DECOMPOSITION OF CALCIUM CARBONATE IN COCKLE SHELL

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DECOMPOSITION OF CALCIUM CARBONATE IN COCKLE SHELL

AHMAD HAMIDI BIN ZULKIFLE

Thesis submitted in partial fulfilment of the requirements for the award of the degree of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering UNIVERSITI MALAYSIA PAHANG

MAY 2013

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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Date	: 31 MAY 2013

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature:Name: AHMAD HAMIDI BIN ZULKIFLEID Number: KA10081Date: 31 MAY 2013

Dedication

Dedicated to my family, supervisor, lecturer and friends =)

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ABSTRACT

Cockle shell or scientifically known as Anadara granosa is a local bivalve mollusc having a rounded shell with radiating ribs. The production of cockle shell in Malaysia was great and keeps increasing by year. In Malaysia, cockle shell was treated as waste with unpleasant smell and mostly left to natural deteriorates. Small number of study utilizes cockle shell as source of CaO. Hence, this study was conducted to propose a cockle shell as an alternative source of CaCO₃ by the calcination process. Calcination of CaCO₃ is a process of producing CaO which is subjecting a substance to the action of heat. This will done by using a muffle furnace. However, the efficiency of the process depends on the variable involved. Therefore, this paper aims to illustrate the effects of few variables on calcination reaction of CaCO₃ via thermal gravimetric analyzer (TGA) in order to optimize the process. In the present work, the vast availability of waste resources in Malaysia which is cockle shell were used as CaCO₃ sources. The experimental variables such as particle size, temperature and heating rate is put under study toward decomposition rate. The decomposition of calcium carbonate was investigated by using a particle size with 300, 425-600, and 1180µm in thermal gravimetric analyzer (TGA). The experiments were test with different temperature (700, 800 and 900°C) to study the decomposition rate of CaCO₃. Experiment has been conducted in inert atmosphere (N2 gas). Analysis of XRF was conducted to determine the mineral composition of powder cockle shell. The surface morphology of raw cockle shell and calcined cockle shell was illustrated by SEM. Mineral composition of cockle shell by XRF showed that cockle shell was made up of 59.87% calcium (Ca). Thermal gravimetric data shows that smaller particle size experienced rapid weight loss compared to larger particle. The higher calcination temperature promotes higher calcination rate as this will increase the particles kinetic energy and thus, accelerates decomposition of CaCO₃ to CaO. The SEM analysis conclude that the higher calcination temperature give the structure of the sample more porous. Hence, more CO₂ will be released to give the more conversion to CaO.

ABSTRAK

Kerang atau saintifik dikenali sebagai Anadara granosa adalah moluska kerang tempatan mempunyai cengkerang bulat dengan terpancar tulang rusuk. Pengeluaran kerang di Malaysia adalah besar dan terus meningkat dari tahun ke tahun. Di Malaysia, kerang telah dianggap sebagai sisa dengan bau yang tidak menyenangkan dan kebanyakannya dibiarkan memburuk semula jadi. Sebilangan kecil kajian menggunakan kerang sebagai sumber CaO. Oleh itu, kajian ini telah dijalankan untuk mencadangkan kerang sebagai sumber alternatif bagi CaCO₃ oleh proses pengkalsinan ini. Pengkalsinan CaCO₃ adalah proses menghasilkan CaO yang menundukkan bahan untuk tindakan haba . Ini akan dilakukan dengan menggunakan relau meredupkan . Walau bagaimanapun, kecekapan proses yang bergantung kepada pemboleh ubah yang terlibat. Oleh itu, kertas ini bertujuan untuk menggambarkan kesan beberapa pembolehubah pada reaksi pengkalsinan CaCO₃ melalui terma penganalisis gravimetrik (TGA) untuk mengoptimumkan proses. Dalam karya ini, ketersediaan besar sumber air di Malaysia yang kerang telah digunakan sebagai sumber CaCO₃. Pembolehubah eksperimen seperti saiz zarah, suhu dan kadar pemanasan diletakkan di bawah kajian ke arah kadar penguraian. Penguraian kalsium karbonat telah disiasat dengan menggunakan saiz zarah dengan 300, 425-600, dan 1.180 µm terma penganalisis gravimetrik (TGA). Eksperimen yang mengikuti ujian dengan suhu yang berbeza (700, 800 dan 900 °C) untuk mengkaji kadar penguraian CaCO₃. Kajian dijalankan dalam suasana lengai (gas N). Analisis XRF telah dijalankan untuk menentukan komposisi mineral kerang. Morfologi permukaan kerang mentah dan kerang calcined telah digambarkan oleh SEM. Komposisi mineral kerang dengan XRF menunjukkan bahawa kerang terdiri daripada 59.87 % kalsium (Ca). Data gravimetrik terma menunjukkan bahawa saiz zarah yang lebih kecil mengalami kehilangan berat badan yang cepat berbanding dengan zarah yang lebih besar . Suhu pengkalsinan yang lebih tinggi menggalakkan kadar pengkalsinan yang lebih tinggi kerana ini akan meningkatkan zarah tenaga kinetik dan dengan itu, mempercepatkan penguraian CaCO3 untuk CaO. Analisis SEM membuat kesimpulan bahawa suhu pengkalsinan yang lebih tinggi memberikan struktur sampel lebih poros . Oleh itu, lebih banyak CO2 akan dikeluarkan untuk memberi penukaran yang lebih untuk CaO.

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LIST OF ABBREVIATIONS

Thermal gravimetric analyzer
Scanning electron microscope
X-ray fluorescence
Nitrogen
Calcium oxide
Calcium carbonate
Carbon dioxide
Magnesium
Phosphorus
Potassium
Sodium
Degree celcius
Micro meter
Cockle shell
Calcium

1 INTRODUCTION

1.1 Background

Cockle shell or scientifically known as Anadara granosa is a local bivalve mollusc having a rounded shell with radiating ribs. In Malaysia, cockle shell as known as 'kerang' belonging to the family Arcidae (Awang et al., 2007). It is a cheap protein source which is quite common to be prepared as local dishes (Mohamed et al., 2012). Seashell contained of CaCO₃ which has enable it to be applied for quite a number of purpose such as biomaterial for bone repair (Awang et al., 2007) and also for industries and daily practice such as in waste water and sewage treatment, glass production, construction material, agricultural, and more. The industrial application of CaCO₃ are wide ranging, including paper, paints, ink, plastics, medicines, feedstuff, adhesives and rubbers (L. Xiang et al., 2005). CaCO₃ is one of the most abundant minerals in nature and has three polymorphs which is calcite, aragonite and vaterite (H. Bala et al., 2005). It's found in muddy bottoms of coastal regions of South East Asian particularly Malaysia, Thailand and Indonesia. The history of cockle culture in Malaysia started in 1948 in Perak. Awang-Hazmi et.al had determined the mineral composition of Anadara granosa from from three major cultivation areas in West Coast of Peninsular Malaysia which are Penang, Kuala Selangor and Malacca. As reported in 2010, Malaysia had produced 78,024.70 metric tonnes of cockle for seafood industry (Izura and Hooi, 2008). 4000-5000 hectares of the west coast of Peninsular Malaysia were used for cockle culture (FAO, 2006). Chemical property analysis using x-ray fluorescene (XRF) shows cockle shell is made up of 97% Calcium (Ca) element and CaO is produced after decomposition was conducted (Mohamed et al., 2012).

Thermal decomposition of a cockle shell is called calcination. Calcination of $CaCO_3$ is a process of producing CaO – a widely used substances in high temperature applications (S. Yusup et al. 2012). Cockle shell decomposition is a gas-solid reaction in which the solid is the reactant. The reaction involves mass- and heat-transfer processes between a solid cockle shell particle and the calcination gas. The calcination of a cockle shell particle involves several steps, each of which is potentially rate-controlling. They are: (1) heat transfer from the bulk gas to the external surface and from the external surface to the reaction interface; (2) thermal decomposition of $CaCO_3$

at the reaction interface; and (3) mass transfer of CO_2 from the reaction interface to the bulk gas (Garcia-Labiano et al., 2002). However, the efficiency of the process depends on the variable involved and the assumption made. Therefore, the effects of few variables on calcination reaction of CaCO₃ via thermo-gravimetric analyzer (TGA) was consider in order to optimize the process. In the present work, cockle shells were used as CaCO₃ sources. The experimental variables such as particle size and calcination temperature were employed.

1.2 Motivation and statement of problem

In Malaysia, cockle shell is abundantly available as a by-product from seafood industry and regarded as waste and mostly left at dumpsite to naturally deteriorate. According to L. Xiang et. al (2005), CaCO₃ is an abundant mineral comprising approximately 4% of the earth's crust. The study on thermal decomposition CaCO₃ has been extensively conducted in recent years (Garcia-Labiano et al., 2002). There are several sources of CaCO₃ for the production of CaO such as limestone, cement-kiln dust, seashells and more. Recent studies only focused on the use of shells from eggs, crabs, mussels and oysters as alternative sources for CaO. Although there are, in theory, many uses for shell, there is no singular solution to treat or utilise these materials as byproducts and treated as waste. Nowadays, number of studies that utilize cockle shells as feedstock for CaO production is still limited. The common natural resources of CaCO₃ that have been applied this day are such as dolomite, limestone, magnesite, and also cement kiln dust. Industrial CaO is produced via thermal decomposition of calcium carbonate sources such as limestone which is obtained through mining and quarrying limestone hill. The most common CaO precursors are limestone and dolomite because of their availability and low cost. However, mining of these carbonate rocks will contribute to the environmental damage. The valorisation of cockle shells for the production of calcium carbonate has not activity performed at industrial level by the sector as the problem statement reported here, solely some specific literature describing a productive process of this type to get CaO. Therefore, cockle shells currently are found to be the best candidate as the alternative material as they made up of 95-99% by weight of CaCO₃. Only very recently, some initial studies were done to investigate the potential of this material. Cockle shell is a major financial and operational burden on the shellfish industry. Malaysia is having 1055 number of farmers working on cockle cultivation agriculture which involving 6000 hectare of cultivation area (Izura and Hooi, 2008). However, these do not only indicate the vast availability of cockles but also the amount of waste shells generated.

