INFLUENCE OF TEMPERATURE AND HEATING RATES ON CALCINATION OF WASTE COCKLE SHELLS TO CALCIUM OXIDES

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ABSTRACT

Cockle shells or *Anadara granosa* has been touted as an alternative for the calcium carbonate sources instead of using the limestone. Mining large quantities of rocks can contribute to the environmental damage and engage with the high cost for environmental compliance. Li *et al*. (2009) also proved that seashells to have higher composition of calcium oxides compared to the limestones. In this research, the shells of Malaysian blood cockle, *Anadara granosa,* were used as the starting material. The present study was done to evaluate the influence of operating conditions on the minerals of *Anadara granosa* shells by heat treatment at various temperatures and heating rates, and to subsequently use the resulting material for the formation of calcium oxide. CaO associated with carbonaceous material has been of recent interest in applications such as transesterification catalysts and sorbents for sulphur dioxide. The utilisation of the economic resources of waste bio-minerals from blood cockle shells is expected to promote the commercial application of the resulting calcium oxides. Calcination of cockle shells was analysed with TGA with different range of temperature (700, 750, 800, 850 and 900^{o}C) and heating rates at 10^{o}C/min and 20^{o}C/min. Overall, the better performance is shown at the calcination temperature of 800^{o}C for 39 minutes and heating rate of 20^{o}C/min under N_2 gas flow of 40mL/min. Then, the characterization of the cockle shells are done by the FTIR spectrophotometer which is performed in a range of 4000cm^{-1} to 400 cm^{-1} with a resolution of 2 cm^{-1} and averaging of 62 scans. As result, the FTIR analysis showed that the waste cockle shell from the seashore gave the peak of 1472.99cm^{-1}.

ABSTRAK

Kulit kerang atau *Anadara granosa* telah disebutkan sebagai alternatif bagi sumber kalsium karbonat dan bukannya menggunakan batu kapur. Perlombongan kuantiti batu-batu yang banyak boleh menyumbang kepada kerosakan alam sekitar dan melibatkan diri dengan kos yang tinggi untuk pematuhan alam sekitar. Li *et al.* (2009) juga membuktikan bahawa kulit kerang mempunyai komposisi kalsium oksida yang lebih tinggi berbanding dengan batu kapur. Dalam kajian ini, kulit kerang di Malaysia, *Anadara granosa*, telah digunakan sebagai bahan permulaan. Kajian ini dilakukan untuk menilai pengaruh keadaan operasi pada mineral daripada *Anadara granosa* dengan rawatan haba pada pelbagai suhu dan kadar pemanasan, dan kemudiannya menggunakan bahan yang terhasil untuk pembentukan kalsium oksida. Kalsium oksida berkaitan dengan bahan karbon telah menunjukkan kepentingannya baru-baru ini dalam aplikasi seperti pemangkin transesterifikasi dan penjerap untuk sulfur dioksida. Penggunaan sumber ekonomi sisa bio- mineral dari kulit kerang dijangka menggalakkan aplikasi komersil kalsium oksida yang dihasilkan. Pengkalsinan kulit kerang dianalisis dengan TGA dengan pelbagai berbeza suhu (700, 750, 800, 850 dan 900^{o}C) dan kadar pemanasan pada 10^{o}C/min dan 20^{o}C/min. Secara keseluruhan, prestasi yang lebih baik ditunjukkan pada suhu pengkalsinan yang 800^{o}C selama 39 minit dan kadar pemanasan 20^{o}C/min bawah aliran gas N_2 daripada 40mL/min. Seterusnya, pencirian kulit kerang yang dilakukan oleh spektrofotometer FTIR yang dilakukan di dalam pelbagai 4000cm^{-1} untuk 400cm^{-1} dengan resolusi 2cm^{-1} dan purata 62 imbasan. Hasilnya, analisis FTIR menunjukkan bahawa sisa kulit kerang dari tepi pantai memberikan puncak 1472.99cm^{-1}.

