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Calcium Oxide from Waste Shells as Potential Green Catalyst for Biodiesel Production

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Abstract: This paper concentrating on the characterizing the effect of various calcination temperatures on calcium oxide (Ca-O) derived from waste shells as an alternative economic heterogeneous catalyst. The characterization of green-based heterogeneous catalysts, prepared from waste mussel shells, is investigated in this case study. The waste mussel shell catalyst was prepared for 4 hours at different high calcination temperatures of 900, 950, and 1000°C with continuous nitrogen gas supply at a 5°C per minute heating rate. Catalyst characterized by different methods: a study of X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), and Fourier Transform Infrared Spectroscopy (FTIR). From the results, a trend of different temperatures for the calcium oxide catalyst derived from the mussel shells was analyzed to the optimal condition of the 950°C calcination process. The diffraction pattern of calcium oxide derived from decomposition at 950°C showed a trend close to calcium oxide developed by the Joint Committee on Powder Diffraction Standard (JCDPS), which between 32.3, 37.5, 54.0, 64.0, 67.2, 79.5 to 88.5 degrees in 2 theta ranges. A specific high-intensity FTIR spectrum occurs at a wavelength of 3642.84 cm⁻¹ of decomposed calcium oxide of 950°C, similar to the particular vibration of Ca-O. Besides, a high surface area and pore diameter at 950°C calcination temperature was revealed in the morphology surface of the developed catalyst. The findings show that waste shells derived from mussels are feasible as a potential catalyst and expect to achieve a high yield conversion during the transesterification process.

Keywords: Calcium Carbonate, Calcium oxide, Biodiesel, Catalyst, Mussel shell, Calcination, Heterogeneous

1. Introduction

Energy and its sustainable growth are some of the most critical components of humanity. The energy supply crisis is worsening today and is one of the most significant challenges we face. Fuels are vital because they can burn and generate large amounts of energy. Many daily tasks, particularly goods and people, rely on the transport of fuel. As the number of oils discovered worldwide decreases with growing demand, alternative fuels must be generated. Oil resources in the coming years are expected

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to be reduced. Biodiesel is a source of renewable energy as safe as conventional diesel. Today it is well known as the carbon-neutral, biologically degradable, non-toxic, and usually sulphur free and aromatic coal, despite the growing worldwide concern for the protection of non-renewable natural resources and environmental sustainability (Mueanmas et al., 2010).

During the transesterification process, homogenous catalysts and heterogeneous catalysts can be used. A catalyst is often defined as material or substance that reduces its stimulating energy to accelerate the chemical reaction process. The most economic problem is that the standard shape used in the industry is a homogeneous catalyst. The use of homogeneous catalysts also includes they are non-reusable, non-ecological, and lead to colossal wastewater from purification (Rahman et al., 2019). Heterogeneous catalysts gain interest because they are highly active, withstand high temperatures, and need no catalytic recovery or water treatment. The catalyst produced naturally from waste shells opens the door and utilizes sustainable catalyst wastes simultaneously. Every year, the shellfish and mollusks produce over 100 million pounds of waste (Perea et al., 2016).

Seeking ways to reuse waste seashells has been increasingly explored. In Malaysia, some dishes use this kind of seafood as the main ingredient for daily meals. By using shell waste as a catalyst raw material, synthesis is such an attractive alternative method for low-cost biodiesel catalyst development. The use of green waste as heterogeneous catalysts has recently been a focus on sustainable initiatives. While minimizing catalyst costs, using all these waste materials emphasizes a healthy and environmentally friendly process. Waste shells are a calcium-rich resource that provides a great source of heterogeneous catalyst calcium oxide (Perea et al., 2016). A detailed study on the relationship between catalyst features and catalytic activity, along with optimizing catalyst preparation, would also be necessary for this research.

2. Waste Shell as Heterogeneous Catalyst

A ton of human-produced waste can be used efficiently to fulfil energy requirements, which can come from different sources, solid, liquid, or gaseous. The use of heterogeneous waste catalysts was of recent concern so that the production of biodiesel would be more sustainable. The waste shell was evaluated as an efficient catalyst for the conversion of vegetable oil to methyl esters. Some of the main contributors to waste shell include eggshells, mussel, snail, oysters, crab, and many more. The chicken eggshells consist mainly of calcium carbonate, which produces durable calcium oxide when calcined above 700°C (Correia et al., 2014). According to the past findings conducted by (Niju et al., 2014), by applying 900°C calcination temperature for 2.5 hours, catalyst concentration 5wt.% and 12:1 molar ratio, 65°C reaction temperature and 1 hour reaction time, the biodiesel yield was 67.57% for commercial and 94.52% for eggshell-derived CaO. In Malaysia, the retail value of cockles alone in 2007 was estimated at over 32 million US dollars (Boey, Maniam, Hamid, et al., 2011). As a factor, waste shell production is abundant, and the plentiful supply makes it possible to use or co-use the shell as a catalyst in biodiesel production. According to the study, at a reaction temperature of 1 hour, the waste shell catalyst is at 50°C, and the oil methanol ratio is 9:1, 78.05 % of the biodiesel yield has recorded. The maximum yield of 3:1 methanol per oil ratio is 73.95% at a reaction temperature of 60°C for commercial CaO in 3 hours (Ngadi et al., 2017). The physical nature of snail shells that are common species found in open seas and ponds. In a different view, these shell types are commonly seen as decorative objects and jewellery and make everyone have a little interest.

