

Synthesis and Characterisation of Calcium Oxide Catalyst Derived from Waste Oyster Shells for Transesterification of Glycerol

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Glycerol, the main by-product of biodiesel production, has experienced saturation in the market, hence affecting the biodiesel industry. Conversion of glycerol into value-added products, such as glycerol carbonate (GC), should be implemented to overcome this issue. Besides, the use of heterogeneous catalysts obtained from waste can reduce the cost and impact on the environment. Although basic homogeneous catalysts show high catalytic activity, they are hard to separate and unrecoverable. Hence, calcium oxide (CaO) was used as the catalyst in this research. The CaO catalyst derived from waste oyster shells (CaO-WOS) was prepared through calcination at 950 °C for 3 h, and TGA, BET, FTIR, XRD, and SEM were conducted for the characterisation of the catalyst. In this study, CaO-WOS and commercial CaO were used as the catalysts for synthesising GC through the transesterification of glycerol and dimethyl carbonate (DMC). The reaction was conducted under identical conditions (DMC-to-glycerol molar ratio of 2.5:1, reaction temperature of 40–60 °C, reaction time of 3 h, and catalyst loading of 4% molar ratio of the initial amount of glycerol). The crystallinity of both catalysts is identical as similar peaks appeared. The XRD and FTIR results confirmed the presence of CaO in the catalyst. The catalytic activity was compared by analysing the ¹H NMR spectra of the GC produced to obtain the predicted percentage molar concentration of GC. The predicted molar concentrations of GC for the transesterification conducted using commercial CaO and CaO-WOS are 97.0% and 72.5%, respectively. Hence, CaO-WOS is a good potential catalyst in the transesterification of glycerol into GC.

Keywords: Calcium oxide; waste oyster; transesterification; glycerol carbonate

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In this millennial era, the climate change crisis has been the biggest concern in the world. The burning of fossil fuels is one of the main contributors to the emission of greenhouse gases (GHGs) that caused climate change. Methyl ester, which is also commonly known as biodiesel, is a greener and more environmentally friendly alternative to fossil fuels, which was invented by Dr. Rudolf Diesel [1]. According to [2], the use of biodiesel could decrease the emission of GHGs by about 78%. Consequently, biodiesel has been widely used in substituting fossil fuels.

However, the production of biodiesel has resulted in the mass production of its main by-product (i.e., glycerol) by 10 wt.% [3]. In other words, 10 kg of glycerol is produced for every production of 90 kg of biodiesel. With the high demand for biodiesel, the production of glycerol as its by-product is concerning due to its large production. Figure 1 shows the prediction of the global production of glycerol, where approximately 4.0 billion L of glycerol will be produced

by 2020 [4]. Other than that, the price of glycerol is also predicted to decrease over the year. Due to this, the biodiesel sector would be greatly affected. Thus, the conversion of glycerol into value-added products is very critical to reduce the negative impact on the environment due to improper disposal of glycerol, to save the cost of its disposal [5], and to make the biodiesel production industry more competitive.

Glycerol or glycerine can undergo many types of reactions for conversion into value-added products, such as transesterification, esterification, oxidation, and valorisation [6]. Transesterification is one of the uncomplicated processes to synthesise glycerol carbonate (GC), a value-added product from the conversion of glycerol. Glycerol carbonate is one of the most expensive value-added products as it can be used in many different fields, such as cosmetics, pharmaceuticals, food, and chemical industries [7]. Thus, the production of GC could increase the value of glycerol in the industry.

Glycerol conversion is a catalytic reaction involving homogeneous and heterogeneous catalysts. Calcium oxide (CaO) can be a good basic catalyst in transesterification as it contains many active sites that can enhance the rate of reaction. In addition, CaO derived from waste oyster shells is eco-friendly and cost-effective. Furthermore, marine waste (e.g., waste oyster and scallop shells) has given a negative impact on the environment as most of the time, these wastes will be discarded in landfills, thrown in the land, or dumped back in the sea [8]. The negative impacts of improper disposal of these marine wastes include contamination to other marine organisms, as well as the production of unpleasant odours, leading to water and soil pollution. However, this issue can be overcome as the main composition of waste marine shells is calcium carbonate (CaCO₃), which can be calcined to produce approximately 90–94 wt.% CaO that can be used as value-added chemicals [9], [10].

Basic homogeneous catalysts are commonly used in the transesterification process as they can accelerate the rate of reaction at mild temperature and pressure due to the contact between the reactants and the catalyst being at maximum [11]. However, homogeneous catalysts are hard to separate and even almost impossible to be recovered, as well as non-reusable and less economic. Despite having a lower rate of reaction compared to homogeneous catalysts, acid heterogeneous catalysts are often used

in the industry due to the active acid sites present, which can lower the contamination in the product [12]. However, the use of acid heterogeneous catalysts leads to a very low rate of reaction. Hence, the function of the catalyst to accelerate the reaction is defective. Due to the disadvantages of homogeneous catalysts and acid heterogeneous catalysts, this research used a common basic heterogeneous catalyst (i.e., CaO) which has a high catalytic activity due to the presence of high surface basicity [13]. In transesterification, CaO is the most reviewed alkaline-earth metal oxide catalyst [10]. It is also commonly used in transesterification because it has a lot of advantages, such as low solubility, high basicity, and recovery [14].