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$CaCO_3$	Calcium Carbonate
CaO	Calcium Oxide
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermal Gravimetric Analyser
w_i	Initial Weight
w_t	Current Weight
w_f	Final weight
$d\alpha/dt$	Decomposition Rate of Cockle Shell Powder
dw_t/dt	Differential Data of TG Curves

1 INTRODUCTION

1.1 Motivation and statement of problem

Marine aquaculture is the main industrial sectors in coastal areas in Malaysia. In addition, the farm of shellfish are about to produce large amounts of waste shell that account for hundreds of thousands of tons per year (Kwon *et al*., 2004). These seashells do not have any other important uses and also discarded as waste products from the marine aquaculture that presents a major disposal problem. The dumped and untreated waste seashells caused disturbing smells and view. For the sustainable development in the future, the industry had recognizes that our sectors must take into account of the environmental factors, including intelligent of monitoring ecosystem resources and also the environmentally benign recycling of natural waste seashell. The recycling of waste seashells has arisen as an issue that occurs in the area of marine aquaculture. Thus, recently, the regulations and strategies on waste seashell have opened up new opportunities for sustainable development through the management and treatment of aquaculture. In order to address the environmental impact of the lifecycle of the seashell production and use of seashells, the consideration of the environmental benefits that would exist if the seashells were given value through use in other industrial processes, and the possibility that recycling of waste can cause more environmental impact of discarding waste due to the lack of previous studies.

In addition to environmental problems, previous studies exposed that the seashells have a high potential to be utilised as a cheap source of calcium carbonate ($CaCO_3$) for industrial applications. Recently, most of studies are focused on the use of seashells as alternatives sources for calcium carbonate. For examples are cockles, eggs, mussels, crabs and oysters shell. As the cockles alone are contributed about 14% of marine aquaculture production in Malaysia (Department of Fisheries Malaysia, 2009) and also has retail value estimated to be over 32 million USD dollars (Boey *et al*., 2011) which are given an abundant supply of blood cockle shells. Further, since there is still a few studies that discussing on the potential biomass resources from the waste cockle shells. Thus, this research studied the influence of temperature and heating rate on the production of calcium oxide (CaO) from the cockle shells by using Thermal

Gravimetric Analyser (TGA). Then, the Fourier transform infrared (FTIR) spectrophotometer is introduced as the way of analysing the characterization of calcium oxide from waste cockle shells. Moreover, a part from high-priced crab and molluscs such as oyster, cockle is chosen due to its inexpensive resources and also consumed as part of the daily diet.

At present, research with respect to cockle shells, in which the primary component is approximately 95-99% calcium carbonate, is in its infancy (Mohamed *et al.*, 2012). Besides, calcium carbonate is one of the most abundant minerals in nature and has three polymorphs: calcite, aragonite and vaterite. Common natural sources of the calcium carbonate that have been useful these days are such as limestone, dolomite, and magnetite. The calcium oxide is normally been produced via thermal decomposition of calcium carbonate sources such as limestone which is obtained through mining and quarrying limestone hill. The limestone which contained about 93-94% by weight of calcium carbonate will convert into calcium oxide. By mining those carbonate rocks will contribute to the environmental damage such as wide deforestation and top soil loss, and high cost for environmental compliance. So that, the special consideration should be devoted to the disposal or processing which gives them the potential to exploit the cockle shells as biomass resources in the calcium oxide production from the decomposition of calcium carbonate (Barros *et al.*, 2009; Nakatani *et al.*, 2009). This consideration fits to be the best applicant as the alternative resources as the composition of calcium oxide in cockle shell is significantly higher than the limestone (Li *et al.*, 2009)

Additionally, there are several studies on the recycling of the seashells have been conducted (Barros *et al*., 2009; Chong *et al*., 2006; Fujita *et al*., 1990; Jung *et al.*, 2006; Kwon *et al.*, 2004; Presznhuk *et al*., 2003; Yang *et al.*, 2005). Among of these studies, the objective is to exploit the waste seashells as biomass resources in the production of calcium oxide from decomposed calcium carbonate by considering also the recovery of the waste and re-use of materials as raw materials in other industries as well as the use in the green technology, as an alternative scenario. Therefore, the source of pollution is minimized and exploited the waste seashells as resources.

On the other hand, due to its varied polymorph properties, research on the utilisation of calcium carbonate from seashells has been of recent interest and widely used in diverse applications such as an active ingredient in agricultural lime (West and McBride, 2005), as a heterogeneous catalyst for biodiesel production (Nakatani *et al.*, 2009; Boey *et al.*, 2009), and as a biomaterial for use in bone repair (Awang-Hazmi *et al*., 2007). These studies also solve the problems of water eutrophication by converting waste seashells into a sustainable reagent for the efficient removal of phosphates from wastewaters (Kwon *et al*., 2004). On the other hand, some of the waste seashells are replaced for limestone application in fertilizers plant for waste shells recycling (Yoon *et al*., 2003) and chicken feed (Kwon *et al*., 2004). Besides, the waste seashells can be used as a substituent for aggregates in construction materials (Yoon *et al*., 2003, 2004; Yang *et al*., 2005) or cement clinker (Cheon and Song, 2003). These ultimate solutions are to convert the waste shells into the products that are both beneficial and economically viable.

