, due to the calcination that promotes the conversion of CaCO₃, a compact and dense material in CaO, which is a porous and more reactive material. The porosity of CaO is related to the release of CO₂ from the internal structure, therefore calcination occurs by reducing the particle volume, which allows the appearance of interstices also known as pores [34].

There was an agglomeration of particles of CaO obtained at 1000°C, which indicates that sintering of the material had occurred. The necks that develop between the adjacent grains continue to grow during sintering, so that the distance between grain centers is reduced, and they can reduce the surface area and porosity [35].

The increase of the calcination temperature caused coalescence of the particles, which may have reduced the specific area [34].

The TGA curve and differential thermal analysis (DTG) of *in natura* eggshells, Figure 4A, showed two regions of mass loss. In the first event, the material showed a mass loss of 1.95% in a range of 30–400°C, related to the loss of volatile materials such as water and organic matter. The mass loss obtained in the first event is lower than that found by Correia [36], who reported that mass loss in *in natura* eggshells was 4.2%. This difference was because of the removal of the membrane adhered to egg shell, which already consists of carbohydrates and proteins, i.e. are rich in organic matter [37]. In the second event, mass loss occurred between 400°C and 800°C, specifically at 782.3°C, in which there was a mass loss of 42.88%. This loss is related to the CO₂ released from CaCO₃ decomposition. This result was similarly found by Correia [36]. The total of *in natura* eggshell mass loss was 44.83%.

The amount of CaCO₃ was calculated from the loss of CO₂ from the *in natura* eggshell TGA curve by Eq. (2) [38]:

$$\% \text{CaCO}_3 = \% m_{\text{CO}_2} \frac{MM_{\text{CaCO}_3}}{MM_{\text{CO}_2}} \quad (2)$$

In this equation, $\% m_{\text{CO}_2}$ is the mass loss related to the release of CO₂ (%), MM_{CaCO_3} is the molar mass of CaCO₃ (g/mol) and MM_{CO_2} is the molar mass of CaCO₃ (g/mol).

The CaCO₃ content in *in natura* eggshell was 97.52%. This value was similar to the one reported by Correia et al. [17].

The thermal stabilities of C800, C900 and C1000 evaluated by TGA and DTG are represented in Figure 4, with a total mass loss of 4.76%, 7.64% and 1.73%, respectively.

Figure 2: Crystallite size of the eggshell calcined at 800°C, 900°C and 1000°C.

Figure 3: Scanning electron microscopy (SEM) image of *in natura* eggshell expanded (A) 500× and (B) 2000×. SEM image of eggshell calcined at 800°C expanded (C) 500× and (D) 2000×. SEM image of eggshell calcined at 900°C expanded (E) 500× and (F) 2000×. SEM image of eggshell calcined at 800°C expanded (G) 500× and (H) 2000×.

Figure 4: Thermogravimetric analysis (TGA) of (A) *in natura* eggshell, (B) eggshell calcined at 800°C, (C) eggshell calcined at 900°C and (D) eggshell calcined at 1000°C.

Figure 5: Chemical composition of methyl esters in prepared cottonseed oil using calcium oxide at different temperatures, areas obtained by chromatographic analysis in gas chromatography with flame ionization detector (GC-FID).

This loss is attributed to the decomposition of $\text{Ca}(\text{OH})_2$ and CaCO_3 . All catalysts had good stability. These curves were similarly found by Sharma et al. [6].

3.2 Biodiesel synthesis

Cotton oil biodiesel chemical composition is illustrated in Figure 5. It was observed that cotton oil biodiesel showed a predominance of linoleate methyl ester. Methyl ester levels for different biodiesel were close and above the minimum acceptable by American Society for Testing and Materials (ASTM) D6751 specification.

Table 1 shows a comparison between cotton oil biodiesel obtained from this work and that in literature using CaO as a catalyst obtained from eggshells.

Note that in this work, all biodiesels presented an ester content higher than [5] and similar to [17]. Free glycerol

Table 1: Comparison between biodiesel of oil obtained in this work and literature.

Oil	C	M.R.	T (°C)	t (h)	%C (wt%)	A.I. (rpm)	E (%)	Reference
Palm	CaO	18:1	–	–	15	–	96.7	[5]
Sunflower	CaO	9:1	60	3	3	1000	97.75	[17]
Cotton	C800	9:1	60	3	3	–	97.83	This work
Cotton	C900	9:1	60	3	3	–	97.23	This work
Cotton	C1000	9:1	60	3	3	–	98.03	This work

%C, Concentration of catalyst; A.I., agitation intensity; C, catalyst; C800, CaO obtained from calcined eggshell at 800°C; C900, CaO obtained from calcined eggshell at 900°C; C1000, CaO obtained from calcined eggshell at 1000°C; E, ester content; M.R., molar ratio alcohol:oil; t, reaction time; T, reaction temperature.

Figure 6: Proton nuclear magnetic resonance (^1H -NMR) spectrum of commercial cotton oil used in transesterification reactions. (A) 5.39–5.24 ppm: $\text{HC}=\text{CH} + \text{CH}-\text{O}$; (B) 4.30–4.11 ppm: CH_2-O ; (C) 2.76–2.75 ppm: $\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}$; (D) 2.31–2.28 ppm: $\text{CH}_2-\text{C}=\text{O}$; (E) 2.06–1.99 ppm: $\text{CH}_2-\text{C}=\text{C}$; (F) 1.64–1.58 ppm: $\text{CH}_2-\text{C}-\text{C}=\text{O}$; (G) 1.29–1.24 ppm: $-\text{CH}_2-$; (H) 0.89–0.85 ppm: CH_3 .