The potential to exploit the vast availability of waste resources in Malaysia which is cockle shell as the potential biomass resources for $CaCO_3$ and CaO was great and lastly, converted to become the value added product. In Malaysia, the shells are treated as waste and mostly left at dumpsite to naturally deteriorate. The shells that been dumped and left untreated may cause unpleasant smell and disturbing view to the surrounding. Thus, in this study, cockle shells were chosen as the new potential source of CaO instead not using other sources of $CaCO_3$. Hence, it can use as the potential source of CaO. Cockle shells which are rich in minerals content such as Ca, C, Mg, P, K, Na and more was suitable for the purposes of industries and daily practice. The experimental variables such as calcination temperature and particle sizes were put under study in order to optimize the calcination process. As Malaysia is rich in waste cockle shells, and also the production of cockle shell was great by year, the potential to exploit them for the production of CaO is great. Hence this program aims to utilise the $CaCO_3$ in cockle shell as new potential source of CaO. This project helps meet the medium term objective for cockle shells by raising awareness of possible ways to generate economic return from waste and in the development of a regional approach to facilitate further development.

1.3 Objective

The following are the scope of this research:

• To propose cockle shell as new potential source for calcium oxide, CaO.

1.4 Scope of this research

The following are the scope of this research:

- Use calcination process to produce CaO.
- Characterize the minerals content in cockle shell.
- Study the effect of temperature and particle size to produce CaO from cockle shell

1.5 Main contribution of this work

The following are the contributions

1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 presented the background of this study, objective of this research, scope of research and the main contribution of this research. This will including the background of cockle shell, uses of $CaCO_3$ in industrial applications, cockle shell decomposition and also mass and heat transfer process in cockle shell decomposition.

Chapter 2 presented the overview of how the study has been analyzed including the type of cockle shell, the availability of cockle shell which is the main material going to be use in this study. The process on how the CaO can be synthesized from cockle shell also include in this chapter. This will including the review on calcination process and the condition on calcination, This chapter will also including the comparison of previous work from any researchers.

Chapter 3 presented the overall method of calcination process. The preparation of material, characterization of cockle shell, research flow diagram, and also the equipments used which are thermal gravimetric analyzer (TGA), x-ray fluorescence (XRF), furnace, sieve shaker, and scanning electron microscope (SEM) were also presented in this chapter. This chapter shows the presented work on how to get the main product which is CaO.

Chapter 4 presented the results and discussion from what the research have been done. In this chapter, the comparison of this work from previous study has been analyzed. Analysis of mineral content in cockle shell, analysis on thermal gravimetric analyzer, and the surface morphology of cockle shell all were discussed in this chapter.

2 LITERATURE REVIEW

2.1 Overview

This section is divided into two parts and describes prior theoretical and experimental work related either directly to calcium carbonate decomposition or to gas-solid reactions in general, restricted only to their bearing on the reaction being studied. The largest part of this section is devoted to a review of the experimental literature on calcium carbonate decomposition. It is interesting to note that the rich literature on calcium carbonate decomposition appears to be driven by theoretical considerations. The other part also included the background of seashell, cockle shell and also calcination process.

2.2 Sea shell

Seashells are the external skeletons of a class of marine animals called Mollusks. It is composed largely of CaCO₃. Typical seashells are composed of two distinct layers, with an outer layer made of calcite (a hard but brittle material) and an inner layer made of a tough and ductile material called nacre. Nacre is a biocomposite material that consists of more than 95% of tablet shape aragonite, CaCO3, and a soft organic material as matrixSeashells are quite well developed and applied to other countries for various purposes. The chemical composition of shells is >90% CaCO₃ by weight (Falade, 1995; Yoon et al., 2003, 2004; Yang et al., 2005; Ballester et al., 2007; Mosher et al., 2010). There are various type of sea shell including short-necked clamp, oyster, green mussel, scallop shell and cockle. CaCO₃ content can be used for various purpose including plastics, medicines, paints and more. In the case of molluscs, the processing installations generate significant amounts of shell waste that account for more than 80,000 tons a year and could be recovered by different methods in an environmentally sound manner (Barros et al., 2009).

Mollusks are marine animals that have a very soft body. Various dangerous factors, e.g., attacks from fishes or other predators or impact from a falling rock continuously threatens their soft tissues. Nature has wisely devised a suitable protection for mollusks in the form of a hard ceramic layer known as a seashell or simply a shell. To this date, about 60,000 species of mollusk shells have been found in nature, with a great variety of shell sizes and shapes. Mollusk shells are categorized into several

classes but most mollusk species fall within three main categories: bivalves, gastropods and cephalopods (Figure 2-1). Complicated spiral-like shapes are found in cephalopod class whereas bivalve and gastropod shells possess simpler shapes.



Figure 2-1: Categories of mollusc

Several attempts were made to capture the shapes of seashells using mathematical formulations (V. Helm et al., 1998). In addition to shape, seashells exist in a variety of sizes starting from less than 1 mm (micromollusks) up to 25 cm in shell of abalone. The strength of shells is a function of the shape and the size of the shell, and of the materials it is made of. Depending on the living environment of the mollusc shells, various types of loading may be applied on the shell structure. For instance, seashells are prone to an impact load from the falling of rocks, attacks from other marine animals such as sharks and crabs or hydrodynamics loads of high-energy environments. The shell structure is adapted to that living condition to withstand feasible threats from nature. Excessive mechanical load will of course break the shell, following failure patterns which also depend on the structure and geometry of the shell. In the case of a sharp penetration, the shell may fracture only in a small region of the structure while the other parts remain intact. On the other hand, distributed loading may crush the shell into several pieces. Zuschin (2002) performed numerous compressive and compaction experiments on three seashell species, i.e., Mercenaria mercenaria, Mytilus edulis and Anadara ovalis, to obtain their strength, failure pattern and the predictor parameter on the strength of the shell. Among all the structural and geometrical parameters of the shell, shell thickness was revealed to be the most significant predictor of the shell strength.

As simplified in Table 2-1, Barros et al. (2009) 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 (Mokhtar., 2009).

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

Table 2-1: Application of seashell in other countries

Source: Barros et al. (2009)

2.3 Cockle shell

Anadara granosa or locally known as 'kerang' is a local bivalve molluscs (Faridah and Nurul, 2008). A cockle 'Kerang', is a common edible European bivalve mollusc, having a rounded shell with radiating ribs. Anadara granosa locally known as kerang in Malaysia is a bivalve belonging to the family Arcidae (Awang et al., 2007). It contained almost 95-99% by weight of CaCO₃. Cockles are composed of two distinct material. The shell consists of calcium carbonate in the form of aragonite, calcite and vaterite. In Malaysia, cockle shell is abundantly available as a by-product from seafood industry. It is a cheap protein source which is quite common to be prepared as local dishes (Mohamed et al., 2012). *Anadara granosa*, is also an important of protein source. It's found in muddy bottoms of coastal regions of South East Asian particularly Malaysia, Thailand and Indonesia.

According to L. Xiang et.al (2005), CaCO₃ is an abundant mineral comprising approximately 4% of the earth's crust. The industrial application of CaCO₃ are wide ranging, including paper, paints, ink, plastics, medicines, feedstuff, adhesives and rubbers (L. Xiang et al., 2005). Although there are, in theory, many uses for shell, there is no singular solution to treat or utilise these materials as by-products and treated as waste. 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 2-2. 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 CaCO₃-based resources.

Sample	CaO	MgO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	Others
MV Shell	52.41	0.22	0.11	0.07	0.17	0.37	0.33
Mussel shell	50.45	0.18	0.78	0.09	0.12	0.24	0.82
Scallop shell	54.53	0.27	0.00	0.04	0.16	0.49	0.47
MM limestone	48.83	4.8	2.76	0.28	0.54	0.02	0.36
JN limestone	50.28	2.54	4.21	0.51	0.95	0.01	0.32

Table 2-2: Comparison of oxides content in seashell and limestone

Source: Li et al. (2009)

The study on thermal decomposition CaCO₃ has been extensively conducted in recent years (Garcia-Labiano et al., 2002). There are several sources of CaCO₃ for the production of CaO such as limestone, cement-kiln dust, seashells and more. Recent studies only focused on the use of shells from eggs, crabs, mussels and oysters as alternative sources for CaO. Nowadays, number of studies that utilize cockle shells as feedstock for CaO production is still limited. In Malaysia, the shells are treated as waste and mostly left at dumpsite to naturally deteriorate. In this study, cockle shells were chosen as the new potential source of CaO instead not using other sources of CaCO₃. Hence, it can use as the potential source of CaO. Cockle shells which are rich in minerals content such as Ca, C, Mg, P, K, Na and more was suitable for the purposes of industries and daily practice. Seashell contained of 95-99% by weight of CaCO₃ which has enable it to be applied for quite a number of purpose (Barros et al., 2009; Nakatani et al., 2009). As Malaysia is rich in waste cockle shells, the potential to exploit them for the production of CaO is great. Chemical property analysis using x-ray fluorescene (XRF) shows cockle shell is made up of 97% Calcium (Ca) element and CaO is produced after decomposition was conducted (Mohamed et al., 2012).