Furthermore, the calcinations of calcium carbonate are a process of producing calcium oxide (Mohamed *et al*., 2012). As stated by Mohamed *et al.* (2012), the higher heating rate elevated the temperature of the reaction faster than the slow heating rate. In addition, the calcinations rate increases as the heating rate increases. Higher calcinations temperatures promote higher rates of calcinations as this will speed up the decomposition of calcium carbonate to calcium oxide and consumed shorter operating time (Mohamed *et al*., 2012). Therefore, the selection of calcination temperature is significantly essential before starting the experimental progress. Besides, the particle sizes of the samples also one of the factors that affected calcination process since the particle sizes are directly influence the reaction rate. The smallest sizes of the samples are experienced rapid weight loss and show the highest calcination rate compared to the largest sizes. Then, the small particles commonly have largest surface area which contributes to the highest uptake of heat in order to promote the decomposition (Rashidi *et al*., 2011).

In Malaysia, cockle contributes to about 14% of marine aquaculture production (Department of Fisheries Malaysia, 2009) and the cockles has retail value estimated to be over 32 million USD dollars (Boey *et al*., 2011). Therefore, there is an abundant supply of blood cockle shells. In addition, the shells do not have any other important uses and are normally discarded as waste. The dumped and untreated waste shells caused unpleasant smells and destructive view to surroundings. Due to the abundance of these seashells, they have a high potential to be utilised as a cheap source of calcium carbonate, $CaCO_3$ for industrial applications. Calcium carbonate, $CaCO_3$, commonly found in rocks occurs naturally as the main component of crustacean shells. The calcium oxide is normally been produced via thermal decomposition of calcium carbonate sources such as limestone which is obtained through mining and quarrying limestone hill. By mining those carbonate rocks will contribute to the environmental damage and high cost for environmental compliance. To the best of our knowledge, there were limited studies related that exploit the vast availability of waste cockle shells from marine aquaculture as potential biomass resources for calcium carbonate and calcium oxide compared to other seashells such as scallop shell and oyster shell.

1.2 Objectives

The major aim of this research project is to evaluate the influence of operating conditions (temperature and heating rate) on the production of calcium oxide using waste cockle shell as raw materials via calcination using Thermal gravimetric analysis (TGA).

1.3 Scope of this research

The scope of this research includes the production of calcium oxide from cockle shells via calcination using Thermal Gravimetric Analyser (TGA) and characterization of cockle shells using Fourier transform infrared (FTIR) spectrophotometer. For the TGA method, the sample collections of cockle shells from the seashore were washed to remove dirt. The samples were then dried, crushed and grinded to form powders and then sieved in order to segregate according to sizes of 0.315mm. Then, each different samples are analysed at different range of calcinations temperature (700, 750, 800, 850, 900 and 900°C) at 10^{o}C/min and 20°C/min under nitrogen gas flow at 40ml/min respectively (Rashidi *et al*., 2011). On the other hand, before FTIR spectrophotometer is done, the fine powder of dried calcium oxide is mixed with potassium bromide (KBr) powder. Then, the samples are characterized at range of 4000 cm^{-1} to 400 cm^{-1} at a 2 cm^{-1} resolution and averaging 62 scans.

2 LITERATURE REVIEW

2.1 Seashells

Seashells are more than just pretty souvenirs to take home from a trip to the beach. Seashells also a high value added product like calcium carbonate and calcium oxide where it is an eco-friendly solution to the problem of disposal in Malaysia. Based on the research by Horne (2006), the seashells such as cockles, crabs and oysters are the exoskeletons of marine animals' type called mollusks, where the skeletons of mollusks are outside of their bodies. Some of the molluks are live in the water and others live on the seashore. The seashells act as a protective outer layer produced by an animal that lives in the sea and these seashells are also a part of the animal body. The seashells are left behind, when the mollusk are died. Similar goes to the land animals where they also leave their skeletons behind when they died.

There are two types of mollusks, which are bivalves and univalves. Most mollusks are bivalves, where the mollusk's shells are divided into left and right valves that form a whole shell. For examples are mussels, scallops, cockles and oysters. On the other hand, univalves just have a one-piece shell which is usually a spiral-type shell, often looking something like a stronger, larger and more elaborate snail's shell.

