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# Decomposition Of Calcium Carbonate In Cockle Shell: Study On Calcination Temperatures

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**DECOMPOSITION OF CALCIUM CARBONATE IN COCKLE SHELL: STUDY ON  
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**JULY 2021**

**DECOMPOSITION OF CALCIUM CARBONATE IN COCKLE SHELL: STUDY ON  
CALCINATION TEMPERATURES**

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## DECLARATION

I declared that this report is my original work and all references have been cited adequately as required by the University.



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## **DEDICATION**

A special dedication to my beloved mother (Sharifah Mazian binti Syed Nordin), father (Ahmad bin Halip) and family members that always inspire, love and support me. I also give special thanks to Dr. Nadia Razali, Mrs. Nurhanim Zulaikha binti Kamarulzaman, my friends and fellow technicians for the endless support, guidance, and tips to help me finish this project splendidly. Thank you for all your love, support, care, and belief in me.

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## ABSTRACT

The most common application of the calcination process, known as thermal decomposition, was the decomposition of limestone (Calcium Carbonate,  $\text{CaCO}_3$ ) into lime (Calcium Oxide,  $\text{CaO}$ ) and carbon dioxide,  $\text{CO}_2$ . The cockleshell composition was investigated in this study as an alternate source of  $\text{CaCO}_3$ . The ideal condition for calcination of cockle shells was studied under two parameters: particle size (granules and powder) and temperature (600, 675, 700, 750, 800, 825, 900) °C. Besides that, the chemical and physical characteristics of the raw and calcined samples were studied. The Fourier-Transform Infrared Spectroscopy (FTIR) was used to analyze the presence of  $\text{CaCO}_3$  and  $\text{CaO}$ . The Ca-O peak is detected at around 710  $\text{cm}^{-1}$ . The regression analysis on the percentage of mass loss after calcination and the percentage of  $\text{CaO}$  obtained showed that only the manipulation of temperature significantly affects the thermal decomposition process in getting optimum conditions for  $\text{CaO}$ . Based on this study, the ideal temperature calcination process for the cockle shell is 893.9°C.



## ABSTRAK

Aplikasi paling biasa bagi proses pengkalsinan atau dikenali sebagai penguraian terma, ialah penguraian batu kapur (Kalsium Karbonat,  $\text{CaCO}_3$ ) kepada kapur (Kalsium Oksida,  $\text{CaO}$ ) dan karbon dioksida,  $\text{CO}_2$ . Komposisi kulit kerang telah dikaji dalam kajian ini sebagai sumber alternatif  $\text{CaCO}_3$ . Keadaan ideal untuk pengkalsinan cengkerang kerang dikaji di bawah dua parameter: saiz zarah (butiran dan serbuk) dan suhu (600, 675, 700, 750, 800, 825, 900) °C. Selain itu, ciri kimia dan fizikal sampel asli dan terkalsin telah dikaji. Spektroskopi Inframerah Transformasi Fourier (FTIR) digunakan untuk menganalisis kehadiran  $\text{CaCO}_3$  dan  $\text{CaO}$ . Puncak Ca-O dikesan pada sekitar  $710\text{ cm}^{-1}$ . Analisis regresi terhadap peratusan kehilangan jisim selepas pengkalsinan dan peratusan  $\text{CaO}$  yang diperolehi menunjukkan hanya manipulasi suhu adalah signifikan dalam mempengaruhi proses penguraian terma dalam mendapatkan keadaan optimum bagi  $\text{CaO}$ . Berdasarkan kajian ini, proses pengkalsinan suhu yang sesuai untuk kulit kerang ialah 893.9 °C.

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## LIST OF ABBREVIATIONS

<b>CaCO<sub>3</sub></b>	Calcium Carbonate
<b>CaOH</b>	Calcium Hydroxide
<b>CO<sub>2</sub></b>	Calcium Dioxide
<b>H<sub>2</sub>O</b>	Water
<b>CSG</b>	Cockleshell granule
<b>CSP</b>	Cockleshell powder
<b>TGA</b>	Thermogravimetric Analysis
<b>XRD</b>	X-Ray Diffraction



## CHAPTER 1

### INTRODUCTION

#### 1.1 OVERVIEW

*Anadara granosa* (Linnaeus, 1758) is the scientific name of blood cockle, important aquaculture species in Southeast Asia. According to the Malaysian Department of Fisheries, blood cockles covered approximately 70% of shellfish culture production in 2017. The strong demands for cockles in the food business are their supply availability, delicious taste, nutritional content, and inexpensive cost (Smellie, 2012).

However, the aquaculture industry's enormous production of cockles will increase waste production because more undesirable cockle shells will be abandoned. The garbage generated will impact the environment and contaminate the environment. One of the significant problems caused by abandoned cockle shells is a foul odour that disturbs the surrounding area (Rashidi et al., 2011).

Furthermore, the Solid Waste Management and Public Cleansing Corporation (SWCorp), according to a study published by Berita Harian Online on 2 January 2020, estimates that Malaysians produce 38142 tonnes of waste per day. On that basis, it was calculated that a Malaysian produce approximately 1.17kg of garbage every day. Food trash accounted for 16 973 tonnes, or 44.5% of the total garbage, with waste cockle shells estimated to be one of the food wastes created.

Before this, the cockleshell will be discarded because it has no market value and cannot be utilized to produce anything. However, a recent study discovered the cockleshell's applications. According to a prior study, CaCO<sub>3</sub> made up most of the cockleshell's composition. Therefore, the cockle shells contain a high amount of CaCO<sub>3</sub>, about 95% (Suteu et al., 2011). Furthermore, a prior study discovered that this untreated waste cockleshell could be used as a biomass source for bone healing material (Mokhtar, 2009). This bone-repair substance was created with cancer patients in mind.

The CaCO<sub>3</sub> in the waste cockle shell can be decomposed to become calcium oxide. The equation for the cockleshell decomposition process, also known as CaCO<sub>3</sub> decomposition, is shown in Equation 1.



The decomposition of CaCO<sub>3</sub> into CaO via thermal is called the calcination process. CaO will be employed in various applications, including glass manufacture, agriculture, wastewater and sewage treatment, construction materials, and more (USDA, 2009). Because it is an endothermic reaction, this calcination process favours high temperatures. Low CaCO<sub>3</sub> decomposition pressure is required for a forward equilibrium process (Stanmore & Gilot, 2005).

This research investigated the calcination process using various factors, including sample particle size, contact duration (hour), and temperature (°C). As a result, numerous factors will be employed to determine the optimum calcination condition during the experiment.

## **1.2 RESEARCH BACKGROUND**

The majority of garbage produced globally comes from various sources, including home, industrial, agricultural, and aquaculture. Some trash can be recycled and reused, while the non-recyclable material will be disposed of in landfills. For example, Malaysia's solid waste management said that just 5.5% of garbage would be recycled, while the remaining 94.5% would be disposed of in landfills (Hoo et al., 2017).

Seashells from the food industry are waste that is commonly discarded and disposed of in landfills. Recent research has discovered that seashells contain a significant amount of  $\text{CaCO}_3$ , which can be used for various reasons. Cockles, oysters, scallops, and mussel shells are among the seashells studied, as are their applications. Each country might use a different type of shell according to the abundance of the species in their country. According to a recent study by Malaysian researchers, calcined cockle shells could be used as biomaterials in creating bone scaffolds (Penny Goerge et al., 2019). In addition, Maryam Muhammad Mailafiya et al. (2019) discovered cockle shell-derived calcium carbonate (Aragonite) nanoparticles that could be useful in nanomedicine.

The potential of seashells as a raw material has been extensively researched. The summary of the uses of these seashells for various purposes ranging from cement to fertilizers is listed in Table 1.1.

**Table 1.1** The simplified utilization of seashells in other countries

Type of seashells	Uses	Country	Researchers/Citation
Cockleshell	The potential as biomass resource that can be used for the bone repair composition for cancer patients	Malaysia	Mokhtar (2009)
	The findings on cockle shell-derived calcium carbonate (Aragonite) nanoparticles that help in nanomedicine		Maryam Muhammad et al., 2019
	The cockleshell is the potential biomaterial in bone scaffold fabrication.		Penny Goerge et al., 2019

Oyster shell	The oyster shell powders can be used for water quality improvement of the lakes by algal blooms removal.	Korea	Jae-Hoon Huh et al., 2016.
	The oyster shells can be reused to manufacture an artificial stone in tabletops and workbenches.		Thamyres H. Silva et al., 2018.
	The calcined oyster shell can be used as a novel eco-friendly antimicrobial agent for packaging.		Kambiz Sadeghi et al., 2019
Scallop shell	The calcined scallop shell can be used as a disinfectant, an antibacterial agent, fungicide, dioxin, and a formaldehyde inhibitor.	Japan	Kauyuki & Masami, 2001.
	The compressive strength of concrete.		Sugiyama, 2004
Mussel shell	Reused to transform into high purity calcium carbonate to obtain commercial value-added product	Spain	Barros et al., 2009
	The production of mussel waste-derived mortars is found.		Ballester et al. 2007

Based on Table 1.1 above, the Korean researcher has investigated the uses of waste oyster shell powders for water quality improvement of the lakes by algal blooms removal (Jae-Hoon Huh et al., 2016). Besides, Japanese researchers have found the uses of calcined scallop shells as a disinfectant and an antibacterial agent, and many other uses (Kauyuki & Masami, 2001). In addition, the studies from Spanish researcher has found the benefits of mussel shells by reusing and transforming them into high purity calcium carbonate to obtain the commercial value-added product (Barros et al., 2009). These are some of the findings on using the varied type of wasted shell of shellfish from different countries.

### 1.3 PROBLEM STATEMENT

Limestone and granite are the two most common quarry rocks found in Malaysia. Limestone is the primary raw material in cement, chalk, rubber paint, and plastics (Wan Ibrahim, 2009). The limestone consists of  $\text{CaCO}_3$ , usually obtained by mining and land excavation.

The resources of the limestones are abundant throughout Malaysia. According to Malaysia's Department of Minerals and Geoscience (2015), Kedah, Perlis, Perak, Selangor, Sabah, Kelantan, and Negeri Sembilan have 30 480 million tonnes.

Even Malaysia has abundant limestones resources; this resource may be depleted. These resources' long-term viability and availability may dwindle over time. The demand for cement and other products that use limestone as a raw material is expected to increase limestone consumption. For example, the uncontrolled production in Lembangan Langat in 2005 can lead to the extinction of the limestone resources (Wong et al., 2005). The state will have to import limestone from other states, which will increase the cost of the project, including transportation costs.

Furthermore, the diminishing mineral supplies, mainly limestone, have prompted researchers to investigate alternative raw materials or develop synthetic compounds to replace and limit the usage of natural resources. Some examples are synthetic gypsum as raw material to create blocks that can be used in the construction (Lushnikova & Dvorkin, 2016) and silica powder to replace the types of cement (Bent et al., 2017). However, a limited number of synthetic compounds can be employed, and researchers continue to investigate the efficacy, availability, and repercussions of using these synthetic chemicals.

Other than that, Malaysia is known for its richness of cockle production (*Anadara Granosa*), which could reach a thousand tonnes per year. Data from Awang-Hazmi et al. (2007) studies suggest that Malaysia has an abundance of marine species of cockle, where the intertidal mudflats at coastal regions in the West Coast of Malaysia are known as their habitat. This cockle meat will be consumed as food while the

cockleshell will be dumped as waste. According to Cox (2009), these by-products are discarded because they have no commercial values.

The excess of cockle production, on the other hand, might result in a lot of cockle shell waste, which can generate many difficulties for society and the community. Wasted cockle shell, for example, is a source of environmental concern in coastal areas and landfills, according to Nor Hisham (2017) and Nor Hazurina (2012). Besides, decreasing the water quality due to the inappropriate disposal method can affect the growth of shellfish (Folke & Kautsky, 1989).

Moreover, untreated cockle shell that has been left untreated for a lengthy time and disposed waste cockle shell can emit an objectionable odour into the environment and surroundings. The deterioration of the cockle meat or the microbial decomposition of salts into gases like ammonia, hydrogen sulphide, and amines caused the foul odour. (Mokhtar, 2009; Hamester et al., 2012).

The study of the application of this waste cockle shell to produce beneficial material for the goods will reduce the number of waste cockle shells at the landfills.

#### **1.4 RESEARCH AIM, OBJECTIVES, AND HYPOTHESIS**

This research aims to study the best conditions to obtain optimum calcium oxide from a calcined cockle shell.

