A Comparison of the use of Eggshells and Cockleshells in the Catalytic Transesterification of Waste Cooking Oil to Produce Biodiesel

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Abstract

Using transesterification to produce biodiesel has attracted considerable attention due to its high conversion rate, relatively low cost, mild reaction conditions, the resulting product properties (which are close to those of mineral diesel), and its applicability to industrial-scale production. In this research, a calcium oxide (CaO) catalyst was prepared from the natural calcium carbonate ($CaCO_3$) sources of waste eggshell and cockleshell that was calcined at 800°C for 2-5 hrs. Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) techniques were used to assess the prepared samples and to compare these with standard CaO. The catalyst and waste oil, mixed at a ratio of 15:85 by weight, and a molar ratio of methanol to waste oil of 15:1, with 95% methanol solvent, were used in the transesterification reaction and heated at 65°C for 3 hrs. The results show that pure CaO catalyst produced from waste eggshell that was calcined at 800°C for 5 hrs. can be used to transesterify waste cooking oil to biodiesel, tested according to the ASTM D6751 and EN 14214 standards.

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Introduction

Fossil fuels, that is petroleum, coal and natural gas, are the world's main energy sources. These non-renewable sources of energy provide 77.24% of total energy used globally, while a further 13.83% is derived from renewable energy such as hydro, solar, wind and biomass (Ministry of Energy, Department of Alternative Energy Development and Efficiency, 2016). At present, guidelines are in place to solve problems with depleting energy resources by using alternative energy or by using waste or biomass materials for future energy generation. Among these, the fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE) are potential renewable energy sources for use in biomass power production, and these may be derived from several oil crops, including palm oil, jatropha, soybean, coconut and rubber seed (Ong et al., 2011), along with waste cooking oil and animal fats. This biodiesel oil can be used to replace diesel fuel in full or mixed with mineral diesel at different ratios, and can be used directly with diesel engines without the need to alter the engines in any way (Srithar et al., 2017) because of the similar combustion and energy properties of mineral and biodiesel (Jaichandar and Annamalai, 2011). Indeed, earlier research reports that relative to diesel fuel, the use of biodiesel may result in significantly lower emissions of particulates, CO_2, SO_x and CO (Chauhan and Shukla, 2011), these being the main causes of global warming.

CaO acts as a heterogeneous catalyst and has been studied for many decades due to its being used as a catalyst in the transesterification from fatty acid to fatty acid methyl ester. CaO has advantages in this application, including the fact that it is reusable, easy to separate after the reaction, and available at low-cost (Boey et al., 2011) because it can be prepared from $CaCO_3$ rich raw materials, for example eggshells, mussel shells, crab shells, oyster shells, clam shells, animal bones, dolomites and marlstones (Jaggernauth-Ali et al., 2015) and limestone (Valverde et al. 2015). It may also be used as a substitute for homogeneous alkaline or acid catalysts (the use of which may pose problems), to overcome difficulties in separating the catalyst from the product mixture and as a response to problems related to environmental disposal (Jaggernauth-Ali et al., 2015). As reported in previous studies, the physical properties of a good catalyst are that it is composed of

small particles with a high surface area (Pandit and Fulekar, 2019; Yi et al., 2018; Ayodeji et al., 2018; Fadhil et al., 2018) as this helps catalytic purification.

In this research, we used waste cooking oil left over from the production of fried rice crackers (*khaw tan*), with these materials sourced in Muang district, Lampang province and then used to prepare biodiesel using CaO to catalyse the transesterification process. For use as heterogeneous catalysts, the CaO was prepared from waste chicken eggshells and cockleshells and samples were calcinated at 800°C for 2, 3, 4 and 5 hrs.

Experimental methods

Catalytic Preparation

The CaO catalytic particles were prepared from waste cockleshell and eggshell. Both of these were washed with water and dried under air prior to being split into batches and calcined using an RWF 1100 Carbolite furnace at 800°C for 2, 3, 4 and 5 hrs. These samples were then ground thoroughly with a mortar to produce a powder.