2.3.1 Production of cockle shell in Malaysia

The history of cockle culture in Malaysia started in 1948 in Perak. Awang-Hazmi et.al had determined the mineral composition of Anadara granosa from three major cultivation areas in West Coast of Peninsular Malaysia which are Penang, Kuala Selangor and Malacca. In 2006, Malaysia had produced 45,674.58 metric tonnes of cockle for seafood industry (Izura and Hooi, 2008). 4000-5000 hectares of the west coast of Peninsular Malaysia were used for cockle culture (FAO, 2006).

Cockle shell is a major financial and operational burden on the shellfish industry. Malaysia is having 1055 number of farmers working on cockle cultivation agriculture which involving 6000 hectare of cultivation area (Izura and Hooi., 2008). 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. Hence this program aims to utilise the CaCO₃ in cockle shell as new potential source of CaO. Cockle shell has to undergo calcination process- a widely used substances in high temperature applications. This project helps meet the medium term objective for cockle shells by raising awareness of possible ways to generate economic return from waste and in the development of a regional approach to facilitate further development. Figure 2-2 indicates the production of cockle shell in Malaysia from 2005 to 2012 (Annual Fisheries., 2012). Based on this statistic, the production of cockles started to decline from 2010 till 2012 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 spatfall areas, reducing operational costs, and increasing research on development of more spat-fall areas. Table 2-3 shows that production of cockle shell (tonnes) by state in Malaysia from year 2005 to 2012.

Year	Kedah	Penang	Perak	Selangor	Johor	Total
2005	232.04	10,991.65	37,415.73	9,398.48	1,477.95	59,515.85
2006	69.70	11,597.11	31,512.42	1,827.00	668.26	45,674.49
2007	132.91	12,670.42	33,711.51	3,021.32	84.00	49,620.16
2008	170.70	12,675.25	33,403.55	14,750.50	138.32	61,138.32
2009	651.70	6,762.50	26,702.77	30,742.43	56.98	64,916.38
2010	1,295.39	8,886.39	26,387.36	41,410.06	45.50	78,024.70
2011	659.19	7,682.27	21,759.37	26,505.53	938.04	57,544.40
2012	389.97	7,737.34	22,068.56	11,842.66	93.50	42,132.03
Sources Appuel Fisheries (2012)						

Table 2-3: Cockle production (tonnes) by states in Malaysia

Source: Annual Fisheries (2012)



Figure 2-2: Production of cockle shell in Malaysia

There are over 200 living species known. They are categorised into six groups wellknown in the world (see Table 2-4) which are Vongole, Pipi (Donax deltoids), Surf clam (Dosinia caerulea), Sydney cockle (Anadara trapezius), Blood cockle (Kerang) and Razor clam (Pinna bicolor).

Groups of cockle	Description
Vongole	Members of the venus shell family. Found
	around the southern Australian coast from
	Fraser Island in Queensland to Cape
	Leeuwin in WA (including Tasmania) and
	harvested from sheltered or sandy subtidal
	sediment of tidal flats and estuary mouths.
	Known as sand cockle
Pipi (Donax deltoids)	Its smooth, wedge-shaped, cream to pale
	brown shell can sometimes be slightly
	yellow or green and have pinky-purple
	bands and averages 5-6 cm in diameter.
	Mainly hand-harvested from the intertidal
	zone of sandy surf beaches.

Table 2-4: Types of cockles

Surf clam (Dosinia caerulea)	Its rough, circular shell. About 3-4.5 cm in
	diameter. Varies in colour from cream
	through greyish white or pale yellow to
	light brown and has sculpted, concentric
	ridges. Found in the Mediterranean.
Sydney cockle (Anadara trapezius)	Its shell can be up to 8 cm in diameter and
	has prominent, outward-radiating ribs.
	Found in estuaries, mud flats and seagrass
	beds.
Blood cockle (Kerang)	It named for the reddish liquid released
	when it opened and sometimes reddish
	tinge of its shell, which is usually about 6
	cm in diameter. Found intertidally in
	northern Australia, eastern Asia such
	Indonesia and Malaysia.
Razor clam (Pinna bicolor)	Called razor fish. Has a long narrow shell,
	roughly the shape of an old-fashioned
	cutthroat razor and is harvested in sand or
	mud near the low water mark on very
	sheltered bays in SA.

Artificial reef is a structure that is submerged in the sea or rivers; used to preserve and promote the breeding of marine life. In Malaysia, this method has proven effective since it was introduced in the early 70s (Chou, 1997). Each year, the government has allocated a large budget in supporting this continuous effort to increase marine productivity and benefit the eco-tourism in the country. In 2009 alone, the government has approved RM15 million in the second economic stimulus package for artificial reefs development (Fauzi, 2009). Basically, any materials that are dumped into the water can be defined as artificial reef. Waste products such as used tyres, old vehicles and refrigerator have been used for cheap option of artificial reef which is considered as one form of pollution. If these materials do not manage properly, it can cause adverse impact to the environment. Another option for artificial reef is concrete structures. It could be higher in cost but their ability of being easily constructed according to various configurations and its durability has made them increasingly used

for artificial reefs (Chou, 1997).Studies on cockle shell as part of the construction material for artificial reef is relatively new. The potential of the shell in concrete composite has not yet been exploited. The shell is chosen due to its properties that suggest the material compatibility to be applied for the purpose. Thus, this study focused on exploration and experimentation of integrating cockle shells in the construction of concrete artificial reefs as an eco-friendly and economic alternative.

2.4 Characterization of cockle shell

2.4.1 Surface morphology

The morphology of raw cockle shell and calcined cockle shell at 700, 800, and 900°C was examined by SEM (Figure 2-3). The natural shell displays a typical layered architecture. With the calcination temperature rising from 700 to 900°C, the microstructures of natural shell are changed significantly from layered architecture to porous structure. The calcined cockle shells were irregular in shape, and some of them bonded together as aggregates. However, the smaller size of the grains and aggregates could provide higher specific surface areas. Since all samples are considered to be less-porous or even nonporous, the size of the particle should directly respond to the surface area. There are three crystal structure of $CaCO_3$ which is aragonite, calcite and vaterite.



Figure 2-3: Surface morphology of cockle shell

Based on the XRF and SEM results on previous study, 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 CaCO₃ which is one of the orthorhombic polymorphs of CaCO₃ 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. The shells form this by-product industry are treated as waste and mostly left at dumpsite to naturally deteriorate. It is hard to dispose due to its strong property. The application of this material is still very limited although there is an attempt to use it in craft production. Only very recently, some initial studies were done to investigate the potential of this material.

2.4.2 Mineral content in cockle shell

The X-ray fluorescence (XRF) analyses provide the mineral compositions of the cockle shell. The mineral composition reported as element of cockle shell. Previous study shows that cockle shell were made up of CaCO₃, which is one of the sources of CaO. Recent report study by Zuki et al. (2004) stated that the mineral composition of Anadara granosa is almost similar to that of coral. Thus, the finding suggests the possibility of using cockle shell as alternative biomaterials for production of CaO. From previous study done by Zuki et al, almost 98.68% of CaC content in cockle shell. Awang-Hazmi et al who also performed mineral composition cockle shell determine that 98.70% of CaC. Meanwhile, S.Yusup et al also determine that mineral content in cockle shell contained 98.99% of CaC content in cockle shell. Table 2-5 illustrated mineral composition from previous study.

Author						
	CaC	Mg	Na	Р	K	Other
Minerals						
(0/ wt)						
(70WL)						
Zuki et al	98.68	0.20	0.87	0.02	0.04	0.20
Awang-Hazmi et al	98.70	0.05	0.9	-	-	< 0.1
S.Yusup et al	98.99	0.51	-	-	-	< 0.1

Table 2-5: Minerals content in cockle shell

2.5 Uses of calcium carbonate (CaCO₃)

Although there are many different uses for calcium carbonate, the production are still very limited. There are many other uses for calcium carbonate ranging from the manufacturing process for fibre glass to pigmenting paint. Calcium carbonate makes up about 20 percent of the pigments used in the paint industry. Calcium carbonate is used to extend the resin or polymers because of its controlled colour and low cost. Calcium carbonate also is used to control the sheen or gloss in flat paints. Seashell contained of 95-99% by weight of CaCO₃ which has enable it to be applied for quite a number of purpose (Barros et al., 2009; Nakatani et al., 2009). Previous study in Malaysia has showed that this material has potential as biomaterial for bone repair (Awang et al., 2007). The suitability of cockle shell as calcium-based adsorbent is confirmed by its high calcium content, as reported by Awang-Hazmi et al. Calcium oxide is recognized as an efficient carbon dioxide 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 (Mohamed et al., 2012). CaO which is used in industries and daily practice such as in waste water and sewage treatment, glass production, construction material, agricultural, and more. In various studies of other seashell types like oysters, scallops and mussels revealed that they are quite well developed and applied indiverse industry around the world for fertilizers, construction materials, cement clinkers and tiles (Barros, 2004). The paper industry is a major consumer of mineral pigments. In paper coating applications, calcium carbonate, fine ground from 0.5 to 3.5 microns (the average width of a human hair is 100 microns), is used to make a whiter, brighter sheet. In paper filling applications, calcium carbonate can improve the whiteness of the sheet and reduce costs by replacing expensive fiber and pigments. The chemical properties of calcium carbonate are used to produce non-acidic paper.