##### **1.4.1 OBJECTIVES**

These are the two main objectives of this research. The objectives are:

- 1) To analyze the physical (proximate analysis: pH, bulk density, ash, fixed carbon, moisture content, volatile matter ) and chemical characteristics (FTIR, TGA, XRD) of the raw and calcined cockle shells. The cockle shells will be calcined based on varying parameters at the constant mass (20g) for 4h of the contact hour;
  - particle size (cockle shell granule and cockle shell powder)

- temperature (600°C, 675°C, 700°C, 750°C, 800°C, 825°C and 900°C )
- 2) Predicting and optimizing the CaO yield from the calcination process of waste cockle shell with statistical analysis such as regression analysis with response optimization

#### **1.4.2 HYPOTHESIS**

There are two hypotheses of this research. The hypothesis is:

- 1) The increase in the particle size of the cockleshell sample increases the mass loss of the sample. This situation occurs because the cockleshell powder will be compacted while there will be some opening surface for the granule due to the uneven surface. This caused the cockleshell granule to have a larger surface area turned into ashes (CaO), resulting in the high weight loss for the sample. Thus, the calcined cockle shell granule will lose high weight instead of cockle shell powder.
- 2) The increase in temperature increases the mass loss of the sample. This situation occurs as the higher temperature sample produces higher heat produce which causes the cockleshell sample to be turned into ashes (CaO), resulting in the high weight loss for the sample. Thus, there will be a Ca-O bond present at temperatures 800° C and 900° C in the FTIR analysis spectrum for calcined cockle shells.

#### **1.5 SCOPE OF STUDY**

This research only studies the blood cockles in *Anadara Granosa'* family because the study only considers one of the types of cockles in Malaysia. However, the study also includes calcination using a Thermal Gravimetric Analyser (TGA), Fourier transforms infrared (FTIR) spectrophotometer characterization, phase identification of a crystalline material, and calcium determination oxide neutralization.

## **1.6 SIGNIFICANCE OF STUDY**

This research set out to study the effectiveness of calcined cockle shells as a potential alternative for raw materials. Most cockle shells will be discarded as food waste because people usually think that the cockle shells have no value and cannot serve any purpose anymore. Therefore, it is hoped that this research will contribute to a deeper understanding of the cockleshell potential as a raw material candidate, thus helping reduce the amount of cockle shell waste, especially in the dumping area. Therefore, this study will play a critical role in creating a cleaner environment and lesser pollution caused by the food and aquaculture industry. Besides, this study also will help the ill effect on the environment due to the continuous and unending quarrying and mining process in Malaysia.

## **1.7 THESIS STRUCTURE**

This thesis consists of five chapters. Chapter 1 initiates the general view regarding the significances of using cockleshell in obtaining calcium oxide and the research background related to utilizing the shellfish. Besides, some problem statements give the general idea regarding cockleshell as one of the sources of food waste, the depletion of the natural resource (limestone), and the lack of the foundations on the chemical-based calcium carbonate. Therefore, the significance of this research is on utilizing food waste in the preparation of biomaterial and as an alternate way of obtaining calcium oxide. Following this, there are two objectives whereby the main aim is to get the optimum conditions for the calcination of the cockle shells.

Chapter two reviews the literature related to the characterization of calcium carbonate derived from cockle shells as its raw material. The study starts with the statistic of the production of cockles in Malaysia and its habitat. Following this, the mineralogy of lime is also being discussed in this chapter. The cockleshell's composition is also discussed in this chapter. This chapter also includes a review of the literature from other researchers on the analysis employed in this study.

Chapter 3 provides the details of the methodological approaches employed for this research. The methodology in conducting this research categorizes by phase by phase, which begins with the procurement of raw material and pre-treatment of raw materials. Next, the TGA analysis is included before the calcination process. Finally,



the analysis for the result involves chemical characterization, which includes FTIR, XRD, and neutralization with acid.

Chapter 4, as the core of the thesis, provides the discussion for the results and data acquired from chapter 3 with the literature of earlier studies as reference. Lastly, the finding from this study is concluded in chapter 5. Finally, any relatable recommendation for improving this research is also mentioned.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 COCKLE

##### 2.1.1 BLOOD COCKLE IN MALAYSIA

In general, the cockle is called kerang by the Malaysian. One cockle species is the blood cockle (*Anadara granosa*), containing haemoglobin red bodily fluid. This type of blood cockle is a marine species that belongs to the *Arcidae* family (Suwanjarat et al., 2019). According to Awang-Hazmi et al. (2007), this cockle inhabits intertidal mudflats of coastal regions in the Southeast Asian Coast ranging from Thailand, the West Coast of Malaysia, and Indonesia. Besides, this species was distributed in Northern Australia, the Middle East, Southeast Asia, East Asia, and South Asia (Faulkner, 2010). One of this cockle's habitats in Malaysia is the Matang mangrove (Man et al., 2012; Tatsuya et al., 2014)

To date, several studies have investigated this type of cockle every year regarding the habitats, the factor that affects their production, the uses of their shell waste, and many more. For example, Munawar Khalil (2013) studied the reproductive cycle of the cockle that was conducted at three different muddy areas, such as Pulau Pinang (Malaysia), Banda Aceh (Indonesia), and Lhokseumawe (Indonesia) from June 2009 to September 2010. Besides, Yurimoto et al. (2014) have studied the factors contributing to the mass mortality event of the cockle that happened in aquaculture ground in Selangor in mid-February 2012.

Moreover, Watanabe (2009) research has established that the blood cockle is an important species for the bivalve aquaculture industry due to its famous food in

Southeast Asia. Due to the abundance of cockle production, the people can easily use them in the meals and cuisines such as char kuey teow, coconut gravy ('Masak lemak) or the boiled cockle can also be eaten with the Tamarind juice. Every year, the consumption of the cockle in Malaysia can reach 50% of its local production (Food and Agriculture Organization, 2015). This cockle is also a cheap protein source widespread in Thailand (Monnat et al.,2020).

The marine aquaculture operations of cockles on the West Coast of Malaysia in 2019 are summarised and given in Table 2.1 (Department of Fisheries in Malaysia, 2020).

**Table 2.1** The reports regarding cockle productions and the culturist (DOFM,2020)

STATES	COCKLE PRODUCTION (TONNES)	CULTURED AREA (HECTARE)	NO. OF CULTURIST
SARAWAK	3.1	0	0
JOHOR	516.07	1,451	13
SELANGOR	330.68	2,383	50
PERAK	10,503.03	2,466	115
PULAU PINANG	2,418.87	882	34
KEDAH	0	63	4
<b>TOTAL</b>	<b>13,771.74</b>	<b>7,245</b>	<b>216</b>

Based on Table 2.1, the total cockle production in Malaysia by the end of 2019 is 13,771.74 tonnes. Perak is the state with the most significant cockle production, which produced 10,503.03 tonnes of cockles. Perak also is the central cockle cultivation area which involves an area of 2,466 hectares with 115 culturists.

The data regarding the price in Malaysia for each type of seashells from Fisheries Development Authorities of Malaysia (2019) in Table 2.2 below show that the price for the cockle shell is lower than other types of seashells.

**Table 2.2** The price for each type of seashells provided by the Fisheries Development Authorities of Malaysia (2019)

Type of seashells	Price (RM/kg)
Cockle	13.00
Bamboo clams	19.90
Mussel	40.00
Scallop	128.00
Abalone	290.00

Based on Table 3, the price for cockle in 2019 is RM13/kg. However, the price might differ in some regions due to the availability.

### **2.1.2 COCKLESHELL STRUCTURE**

The cockleshell has an oval form and is quite thick, measuring about 2mm in thickness. The cockleshell is typically 45-60 mm long and 35-50 mm broad on average. The cockleshell's outer structure is white to yellowish-brown, while the interior is white.

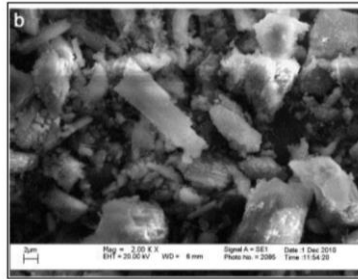
### **2.1.3 COCKLE SHELL COMPOSITION**

In its most prevalent form, Calcium carbonate, limestone, is one of the most abundant minerals found worldwide. Furthermore, previous research has shown that the crustacean shell is primarily composed of calcium carbonate, in addition to limestone (Sy-Mohamad et al., 2016).

According to Chen and Xiang (2009), calcium carbonate polymorphs are classified into three types: calcite, aragonite, and vaterite. These polymorphs can also be distinguished based on their characteristics (Shafiu Kamba, et al., 2013). For example, the calcite crystal is thermodynamically stable under ordinary settings, but the aragonite crystal is a high-pressure polymorph that is less durable than calcite. In addition, the vaterite can shift into two additional polymorphs simultaneously, making it the least stable.

According to Nor Hisham et al. (2017), the limestone comprises calcite crystal, the most stable  $\text{CaCO}_3$  polymorphism, while the cockleshell is made up of aragonites crystal.

The previous statement from Nor Hisham et al. has supported the study from Nurul et al. (2011), Zubaidi and Tabakhah (2015). They have clarified that the raw cockle shell comprises aragonite by analysing its crystal structure using XRD. Figure 2.1 shows the surface morphology of the cockle shells powder obtained by Nurul.



**Figure 2.1** The surface morphology of the cockle shells powder (Nurul et al., 2011)

#### 2.1.4 COCKLE SHELL UTILIZATION

The previous study from many researchers has found many uses of the cockleshell in various fields. Some of the founding in last years (2010-2019) summarize in Table 2.3 below.

**Table 2.3** The list of the researchers and their founding

RESEARCHERS/YEAR	FOUNDINGS
Taboada et al., 2010	The study shows that cockleshell contains enough calcium content that can help to balance the pH levels of soil, improves the nitrate uptake of the plant, and strengthens plant cell walls
Lertwattanakruk, et al., 2012	The ground cockleshell can be used as cement replacement to save cost due to the presence of aragonite. In addition, the calcite crystals in cockleshells have higher strength and densities compared to limestone.
Mohammed, et al., 2014	The current treatment to remove dyes from wastewater uses physical or chemical treatments such as membrane filtration and reverse osmosis. However, most of the treatment is not applicable at a large scale because of expensive costs
Moideen et al., 2015	The uses of crushed cockle shells to reduce the chemical oxygen demand (COD) in wastewater treatment.
T. Singhasiri et al., 2016	The uses of cockle shells as heterogeneous solid catalysts for a transesterification reaction to produce biodiesel from food processing waste oil

Y. Tiandho et al.,2018	As a natural coagulant, wasted cockle shells behave as a bio sorbent and a neutralizer of polluted water in Bangka Belitung Islands, Indonesia.
Faridah Ghafar et al., 2019	The utilization of calcium oxide derived from waste cockle shell as the heterogeneous base catalyst to produce bio lubricant from waste cooking oil (WCO) as the feedstock

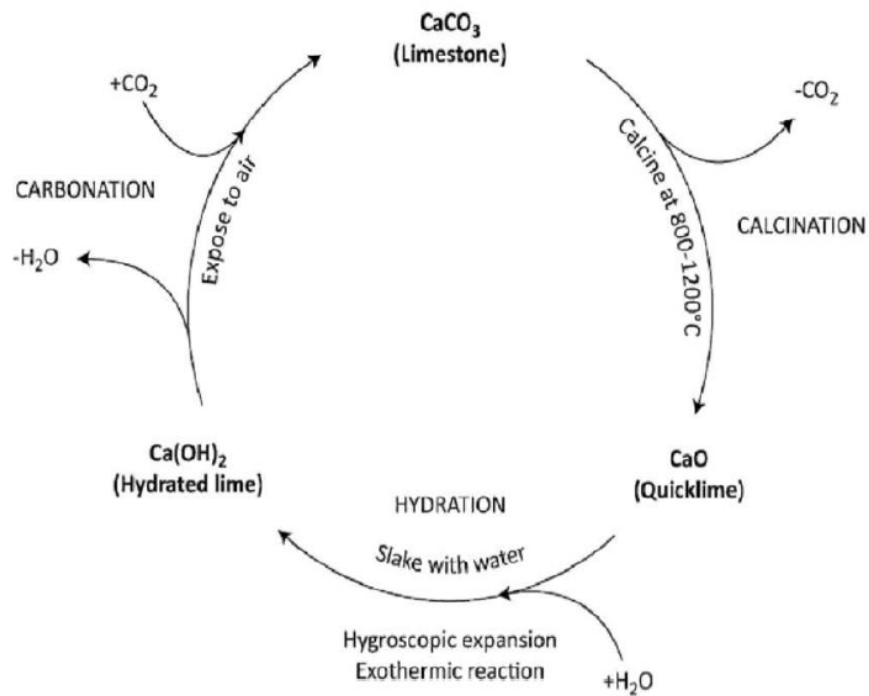
In the same vein, the recent study from S.Murugan et al. (2020) found that the crushed and uncrushed cockle shells were used as a replacement material for coarse aggregate in preparing M40 grade eco-concrete.

