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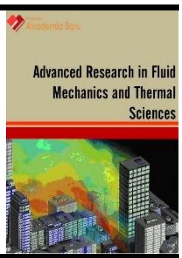

Optimization of Calcination Temperature of Eggshell Catalyst and Palm Oil Biodiesel Production for Blending of B10 Petroleum Diesel Fuel

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ABSTRACT

Palm biodiesel is presently the highlight of current diesel trends, more so in Malaysia. The study of this field is increasing day by day to find ways to reduce its production cost. This study is conducted to analyze the trend of different calcination temperatures to the production of calcium oxide catalyst derived from waste eggshells. The different temperatures are then further analyzed to determine which is the most optimum calcination temperature. Catalyst characterization was conducted by using SEM, XRD and FTIR. It is found that from three different calcination temperatures (900°C, 920°C, 950°C), 920°C is determined to be the most optimum as it gives out the higher yield of calcium oxide while using less energy consumption. The selected optimum catalyst is then utilized to synthesize biodiesel derived from palm olein oil through the process of transesterification. Nine different parameters of transesterification process with different molar ratios and catalyst wt.% content had been conducted and nine different samples are prepared. From these nine samples, one parameter was chosen to be the optimum. Parameters with 12:1 molar ratio, 4wt.% catalyst content, 60°C fixed reaction temperature and 600rpm fixed constant stirring speed are deemed to be the most optimum which yielded 98.89% of biodiesel. This sample is then tested for its properties to determine whether it complies with the ASTM standard before it is blended into petroleum diesel. Properties being tested includes kinematic viscosity, water content, flash point, density and fatty acid methyl ester (FAME) content. The sample is then mass produced to be blended with pure diesel (B0) with fixed ratio of 9:1, in house blend of B10 petroleum diesel fuel is made. The blend was renamed EB10. This biodiesel fuel blend was also tested for its properties to determine if it is safe to be used in consumers vehicles. And it is shown that it is safe to be applied on a daily basis. The blend was also compared to the quality of market available diesel fuel (BHP), and EB10 was proven to have the same quality.

Keywords:
Eggshell catalyst; Calcination; Palm biodiesel; Diesel fuel

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1. Introduction

In the present time, common fuel that the world is using is made of natural resources such as petroleum and coals categorised as fossil fuels. These fossil fuels are reducing as days go by and are close to depletion, thus an alternative should be found in exchange. Due to the lack of supply and intricate manufacturing processes besides needing a ginormous plant, therefore fossil fuels cost higher and become a burden to consumers [15].

Nowadays, biodiesel is coming into the spotlight due to its properties which is much safer and has the same combustive ability as fossil fuels. It is also an alternative resource because of its smaller production cost and the natural resources are vastly available [21]. Biodiesel could be produced from vegetable oils such as palm oil, soybean oil, rapeseed oil and coconut oil, it could also be made from animal's fat and used cooking oil [7]. Catalyst is used as a complementary in the production of biodiesel. There are two general types of catalysts, the conventional homogeneous catalyst and the heterogeneous catalyst [25].

Catalyst is a substance or additive material to a reaction which aids in bringing up the rate of chemical changes without being used up or depleted and could be recovered at the end of the chemical reaction [8]. In chemical terms, a heterogeneous catalyst refers to a form of catalyst where the phase of the catalyst differs from the reactants in chemical reaction. The phases here refer not only to solid, liquid and gas but also immiscible liquids such as oil and water. The great majority of heterogeneous catalysts currently in practical uses are solids and the great majority of reactants are liquids or gases [4]. However, majority of heterogeneous catalyst are solids and many variations exist, such as solid and gas phases, solid and solution phases as well as immiscible liquid phases [2]. A catalyst that is in a separate phase from the reactants is said to be a heterogeneous or contact catalyst. Advantages in using heterogeneous catalyst is that it does not corrodes and could be easily separated from the fluids. In fact, heterogeneous catalyst could be used in biodiesel production for oils that has high content of free fatty acids (FFA).

Currently, transesterification is the preferred choice in producing biodiesel. It is a process that mixes oils (vegetable oil/ animal fats) with alcohol (mostly using methanol or ethanol) with the presence of catalyst to change it into ester fats. This mixture will be separated into two parts which is the glycerine and alcohol mixture, and esters. Glycerine with higher density will sink while the alcohol ester mixture with lower density will float to the top [5]. Moreover, the alcohol and ester mixture will need to undergo a separation process. Alcohol which is obtain could be stored and reuse. Meanwhile the ester that is obtained will be sent to clean and filter. Esters that had been clean is the biofuel. This biofuel could be directly applied or blended with diesel before using it as fuel. Another element which is being taken into account in producing biodiesel is to make sure that the biodiesel produced is on par with the fixed international standard.