2.1.1 Growth of Seashells

Furthermore, seashells are primarily made of calcium carbonate and other minerals that found in the sea and also with a minor quantity of protein. The proteins and mineral extracellularly are secreted from mantle tissue that located under and in contact with the shell in order to form the shell. Think of laying down the protein and pouring mineral over it. Thus, seashells grow from the bottom up, or by adding material at the margins. This pattern of growth results in three different shell layers: an outer proteinaceous periosteum (uncalcified), a prismatic layer (calcified) and an inner pearly layer of nacre (calcified). The composition can be thickened, enlarged and repaired, but does not play a part in the metabolism of the animal. When the mollusk eventually dies, the shell is usually the only part that remains intact.

Currently, there is some understanding that shells are forms from the protein matrix of bone and seashell is secreted out from the cells. During guiding and directing calcification, these proteins have a tendency to bind the calcium ions. This binding of calcium ions to the protein matrix can develops the crystal formation according to specific hierarchical arrangements. During the shells development, the isolation of many proteins is playing their role. It is appears to be protein-determined whenever the calcium carbonate crystal (calcite) which in the prismatic layer, or the aragonite which in the nacre of a seashell. The type of calcium carbonate crystal formed when the secretion of different type of proteins at different times and places in the seashells (Horne, 2006).

By adding new organic matrix and mineral to the outer margins of the shell will make the seashells gradually increase and extend their shells. First, the strengthening is made up of an uncalcified layer of conchiolin--protein and chitin which is naturally produced polymer. Then, followed by the highly calcified prismatic layer and then further by the final pearly layer, or nacre. The crystal aragonite platelets which are function similarly to diffraction grating in dispersing visible light caused the iridescence of the nacre occurs incidentally (Horne, 2006). Then, as stated by Schowalter-Hay (2011), the given enough time and pressure on the layers of cemented shells and coral bodies may transform into calcium carbonate, a sedimentary, carbonate rock mainly composed of calcium carbonate precipitated by these organisms. These rocks that stem from such organic matter are called biogenic.

2.2 Cockle Shells

This cockle shell scientifically known as *Anadara granosa* is local mollusc shells, exist in coastal areas in Southeast Asia, particularly Malaysia, Thailand and Indonesia. In 2006, Malaysia has produced 45,674.58 metric tonnes of shells for the seafood industry (Izura, 2008). The shells form these industrial products are considered as waste and mostly abandoned at dumpsite to naturally deteriorate. It is difficult to dispose because of the strong property.

On the other hand, based Izura and Hooi (2008), the statistics for production of waste cockle shell have started to drop from the year of 2002 to 2006 because of the limited area suitable for the development of culture in Peninsular Malaysia and also the areas of insufficient spat-fall in Sabah and Sarawak. The reduction of mangrove forests and greater operating costs help to provide seed shells also contributed to decrease in the production of shellfish. However, Izura and Hooi (2008) state that Malaysia is predictable to produce about 130,000 tonnes of cockle alones in the Ninth Malaysia Plan.

2.2.1 Mineral Contents in Cockle Shells

The cockle shells have found abundantly in Malaysia as a by-product of the marine aquaculture. This waste has not been exploited in other application except that it has been used in small-scale craft production. Mineral composition of the cockle shells composed of calcium (Ca), carbon (C), magnesium (Mg), silica (Si) and oxygen (O), which is similar to sand, stone and cement suggests potential as an alternative raw material sources of calcium oxide (Sahari, 2013).

Additionally, biological systems are able to produce inorganic materials such as calcium carbonate and morphological structure and polymorphs. Besides, biological systems in the marine aquaculture such as cockle shells, oyster shells, coral, and mollusc shells, in which the main component is calcium carbonate and other organic components, such as anionic proteins and glycoprotein (Fukui & Fujimoto, 2012).

Moreover, calcium carbonate that contained in the cockle shells has three anhydrous crystalline phases which are calcite, aragonite and vaterite. The calcite is thermodynamically stable under ambient condition. Then, the aragonite is a high pressure polymorph that is less stable than calcite. While the vaterite is stable at least between three polymorphs and also has the ability to transform into one of the other two polymorphs.

According to Kamba *et al*. (2013), cockle shells are composed of a greater percentage of aragonite calcium carbonate polymorphs. Based on the analysis of powdered calcium carbonate from cockle shells and also the analysis on the commercial calcium carbonate, the cockle shells are made up of aragonite form of calcium carbonate, which is more compact and less stable than calcite. These characteristics make it potential biomaterials for medical uses and also as calcium oxide resources.