## 2.2 CALCIUM CARBONATE

Calcium carbonate,  $\text{CaCO}_3$ , makes up the majority of the cockleshell. As a result, it could be used as an alternative raw material to limestone, such as a biomaterial for tissue engineering (Hemabarathy et al. 2014; Mohamed et al. 2012).  $\text{CaCO}_3$  may also be easily transformed into biocompatible nanoparticles for application in medical, pharmaceutical industries, and drug delivery systems, thanks to the current focus on nanotechnology (Fukui & Fujimoto 2012).

Besides, the limestone and  $\text{CaCO}_3$  synthesize through the reversible calcination-carbonation process (Rashidi et al., 2011). Calcination is an endothermic reaction that utilises much energy at a high temperature. Thus, calcium carbonate synthesizes calcium oxide ( $\text{CaO}$ ) and carbon dioxide ( $\text{CO}_2$ ). When the  $\text{CaO}$  obtained from the calcination process reacted with water for the hydration process, the slake or hydrated lime, calcium hydroxide ( $\text{Ca(OH)}_2$ ), will be produced.

Then, the presence of  $\text{CO}_2$  in the surrounding will cause the carbonation process to occur. The final  $\text{Ca(OH)}_2$  and  $\text{CO}_2$  reactions are  $\text{CaCO}_3$  and water. When the carbonation occurs, the lime cycle process will be closed by returning to its starting point. The lime cycle of the calcium carbonate process is shown in Figure 2.2 below.



**Figure 2.2** The lime cycle of calcium carbonate (Schotsmans et al., 2012)

### 2.3 REVIEW OF $\text{CaCO}_3$ CHARACTERIZATION

Many methods can characterize the  $\text{CaCO}_3$  and  $\text{CaO}$  of the samples containing  $\text{CaCO}_3$ . For example, a transmission electron microscope (TEM), an energy dispersive X-ray analyser (EDX), X-ray diffraction (XRD), scanning electron microscopy equipped with energy dispersive Xray (SEM-EDX) and Fourier transmission infrared spectroscopy (FTIR).

The summary and comparison of a few ways in  $\text{CaCO}_3$  characterization are shown in Table 2.4 below.

**Table 2.4** The comparison of a few ways in CaCO<sub>3</sub> characterization

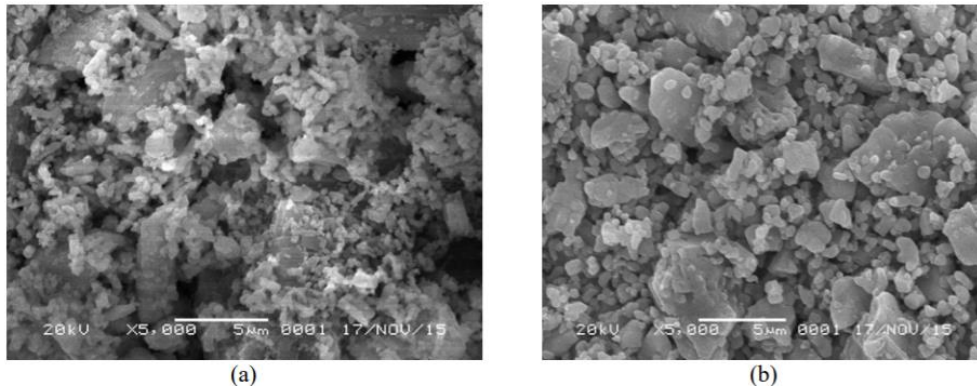
METHODS/ ANALYSIS	OBJECTIVE	EXPECTED FINDINGS	RESEARCHER
Variable pressure scanning electron microscopes (VPSEM)	The surface characterization of a wide range of materials	Study surface morphological changes on the sample after coating the powder with gold.	Islam et al., 2013
X-ray diffraction (XRD)	To analyze the crystal structure shown by the shell, which is made up of aragonite	The waste cockle shells contain one of the polymorphs of CaCO <sub>3</sub> , which is aragonite	Mohamed et al., 2012
		The composition of uncalcined cockle shell mainly consists of CaCO <sub>3</sub> with the absence of peak of CaO.  The composition of calcined catalyst consists of the CaO when the temperature is at and above 700°C.	Boey et al. (2011)
Energy-dispersive X-ray analyser (EDX)	While the scanning electron microscopy equipped with energy dispersive X-ray (SEM-EDX) is the analysis of determining the structure and elemental composition of the shell	SEM results showed that aragonite have a needle-like structure and the the structure changed after the calcination process.  EDX results showed that calcium carbonate was existent, but the proportion changed after the calcination process.	Mohamed et al., 2012
Fourier transmission infrared	To reveal the presence of	The FTIR spectrum of the calcined commercial CaCO <sub>3</sub> and the calcined eggshell showed the	Witoon (2011)



spectroscopy (FTIR)	CaCO <sub>3</sub> groups in shell	<p>exact wavenumber of 500 cm<sup>-1</sup>, which shows that the calcined commercial CaCO<sub>3</sub> and the calcined eggshell have a very similar chemical nature.</p> <p>Calcium oxide is the most abundant component in calcined eggshells, about 97.4%.</p> <p>The existence of the calcium carbonate is confirmed by the relation to the high amount of calcium oxide in the calcined eggshell.</p>	
Brunauer–Emmett–Teller (BET)	The measurement of the specific surface area of materials	<p>An adsorbent with a high surface area would have a better adsorption capacity because it had a higher contact area.</p> <p>The existence of impurities clogged the material's surface and reduced the material surface area.</p> <p>The activation process could remove the impurities. Ex: Calcination</p>	Lia et al.; 2020
Thermo Gravimetric Analysis (TGA)	Thermal analysis of the cockleshell sample during the calcination process	The optimal point for cockleshell basically at 850°C, time of 40 min, a heating rate of 20°C/min and size < 0.125mm	Rashidi et al., 2011

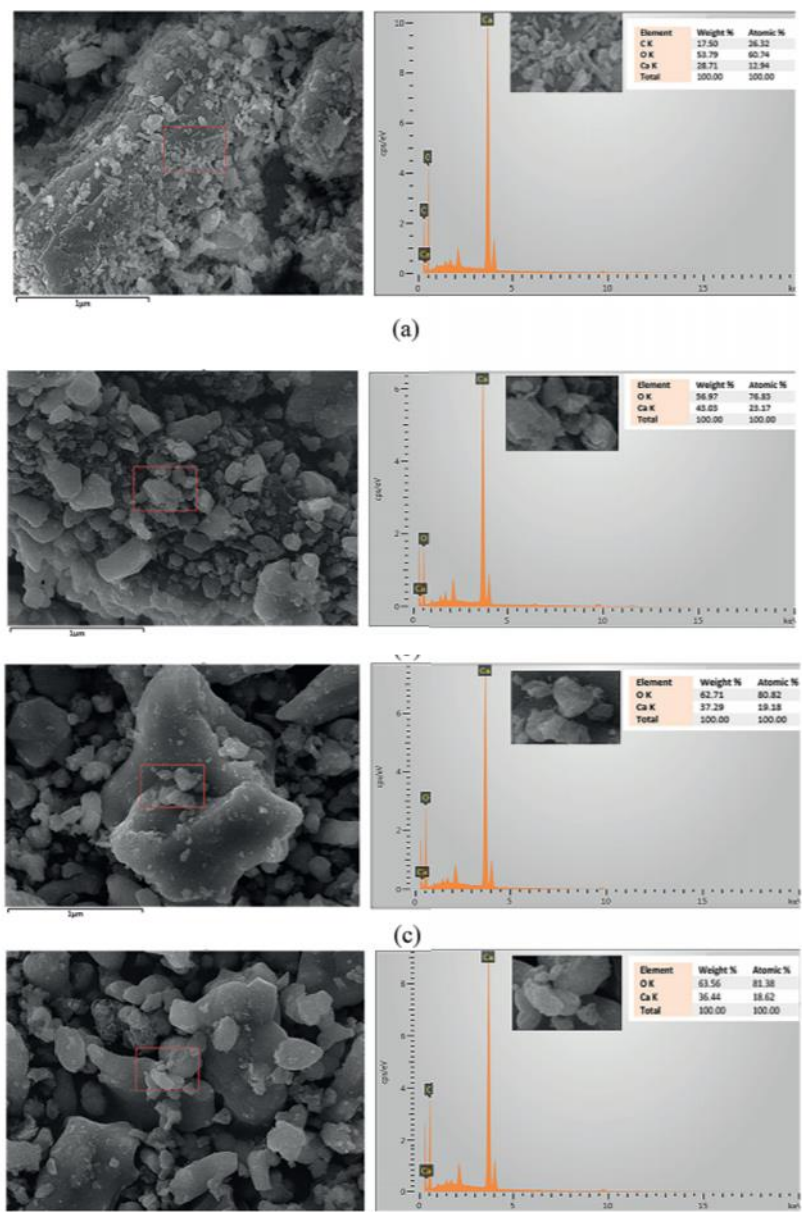
Based on the summary from the table above, many ways can be used in the CaCO<sub>3</sub> characterization. One of them is the scanning electron microscope (SEM), a standard method for imaging the microstructure and morphology of the materials. For example, the SEM morphology of dried Biogenic Cockleshell (BCS) and heat-treated

BCS powders at 500°C are shown in Figure 2.3 from Asmi and Zulfia (2017). The heat-treated BCS sample had a cubic-like morphology with an average grain size of 1.48  $\mu\text{m}$ , whereas the dried BCS sample had a rod-like morphology with an average grain size of 1.85  $\mu\text{m}$ .



**Figure 2.3** The SEM of (a) dried and (b) heat-treated blood cockle shell powder at 500°C

Besides, Sarah Dampang et al. (2021) also found the result for the surface morphology of seashell powder before and after the calcination process where seashells were calcined at the seashells calcined at 800°C, 900°C, and 1000°C. The results are shown in the figure below.



**Figure 2.4** SEM-DEX results for compounds (a) before calcination and after calcination process at (b) 800°C, (c) 900°C, and (d) 1000°C.

Based on Figure 2.4 (a) above, the most dominant elements for the seashells before the calcination were O (52.07%), Ca (27.86%), and C (18.43%). In turn, Figure 2.4 (b) showed that O composition was 56.97% and Ca was 43.03% for the seashells calcined at 800°C. For seashells calcined at temperatures of 900°C and 1000°C, there were no significant differences in O and Ca content.

## **2.4 CALCIUM OXIDE**

Quicklime is a colourless chemical substance made up of calcium oxide (CaO). Nowadays, research focuses on utilising of calcined seashells as calcium oxide substitutes. An example of alternative sources is the shell of the cockles, mussels, crabs, and oysters. According to Mohamed et al., 2021, the calcium oxide that decomposes from CaCO<sub>3</sub> in cockle shells has low impurities compared to the commercial calcium oxide. The reason is that impurities such as silica, alumina, and iron are often contained in commercial CaO.

Based on the study done by Witoon (2011) and Rashidi et al. (2011), calcium oxide was used for the carbon dioxide looping cycle because there are many advantages for using calcium oxide such as the reduction of the energy requirement, have a wide range of potential operating temperatures and so on.

The utilization of calcium oxide in various fields of industries is very established. For example, the use of calcium oxide as a dehydrating agent and absorbent in the chemical industry. Furthermore, the use of calcium oxide as an absorbent has been proven to effectively absorb carbon dioxide based on a few previous studies, such as from Mohamed et al. (2012). He states that calcium oxide is widely used in absorbing carbon dioxide.

According to Boey et al. (2011), the calcium oxide resource from the abundantly available cockle shell can perform as a heterogeneous catalyst in biodiesel production (methyl esters) by using the transesterification process of palm olein.

## **2.5 CALCINATION PROCESS**

In general, the calcination process is where the calcium oxide and calcium dioxide are synthesized from the calcium carbonate in the cockleshell through thermal decomposition. Based on Garcia-Labiano et al. (2002) study, the calcination at atmospheric pressure can be achieved at temperatures 800-900°C due to the lower resistance of external mass transfer. However, after the calcination process, the limestone containing a primary calcium carbonate will lose up to 44% of its original weight (Galván-Ruiz et al., 2009).

According to Chong and Specht's study in 2006, the resistance caused by the particle size of the samples during the calcination process can be minimized by grinding the samples into a millimetre range of particle size.

From the previous study, the factors that can affect the calcination process are temperature, the weight of the samples, the contact time, and the size of the samples.

## **2.6 FACTORS AFFECTING CALCINATION PROCESS**

### **2.6.1 TEMPERATURE**

Some researchers have done many previous studies on how the calcination process's temperature can affect the decomposition of the samples that contain calcium carbonate. According to Rashidi et al. (2011), this calcination process depends on the reaction temperature, defining the qualities of the sorbent. Thus, the temperature for the calcination process should be selected thoroughly when conducting the experimental work.

