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Using discarded oyster shells to obtain biodiesel

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ABSTRACT

Objective: To evaluate the CaO made from oyster shell (*C. virginica*) as a heterogeneous catalyst in the transesterification of edible vegetable oil used for the production of biodiesel.

Design/methodology/approach: A completely randomized experimental design was used, which grouped 3 treatments with 3 repetitions, generating a total of 9 experimental units. The response variable was the performance of the transesterification reaction that was evaluated with 2%, 3% and 4% of CaO obtained from oyster shells. The density, kinematic viscosity, acidity, and conversion efficiency to methyl esters were determined by ^{1}H NMR of the products of each treatment.

Results: The treatment with 3% catalyst showed the highest reaction yield (92.2%) compared to the treatments with 2% (86.8%) and 4% catalyst (87.13%). The ^{1}H NMR spectra confirmed the presence of methyl esters in the product of the three treatments. The treatment with 3% and 4% by weight of catalyst presented products with similar characteristics with acceptable values of density, viscosity and acid number in accordance with the ASTM D6751 and EN1421 standards.

Study limitations/implications: A concentration of 2% by weight of CaO generates a conversion percentage far from the content of methyl esters established by the ASTM D6751 and EN14214 Standards (>96.5%).

Findings/conclusions: ^{1}H NMR results indicate that the conversion efficiency to methyl esters is positively affected by the amount of catalyst. In the treatments with catalyst loading greater than 2%, the conversion to methyl esters increased significantly to values around 90%.

Keywords: oyster shells, used edible vegetable oil, transesterification, methyl esters.

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INTRODUCTION

Greenhouse gas (GHG) emissions related to fossil fuel consumption are on the rise (British Petroleum, 2019). According to the Global Renewable Energy Status Report (2018), about 50% of fossil fuel consumption is due to transportation. To limit this fossil fuels dependence, the development of bioenergetics has been motivated. Biodiesel is considered a renewable, sustainable, biodegradable, non-toxic and clean form of energy (Chozhavendhan *et al.*, 2020).

Transesterification of triglycerides with short-chain alcohols (methanol and ethanol), in the presence of a catalyst, is the most widely employed method for biodiesel production (Akubude *et al.*, 2019; Borah *et al.*, 2018). On a global scale, 99% of this bioenergy is

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obtained from edible oils (Ashraf, 2019). Homogeneous catalysts such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) are widely used for obtaining high reaction yields in short times. However, they have problems in biodiesel separation, high product purification cost and zero catalyst reuse (Akubude *et al.*, 2019; Ogunkunle and Ahmed, 2019). To replace these catalysts, research has been focused on heterogeneous catalysts solids with basic properties derived from waste materials.

Due to their high calcium carbonate ($CaCO_3$) content, oyster shells represent a potential source of calcium oxide (CaO) (Ramón *et al.*, 2016). The present research evaluated CaO obtained from *Crassostrea virginica* oyster shells as a heterogeneous catalyst to produce biodiesel through the transesterification of used edible vegetable oil.

MATERIALS AND METHODS

Oyster shells (*Crassostrea virginica*) derived from human consumption were used. The edible vegetable oil used was collected from dwelling houses. The shells were washed with tap water to remove dirt particles and dried in the sun for six hours for two days. The oil was vacuum filtered to remove food residues and heated on a stirring electric grill at 105±10 °C for 30 min to remove the water content.

Catalyst Preparation

The oyster shells were crushed, passed through a manual mill, sieved through a number 60 (250 microns) mesh, and calcined in an oven at 900 °C for 2 h. They were later kept in vacuum-sealed test tubes (Figure 1).

CaO catalyst characterization

The morphology, microstructure and elemental composition of the catalyst were determined by SEM-EDX. A JEOL JSM-610 LA scanning electron microscope was used. The crystallinity was analyzed in an XRD with a Bruker model D-8 Advance diffractometer,

Figure 1. Preparation of CaO catalyst derived from oyster shells.

Cu K-alpha1 tube. The constituent substances of the catalyst were determined by FT-IR with an Agilent Cary 630 FT-IR spectrophotometer following the ATR (Attenuated Total Reflection) technique.

Characterization of the used edible vegetable oil

Based on the methods of the norms ASTM D1298, ASTM D445, NMX-F-211-SCFI-1987, NMX-F-101-SCFI-2012 and NMX-F-154-SCFI-1987, respectively, the density, viscosity, moisture % and volatile material, acid index and peroxide index of the edible vegetable oil used were determined.

