Note from the field

Effects of experimental variables on conversion of cockle shell to calcium oxide using thermal gravimetric analysis

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ABSTRACT

Calcination of $CaCO_3$ is a process of producing CaO — a widely used substance in high temperature applications. However, the efficiency of the process depends on the variable involved and the assumption made. Therefore, this paper aims to illustrate the effects of few variables on calcination and carbonation reaction of $CaCO_3$ via thermo-gravimetric analyzer (TGA) in order to optimize the process. In the present work, cockle shells were used as $CaCO_3$ sources. The experimental variables i.e. particle size, heating rate, calcination and carbonation temperature were employed. A minimum of two runs of experiments for each variable were conducted and the standard deviation for all of the runs are found to be less than 1. Analysis of XRD, XRF and EDX indicates the conversion of $CaCO_3$ in cockle shells to CaO after calcination. The optimum adsorptive capacity of synthesized CaO for CO_2 at the optimum conditions is 0.72 kg CO_2/ kg CaO.

1. Introduction

The study on thermal decomposition of calcium carbonate ($CaCO_3$) has been extensively conducted in recent years (Garcia-Labiano et al., 2002). As Malaysia is rich in waste cockle shells, the potential to exploit them as raw materials in calcium oxide (CaO) production is great. To date, number of studies that utilize cockle shells as feedstock for CaO production is still limited. Recent studies only focused on the use of shells from eggs, crabs, mussels and oysters as alternative sources for CaO. Fig. 1 indicates the production of cockles in Malaysia from 1990 through 2006 (Izura and Hooi, 2008). Based on this statistic, the production of cockles started to decline from 2002 till 2006 due to limited suitable culture area for expansion in Peninsular Malaysia and inadequate spat-fall areas in Sabah and Sarawak. Higher operational costs and reduction of mangrove areas that helps to supply the cockle seeds also contribute towards the decline in cockles' production. However, Malaysia expected to produce 130,000 tons of cockles during the Ninth Malaysia Plan. Thus to realize the target, several

steps had been recommended such as reserving and gazetting spat-fall areas, reducing operational costs, and increasing research on development of more spat-fall areas (Izura and Hooi, 2008). Additionally, Li et al. (2009) found that the composition of CaO in sea shells is higher compared to other naturally occurring sources such as limestone as indicated in Table 1. The combination of Li's result and other similar findings such as scallop shells, sea shells and crab crust and legs (Sasaki et al., 2002; Jeon and Yeom, 2009) on the composition of calcium-based compound in marine shells justifies the use of cockle shells as a potential biomass for $CaCO_3$-based resources.

The major aim of this study is to determine the influence of operating conditions on the production of CaO using cockle shells as raw material via the analysis of thermo-gravimetric (TG) and differential thermo-gravimetric (dTG) curves.

2. Material and methods

The cockle shells were dried and prepared as described by Mohamed et al. (2012). In addition, three analyses were carried out in this study: X-Ray Fluorescence (XRF, Bruker S4 Pioneer), X-Ray Diffraction (XRD, Bruker d8 Advance), Scanning Electron Microscopy (SEM, Leo 1430VP) and Energy Dispersive X-ray (EDX, Oxford

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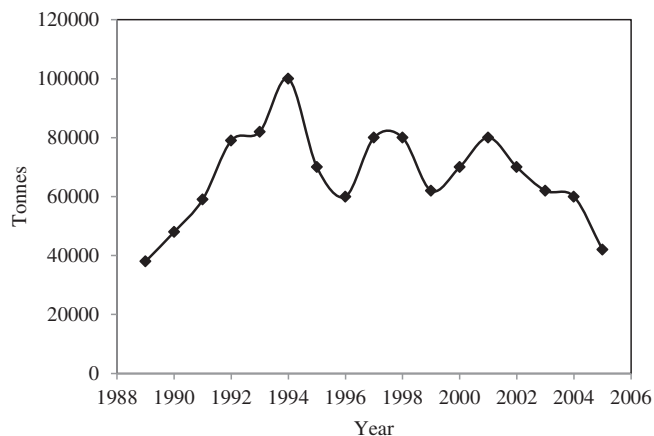
Fig. 1. Production of cockles in Malaysia (Izura and Hooi, 2008).

Table 2
Experimental parameters of the calcination and carbonation process, optimum experimental conditions and CO_2 adsorptive capacity.