In a previous study has reported the optimal calcination temperature for river snail found to be at 800°C by using the transesterification process with waste cooking oil as feedstock. On the research done by (Kaewdaeng et al., 2017), the FAME yield achieved to 98.19% by using 3wt.% catalyst loading, 9:1 molar ratio, 65°C reaction temperature and 1 hours reaction time. In other results revealed decreasing of yield from 98% to 77% during the 9th cycle, reused back the catalyst in optimizing the parameter of

3wt.% catalyst loading, 900°C calcination temperature, 7 hours reaction time, and 6:1 molar ratio (Laskar et al., 2018). A massive number of scallop shells are produced in the North of Japan each year, and this type of shell is usually stranded on the roadside, causing a horrible odor (Sirisomboonchai et al., 2015). CaO catalytic performance is stated to be maximized from 900°C to 1100°C, similar to the optimum scallop shell calcination temperature (Zhu et al., 2006).

By blending palm oil as feedstock and calcinated catalyst derived from waste scallop shell at 1000°C will result to 95.44% of yield. Crab shell materials are very long-lasting and contain chitin and calcium carbonate as the main element (Vijayaraghavan et al., 2006). Characteristics have shown that calcium carbonate, which has been converted into calcium oxide for 2 hours, has been the principal element of the shell if it is activated above 700°C (Boey et al., 2009). From the findings from the past research, with the concentration following reaction temperature 65°C, 0.5:1 methanol to oil mass proportion, and 2.5 hours of reaction time, the calcinated crab shells (at 900°C) were able to trans-esterify palm olein to 98.8 wt. % purity (Boey, Maniam, & Hamid, 2011). The statistics show that 300,000 tons of oyster shells were disposed of every year, and microbial decomposition occurred and that highly toxic gases like NH₃ and H₂S were developed (Silva et al., 2019). The principal component (approximately 96%) of oyster shells is calcium carbonate (CaCO₃), which can be converted into calcium oxide for biodiesel production (Buasri et al., 2015). The CaCO₃ catalyst is converted into CaO at temperatures of 900°C for 2 hours after calcination (Buasri et al., 2015). The result revealed that the biodiesel yield is above 70% and 98.4% pure in 5-hour reaction time by using 25wt. % of the calcinated oyster shell (at 700°C) at 6:1 methanol: oil molar ratio.

3. Materials and Methods

The case study covers on the particular method for preparing, characterizing and working principle of equipment that will be used to make catalysts for calcium oxide catalysts derived from waste shells. Dry mussel shells powder (250g) was put in a silica cup and then decomposed at several temperatures (900, 950, and 1000°C) using a high-temperature electric furnace. At room temperature, the calcined waste shell was cooled and stored over silica gel in desiccators. The catalyst was then characterized by using XRD powder, followed by identification by using FTIR spectroscopy and SEM-EDX. The XRD powder pattern for calcinated mussel shells at different temperatures as compared to the XRD calcium oxide powder pattern developed by (Lesbani et al., 2016). The X-ray diffraction (XRD) analysis will be performed with the condition of data collected over a two theta range of 10° to 90°, step size of 0.02° and scanning speed of 4°/min. Calcium oxide characterization was performed using FTIR spectrophotometer Perkin Elmer Spectrum 100 series between the limits of scan range are between 600 to 4000cm⁻¹, X-Ray Model Bruker D8 Advance, and SEM-EDX Hitachi VP-SEM SU1510. For the SEM image and EDX analysis of the sample, magnification of ×2000 and ×5000 is used.

3.1 Impact Preparation of Calcium Oxide as Green Waste Shell Catalyst

In this paper, calcium oxide is derived from a mussel shell catalyst as a source for a green waste shell. A group of mussels (500 gm each) was collected from Kampung Sungai Lurus in Senggarang, Batu Pahat, Johor, Malaysia. Its geographical coordinates are 1 ° 46 '10' 'North, 102 ° 58' 9 " East. Mussel shells are then washed regularly for several times until they have been cleaned and impurities removed. For a day, it is dried in daylight to extract moisture before it burns inside the oven at 100°C in 4 hours located at the Laboratory of Polymer and Ceramic Faculty of Mechanical and Manufacturing (FKMP) UTHM. Next, the catalysts are determined by the three different calcination temperatures used, which are 800°C until 1000°C. The range of powder size produced is then sieved between 150 to 250 microns. The powder is then calcinated in an aluminium crucible for three hours, at a temperature of 900°C to 1000°C at 5°C heating rate by using a high-temperature furnace. After the calcium oxide derived from waste shells is burned, it had been cooled to the ambient temperature for a day and then

placed in a desiccator for use. Then, the calcined powders will be ground using mortar machines and sieved by particulate measurement in the range of 100 to 140 micrometers to complete the catalyst preparation process. The overview of the procedures to be used in catalyst preparation is given in Figure 1. Catalyst preparations are started at different temperatures with processing, washing, drying, grinding, and calcinating.

