



Application of oyster shell waste as a heterogeneous catalyst in the biodiesel production from used cooking oil

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ARTICLE INFO

Article history:

Received 15th April, 2022

Received in revised form 02th Jun, 2022

Accepted 30th Jun, 2022

Available online 22th July, 2022

Keywords:

Natural oyster shell powder

Biodiesel production

X-ray diffraction

FT-IR

SEM

ABSTRACT

The generation of shell waste was investigated using calcium oxide from tropical oyster shells. The following preparations were used: A natural oyster shell powder, a tropical oyster shell powder, calcined in a programmed oven for 2 hours at 800 °C. a recyclable heterogeneous catalyst, was created from shellfish using a simple heat treatment approach. Based on thermal gravimetric analysis (TGA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM), the resulting catalyst (osp800) was evaluated. The calcined oyster shell were used to produce biodiesel by the reaction of transesterification variables (MeOH/oil ratio, catalyst amount, and reaction time) with a yield of 98% of biodiesel. According to the results of the experiments, we noticed that the increase of the methanol/oil molar ratio improved efficiency, reaching a maximum where the ratio was 12:1 (MeOH/oil) with a 5% catalyst. The oyster shell catalyst can be readily recovered and re-utilized in the transesterification reaction up to seven times without losing its activity. The use of oyster shell waste in catalyst preparation could reduce the cost of the catalyst while reducing contaminants. The result would be cost-effective and environmentally friendly biodiesel.

1. Introduction

Currently, there is considerable environmental concern about the waste generated by the consumption of seafood products. According to a study in Thailand, oyster and white crab harvests will total 27,730,000 kg and 132,000 kg, respectively, in 2020 [1]. The growth in consumption levels has led to the accumulation of shellfish waste on the coast and shrimp shells in large quantities, which poses environmental pollution problems [2,3]. However, this waste can be used because it contains essential components, such as calcium carbonate (CaCO₃) from tropical oyster shells and deacetylated chitin from shrimp shells. However, these wastes can be utilized because they contain essential components, such as calcium carbonate (CaCO₃) from tropical oyster shells and deacetylated chitin from shrimp shells. When heated or incinerated at high temperatures (700 °C and above), calcium carbonate turns into calcium oxide (CaO) [4]. As a result, there is a lot of interest in researching and developing cost-effective and ecologically friendly CaO-based heterogeneous catalysts from sustainable resources for biodiesel generation. In previous years, several researchers have produced unique natural CaO-based catalysts to reduce expenses, such as waste mud crab shells, waste fish scales, waste animal bones, and waste shells of mollusks and oysters [5,6].

Biodiesel is a fuel that is both ecologically benign and biodegradable. It degrades approximately four times faster than diesel. It is frequently synthesized from fats or oils using methanol and a catalyst to make fatty acid methyl esters (FAME) and glycerol as a by-product [7]. In the biodiesel production transesterification reaction, it is possible to use both homogeneous (acidic or basic) and heterogeneous (acidic, basic or enzymatic) catalysts. The most prevalent way of producing biodiesel is base-catalyzed homogeneous transesterification. It

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moves quickly and produces very high yields in short reaction periods. It has been noted that homogeneous catalysts frequently generate a variety of issues, including equipment corrosion due by wasted catalyst deposition. As a result, the employment of heterogeneous catalysts can result in higher product [5,8].

In this work, the CaO catalyst was typically prepared from an oyster shell by calcination at 800 °C. This catalyst was utilized as a feedstock to produce biodiesel from waste cooking oil using the transesterification reaction. The effects of reaction time, methanol/oil molar ratio, catalyst loading, and oyster shell catalyst reusability were investigated thoroughly. Furthermore, biodiesel was synthesized from wasted cooking oil, and its parameters such as flash point, kinematic viscosity, cloud point, pour point, and density were measured. The findings were matched to the ASTM D 14214 and ASTM D 6751 standards [9].