Although commercial CaO is inexpensive and can be easily purchased, the development of more sustainable sources of catalysts would be beneficial to the industry and the environment. In addition, the composition of CaO in waste oyster shells is almost similar to that of commercialised CaO as it contains about 94% CaO [9]. Thus, this research developed an eco-friendly basic CaO catalyst derived from waste oyster shells.

In this study, the CaO catalyst derived from waste oyster shells (CaO-WOS) was used for the transesterification of glycerol to GC. The catalytic activity of the catalyst was compared to commercial CaO.

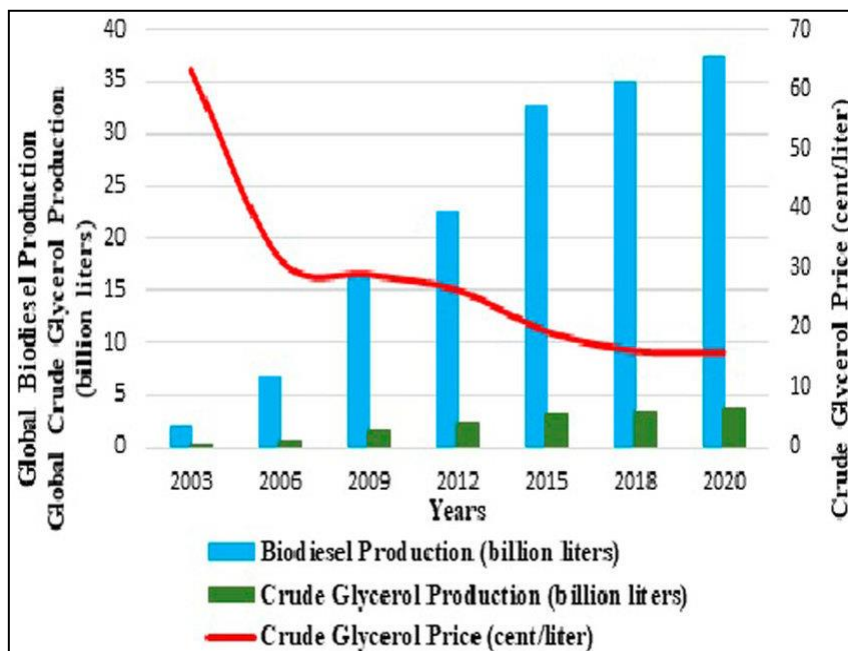


Figure 1. The predicted global biodiesel and crude glycerol production and price
Source: [4].

MATERIALS AND METHODS

Preparation of Waste Oyster Shell-Derived Catalyst

The method used for converting waste oyster shells to CaO is calcination [15], [16]. Prior to, first, the waste oyster shells were cleaned using tap water, followed by 10% w/v sodium hydroxide solution and distilled water to remove any organic materials, dirt, and contaminants on the shells. The shells were then dried in an oven at 100 °C for 4 h. Next, the dried shells were crushed and powdered in a grinder. The calcination of the crushed shells was carried out at 950 °C for 3 h in a furnace.

Catalyst Characterisation

The thermogravimetric analysis (TGA) of the prepared CaO-WOS and commercial CaO was conducted at a heating rate of 10 °C min⁻¹ until 1,000 °C. The graph of the weight loss of catalysts against temperature and differential scanning calorimetry (DSC) was plotted. The pore size distribution, total pore volume, and specific surface area of the catalysts were determined with Brunauer-Emmett-Teller (BET) analysis. In this analysis, -196 °C of liquid nitrogen circulated bath was prepared and used. Approximately 0.5 g of the catalyst sample was degassed to remove any moisture and impurities at 150 °C under vacuum conditions. The BET surface area, the total pore volume, and the average pore diameter of the catalysts were determined based on the adsorption-desorption isotherm and further calculated using the BET method. The determination of the catalysts' crystalline properties and their purity was conducted using X-Ray diffraction (XRD). The analysis was performed at 45 kV and 40 mA of Cu-K α radiation in the range of 20°–90° with a scanning rate of 2 s. Fourier transform infrared spectroscopy (FTIR) analysis was conducted on the catalysts to determine the stretching of the functional groups present in the catalysts in the wavenumber range of 450–4000cm⁻¹. The morphology and topology of the catalysts were determined using scanning electron microscopy (SEM). In this analysis, a small amount of catalyst was placed on the surface of the carbon tape fixed on the metal stub. A thin layer of gold was coated on the catalyst to avoid any electron charging during scanning. The images of the catalyst were captured at 2,500 \times magnification for both catalysts.

Transesterification of Glycerol with Dimethyl Carbonate

A 250-mL three-necked flask equipped with a condenser

and a water bath was used in the transesterification of glycerol and DMC with a DMC-to-glycerol molar ratio of 2.5:1. The reaction was conducted for 3 h at 40–60 °C. The CaO catalyst loading was added at 4% molar ratio of the initial amount of glycerol. The product was filtered to isolate it from the catalyst or to remove the catalyst.

