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DECOMPOSITION STUDY OF CALCIUM CARBONATE IN COCKLE SHELL

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Abstract

Calcium oxide (CaO) is recognized as an efficient carbon dioxide (CO_2) adsorbent and separation of CO_2 from gas stream using CaO based adsorbent is widely applied in gas purification process especially at high temperature reaction. CaO is normally been produced via thermal decomposition of calcium carbonate ($CaCO_3$) sources such as limestone which is obtained through mining and quarrying limestone hill. Yet, this study able to exploit the vast availability of waste resources in Malaysia which is cockle shell, as the potential biomass resources for $CaCO_3$ and CaO. In addition, effect of particle size towards decomposition process is put under study using four particle sizes which are 0.125-0.25 mm, 0.25-0.5 mm, 1-2 mm, and 2-4 mm. Decomposition reactivity is conducted using Thermal Gravimetric Analyzer (TGA) at heating rate of 20°C/minutes in inert (Nitrogen) atmosphere. Chemical property analysis using x-ray fluorescence (XRF), shows cockle shell is made up of 97% Calcium (Ca) element and CaO is produced after decomposition is conducted, as been analyzed by x-ray diffusivity (XRD) analyzer. Besides, smallest particle size exhibits the highest decomposition rate and the process was observed to follow first order kinetics. Activation energy, E, of the process was found to vary from 179.38 to 232.67 kJ/mol. From Arrhenius plot, E increased when the particle size is larger. To conclude, cockle shell is a promising source for CaO and based on four different particles sizes used, sample at 0.125-0.25 mm offers the highest decomposition rate.

Keywords: Decomposition, Kinetics, Calcium carbonate, Particle size, Cockle shells, TGA.

1. Introduction

Cockles or *anadara granosa* is a type of bivalve shellfish that grows well in muddy coastal area. It is a cheap protein source which is quite common to be

Nomenclatures

dw_t/dt	Weight loss rate, mg/min.
$d\alpha/dt$	Conversion rate, 1/min.
E	Activation energy, kJ/mol
k	Specific rate constant, min^{-1}
R	Gas constant, J/mol K
w_f	Final weight of the sample, mg
w_i	Initial weight of sample, mg
w_t	Current weight of the sample size, mg

Greek Symbols

α	Weight fraction of reacted shell powder

prepared as local dishes. Malaysia is expected to produce 13000 metric ton of cockles during Ninth Malaysia Plan [1]. Selangor aims to produce 10 mt/ha/yr of cockle during 2010 [2]. Till 2007, Malaysia is having 1055 number of farmers working on cockle cultivation agriculture which involving 6000 hectare of cultivation area [3]. However, these figures do not only indicate the vast availability of cockles but also the amount of waste shells generated. The shells that been dumped and left untreated may cause unpleasant smell and disturbing view to the surrounding.

As simplified in Table 1, Barros et al. [4] described that seashells are quite well developed and applied in other countries for various purposes. In Malaysia recently, it was found that cockles shell is the potential biomass resource for bone repair material especially made for cancer patients [5].

Table 1. Application of Seashells in other Countries [4].

Type of Seashell	Country	Application
Oysters	Japan	Cement clinkers
	Korea	Fertilizers, water eutrophication
Scallops	UK	Construction road forestry
	Peru	Obtain lime as the input for other industrial sector
Mussels	Spain	Animal feed additives, liming agent, constituent
	US	fertilizers
	Holland	Soil conditioner, liming agent
		Mussel tiles

Seashell contained of 95-99% by weight of $CaCO_3$ which has enable it to be applied for quite a number of purposes [4, 6]. Equation (1) represents the decomposition process of cockle shell which is denoted by decomposition of $CaCO_3$. Via thermal decomposition process known as calcination, $CaCO_3$ can be converted into CaO which is used in industries and daily practice such as in waste water and sewage treatment, glass production, construction material, agricultural and more [7]. CaO also been used as the based material to adsorb carbon dioxide, CO_2 [8, 9]. The existing technology of CO_2 adsorbent like using amine-based adsorbent, activated carbon, and molecular sieve can only withstand low-temperature process (40°C-160°C) [8]. Inversely, limestone and dolomite is resistible to high-temperature process (500°C-1000°C) [8] other than it can be regenerated and sustained to a number of CO_2 adsorption and calcination cycles [9].