2. Experimental

2.1 Preparation of CaO Catalysts

The oyster shells were collected as waste from Oualidia Located 158 kilometers from Casablanca, Morocco, between El Jadida and Safi. The discarded shells were cleaned with water to remove dust and contaminants before being dried for 12 hours in an oven at 80 °C. Dried oyster shells were crushed and sieved through screens ranging from 100 to 200 mesh (38-75 μ m). A calcination process was used to produce the solid catalyst. Spent shells were calcined for 2 hours at 800 °C in an air environment at a heating rate of 10°C/min [10]. The result (CaO catalyst) was a white powder. Before use, the calcined sample was maintained in a closed container to prevent reactivity with CO₂ and moisture in the air [11]. Figure 1 depicts the waste shell-derived catalyst preparation method.



Fig. 1. Preparation of CaO catalyst derived from oyster.

2.2 Characterization of CaO Catalysts

X-ray diffraction (XRD) analysis was performed at room temperature using a Shimadzu 6100 diffractometer equipped with a copper anticathode ($\lambda_{\text{CuK}\alpha} = 1.541838 \text{ \AA}$) with a scan step of 0.02°s^{-1} , from 5 to 70 (2θ) and at (40 kV and 30 mA). Identification of minerals in the samples was performed by comparison of the XRD patterns obtained with the Joint Committee on Powder Diffraction Standards (JCPDS-ICDD) database. Fourier transform infrared spectroscopy (FTIR) was performed on a Jasco FT/IR 4600 spectrometer equipped with the ATR module (Pro One). The FTIR spectra of the sample were obtained with a resolution of 4 cm^{-1} and collected in the range of $4000\text{--}400 \text{ cm}^{-1}$. Thermogravimetry/differential thermal analysis (TG/DTA) was performed using the LabsysTM Evo (1F) SETARAM equipment. Scanning electron microscopy (SEM) was used to examine the microstructures of the calcined waste shells. SEM images of the representative sample were obtained by the JEOL JFC-2300HR.

2.3 Experimental procedure of biodiesel

2.3.1 Pre-treatment of Soybean Waste Cooking Oil (SWCO)

Soybean oil used 2–3 times was collected from a nearby restaurant. The waste oil was filtered using filter paper to separate suspended impurities. Then, to remove small particles, the oil was centrifuged at 3000 rpm for 30 min to obtain an oil-free of solid impurities and particles, and then heated at 100 °C for 30 min to remove the contained water.

2.3.2 Synthesis of Biodiesel

The most common process of producing biodiesel is the trans-esterification of vegetable oil with the presence of catalyst and alcohol [12]. Generally, to reduce capital and operating costs for the biodiesel plant, the process is carried out at a low temperature and atmospheric pressure

However, it is preferable to use little excess of alcohol to shift the equilibrium towards the formation of esters since the process reactions are reversible. Based on the alcohol excess, the forward reaction is pseudo-first-order and the reverse reaction is found to be second-order. Additionally, it was found that trans-esterification reactions might be rapid with the presence of alkali catalyst [13]. The biodiesel used in the current study was prepared from SWCO and methanol 99% in the presence of 5% of CaO heterogeneous using the trans-esterification process for 2 h. The optimal chosen conditions that lead to a yield of 97% of biodiesel are a volume ratio of 12:1, a temperature between 60 and 65 °C [14]. The reaction product was exposed to air for 30 min to evaporate excess methanol. Then, it was allowed to lay for 6 h to generate the two distinctive phases.

2.4 Biodiesel Characterization

2.4.1 Physicochemical parameters

The physicochemical properties as viscosity, density, and acid value, of the biodiesel prepared from local WCO, were established by following the well-known methods. The obtained results are summarized in Table 1 [15]. It is noticed that the physicochemical characteristics of the WCO biodiesel conform to the standard ASTM D6751-02. However, the major physical and chemical features are in great accord with the standards [16].

2.4.2 Characterization of biodiesel

The functional groups that characterize the biodiesel were identified using the Jasco 4600 FT/IR (infrared) method. For the chemical composition analysis, we used a CLARUSTM GC-680 WITHQ-8 MS PERKIN ELMER integrated GC/MS system with a flame ionization detector and a Rix®-5Sil MS capillary column (0.25 mm ID, 30 m long, 0.25 m film thickness). Helium was used as the carrier gas at a flow rate of 3 ml min⁻¹ with a split ratio of 67.