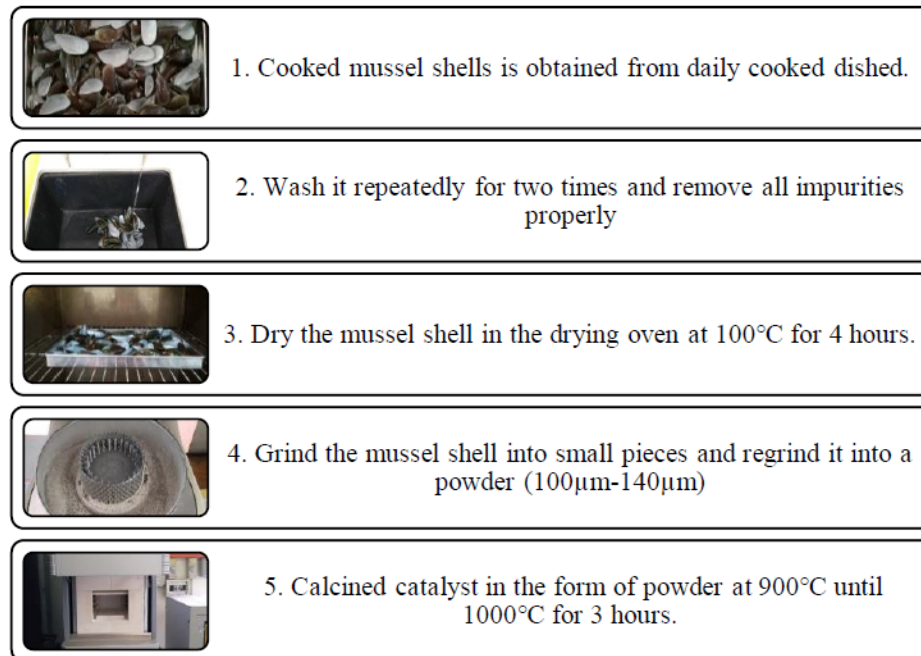


Figure 1: Waste shells catalyst derived preparation

4. Results and Discussion

A total of three samples of heterogeneous green-based mussel shell catalysts were prepared with different calcination temperatures. The experiment was successfully carried out at 900, 950, and 1000°C during the calcination process. After calcination, it can be seen clearly that the colour of the mussel shells is shifting from dark grey to white as shown in Figure 2. Calcination provides the finest particle for 1000°C; it is followed by 950°C and 900°C, respectively. It is due to traces of organics that are not presented in bright samples obtained at high temperatures.



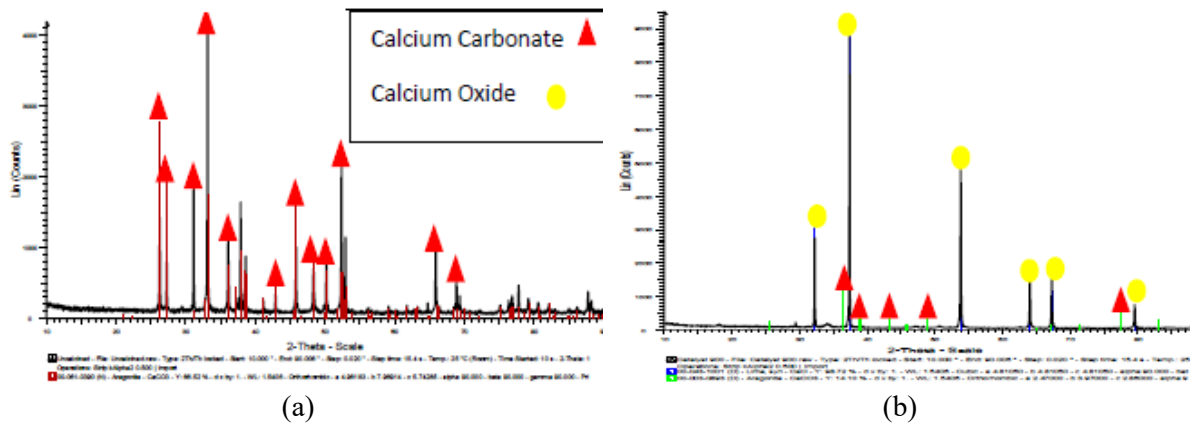
Figure 2: Natural catalyst (left) and calcined catalyst (right)

4.1 XRD Analysis for CaO Produced from Waste Shell

To determine the phase present in the samples, XRD analysis was performed for the three samples of different temperature calcined mussel shells catalyst. Peaks of CaO should be present at intensities of 2 theta ranges between 32.2°, 37.3°, 53.8°, 64.1°, and 67.3° according to JCPDS (Lesbani et al., 2016). In Figure 3(a), XRD analysis shows that natural mussel shell composition consists primarily of CaCO₃ with aragonite crystalline structure but without CaO peaks, as indicated by a 2-theta range dominant peak at 33.0°. These results were similar to what the previous study (Haslinda Shariffuddin et al., 2018) reported. Multiple spikes of unreacted (CaCO₃) in calcite type were shown by diffractogram from mussel shells waste calcinated at 900°C, that can be classified at 2 theta range between 25.2°, 36.5°, 39.0°, 43.2°, 45.9°, 48.9°, 77.5°, and 83.2° as seen in Figure 3(b). The catalyst produced calcite (CaCO₃) at 2 theta ranges which indicated that the CaCO₃ to CaO decomposition was not fully completed. The hard physical structure of the mussel shells is possibly due to the difficulty to decompose even at high temperature (Lesbani et al., 2016). As for the catalyst of mussel shells calcined at 950°C, better results have been reported in Figure 3(c) with less CaCO₃, suggesting that almost all reacted and synthesized to CaO.