Furthermore, there is a finding on the composition of calcium oxide in seashells which is higher than limestone (Li *et al.*, 2009). But, there is limited study that related to the decomposition of calcium carbonate from cockle shell by using calcium carbonate as the main calcium oxide resources. Most studies have focused on the chemical reactions uses, where the salts of calcium and carbonate ions are performed as the precursors for the decomposition of calcium carbonate. In fact, calcium carbonate which is abundant in nature is commonly adopted in industrial processes as the solid absorbent through the reversible calcinations-carbonation process as shown below:

Endothermic calcination:

$CaCO_3\,(s) \leftrightarrow CaO\,(s) + CO_2\,(g)$ $\Delta H = 178$ kJ/mole **(Equation 2.1)**

Exothermic carbonation:

$CaO\,(s) + CO_2\,(g) \leftrightarrow CaCO_3\,(s)$ $\Delta H = -178$ kJ/mole (**Equation 2.2)**

2.2.2 Uses of $CaCO_3$

The use of this material is still very limited, although there have been attempts to use them in craft production. Only recently, some preliminary studies have been performed to investigate the potential of this material. For example, a study in Malaysia has shown that this material has potential as biomaterials for bone repair (Awang *et al.*, 2007). In various studies on other types of seashell such as oysters, scallops, mussels and cockles revealed that they are quite developed and used in a variety of industries as an alternative source of calcium oxide from the decomposition of calcium carbonate around the world for fertilizer, building materials, cement clinkers and tiles (Barros *et al.*, 2004).

Additionally, there are several studies on the calcium-based compound composition in marine aquaculture and also as justifying the use of cockle shells as potential biomass resources for calcium carbonate-based (Li *et al.*, 2009). Calcium carbonate contained a lot of inorganic biomaterials with different morphological structure that has attracted the interest of other researchers in the various fields. The wider use of calcium carbonate in many industries, such as paints, rubber, and plastics industries are the cause of this benefit. The calcium carbonate that has been detected to be biocompatible for use in medicine, the pharmaceutical industry, and also drug delivery systems showed the focus of interest in nanotechnology (Xu *et al.,* 2006).

2.3 Review of Calcination Process (Decomposition)

Calcium oxide from cockle shells (*Anadara granosa*) or other seashells can be produced by using Thermal Gravimetric Analysis (TGA) and also by combustion with air in an electric furnace.

Thermal Gravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled environment. Measurements are primarily used to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. However, the calcinations temperature and heating rate are the main focus of this calcination process of waste cockle shells.

Based on Rashidi *et al.* (2011) and Mohamed *et al.* (2012), the reactivity of decomposition of cockle shell was conducted using the Thermal Gravimetric Analyser (TGA). Based on Rashidi *et al.* (2011) literature, she has studied the performance of calcination process with respect to various temperatures, heating rate, particle size and duration of time. From her reviewed, she found that the optimal point for the production of calcium oxide from waste cockle shell basically at 850^{o}C, 40 minutes time period, the heating rate at 20^{o}C/min and size below than 1.25mm under nitrogen gas flow of 50mL/min. Based on her research, it can be concluded that the calcination of sample performance is highly dependent on several variables such as reaction temperature, duration for the process to take place, the heating rate and particle size. Overall, operating parameters directly affects the sample decomposition, sintering effects, surface area, pore volume and distribution as well as the rate of reaction.

While Mohamed *et al.* (2012) has investigated on the effect of different particle sizes towards decomposition process. Based on her studied, she found that the ideal operating conditions for the decomposition of cockle shell is at calcinations temperature of 850^{o}C with heating rate of 20^{o}C/min by using particle size of below 0.125 mm in inert (N_2) atmosphere by using TGA.

Based on Boey *et al.* (2011) research, the decomposition of waste cockle shell was analysed from 30^{o}C to 900^{o}C with heating rate of 20^{o}C/min under N_2 condition by using the TGA instrument. Then, similar to her second study that stated that the waste cockle shells is a calcium-rich biomass and also has high potential as calcium oxide resources.

According to Nakatani *et al.* (2008), powdered shell was analysed under combustion with air in an electric furnace at a given temperauture (100, 500, 700, 800, 900 and 1000^{o}C) for 3hours. From the results, it showed that the dramatically increased of weight-loss (45%) during the combustion temperature from 700^{o}C to 900^{o}C.