Mohamed et al. (2012) stated that the calcination process could decompose some fraction of the seashells into calcium oxide. Based on his studies, a rapid weight change happened when the cockle shells powder was calcined at the increasing temperature between 700°C to 900°C. However, there is no change in the weight of the cockleshell when it calcined at 900°C and onwards.

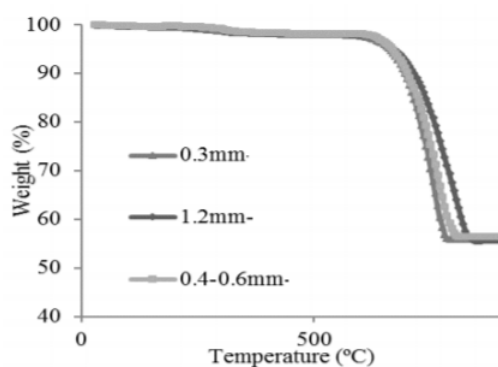
While Boey et al. (2011) study the effect of temperature on the calcination process using Thermal Gravimetric Analysis, temperature ranges from 575–800°C can affect the calcination process where the most decomposition process occurred at temperature 750°C.

### **2.6.2 PARTICLE SIZE**

Other than the temperature and contact time of the calcination process, the particle sizes of the samples influence the reaction rate of cockle shell decomposition.

According to Rashidi *et al.* (2011), the larger the particle size of the cockleshell powder, the slower the weight loss percentage and the lower the calcination rate. Besides that, she also stated that the wider surface area of smaller particle size would go to a higher uptake of heat while promoting decomposition.

Based on SY Mohamad (2016) study, she analyzed three different particle sizes: 0.3 mm, 0.4-0.6 mm, and 1.2 mm at 900 °C to investigate the effect of particle sizes on the calcination process. The results shown in Figure 2.5 is the TG Curve that proved that particle sizes influence the weight loss percentage of the samples tested.



**Figure 2.5** TG Curves for different particles sizes at 900°C and 20°C/min (Sy Mohamad, 2016)

Figure 2.5 shows that smaller-sized particles will have a rapid weight change compared to larger ones.

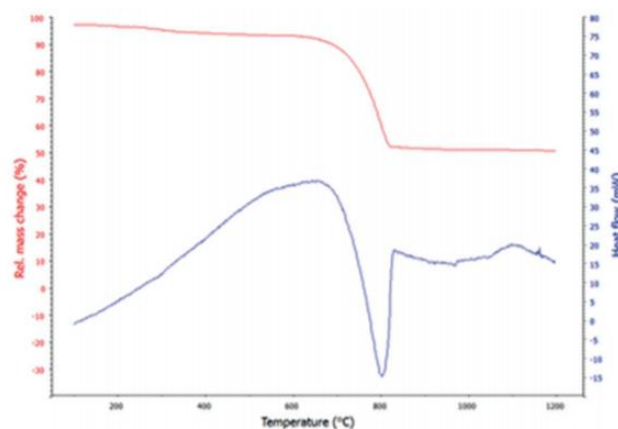
## 2.7 THERMAL GRAVIMETRIC ANALYSIS (TGA)

In general, Thermal Gravimetric Analysis (TGA) can be used in the research to measure the amount and rate of change in the weight of a materials sample as a function of temperature or time in a controlled environment. The data obtained can determine the composition of the materials sample and predict their thermal stability from low temperature until up to 1000°C. Furthermore, due to the decomposition, oxidation, or dehydration of the materials sample selected in this analysis, the weight loss or gain of the material sample can be analyzed.

However, in studying calcination conditions on the decomposition of calcium carbonate in waste cockle shell to calcium oxide, the analysis focuses on the calcination temperature and heating rate. Therefore, a thermal Gravimetric Analyzer can study the reactivity of decomposition of cockle shells (Rashidi et al., 2011; Mohamed et al., 2012).

The performance of the calcination process concerning various temperatures, heating rate, particle size, and duration of time have been studied by Rashidi et al. (2011). From the founding, he concluded that the optimal point to produce calcium oxide from waste cockle shell is basically at the temperature of 850°C, period time of 40 minutes, the heating rate at 20°C/min, and its size below 1.25mm under nitrogen gas flow at 50mL/min. Based on that study, the calcination of sample performance depends on several parameters: the reaction temperature, the duration for the process to take place, the heating rate, and particle size.

Other than that, the study from Sarah Dampang et al. (2021) shows in Figure 2.6 below that a significant change in mass begins to occur around temperatures of 780°C. The release of CO<sub>2</sub> molecules causes CaCO<sub>3</sub> to decompose into CaO, resulting in a mass drop. (Bazargan et al., 2015). The temperature of 800.5°C with a calcination period of 78 minutes gave the most significant mass changes for the seashells. After reaching a temperature of around 900°C, the mass change curve appears to have remained relatively constant. The curve shows that the CaO compound does not change at temperatures between 900°C and 1200°C (Dümichen et al., 2015).

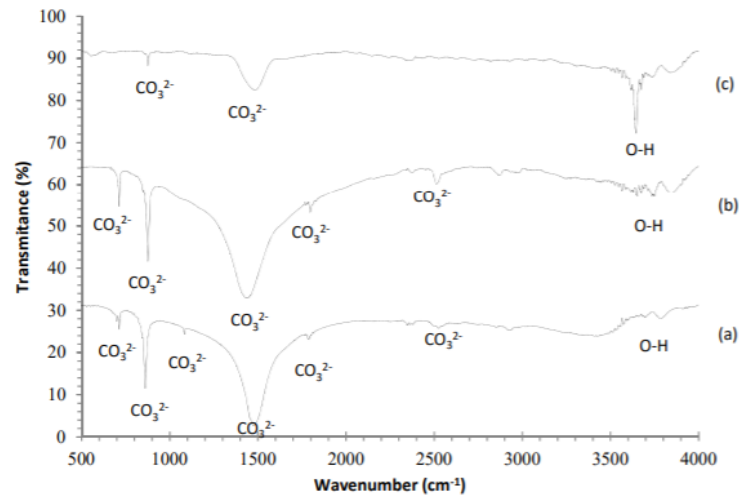


**Figure 2.6** TGA Analysis of calcination process under different temperature





IR spectrum will change with the increase in calcination temperature, similar to Asmi and Zulfia (2017) findings. Figure 2.8 below shows the FTIR spectra from their studies.



**Figure 2.8** FTIR spectra of (a) dried, (b) heat-treated blood cockle shell at 500°C, and (c) heat-treated blood cockle shell at 800°C.

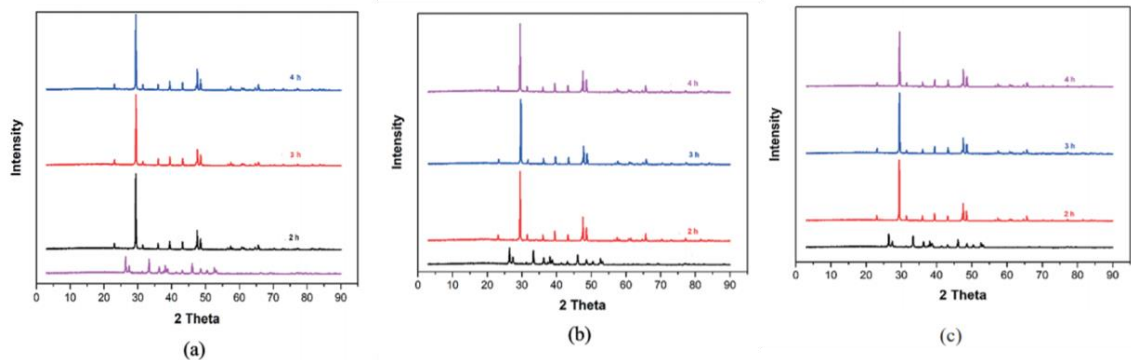
Figure 2.8 (c) shows two small frequency bands at  $876\text{ cm}^{-1}$  and  $1482\text{ cm}^{-1}$ . These peaks are shorter than the dried blood cockle shell sample and heat-treated blood cockle shell at  $500^{\circ}\text{C}$ ; this result can be attributed to the decomposition of  $\text{CaCO}_3$  becoming  $\text{CaO}$  by releasing  $\text{CO}_2$ . Thus, the calcination at the temperature  $800^{\circ}\text{C}$  will produce more  $\text{CaO}$  than the calcination at temperature  $500^{\circ}\text{C}$ .

## 2.9 X-ray Diffraction (XRD)

Some researchers used X-ray Diffraction (XRD) to characterise the calcium carbonate of cockle shells. For example, Wang et al. (2021) conducted the crystallinity analysis using XRD ( $2\theta$  range of  $0\text{--}90^{\circ}$  at a scanning speed of  $1^{\circ}\text{ min}^{-1}$ ). The results from Sarah Dampang et al. (2021) from her studies, Figure 2.9, showed the XRD characterization patterns of seashells before and after the calcination process. The results displayed that calcium carbonate ( $\text{CaCO}_3$ ) was contained in the shells. In the  $\text{CaCO}_3$  phase, the highest peaks are at angles of  $29.4^{\circ}$ ,  $39.4^{\circ}$ ,  $43.2^{\circ}$ ,  $47.5^{\circ}$ , and  $48.5^{\circ}$ .

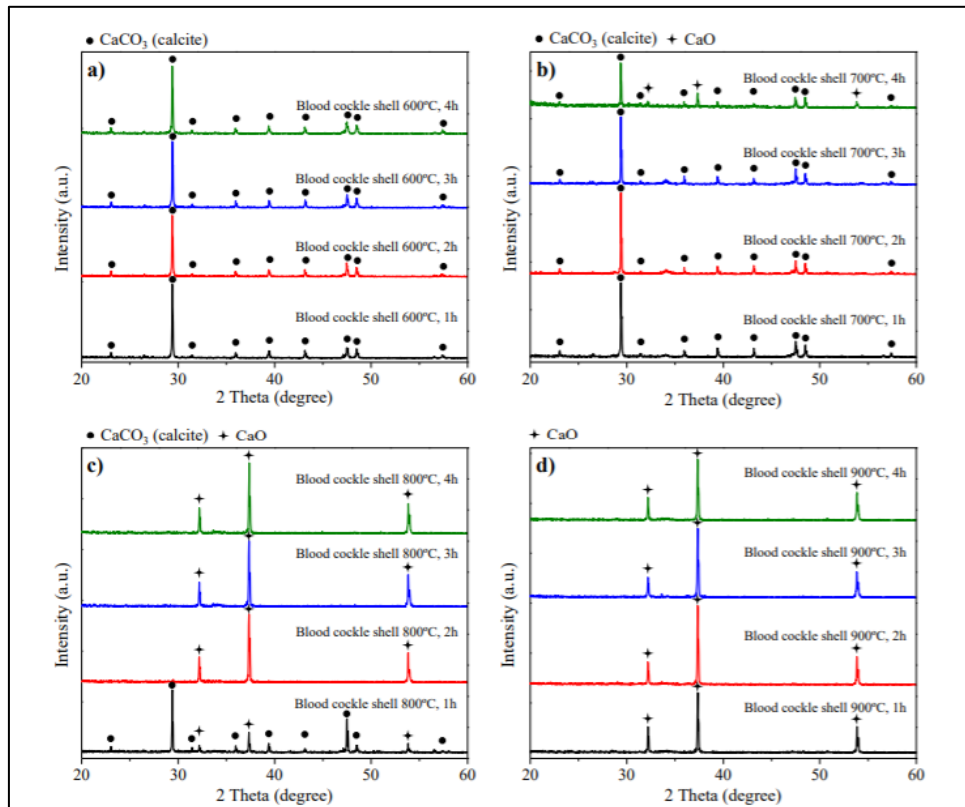
Meanwhile, the  $\text{CaO}$  phase with a minimal intensity is at the angle of  $58.1^{\circ}$  and  $64.6^{\circ}$ . The appearance of the  $\text{CaO}$  phase was obtained because several  $\text{CaCO}_3$  compounds have changed phase after the calcination process (Berent et al., 2019).

The XRD results indicated that temperature and calcination time variation did not have a significant effect because the obtained peaks were almost the same.



