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STUDY OF CALCINATION CONDITION ON DECOMPOSITION OF CALCIUM CARBONATE IN WASTE COCKLE SHELL TO CALCIUM OXIDE USING THERMAL GRAVIMETRIC ANALYSIS

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ABSTRACT

Calcium oxide (CaO) is usually produced via thermal decomposition of limestones obtained through mining and quarrying. However, this study manages to exploit the vast availability of natural calcium sources (*Anadara granosa*) or locally known as cockle shell in Malaysia. The efficiency of the calcination process that transforms calcium carbonate ($CaCO_3$) to calcium oxide (CaO) was often depended on the variable involved. Therefore, we wish to demonstrate the effects of experimental variables (calcination temperature, heating rates and particle sizes) on calcination of $CaCO_3$ via thermos-gravimetric analyser (TGA). Analysis of XRF, XRD and SEM were also conducted on the CaO produced after calcination.

Keywords: calcination, calcium oxide, decomposition.

INTRODUCTION

Calcium carbonate, $CaCO_3$, commonly found in rocks occurs naturally as the main component of crustacean shells. Due to its varied polymorph properties, the mineral is widely used in diverse applications such as an active ingredient in agricultural lime (West and McBride, 2005), as a heterogeneous catalyst for biodiesel production (Nakatani *et al.,* 2009; Boey *et al.,* 2011), as a biomaterial for use in bone repair (Awang-Hazmi *et al.,* 2007) and as a biosorption material to remove heavy metal ions (Mahtab *et al.,* 2012). Research on the utilisation of $CaCO_3$ from seashells has been of recent interest, for example in the utilisation of the mineral from crab shells as a catalyst (Boey *et al.,* 2011) and a biosorption material (Yan-jiao, 2011). Apart from high-priced crab and molluscs such as oyster, cockle is inexpensive and consumed as part of the daily diet. In Malaysia, cockle contributes to about 14% of marine aquaculture production (Department of Fisheries Malaysia, 2009). Therefore, there is an abundant supply of blood cockle shells. In addition, the shells do not have any other important uses and are normally discarded as waste. Due to the abundance of these seashells, they have a high potential to be utilised as a cheap source of $CaCO_3$ for industrial applications.

Cockle shells or *Anadara granosa* has been touted as an alternative for the calcium carbonate sources instead of using the limestone. Mining large quantities of rocks can contribute to the environmental damage and engage with the high cost for environmental compliance. Li *et al.* (2009) also proved seashells to have higher composition of calcium oxides compared to the limestones. In this work, the shells of Malaysian blood cockle, *Anadara granosa*, were used as the starting material. The present study was done to evaluate the influence of operating conditions on the minerals of *Anadara granosa* shells by heat treatment at various temperatures, particle sizes and heating rates, and to subsequently use the resulting material for the formation of calcium oxide (CaO). CaO associated with carbonaceous material has been of recent interest in applications such as transesterification catalysts (Wei *et al.,* 2009; Wan and Hameed, 2011) and sorbents for sulphur dioxide (Marcias-Pérez *et al.,* 2008). The utilisation of the economic resources of waste bio-minerals from blood cockle shells is expected to promote the commercial application of the resulting calcium oxides.

To the best of our knowledge, there are few reports on the exploitation of the vast availability of waste cockle shells from marine aquaculture as potential natural resources for calcium oxide compared to other seashells such as scallop shell and oyster shell. Therefore, this study was carried out with intent to determine the influence of different calcination condition (temperature, heating rate and particle sizes) on the production of calcium oxide using cockle shell as raw materials based on thermo-gravimetric analyses.