$$CaCO_3\ (s) \leftrightarrow CaO\ (s) + CO_2\ (g) \quad (1)$$

Stanmore et al. [10] mentioned that kinetics of calcination is complicated by three factors which are concentration of CO_2, sizes of the particle and also impurities. Calcination favours high temperature as it is an endothermic reaction and it needs low decomposition pressure of $CaCO_3$ in order to drive the equilibrium reaction forward [10]. Garcia-Labiano et al. [11] claimed that atmospheric pressure can avoid the resistance of external mass transfer resistance. Previous studies found that atmospheric pressure could be achieved when calcination temperature reached 800-900°C [10, 12]. Besides, Cheng and Specht [13] stated that the resistances introduce by particle size of the sample can be avoided by having the sample size in millimetre or micrometer range. However, the extent of particle size effect is uncertain since it also depend on the calcination condition such as temperature, flow rate and calcination atmosphere [13].

Thus the objective of this paper is to demonstrate the effect of one of the factors that influence decomposition of cockle shell which is particle sizes by demonstrating the fraction of decomposed sample according to temperature changes, the highest temperature that cockle shell can resist and the kinetic analysis of the process. It also aims to illustrate that cockle waste shell which is abundantly available in Malaysia, is rich with Ca and posses an added value to the environment.

2. Materials and Methods

2.1. Preparation of material

Waste cockle shells that used in this experiment were taken from a stall in Perak. The shells were washed with raw water to remove dirt and been dried using oven at 110°C for 2 hours. It were crushed using pestle and mortar which was then been ground into the powder form using Rocklab grinder. The powder was sieved in the shaker sieve for 10 minutes to segregate according to the ranges of particle sizes.

2.2. Experimental method

There were two characterization analysis that have been done in this study which were using x-ray fluorescence (XRF) and x-ray diffraction (XRD). The chemical composition of cockle shell was analysed using x-ray fluorescence, XRF (Model: Bruker S4 Pioneer, USA) while the crystal structure of the sample were estimated using x-ray diffraction, XRD (Model: Bruker D8 Advance, USA), which was run in 2 theta range 1 to 80° with step size of 0.05 and step time of 1 s.

Calcination of cockle shell were analyse by conducting the thermal decomposition using thermo-gravimetric analyzer, TGA (Model: Perkin Elmer Pyris 1 TGA). 10-20 mg of shell powder in the size of 0.125-0.25 mm was placed in the ceramic sample holder. It was heated up to 850°C at 20°C/min under nitrogen gas flow at 20 ml/min. Nitrogen was used to ensure inert environment around the sample. The sample was cooled down to room temperature after been hold for 30 minutes at 850°C to ensure the completion of the process. The procedures were repeated for different particle size at the same heating rate.

3. Results and Discussion

3.1. Characterization of cockle shell

Chemical analysis using XRF has been conducted to estimate the mineral composition in cockle shell. The finding demonstrates that cockle shell is made up of calcium, which is the same outcome with other study such as Awang-Hazmi et al. [14] who also performed chemical analysis on cockle shell in Malaysia. Table 2 indicate the comparison of chemical analysis obtained in this study and the one conducted by Awang-Hazmi et al. [14].

Table 2. Chemical Analysis of Cockle Shells by XRF.

Author / Mineral (%wt)	CaC	Mg	Si	Na	Others
Current study	98.99	0.51	0.078	-	< 0.1
Awang-Hazmi et al. [14]	98.70	0.05	-	0.9	< 0.1

The analysis of crystal structure using XRD illustrates that raw cockle shell is made up of aragonite, $CaCO_3$. It is one type of crystal form of calcium carbonate other than calcite and vaterite. Even though calcite is the most stable polymorphism of calcium carbonate, aragonite has higher density and hardness which make it very suitable material in plastic, paper, glass fiber and other industry [15]. The analysis also indicates the presence of lime, CaO, in the calcined cockle shell. Thus, these findings suggest that thermal decomposition of cockle shell converts $CaCO_3$ contained into CaO.