Catalytic Characterization

The crystal phases and crystalline sizes of the prepared CaO samples were assessed through powder X-ray diffraction and measured using a Rigaku MiniFlex 600 with Cu-K$_\alpha$ radiation in the range of 2θ = 20-80°, and with X–rays generated from Cu K$_\alpha$ irradiation (λ = 1.5406 Å) operated at 40 kV and 15 mA, with a 2θ range scan of 20–80°, step scanned at 0.02°, and speed scanned at 20°/minute. After this, phase identification was carried out by comparing the results with the diffraction pattern (JCPDS card) database. The functional groups of these samples were assessed using Fourier transform infrared spectrometry (FT-IR) on a Shimadzu FTIR-8900 Fourier transform infrared spectrophoto-meter. This used the KBr-pellets method with a scanned range of 400-4000 cm^{-1}. The morphology of the obtained CaO samples were photographed with a JSM 5910 LV scanning electron microscope running at 15 kV. The elemental compositions of the formed

CaO samples were then analyzed with an energy dispersion spectrophotometer (EDS) equipped SEM.

Transesterification Activity

We modified the method for carrying out the biodiesel transesterification reaction reported in Roschat et al., 2019. In the transesterification condition, the catalytic CaO sample was mixed with waste oil at a ratio of 15:85 by weight and a molar ratio of methanol to waste oil of 15:1. The mix was heated at 65°C for 3 hrs. and the quality of the resulting biodiesel was analyzed following the ASTM D6751 and EN 14214 standards.

Results and Discussion

XRD

Figure 1 displays the XRD patterns of the CaO catalyst prepared from the two different CaO precursors of eggshells and cockleshells, which were calcined at 800°C for 2 to 5 hrs. It was found that the main peaks were observed at 2θ = 28.70°, 47.08°, 62.76° and 71.88°, which correspond to natural $CaCO_3$ precursors as per JCPDS card no. 47-1743. Another three peaks were found at 2θ = 34.12°, 50.84° and 54.36°, which correspond to calcium superoxide ($Ca(O_2)_2$), according to JCPDS card no. 21-0155. When heated for 2-3 hrs., lower intensity peaks appeared at 2θ = 53.96° and 64.20° and these can be attributed to CaO (JCPDS card no. 48-1467). When waste eggshell $CaCO_3$ was heated for 5 hrs., the pure CaO phase of a cubic system with a face-centered lattice (Chavan et al., 2015) appeared and this was confirmed with main peaks at 2θ = 32.34°, 37.48°, 53.96°, 64.20° and 67.48° (JCPDS card no. 48-1467). In addition, the peaks at 2θ = 28.70°, 34.12°, 47.08°, 50.84°, 62.76° and 71.88° disappear, indicating that the thermal decomposition of $CaCO_3$ into CaO and CO_2 was complete, as shown in Equation (1).

$$CaCO_3(s) \xrightarrow{\triangle} CaO(s) + CO_2(g) \qquad (1)$$

However, when analyzing the calcined waste cockleshell precursor, heating to the same temperature and for the same times resulted in mixed phases of $CaCO_3$, $Ca(O_2)_2$ and CaO still being observed and so the choice of raw material used as the $CaCO_3$ precursor significantly affects the preparation of a pure calcined CaO catalyst.

Based on the XRD results, the crystallite sizes of the CaO were calculated using the Debye–Scherrer equation, as per Equation (2) (Habte et al., 2019):