MATERIALS AND METHODS

Preparation of cockle shells

Cockle shells were purchased from a local vendor in Balok, Kuantan. The shell powder was prepared according to the method described by Rashidi *et al.* (2011). The cockles were washed thoroughly with tap water, scrubbed using brush to remove impurities and boiled for 15 minutes at 100 °C. The cockles were then cooled at room temperature before the contents of the cockles were removed leaving behind only the shells. The shells once again cleaned using distilled water and then sun-dried for one day. Drying is important to prevent the agglomerate during the grinding process. The cockles were crushed into small pieces with pestle and mortar before being grounded into powder form. The powder obtained was then sieved into three different of particle sizes (0.3 mm, 0.425-0.6 mm, and 1.18 mm) using a

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stainless steel sieve shaker (Retsch AS 200). The calcium carbonate powders were finally packed into a polyethylene plastic bag for further analyses.

Materials characterization

Three characterization analyses were carried out in this study: X-Ray fluorescence (XRF), X-ray diffraction (XRD) and Scanning electron microscope (SEM). The chemical composition of cockle shell was analysed using X-Ray Fluorescence (XRF, Bruker S8 Tiger) while the x-ray diffraction (XRD) of the crystal structure of the waste cockle shell were performed on a Rigaku (Miniflex II, England), run over 2θ range from 3 to 80° with step size of 0.05° and at a scanning speed of 1°/min. The surface morphology and crystal structure of the samples were visualised using SEM (Zeiss Evo 50, Carl Zeis, USA).

Calcination of cockle shell via thermal gravimetric analyzer (TGA)

Calcination of cockle shells were analyzed with a thermal gravimetric analyzer, TGA (Model: TGA Q 500). Approximately 5 mg of shell powder was placed in the ceramic holder. Then, it had been heated up to the desired temperature at desired heating rate under N_2 gas flow of 40mL/min. Nitrogen is used to ensure inert environment around sample. The procedure was repeated at different operating conditions as shown in Table-1.

Table-1. Experimental parameters of the calcination.

Parameters	Experimental value
Heating rate (°C/min)	10 and 20
Calcination temperature (°C)	700, 800, 900
Particle sizes (mm)	0.3, 0.4-0.6, 1.2

RESULTS AND DISCUSSIONS

Characterization of cockle shell

XRF analysis was conducted to qualitative and quantitatively estimated the chemical compositions in the calcined cockle shell. XRF results presented in Table-2 demonstrated that calcined cockle shell is composed generously by CaO (97.57%). The findings proved that high amount of calcium present in shells as mentioned by Li *et al.* (2009) and Mohamed *et al.* (2012). The large amount of CaO is associated with the presence of calcium carbonate, which is the main component of the waste cockle shell confirmed by the XRD results. The calcined cockle shells also contained trace amounts of MgO, P_2O_5, SO_3, K_2O, Na_2O, Fe_2O_3, SiO_2, Al_2O_3, SrO, Cl, ZrO_2, Cr_2O_3, CuO, MnO, NiO and MoO_3.

Table-2. Chemical composition of calcined cockle shell.

Compound	Concentration (wt. %)
CaO	97.57
MgO	0.32
P_2O_5	0.19
SO_3	0.12
K_2O	0.03
Na_2O	1.22
Fe_2O_3	0.04
SiO_2	0.13
Al_2O_3	0.1
Others	0.28

XRD patterns of calcined cockle shells are given in Figure-1. Findings revealed that increment in calcination temperature from 800 ºC to 900 ºC caused complete transformation of $CaCO_3$ to CaO. It was observed that the major component of calcined cockle shell at 900 ºC was CaO species (Figure-1). Narrow and high intense peaks observed from calcined cockle shell as shown in Figure. 1(B) indicated that the material was well-crystallized during the heat treatment process (Khemthong et al., 2012).