Transesterification of the evaluated edible vegetable oil

An experimental design was established with nine experimental units (EU), described in Table 1. Three catalyst concentrations were evaluated, estimated by various authors as having the best reaction performance using CaO (Buasri *et al.*, 2015; Lani *et al.*, 2017; Yusuff and Popoola, 2018; Tan *et al.*, 2019).

Transesterification was carried out in a 500 mL three-way reactor (equipped with a magnetic stirrer and a thermometer), connected to a water-cooled reflux condenser (Figure 2). 50 g of the recycled edible vegetable oil was used for each EU (Yusuff and Popoola, 2018).

The type of alcohol, reaction time (2 h) and temperature (65 °C) was kept constant, following Farooq and Ramli (2015), Yusuff and Popoola (2018) and Tan *et al.* (2019). Alcohol: oil molar ratio of 36: 1 was used at a stirring speed of 700 rpm. The catalyst was separated by filtering in a vacuum. The product of each EU was passed to a separatory funnel. The denser (lower) phase was dried at 100 °C and the less dense (upper) heated to 70 °C to remove excess methanol for 30 min.

Table 1. Experimental treatments of the evaluated oil transesterification.

Treatments	Concentration	Repetition
A2	2% CaO catalyst	3
B3	3% CaO catalyst	3
C4	4% CaO catalyst	3

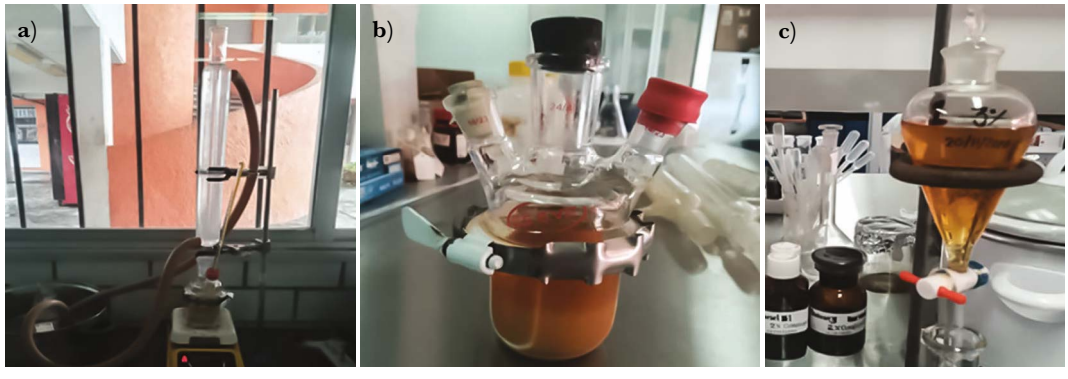

Figure 2. Transesterification. a) Reactor, b) product, c) phase separation.

Statistical analysis

The reaction yield was analyzed through a simple analysis of variance (ANOVA) to find statistically significant differences between treatments (catalyst percentage). The means comparison was assessed using Tukey's test, with a 5% significance (α=0.05). The data were then analyzed in the Statgraphics® Centurion XVIII.1.06 (Statpoint Technologies, 2010) statistical program.

Biodiesel Characterization

The methyl esters content was determined by proton nuclear magnetic resonance (^{1}H NMR), following equation 1. Kinematic viscosity, density, and acid index were analyzed following the methods established in the ASTM D445, NMX- F-075-SCFI-2012 and NMX-F-101-SCFI-2012 norms, respectively.

$$\%Conversion = \left(\frac{2A_{CH_3}}{3A_{\alpha-CH_2}} \right) * 100 \qquad \text{Equation 1}$$

A_{CH_3} is the integration value of the protons of the methyl esters and $A_{\alpha-CH_2}$ is the integration value of the methylene protons (Farooq and Ramli, 2015).

RESULTS AND DISCUSSION

CaO catalyst characterization

During the calcination process, the oyster shells lost an average of 44.5% of their weight, due to CO_2 release during the gas phase (Galván and Velázquez, 2011). In the SEM images (Figure 3), the formation of particles of divergent sizes and shapes is observed, possibly as the result of a non-uniform exposure of the samples to the calcination temperature (Singh and Verma, 2019). Figure 3.1d at 200x shows a porous catalyst, which is related to abundant active reaction sites (Aderibigbe, 2020).

EDX analysis (Figure 4) exposes a high concentration of Ca and O ions. The presence of these elements as main constituents indicates that the oyster shell was converted to CaO. The Ca content is similar to that reported by Singh and Verma (2019) (54.76%), for calcined eggshells.