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta} \qquad (2)$$

where λ is the wavelength of the Cu K_α incident X-rays (λ = 1.5418 Å), β_{hkl} is the full-width-at-half-maximum (FWHM) of the CaO peak (200) plane (in radians), θ corresponds to the CaO peak at 2θ = 37.48°, and K is a constant, which has been assumed to be 0.9 (Habte et al., 2019)
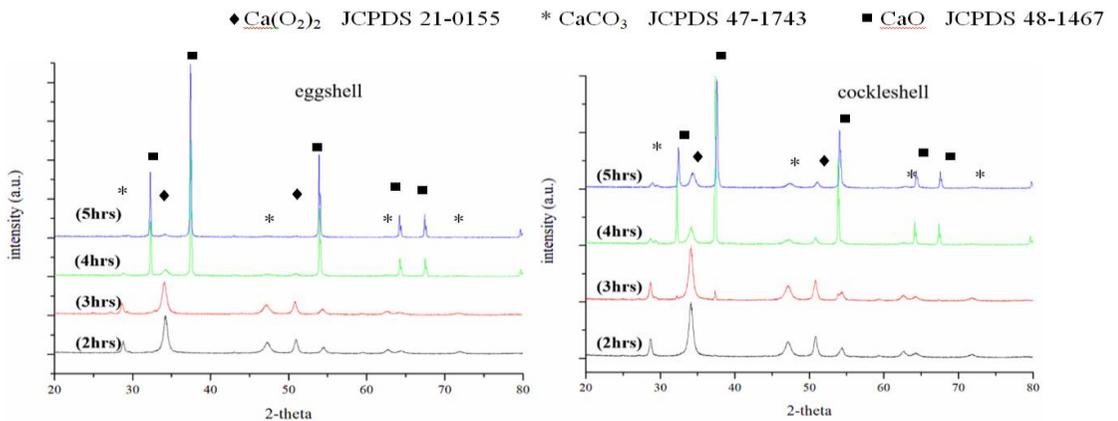

Figure 1 XRD patterns of the calcined CaO catalyst derived from eggshell and cockleshell and heated at 800°C for 2-5 hrs.

From Debye-Scherrer's formula above, it was found that the crystallite sizes were in the range of 58-67 nm. This was confirmed by the SEM images, as shown in Figures 3-4 and Table 2, and can be explained by the agglomeration of nuclei due to the decarbonization process.

FT-IR

The FT-IR spectra of the waste eggshell and the raw cockleshell used as precursors and prepared as a CaO catalyst by heating at 800°C for 2-5 hrs were compared with standard CaO and the results are shown in Figure 2.
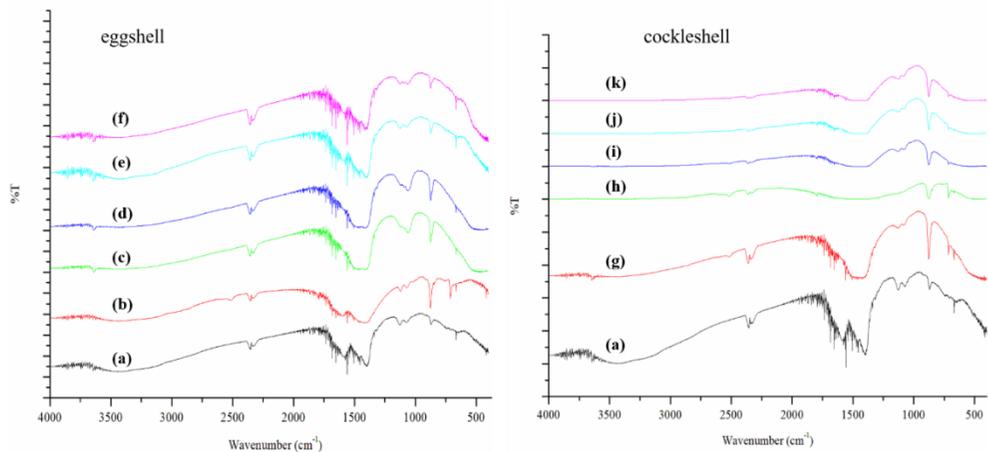
Figure 2 FT-IR spectra of (a) standard CaO (KemAus/Australia), (b) waste eggshell, (c) calcined CaO catalyst made from eggshell and heated at 800°C for 2, (d) 3, (e) 4 and (f) 5 hrs., (g) cockleshell waste, (h) calcined CaO catalyst made from cockle shell waste and heated at 800°C for 2 (i) 3, (j) 4 and (k) 5 hrs.