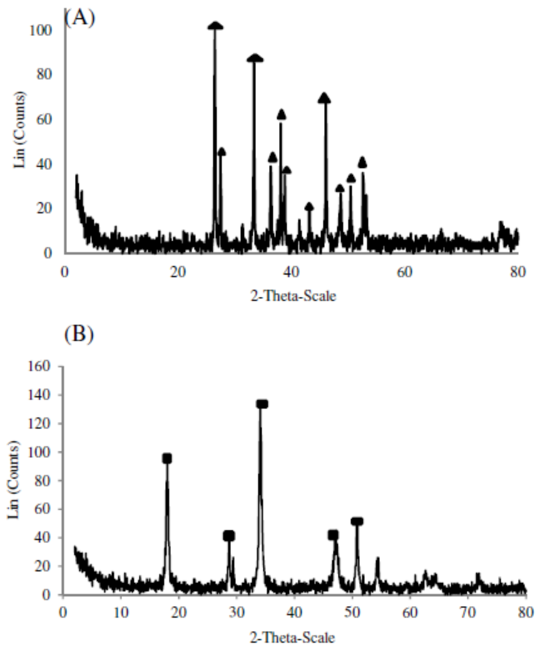

Fig. 1. XRD Spectra of (A) Cockle Shell and (B) Decomposed Cockle Shell at 850°C (▲ = $CaCO_3$ and ■ = CaO).

3.2. Thermal decomposition of cockle shell

Thermal decomposition of carbonate usually is assumed to suit Shrinking Core Model (SCM) where it visualizes the reaction begin to occur at the outer layer of the particle then move into the solid which finally leaving the completely converted material and inert solid that is known as 'ash' [16]. Figure 2 illustrates weight loss of the sample during the process. By taking sample with particle size of 2-4 mm as the example, the initial process started with a very small weight loss which is due to the moisture content that still left in the sample. As the temperatures increase between 700°C to 900°C , rapid weight change occur as the volatile material in the sample attempt to escape as decomposition begin to take place. However, the sample weight seemed to be constant after the temperature reach 900°C. It signifies that the process was already done and sample left is known as 'ash' [16].

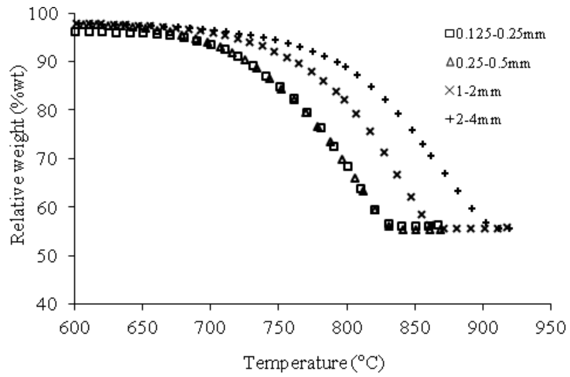

Fig. 2. TG Curves of Cockle Shell Powder Decomposition.

Weight loss of the sample indicates the fraction of sample that been decomposed during the process [17]. By assuming that there were no impurities forming during the process, Fig. 3 represents the fraction of decomposed sample which was most probably involving the conversion of $CaCO_3$, contained in the cockles shell into CaO. The assumption was supported by the analysis that been done using XRD as described in Section 3.1.

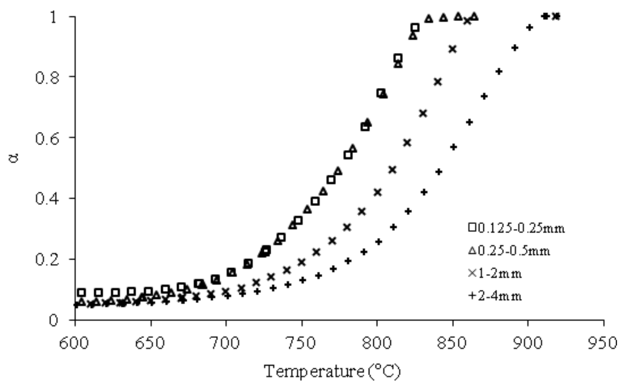

Fig. 3. Fraction of Sample Decomposed according to Temperature Change.