On the other side, after the calcination process at a temperature of 950°C, calcined mussel shell powders showed peaks at 2 theta range between of 32.3°, 37.5°, 54.0°, 64.0°, 67.2°, 79.5° and 88.5° which conformed to the CaO crystallite structure due to the transformation of calcium carbonate into calcium oxide. In contrast, small amounts of CaCO₃ remained in the form of calcite at peaks of 30.90°, 41.0°, 49.0°, 62.30°, and 30.90°. As for powder calcined at 1000°C, an only small amount of CaCO₃ was detected at 2 theta range between of 30.80°, 41.0°, 49.0, 62.1 and 82.2° as can be seen in Figure 3(d). The powder samples at this temperature showed the large presence of CaO, which were detected at the peak of 32.1°, 37.5°, 54.0°, 64.0°, 67.5°, 79.5° and 88.5° from 2 theta ranges. From all three diffractograms, the peaks for calcium oxide were identified, located similar to (Lesbani et al., 2016). It can be concluded from the three graphical XRD that the best calcination temperature was 950°C. Comparing calcination graph at 900°C and 950°C, it is apparent that at 950°C calcination produced more CaO than 900°C where it can still clearly found that a reasonable number of unconverted CaCO₃ remains.

In consideration of conversion CaO yield, the percentage rate of catalyst conversion at 950°C is 109.93% higher than the catalyst at 900°C, which is only 98.72% conversion yield. The development of CaO derived from waste mussel shells only showed slightly different for calcination between 950°C and 1000°C. Although calcined powder at 1000°C shows the sharper peak of intensities where the value almost reached 11200 (arb units) as compared to only 8500 (arb unit) calcined powder at 950°C, it still produced unreacted of CaCO₃. The main reason for this XRD comparison was to help improve the sustainability of biodiesel production by choosing lower temperature calcination to reduce the consumption of energy by indirectly aiming to reduce the costs of the entire process.



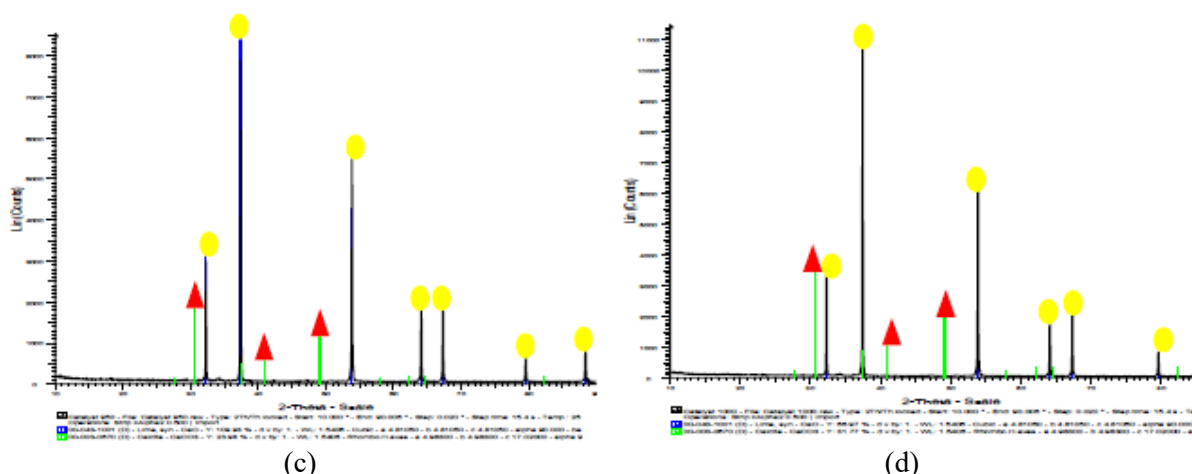


Figure 3: Mussel shell catalyst at (a) natural (b) calcined 900°C (c) calcined 950°C (d) calcined 1000°C

4.2 FTIR Analysis

FTIR analysis was conducted for the three samples of calcinated mussel shells powder with different temperatures, including natural without calcinated. For the natural mussel shells as seen in Figure 4(a), the main absorption band detected at 1446.41cm^{-1} can be traced to the bending vibrations of CH_2 deformation and the other two leading absorption bands observed at 857.91 and 712.54cm^{-1} can also be related to the out of the plane band and in-plane vibration modes for CO_3^{2-} ions. These results attributed to the presence of CaCO_3 in the mussel shells. The results were similar to what the previous study (Laskar et al., 2018) reported on a study of snail shells as a waste catalyst for biodiesel. The sharp peaks of 3641.67cm^{-1} were obtained in Figure 4(b) indicates that the hydroxyl group (Free O-H) was present where $\text{Ca}(\text{OH})_2$ was caused by water absorption, which was proportionate to the powder when calcination temperature was applied at 900°C . There is no such peak observed in the natural catalyst spectrum at the location of 3600cm^{-1} . Moreover, the band at 1471.90cm^{-1} indicated the CH_3 band, and the band centred at 874.19cm^{-1} showed the carbonate ions in the functional group of (C-H). The findings for 900°C calcinated catalysts are close to research on the heterogeneous catalyst cockle shell (Ngadi et al., 2017).