Figure 2-4: Uses of calcium carbonate in industrial application

2.6 Review of cockle shell calcination studies

According to Yan et al. (2010), calcination is described as a five-step process which involves (i) heat transfer from surrounding to external surface of particle, (ii) heat transfer from exterior surface to interior samples interface, (iii) heat absorption and thermal decomposition at the interface layer, (iv) diffusion of formed CO_2 through porous layer of calcium oxide (CaO) and (v) diffusion of CO_2 towards the surrounding.

The importance calcination performance is in two aspects:

(1) Calcination kinetics, which determine the time required for calcination

(2) The physical structure change during calcination, which determines the reactivity of the CaO produced.

Calcination of cockle shell has been studied extensively. Decomposition equilibrium, chemical kinetics, the microstructure of the calcine, and the transport processes associated with the calcination have been investigated by numerous researchers1'98. However, most studies have been conducted on the calcination of cockle shell particles at lower calcination temperatures. Relatively less work has been conducted on the calcination of small particles at high calcination temperatures.

Therefore, for reasons of both practical interest and fundamental understanding, it was timely to study the calcination of small particles under high temperature, short residence time conditions. The focus of this study was, therefore, the calcination behavior of cockle shell under conditions using the furnace. Particle sizes of 0.3, 0.4-0.6, and 1.2 mm and temperatures of 700, 800, and 900°C were used. Naturally occurring cockle shell exist in different varieties, each having a unique physical structure and chemical composition. An extensive review of the different types of shell has been given by (Boynton et al).

 $CaCO_3$ can be generally found in three distinct crystalline phases *i.e.* calcite, aragonite and vaterite (shown in Figure 2-5). Calcite is the most stable and most commonly found in nature. Aragonite, however, can only be found in precipitate $CaCO_3$ or seashells whereas vaterite is found from synthesized $CaCO_3$ and does not occur naturally. The crystallized form of $CaCO_3$ is called a calcite. Together with this major constituent, naturally occurring cockle shell also contain some impurities (quartz, clay and trace elements), with total amounts ranging from less than 1 to up to 2.0 %.



Figure 2-5: Crystal structure of calcium carbonate

Thermal decomposition of a cockle shell is called calcination. The calcination of cockle shell is through the endothermic reaction $CaCO_3 \leftarrow \rightarrow CaO + CO_2$. If the partial pressure of CO_2 is less than the equilibrium value, the reaction will proceed. The equilibrium decomposition pressure of CO_2 as a function of the decomposition temperature is shown in Figure 2-6. Good agreement on calcite decomposition equilibrium has been reached among various researchers. The calcination of cockle shell involves single steps. The only step is the decomposition of the calcium carbonate $CaCO_3 \leftarrow \rightarrow CaO + CO_2$. A review of this study is given by Bandi and Krapf. The equilibrium decomposition temperature has been reported to be in the range of 893 to 1,073 K, depending on the CO_2 partial pressure and the experimental conditions, and no agreement has been reached on the correlation between the decomposition temperature and the equilibrium decomposition pressure of CO_2 .



Temperature (K)

Figure 2-6: The equilibrium decomposition pressure of CO₂ as a function of the decomposition temperature temperature CaCO₃

The physical process of cockle shell calcination is generally described as follows. For a spherical sample geometry, calcination begins on the surface and proceeds inwardly in a symmetrical fashion. A thin layer of highly porous calcium oxide forms on the surface of the sample. As the reaction progresses, the thickness of this layer increases and the diameter of the unreacted core decreases. A distinct interface exists between the two phases. Heat must be absorbed at this interface and CO_2 must diffuse out from this interface in order for reaction to proceed.

Calcination of $CaCO_3$ is a process of producing CaO - a widely used substances in high temperature applications.

$$CaCO_3(s) \leftarrow \rightarrow CaO(s) + CO_2(g)$$

According to S. Yusup, 2012, cockle shells were washed until all traces of dirt and dust removed. The clean samples were sun-dried for 2 days followed by oven-dried at 110°C for 2 hours. The samples were crushed and grounded to different particle sizes (< 1.25 mm- 4 mm) using pestle and mortar and Rocklab rotation grinder. A sieve shaker (CISA

Cedaceria Industrial, Spain) was used to separate the particle to corresponding sizes distribution for 10 minutes of sieving duration. The samples was placed EXSTAR 6000 thermal gravimetric analyzer (TGA) in ceramic sample holder. It was then heated up to desired calcination temperature, heating rate and constant nitrogen gas flow. In another study, 250 g of cockle shells was washed, scrubbed to remove dirt, boiled for 10 min and then cooled with room temperature. The shells were then washed thoroughly with distilled water and dried in an oven (Memmert UM500, Germany) for 7 days at 50°C. The cockle shells were finely ground using a blender (Blendor, HCB550, USA). The powders was sieved using a stainless laboratory test sieve with an aperture size of 90 μm (Endecott Ltd., London, England) to obtain micron-sized (10-90 μm in diameter) powders (Mohamed et al., 2012). However, based on Awang-Hazmi (2007), the cockles was washed and scrubbed free of dirt. Then they were boiled for 5 min and cooled at room temperature before the contents of the cockles were removed leaving behind the shells. The shells were washed thoroughly with clean water and then oven dried at 50°C for three days. The cockles were ground using Blendor until they turned into powder form. The powder from the shells was then sieved at 850 µm after which they were packed into McCartney bottles and sterilized or one hour in the oven at 105°C.

Author Parameters	Calcination temperature (°C)	Particle size (mm)	Heating rate (°C/min)
M.Mohamed et al (2012)	700	0.125-0.25	20
Awang-Hazmi et al (2007)	750-950	<0.125	20
S.Yusup (2012)	850	<1.25	20

Table 2-6: Experimental condition for calcination of synthesized CaO

2.7 Cockle shell decomposition

2.7.1 General cockle shell calcination

Calcium carbonate, thermally decomposes, or calcines, to calcium oxide by releasing carbon dioxide (Equation 1). The calcination reaction is reversible and endothermic reaction. In this study, cockle shell decomposition, or calcination, always refers to the decomposition of calcium carbonate to calcium oxide.

Stanmore et al. 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 CaCO₃ in order to drive the equilibrium reaction forward [10]. Garcia-Labiano et al. (2010) 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 (Stanmore et al., 2005). Besides, Cheng and Specht (2006) 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.

2.7.2 Mass and heat transport process in cockle shell decomposition

Cockle shell decomposition is a gas-solid reaction in which the solid is the reactant. The reaction involves mass and heat transfer processes between a solid cockle shell particle and the calcination gas. The sequence of steps to convert cockle shell to calcium oxide includes five sub-processes as shown in Figure 2-7 (b).

- 1. Transport of heat from the bulk gas at temperature T_A by radiation and convection to the solid surface (at radius, r_s) at temperature T_s (symbolized by α).
- 2. Transport of heat by conduction into the cockle shell particle to the reaction front (at radius of r_F) at temperature T_F through a porous layer of cockle shell (symbolized by λ).
- 3. Dissociation reaction of CaCO₃ to CaO and CO₂ at the reaction interface (symbolized with k). The difference between the equilibrium partial pressure of CO₂, $P*_{CO_2}$, (Figure 2), and the partial pressure of CO₂ at the reaction interface, P_F , is the driving force of cockle shell calcination reaction (Equation 1). The enthalpy of the calcination reaction is considered much larger than the internal energy, hence the heat transport into cockle shell particle is negligible and the

core temperature, T_M is only slightly lower than $T_{S_1} P_F$ is higher than the partial pressure of CO₂ at the gas-solid interface, P_S and in the bulk gas, P_A because CO₂ is generated in-situ during the calcination rection.

- 4. Transport of generated CO_2 at the reaction interface through the porous cockle shell layer to the outer surface of the particle (symbolized with D_P) to maintain the continuity of calcination reaction at the rreaction interface.
- 5. Transport of CO_2 by a convection transport from the outer surface of the particle to the bulk gas with a partial pressure of CO_2 of P_A (symbolized by β).

The calcination process can be explained using a partially decomposed piece of carbonate, whose profiles of CO₂ partial pressure and temperature are shown in Figure 2-7(b). The specimen comprises a dense carbonate core surrounded by a porous oxide layer. In the calcination reactor at temperature T_A heat is transferred by radiation and convection (symbolized by α) to the solid surface at a temperature of T_S . By means of thermal conduction (λ) heat penetrates through the porous oxide layer at an average temperature of TOX to reach the reaction front, where the temperature is T_F . As the reaction enthalpy is many times greater than the internal energy, the heat flowing further into the core is negligible during reaction. Therefore the core temperature is only slightly lower than the front temperature. Once heat is supplied, the chemical reaction (k) then takes place, for which the driving force is the deviation of CO₂ partial pressure from the equilibrium ($P^* - P_F$). The released CO₂ diffuses (DP) through the porous oxide layer to the surface and finally passes by convection (β) to the surroundings where the CO₂ partial pressure P_A exists.



(b) Figure 2-7: Model of cockle shell decomposition

A shrinking core reaction model has been widely employed to describe thermal decomposition of a cockle shell particle (Ingraham and Marier, 1963; Beruto and Searcy, 1974; Elder and Reddy, 1986; Zhong and Bjerle, 1993; Fonseca, et al., 1998; Eversen, et al., 2006). This reaction model describes conversion of a nonporous cockle shell solid particle in which the reaction occurs at the outer surface and progresses into the interior of the cockle shell. With the progress of the calcination reaction, a layer of porous calcium oxide product is developed around the unreacted core of cockle shell.