Using the same computation method as Samtani et al. [17] and Nobari and Halali [18], fraction of the decomposed sample during the calcination is denoted by α and computed using Eq. (2). The fraction was based on the current weight loss with respect to total weight loss of the sample. Initial weight is denoted by w_i while w_t represents current weight and final weight is denoted by w_f. Sample with larger particle size need higher temperature and longer time to get fully decomposed compared to sample with smaller particle size.

$$\alpha = \frac{w_i - w_t}{w_i - w_f} \tag{2}$$

Figure 4 shows decomposition rate of cockle shell, *dα/dt*, which is computed using Eq. (3). Weight loss with respect to time, dw_t/dt, is the differential data of TG curves which were generated by the software.

$$\frac{d\alpha}{dt} = -\frac{dw_t/dt}{w_i - w_f} \tag{3}$$

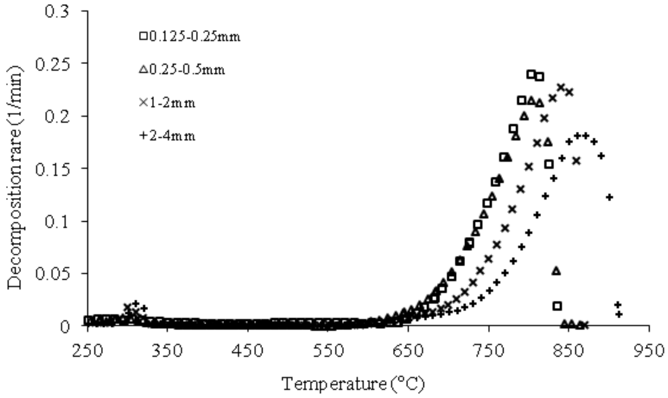

Fig. 4. Decomposition Rate Curve of Cockle Shells with Different Particle Size.

Decomposition rate is increased as the particle size is smaller. The sample with smallest particle size exhibits to have highest maximum decomposition rate among the other sample sizes. It occurred at 800°C with decomposition rate of 0.25/min. It is also observed that the time taken for maximum decomposition rate of the smallest particle size is shorter compared to the sample with larger particle size. Particle sizes really become a factor to the thermal decomposition process as it determines the surface area of the sample. Smaller particle size tends to have large surface area that contributes to high efficiency of heat transfer. It can accelerate the process by reducing the thermal or heat resistance and other resistance such as mass transfer or gas diffusion [13]. The cause of CO_2 partial pressure can be neglected in this study as the process was conducted at 850-900°C in which at this temperature the pressure is considered to be in equilibrium or atmospheric pressure [10, 12].

3.3. Kinetics analysis

Kinetic analysis is important as the process involves thermal effect to the sample. The process take place once the heat supplied is enough. Thus, the kinetic energy needs to be analysed so that best operating condition by controlling particle sizes and operating temperature can be implemented. In this study, kinetic analysis of thermal decomposition was described by Arrhenius equation as been done by many previous researchers before [16, 18, 19]. Rate of reaction, *r*, was represented by the decomposition rate, $d\alpha/dt$, as follows

$$r = d\alpha / dt = kf(\alpha) \tag{4}$$

Rearrange Eq. (4) will yield the equation for reaction constant, *k*

$$k = \frac{d\alpha}{dt} / f(\alpha) \tag{5}$$

The value of $f(\alpha)$ is depending on the type of reaction order of the process which is decided based on best fit curved. Through regression analysis, decomposition of cockles shell was best fit with first order type of reaction. Thus, the particular equation was applied.

Table 3. Mathematical Model for Reaction Mechanism.