Table 2-1: Comparison on different way of preparation of seashells

Type	Methods/Findings	Researcher
Preparation	**Thermal Gravimetric Analyzer (TGA)**	
	- Analysed from 30 to 900^{o}C with heating rate of 20^{o}C/min under N_2 condition.	Boey *et al.* (2011)
	- Calcinations temperature of 850^{o}C with heating rate of 20^{o}C/min by using particle size of below 0.125 mm under inert condition.	Mohamed *et al.* (2012)
	- The optimal point for cockle shell basically at 850°C, time of 40min, heating rate of 20°C/min and size of <0.125mm.	Rashidi *et al.* (2011)
	- Peak temperature of curve found at 780^{o}C	Islam *et al.* (2013)
	Combustion with air in an electric furnace	
	Powdered shell showed dramatically increased of weight-loss (45%) during the combustion temperature from 700^{o}C to 900^{o}C.	Nakatani *et al.* (2008)

2.3.1 Factors Affecting Calcination Process

2.3.1.1 Temperature

As stated by Rashidi *et al.* (2011), this calcination process depends on the reaction temperature, which will define the qualities of the sorbent, whether the samples are in good quality or else. Therefore, the selection of the reaction temperature is more important before conducting experimental work. Also, at a certain temperature at which the surface area is at the highest level, the rate of decomposition is at the top of calcium carbonate and thus will accelerate this calcinations temperature.

While Mohamed *et al.* (2012) stated that the thermal decomposition process can decompose a fraction of the seashells into calcium oxide. From her literature, when the temperatures increase between 700°C to 900°C , it been recorded that the rapid weight change happen as the volatile material in the cockle shells powder where the decomposition start to take place. Though, the cockle shells' weight are constant when the temperature start to reach 900°C and onwards. The result indicates the total decomposition of calcium carbonate to calcium oxide, leaving only the product "ash" Through this thermal gravimetric analysis, the cockle shells start to decompose at 700°C and loss about 55% of the weight.

Based on Boey *et al.* (2011) research, the TGA result shows the effect on the calcination process as the temperature range from 575–800^{o}C and give centered temperature on 750^{o}C, the decomposition of the samples is 42%. When calcium carbonate is transformed to calcium oxide, the stoichiometrical weight loss is 44%.

According to Nakatani *et al.* (2008), the calcination process of powdered shell is done by the combustion with air in an electric furnace, where the results showed the slightly increased of weight loss about 10% from the temperature of 100^{o}C to 700^{o}C, while the dramatically increased of weight-loss (45%) is during the combustion temperature from 700^{o}C to 900^{o}C. But, when the temperature reached above 900^{o}C, the weight-loss remained constant.

2.3.1.2 Heating Rate

Furthermore, the heating rate is really important due to its influenced on cockle shell powder decomposition during calcination process. Based on Rashidi *et al.* (2011), the heating rate is essentially important because it affects the decomposition of these samples during the calcinations process. Larger heating rates typically have maximum calcinations rate, shorter operating time to achieve the desired calcinations temperature. Basically, when higher heating rate used, the process itself will quickly occur and thus, take a shorter operating time to reach the desired temperature.

Mohamad *et al*., (2012) describes that calcination process occurs more rapidly with higher heating rates as the same decomposition amount can be reached within a shorter time. Therefore, applying the suitable heating rate for the calcination process is significantly important. Based on her studied, the most suitable heating rate for the calcination process is 20^{o}C/min. Besides, Mohamad *et al*., (2012) also stated that the higher heating rate elevate the temperature of the reaction faster than slower heating rate and hence, decreases the time taken for the reaction to complete.

2.3.1.3 Particle Size

Moreover, the particle sizes are also one of the important parameter in the calcination process. This is due to its influenced on the reaction rate of cockle shell decomposition. Based on Rashidi *et al*. (2011), the smaller particle size of the cockle shell powder will experienced rapid weight loss percentage and also will show the higher calcination rate compared to the larger particle size. Besides that, she also stated that the wider surface area of smaller particle size will goes to a higher uptake of heat during promoting the decomposition.

While Mohamed *et al.* (2012) stated that the particle size is affected the calcination process, in which the smaller particle size of sample demonstrates the greater decomposition rate within shorter duration time and at lower temperature compared to the larger particle size of sample. From her results, it is stated that the uppermost decomposition rate is 0.25/min for the smallest particle sizes of 0.125-0.25 mm at heating rate of 20°C/min have been shown in this study.

Furthermore, Yan *et al.* (2010) stated that the intermediate particle size will have reaction and also limitations of mass transfer. He also suggested that the smaller particle size has less pore diffusion resistance that affects the mass transfer to the pores, since the calcination rate is also heavily affected by the pore structure.

On the other hand, Hassibi (1999) stated that the differences in the particle size will influence the heat penetration towards the samples. When at the constant residence time and calcination temperature, the outer layer is only converted to CaO, while the samples interior will remain as $CaCO_3$. This is due to the heat is not completely penetrate core of the larger samples. So that, it is assumed that the smaller particle size will agglomerate during calcination process. Hence, it may reduce the surface area of the samples and thus limits the heat and mass transfer.