**Figure 2.9** XRD results for compound before and after calcination process at 800°C, 900°C, and 1000°C.

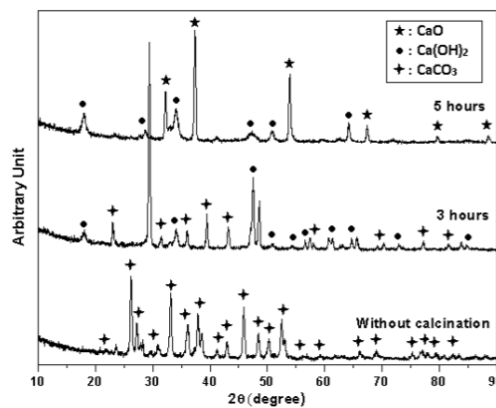
Based on Teerawat et al., (2018) study, only the characteristic peaks associated with the CaO phase were observed in the XRD results when the calcination temperature was at 900°C for all holding periods. This result can be seen in Figure 2.10 below.



**Figure 2.10** The XRD patterns of blood cockle shell after calcination at (a) 600°C, (b) 700°C, (c) 800°C and (d) 900°C with various holding times. (Teerawat et al., 2018)

The XRD results show the characteristic peaks associated with the complete disappearance of the  $\text{CaCO}_3$  phase after calcination at  $800^\circ\text{C}$  for 2 hours. Besides, the calcite and amorphous are entirely formed from aragonite at  $600^\circ\text{C}$  and  $800^\circ\text{C}$ , respectively. Thus, it indicates that temperature and holding time were essential for the calcination process.

The findings by Teerawat also was similar to the results by Y Tiandho et al. (2018), as shown in Figure 2.11. The cockleshell contains only the  $\text{CaCO}_3$  phase in the aragonite structure before the calcination. After calcination at  $700^\circ\text{C}$  for 3 hours, the  $\text{CaCO}_3$  compound becomes calcite, and some  $\text{CaCO}_3$  begins to decompose into calcium oxide. Aragonite phase changes to calcite due to heat treatment have also been observed by Parker (2010). In 5 hours, the entire  $\text{CaCO}_3$  compound has been decomposed into calcium oxide for calcination.



**Figure 2.11** XRD diffraction pattern of cockle hell: before and after calcination

## **CHAPTER 3**

### **METHODOLOGY**

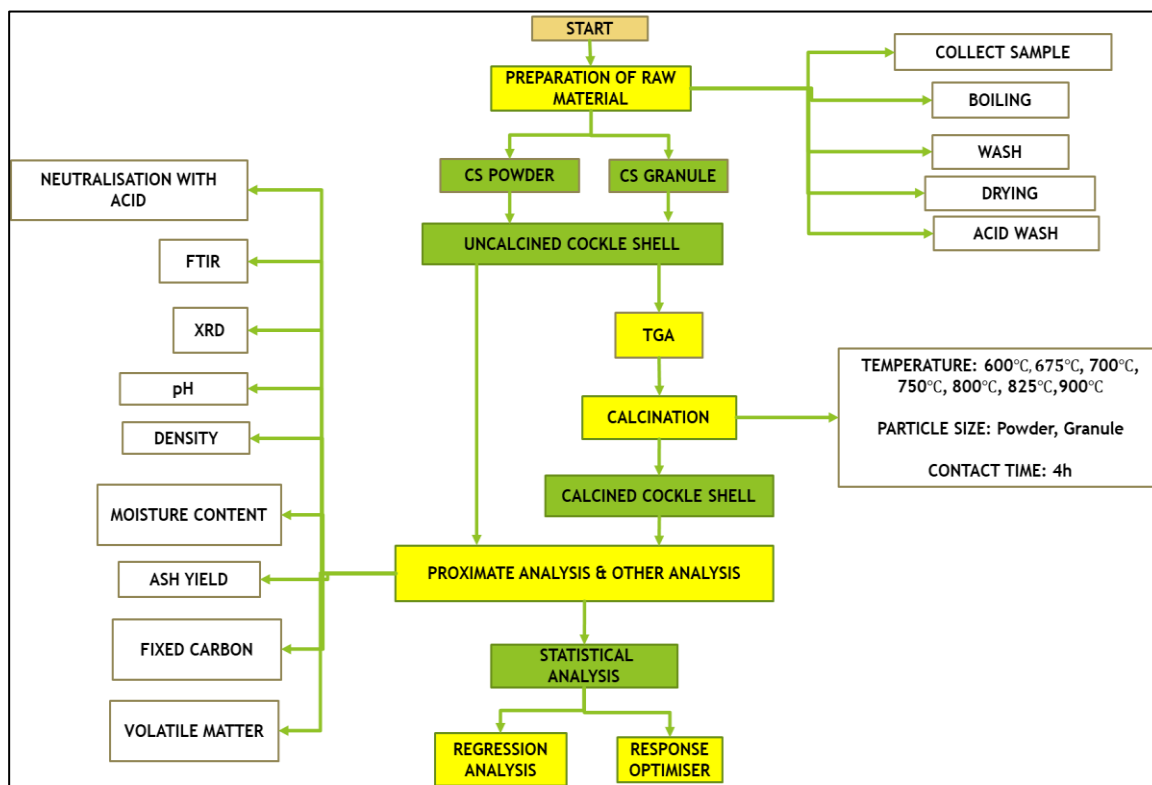
#### **3.1 OVERVIEW**

In this section, the procedures are explained based on the five phases of the experiment.

- The first phase: to collect the cockleshell and undergo a pre-treatment process.
- The second phase: the cockleshell is ground and separated to get cockle shell powder and cockle shell granule.
- The third phase: the sample were undergone thermal gravimetric analysis. Then, the cockle shell powder and cockle shell granule were calcined
- In the fourth phase: the physical and chemical characteristics of the uncalcined and calcined cockle shells sample will be determined under proximate analysis. Moreover, in this phase, the infrared spectrum of absorption and the emission and phase identification of the crystalline material is measured.
- The fifth phase: all data taken and tabulated in the tables were used for statistical analysis using regression analysis and response optimizer. At the same time, response surface methodology was done to determine the optimum conditions for extracting chitosan from the cockle shell.

### 3.2 THE RESEARCH WORK FLOWCHART

The details for the experimental procedure will be shown in Figure 3.1 below.



**Figure 3.1** The flow chart of the experimental procedure

### 3.3 THE WORKFLOW OF THE RESEARCH

Table 3.1 shows the research workflow, which includes the objectives from this study with the method corresponding to the goals and the expected outcomes from the method used.

**Table 3.1** The workflow of the research.

OBJECTIVE	METHODOLOGY	EXPECTED OUTCOME(S)	
1	To analyze the physical and chemical characteristics of the uncalcined cockleshells	Proximate Analysis	Moisture, volatile matter, ash, and fixed carbon
2		Calcination Process	Synthesized CaO

	To analyse the physical and chemical characteristics of the calcined cockleshells based on varying parameters: <ul style="list-style-type: none"> <li>• Particle Size</li> <li>• Temperature (°C)</li> </ul>	Approximate Analysis	Moisture, volatile matter, ash, and fixed carbon
		Fourier-Transform Infrared Spectroscopy (FTIR) Test	Obtaining an infrared spectrum of absorption/emission of eggshell samples after the calcination process
		Thermo Gravimetric Analysis (TGA)	Thermal analysis of the eggshell sample during the calcination process
		X-ray Powder Diffraction (XRD)	Phase identification of a crystalline material and providing unit cell dimensions info
3	Optimization of CaO extract from cockleshells	Statistical Analysis	Normal distribution curve with standard deviations
		Response Optimiser	To determine the optimum condition for the extraction of chitosan from cockleshell

### 3.4 THE RAW MATERIAL AND CHEMICALS

The list of the raw material and chemicals used in the research project will be shown in Table 3.2 below.

**Table 3.2** List of the raw material and chemicals

<b>RAW MATERIAL</b>	Cockle
<b>CHEMICALS</b>	Acetic acid
	Sulphuric Acid
	Potassium Bromide
	Phenolphthalein
	Nitrogen
	Sucrose

### 3.5 EQUIPMENT AND APPARATUS

A list of the equipment and the apparatus used throughout the research will be shown in Table 3.3 below.

**Table 3.3** The list of equipment and apparatus

EQUIPMENT	APPARATUS
Analytical balance	Desiccator
pH meter	Crucible
Drying oven	Tongs
Muffle furnace	Measuring cylinder
Fourier Transform Infrared Spectroscopy (FTIR)	Beaker
Thermal Gravimetric Analysis	Stirrer
Electrical Powder Grinder	250ml flask
	Spatula
	Filter paper and filter funnel

### 3.6 EXPERIMENTAL WORK

#### 3.6.1 1ST PHASE: RAW MATERIAL COLLECTION AND PRE-TREATMENT PROCESS

The alternate calcium carbonate source for this study is the cockle shells. Thus, the cockles were bought from Market Banting, Selangor in this phase. However, the sample can also be obtained from seafood restaurants or fishmongers. After taking out the cockle meat, cockle shells samples were collected and underwent a pre-treatment process. The pre-treatment process was conducted within 12 hours after the cockle shells were discarded to avoid mass decaying due to traces of interference materials. Then, the obtained seashells were cleaned using tap water and dried under the sun (Kadir et al., 2020; Wang et al., 2019).

The cockle shells were washed thoroughly with water and scrubbed with a brush until all dirt and impurities were removed. Afterwards, they were boiled in 100°C boiling water for 15 minutes to sterilize the sample and remove unwanted substances.



**Figure 3.2** (a) The fresh cockle, (b) The cleaned cockleshell

The cleaned cockle shell samples were then sundried for 24 hours or until they dried (Titah et al., 2018). The cockle shells samples were kept under room conditions after being treated. Then, the cockle shells were rewashed with diluted acetic acid (vinegar). 1L of water was used to dilute 10 mL of vinegar to prepare the diluted vinegar. After washing with vinegar, the cockle shells were dried again under the sun for 24h and then stored in the glass jar with silica gel.

### **3.6.2 2ND PHASE: COCKLE SHELL POWDER AND COCKLE SHELL GRANULE**

The preparation of cockle shell powder and cockle shell granule was conducted according to the process introduced by Islam et al. (2013). However, instead of using the pestle and mortar, the electrical grinder 2000W was used. In this phase, the cockle shells samples were grounded using an electrical powder grinder 2000W for around 30 seconds. Then, the sample was sieved to obtain 0.3-1.0cm of cockle shell granules. The rest of the sample continued grinding into a cockle shell powder.





**Figure 3.3** The electrical powder grinder 2000W.

Figure 3.3 above shows the electrical powder grinder 2000W used to grind the cockleshell. Figure 3.4 below shows the cockleshell in the electrical powder grinder before and after ground to granule and powder.



**Figure 3.4** (A) The cockleshell before grinding. (B) The obtained cockleshell granule. (C) The obtained cockle shell powder

### **3.6.3 3RD PHASE: THERMO GRAVIMETRIC ANALYSIS (TGA) AND CALCINATION PROCESS**

#### **3.6.3.1 THERMOGRAVIMETRIC ANALYSIS (TGA)**

Thermogravimetry is a technique to measure the change in weight as a function of temperature or time. This method will generally determine the weight difference of a sample exposed to a steady temperature rise or the thermal analysis method. This method was applied in this study by following the study from Mustakimah

(2012). The temperature range was modified but maintained the heating and carrier gas flow rates.

This method will be started by weighing 10 mg of uncalcined cockle shells sample. Then, the furnace door will be opened by pressing the intelligent sense terminal button and placing the sample in the crucible. Once the furnace reaches the test heating rate, the test will be started. First, the TGA will be set with 20 °C/min for heating and carrier gas flow rates (nitrogen gas) with 20 ml/hr. Then, the TGA will be started from 30 °C to 1000°C. Finally, we will analyse the data that we will obtain.

### 3.6.3.2 CALCINATION PROCESS

A 40 grams sample was placed on the crucible and placed in the electric furnace at atmospheric oxygen conditions for the calcination process. As a result, the cockle shells will convert to pure CaO and produce carbon dioxide, as shown in the Equation 1 reactions. In this project, the cockleshell granule and powder samples were calcined at different temperatures (600°C, 675°C, 700°C, 750°C, 800°C, 825°C, and 900°C) for a contact time of 4h. The summary of the sample conditions is summarized in Table 3.4.