3 Results and discussion

3.1 Characterization of CaO Catalysts

3.1.1 XRD analysis of catalyst

Figure 2 illustrates the X-ray diffraction (XRD) patterns of unburned and burned catalysts. Uncalcined and calcined oyster shells at 100-800° C show similar XRD patterns. The main peaks were observed at $2\theta = 29.50, 36.04, 39.48, 43.24, 47.6, 48.6$ and 57.44 . These peaks were the characteristic calcium carbonate peaks corresponding to JCPDS File No. 85-1108. Calcium oxide peaks and some calcium hydroxide peaks appeared when the shell was calcined at 800 °C.

The peaks for the oyster shells calcined at 800 °C appeared at 2θ of calcination = $32.16, 37.32, 53.84$, which are the characteristic peaks of calcium oxide. are the characteristic peaks of calcium oxide (JCPDS file no. 48-1467) [17].

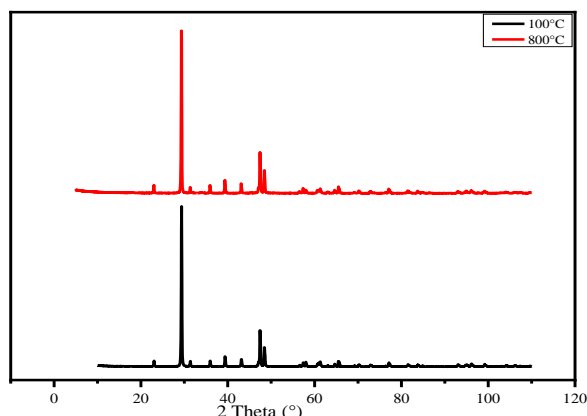


Fig. 2. XRD patterns for shell calcined at different temperatures.

3.1.2 TG-DTA Analysis

TG-DTA was employed in order to determine the appropriate calcination temperature to produce the CaO catalyst from oyster shell waste (Figure 3). According to the TG curve, the first weight loss step was found between 150-260 °C, the second and the third were found between respectively 300-400, 550-700 °C the weight losses correspond to the decomposition of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and CaCO_3 , respectively. Above 700 °C, the sample weight remained almost constant, while the maximum peaks in the DTG curves were around 595-730 °C. The TG-DTA curves confirmed that a temperature above 700 °C is required to transform CaCO_3 to CaO. A temperature of 800 °C was selected as a suitable calcination temperature to produce CaO catalyst from the Oyster shells [18].

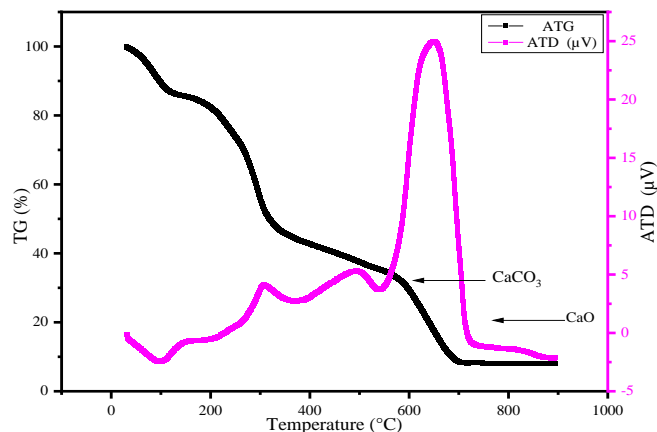


Fig. 2. TG and DTG curves for Oyster shell.

3.1.3 FT-IR analysis of the catalyst

Figure 4 illustrates the FT-IR spectra of (a) oyster shell and (b) oyster shell calcined at 800 °C. The primary absorption bands in the uncalcined catalyst are at 1442, 875, and 712 cm^{-1} , which are attributed to the asymmetric stretching, out-of-plane bending, and in-plane bending vibrational modes of the CO_3^{2-} molecules, respectively. A strong OH stretching band appears at 3638 cm^{-1} after calcination at 800 °C; also, the oyster shells lose carbonate and the absorption bands of the CO_3^{2-} molecules move to a higher energy. The lower mass of the functional group linked to the CO_3^{2-} ions was ascribed to this. Calcination at 800 °C causes the bands to move to higher energy levels.