The observed broadband centering at 1396.9 cm^{-1} is characteristic of C–O bonds and shows a bond between the oxygen atom of the carbonate group (CO_3^{2-}) and the calcium atom. The two sharp peaks at 711.7 and 873.7 cm^{-1}, and at 715.5 and 860.2 cm^{-1} can be attributed to asymmetric vibrations of the carbonate group (CO_3^{2-}) of the eggshell (Habte et al., 2019) and the cockleshell, as shown in figures 2(b) and 2(g). However, the peak of intensity at 873.7 cm^{-1} decreases with increased heating time, and in addition, the calcined CaO sample shows peaks at 1128.6 and 1057.0 cm^{-1} which were ascribed to C–O bonds, indicating the carbonation of calcium

oxide nanoparticles (Mirghiasi et al., 2014). The chemical compositions were confirmed by the EDS spectrum, as shown in Figure 5 and listed in Table 1. The tiny peak at 2352.9 cm^{-1} might be due to atmospheric CO_2 (Darezereshki, 2010) and what appeared to be the bending vibration of a hydroxyl group (—OH) at 3421.5 cm^{-1} may have been caused by the absorption of a water molecule on the surface of the CaO to form calcium hydroxide (Ca(OH)$_2$), as shown in Equation (3).

$$CaO_{(S)} + H_2O_{(g)} \longrightarrow Ca(OH)_{2\ (aq)} \qquad (3)$$

**SEM-EDS**

Figures 3-4 show the SEM images of the waste eggshell, the waste cockleshell, and the CaO calcined at 800°C for 2-5 hrs compared to standard CaO. The SEM images show how the hexagonal layers of the $CaCO_3$ can change to rod-like shapes as the calcined CaO is agglomerated in the calcination process (Valverde et al., 2015). The crystalline size of the calcined CaO is also significantly smaller than standard CaO.
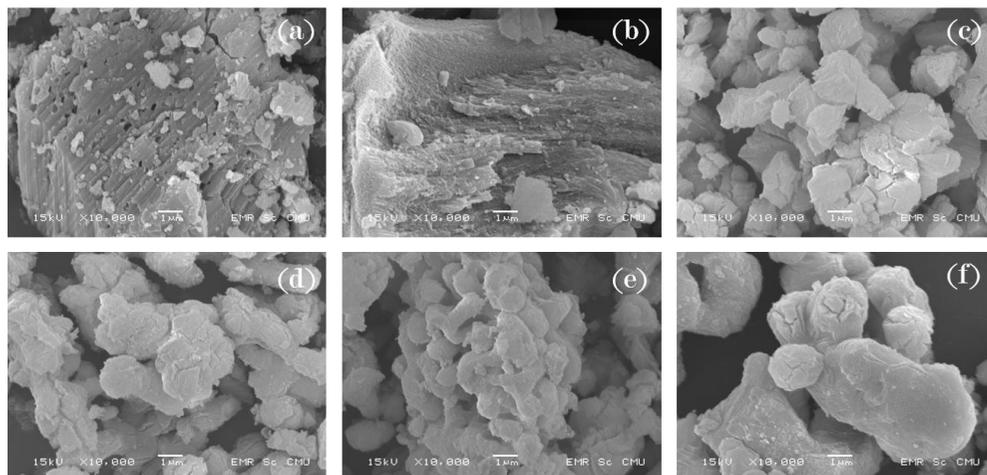
Figure 3 SEM images of (a) the waste eggshell $CaCO_3$ precursor, (b) standard CaO, (c) the calcined CaO made from eggshell waste heated at 800°C for 2, (d) 3, (e) 4 and (f) 5 hrs.
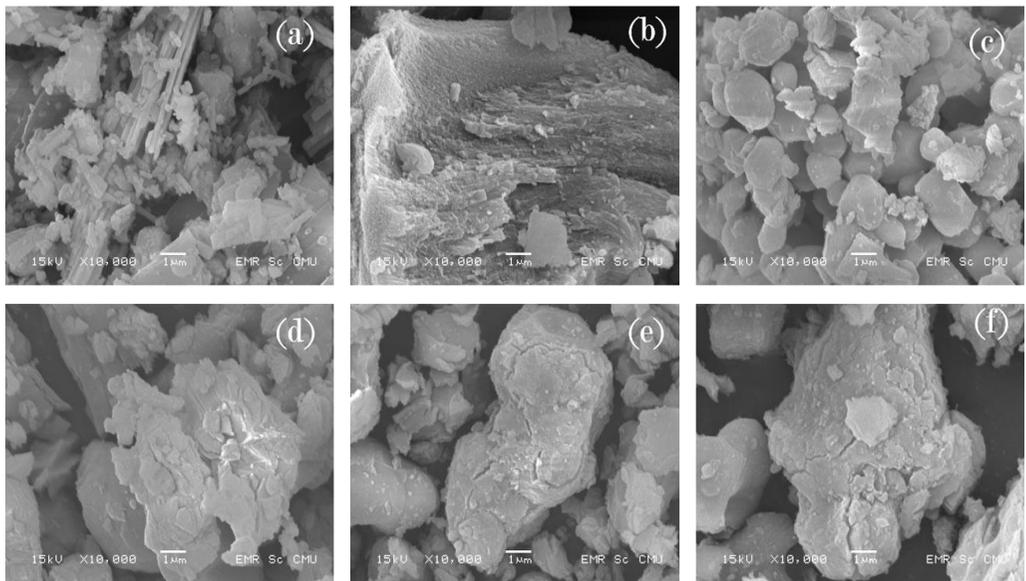
Figure 4 SEM images of (a) the waste cockleshell $CaCO_3$ precursor, (b) standard CaO, (c) the calcined CaO from waste cockleshell heated at 800°C for 2 hrs., (d) 3, (e) 4 and (f) 5 hrs.