**Table 3.4** The sample conditions.

NO.	SAMPLE CODE	PARAMETER	
		TEMPERATURE	PARTICLE SIZE
1.	CSG 600	600°C	GRANULE
2.	CSG 675	675°C	
3.	CSG 700	700°C	
4.	CSG 750	750°C	
5.	CSG 800	800°C	
6.	CSG 825	825°C	
7.	CSG 900	900°C	
8.	CSP 600	600°C	POWDER
9.	CSP 675	675°C	
10.	CSP 700	700°C	
11.	CSP 750	750°C	
12.	CSP 800	800°C	

13.	CSP 825	825°C	
14.	CSP 900	900°C	

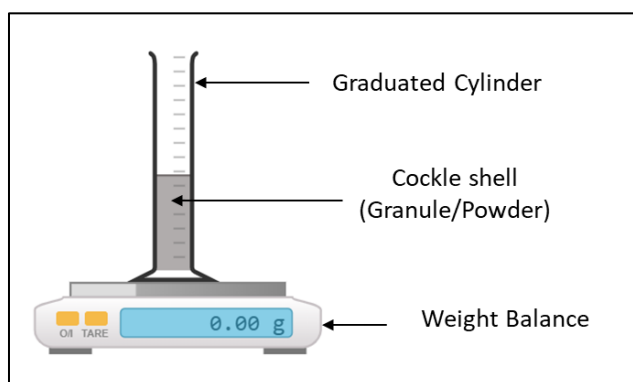
### 3.6.4 4TH PHASE: PROXIMATE ANALYSIS AND OTHER ANALYSIS

#### 3.6.4.1 BULK DENSITY

For this method, the density of the cockleshell sample was calculated. Firstly, the weight of the 25ml measuring cylinder was measured, and then 4-7 ml of cockle shell sample was filled in the measuring cylinder. Later, the weight of the measuring cylinder with the cockle shell sample was measured, and all the readings were recorded. Then, the bulk density will be obtained by using the formula as shown below:

$$\text{Bulk density} = \frac{\text{Weight of a cockle shell sample}}{\text{The volume of a cockle shell sample}} \quad (\text{Eq.2})$$

Figure 3.5, shown below, was the schematic diagram of the apparatus and material used to calculate the bulk density of the cockle shell sample.



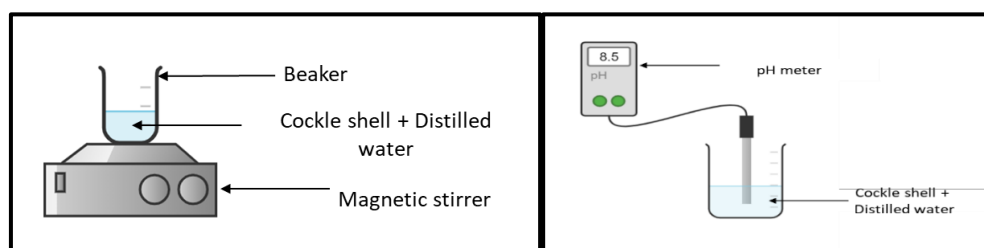
**Figure 3.5** The schematic diagram for calculating bulk density.

#### 3.6.4.2 pH

For this method, the pH of the cockleshell sample was identified. The pH is an indicator of the acidity and basicity of the cockle shell samples. It was determined by using 10 grams of cockle shell powder sample. The sample was put in the 25 ml beaker, and 10 ml of distilled water was added to the beaker. Next, the mixture was

stirred quickly for 30 minutes. Then, the pH meter reading would be taken using a pH meter (Mettler Toledo).

This method was used to determine the cockleshell granule sample's pH, but the granule sample needed to be crushed to powder. Figure 3.6 below shows the steps in measuring the pH of the sample.



**Figure 3.6** (A) The cockleshell and distilled water were stirred (B)pH meter used in the reading of pH of the mixture

### 3.6.4.3 PROXIMATE ANALYSIS

The proximate analysis of the uncalcined and calcined cockle shell granules and cockle shell powders will identify their physical characteristics. The proximate analysis of the uncalcined and calcined cockle shell granules and cockle shell powders were conducted according to ASTM D1762-84 to identify their moisture, ash, volatile matter and carbon content.

#### i. MOISTURE CONTENT

In this method, the empty crucible was weighed, and around 2 – 2.2 grams of calcined cockle shell sample was added to the crucible. After that, the crucible was placed in the oven for 4 hours at 105°C. After 4 hours, the crucible was taken out and cooled in the desiccator. Then, the final mass of the crucible and the calcined cockleshell sample were weighed, and the final mass of the cockleshell sample was calculated. Finally, the moisture content of the cockleshell sample was calculated with the equation shown below.

$$\text{Moisture content, MC} = \frac{W-d}{d} \times 100\% \quad (\text{Eq. 3})$$

W= wet weight  
d = weight after drying

## ii. VOLATILE MATTER

In general, the volatile matter measures the non-water gases produced from the cockle shell sample during heating. It is calculated as the percentage weight of gas emissions from the cockle shell sample emitted in an oxygen-free atmosphere during heating to 950°C, except for humidity at a standardized temperature.

The evaporating dish was weighed in this method, and around 2g of cockle shell sample was filled into evaporating dish. Then, the new weight of the evaporating dish and the cockleshell sample was measured, and the wet weight of the cockleshell sample was calculated. After that, they were heated at 950°C in an oxygen-free atmosphere. Then, the final weight of the evaporating dish and the cockleshell sample was weighed, and the weight of the cockleshell sample after drying was calculated. Finally, the volatile matter of the cockleshell sample was calculated by using the equation shown below.

$$\text{Volatile matter} = \frac{\text{Weight of preheated sample} - \text{Weight of the sample after heating}}{\text{Weight of precombustion sample}} \quad (\text{Eq. 4})$$

## iii. ASH CONTENT

In this process, the ash content of the cockleshell samples was identified. The ash content is the amount of inorganic waste material contained in the samples. The process was started by weighing the cockle shell sample. Next, the sample was heated in the air using a muffle furnace under rigidly controlled time conditions with a controlled temperature of is about  $550 \pm 10$  °C for 4 hours. Then, the residue that remains after heating was weighed. Finally, the ash content was estimated using the equation shown below.

$$\text{Ash} = \frac{M(\text{dry}) - M(\text{ash})}{M(\text{dry})} \times 100\% \quad (\text{Eq. 5})$$

$$M(\text{ash}) = \text{weight of ash}$$
$$M(\text{dry}) = \text{weight of the original sample}$$

#### iv. **FIXED CARBON**

In general, this method was used to calculate the amount of non-volatile carbon remaining in the uncalcined cockle shell sample, also known as fixed carbon. The formula to get the percentage of the fixed carbon in the sample is the difference between 100 and the percentage of the moisture, volatile matter, and ash, as shown in the formula below.

$$\text{Fixed carbon (\%)} = 100 - (\% \text{ moisture} + \% \text{ volatile matter} + \% \text{ ash}) \quad (\text{Eq. 6})$$

#### **3.6.4.4 FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR) TEST**

The cockleshell sample was characterized and analyzed using Fourier Transform Infrared Spectroscopy (FTIR) in conjunction with functional group analysis (Ajao et al., 2018). The FTIR analysis can determine the characterization of the calcined cockle shells, measuring the wavelengths that the cockle shells absorb or emit in the infrared region. In this method, calcium oxide in the calcined cockle shells of granule and powder will be identified.

The cockleshell was mixed with Potassium Bromide (KBr) powder to determine the composition of the cockleshell. Afterwards, the mixed powder was placed in the drying oven to remove moisture. Then, it was placed on the FTIR plate and was pressed about 1.7 tonnes with the compression machine. Then, they were put in the Fourier Transform Infrared Spectrometer, and the data obtained were analyzed.



**Figure 3.7** (A) Compression machine (B) Fourier Transform Infrared Spectrometer

Figure 3.7 (A) and (B) were the equipment that has been used in this test besides the drying oven.

#### **3.6.4.5 X- RAY POWDER DIFFRACTION (XRD)**

In this study, the X-ray Powder diffraction method was used to determine the phase identification of a crystalline material and provide unit cell dimensions' info. According to Wang et al. (2012), the XRD was conducted for the crystallinity analysis of the cockleshell. First, the technique was operated by irradiating an incident X-ray sample. Then, the X-ray amplitude and dispersion angles that exit the material was calculated. The characteristic of crystalline XRD peaks showed that the cockleshell is a rich source of calcium carbonate (Supattra Wongsanmai, 2017).

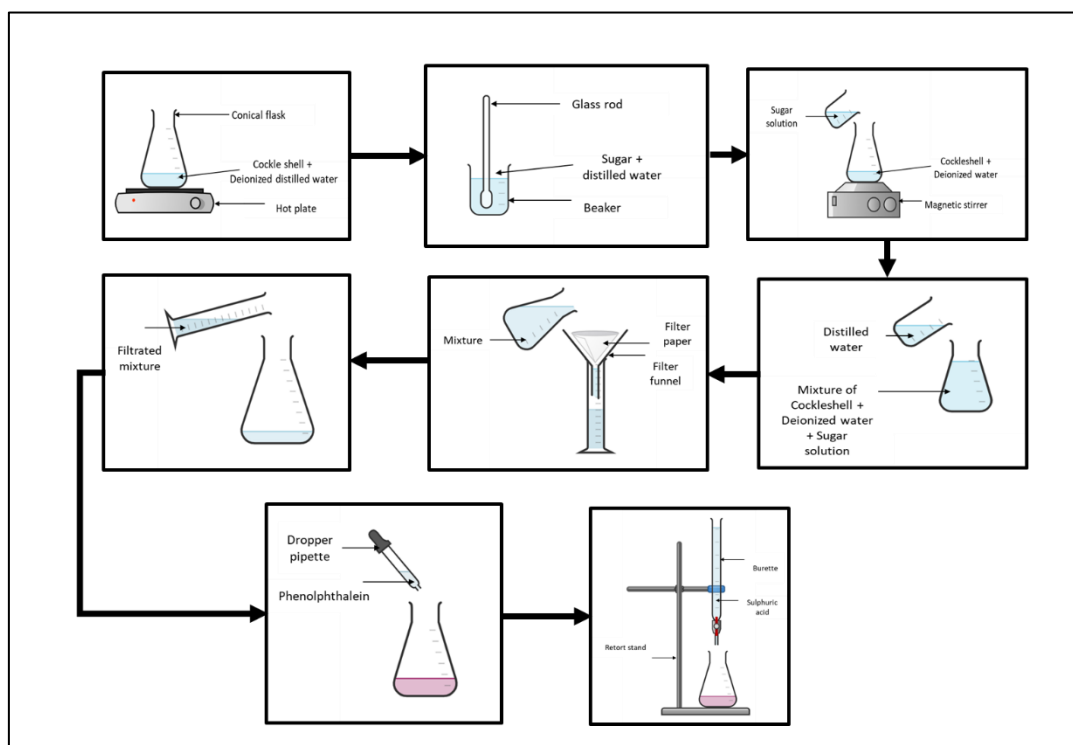
#### **3.6.4.6 NEUTRALISATION WITH ACID (DETERMINATION OF CAO)**

The rapid sugar test (using sulphuric acid) was used to determine the available lime (CaO) from the calcined cockle shell sample. In this method, the hydrochloric acid (HCl) will replace the sulphuric acid,  $H_2SO_4$ , because it can give the available CaO values up to 3% more than those obtained when HCl is used.

To begin this method, 2.5 gram of calcined cockle shell sample was filled into a 250 ml flask, and 40ml of CO<sub>2</sub> -free water was added. It boiled for 3 minutes. Then, it was cooled to room temperature. Once cooled, 50% of the sugar solution was added to the sample in the flask. 50% of the sugar solution was obtained from the mix of 20 g of sucrose (sugar) in 20 ml of water. Then, they were shaken for 30 minutes. Later, more water was added up to the 250 ml mark, and the mixture was filtered through a No.1 Whatman paper. However, the first 15–30 ml of filtrate was discarded, and the 25 ml of the later filtrate was pipetted into a flask. Then, five drops of phenolphthalein were added to the flask, and it was titrated with 0.357N sulphuric acid. The calculation used to calculate the available lime contained in the calcined cockle shell is shown in the equation below.

$$\text{The available lime, as CaO,} = \text{ml of 0.357N acid, on the burette,} \times 4 \quad (\text{Eq. 7})$$

Figure 3.8 below shows the schematic diagram of the steps for the neutralisation process.



**Figure 3.8** The steps for the neutralisation process



### **3.6.5 FIFTH PHASE: STATISTICAL ANALYSIS AND RESPONSE OPTIMISER**

All data of the results obtained were tabulated in the tables, and the graphs were plotted. Then, the statistical analysis of the percentage of mass loss and CaO using regression analysis with the aid of MINITAB was done. Besides that, one-way ANOVA analysis was done for pH, bulk density and proximate analysis results of the CSP and CSG. Afterwards, the charts and graphs plotted and tabulated in this analysis were discussed. The optimal condition for the temperature and sample type was calculated using a response optimiser.

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 INTRODUCTION

In this chapter, cockle shells act as alternate  $\text{CaCO}_3$  to be synthesized into  $\text{CaO}$  by thermal treatment or calcination. Two main parameters were utilized to determine the ideal calcination condition for the cockle shell: surface area (granules and powder) and temperature ( $^{\circ}\text{C}$ ). The characterization and analysis of the sample were done both before and after the calcination process.