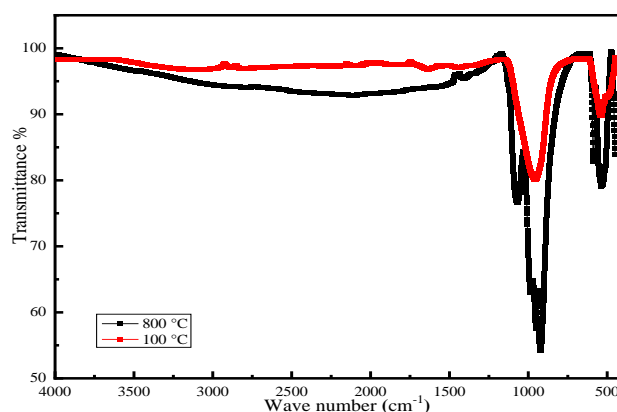


Fig. 3. FT-IR patterns for (a) oyster shell, (b) calcined eggshell at 800 °C.

3.1.4 SEM analysis of catalyst

The catalyst was examined using scanning electron microscopy (SEM) was used to examine the morphology of the oyster shell catalyst, as shown in Figure 5. The calcined oyster shell is made up of a variety of sizes and shapes. Smaller grain sizes and aggregates, in general, may provide more specific surface areas. The particle size should be proportional to the area of contact. The pores are well formed, indicating the amorphous nature of the catalyst particles, as seen in the images [19].

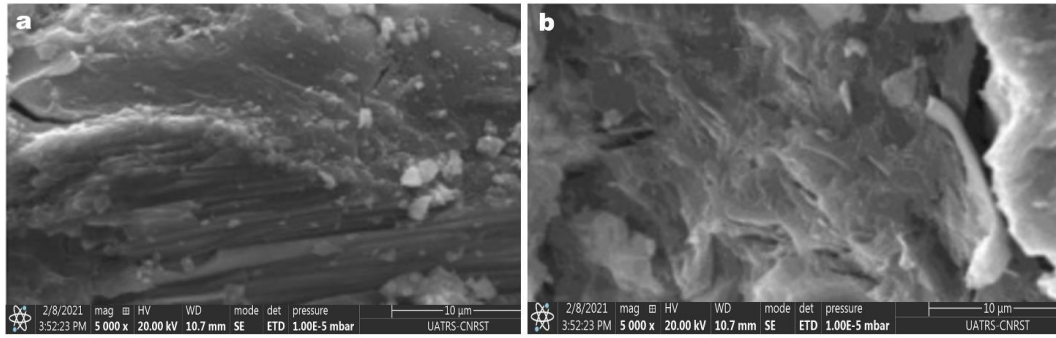


Fig. 4. SEM images natural (a) and calcined oysters shell at 800 °C.

3.2. Characterization of biodiesel

3.2.1 Physicochemical parameters

In order that biodiesel can be used in diesel engines, the fuel must meet various specifications outlined in biodiesel standards, primarily the American biodiesel standard (ASTM D6751) and the European biodiesel standard (EN14214) [17,18]. Table 3 summarizes the properties of the FAME fuel discovered in this study, with a comparison to the recommended international biodiesel standards ASTM D6751 and EN14214. The majority of its properties, as can be seen, fall within the range of fuel properties described in the most recent biodiesel standards.

Table 1

Physicochemical properties.

	Standard Test Methods	Unit	Results
Density at 20 °C	ASTM D4052	kg/m ³	890.20
Viscosity at 40°C	ASTM D455	(mm ² /s)	4.35
Acid value	ASTM D664	(mg KOH/g)	0.453
Ester content	EN 14103	(wt.%)	93.50
Cold Soak Filtration Test	ASTM D7501	°C	-3
Flash point	EN ISO 2719	°C	70

3.2.2 FT-IR analysis

Figure 6 shows the infrared spectrum of biodiesel. The stretching vibration of C-O of the ester at 1234, 1119, and 1026 cm⁻¹, and the carbonyl group of the ester (C=O) at 1744 cm⁻¹. Other functional group peaks in the biodiesel were recorded in the spectra, including the sp² C-H stretching vibration at 3194 cm⁻¹, the sp³ C-H stretching vibration at 2916, 2855, 2731, and 2677 cm⁻¹, and the C-C stretching vibration at 1597 cm⁻¹. CH₂ has a bending vibration of 1458 cm⁻¹, CH₃ has a bending vibration of 1373 cm⁻¹, C-C has a bending vibration of 872 cm⁻¹, and (CH₂)_n has a bending vibration of 725 cm⁻¹. The peak at 3472 cm⁻¹ could normally be attributed to the O-H bands. The O-H groups are suspected to be FFAs in the biodiesel and residual glycerol is present in the biodiesel [20-22].