Table 1 Comparison of the EDS data for the prepared CaO catalyst with standard CaO, and the $CaCO_3$ waste materials.

Conditions	Weight%			Atomic%		
	Carbon	Oxygen	Calcium	Carbon	Oxygen	Calcium
Standard CaO	3.19	42.71	54.10	6.20	62.30	31.50
Waste eggshell	11.40	46.17	42.43	19.39	58.98	21.63
Eggshell/800°C for 2 hrs.	6.62	46.98	46.40	11.86	63.22	24.92
Eggshell/800°C for 3 hrs.	6.33	46.22	47.45	11.45	62.81	25.74
Eggshell/800°C for 4 hrs.	4.35	45.35	50.30	8.14	63.67	28.19
Eggshell/800°C for 5 hrs.	2.96	45.36	51.72	5.56	64.90	29.54
Waste cockleshell	14.51	46.73	38.76	23.70	57.32	18.98
Cockleshell/ 800°C for 2 hrs.	11.83	48.48	39.69	19.67	60.54	19.79
Cockleshell/ 800°C for 3 hrs.	9.04	45.06	45.90	15.96	59.75	24.29
Cockleshell/ 800°C for 4 hrs.	7.24	48.77	43.99	12.70	64.19	23.11
Cockleshell/ 800°C for 5 hrs.	4.89	48.47	46.64	8.86	65.86	25.29