In Figure 4(c), the high-intensity band at 3642.84cm^{-1} showed free O-H (hydroxide) bands for the 950°C calcinated catalyst, where the percentage of transmittance 92.49% which is higher than catalyst calcinated at 900°C which is only 91.11% . The CH_2 and C-H bending vibration at 1417.55cm^{-1} and 874.19cm^{-1} define the presence of alkanes and alkene functional class, which is caused by the carbonization of atmospheric during the synthesis. Lastly, for the calcination temperature 1000°C catalyst, there are two new peaks occur at the range of wavelength 3677.31cm^{-1} and 3873.03cm^{-1} with the percentage of transmittance for each peak is 93.57% and 93.53% . Based on the IR spectra, the dominant peak occurs at 3646.25cm^{-1} , which is revealed the intensity band of free O-H (hydroxide). Besides, the new peak also detected at the wavelength of 2162.48cm^{-1} with a percentage of transmittance 94.49% . In comparison, the FTIR spectrum of three different calcination temperatures showed similar trends with the FTIR spectrum obtained from other types of waste shells, which is the research done beforehand. Meanwhile, a catalyst calcined at 1000°C tracks the higher percentage of transmittance hydroxide O-H bands compared to 900°C and 950°C , as shown in Figure 4(e). This wavelength range was also reported in the eggshell and mud crab shell analysis (Correia et al., 2014) as a waste shell catalyst. This finding is also supported by research (Boey et al., 2009b) that the sharp band at 3641cm^{-1} area linked with the OH water physisorbed stretch on the CaO surface. From all the results shown, calcium oxide from waste mussel shells can be one of the promising green-based catalysts for the next transesterification process.

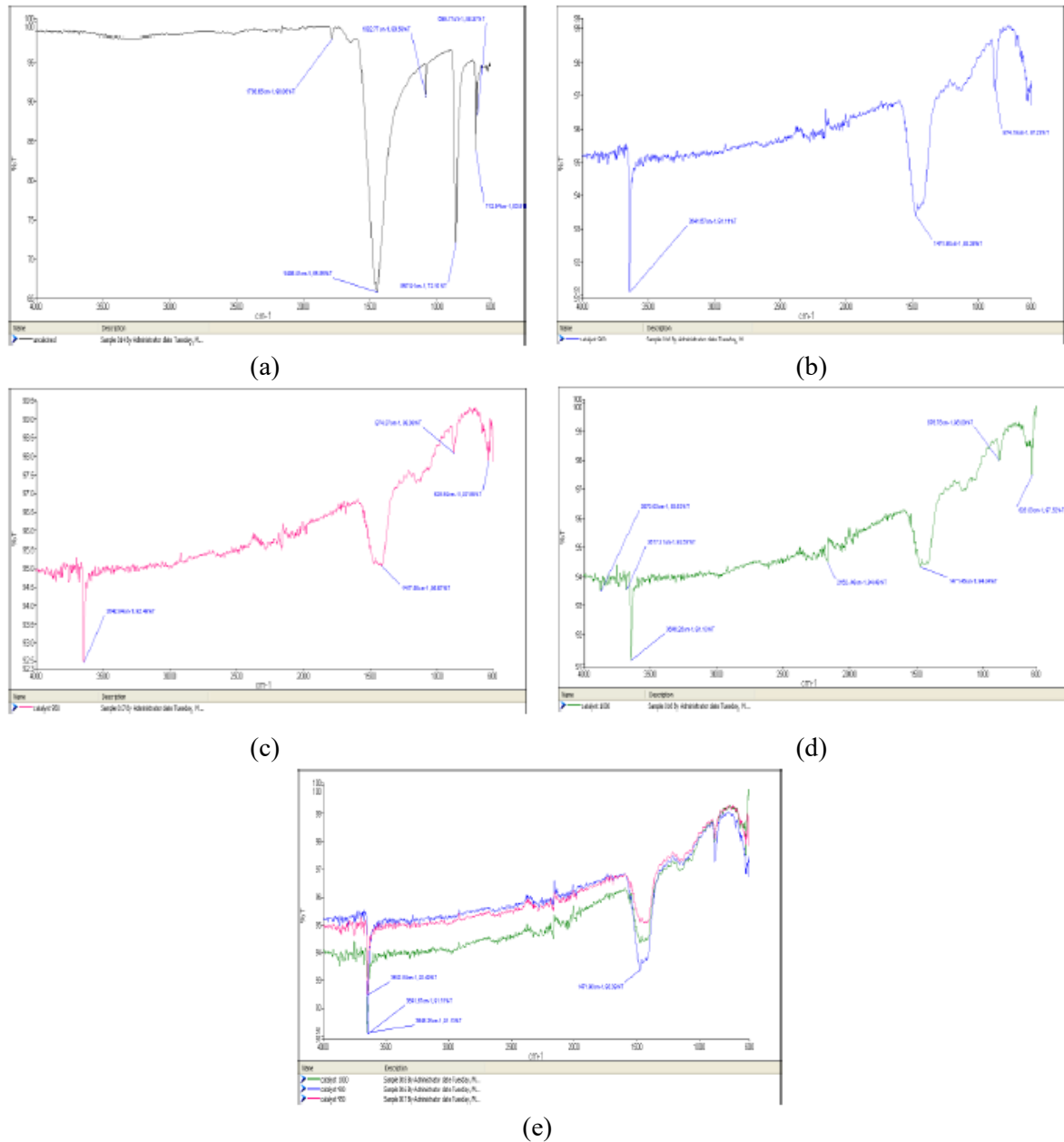


Figure 4: Functional group wavelength for (a) Natural catalyst (b) Catalyst at 900°C (c) Catalyst at 950°C (d) Catalyst at 1000°C (e) Comparison catalyst 900, 950 & 1000°C

4.3 SEM Analysis

The SEM image analysis was done with the catalyst developed to study whether the effect of temperature calcination would be affecting the shell powder surface morphological. Figures 5 and 6 demonstrate the surface morphology of three calcined calcium oxide and natural powder samples derived from waste mussel shells. Two different magnifications, 2000X and 5000X, have been analyzed for the surface morphology of each sample. The mussel shells catalyst contains various sizes and shaped particles for both natural and calcined powder. It may be due to the various size range of the powder catalyst during the sieving process, which is between 100 to 140 micrometers. Besides, the temperature distribution was the main reason why the irregular shapes obtained from the SEM image due to the calcination process inside a high-temperature furnace, the catalyst powder inside an alumina crucible without cover reveals more heat exposed at the top of the catalyst powder rather than at the bottom. The presence of large porosities in relative to increasing the temperature of calcination gives the higher porous structure shown in the morphological of the sample.