Figure 7: Proton nuclear magnetic resonance (^1H -NMR) spectrum of biodiesel sample obtained from cotton oil using calcium oxide. (A) 5.37–5.31 ppm: $\text{HC}=\text{CH}$; (B) 3.61 ppm: CH_3-O ; (C) 2.77–2.74 ppm: $\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}$; (D) 2.31–2.27 ppm: $\text{CH}_2-\text{C}=\text{O}$; (E) 2.06–1.99 ppm: $\text{CH}_2-\text{C}=\text{C}$; (F) 1.62–1.59 ppm: $\text{CH}_2-\text{C}-\text{C}=\text{O}$; (G) 1.30–1.24 ppm: $-\text{CH}_2-$; (H) 0.89–0.85 ppm: CH_3 .

Figure 8: Glycerin content in the biodiesels.

content in biodiesel was also close and relatively small, as shown in Figure 6. The low glycerol content is due to use of the resin for biodiesel purifications, which had a strong acidic character, since resin is efficient in removal of free glycerin [39]. According to Norma ASTM D6751, this glycerol content is still above the minimum acceptable by specification.

In order to confirm the results obtained through chromatographic analyses of cotton oil and purified biodiesel, samples were evaluated by ^1H NMR, illustrated in Figures 7 and 8.

In the cotton oil spectrum, the signals related to hydrogens of triacylglycerides were observed. The signals

Figure 9: Calcium content in crude biodiesel.

4.30–4.11 ppm (B), related to hydrogens of the $\text{CH}_2\text{-O}$ group present in triacylglycerides, do not appear in the biodiesel ^1H NMR spectrum. In reference to the spectrum, there was signal appearance in 3.61 ppm, referring to hydrogens of the OCH_3 group. In this way, it was possible to ratify the high purity of biodiesel samples [40].

3.3 Leaching of calcium in biodiesel

The calcium content for all crude biodiesel, as shown in Figure 9, is higher than the ASTM D6751 specification for calcium content in biodiesel.

It was observed that calcium contents were higher than the value reported in [41, 42]. The catalytic reaction is the result of the heterogeneous and homogeneous contributions. The heterogeneous contribution refers to a reaction that occurs in the surface of the catalyst and the homogeneous contributions refer to a reaction that involves the leached species [30, 41]. However, the homogeneous contribution is much smaller than the heterogeneous contribution when the catalyst loading is larger than 1 wt% (catalyst/oil weight ratio) of CaO [41]. For this reason, 3 wt% (catalyst/oil weight ratio) was used in this work.

A cloudy, white opaque and gelatinous aspect of crude biodiesel was evidence of the presence of calcium. This aspect is due to CaCO_3 formation [30].

3.4 Biodiesel characterization

Table 2 shows biodiesel physicochemical properties. All biodiesels showed a clear appearance and absence of impurities such as suspended materials, sediment or turbidity.

The biodiesel specific mass at 20°C ranged from 883 kg/m^3 to 895 kg/m^3 , thus meeting the ASTM D6751 requirements.

Table 2: Physical and chemical properties of different biodiesels.

Physicochemical properties	BC800	BC900	BC1000	ASTM specification
Aspect	Clean and free of impurities	Clean and free of impurities	Clean and free of impurities	–
Acid value (mg KOH/g)	3.65	15.92	2.74	0.5
Specific mass at 20°C (kg/m^3)	883	887	895	850–900
Kinematic viscosity at 40°C (mm^2/s)	4.66	5.72	7.52	3–6
Calcium + magnesium Content (mg/kg)	0	0	0	5

ASTM, American Society for Testing and Materials; BC800, biodiesel obtained from eggshell calcined at 800°C ; BC900, biodiesel obtained from eggshell calcined at 900°C ; BC1000, biodiesel obtained from eggshell calcined at 1000°C .

The acid values of different biodiesels are shown in Table 2. All biodiesels were above the ASTM D6751 specifications, due to the use of strong acidic resin in the purification process. Resin promotes the exchange of calcium ions, present in biodiesel, by the acid protons, present in functional groups of the resin; consequently, biodiesel has a high acid value. As shown in Table 2, biodiesels with higher acid values were those with high calcium content. Biodiesel obtained from eggshell calcined at 900°C (BC900) has calcium leached at 6009.54 ppm, after undergoing a through purification process with a higher resin acid value. In biodiesel obtained from eggshell calcined at 800°C (BC800) the acid value was close to that found by Alba-Rubio et al. [43], who found an acid value of 3.8 mg KOH/g. All biodiesels showed acid values higher than the 0.2 mg KOH/g reported in [43].

The biodiesel kinematic viscosity at 40°C obtained from C800 and C900 met the ASTM D6751 requirements. Biodiesel obtained from C1000 was above ASTM D6751 biodiesel specification, as Table 2 shows. It is believed that the high viscosity for biodiesel obtained from eggshell calcined at 1000°C (BC1000) is due to the presence of soaps in accordance with the report of [44].

The content of biodiesel calcium and magnesium met ASTM D6751 requirements. Therefore, biodiesel free from calcium and magnesium will not cause damage to the engine and will not clog injectors.

A solution to bypass the acidity is to use a resin that is less acidic and, as for viscosity, carry out removal of the soaps.

4 Conclusion

This work showed that CaO at different calcination temperatures can be successfully obtained from *in natura* eggshells and food industry residues.

In addition, all catalysts obtained presented excellent morphology and good stability. The ester biodiesel contents were similar. Since cotton oil was a promising raw material to be used in biodiesel production using CaO catalysts, originally from eggshells, all tested catalysts showed promise in the synthesis of biodiesel from cottonseed oil.

Although C1000 solubilized a smaller amount of Ca in the product, C800 is probably a better choice, since it is obtained with a much lower energy expenditure; it showed an excellent catalytic activity and the biodiesel obtained showed the best quality.

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