The XRD patterns of the catalyst (Figure 5) show peaks at $2\theta \cong 32°$, 37°, 54°, 63° and 67°, characteristic of CaO (Farooq *et al.*, 2018). Which is consistent with the high Ca and O content reported by the EDX technique. The narrow and high-intensity peaks define the crystalline structure of the catalyst (Buasri *et al.*, 2015).

The spectrum of the FT-IR analysis (Figure 6) presents similarities with those reported by Tan *et al.* (2019), for chicken bones and fish bones, with the bands for 1409 cm^{-1} and 995 cm^{-1} resulting from the Ca-O vibration.

Used edible vegetable oil characterization

The used edible vegetable oil had an acid index (0.72 mg KOH/g) less than acceptable (<2.0 mg KOH/g) (Banerjee *et al.*, 2019); and a free acids percentage (0.36%) below

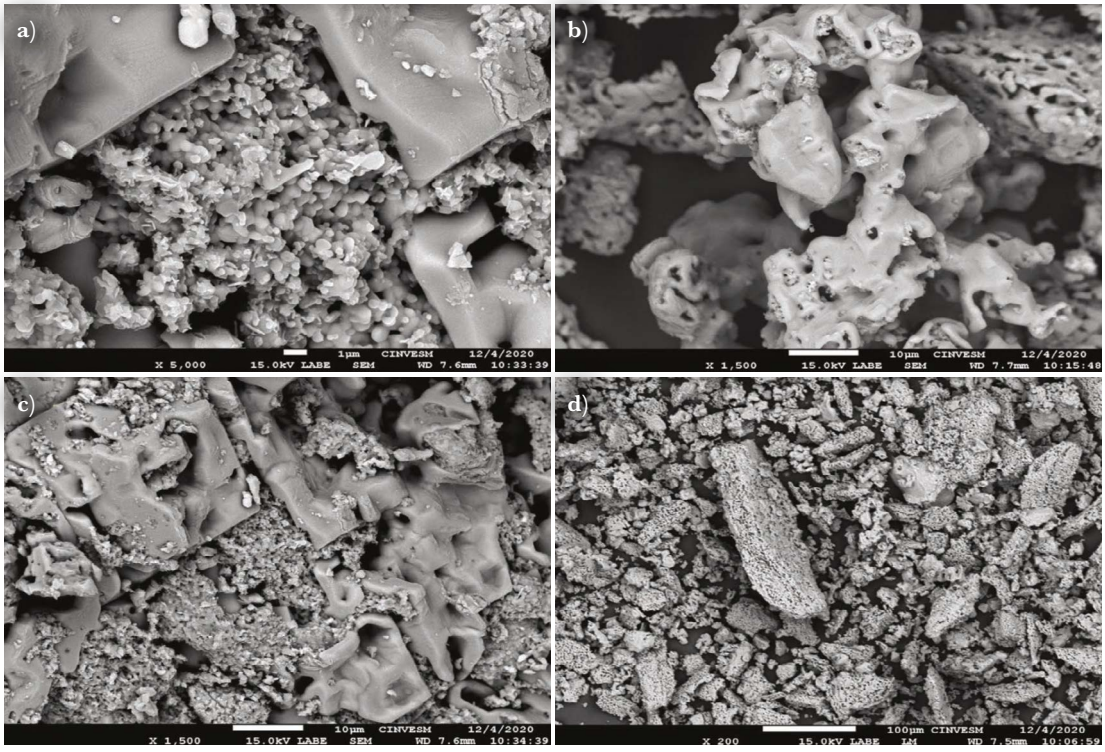

Figure 3. SEM images of oyster shell derived CaO catalyst.

Elemento	% en peso	% atómico
O K	43.17	64.70
Na K	0.80	0.83
Mg K	1.55	1.53
Si K	1.37	1.17
Ca K	53.11	31.77
Total	100 %	

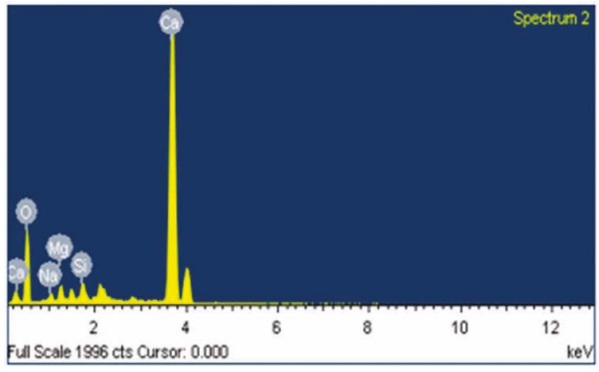

Figure 4. Elemental composition of calcined oyster shells.