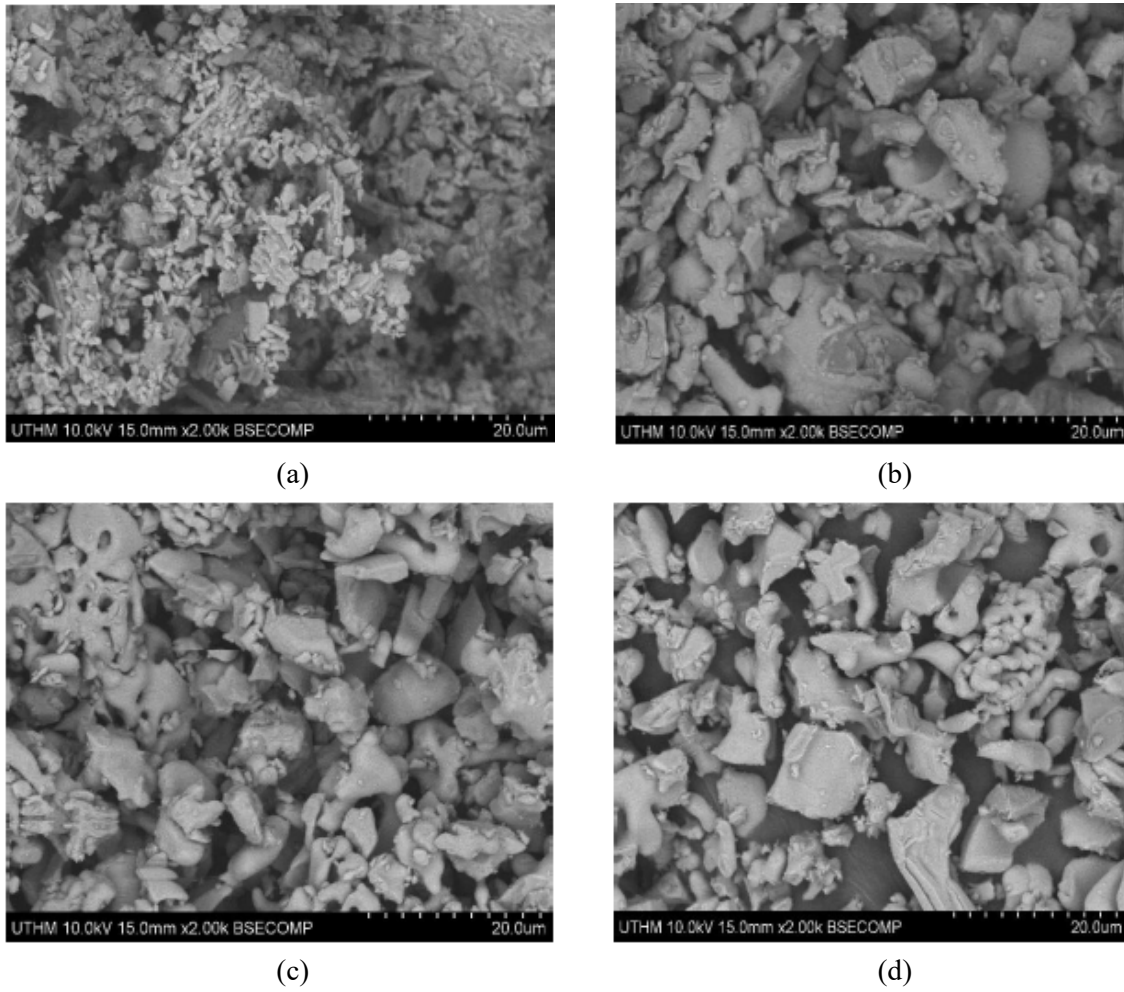
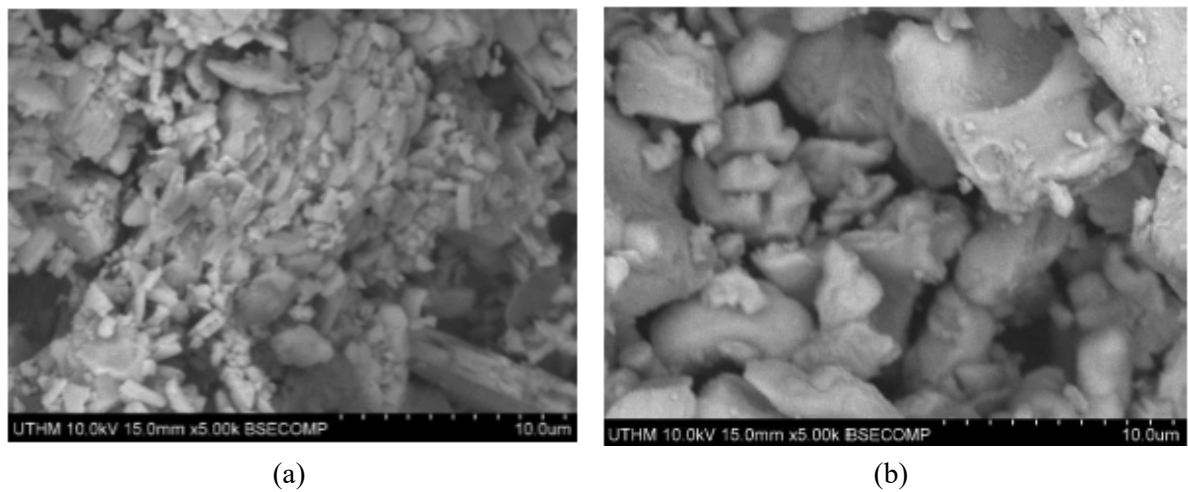