Order of reaction	$f(\alpha)$
Zero order	**1**
First order	**$1-\alpha$**
Second order	**$(1-\alpha)^2$**

Linear form of Arrhenius equation that to be fitted in is as follows

$$\ln k = \ln A - E / RT \tag{6}$$

By replacing *k* with Eq. (5) in Eq. (6), the Arrhenius equation formed is

$$\ln \frac{d\alpha / dt}{f(\alpha)} = \ln A - E / RT \tag{7}$$

Figure 5 shows A plot of ln $[(d\alpha/dt) \,/\, f(\alpha)]$ or ln *k* versus $1/T$ was then constructed by using Eq. (7). The slope of the plotted graph indicates the activation energy, *E*, of the process and the intercepts of y axis represents exponential A which is the value on ln *k*, rate constant. Regression analysis demonstrates first order reaction mechanism fits the best with the kinetics of cockle shell decomposition. In addition, the analysis illustrates that larger particle size has the steeper slope which denotes the higher value of activation energy and reaction constant. Based on first order of reaction described in Table 4, Demir et al. [19] also found the same decomposition behaviour. At constant heating rate, activation energy is increased once particle size of the sample is larger. The finding of Demir et al. [19] is described in Table 5.

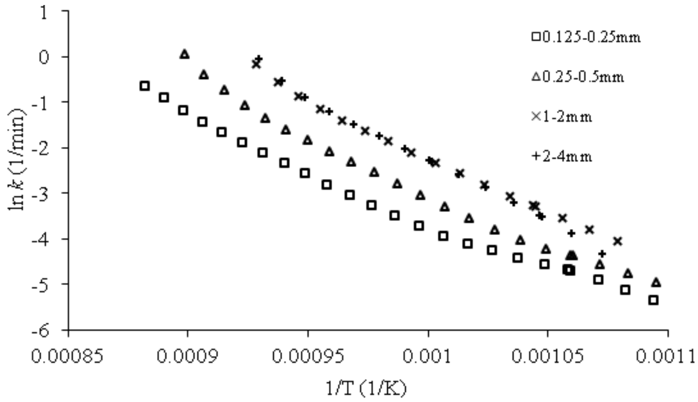

Fig. 5. Arrhenius Plot for Cockle Shell Decomposition.

Table 4. Analysis of Kinetic Values based on Arrhenius Plot obtained in this Study.

Order of Reaction	Zero				First				Second			
Particle size (mm)	2-4	1-2	0.25-0.5	0.125-0.25	2-4	1-2	0.25-0.5	0.125-0.25	2-4	1-2	0.25-0.5	0.125-0.25
Regression (R^2)	0.978	0.990	0.997	0.994	0.996	0.995	0.982	0.982	0.982	0.975	0.945	0.957
ln k (min^{-1})	18.497	15.128	15.85	14.369	25.725	22.346	20.45	18.03	32.953	29.564	25.043	21.691
E(kJ/kmol)	176.05	147.52	158.87	150.69	232.67	204.11	194.07	179.38	289.30	260.70	229.25	208.09

Table 5. Activation Energy Values of Previous Study on Calcination of Dolomite Obtained by Demir et al. [19].

Particle size (μm)	Heating rate (°C/min)	E (kJ/mol)	r^2
-850 + 600	10	278.37	0.9997
-500 + 355	10	272.22	0.9992
-230 + 180	10	268.38	0.9989
-150 + 125	10	264.94	0.9977

4. Conclusions

Based on the XRD analysis, cockle shell do contained of calcium carbonate in the crystal form of aragonite. The thermal decomposition process that been done managed to decompose a fraction of the sample into calcium oxide. Through thermogravimetric analysis, cockle shells begin to decompose at 700°C and loss 55% of the weight regardless the particle sizes. The findings confirmed that particle size influenced the process. Sample with smaller particle size demonstrates higher decomposition rate in shorter time and at lower temperature compared to the larger particle size. In this case, the highest decomposition rate is 0.25/min for the particle sizes of 0.125-0.25 mm at heating rate of 20°C/min. Based on the best fitted line, decomposition of the shell powder is found to exhibit first order mechanism. Plus, larger particle size caused the activation energy to be higher. Thus the sample consumed more energy to initiate the process.

Future work will focus on determining the efficiency of the shell powder in capturing carbon dioxide. Then, the results will be compared with the commercial adsorbent applied in the industries.