Calcination process			Adsorptive capacity (at optimum condition and carbonation temperature = 650 °C)
Parameters	Experimental value	Optimum condition	
Particle size (mm)	<0.125, 0.5–1.0, 2.0–4.0	<0.125	0.72 kg CO_2/kg synthesized CaO
Heating rate (°C/min)	10, 20, 50	20	
Calcination temperature (°C)	750, 850, 950	850	
Carbonation temperature (°C)	500, 650, 850	650	

Inca). The crystal structure of the sample was estimated using XRD in 2θ range of 1–80° with a step size of 0.05 and a step time of 1 s. Calcination of the shells was carried out in Perkin Elmer Pyris 1 Thermo-gravimetric analyzer (TGA). 5–10 mg of sieved shell powder was placed in the ceramic sample holder. Subsequently, the powder was heated up to the desired temperature at desired heating rate under N_2 gas flow of 50 ml/min. The sample was cooled down to room temperature after 30 min of holding time. The procedure was repeated at different operating conditions as shown in Table 2. Under the optimal calcination conditions, CO_2 adsorption capacity of the synthesized CaO was investigated at various operating temperature i.e. 500, 650 and 850 °C under CO_2 gas flow of 50 ml/min.

3. Results and discussion

Based on the XRF and XRD results, the composition of cockle shell is proven to be rich in calcium and presence of CaO is detected in calcined cockle shells (Mohamed et al., 2012). The findings agree with Li et al. (2009) which shows high amount of calcium in shells. Based on XRD spectra, raw cockle shells contain aragonite ($CaCO_3$) which is one of the orthorhombic polymorphs of $CaCO_3$ other than calcite and veterite. Despite its relative instability, aragonite is still the most suitable compound for CaO production compared to the calcite or veterite.

SEM was used to visualize the changes on surface structure of the cockle shells. Aragonite is known to have needle-like structure as shown in Fig. 2(a). Yet, the structure changed after the calcination process. The surface is much smoother with uniform shapes as shown in Fig. 2(b).

EDX results showed that $CaCO_3$ was present but the proportion changed after calcination. Calcination increased the amount of calcium (Ca) and reduced the weight percent of carbon (C) of the sample as shown in Table 3.

Based on the observation of TG curves in Figs. 3–5, cockle shells experienced two phases of weight loss. During the first phase, the sample weight started to decrease at temperature around 200–300 °C prior of rapid decomposition once the temperature

Table 1
Comparison of oxides content in sea shells and limestone (Li et al., 2009).

Sample	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	Na_2O	Others	LOI
MV shell	52.41	0.22	0.11	0.07	0.17	0.37	0.33	46.32
Mussel shell	50.45	0.18	0.78	0.09	0.12	0.24	0.82	47.32
Scallop shell	54.53	0.27	0.00	0.04	0.16	0.49	0.47	44.04
MM limestone	48.83	4.8	2.76	0.28	0.54	0.02	0.36	42.41
JN limestone	50.28	2.54	4.21	0.51	0.95	0.01	0.32	1.18