Figure 5: SEM Analysis for natural (a), calcined at 900°C (b), calcined at 950°C (c) and calcined at 1000°C (d) (2000X Magnification)



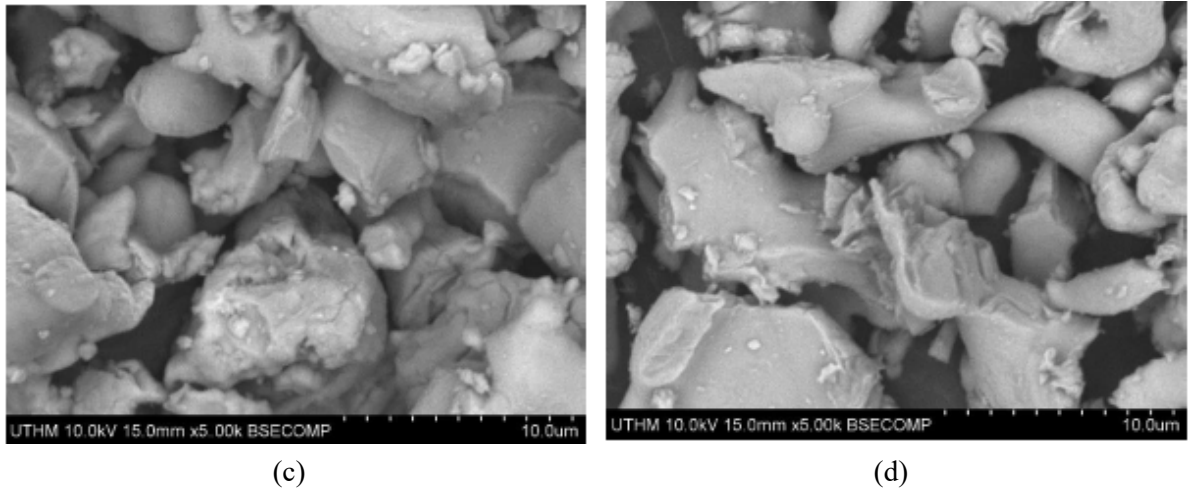


Figure 6: SEM Analysis for natural (a), calcined at 900°C (b), calcined at 950°C (c) and calcined at 1000°C (d) (5000X Magnification)

The same morphology structure was examined in previous work done by (Buasri et al., 2013) to study calcium oxide derived from the mussel, cockle, and scallop shell for biodiesel production. For the observation of natural waste mussel shell catalysts, the morphology was shown to seem a bulky substance with a heavily layered architecture. The average pore diameter and particle area of the natural and calcined catalysts were stated in Table 1. In the case of powder calcined at 900°C, the structure was also irregular shaped similar to powders calcined at 950°C and 1000°C, where it can be seen that it was almost in the shape of a 'dog-bone' and some particles are bonded as aggregates.

Table 1: Physical properties of waste mussel shell catalyst

Physical property	Type of Catalyst			
	Natural Mussel Shell	Calcined Mussel Shell 900°C	Calcined Mussel Shell 950°C	Calcined Mussel Shell 1000°C
Area (mm ²)	4.455×10 ⁻⁴	0.001	0.002	0.006
Pore diameter (mm)	0.019	0.040	0.067	0.076

Among the waste mussel shell-derived catalyst, calcinated powder at 1000°C had a large area (0.006mm²) and pore diameter (0.076mm) presented in an irregular area and pore size. The natural catalyst present lower values for the area (4.455×10⁻⁴mm²) and pore diameter (0.019mm) compared to the calcinated catalyst. Both Figure 4.10 & 4.11 indicates different surface morphologies by observing the three various calcinated temperatures that catalyst waste mussel shells. Calcination temperature can be seen as an increase in the trend of area and pore size of powders.

4.4 EDX (Energy Dispersive X-ray analysis)

The CaO composition in its elemental state, calcium (Ca), oxide (O), and natural substance (C) can be obtained from the EDX analysis. Calcium is discovered to be the primary element present in all catalysts developed from mussel shells, prepared at three different temperatures. However, other elements came up in smaller proportions. For a mussel shell derived CaO as shown in Figure 7, spectrum signals of Ca, C and O have been observed, the weight percentage of each product in the synthesis catalyst shows that a natural sample is higher in C than another synthesis catalyst powder but less in Ca. Meanwhile, at 900°C, the composition of C is decreases compared to natural, and the value of the weight percentage recorded is 6.85% in the sample. However, there is a decrease in the composition of Ca, where the value indicates around 55.39wt. %, but higher of element O, which is 42.22wt. % reported. At 950°C, sample carbon levels unexpectedly disappear. In comparison, the quantity of O decreased from catalyst powder of 900°C, and Ca is the highest compared to natural and synthesis catalyst powder where the value of 68.27wt. % recorded.