Product Analysis

The GC produced from the transesterification process was confirmed using proton nuclear magnetic resonance (¹H NMR), where dimethyl sulphoxide (DMSO) was used as a solvent, and the results were compared to previous studies. The catalytic activity of commercial CaO and CaO-WOS was compared. The comparison of the catalytic activity was based on the percentage molar concentration of GC obtained from the transesterification process using constant parameters. These percentages can be calculated from the results obtained from ¹H NMR using the following formula, where I_{Hd} is the integration of Hd from GC, I_{Hg} is the integration of Hg from glycerol, and I_{He} is the integration of He from GC [17].

$$\% \text{ molar concentration GC} = \frac{I_{\text{Hd}}}{I_{\text{Hg}} + I_{\text{He}}} \times 100\%$$

RESULTS AND DISCUSSION

Characterisation of CaO-WOS

Thermal Analysis

According to Figure 2, the TGA plot and DSC curve for commercial CaO show that the weight loss experienced by the catalyst at around 450 °C is due to the loss of organic compounds present in the catalyst, while the weight loss at 700 °C is due to the loss of carbon dioxide (CO₂) and the carbonate starts to be converted into CaO [18]. At 700 °C, commercial CaO achieved a constant weight loss. Figure 3 presents the TGA plot and DSC curve for CaO-WOS, which also shows similar weight loss. However, CaO-WOS experienced an increment in the percentage of weight loss after 700 °C, which may occur due to the buoyancy effect as the gas surrounding the sample becomes less dense [19]. The DSC curve for both catalysts supports the TGA plot based on the endothermic peaks observed at approximately 450 and 700 °C. The results are in agreement with a previous study [18]. Hence, these results align with the calcination temperature used to convert CaCO₃ into CaO, where the calcination temperature should be above 700 °C for complete conversion.

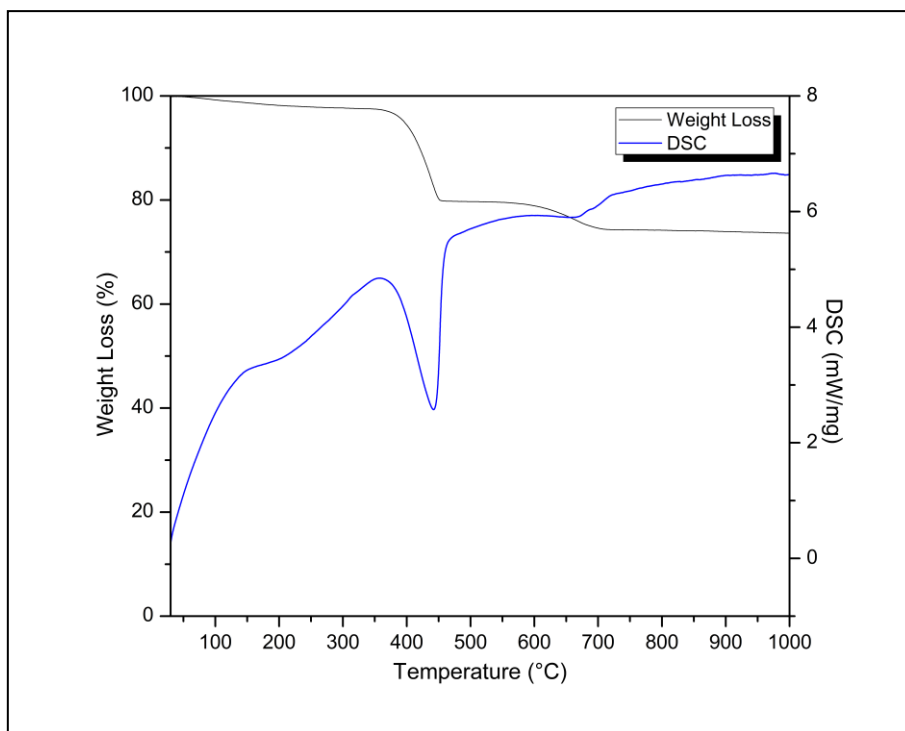


Figure 2. TGA plot and DSC curve for commercial CaO.