Figure 5 and Table 1 confirm the chemical compositions of the waste $CaCO_3$ materials and the calcined CaO catalyst. The waste $CaCO_3$ materials were changed to CaO and decarbonized by the release of CO_2 gas and this was confirmed by the observed carbon contents decreasing by weight% from 11.40% to 2.96% and from 14.51% to 4.89% for the eggshells and cockleshells, respectively.
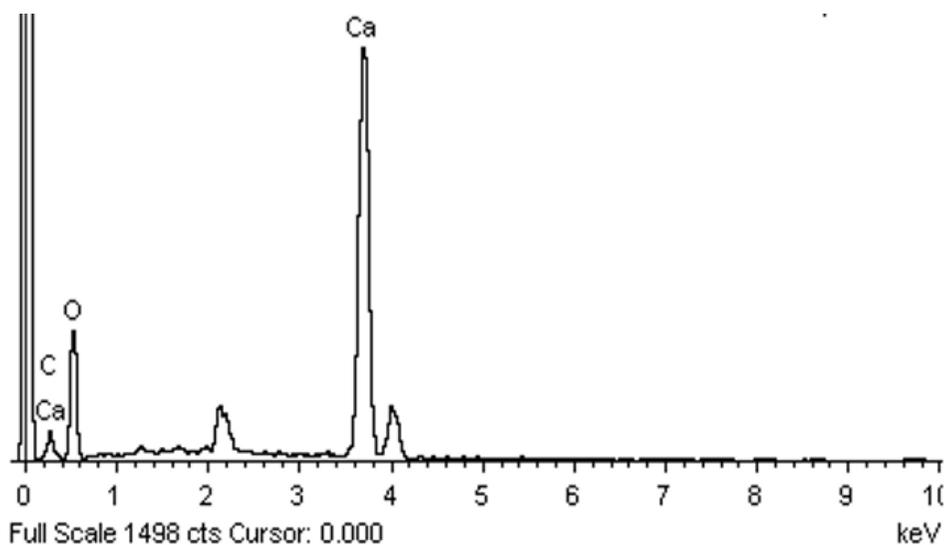
Figure 5 EDS spectrum of the calcined CaO catalyst made from eggshells heated at 800°C for 5 hrs.

The carbon content of the calcined CaO made from raw eggshell heated at 800°C for 5 hrs. was similar to standard CaO and the Ca/O ratios obtained are listed in Table 1.

%FFA

Waste cooking oil resulting from the production of fried rice crackers (*khaw tan*) that was sourced in Muang district, Lampang province was used for the preparation of the biodiesel. The percentage of free fatty acid (%FFA) in the prepared biodiesel was determined using the American Society for Testing and Materials (ASTM D6751) and the European Standard (EN14214) methods, as shown in Table 2. It was found that the decarbonized eggshell waste heated to 800°C for 5 hrs gave the purest and most actively transesterified CaO catalyst and this then yielded a higher biodiesel product

(similar to that resulting from the use of standard CaO) while shorter calcination times tended to introduce impurities and this lowered biodiesel yields. This production technique also has the advantage that waste $CaCO_3$ raw materials sourced from households and restaurants are easy to find.

Table 2 The %FFA of biodiesel made using calcined catalytic transesterification from different $CaCO_3$ waste precursors and heated to 800°C for various calcination times.

Conditions	The calcined catalyst	Crystallite sizes of CaO (D_{200})	Weight of biodiesel (g)	%FFA
Control	CaO Standard	N/A	2	0.346
Eggshell 2 hrs.	CaO + $CaCO_3$ and $Ca(O_2)_2$	N/A	2	0.730
Eggshell 3 hrs.	CaO + $CaCO_3$ and $Ca(O_2)_2$	N/A	2	0.641
Eggshell 4 hrs.	CaO + $Ca(O_2)_2$	65 nm	2	0.474
Eggshell 5 hrs.	CaO	67 nm	2	0.384
Cockleshell 2 hrs.	CaO + $CaCO_3$ and $Ca(O_2)_2$	N/A	2	0.859
Cockleshell 3 hrs.	CaO + $CaCO_3$ and $Ca(O_2)_2$	N/A	2	0.641
Cockleshell 4 hrs.	CaO + $CaCO_3$ and $Ca(O_2)_2$	65 nm	2	0.602
Cockleshell 5 hrs.	CaO + $CaCO_3$ and $Ca(O_2)_2$	58 nm	2	0.551

Conclusion

The optimum transesterified CaO catalyst for biodiesel preparation was found to be that made from waste eggshell calcined at 800°C for 5 hrs. This was due to the pure phase of the active catalytic CaO, which compared favorably to the less pure catalyst obtained from waste cockleshell, and its smaller size at the nanoscale, which should provide greater surface area.

Acknowledgement

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