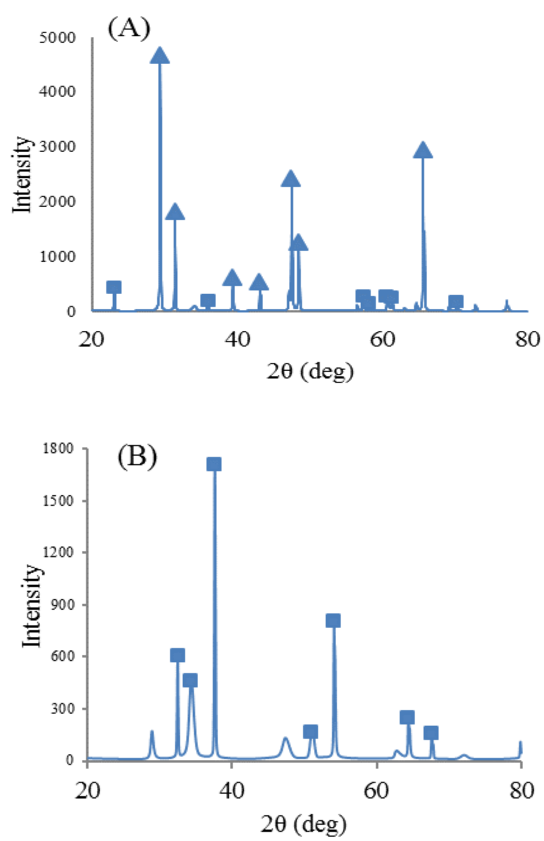

Figure-1. XRD Spectra of calcined cockle shell at (A) 800 °C and (B) 900 °C (■: CaO, ▲:$CaCO_3$).

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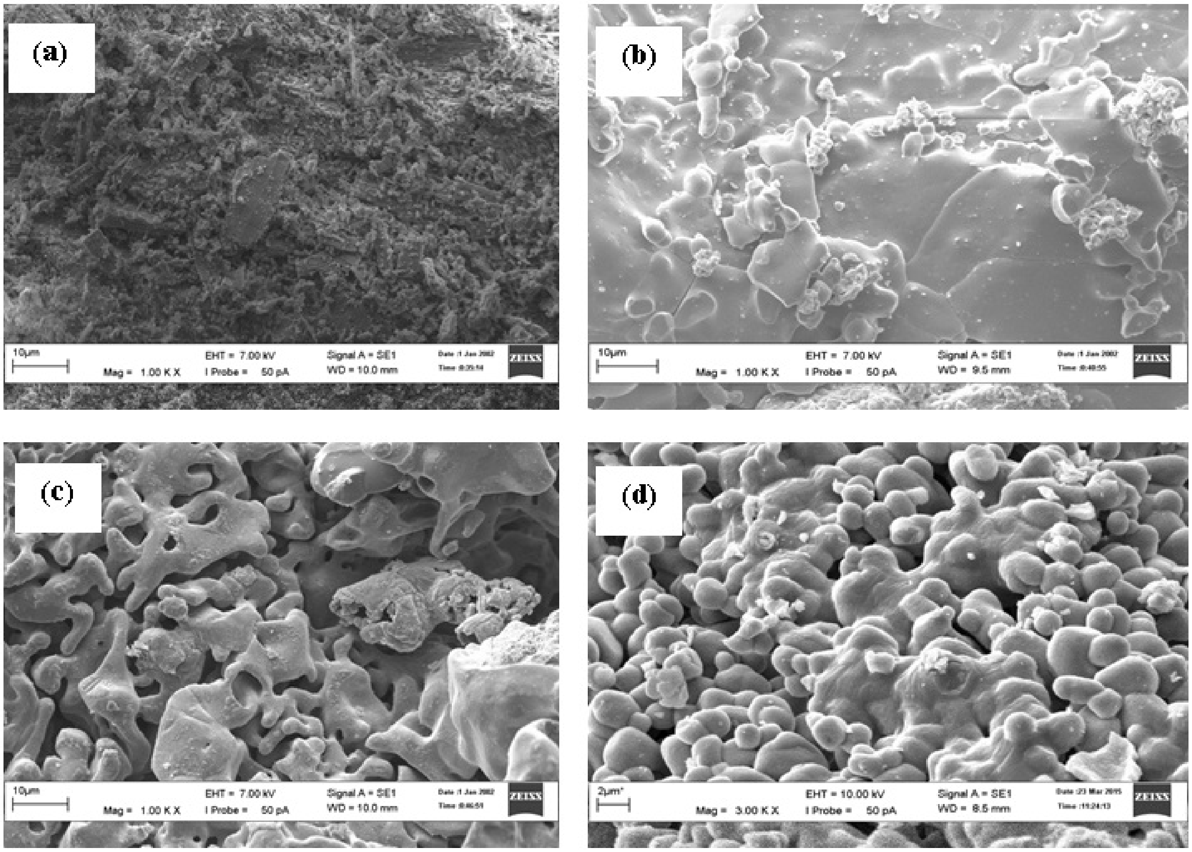