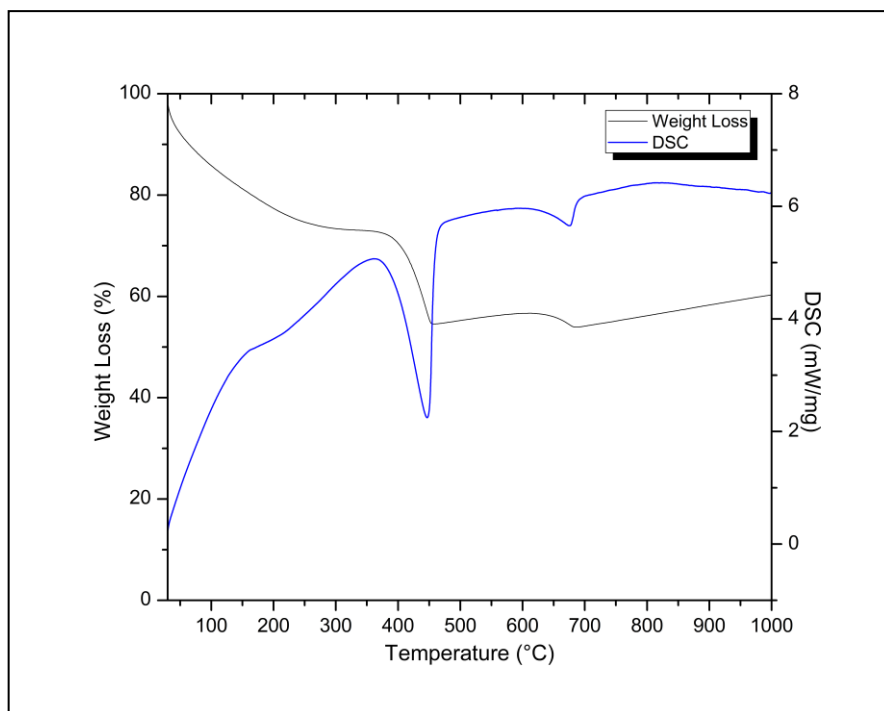


Figure 3. TGA plot and DSC curve for CaO-WOS.

BET Surface Area Analysis

The physical properties of the prepared catalysts determined using the BET nitrogen adsorption isotherm are presented in Table 1. The BET surface area, total pore volume, and average pore diameter of

commercial CaO are 3.2984 m²/g, 0.0173 cm³/g, and 37.3620 nm, respectively, and 2.9353 m²/g, 0.0112 cm³/g, and 19.9113 nm, respectively, for CaO-WOS. The trend shows that the BET surface area of CaO-WOS is smaller than commercial CaO. The results are in agreement with a previous study done by [16], as

shown in Table 1. The average pore diameter for commercial CaO and CaO-WOS is in the range of 2–50 nm, which proves that both catalysts are mesoporous materials. The isotherm plot as shown in Figure 4 and Figure 5 reveals that the catalysts exhibit an almost similar type of isotherm, which is a Type IV

isotherm. The isotherm plot displays a hysteresis loop, which is the Type H2 isotherm according to the IUPAC classification. Type H2 isotherm indicates the presence of non-uniform cylindrical pores.

Table 1. BET results for commercial CaO and CaO-WOS.

Catalyst	Commercial CaO	CaO-WOS	Reference [16]
BET Surface Area (m²/g)	3.2984	2.9353	3.000
Total Pore Volume (cm³/g)	0.0173	0.0112	0.008
Average Pore Diameter (nm)	37.3620	19.9113	11.000

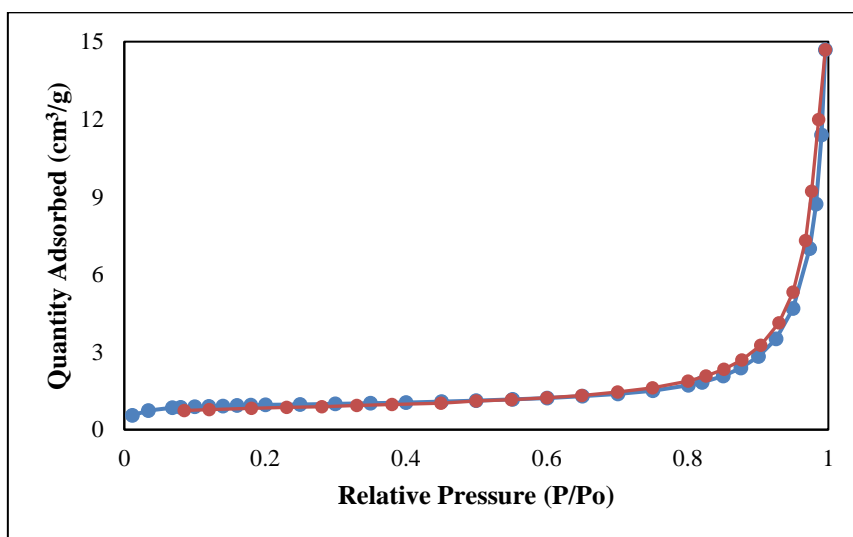


Figure 4. Nitrogen adsorption isotherm linear plot for commercial CaO.

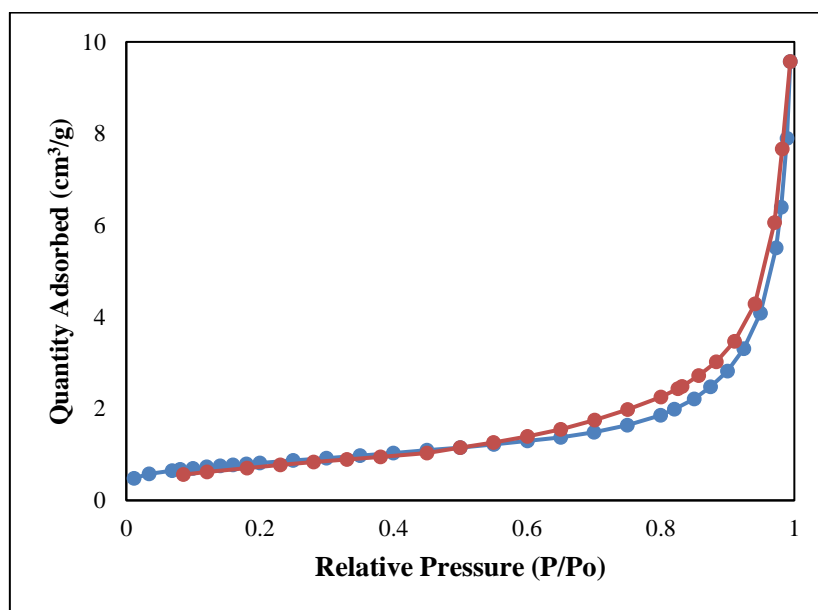


Figure 5. Nitrogen adsorption isotherm linear plot for CaO-WOS.