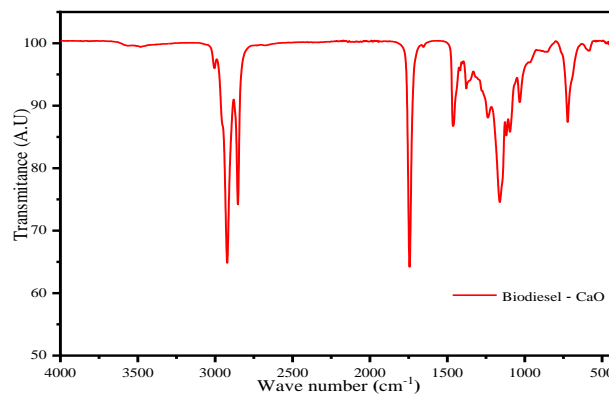


Fig. 5. Infrared spectrum of biodiesel.

3.2.3 GC–MS Analysis

GC-MS measurements were performed to investigate the chemical composition of the synthesized biodiesel. The chromatogram obtained is illustrated in Figure 7. The existence of four major chemicals has been discovered. The proportionate peak is related to the amount of SWCO fatty acid methyl esters present. The FAMES were identified by analyzing the standards under the identical experimental circumstances and weighting the corresponding retention time data. Furthermore, the acquired findings are summarized in Table 2. The overall FAME concentration in the SWCO biodiesel generated after 2 hours of reaction time was 98 percent, with methyl linoleate being the predominant component.

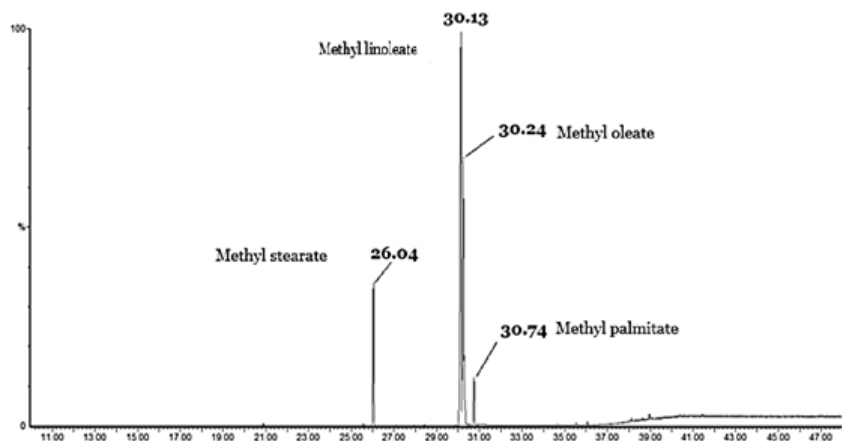


Fig. 6. GC–MS spectrum of SWCO biodiesel.

Table 2

FAMES composition of WCO biodiesel.

Peak Number	R.T (Min)	Identified Compounds	Corresponding Acid
1	26.04	methyl stearate	$C_{19}H_{38}O_2$
2	30.13	methyl linoleate	$C_{19}H_{34}O_2$
3	30.24	methyl oleate	$C_{19}H_{36}O_2$
4	30.74	methyl palmitate	$C_{17}H_{34}O_2$

4 Conclusion

The calcined oyster shells were employed as a catalyst in the biodiesel transesterification of SWCO. Because of their easy availability and non-corrosive character, they are low-cost, it can be assumed to be useful for biodiesel transesterification. The result was a 96 percent biodiesel yield by transesterification at 60 °C in 2 hours using a 3% catalyst and a methanol to oil molar ratio of 12:1. The results show that the catalyst made from oyster shells may be successfully recovered and reused in the transesterification reaction up to eight times without apparent loss of activity. According to international standards, the biodiesel proprieties, were good in comparison to those of conventional diesel.

Conflicts of interest statement

The authors declare no competing financial interest.

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