Figure-2. SEM images of (a) raw cockle shell and calcined cockle shell at (b) 700 ºC, (c) 800 ºC and (d) 900 ºC.

The morphological characteristic of decomposed cockle shell calcined at 700 ºC, 800 ºC and 900 ºC was examined by SEM. Natural cockle shell displays needle-like structure known as aragonite as shown in Figure-2(a). However, the structures of the cockle shell are observed to change drastically with increasing of calcination temperature from 700 ºC to 900 ºC. The surface of calcined waste cockle shell presented much smoother surface, irregular shape with some of them bonded together to form large aggregates. Moreover, findings illustrated in Figure 2 were found similar to the calcined limestones reported by Sun *et al.* (2008). In his works, Sun et al. (2008) validated that the almost spherical grain shapes with some grain-neck growth were resulted from the sintering during calcination process.

In this study, the effect of particle sizes on the calcination process was investigated by analyzing three different particle sizes: 0.3 mm, 0.4-0.6 mm and 1.2 mm at 900 °C. The TG curves showed in Figure-3 proved that particle sizes definitely influences the weight loss percentage of the samples tested. It is observed that smaller sized particle experienced rapid change of weight compared to the larger particle size. These findings agreed with Mohamed *et al.* (2012) that exhibits smaller sized particle was observed to reach similar conversion as larger sized particle within a shorter time. This observation is probably due to the large surface area associated with smaller sized particles that contributes to a higher rate of heat exchange required in promoting decomposition (Mohamed *et al.,* 2012).

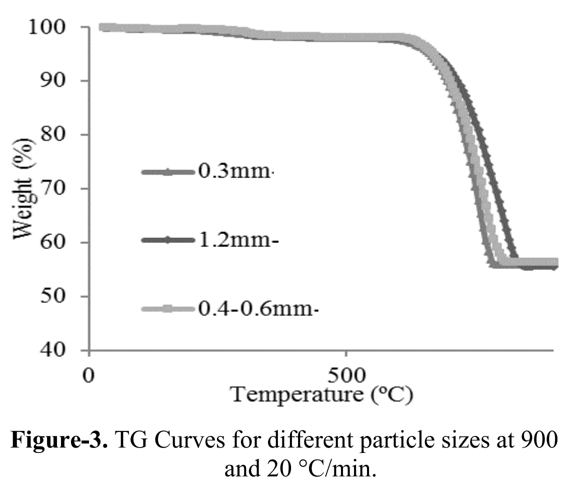

Figure-3. TG Curves for different particle sizes at 900 °C and 20 °C/min.

Figure-4 illustrates the effect of heating rate on calcination and undoubtedly proved that calcination rapidly occurs with higher heating rates as the same decomposition amount can be reached within a short duration of time. In this study, the results obtained showed

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that the higher heating rate of 20 ºC/min gave the fastest duration of time (36 minutes) for the decomposition of cockle shell into the calcium oxide compared to the heating rate of 10 °C/min which takes about 70 minutes. As mentioned by Mohamad *et al.,* (2012) higher heating rate elevated the temperature of the reaction faster than slower heating rate and hence, decreases the time taken for the reaction to complete. Therefore, selection of suitable heating rates is rather critical for the calcination process. In addition, the dTG curves obtained from this study were found to be similar with previous study as reported by Hatakeyama and Liu (1998) whom stated that narrower and sharper reaction profiles were obtained with increasing heating rates.