Figure 2-8: Shrinking core model mechanism

The shrinking core model was developed for solids that are non-porous, although the model can be used where the rate of the chemical reaction is much slower than the diffusion of the gas through the newly formed product (Smith, 1981). The main feature is that the reaction occurs at an interface between a spherical un-reacted core (CaCO₃) and a surrounding solid product (CaO). As the reaction progresses and the un-reacted core shrinks, the zone of reaction moves towards the centre of the solid.

2.7.4 Structural changes during calcination

During heating and calcination of cockle shell particles, several changes occur. During heating, the free moisture is vaporized and a small amount of organic matter, which exists in most stones, is volatilized. In some cases, H₂O trapped in the lattice of the material also vaporizes during heating. During calcination, the $CaCO_3$ crystal structure is transformed into the CaO crystal structure and CO2 is generated by the decomposition reaction and is released from inside of the particles. In addition, thermal stress is built up within the particles. These are potential causes of particle fragmentation. By heating large cockle shell particles and calcite crystals to 1,073 K, Hedin demonstrated that thermal stress disintegrated some of the samples into dust. He observed that the particles being disintegrated were those with large crystals. By contrast, particles with small crystals of 2.5 mm or less did not fracture for the same heating conditions. By SEM analysis, they found that cracks or fissures developed as a function of calcination time. Liu et al. calcined two cockle shell (150 to 250 in size range) in a TGA at a heating rate of 200 K/min and found that the cracking pattern was related to grain size, grain-grain interlocks and the particle size of the raw materials. Coutant et al. calcined small cockle shell particles in a dispersedphase reactor which was designed to simulate a high heating rate furnace injection process. They took photomicrographs of the collected samples to characterize the particle fragmentation.
The SEM micrographs indicated that the particle sizes of three cockle shell had decreased, while those of five cockle shell did not show.

2.7.5 Physical property changes during calcination

Most cockle shell possess very low porosities. Some porosity is generated during the calcination process. When CaCO₃ decomposes, it loses 44 % of its weight as carbon dioxide. Due to the marked difference between the molar volume of CaCO₃ ($36.9 \text{ cm}^2/\text{mol}$) and CaO ($16.9 \text{ cm}^2/\text{mol}$), the calcine formed has a porosity up to 54 % and a pore volume up to 0.36 cm²/g.

The development of the porous structure during calcination may be described as follows. The decomposition of $CaCO_3$ begins at active centers or nuclei which are formed on the external surface and on the internal surface originating from interstices and lattice imperfections. It proceeds from these centers, both along the surface and into the solid interior. The newly formed product (CaO) transforms its structure from a pseudo-lattice of $CaCO_3$ to a thermodynamically stable form of CaO via a transition process. The transition has been proposed as both immediate or lagging behind the

decomposition. Though much effort has been made to determine the exact nature of the process, no agreement on the transition mechanism has been reached. The observed structure of the calcine can be described as micrograins of CaO joined together by necks in a non-uniform matrix. The micrograins are crystallites of CaO. The size of the crystallites has been estimated to be in the range of 100 to 500 A for newly formed CaO at mild calcination conditions. The voids among the micrograin matrix constitute the major porosity of the calcine. Accompanying the development of this porous matrix is the creation of a large internal surface area.

The porous CaO occurs in two stages. The initial stage is characterized by the development of micropores within the CaO grain clusters and a macropore network between clusters. During this stage, the surface area changes without porosity loss. The second stage is characterized by the coalescence of fused clusters and the elimination of macropores. During this stage, both porosity and surface area decrease. Detailed mechanisms for the development of the porous structure of the calcine and porosity loss due to sintering have not been fully established, but they are reported to be influenced by the initial structure of the material, the calcination temperature, the holding time, the surrounding gas composition, the impurities in the cockle shell, etc. From a practical point of view, there are three parameters which describe the physical structure of the

calcined particles from a reactivity viewpoint. They are surface area, porosity and pore size distribution. The surface area affects the rate of decomposition. The porosity affects the amount of reaction product that can be accumulated on the interior particle surface. The pore size distribution controls the accessibility of the internal surface to the reactants diffusing through the pores and the closure of pore entrances which stops further access of the reactants.

2.7.6 Calcination temperature

The reaction temperature is crucial since they are directly related to the surface area and pore distribution of the samples. It has been reported in the literature that the threshold point in which the solids may begin sintering is 1154° C for CaO and 533° C for CaCO₃ (R.Barker,1973). Therefore, the selection of reaction temperature is significantly essential before running the experimental works. Also, at particular temperature in which the surface area is at the highest, the decomposition rate of CaCO₃ is at the peak and thus will accelerate the calcination temperature.

Authors	Calcination temperature (°C)
S. Yusup	750, 850, 950
Current study	700, 800, 900

Table 2-7: Comparison study of calcination temperature from other research

2.7.7 Heating rate

Heating rate is important variables since it influences the samples decomposition during the calcination process. Larger heating rate is commonly has the maximum calcination rate, shorter operating time to reach the desired calcination temperature (S.Yusup et al., 2011). According to S.Yusup (2011), when higher heating rate is applied, the process itself will rapidly take place and thus, consume shorter operating time to reach the desired temperature.

AuthorsHeating rate (°C/min)S. Yusup20Current study20

Table 2-8: Comparison study of heating rate from other research

2.7.8 Particle sizes

Particle sizes are basically one of the critical variables in the calcination process since they directly influence the reaction rate (S.Yusup et al.2011). The smallest the particle size, the better the result in percentage of weight gain and also exhibit the almost calcination rate.

Authors	Particle sizes (mm)
S. Yusup	0.125-0.25, 0.25-0.5, 1-2, 2-4
Current study	0.3, 0.4-0.6, 1.2

Table 2-9: Comparison study of particle size from other research

2.7.9 Equipment used in calcination process

2.7.9.1 Thermal gravimetric analyzer (TGA)

Thermal gravimetric analysis (TGA) is an analysis technique where a sample mass is recorded as a function of temperature. A substance, in a controlled environment, is heated or cooled at a controlled rate (preferably linear) and the weight of the sample is recorded as a function of time or temperature (Blazek, 1973). The thermal gravimetric curve gives information on the sample composition, thermal stability, and thermal decomposition (Blazek, 1973).

TGA is performed by weighing a sample on a sensitive weight-measurement device known as a thermobalance (Wendlandt, 1986). The balance and sample are placed in a vessel for heating or cooling. The atmosphere within the vessel can either be fixed (static) or flowing (dynamic) (Wendlandt, 1986). For both cases, the system is purged with a desired gas prior to testing. If a dynamic atmosphere is used, the gas flow rate is adjusted to maintain a steady stream of gas flowing through the system. The temperature programming routine is then initiated.

Many factors are very influential in this process and need to be taken into careful consideration. The choice of gas to be used (whether reactive or inert), sample size, particle size, sample thermal conductivity, heat of reaction, and the reactivity of the sample mass or volatilized species with the apparatus are only a few of many considerations when performing this procedure (Wendlandt, 1986).

Although TGA is strictly the determination of sample mass as a function of system temperature, the use of this procedure in conjunction with other analysis

techniques can yield a great deal of information about a system. Often, the exiting gas stream is sent directly to an analyzer to determine the composition of the volatilized species. This yields information both about the temperature of the decomposition and the chemical nature of the decomposition.

Differential thermal analysis (DTA) is also a related, supplemental analysis technique, that is usually performed simultaneously with TGA. This technique consists of measuring the temperature difference between the experimental sample and a thermally inert reference sample. This difference is recorded as a function of time or temperature (sample, reference, or furnace) for a uniform heating or cooling routine. These temperature differences are indicative of endothermic or exothermic enthalpy changes. Endothermic effects are generally characteristic of phase transitions, dehydration, reduction, or certain decomposition reactions. Exothermic effects generally imply crystallization, oxidation, or some decomposition reactions (Wendlandt, 1986).



Figure 2-9: Flow diagram during TGA analysis

2.7.9.2 X-ray fluorescence (XRF)

X-ray fluorescence (XRF) is a technique used for qualitative determination of major and minor elements in samples. A schematic diagram of XRF is shown in Figure 2-10.



Figure 2-10: X-ray pathways during XRF analysis

During an XRF analysis, the sample is introduced into the target area of an X-ray tube. The sample is then irradiated with a beam of X-rays from an X-ray tube or a radioactive source. The elements in the sample are then excited by absorption of the primary beam and emit their own characteristic fluorescence X-rays. These fluorescent x-rays are then detected and analyzed by the spectrometer. Because the relationship between emission wavelength and atomic number is known, isolation of individual characteristic lines allows the unique identification of an element; and elemental concentration can be estimated from characteristic line intensities. As a result, a qualitative and quantitative elemental analysis of the sample is obtained (Skoog et al., 1998; Gunzler and Williams, 2002).

2.7.9.3 Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are similar in principle to optical or light microscopy, except that an electron beam rather than visible light is used as a probe. The use of an electron beam rather than electromagnetic radiation in the visible spectrum allows far greater resolution, due to the shorter wavelength of the beam.

Electron microscopes are similar in theory and design to conventional microscopes. They are used to magnify images of small objects and thus electron microscopes are composed of the same general components. Electron microscopes consist of a radiation source (electron beam as opposed to visible light), lenses (magnetic or electrostatic fields rather than glass), and an image viewer (fluorescent screen or photograph) (Fischer, 1966).

Scanning electron microscopes are used to obtain good resolution, high magnification images of material surface morphology. TEM is often used in the area of

carbon science to examine the lamellar microstructure within a carbonaceous material. TEM micrographs are often generated to show images of the lattice fringes (edges of graphitic lamellae) and to help determine imperfections in a carbonaceous material.