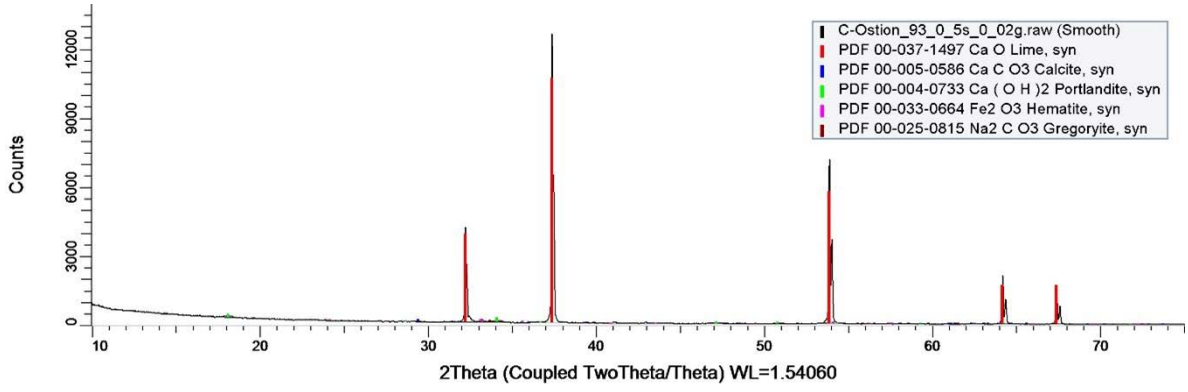

Figure 5. Diffractogram of a calcined sample of oyster shells.

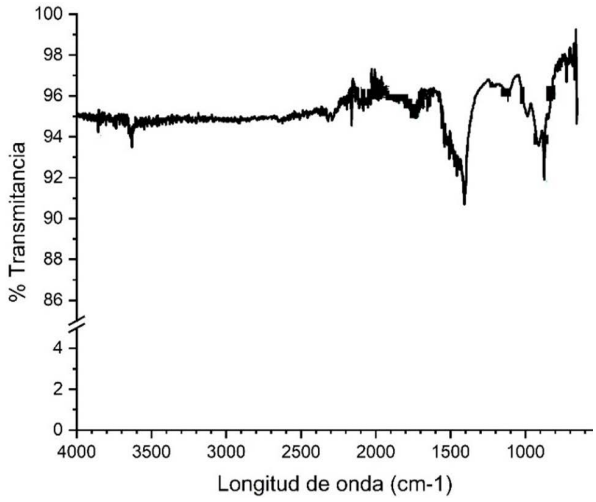

Figure 6. Spectrum of calcined oyster shell sample.

that reported by Yusuff and Popoola (2018) of 1,924%. It showed a moisture content of 0.1289%, lower than the 2.0% suggested as acceptable by Banerjee *et al.* (2019) and 0.64% documented by Tan *et al.* (2019). The density was found within the range established by the NMX-F-475-SCFI-2011 Standard (0.914-0.925) for virgin oils and was lower than the density indicated by Tan *et al.* (2019) (950 kg/m^3). The mean kinematic viscosity (39.36 mm^2/s) was located within the typical values (27.2- 53.6 mm^2/s) for fats and oils (Lanjekar and Deshmukh, 2016), and below that indicated by Farooq and Ramli (2018) (42.01 mm^2/s).

The high peroxide index (18.23 meqO_2/kg) was like those obtained by Torres *et al.* (2016), (10.5 to 19.5 meqO_2/kg) in samples of used vegetable oils from a pilot plant for biodiesel production. Although, lower than the 40 meqO_2/kg reported in the bibliography for oils in which undesirable characteristics are detected after 180 days of storage (Rivera *et al.*, 2014). The results indicate that the raw material did not show a significant deterioration that significantly affects the transesterification reaction.

Edible vegetable oil transesterification

Considering the final mass of both phases, after the heating process indicated by the methodology, treatment B3 showed a high reaction performance compared to treatments A2 and C4 (Table 3).

Table 2. Physicochemical properties of the used edible vegetable oil.

Properties	Units	Value
Density at 15 °C	kg/m^3	928.58
Viscosity at 40 °C	mm^2/s	39.36
Moisture and volatile material	%	0.1289
Acid index	mg KOH/g	0.7230
Peroxide index	meqO_2/Kg	18.2388

Table 3. Results of reaction yield by treatment.