For the last calcined temperature of 1000°C, the element C is present with a higher quantity compared to the calcined catalyst of 900°C is around 3.27wt. %. However, O and Ca were almost similar to the previous 950°C calcined catalyst. It can be concluded, the calcination at a temperature of 950°C was found to be more efficient in terms of the composition of Ca and O without the content of C. According to past results, 51.94 wt. % of Ca were presented in a mussel shell calcinated at 900°C for four hours (Patil et al., 2020). As a result, the higher weight percentage of Ca can be achieved by increasing the temperature to 950°C, which is 16.37wt. % higher from past research. Also, the presence of carbon could still be found in every spot of calcined shell powder, showing the possibility of some traces of unreacted calcite on the sample and possibly caused by handling contamination (Haslinda Shariffuddin et al., 2018). From the observation, it is unfavourable to increase the temperature from 950 to 1000°C as it increases the carbon content of the sample shown by the summary table. The increase of calcination temperature to 1000°C decreased the distribution of Ca in the sample, while a significant increase in C was observed.

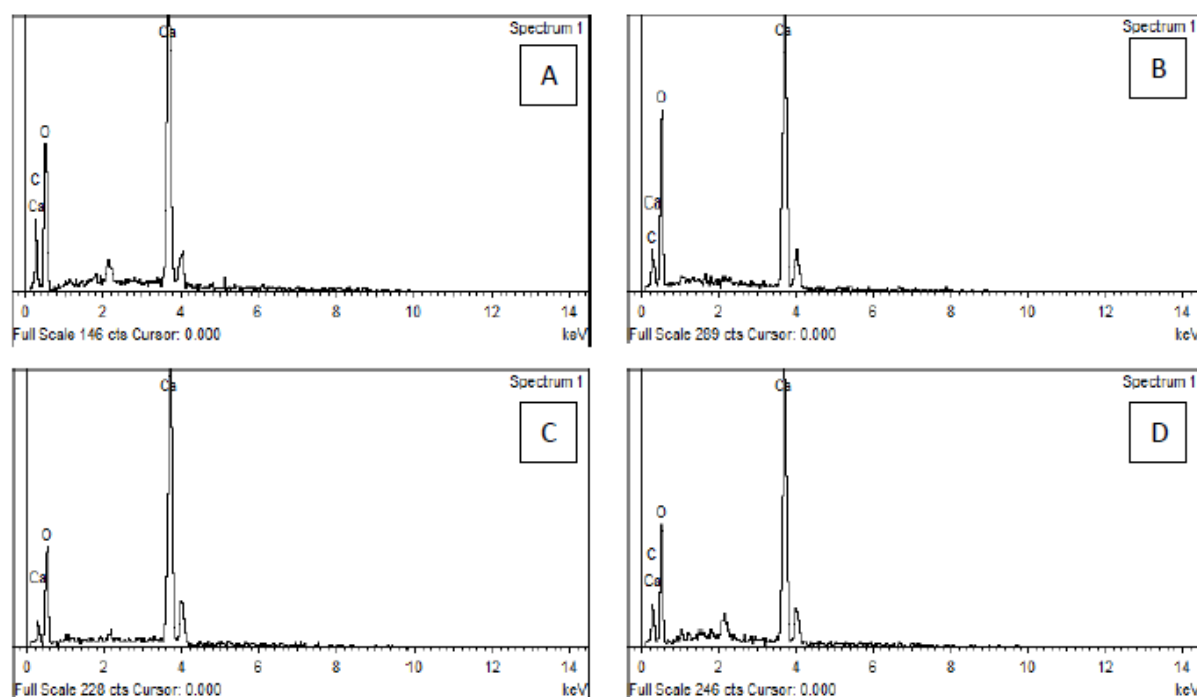


Figure 7: EDX Result (A = natural, B = 900°C calcined, C = 950°C calcined, D = 1000°C calcined)

5. Conclusion

Based on the research results, it could be concluded that the main component of the calcined muscle shell catalyst is calcium oxide as a conversion of calcium carbonate after the calcination process, which can be found in three different temperature treatments. The waste muscle shells have great potential to be used as a sustainable and economical biocatalyst for the next transesterification process. Characterization research on the catalytic activities can also show that the correct calcination temperature gives better physical and chemical properties of the developed catalyst, which is assumed to result in a higher conversion of biodiesel. Three different calcining temperatures, 900°C, 950°C, and 1000°C were used in this study. The ideal mussel shells calcination temperature is determined to be 950°C for 4 hours with a heating rate of 5°C per minute. It is because, at calcination temperature 950°C, it is apparent that the amount of calcium carbonate particles unconverted to calcium oxide is less high compared to 900°C and 1000°C catalysts. Moreover, the characterization of mussel shells as a catalyst in the production of biodiesel at 950°C calcination temperature also has an XRD pattern similar to that of JCPDS calcium oxide.

Another factor that recommends the calcination temperature of 950°C is because it can be considered desirable, as it contains high amounts of Ca, O, and free from C for the CaO samples. Thus, the approach to achieve calcination at lower temperatures with high yields must be aligned with this study to make it an aspect of economical and sustainability for catalyst synthesis since most researchers attempt to discover the reliable, social, and environmental benefit alternatives catalyst for biodiesel. A feasibility study project can, therefore, verify that the mussel shells can be converted into a green-based catalyst for the development of biodiesel production.

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