Previous study shows that calcium-containing catalyst has shown advantages such as good catalytic activity and reusability [10]. Studies on the usage of eggshell catalyst for palm biodiesel production had been conducted by Khemthong *et al.,* [11] and Ngadi *et al.,* [17], both using only one calcination temperature which is 800°C. Both of these studies showed different result, where Khemthong *et al.,* [11] obtained 96.7% palm biodiesel and Ngadi *et al.,* [17] obtained 75.85%. These two results show a very vast difference in biodiesel FAME output, noting that Khemthong *et al.,* [11] achieved this with the assistance of microwave irradiation. Latest optimization study for eggshell catalyst was conducted by Castro *et al.,* [3]. In this study, eggshells were calcined between the temperature range of 800 to 1000°C. Quoting the author, "Although C1000 solubilized a smaller amount of Ca in the product, C800 is probably a better choice since it is obtained which much lower energy expenditure.". taking from this probability of producing a same quality of catalyst with lower calcination temperature, this current study explores the calcination temperature between the smaller range of 900°C to 950°C. Analyzing from both the results of biodiesel production from Khemthong *et al.,* [11] and Ngadi *et al.,* [17], further optimization of calcination temperature is done for the eggshell catalyst to be used in transesterification of palm oil for blending of B10 diesel fuel.

2. Methodology

2.1 Preparation of CaO Catalyst from Waste Eggshell

Three different calcium oxide catalyst had been produced for this research. The catalysts are differed by the calcination temperature used. For the synthesis of eggshell calcium oxide catalyst, the eggshells are first collected from the local hawker stall, washed, cleaned and dried. It is then grinded to powdered form, sifted to 150-micron size. Then the powder was calcined in air at 900°C, 920°C and 950°C at a rate of 5°C/min, for 3 hours in an alumina crucible. The catalyst is then cooled to room temperature and then stored in a desiccator to prevent contact with moisture for future use.

2.2 Transesterification of Palm Oil

The 'transesterification' is also called as methanolysis or alcoholysis [9]. In this work, palm oil and methanol are the main ingredient for the transesterification process. The free fatty acid (FFA) value for palm oil is 1.128% [16]. Three different molar ratios were used in this research, 9:1, 12:1 and 15:1 methanol to oil ratios. Three different wt.% of catalyst had been used in this study (2%, 3% and 4%) in each mixture. The reaction had taken place for 3 hours in the three-necked flask equipped with the condenser, thermometer and magnetic stirrer. The speed of the stirrer was set to 600 rpm. Temperatures of reaction had been fixed at 60°C. The summary of the transesterification reaction parameters are as follows.

Table 1
Transesterification parameters

Sample No.	Catalyst Content (%)	Methanol: Oil Ratio
1	2%	9:1
2		12:1
3		15:1
4	3%	9:1
5		12:1
6		15:1
7	4%	9:1
8		12:1
9		15:1

After the reaction process is completed, the magnetic stirrer and the heater is switch off. The apparatus is dismantled, and the mixture produced was transferred to a filter funnel. The mixture is left to be cooled and separated into two distinct layers. Glycerol will be brown in colour while biodiesel is in yellow. Next, the bottom layer which is the glycerol is let out slowly and both samples of biodiesel and glycerol is then kept in bottles for further analysis.

2.3 Catalyst Characterization

For catalyst characterization, to analyse the surface area of the prepared catalysts, the scanning electron microscope (SEM) is used to observe the surface morphology of the catalyst. Before running the analysis, little amount of powder was mounted on an aluminium stub on top of self-adhesive and then it is coated with gold. Other than that, the X-ray diffraction (XRD analysis was performed with the condition of data collected over a 2θ range of 3-90°, step size of 0.02° and scanning speed of 4°/min to determine the element content of the catalyst [10]. FTIR analysis had also been conducted by using the Perkin Elmer Fourier Transform Infrared Spectrometer for the catalyst to observe the presented functional group and bands in the samples.

2.4 Determination of Biodiesel Properties

In order to determine whether the produced biodiesel achieved the biodiesel international standard that had been set, some testing of biodiesel properties was made. The properties were tested are the density by using the pycnometer, kinematic viscosity by using viscosity meter *Viscolite* 700 (model VL700-T15), percentage of water content by using water analyser (Mettler Toledo), fatty acid methyl ester content by using gas chromatography with flame ionization diode (GC-FiD) and flash point by using the *Pensky Martens* flashpoint machine. Table 2 below shows the parameters used for FAME analysis by using GC-FiD.

Table 2
Parameters for ester content analysis [20]

Agilent 6890 GC	
Inlet	Split
Detector	FID
Automatic Sampler	Agilent 7683
Liner	Split Line
Column	DB 23: 60m x 0.248m x 0.15um
Inlet Temperature	250°C
Injection Volume	1µL
Split Ratio	1/50
Carrier Gas	Helium
Head Pressure	Constant pressure mode at 230 kPa
Oven Temperature	50°C for 1 min, 25°C/min to 175°C, 4 /min to 230°C, 5 min