X-ray diffraction is a common method used for studying crystalline materials. Xray diffraction is performed by exposing a crystal to an x-ray beam and analyzing the resultant reflected beam, exploiting the fact that the atoms in a crystal act as a three dimensional diffraction grating. The spacing between crystal planes, crystallite size (both approximate diameter and relative depth), and many other qualitative observations can be discerned from x-ray diffraction experiments (Klug and Alexander, 1974).

Thermal gravimetric analyzer (TGA) was used in analyzer the calcination process of CaCO₃. Approximately ± 5 mg of cockle shell with particle size <0.125-4mm were placed in ceramic sample holder. It was then heated up to the desired calcination temperature (700-900°C) at constant heating rate (20°C/min) under a constant nitrogen (N₂, 99% purity supplied by Linde Sdn. Bhd.) stream flow of 40-60 ml/min. Once the system reached an equilibrium state, the sample was cooled down to room temperature.

The mineral composition in cockle shell was detected by using X-ray fluorescene (XRF).

The surface morphology of cockle shell was illustrated by using scanning electron microscope (SEM) to determine the surface structure and also the porosity of the sample.



(a)

(b)





3 MATERIALS AND METHODS

3.1 Overview

This chapter introduces the research methodology used for this research as well as to introduce the research strategy and technique applied. This will included how it has sample collection, analysis and development of process. The subsequent three sections describe the preparation of sample, guidelines for the calcination process and also the characterization of cockle shells.

3.2 Experimental



Figure 3-1: Research flow diagram

3.2.1 Preparation of cockle shells

Cockle shells were obtained from a wet market located in Balok, Kuantan. The cockles was washed by tap water and being scrubbed using brush to remove dirt. Then they were boiled for 15 minutes at 100°C and cooled at room temperature before the contents of the cockles were removed leaving behind the shells. The shells were washed thoroughly with clean water and then sun-dried for one day. Drying is important to prevent the agglomerate during the grinding process. The cockles were grounded using pestle and mortar into small pieces before being crushed using crusher until they turned

into powder form. Figure 3-2 and Figure 3-3 showed the cockle shell being prepared starting from washing them to the last step which is turn the cockles into powder form.

3.2.2 Particle size distribution

The powder from the shells was then sieved in the sieve shaker (Retsch AS 200) for 5 minutes of sieving duration to segregate according to the ranges of particle sizes which is summarized in Table 3-1. The samples were then packed into sample bag with 1kg each.

Author	Range of particle size (mm)		
Current study	0.3, 0.425-0.6, and 1.18		
S.Yusup	0.125-0.25, 0.25-0.5, 1-2, and 2-4		

Table 3-1: Range of particle sizes based on study



Figure 3-2: (a) Cockle shell was washed and cleaned (b) Cockle shell was crushed



Figure 3-3: (c) Sample was sieved to three different particle sizes (d) Cockle shell turned into powder

3.2.3 The calcination process

A laboratory muffle furnace of dimension 275 x 380 x 350 mm manufactured by Nabertherm, Germany was used. Each sample was weighed about 10g by using

electronic balance. The shell powder in the size of 300μ m was placed into a small porcelain. It was then heated up to 900°C at heating rate of 20°C/min and under N₂ gas flow at 20ml/min. Nitrogen was used to ensure inert environment around the sample. The samples were hold for 30 minutes of holding time and cooled down to room temperature to ensure the completion of the process. The samples were removed from furnace and the weight of the sample was recorded after the completion of the process. The procedure were repeated for different particle size and temperature at the same heating rate as shown in Table 3-2. Figure 3-4 showed that the samples were then placed into porcelain after being weighed by analytical balance. The samples were then placed into muffle furnace according to temperature and particle sizes.

3.2.3.1 The calcination process

Samples of the three particle sizes were calcined, at constant heating rates, to one of three different ultimate calcintion temperature, different particle size, and hold at that temperature for 30 minutes. The three ultimate temperatures were 700, 800, and 900°C. The calcination condition are shown in Table 3-2.

Calcination	Calcined	Particle	Heating rate(-
temperature(°C)	duration(min)	size(µm)	°C/min)	
700	30	300	20	
800	30	300	20	
900	30	300	20	
900	30	300	20	
900	30	425-600	20	
900	30	1180	20	

Table 3-2: Experimental condition to study the effect of calcination process



Figure 3-4: (a) The samples was placed into porcelain (b) Calcination process was conducted by furnace

3.3 Analysis

3.3.1 Thermal gravimetric analysis (TGA)

The decomposition of coal samples in this study were carried out in a thermogravimetric analyzer. The technique continuously records the variation in mass of a sample while the sample is in a controlled atmosphere and also subjected to a temperature program. The temperature of the sample is usually increased linearly with time; however, isothermal studies can also be conducted. A plot of mass or mass percentage as a function of time or temperature (called a thermogram or a thermal decomposition curve or TG curve) is then recorded, showing a decomposition pattern of the sample analyzed under a given atmosphere. The main components of a thermogravimetry instrument includes: a sensitive analytical balance or thermobalance, furnace, thermocouple, sample holder, a purge gas system for providing an inert or reactive atmosphere, a microprocessor and a computer for data acquisition and display.

The sensitivity of the thermobalance is usually of the order of one microgram, and samples ranging from 5 milligram to 10 grams may be analyzed. The sample holder is housed in the furnace; however it is thermally isolated from the furnace. The temperature of the thermogravimetric furnace ranges from ambient temperatures to 1500° C and higher, with heating rates to as high as 200° C/minThe temperature that is recorded during the analysis represents the actual temperature of the sample. The temperature of the sample is measured with a small thermocouple which is located as close as possible to the sample holder, and the temperature measured usually falls within $\pm 2^{\circ}$ C of the operating range (Skoog et al., 1998).

Calcination of the shells was analysed by carried out in Thermo-gravimetric analyzer, TGA Q500 USA. Sieved shell powder was weighed using analytical balance about 50 mg in the size of 300, 425-600, and 1180 μ m was placed in the aluminum sample holder. Subsequently, the sample was then heated up to temperature of 700, 800, and 900°C at heating rate of 20°C/min under N₂ gas flow of 40 to 60 ml/min. The sample was cooled down to room temperature after 30 minutes of holding time. The weight of the sample was recorded during heating as a function of temperature. The procedure was conducted at different operating conditions as shown in Table 3-2.



Figure 3-5: Analysis of calcination was conducted by using TGA

3.3.2 Characterization of calcium carbonate

The following instruments were employed for the observation and characterisation analysis of the calcium carbonate including surface morphology and CaO content of a sample, which were Scanning Electron Microscope, SEM and x-ray fluorescene, XRF.

3.3.2.1 Scanning electron microscope (SEM)

Visualizing the surface morphology and crystal structure of the samples which were aragonite, vaterite, and calcite were estimated using SEM (Zeiss Evo 50, Carl Zeis, USA) at Microscopy Laboratory, Central Laboratory, UMP. The surface morphology of samples, which is an important surface property and very useful for understanding their defect structure, grain size, surface area, etc. The particle morphology of the raw cockle shells and synthesized cockle shells was observed with SEM. In a typical test, the sample was loaded on a piece of adhesive tape located at the top of an aluminum sample holder. The cockle sample was gold-coated using an Emitech 575 Sputter Coater, to eliminate any electron discharges that could reduce the resolution of the sample's image. The surface morphology of both raw cockle shells and calcined cockle shells were observed with SEM. The specimens with 10mg were glue on a piece of carbon tape located at the top of an aluminum sample holder. The cockle sample was gold-coated using an Emitech 575 Sputter Coater, to eliminate any electron discharges that could reduce the resolution of the sample's image. The sample was analyzed between 50 and 100Pa with an accelerating voltage of 5KV, 7KV, and 15KV electron microscope (Zeiss Evo 50, Carl Zeis, USA) at Microscopy Laboratory, Central Laboratory, UMP facility. The sample holder was placed on the stage. The beam was switched on when Vacuum is complete. The scanning was start. Images were taken by using both the detectors i.e., LFD and ETD in different magnifications (100 X to 1000 X) without pressure, as well as with various pressures (50Pa and 100Pa) at 5KV, 7KV, and 10KV of EHT (high voltage) with a spot size of 4.0 and working distance (WD) 9.0 mm, 9.5 mm, and 10.0 mm.



Figure 3-6: Surface morphology was conducted using SEM

3.3.2.2 X-ray fluorescence (XRF)

Meanwhile, the mineral composition of cockle shell was analysed using x-ray fluorescence, XRF (Bruker S8 Tiger). The XRF analyses provide the chemical compositions of the cockle shells and the samples at different calcination condition. The chemical composition reported as oxides (%wt.) of cockle shells is important to determine the additional content of the metal element. XRF measurements were performed using a Bruker S8 Tiger spectrometer, equipped with a rhodium X-ray tube, on air dry powdered samples fused with lithium tetraborate.



Figure 3-7: Mineral composition of cockle shell by XRF

4 RESULTS AND DISCUSSION

4.1 Overview

This chapter is divided into five sections. The physical changes during the calcination by furnace are examined in section 4.2. The particle size of cockle shell after being crushed are examined in section 4.3. The morphology and reaction layer within the thermal decomposition samples are examined in section 4.4. The thermal decomposition analysis is discussed in Section 4.5. The chemical analysis of cockle shell are examined section 4.3.2.