MV: *Mactra Veneriformis*, MM: Moaming, JN: Jining.
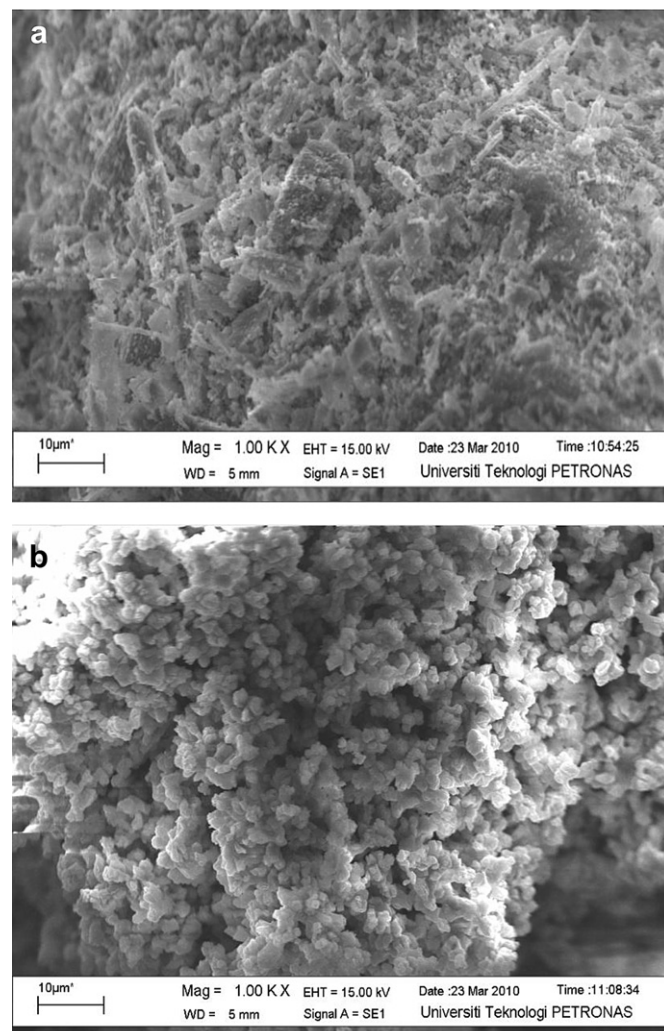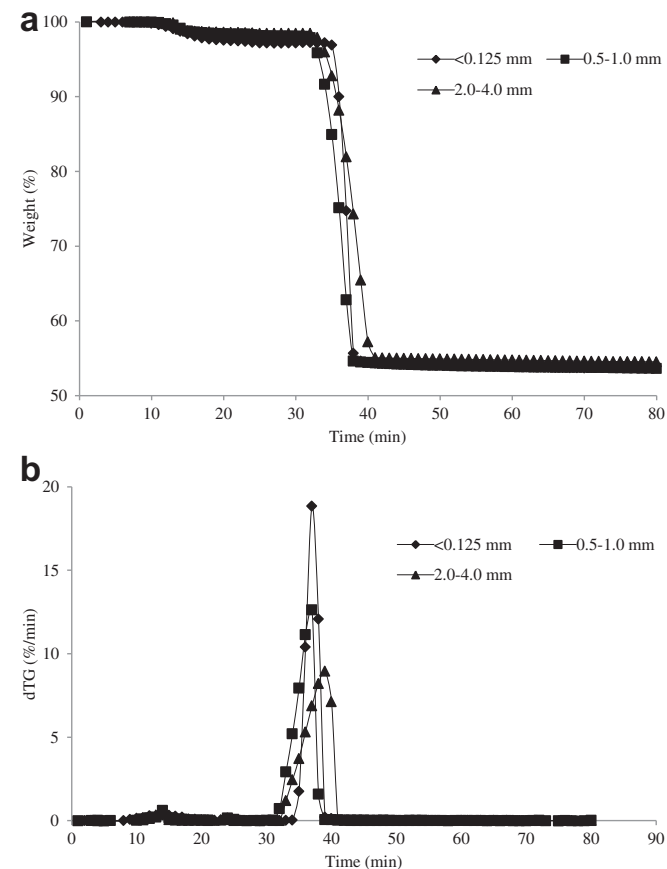
Fig. 2. SEM image of (a) cockle shell (b) calcined cockle shell.

Table 3
EDX analysis of raw cockle shells and calcined cockle shells.

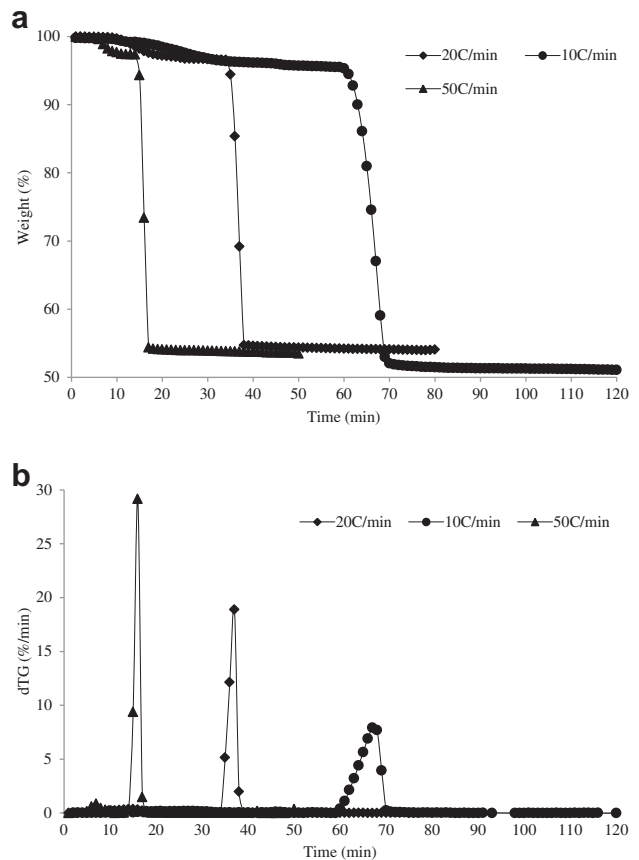| Element	Raw cockle shells (wt %)	Calcined cockle shells (wt %)
C	15.77	13.42
O	55.39	55.54
Ca	28.85	31.03