2.5 Blending of EB10 Diesel Fuel with Fixed Ratio

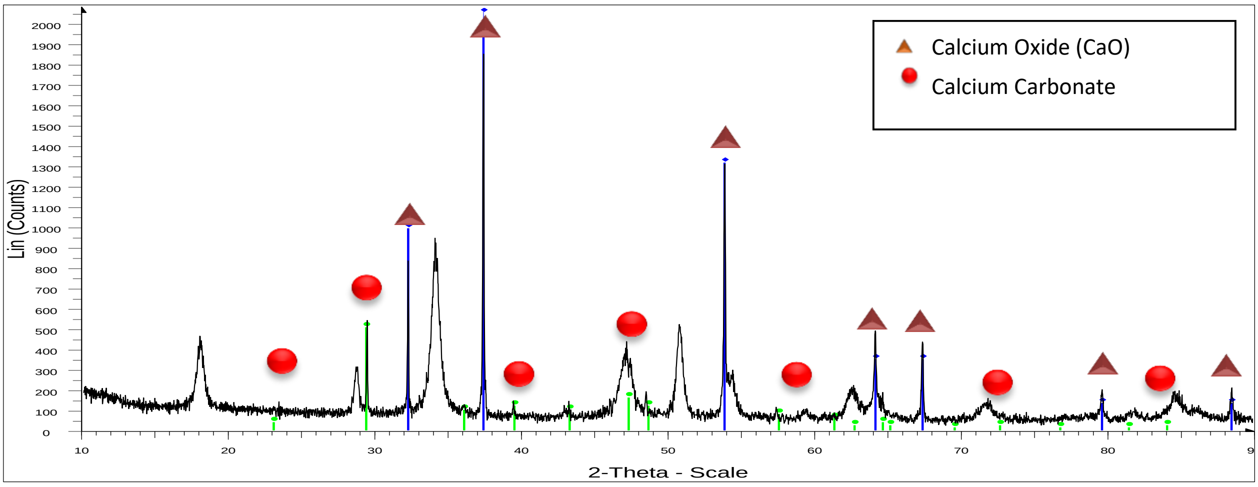
Palm biodiesel produced had been blended with pure diesel (B0) procured from the courtesy of Keretapi Tanah Melayu Berhad (KTMB), Kempas. With fixed ratio, 9 litres of pure diesel (B0) are blended with 1 litre of biodiesel which has been produced through transesterification process. The blending process was done in a 10L mechanical stirrer with heater. The blending is conducted in fixed temperature of 30°C, rotational stirring speed of 200rpm for 2 hours. After the blending is completed, the product was further tested for its properties which includes kinematic viscosity, water content, flashpoint as well as bio-content. The blended diesel fuel was renamed EB10 to avoid confusion. EB10 was then compared with the market sold diesel fuel purchased from BHP petrol station, to be compared on its properties and quality.

3. Results

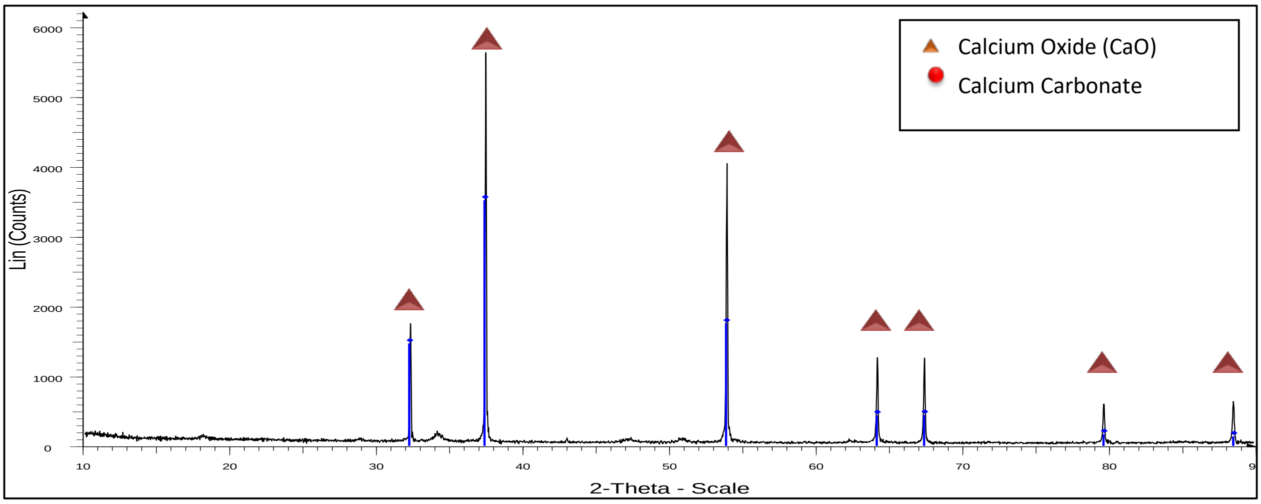
3.1 Characterization of Eggshell CaO Powder

3.2.1 XRD

XRD analysis is being conducted for the three samples of different temperature calcined eggshell powders to identify the phase present in the samples. Traces of CaO element should be clearly shown and present in the XRD graph. Peaks of CaO should be present at the intensities of 2θ = 32°, 37°, 54°, 64°, 67° and 80° [3]. From XRD graphs in Figure 1, it can be clearly observed that all the samples had achieved the designated peaks indicated for CaO. In other words, calcination of raw eggshells powders in three different temperature are deemed to be a success and could be used as catalyst in the next process, transesterification.