2.4 Calcium Oxide

Calcium oxide is a chemical compound that is a colourless, cubic crystalline or white amorphous substance. It is also known as quicklime, or caustic lime, but commercial calcium oxide often contains impurities such as silica, iron, alumina, and magnesia. The commercial calcium oxide is prepared by heating calcium carbonate (limestone) in a special lime kiln to about 500°C to 600°C, decomposes to the oxide and carbon dioxide. (HighBeam Research, 2005)

$$CaCO_3\,(s) \xleftrightarrow{500\text{-}600^{o}C} CaO\,(s) + CO_2\,(g) \qquad \textbf{(Equation 2.3)}$$

Nowadays, most studies are focused on the use of seashells as alternatives sources for calcium oxide (CaO). For examples are cockles, eggs, mussels, crabs and oysters shell. Compared to the commercial calcium oxide, the calcium oxides that decompose from calcium carbonate in cockle shells have low impurities (Mohamed *et al.*, 2012).

Based on a study done by Oliveria *et al*. (2012), the calcium oxide is a raw material used by the chemical industry in the production of lime. Meanwhile, Witoon (2011) and Rashidi *et al*. (2011) stated that the calcium oxide was used for carbon dioxide looping cycle which is due to its potential advantages such as a reduction of energy requirement, wide range of potential operating temperatures, the relatively inert nature of solids wastes and also the elimination of the generation of liquid wastes.

In the chemical industry, the calcium oxide is used as a dehydrating agent and absorbent. As an absorbent, calcium oxide has been proven to effectively absorb carbon dioxide, which helps when the chemical's carbon dioxide is too high to effectively work with. For example, Mohamed *et al.* (2012) states that calcium oxide widely been used in absorption of carbon dioxide, CO_2 which if functioned as the based-material. Then, there is an existing technology of CO_2 adsorbent such as activated carbon, using amine-based adsorbent, and molecular sieve which are can only withstand low temperature process from 40°C to 160°C. Same goes to the literature by Witoon (2011), where the attractive method for CO_2 capture from combustion gases is by the carbonation-calcination looping cycle of calcium-based sorbents. This is because the cost can be reduced during the capture steps compared to conventional technologies. Since the CO_2 concentration in the atmosphere has increased rapidly due to the industrial revolution, then the application of CO_2 sorbent is due to the problem of global warming that caused by CO_2 emission.

Additionally, Boey *et al.* (2011) stated that the cockle shell, which is abundantly available, was exploited as calcium oxide resources and performs as a heterogeneous catalyst in the transesterification of palm olein into biodiesel (methyl esters). Same goes to Nakatani *et al.* (2008), where the transesterification of soybean oil by using combusted waste of oyster shell as a catalyst. This is because of the biodiesel is not only as an alternate or extender but also as a sustainable fuel. Besides that, it is biodegradable, renewable, nontoxic, carbon neutral, higher flashes point, and also have low exhaust emission and environmentally acceptable as a fuel for diesel engines. (Wedel, 1999 and Knothe, 2005)

Moreover, based on Macías-Pérez *et al.* (2008), it is showed that existence of well-dispersed of calcium oxide in the sorbents have recovered SO_2 retention compared to the activated carbon, in which the SO_2 retention happens in surface of calcium oxide between 100^oC and 250^oC, while it is above 300^oC in the bulk calcium oxide. Then, the total calcium conversion is reached at 500^oC and when the temperature reached above 550^oC, the calcium-catalysed carbon gasification by SO_2 happens.

2.4.1 *Review of $CaCO_3$ Characterization*

Calcium oxide from cockle shells and commercial calcium oxide can be characterized using variable pressure scanning electron microscopes (VPSEM), a transmission electron microscope (TEM), an energy dispersive X- ray analyser (EDX), X-ray diffraction (XRD), scanning electron microscopy equipped with energy dispersive X-ray (SEM-EDX) and Fourier transmission infrared spectroscopy (FT-IR).

The X-ray diffraction (XRD) can be used to analyze the crystal structure that shows by the shell which is made up of aragonite and the X-ray fluorescence (XRF) is to analyse the chemical that estimate the mineral composition in shell. While the scanning electron microscopy equipped with energy dispersive X-ray (SEM-EDX) is the analysis of determining the structure and elemental composition of shell. Then, the Fourier Transform Infrared (FTIR) spectroscopy is to reveal the presence of $CaCO_3$ groups in shell and the Transmission Electron Microscope (TEM) is observed the crystals shape in the shell. Last but not least is the Variable Pressure Scanning Electron Microscopy (VPSEM) which is used to study the surface morphological changes on the samples after coating the powder with gold.