4.2 Muffle furnace

Results obtained from a muffle furnace showed that weight of cockle powder was decrease after subjected to heat. The weight decrease gradually from initial mass with 10 g sample as temperature increases. When CaCO₃ decomposes, it loses 44 % of its weight as carbon dioxide. During this stage, both porosity and surface area decrease. Detailed mechanisms for the development of the porous structure of the calcine and porosity loss due to sintering have not been fully established, but they are reported to be influenced by the initial structure of the material, the calcination temperature 700, 800, and 900°C, the holding time of 30 minute, the surrounding gas composition, the impurities in the sorbent, etc. Due to the release of CO_2 gas, the weight of thermal decomposition samples decrease with time. This can be illustrated in Table 4-1. The results indicate that samples lose more weight at higher temperatures. The reaction layer was very porous. The weight changed significantly during the weighing process. The thermally decomposed samples retained their spherical shape during the process. The location of the surface of the solid interface can be assumed to be changing with time. This is necessary assumption in developing the shrinking core model.

Temperature (°C)	Weight loss (g)
700	8.9
800	6.4
900	5.7

Table 4-1: Weight losses against temperature in difference calcination temperature

The physical changes of cockle shell also can be seen with different in colour of cockle powder. Fine powders before calcination process displaying chalky-white and turn to pale grey-green shades after the completion of process. This can be seen through the Figure 4-1 below. This demarcation line can be defined as the reaction boundary. This line is a consequence of the complete release of CO_2 to form pure CaO. The pale grey-green color can be attributed to CaO. This result same as previous research done by Sara et al.



Figure 4-1: Physical appearances of cockle shell powder

4.3 Crusher

The physical appearances of cockle shells are illustrated in Figure 4-2. From results obtained, we can see that a different in size of particles before and after the cockles being crush. The original size of cockles can be seen before subjected to the crusher. Meanwhile, a fine size of particles can be seen after the cockles come out from crusher. This method was repeated three times in order to get the fine particle. In addition, no chemical reaction occurred during this process. This process does not include any chemical reagent. Table 4-2 indicate the comparison of size of particles obtained in this study and the one conducted by S. Yusup et al. (2012).



Figure 4-2: Physical appearances in particle size

Table 4-2: Particle size of cockle shell by crusher

Author	Range of particle size (mm)			
Current study	0.3, 0.425-0.6, and 1.18			
S.Yusup	0.125-0.25, 0.25-0.5, 1-2, and 2-4			

4.4 Surface morphology of cockle shell

The morphology of samples was determined by Zeiss Evo 50, Carl Zeis, USA. The samples examined by the SEM included raw cockle shell and also calcined cockle shell for temperature at 700, 800, and 900°C.

4.4.1 Sample before thermal decomposition

Cockle shell was used in this research because of its high purity (96-100% CaCO₃) and natural abundance. Figure 4-3 (a) is a SEM image showing a typical example of the cockle shell, which consists of fine pores and grains. The size of the fine pores averages around 4-8 μ m in the basic unit. The porosity in cockle shell may be due to original porosity, or to dissolution related to secondary porosity, or both. The normal case is a loss of majority of the original porosity due to cementation and compaction sometime after deposition.

4.4.2 Sample after thermal decomposition

The exterior colour of all of the samples changed from white to grey during the process. All of the thermal decomposition samples were cleaved, examined with SEM image (see Figure 4-3- 4-4). On every fractured sample surface, a grey-black product layer was observed. It is believed that the grey-black colour of the product layer is

caused by the thermal decomposition of CaCO₃. The thickness of the product layer increased proportionally to the duration of thermal decomposition. If the temperature was increased, the rate of development of the product layer increased. It was possible to estimate within 0.05 cm the thickness of the product layer by using this technique. This result was expected, as the reaction layer is composed of CaO. After thermal decomposition occurred for a period of time, most of the whole particles were still spherical in shape, the exceptions were those samples which decomposed at higher temperatures and for longer durations. Distortions from sphericity are caused by impurities in the compound and high temperatures. At times narrow white bands appeared in the dark grey layer.

As previously mentioned, calcination conditions including temperature, holding time, and gas environment significantly impact the surface morphology of cockle shell. The average pore radius increases with temperature. A total of four images of SEM images were obtained for samples raw cockle shell and calcined cockle shell (Figure 4-3 and 4-4) and their corresponding CaO product calcined at 700, 800, and 900°C using N₂ in furnace. The morphologies of cockle shell shown in Figure 4-3 to Figure 4-4 are visually similar to those reported in S.Yusup et al. In Figure 4-3 (a), sample of raw cockle shell appears to have a rougher surface than calcined cockle shell. Raw cockle shell was more porous and sparser than calcined cockle shells. Calcium oxide produced from calcination in N2 gas at temperature 900°C was more porous and had a smoother surface area than the calcium oxide produced at temperature 700 and 800°C. To qualitatively interpret the observation, the physical structure of uncalcined particles was related to the development of the physical structure of the partially calcined particles. As a gas-solid reaction, thermal decomposition can only occur at the solid surface of the particle. Since the uncalcined material has considerable internal surface area, it is expected that this surface will participate in the decomposition process if the calcination is not fully controlled by heat and/or mass transfer processes. This has been confirmed by the structural analysis of the partially calcined particles. On the other hand, the calcination rate on the surface was location dependent, decreasing towards the center of the particle. From a kinetics point of view, rate differences can only be caused by temperature and/or CO₂ partial pressure gradients within the particle. The temperature at the particle center must be lower than that at the external surface and the CO_2 partial pressure must be higher than that at the particle periphery in order for calcination to proceed by the observed pattern. Considering that the decomposition reaction is

strongly endothermic and releases CO_2 , internal temperature and CO_2 partial pressure gradients may exist during calcination.



(a) Raw cockle shell(b) Calcined cockle shell at 900°CFigure 4-3: SEM image of raw and calcined cockle shell



a) Calcined cockle shell at 800°C
 (b) Calcined cockle shell at 700°C
 Figure 4-4: SEM image of calcined cockle shells under inert atmosphere

4.5 Chemical composition

Chemical analysis of cockle shell using XRF has been conducted to estimate the mineral composition in cockle shell. From the result obtained, it can be demonstrates that cockle shell is made up of calcium and carbon, which is the same outcome with other study such as Awang-Hazmi et al. who also performed chemical analysis on cockle shell in Malaysia. Appendix B shows the element compositions of raw cockle shell that had been produced compared to the element composition of synthesized cockle shell. The synthesized cockle shell at temperature 900°C samples contained the

highest amount of CaO which is >91.00%. The composition of CaO obtained is in accordance with the previous study by A.J. Awang et. al and Zuki et. al. Thus, it is suggested that cockle shell has potential to be used as sources of CaO based on their minerals composition.

4.6 Thermal decomposition analysis

4.6.1 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'. According to Barros et al. (2009), sample will experienced weight loss initially at 100-140°C due to the trapped moisture and once the temperature increase from 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 due to prior sun-drying of the sample for one day. 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 represent the decomposed sample. Figure 4-5 illustrated the weight loss of the sample during the process. By taking sample with particle size of 1.2 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 600°C to 750°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'.



Figure 4-5: TG curve of cockle shell powder decomposition at different particle sizes

4.6.2 Effect of particle size

The effect of particle size on thermal decomposition was investigated by testing a series of cockle shell sample at 900°C. The result is given in Figure 4-5. Three ranges of particle sizes (0.3 mm, 0.4-0.6 mm, 1.2 mm) were tested. According to the decomposition mechanism, in which the decomposition of a solid take place at an interface advancing inwards from the outside of each particle, small particles will decompose more quickly than large particles.

Figure 4-5 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 shown by TG curves, smaller sized particle experienced rapid weight loss compared to larger particle size. 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. The effect of particle size

on thermal decomposition was investigated by testing a series of cockle shell samples at 900°C. The results are given in a Figure 4-5. Three ranges of particle sizes (0.3 mm, 0.4-0.6 mm, 1.2 mm) were tested. According to the decomposition mechanism, in which the decomposition of a solid takes place at an interface advancing inwards from the outside of each particle (as discussed earlier), small particles will decompose more quickly than large particles.

Figure 4-5 show the effect of sample size on the wt% of samples. It is observed that for all three types of samples, the decomposition of cockle shell increase slightly with increasing size. This increase is only significant for larger samples. For smaller samples, size does not affect reaction rate. This observation is consistent with the assumption that the particle sizes of the cockle shell influenced the calcination process. Theoretically, for the smaller particle size, low activation energy is required and vice versa for large particle size. This phenomenon can be explained by the collision theory in determining rate of reaction. As smaller particle sizes are utilized, rate of reaction increases due to higher surface area available for the collision process to take place. In addition, the greatest surface area of the samples will significantly improve the heat distribution within them and thus, accelerates better decomposition process. Consequently, the resistance for the reaction to occur is reduced and thus, results in low activation energy. According to Yan et al. (2010) intermediate particle size will have reaction and mass transfer limitations. Furthermore, he suggests that the calcination rate is also heavily influenced by the pore structure, in which the small particle size has less pore diffusion resistance that influences the mass transfer to the pores. Hassibi states that the differences in the particle size do affect the heat penetration towards the samples. At constant residence time and calcination temperature, heat will not completely penetrate core of the larger samples and as a result, only the outer layer is converted to CaO and samples interior will remain as CaCO₃. Therefore, it may reduce the surface area of the materials and thus limits the heat and mass transfer.

4.6.3 Effect of calcination temperature

The thermal decomposition rates of $CaCO_3$ at the test condition (700, 800, 900°C) show differences, as illustrated in Figure 4-6. The measurement of weight loss (%) versus temperature indicate that at temperature 700°C, particle had a weight loss of 95% within 45 minute. Meanwhile at temperature 900°C, particle had a weight loss of 80% within 35 minute. The calcination temperature is sustained for 30 min at each

temperature level to ensure a complete decomposition. As illustrated in Figure 4-6, higher calcination temperature promotes higher calcination rates 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 effect (Borgwardt, 1989; Samtani et al., 2002).