(a)



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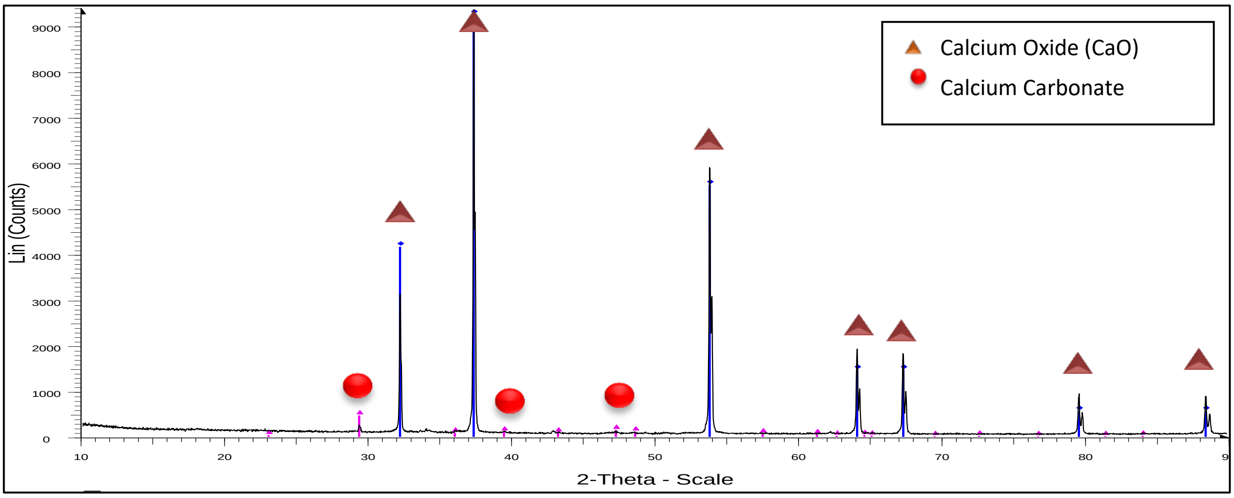

(c)

Fig. 1. XRD graph for calcination of eggshell at (a) 900°C, (b) 920 °C (c) 950°C

Diffractogram obtained from in eggshell waste powder calcined at 900°C shows multiple peaks of unreacted ($CaCO_3$) in calcite form. It can be identified at 2θ = 23°, 29.3°, 39.5°, 47.3°, 57.8°, 72.5° and 84°. As for powder calcined at 920°C, no presence of $CaCO_3$ recorded which indicates almost all of it had reacted and synthesized to CaO. As for powder calcined at 950°C, only small amount of $CaCO_3$ were detected at 2θ = 29.4°, 39.5° and 47.2°. All of the powder samples shows large presence of CaO, which are detected at the same peak for all three diffractogram. Peaks were identified at 2θ = 32.3°, 37.4°, 53.9°, 64.2°, 67.4° and 79.8°. these results were similar to those reported by previous study conducted by Wei *et al.,* [22]. The increase in calcination temperature induces more intense and sharp peaks, this signifies an increment in crystallinity of the material and the removal of $CaCO_3$.

From the three XRD graphs shown, it can be concluded that the most optimum temperature for calcination is 920°C. Comparing between calcination graphs at 900°C and 920°C, it can be clearly seen that calcination at 920°C produced more CaO compared to 900°C where it can be noticed that there are still quite a number of unconverted $CaCO_3$. The production of CaO at calcination of 920°C and 950°C shows only a slight differ. However, although powder calcined at 950°C shows sharper peaks, it still contains some unreacted $CaCO_3$. Hence, 920°C is chosen because one of the main reason this research is made is to help improve the environment, chosing a lower temperature calcination helps to conserve energy and indirectly will help in cutting cost of the whole process.

3.2.2 FTIR

FTIR analysis was conducted for the three samples of different temperature calcined eggshells powder. This analysis was done to identify the presence of bands present in the samples to confirmed that the catalyst synthesized is really CaO. Figure 2, Figure 3 and Figure 4 show the FTIR analysis graphs for three different calcium oxide powders.

Figure 2, Figure 3 and Figure 4 presented the FTIR graph for the three CaO powders produced. There are four specific bonds required to be present in the FTIR graph. The high intensity band at 3643 cm^{-1} indicates the O–H bands from the hydroxide remains. The band at 1417 cm^{-1} indicates the C–O band. The band centered at 866 cm^{-1} indicates the C–O band. The wide and high intensity band at around 500 cm^{-1} indicates the Ca–O bands. This band has the highest intensities in the CaO standard spectrum. (Ruiz, 2009).