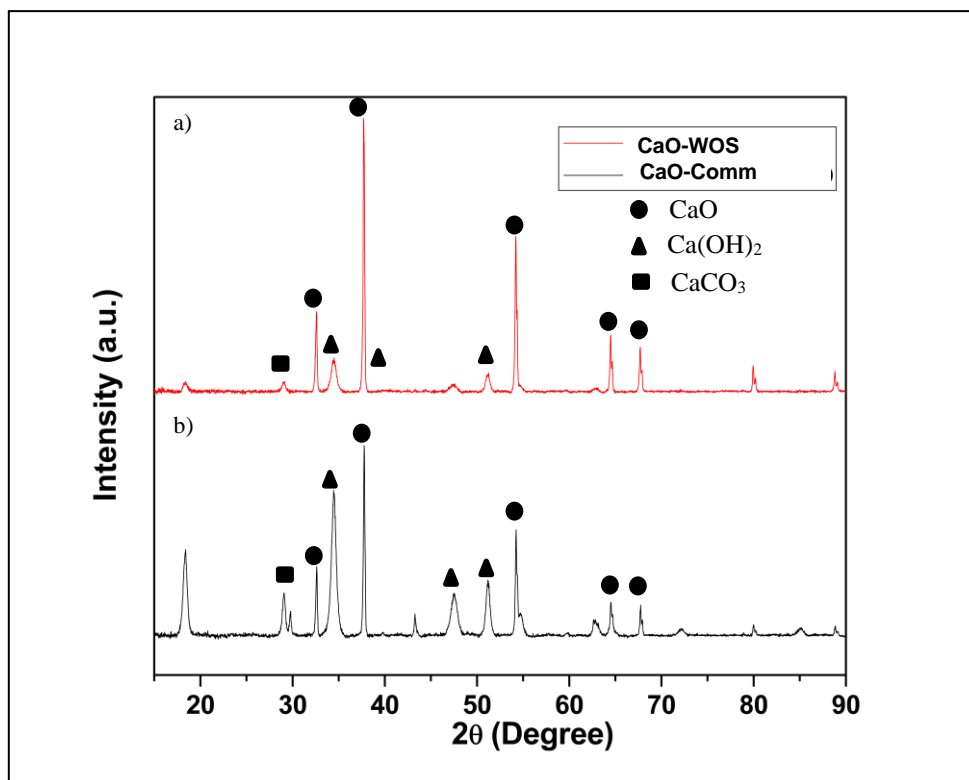


Figure 6. Crystalline peaks of a) CaO-WOS and b) commercial CaO.

Crystalline Structure Analysis

The XRD analysis was done to analyse the crystalline properties of commercial CaO and CaO-WOS. According to Figure 6, there are CaO, Ca(OH)₂, and a trace of CaCO₃ observed in the results, with CaO being the major content and Ca(OH)₂ being the minor content in both catalysts. The circles, triangles, and squares represent CaO, Ca(OH)₂, and CaCO₃, respectively. Based on the XRD analysis, CaO has crystalline properties, as shown by the sharp peaks. The presence of Ca(OH)₂ may be due to the humidity-induced interaction of CaO with water vapour [20]. The XRD results for commercial CaO and CaO-WOS indicate the presence of a small amount of CaCO₃ that was not completely converted to CaO, which may be due to insufficient calcination time. Tables 2 and 3 present the peaks based on the compounds present in the catalysts. Commercial CaO and CaO-WOS show similar peaks that represent CaO, which appeared at $2\theta = 32.4^\circ, 37.6^\circ, 54.3^\circ, 64.6^\circ,$ and 67.9° with a cubic crystal structure (JCPDS No. 01-074-1226). The

results agree with a previous study.

FTIR Analysis

Figure 7 shows the FTIR results with the functional groups labelled at each peak. Various functional groups present in the catalysts can be identified. For commercial CaO and CaO-WOS, the peaks at 3600 cm^{-1} and 3644 cm^{-1} show the physisorption of water molecules (-OH), which may be caused by humidity in the air. Next, at 1479 cm^{-1} and 1462 cm^{-1} , the peaks are due to asymmetric bending out-of-plane, bending in-plane, and stretching vibration of carbonate ion (CO_3^{2-}) from CaCO₃. Furthermore, the peaks at 550 cm^{-1} and 565 cm^{-1} are caused by the stretching of Ca-O bond, which illustrates the vibration characteristics of the CaO phase [20]. The presence of the peaks at $1200\text{ cm}^{-1}, 1127\text{ cm}^{-1}, 1017\text{ cm}^{-1},$ and 877 cm^{-1} in the FTIR graph of CaO-WOS may be due to the presence of C=O in CaCO₃. The FTIR results support the results obtained from XRD, in which a small amount of CaCO₃ is still for the synthesised CaO.