reached 600—700 °C. According to Barros et al. (2009), sample will experience weight loss initially at 100—140 °C due to the trapped moisture and once the temperature increased to 250—410 °C, volatile matter will start to dissociate. Upon increasing the temperature up to 500—540 °C, the remaining organic material also started to dissociate and finally at 650 °C, the sample rapidly disintegrated into CaO. However, in this study, no significance weight loss was recorded by most of the sample at the initial temperature (100—140 °C). This may be due to prior drying of the sample in oven at 110 °C for 2 h.

Borgwardt (1989) believed that the amount of weight loss depends on type of micro-grain array of the sample and assumed that if the micro-grain has a face centred array of uniform spheres, it will have certain values of diameter and molar volumes that control the amount of micro-grain and percentage of weight loss that can be experienced by the sample. Thus, it can be observed that most of the TG curves of calcination illustrated that the sample left with 55% of the original weight which represents the decomposed sample.

Fig. 4. (a) TG curves and (b) dTG curves at different heating rates for particle sizes of <0.125 mm and temperature of 850 °C.

Fig. 3. (a) TG curves and (b) dTG curves for different particle sizes at 850 °C and 20 °C/min.

Fig. 3 illustrates the influence of particle sizes on the calcination process. The experiment shows that particle size influences the percent of weight loss of the samples tested as depicted by TG curves as well as the calcination rate which is represented by DTG curves. As shown by TG curves, smaller sized particle experienced rapid weight loss compared to larger particle size and same observation was indicated by DTG curves which represent the calcination rate of the samples. The smaller sized particle is also observed to reach the same conversion as the larger sized particle within a shorter time. This observation might be due to wider surface area of smaller sized particles which contributes to a higher uptake of heat to promote the decomposition. The same observation was reported by Ar and Dogu (2001) who claimed that the process was influenced by diffusion effect on calcination rate.

Fig. 4 describes the effect of heating rate on calcination and clearly indicates that calcination occurs more rapidly with higher heating rates as the same decomposition amount can be reached within a shorter time. Higher heating rate elevated the temperature of the reaction faster than slower heating rate and thus, reduces the time taken for the reaction to complete. Therefore, applying the suitable heating rate for the process is very important. Furthermore, Samtani et al. (2002) stated that heating rates also influence the shape of dTG curves. The height of the curve (peak) which represents the calcination rate will increase once the heating rate is increased and this similar occurrence was also observed in our study.