#### 4.2 TGA

TGA (thermogravimetry analysis) is a technique for determining a compound's weight change as a function of temperature or time. The raw cockle shell powder was subjected to TGA, and the results are presented in Figure 4.1.

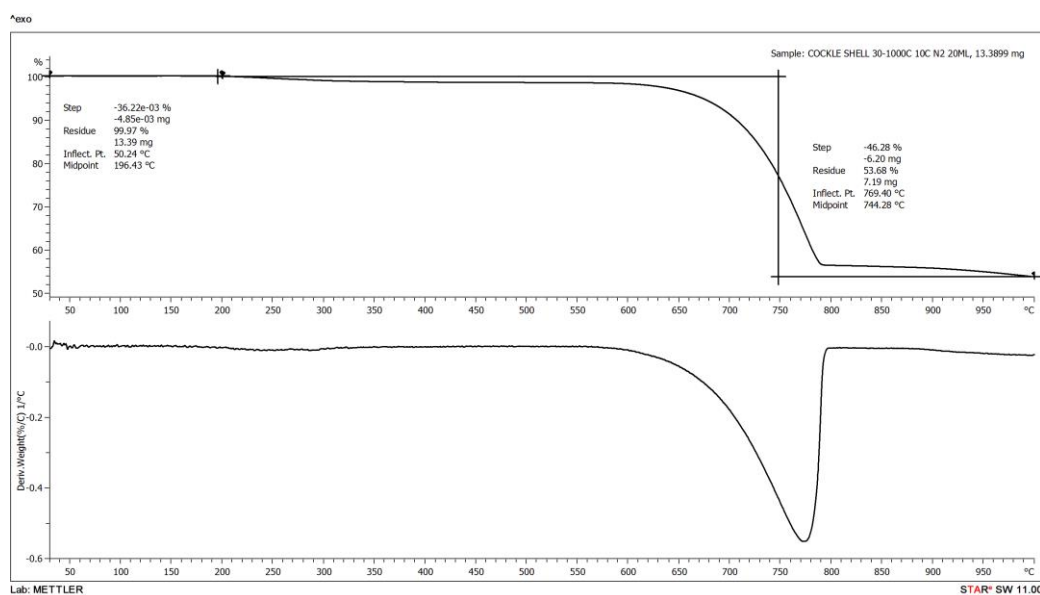


Figure 4.1 TGA results for raw cockle shell powder.

The decomposition of  $\text{CaCO}_3$  was initiated at  $600^\circ\text{C}$  based on TGA study results because the mass began to drop at that temperature. A significant change in mass begins to occur around temperatures of  $750^\circ\text{C}$ . According to Bazargan et al. (2015), the decrease in the mass indicates the decomposition of  $\text{CaCO}_3$  to  $\text{CaO}$  due to the release of  $\text{CO}_2$  compounds where the high-temperature range (above  $700^\circ\text{C}$ ) is required to transform  $\text{CaCO}_3$  to  $\text{CaO}$  (Empikul et al., 2010).

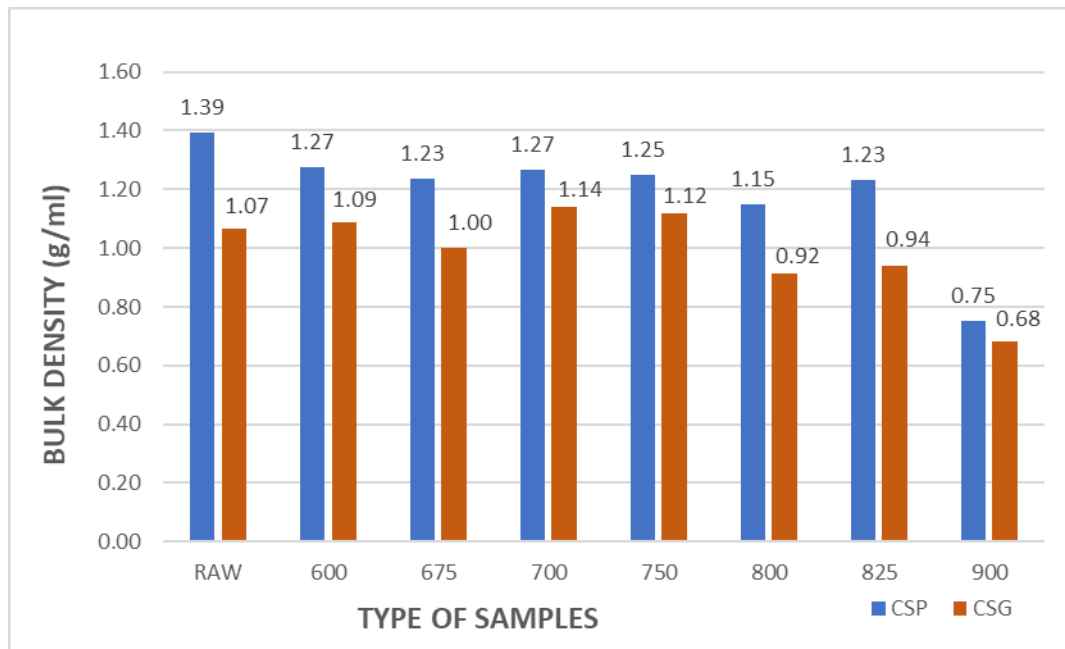
The temperature of  $780^\circ\text{C}$  gave the biggest mass changes for the cockle shells. After passing the temperature of  $780^\circ\text{C}$ , the mass change only around 3% up to temperature  $100^\circ\text{C}$ . This indicates that almost all  $\text{CaCO}_3$  has been decomposed. Based on Dümichen et al., (2015), there is no change in the  $\text{CaO}$  compound from  $900^\circ\text{C}$  to  $1200^\circ\text{C}$ .

The cockle shells had the most significant mass changes when heated to  $780^\circ\text{C}$ . After passing through  $780^\circ\text{C}$  until it reaches  $1000^\circ\text{C}$ , the mass changes by only about 3%. This means that practically all of the  $\text{CaCO}_3$  has been decomposed. According to Dümichen et al. (2015), the  $\text{CaO}$  compound does not change the temperature from  $900^\circ\text{C}$  to  $1200^\circ\text{C}$ .

#### **4.3 BULK DENSITY**

Density is one of the powerful characterizations of solid material as the analysis of density contributes to identifying the substance's physical characteristics. The bulk density considered the solids and pore space of the particles of CSP and CSG. The density for  $\text{CaCO}_3$  is 2.71 g/ml (Myers, 2007); meanwhile, the bulk density measured from raw CSP and CSG is 1.39 g/ml and 1.07 g/ml.

The bulk density of the raw and calcined samples calculated were shown as below;

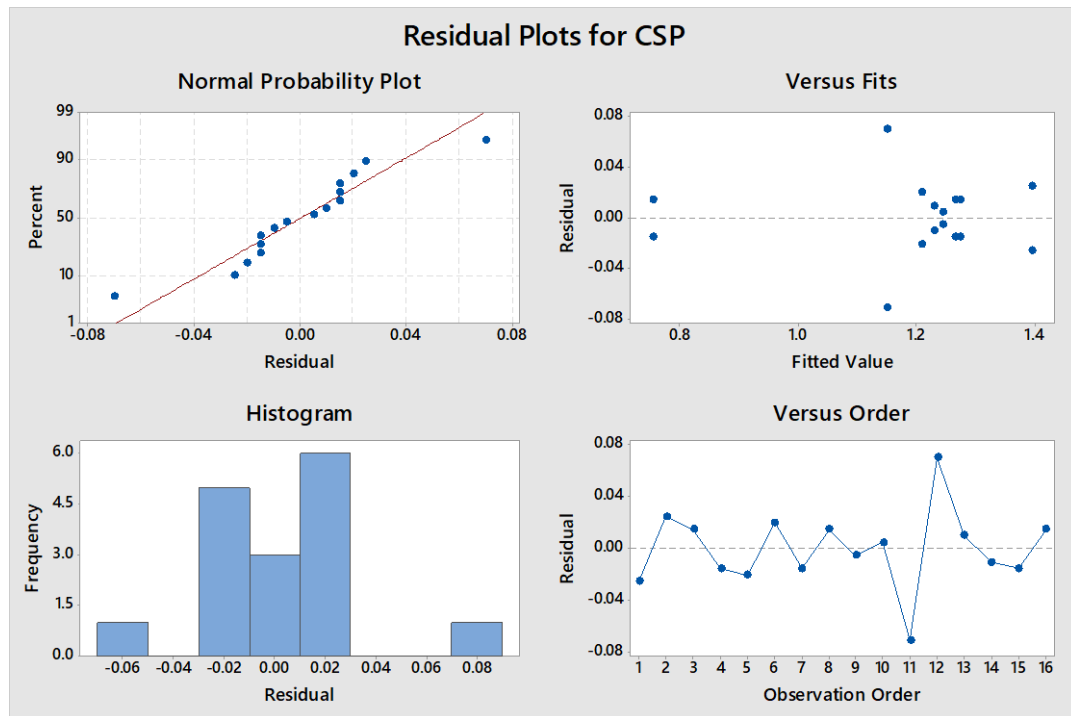


**Figure 4.2** The bulk density (g/ml) for CSP and CSG for the raw sample and each calcination temperature.

Based on Figure 4.2, the bulk density of the raw and calcined samples at the temperature of 600°C to 825°C did not significantly differ. However, the calcined cockle shell at temperature 900°C is the lowest because the porosity is decreased. This is because the particle size of the calcined cockleshell decreases when subjected to a higher temperature of calcination. CSP 900 and CSG 900 have smaller particle sizes than samples calcined at lower temperatures. As the particle size decreased, the pore space between the particle became less compact; thus, the bulk density decreased (Musa, 2019).

Besides that, the bulk density for the CSG is lower than CSP for all the shown samples. This indicates that the greater the particle size, the more free space between the particles, thus affecting the mass of the sample. The sample became less compact; thus, the bulk density decreased.

One-way ANOVA was done to find the effect of temperature towards the bulk density for raw, calcined CSP and CSG. The histogram from Figure 4.3 shows that raw and calcined CSP results were not normally distributed.



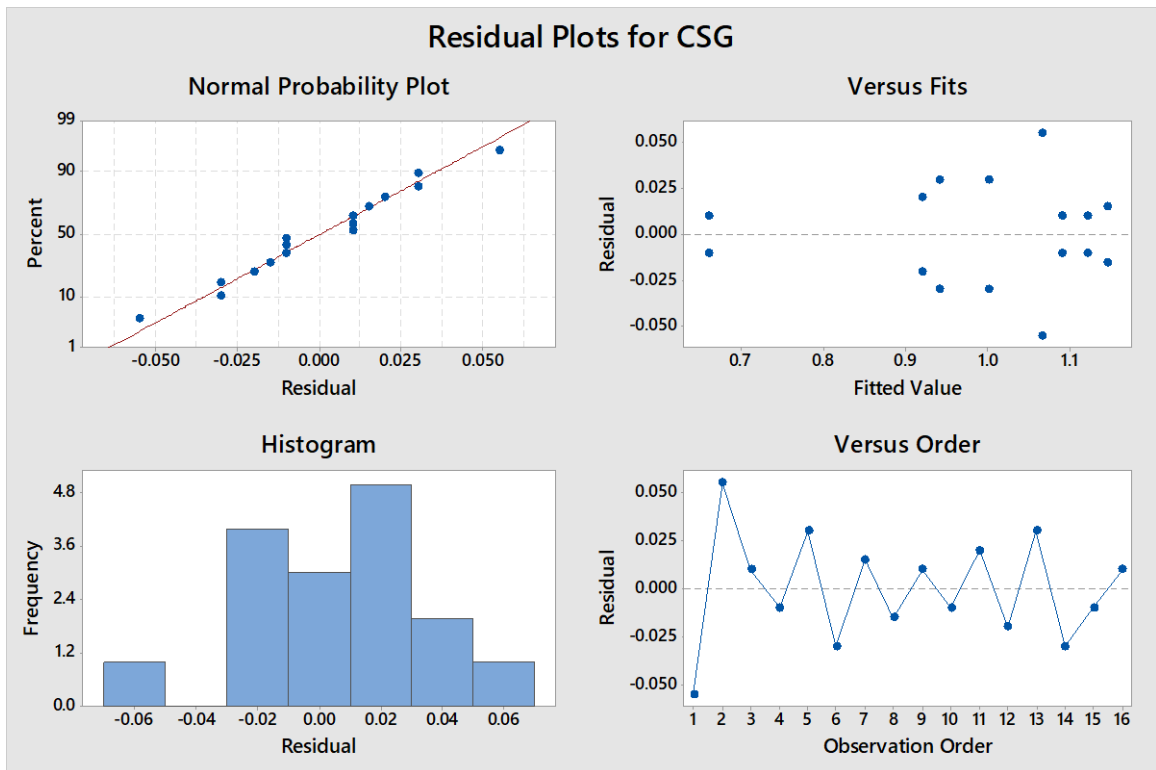
**Figure 4.3** Residual plots of bulk density data for CSP

Based on Table 4.1, the P-value shown was approximately 0, lower than the significant level at 0.05. Hence, the indicated data reject the null hypothesis that each bulk density was statistically equal. This stated that the means of bulk density affected by the difference in temperature were not equal.