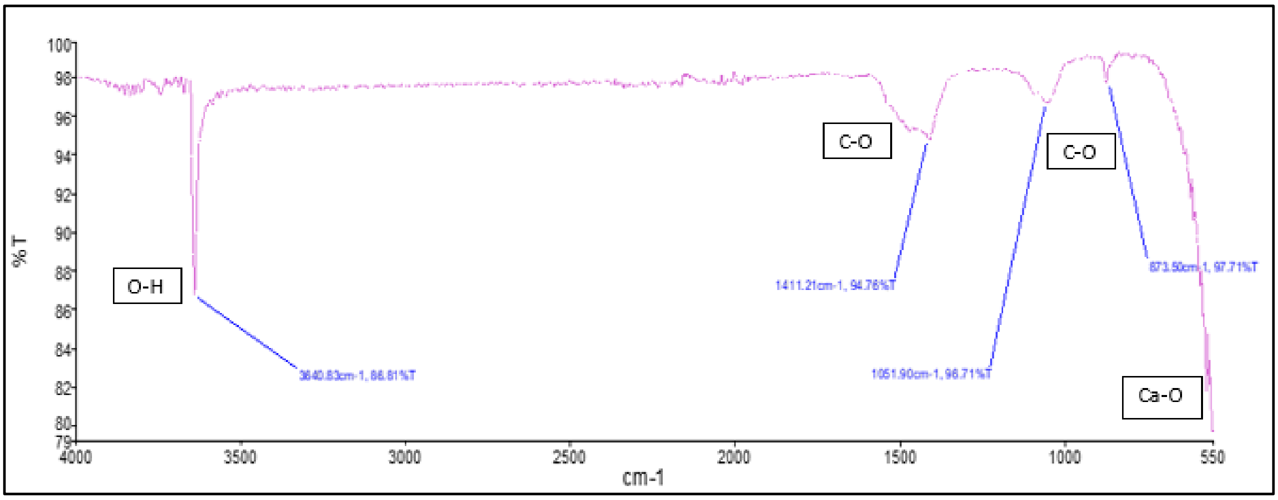

Fig. 2. FTIR transmittance graph for 900°c eggshell powder

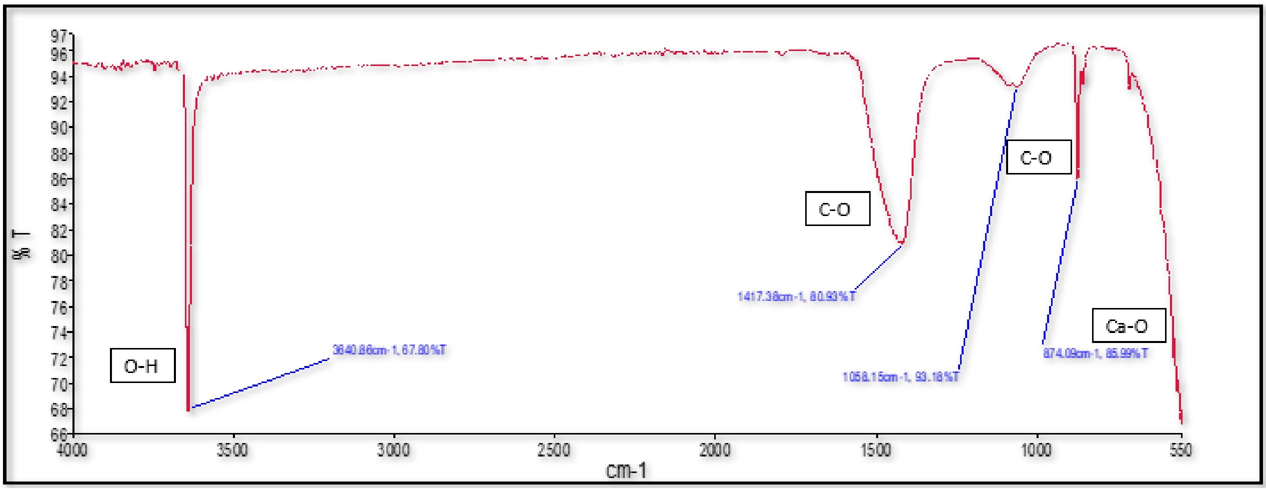

Fig. 3. FTIR transmittance graph for 920°c eggshell powder

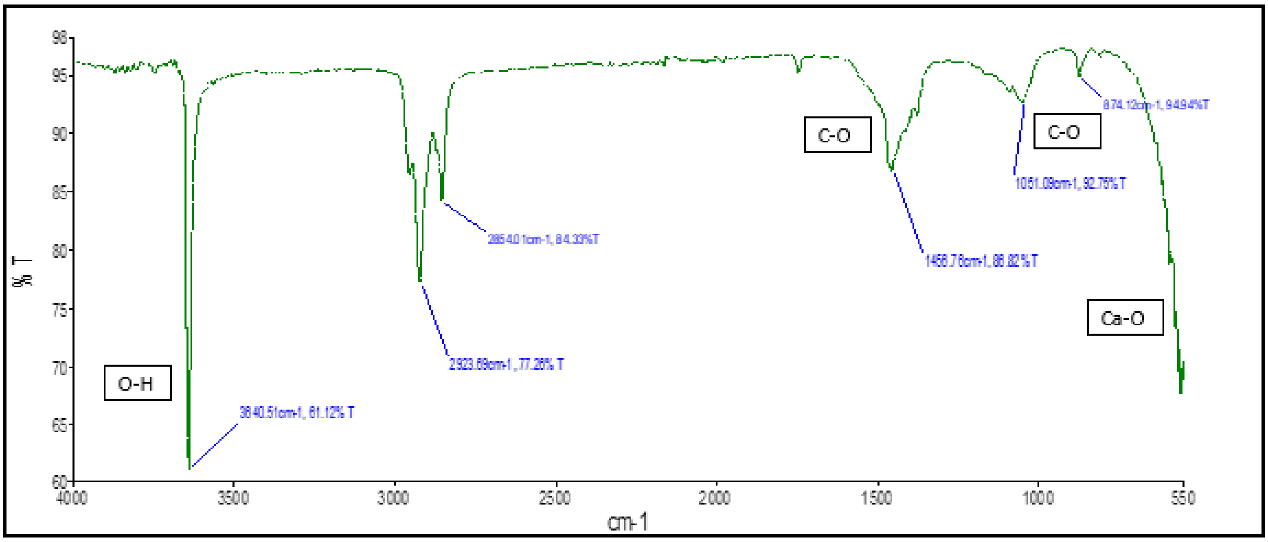

Fig. 4. FTIR Transmittance Graph for 950°C Eggshell Powder

3.2.3 SEM

SEM analysis on the catalyst produced is to observe whether changes in calcination temperature will affect the surface composition and structure of eggshell powders. It is also to observe the size and consistency of the powders. Figure 5 and Figure 6 show the surface morphology of the three different calcined calcium oxide powder samples. The surface morphology of each samples was taken with two different magnifications.

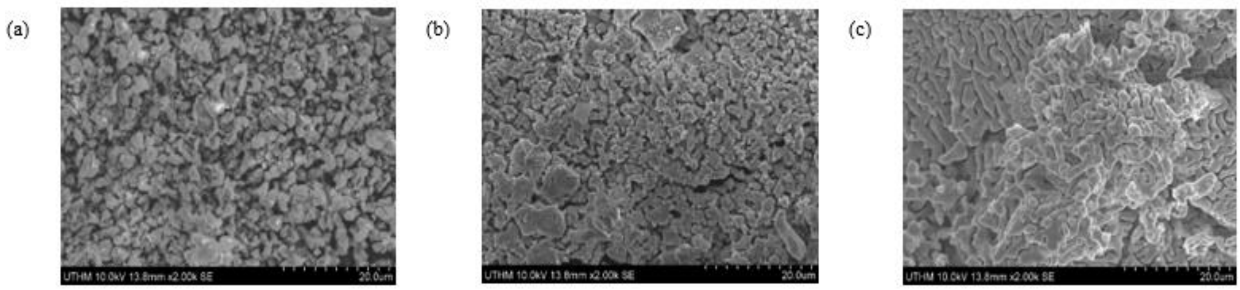

Fig. 5. SEM observations for (a) 900°C, (b) 920°C, (c) 950°C eggshell waste powder (2000X magnification)

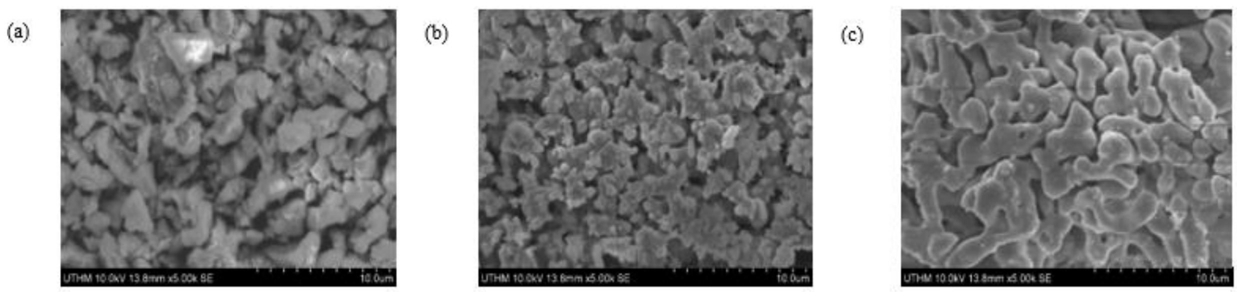

Fig. 6. SEM observations for (a) 900°C, (b) 920°C, (c) 950°C eggshell waste powder (5000X magnification)

The morphology of calcined chicken eggshells was investigated and studied by SEM using magnification of 2000X and 5000X as illustrated from Figure 5 and Figure 6. All three of the samples shows irregularity in the crystal structure with homogeneous distribution. Presence of large porosities were found in all three samples as observed. This morphological structure is similarly discribed in the previous work of Wei *et al*., [22]. For powder calcined at 900°C, the structure is observed to be irregularly shaped as compared to powders calcined at 920°C and 950°C where it can be seen that it is almost spherical in shape. The porosity observed from the SEM morphologies of CaO is related to the release of CO_2 from the internal structure, hence calcination occurs by reducing the volume of the particle, indirectly allows the appearance of interstices knows as pores [18].

There was an agglomeration of CaO particles seen at 950°C calcinated powder, this indicates that sintering of the material had occurred. Neck development between adjacent grains continues to grow during sintering, therefore distance between grain centers is reduced, this indirectly reduces the surface area [19]. Increasing of calcination temperature causes coalescence of particles, which also reduces the specific area [18]. Observing from all the figures, the three different calcined temperatures catalyst of eggshell CaO, each has distict different surface morphologies. An increasing trend surface area of powders could be seen as the calcination temperature were increase.