The effect of calcination temperature on calcination process is exhibited by Fig. 5. The calcination temperature is sustained for
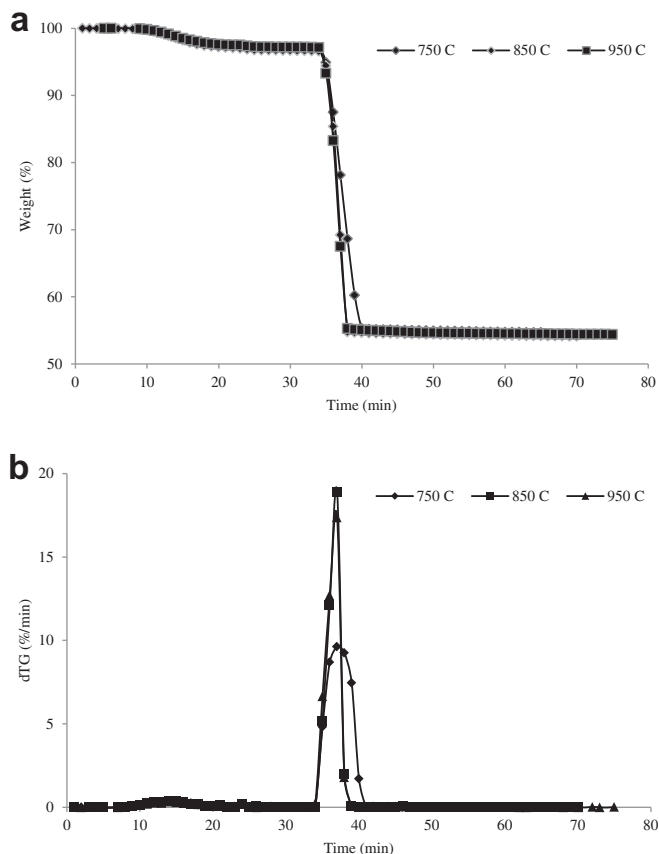
Fig. 5. (a) TG curves and (b) dTG curves at different calcination temperatures for particle size of <0.125 mm at 20 °C/min.
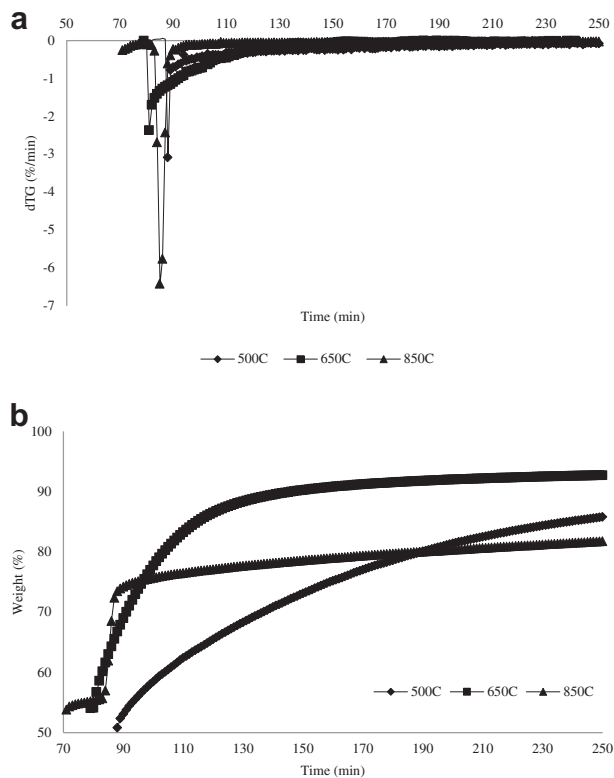
Fig. 6. (a) dTG curves and (b) TG curves at different carbonation temperatures at optimal calcination operating conditions (Calcination temperature = 850 °C, Heating rate = 20 °C/min, Particle size = <0.125 mm).

30 min at each temperature level to ensure a complete decomposition. As illustrated in Fig. 5, higher calcination temperature promotes higher calcination rate as this will increase the particles kinetic energy and consequently, accelerates decomposition of $CaCO_3$ to CaO. However, a very high calcination temperature may lead to sintering and attrition effects (Borgwardt, 1989; Samtani et al., 2002).

In addition, the effect of carbonation temperature on CO_2 adsorption capacity has also been incorporated. Referring to Fig. 6(a), a rapid carbonation reaction is encountered at the elevated temperature and equilibrium is achieved faster compared to low temperature reactions. Yet, according to Fig. 6(b), it is observed that the weight changes increases with temperature up to 650 °C only, and starts to decline at the elevated temperature i.e. 850 °C. Hence, it is expected that the exposure of CaO to CO_2 at the elevated temperature accelerates the sintering process and leads to pore destruction which lead to reduction in CO_2 capture capacity and low reactivity. Meanwhile, under low temperature condition i.e. 500 °C, there is a possibility that thermal energy is insufficient to drive the carbonation reaction. Under optimum calcination and carbonation conditions, maximum CO_2 capture is found to be 0.72 kg per kg adsorbent.

4. Conclusion

The study proved that waste cockle shells are a calcium-rich biomass with high potential as the source for CaO. The optimum operating conditions for decomposition of cockle shell is at calcination temperature of 850 °C, heating rate of 20 °C/min and by using particle size of <0.125 mm under inert condition. The capability of synthesized CaO on CO_2 capture is tested at various carbonation temperatures and the adsorptive capacity is proven to be about 0.72 kg CO_2/kg adsorbent.

Acknowledgement

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