Figure-5 further describes the effect of calcination temperature on the calcination process. Higher calcination temperature observed to encourage higher calcination rate due to the increase of the particle kinetic energy that eventually speed up the conversion from $CaCO_3$ to CaO. Although, it is best to acknowledged that a very high calcination temperature may cause sintering and attrition effects as reported by Bogwardt (1989) and Samtani *et al.* (2002).

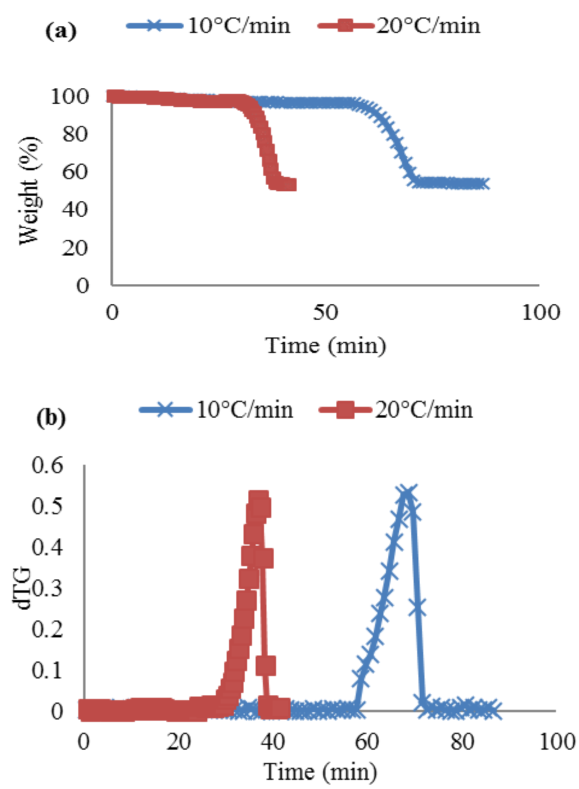

Figure-4. (a) TG Curves and (b) dTG curves at different heating rates for particle sizes of 0.3mm and temperature 900 °C.

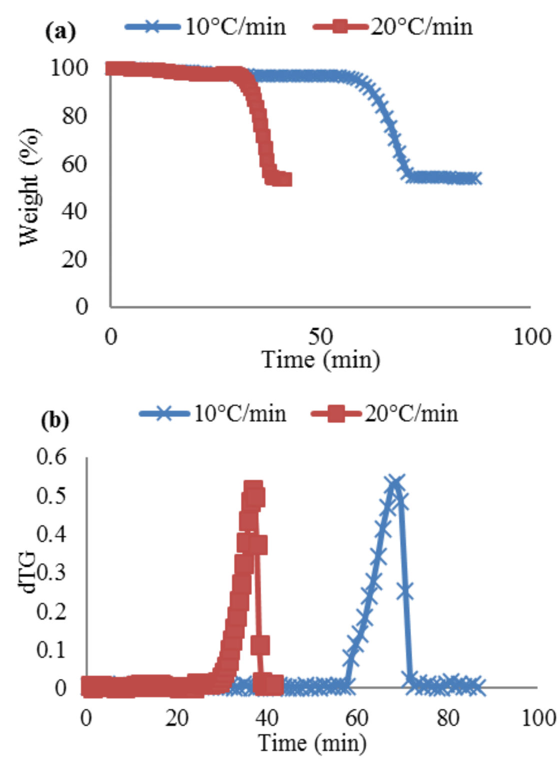

Figure-5. (a) TG Curves and (b) dTG curves at different calcination temperatures for particle sizes of 0.3mm at 10°C/min.

CONCLUSIONS

This study showed that waste cockle shells are a calcium-rich biomass which has the high potential as the source for the calcium oxide (CaO). Based on the TGA findings, it can be concluded that samples performance in calcination is highly dependent on few variables such as reaction temperature, particle sizes and heating rate. The optimum operating conditions for decomposition of cockle shell is at temperature of 900 ºC, heating rate of 20 ºC/min and using particle sizes of 0.3mm under inert condition.

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