3.2.4 Comparison between current study and previous study (catalyst)

There are numerous studies being conducted for calcination of eggshell powders as catalyst for transesterification to produce biodiesel. However, previous study have yet to pair eggshell powder CaO catalyst with palm oil feedstock. Different optimum temperature of calcination was adapted for this study and further study shows that the best temperature for eggshell calcination drops between the temperature of 800°C - 1000°C. Table 3 shows a summary of previous study of calcination temperatures for eggshell powders did for their respective oil feedstock.

Table 3
Comparison of eggshell powder calcination temperature and biodiesel yield between current and previous study

Author	Oil Feedstock	Calcination Temperature (°C)	Yield (%)
Current Study (2019)	Palm Olein Oil	920	98.89
Wei *et al.* [22]	Soybean Oil	> 800	98
		< 600	< 30
Samrat and Srimanta [24]	Waste Vegetable Oil	950	90
Goli and Omprakash [6]	Soybean	900	97.86
Castro *et al.* [3]	Cotton Oil	800	97.83
		900	97.23
		1000	98.08

3.3 Analysis of the Biodiesel Product from Transesterification

Three different molar ratios had been used in this research, 9:1, 12:1 and 15:1 methanol to oil ratios. Also, the amount of catalyst used was also different, 2%, 3% and 4%. A constant temperature of 60°C and stirring rotational speed of 600rpm are used for all sets of process. After the transesterification of all parameters are completed, all of the biodiesel product had been tested for their characteristics as so that it can be confirmed that the biodiesel made are on par with the ASTM standards for biodiesel. Table 4 shows summary of biodiesel samples properties.

Table 4
Summary of biodiesel samples properties

No.	Catalyst Content (%)	Methanol: Oil Ratio	Water Content (ppm)	Kinematic Viscosity (mm^2/s)	Density (kg/m^3)	Flash Point (°C)
1	2%	9:1	0.038%; 384.0	11.2	1013.2	127.9
2		12:1	0.032%; 317.8	4.8	904.4	127.8
3		15:1	0.025%; 250.1	6.2	880.6	127.8
4	3%	9:1	0.035%; 353.5	6.1	938.6	128.0
5		12:1	0.050%; 503.4	4.6	903.2	127.6
6		15:1	0.027%; 270.7	4.9	935.0	127.8
7	4%	9:1	0.021%; 210.7	5.3	945.6	127.8
8		12:1	0.017%; 173.3	4.5	897.4	128.1
9		15:1	0.034%; 343.4	4.9	909.2	127.8

3.3.1 Fatty acid methyl ester content test analysis

From the four biodiesel properties test completed previously, two of the best samples in terms of their properties are selected to be tested for the final property test, the FAME content test. The most important test for the properties of B100 biodiesel is the fatty acid methyl ester (FAME) test.

This test is to show the overall fatty acid present in the sample. Based on the standard for FAME testing EN14078, the minimum ester content in a sample of B100 biodiesel should be greater than 96.5% overall. Table 5 shows the FAME percentage content of the two samples selected.

Table 5
Fatty acid methyl ester content of eggshell biodiesel (ASTM D6751)

Sample	Catalyst Content (%)	Methanol: Oil Ratio	Fame Content (%)
A	3%	12:1	97.84
B	4%	12:1	98.89