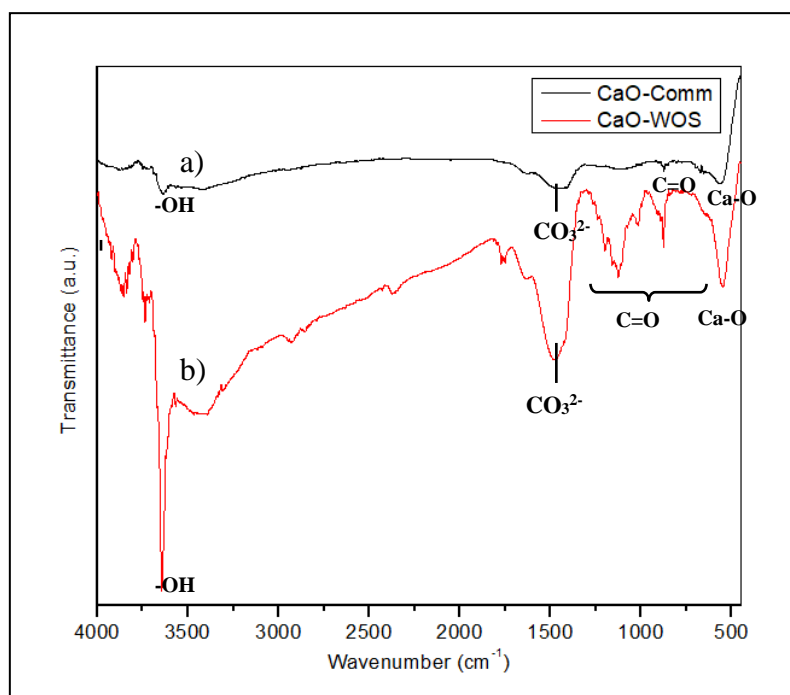


Figure 7. FTIR results for a) commercial CaO and b) CaO-WOS.

Table 2. XRD peaks of CaO-WOS.

Compounds	CaO	Ca(OH) ₂	CaCO ₃	References
2θ	32.4	34.4	29.1	[20],[21]
	37.6	47.3		[20],[21]
	54.3	51.2		[20],[21]
	64.6			[21]
	67.9			[21]

Table 3. XRD peaks of commercial CaO.

Compounds	CaO	Ca(OH) ₂	CaCO ₃	References
2θ	32.4	34.5	29.1	[20],[21]
	37.6	47.6		[20],[21]
	54.3	51.3		[20],[21]
	64.6			[21]
	67.9			[21]

SEM Analysis

According to the results of scanning electron microscopy (SEM) in Figure 8, the morphology of CaO-WOS has an irregular shape and a flake-like structure, while for commercial CaO, the morphology shows an agglomerated structure with an irregular

shape. This may be because CaO-WOS was prepared through grinding and filtering only; hence, it is not as smooth as commercial CaO. Thus, the size of CaO-WOS is much larger than commercial CaO. Other than that, the irregular surface may be caused by the elimination of CO₂ and organic matter through calcination [20].

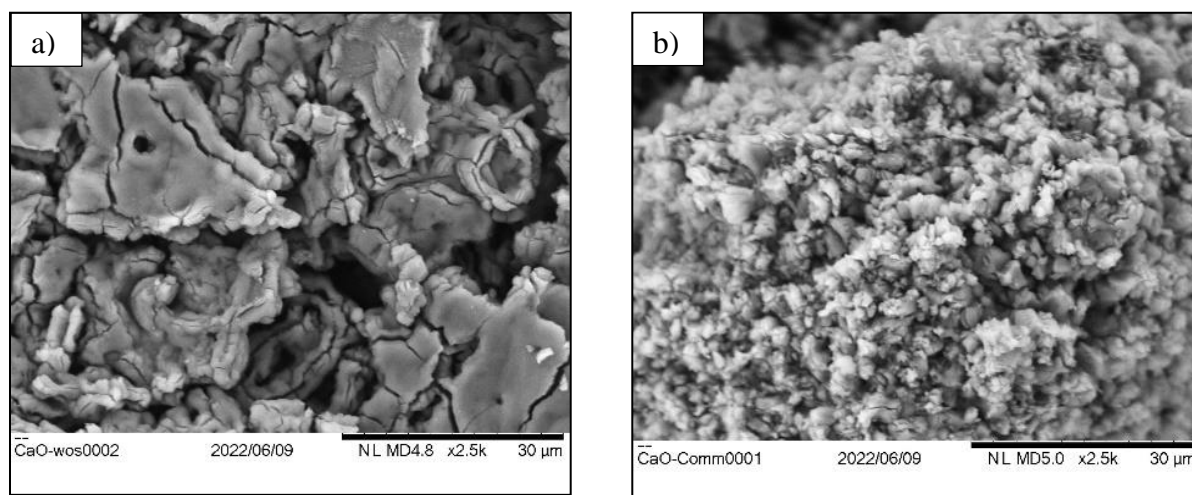


Figure 8. Morphology of a) CaO-WOS (10,000× magnification) and b) commercial CaO (5,000× magnification).