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References

1. Kerajaan sasar hasil 130000 tan metric kerang. *Utusan Malaysia*. 15 December 2007. http://www.seafdec.org.my. (Accessed: 16th Feb 2009).
2. Pelan induk pembangunan Malaysia 2005, www.bernama.com/selangor_maju/pembangunan_pertanian.htm. (Accessed: 14th Feb 2009).
3. Izura, S.N.; and Hooi, T.K. (2008). Shaping the future of cockle industry in Malaysia; Maritime Insitute of Malaysia. http://www.seafdec.org.my. (Accessed: 22nd Feb 2009).
4. Barros, M.C.; Bello, P.M.; Bao, M.; and Torrado, J.J. (2009). From waste to commodity: transforming shells into high purity calcium carbonate. *Cleaner Production*, 17(3), 400-407.
5. Mokhtar, I.L. (2009). Cockle shells help bone heal faster. *New Straits Time*. 28 December 2009. www.nst.com.my. (Accessed: 20th Jan 2010).
6. Nakatani, N.; Takamori, H.; Takeda, K.; and Sakugawa, H. (2009). Transesterification of soybean oil using combusted oyster shell waste as a catalyst. *Bioresource Technology*, 100(3), 1510-1513.
7. Calcium oxide: crops, National Organic Standard Board Technical Advisory Panel Review 2002, USDA National Organic Program, http://www.omri.org/CaO_final.pdf. (Accessed: 10th May 2009).
8. Lu, H.P.; Smirniotis, G.; Ernst, F.O.; and Pratsinis, S.E. (2009). Nano-structured Ca-based sorbents with high CO_2 uptake efficiency. *Chemical Engineering Science*, 64(9), 1936-1943.
9. Dennis, J.S.; and Pacciani, R. (2009). The rate and extent of uptake of CO_2 by a synthetic CaO-containing sorbent. *Chemical Engineering Science*, 64(9), 2147-2157.
10. Stanmore, B.R.; and Gilot, P. (2005). Review: Calcination and carbonation of limestone during thermal cycling for CO_2 sequestration. *Fuel Processing Technology*, 86(16), 1707-1743.
11. Garcia-Labiano, F.; Adanez, J.; Abad, A.; deDiego, L.F.; and Gayan, P. (2002). Calcination of calcium-based sorbents at pressure in a broad range of CO_2 concentrations. *Chemical Engineering Science*, 57(13), 2381-2393.
12. Calcium carbonate: facts, discussion forum, and encyclopedia article, http:// www.absoluteastronomy.com/topics/Calcium_carbonate. (Accessed: 10th March 2009).
13. Chong, C.; and Specht, E. (2006). Reaction rate coefficients in decomposition of lumpy limestone of different origin. *Thermochimica Acta*, 449(1-2), 8-15.

14. Awang-Hazmi, A.J.; Zuki, A.B.Z.; Nordin, M.M.; Jalila, A.; and Norimah, Y. (2007). Mineral composition of the cockle (Anadara Granosa) shells of west coast of peninsular Malaysia and its potential as biomaterial for use in bone repair. *Journal of Animal and Veterinary Advances*, 6(5), 591-594.
15. Keiko, S.; Tomohiko, Y.; and Masami, T. (2002). Synthesis of aragonite from calcined scallop shell at ambient temperatures and their morphological characterization by FE-SEM. *Journal of the Mining and Materials Processing Institute of Japan*, 118(8), 553-558.
16. Levienspiel, O. (1999). *Chemical reaction engineering*, (3^{rd} Ed.). John Wiley, New York.
17. Samtani, M.; Dollimore, D.; Tong, P.; and Alexander, K.S. (1996). The kinetic interpretation of the decomposition of calcium carbonate by use of relationships other than the Arrhenius equation. *Thermochimica Acta*, 282-283, 13-27.
18. Nobari, A.H.; and Halali, M. (2006). An investigation on the calcination kinetics of zinc carbonate hydroxide and calsimin zinc carbonate concentrate. *Chemical Engineering Journal,* 121(2-3), 79-84.
19. Demir, F.; Donmez, B.; Okur H.; and Sevim, F. (2003). Calcination kinetic of magnesite, from thermogravimetric data. *Chemical Engineering Research and Design*, 81(6), 618-622.