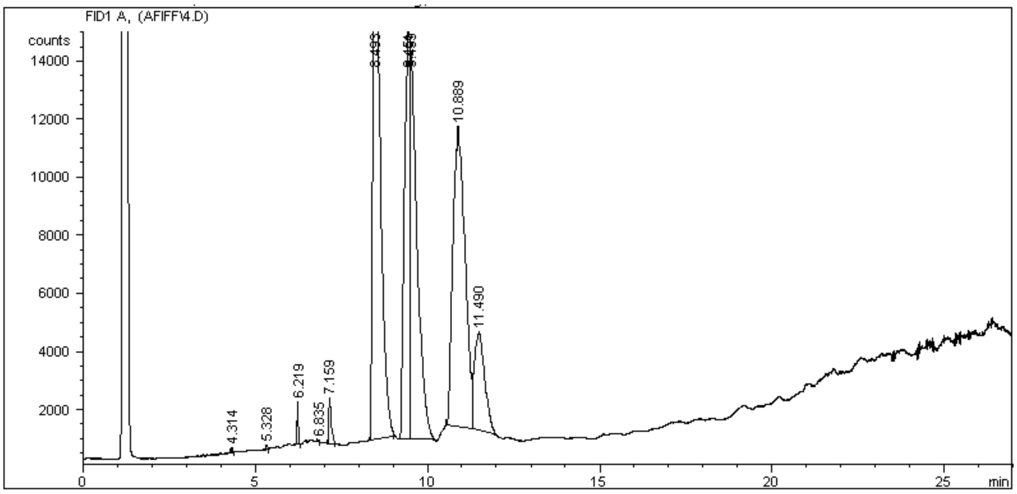

Fig. 7. GC-FiD graph for Sample A

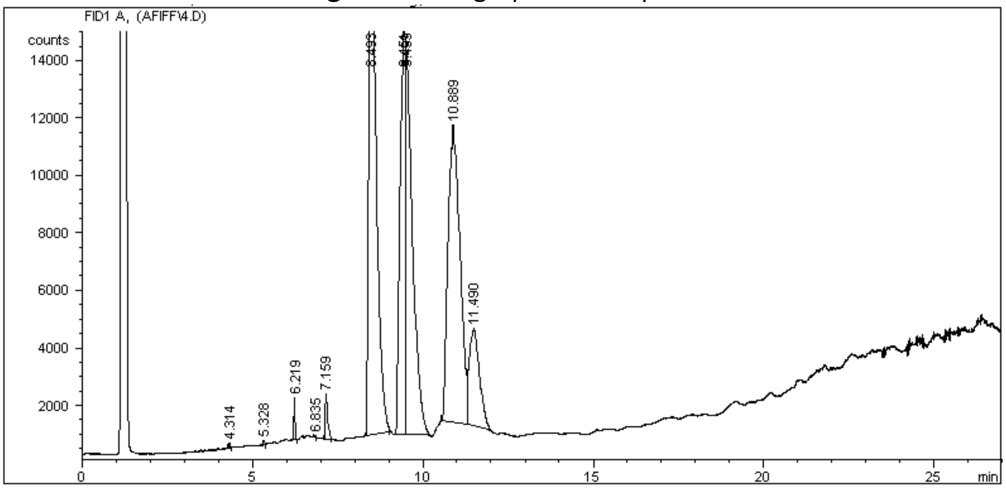

Fig. 8. GC-FiD graph for Sample B

From the two samples selected, the best yield is found to be from sample 8 (4% catalyst content, 12:1 molar ratio) with FAME content value of 98.89%. The percentage values of fatty acids are obtained from the GC-FID graph where the peak area percentages of detected fatty acid are totalled [20]. Analysing from the five properties test conducted, the best biodiesel product is to be chosen to be produced in bulk. The biodiesel made must be on par with the ASTM Standards for biodiesel blending. The biodiesel chosen will me mixed and blend with pure diesel (B0) with the ratio of 9:1 (pure to biodiesel) ratio to produce EB10 diesel fuel. After careful observation and considerations, the biodiesel with parameters of 4% catalyst and 12:1 methanol to oil ratio is picked to be the best. This biodiesel achieved all the standard tested where it has only 0.017% water content, 4.5 kinematic viscosity value, 897.4kg/m^3 density, 128.1°C flash point and contains 98.89% of fatty acid methyl ester. All of the values are within the range of standard set by ASTM.

3.4 EB10 (Eggshell) and B10 (Market) Biodiesel Blend Comparisons

For this research, B10 (10% biodiesel content) fuel diesel had been blended by combining 9 litres of pure diesel (B0) with 1 litres of the optimum biodiesel (EB10) which were chosen and made in bulk beforehand. Why blend it to B10? Because in the current market, B10 is currently the diesel fuel being sold. Hence, by blending this EB10 (palm), we are going to compare it with the market sold B10 (BHP) to see whether the blend is identical to it in quality wise.

In addition, four other characteristic tests are conducted to determine if the biodiesel blend produced is on par with the ASTM standard as so that it is safe to be used in vehicles. The tests include kinematic viscosity test, water content, flash point and Fourier-transform Infrared (FTIR) spectrometer test was conducted to identify the bio-content of the blend. The results of the four petroleum diesel properties test are shown in Table 6.

Table 6
Characteristic comparisons between blended B10 with market B10 (BHP)

	EB10	B10 (BHP)	Standard Test Used	Standard Values
Kinematic Viscosity	4.0 mm^2/s	3.3 mm^2/s	D445	1.9 – 4.1 mm^2/s
Water Content	0.009%	0.01%	D2709	0.05% (max)
Flash Point	77.9°C	78.2°C	D93	> 52°C
Bio-content	10.56%	10%	D7371	10%

From Table 6 above, it can be concluded that the biodiesel fuel blend produced are within the standard set by ASTM D7467-13 Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20). It is confirmed to be safe for application to vehicle and the blending is regarded as a success. From the comparison, we had deduced that the quality of the blend EB10 is almost the same as compared to the market available B10 (BHP).

4. Conclusions

As a whole, it can be concluded that the best and optimum parameters for transesterification of palm oil with eggshell calcium oxide catalyst are obtained from sample 8 which has 4% catalyst content and a 12:1 methanol to oil ratio. The sample has achieved all the standard tested for its properties with 897.4kg/m^3 density, 4.5 mm^2/s kinematic viscosity, 128.1°C flashpoint, 173.3ppm (0.017%) water content and 98.89% fatty acid methyl ester content. This sample was chosen to be produced in bulk to blend with pure diesel (B0) to produce B10 biodiesel fuel (EB10) and compared to the existing market B10 biodiesel fuel for its quality. The blending of EB10 is seen to be successful, as compared to the market available B10 biodiesel, the quality is shown to be similar and by achieving all the standard properties tests, the EB10 blend are deemed to be safe for consumers.

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