Transesterification of Glycerol with DMC

The transesterification of glycerol with DMC was carried out using commercial CaO and CaO-WOS as catalysts. The mass of GC produced using both catalysts is 11.4 and 11.1 g, respectively. The GC produced was further analysed through ^1H NMR.

^1H NMR Analysis

Proton NMR analysis was used to confirm the structure obtained from the transesterification of glycerol and DMC. The proton signals observed are presented in Figure 9. The results obtained are identical to the results of [17], which also used DMSO as the solvent. The solvent peak for DMSO appeared at around 2.5 ppm. The multiplet peaks at 4.39 ppm for commercial CaO and 4.47 ppm for CaO-WOS labelled as Ha are present in GC. At 4.15 and 4.05 ppm, the doublet-of-doublet signals labelled as Hb were observed, which belong to commercial CaO and CaO-WOS, respectively. Another multiplet

signal at 4.64 and 4.60 ppm for each catalyst belongs to a proton with multiple neighbouring protons labelled as Hc. The peaks at 3.44 and 3.33 ppm for commercial CaO and 3.43 and 3.29 ppm for CaO-WOS represent Hd and He, respectively, which are the signals of superimposed glycerol [17]. These signals overlapped because the peaks are so close to each other, along with the additional signal at 3.5 ppm that represents H_2O molecules. The triplet peak at 5.19 ppm for commercial CaO and CaO-WOS is attributed to OH, which is found in the GC compound. Other than that, the signal that appeared at 4.35 ppm for the reaction with CaO-WOS, which is labelled as Hg, is the signal that represents the proton from the glycerol compound. This shows that unreacted glycerol is present in the transesterification reaction using CaO-WOS as a catalyst. Other unidentified peaks may belong to methanol, the side product for the transesterification of glycerol, and DMC. Table 4 shows the summary of the positions of the protons, and the outcome is consistent with a previous study.

Table 4. Protons present in the NMR spectra.

Proton	Position of peaks (ppm)		References (ppm) [17]
	Commercial CaO	CaO-WOS	
Ha	4.39 (m, 1H)	4.47 (m, 1H)	4.33–4.48 (m, 1H)
Hb	4.15 (dd, 1H)	4.05 (dd, 1H)	4.20–4.25 (dd, 1H)
Hc	4.64 (m, 1H)	4.60 (m, 1H)	4.70–4.75 (m, 1H)
Hd	3.44 (m, 1H)	3.43 (m, 1H)	3.55–3.60 (m, 1H)
He	3.33 (m, 1H)	3.29 (m, 1H)	3.40–3.50 (m, 1H)
Hf	5.19 (t, OH)	5.19 (t, OH)	5.25–5.30 (t, OH)
Hg	-	4.35 (m, 1H)	4.35–4.40 (m, 1H)