Based on Islam *et al.* (2011), the EDX results showed that the cockle shells contained more calcium and carbon than the commercial calcium carbonate, whereas the commercial calcium carbonate contained more oxygen than the cockle shells. FT-IR analysis revealed the presence of carbonate groups in both the cockle shells and the commercial calcium carbonate. FT-IR analysis showed the presence of aragonite in the cockle shells and calcite in the commercial calcium carbonate. XRD analysis showed that the cockle shells powder contained aragonite, whereas the commercial calcium carbonate contained calcite. The cockle shells powder was formed with good quality calcium carbonate and contained calcium carbonate in the aragonite phase and then will convert to the calcium oxide.

While, according to Witoon (2011), the FTIR spectrum of the calcined commercial calcium carbonate and the calcined eggshell showed the same wavenumber of 500 cm^{-1}, in which showing that the calcined commercial calcium carbonate and the calcined eggshell have a very similar chemical nature. The calcined eggshell shows that the chemical composition of calcium oxide is the most abundant component which is about 97.4%. Based on the FTIR results, it is confirmed that the existence of the calcium carbonate is related to high amount of calcium oxide in the waste eggshell. This result on the calcined eggshell also showed the small amounts of CuO, MgO, Fe_2O_3, P_2O_5, SO_3, SrO, K_2O. Thus, the waste eggshell can be considered as pure relatively natural carbonate-based material resources from a chemical perspective.

Additionally, based on the XRF and XRD results, the composition of cockle shell is confirmed to be rich in calcium component and calcium oxide existence is discovered in calcined cockle shells (Mohamed *et al.,* 2012). Based on XRD spectra, waste cockle shells contain one of the polymorphs of calcium carbonate which is aragonite other than calcite and veterite. Even though its relative is instable, the aragonite is still the most appropriate compound for production of calcium oxide compared to the calcite or veterite. On the other hand, SEM was used to visualize the changes on cockle shell's surface structure. SEM results showed that aragonite have needle-like structure and the structure changed after the calcinations process. While, EDX results showed that calcium carbonate was existent but after calcinations process, the proportion was changed. This calcinations process reduced the weight percent of carbon (C) by increasing the amount of calcium (Ca) of the sample.

Boey *et al.* (2011) stated that the SEM demonstrated the morphologies existence which is relatively smaller and look like to each other by increasing the catalyst's surface area. Conversely, the uncalcined catalyst exposed a bulky substance at equal magnifications of 3000x. From this observation, it is shown the same results with N_2 physisorption measurement, where there is much higher pore volume and higher surface area were detected for the calcined catalyst as compared to the uncalcined catalyst. Then, the XRD results exposed that the composition of uncalcined cockle shell mainly consists of calcium carbonate with the absence of peak of calcium oxide. However, when the temperature is increased, the calcium carbonate completely transformed to calcium oxide by developing the carbon dioxide. When the temperature at and above 700^{o}C, the composition of calcined catalyst is consisted of the calcium oxide. Then, calcined catalyst has a narrow and high intense peaks was defined the well-crystallized structure of the catalyst. Furthermore, the EDX results showed that the uncalcined sample shows the major component of oxygen, and the chief element of calcium is in the calcined catalyst. Stoichiometrically, it is proved that in calcium carbonate, there is major content of oxygen (48%) and while in calcium oxide, there is calcium is the chief constituent (71%).

Table 2-2: Comparison on different way of characterization of seashells

Type	Methods/Findings	Researcher
Characterization	**X-ray diffraction (XRD)** Analysis of crystal structure shows the cockle shell made up of aragonite	Mohamed *et al.* (2012) Islam *et al.* (2013) Boey *et al.* (2011) Nakatani *et al.* (2008) Xing *et al.* (2013)
	X-ray fluorescence (XRF) Chemical analysis that estimate the mineral composition in cockle shell	Mohamed *et al.* (2012)
	Scanning Electron Microscopy equipped with Energy Dispersive X-ray (SEM-EDX) Analysis of determining the structure and elemental composition of cockle shell	Boey *et al*. (2011) Rashidi *et al.* (2011) Xing *et al.* (2013)
	Fourier Transform Infrared (FTIR) spectroscopy FTIR analyses reveal the presence of carbonate groups in cockle shell	Islam *et al.* (2013)
	Transmission Electron Microscope (TEM) TEM analysis observed the crystals shape	Islam *et al*. (2013)
	Variable Pressure Scanning Electron Microscopy (VPSEM) Study of surface morphological changes on the samples after coating the powder with gold	Islam *et al.* (2013)