Treatments	Yield (%)			Average
A2	86.6	87.8	86	86.8
B3	92.2	93	91.4	92.2
C4	87.8	87	86.6	87.13

With a 95% confidence level, the analysis of variance (ANOVA) of one factor and the Tukey's test, showed that there is a statistically significant difference between the highest reaction yield percentage, which was obtained in treatment B3 (92.2%), compared to the performance of treatments A2 (86.8%) and C4 (87.13%).

Biodiesel characterization

All 1H NMR spectra (Figure 7) exhibited a singlet close to 3.6 ppm, characteristic of the protons of the methoxy group (O-CH_3). As well as a triplet at approximately 2.3 ppm, typical of -CH_2 protons, adjacent to methyl (Santos, 2013; Morales, 2017), which confirms the presence of methyl esters in the three treatments. Only the product of treatment of A2 showed double doublets in the range of 4.1-4.3 ppm related to glyceride protons (Cedrón *et al.*, 2014).

Treatment B3 (3% by weight of catalyst) and C4 (4% by weight of catalyst) presented products with similar characteristics with acceptable values of density, viscosity and acid number following ASTM D6751 and EN 14214 standards (Table 6). Which is related to

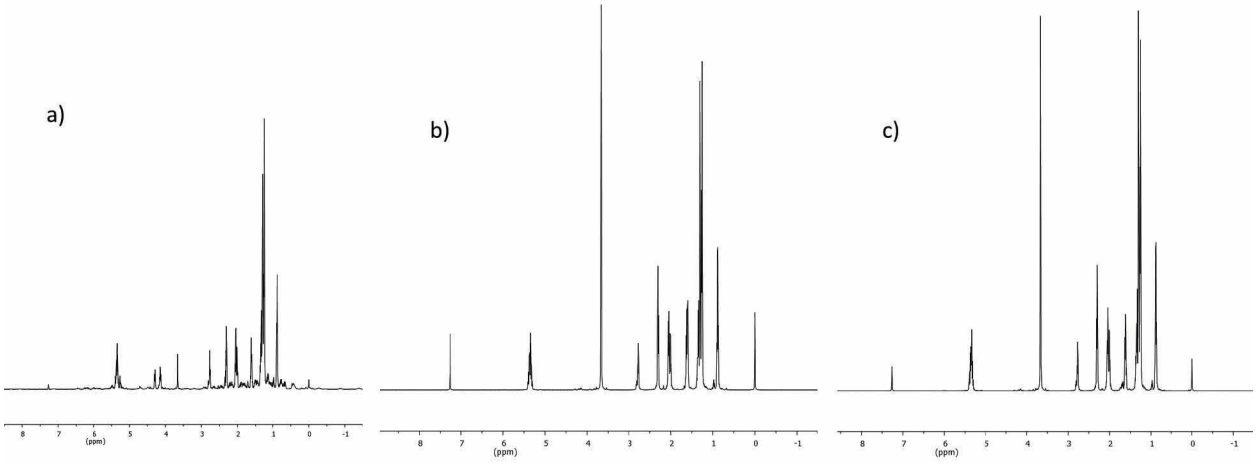

Figure 7. ^{1}H NMR spectra of treatments a) A2 (2% catalyst), b) B3 (3% catalyst) and c) C4 (4% catalyst).

Table 6. Results of the biodiesel characterization.

Treatment	Yield (%)	Density at 15 °C (kg/m^3)	Viscosity at 40 °C (mm^2/s)	Acidity (mg KOH/g)	Methyl esters (%)
A2	86.8	922.3231	18.3096	0.5075	14.63
B3	92.2	890.1291	4.4301	0.3084	90.90
C4	87.13	897.6056	4.3725	0.2985	91.14

Note: Numbers highlighted in bold meet the quality standards established in ASTM D6751 and EN 14214.

high conversion to methyl esters according to ^{1}H NMR results. Although the B3 treatment exhibited a higher and statistically significant performance.

CONCLUSIONS

The XRD, FT-IR and SEM-EDX analyzes confirmed the formation of CaO from the calcined samples of oyster shells at 900 °C. The ^{1}H NMR results indicate that the conversion efficiency to methyl esters is positively affected by the amount of catalyst. In the treatments with catalyst loading greater than 2%, the conversion to methyl esters increased significantly (≥90%). For these treatments, the physicochemical properties of the biodiesel obtained were acceptable as indicated in the ASTM D6571 and EN 1411 Standards. In this sense, local oyster shells (*Crassostrea virginica*), considered as worthless waste, represent a promising source of CaO for the successful synthesis of biodiesel, whose characteristics meet quality standards.

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