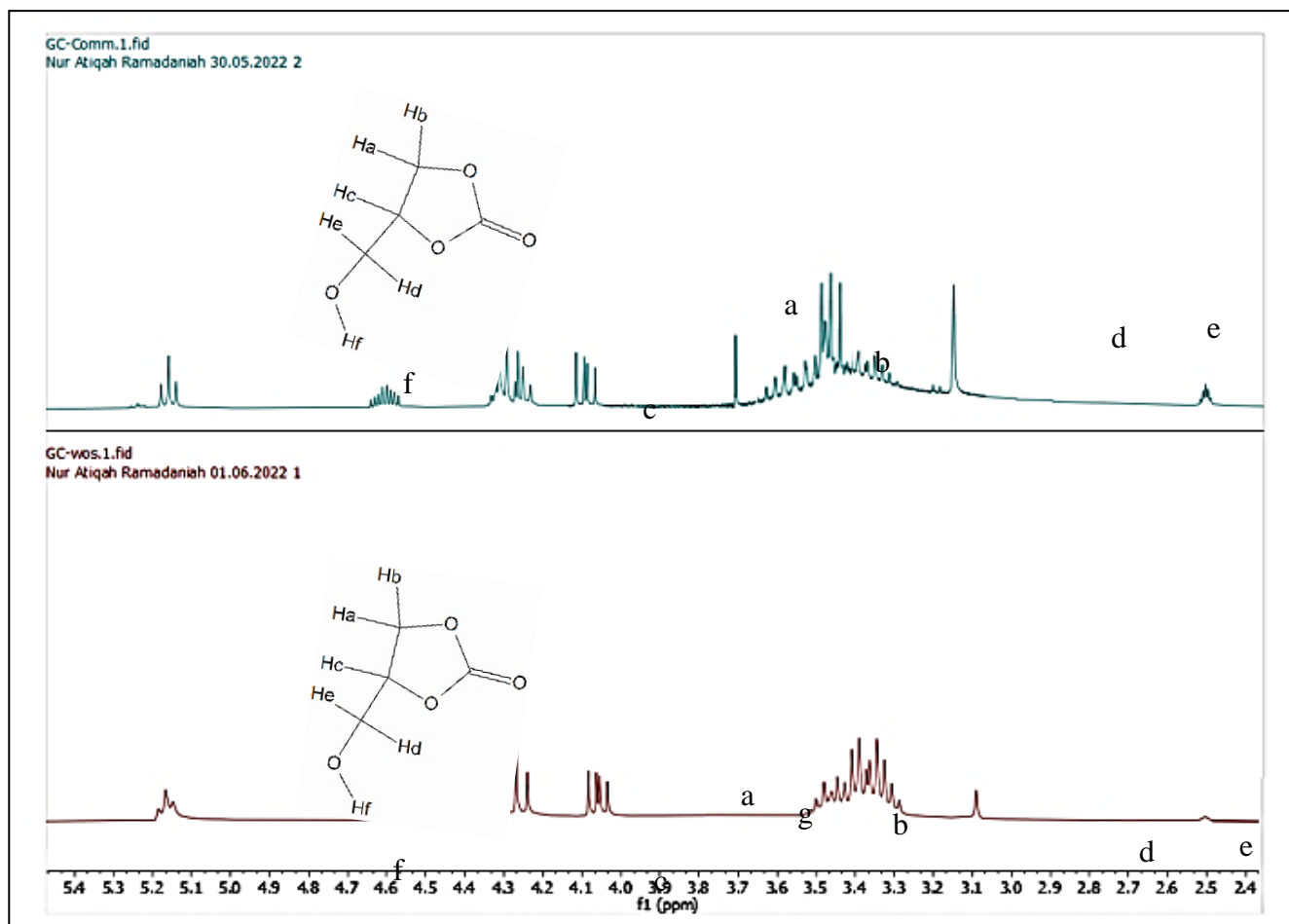


Figure 9. NMR results for i) commercial CaO and ii) CaO-WOS.

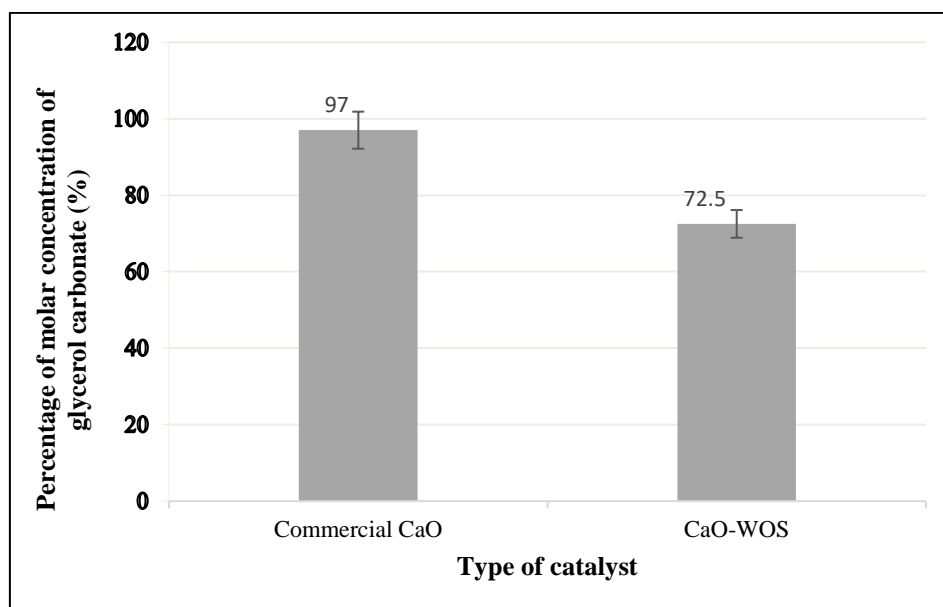


Figure 10. Percentage of molar concentration of glycerol carbonate produced from ¹H NMR.

Comparison of Catalytic Activity.

The integration values of the peaks were used to determine the predicted percentage molar concentration of the GC produced [17]. The specific peaks used are Hd, He, and Hg peaks, where for commercial CaO, the integration values are 0.58, 0.60, and 0 respectively. On the other hand, the integration values for CaO-WOS are 0.87, 0.77, and 0.43 for Hd, He, and Hg, respectively. Hd and He represent the proton attached to C-OH in GC, while Hg represents the proton in glycerol. As a result, the predicted molar concentration of the GC produced with commercial CaO as a catalyst is 97% and 72.5% when using CaO-WOS. Based on the NMR results, the glycerol conversion using CaO is 100% as no Hg peak was present. Hence, from Figure 10, the reaction with commercial CaO shows higher catalytic activity (97%) than CaO-WOS (72.5%).

CONCLUSION

In conclusion, CaO-WOS was successfully synthesised. The characterisation of CaO-WOS was conducted using TGA, BET, FTIR, XRD, and SEM. The characterisation results show similar properties between CaO-WOS and commercial CaO. The analysis of XRD confirmed the presence of CaO in waste oyster shells and can function as a catalyst. Furthermore, the analysis of the product was done using ¹H NMR to determine the molar concentration of the product and analyse the effectiveness of the catalysts. Hence, ¹H NMR can be an alternative for quantification analysis. The catalytic activity of the catalysts was compared by calculating the predicted molar concentration of the GC produced, which is 72.5% for CaO-WOS. This study reveals that CaO-WOS is a good potential catalyst in the transesterification of glycerol with DMC.

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