Lower activation energy values at higher calcination temperature are attributed to the kinetic motion of the samples itself. At higher temperatures, the samples have more energy that hastens their kinetic motion and the calcination process. Therefore, the easiness of the process results in a fast reaction and lower activation energy values. Likewise, Kim found similar findings in which the calcination reaction proceeds slowly at temperature below 850 °C compared to temperature at and beyond 850 °C. The trend of increase in activation energy with respect to temperature is also found in other works. However, a very high calcination temperature may lead to sintering and attrition effect (Borgwardt, 1989; Samtani et al., 2002)



Figure 4-6: TG curves of cockle shell powder decomposition at different temperature

4.6.4 Effect of particle size in conversion

Weight loss of the sample indicates the fraction of sample that been decomposed during the process (Samtani., 1996). Using the same computation method as Samtani et al. (1996) and Nobari and Halali, fraction of the decomposed sample during the calcination is denoted by α . The fraction was based on the current weight loss with respect to total weight loss of the sample. Sample with larger particle size need higher temperature and longer time to get fully decomposed compared to sample with smaller particle size. Figure 4-7 represents the fraction of decomposed sample which was most probably involving the conversion of CaCO₃ contained in cockle shell into CaO. The effect of particle size on thermal decomposition was investigated by testing a series of cockle shell sample at 900°C. The result is given in Figure 4-7. Three ranges of particle sizes (0.3 mm, 0.4-0.6 mm, 1.2 mm) were tested. According to the decomposition mechanism, in which the decomposition of a solid takes place at an interface advancing inwards from the outside of each particles as discuss earlier. Small particles will decompose more quickly than a large particles. The smaller particle size also observed to reach the same conversion as the larger particle size within a shorter time.



Figure 4-7: Conversion of sample at different particle sizes

4.6.5 The effect of temperature on conversion

The effect of temperature on the conversion of CaO was illustrated in Figure 4-8. The result confirm that the higher temperature require a longer conversion time than the smaller temperature. This confirms that ash diffusion control is predominant in the temperature and particle size range studied. The rate of reaction increased tremendously with decreasing particle sizes, as the effect of ash diffusion were minimized. The thermal decomposition rates of CaCO₃ at the test conditions (i.e., temperatures of 700°C, 800°C, and 900°C, calcined in pure nitrogen) show differences, as illustrated in Figures 4-8 More resistance occurs in the higher temperature. A comparison of the curves for 700, 800, and 900°C calcination temperature shows that under similar conditions, the decomposition rate obtained for 700°C is much smaller than that obtained at 900°C. This probably arises due to 0.3 mm particles decomposing more rapidly than 1.2 mm particles (Figure 4-8). The measurement of weight loss (X) versus time at 700°C indicates that the 0.3 mm particles obtained had a weight loss of 95% within 45 minute, but the 0.3 mm particles had a weight loss of 95% after only 35 minute.



Figure 4-8: Conversion of sample at different calcination temperature

4.6.6 Decomposition rate of cockle shell

Figure 4-9 shows decomposition rate of cockle shell. 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 850°C with decomposition rate of 0.021/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. The cause of CO_2 partial pressure can be neglected in this study as the process was conducted at 900°C in which at this temperature the pressure is considered to be in equilibrium or atmospheric pressure.



Figure 4-9: Decomposition rate curve of cockle shell with different particle size

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The focus of this research has been the analysis of the reaction mechanisms of thermal decomposition of calcium carbonate in cockle shell under inert environment condition (N_2 gas). Experiments have been conducted in N_2 atmosphere under two different variables which are the effect of calcination temperature on calcination process and the effect of particle sizes on calcination process. The conclusion of this study may be summarized as follows:

5.1.1 SEM characterization

Raw cockle shell was more porous and sparser than calcined cockle shells. Calcium oxide produced from calcination in N_2 gas at temperature 900°C was more porous and had a smoother surface area than the calcium oxide produced at temperature 700 and 800°C. At temperature 700°C, the surface was less porous. While at temperature 800°C, the surface was porous. The temperature at the particle center must be lower than that at the external surface and the CO₂ partial pressure must be higher than that at the particle periphery in order for calcination to proceed by the observed pattern.

5.1.2 X-ray fluorescence (XRF)

Analysis done by XRF showed that cockle shell was made up of Ca. Almost 59.87% of cockle shell was made of Ca. Based on the result, the study prove that waste cockle shell are calcium-rich biomaterial with high potential as the source of $CaCO_3$ for the production of CaO. The synthesized cockle shell at temperature 900°C samples contained the highest amount of CaO which is average of >91.00%. This will include in Appendix B. The composition of CaO obtained is in accordance with the previous study by A.J. Awang et. al and Zuki et. al. Thus, it is suggested that cockle shell has potential to be used as sources of CaO based on their minerals composition.

5.1.3 Thermal gravimetric analyzer (TGA) analysis

The study has demonstrated that the decomposition of cockle shells are variable, depending on particle size and temperature. The findings confirmed that particle size and calcination temperature influenced the calcination process.

5.1.3.1 The effect of particle size

From the data in this study, smaller particle size experienced rapid weight loss compared to larger particle. The smaller particle size also observed to reach the same conversion as the larger particle size within a shorter time. This observation might due to wider surface area of smaller particle which contributes to a higher chance of heat to proote the decomposition. The experiment shows that sample with smaller particle size demonstrates higher decomposition rate in shorter time and at lower temperature compared to the larger particle size. In this study, the highest decomposition rate is 0.021/min for the particle sizes of 0.3 mm at heating rate of 20°C/min. Thermal decomposition can be accelerated by increasing the temperatures and by decreasing the particle size result to bigger surface area.

5.1.3.2 The effect of temperature

In addition, temperature also influenced the calcination process. The higher calcination temperature promotes higher calcination rate as this will increase the particles kinetic energy and thus, accelerates decomposition of CaCO₃ to CaO.

5.2 Recommendation

By using the Energy Dispersive X-ray fluorescence (EDX) spectrometer to perform qualitative and quantitative analyses for elements comprising a material by measuring re-emitted characteristic X-ray from elements, the mineral composition of cockle shell would be accurate rather than use XRF. XRF cannot analyze elements lighter than Na and also cannot distinguish between various isotopes of element.

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APPENDICES A) TGA Data Analysis











B) XRF Data Analysis

Mineral	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
(%wt)					
CaO	75.51	75.59	75.85	76.01	76.00
Fe ₂ O ₃	1.06	1.04	1.07	1.06	1.04
Na ₂ O	0.86	0.85	0.83	0.87	0.85
MgO	0.11	0.11	0.11	0.11	0.11
SiO ₂	0.38	0.37	0.34	0.40	0.33
K ₂ O	0.03	0.04	0.04	0.03	0.03

Table 4.3.2.1 Mineral composition of synthesized cockle shell (0.3 mm at 700°C)

Table 4.3.2.2 Mineral composition of synthesized cockle shell (0.3 mm at 800°C)

Mineral	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
(%wt)					
CaO	81.65	82.99	82.78	82.39	84.23
Fe ₂ O ₃	1.16	1.16	1.17	1.18	1.14
Na ₂ O	0.76	0.72	0.72	0.72	0.73
MgO	0.11	0.11	0.12	0.12	0.12
SiO ₂	0.32	0.34	0.31	0.33	0.33
K ₂ O	0.03	0.04	0.04	0.03	0.03

Mineral	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
(%wt)					
CaO	92.27	92.78	91.75	92.47	92.96
Fe ₂ O ₃	1.22	1.22	1.36	1.27	1.21
Na ₂ O	0.60	0.59	0.53	0.57	0.67
MgO	0.13	0.13	0.13	0.13	0.13
SiO ₂	0.18	0.19	0.31	0.24	0.17
K ₂ O	0.02	0.02	0.03	0.02	0.03

 Table 4.3.2.3 Mineral composition of synthesized cockle shell (0.3 mm at 900°C)

Table 4.3.2.4 Mineral composition of synthesized cockle shell (0.3 mm at 900°C)

Mineral	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
(%wt)					
CaO	91.21	93.18	91.94	92.23	91.91
Fe ₂ O ₃	1.39	1.19	1.14	1.19	1.25
Na ₂ O	0.50	0.54	0.56	0.59	0.62
MgO	0.13	0.13	0.13	0.13	0.13
SiO ₂	0.37	0.17	0.17	0.20	0.18
K ₂ O	0.04	0.02	0.02	0.02	0.02
Mineral	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
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(%wt)					
CaO	91.80	92.42	92.05	91.79	91.66
Fe ₂ O ₃	0.34	0.33	0.35	0.34	0.33
Na ₂ O	0.62	0.64	0.59	0.59	0.62
MgO	0.13	0.13	0.13	0.12	0.13
SiO ₂	0.17	0.20	0.20	0.16	0.17
K ₂ O	0.02	0.03	0.03	0.03	0.02

Table 4.3.2.5 Mineral composition of synthesized cockle shell (0.4-0.6 mm at900°C)

Table 4.3.2.6 Mineral composition of synthesized cockle shell (1.2 mm at 900°C)

Mineral	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
(%wt)					
CaO	93.36	92.78	92.07	92.38	92.41
Fe ₂ O ₃	0.11	0.11	0.10	0.10	0.10
Na ₂ O	0.55	0.54	0.51	0.44	0.48
MgO	0.12	0.12	0.12	0.12	0.12
SiO ₂	0.07	0.11	0.08	0.09	0.08
K ₂ O	0.02	0.02	0.02	0.01	0.02