**Table 4.1** The analysis of variance for bulk density of CSP

Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	7	0.50144	0.071635	42.61	0.000
Error	8	0.01345	0.001681		
Total	15	0.51489			

The F-value from the F distribution table is 2.62413 because the degree of freedom for 1 and 2 are 7 and 8. Thus, The F-value for CSP is bigger than the value from the F distribution table, which is 42.61. This shows that the temperature is significant for the bulk density of CSP.



**Figure 4.4** Residual plots of bulk density data for CSG

The histogram from Figure 4.4 above shows that raw and calcined CSG results were almost normally distributed. The P-value shown in the table below was approximately 0, lower than the significant level at 0.05. Hence, the indicated data reject the null hypothesis that each bulk density was statistically equal. This stated that the means of bulk density affected by the difference in temperature were not equal.

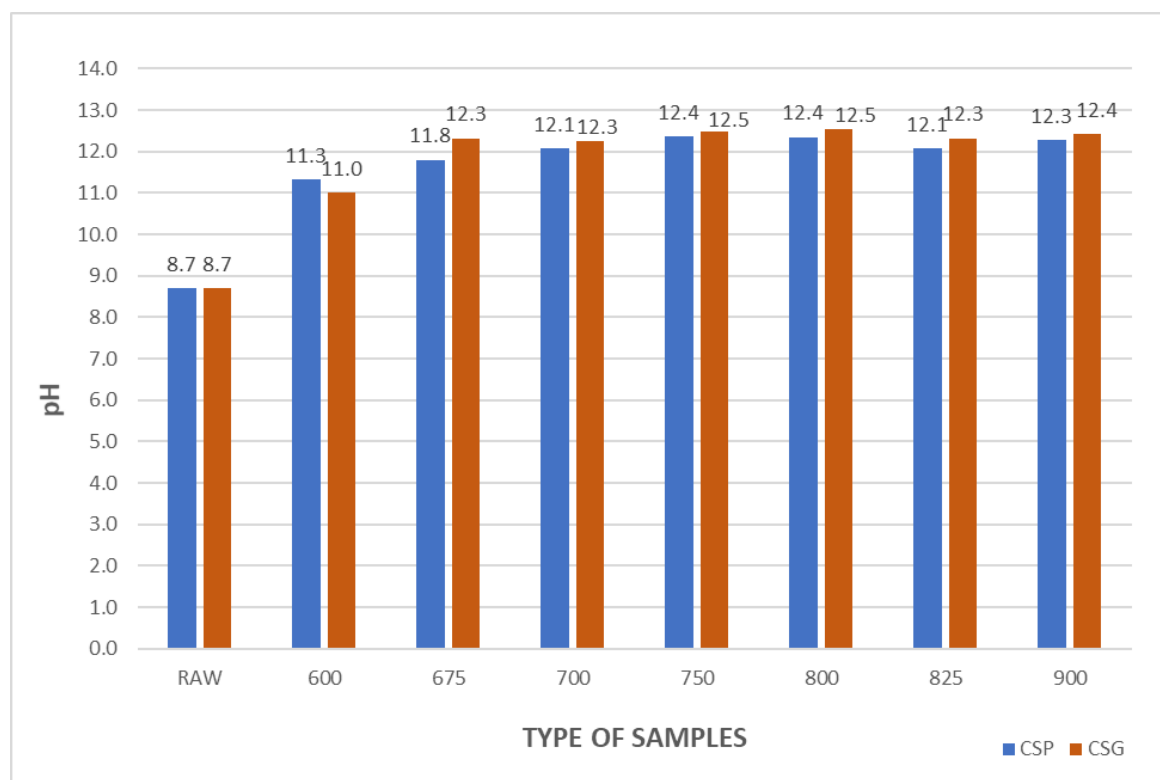
**Table 4.2** The analysis of variance for bulk density of CSG

Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	7	0.34580	0.049400	34.37	0.000
Error	8	0.01150	0.001438		
Total	15	0.35730			

The F-value from the F distribution table is 2.62413 because the degree of freedom for 1 and 2 are 7 and 8. Thus, The F-value for CSG is bigger than the value from the F distribution table, which is 34.37. This shows that the temperature is significant for the bulk density of CSG.

#### 4.4 pH ANALYSIS

The pH of an aqueous sample solution can be determined by using the concentration of hydronium ion concentration in the solution. The pH analysis of the raw and calcined samples was done, and the results of the pH obtained in the study were shown as below;

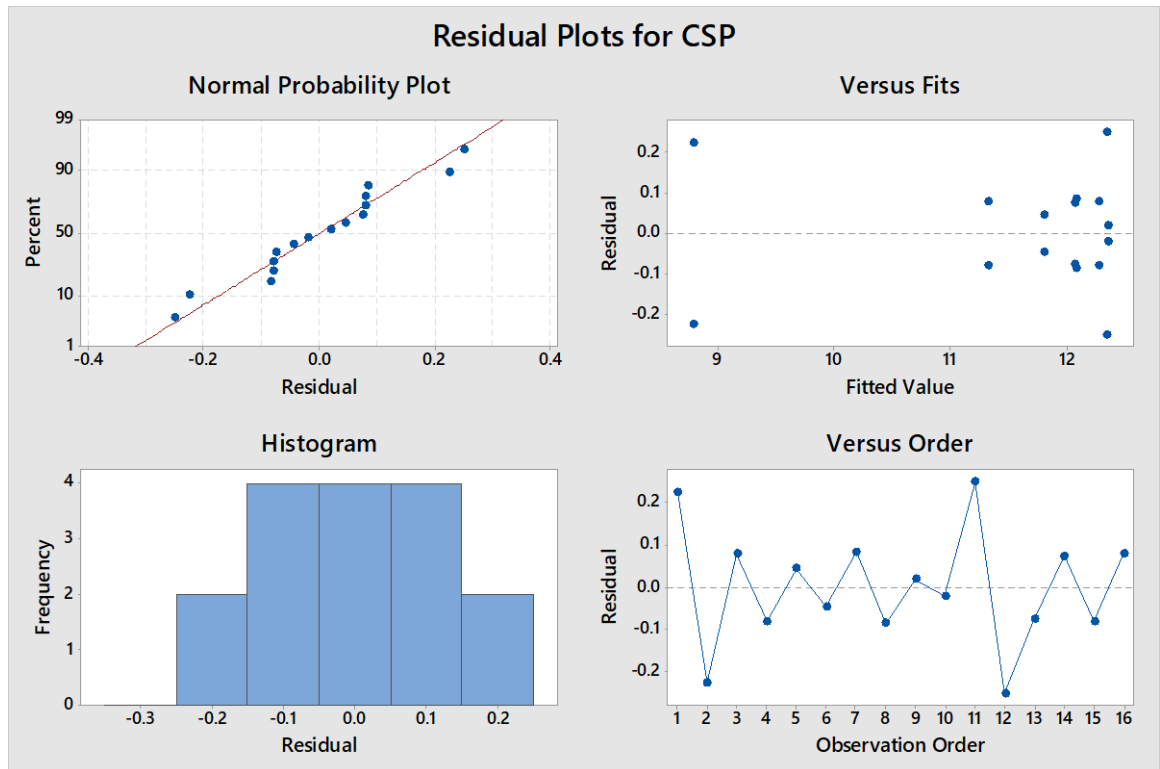


**Figure 4.5** The pH value obtained for each sample.

Based on Figure 4.5, the pH for the raw sample is 8.7, which is slightly lower than the pH of the  $\text{CaCO}_3$  with the purity of 99.99% (calcite), which is 9.91 (Mohd Shuha, 2019) and 9.4 (Musa, 2019) though both classified as a base on the pH scale. Therefore, the base properties indicate that calcium hydroxide ( $\text{CaOH}$ ) originates from the mixture of  $\text{CaCO}_3$  with distilled water.

The pH for the calcined cockleshell samples is higher than the raw sample's pH. It indicates the presence of  $\text{CaO}$  in the calcined sample because the  $\text{CaO}$  is much soluble in distilled water compared to  $\text{CaCO}_3$ , thus producing more  $\text{CaOH}$ .

Besides that, there is no significant difference in the pH between calcined CSG and CSP for calcination at each temperature. However, one-way ANOVA was done to find the effect of temperature towards the pH for raw, calcined CSP and CSG.



**Figure 4.6** Residual plots of pH data for CSP

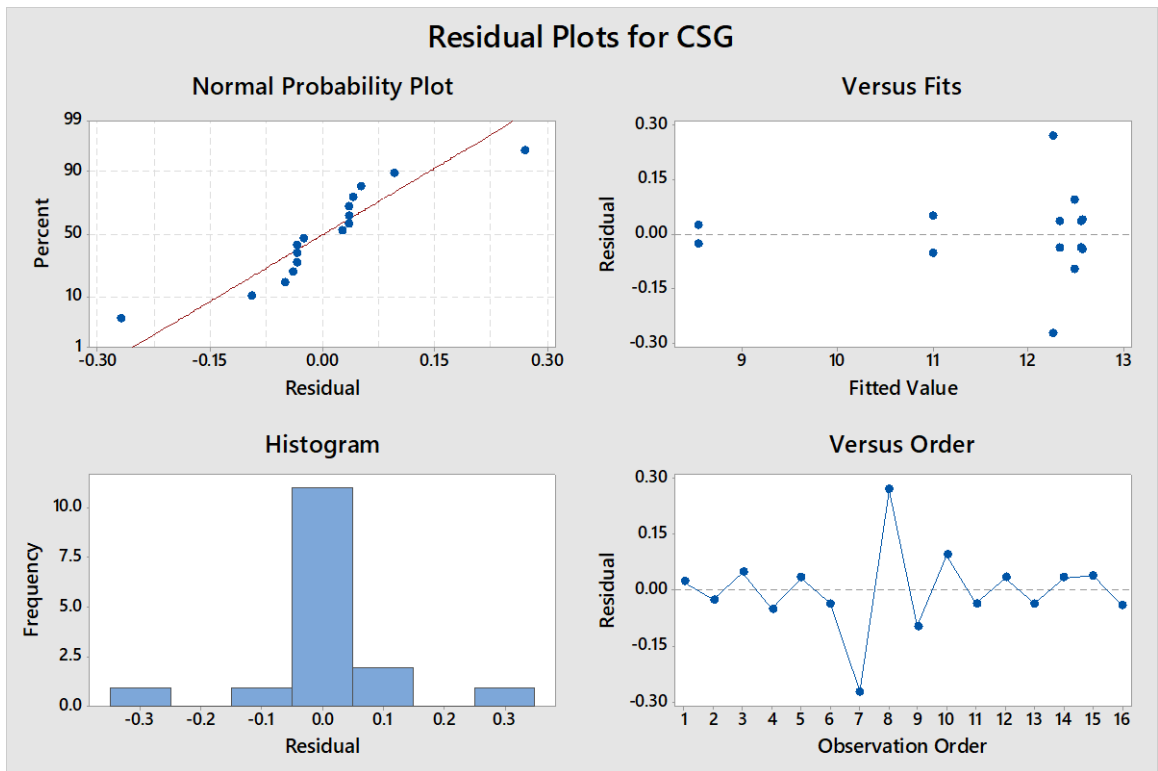
The histogram from Figure 4.6 shows that the raw and calcined CSP results were almost normally distributed. The P-value shown in Table 4.3 was approximately 0, lower than the significant level at 0.05. Hence, the indicated data reject the null hypothesis that each moisture content was statistically equal. This stated that the means of pH affected by the difference in temperature were not equal.

**Table 4.3** The analysis of variance for pH of CSP

Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	7	20.1816	2.88308	81.67	0.000
Error	8	0.2824	0.03530		
Total	15	20.4640			

The F-value for CSP is bigger than the value from the F distribution table, which is 81.67. This shows that the temperature significantly affects the pH of CSP.





**Figure 4.7** Residual plots of pH data for CSG

The histogram from Figure 4.7 shows that raw and calcined CSG results were almost normally distributed. The P-value shown in Table 4.4 was approximately 0, which is lower than the significant level at 0.05. Hence, the indicated data reject the null hypothesis that each pH was statistically equal. This stated that the means of bulk density affected by the difference in temperature were not equal.

**Table 4.4** The analysis of variance for bulk density of CSG

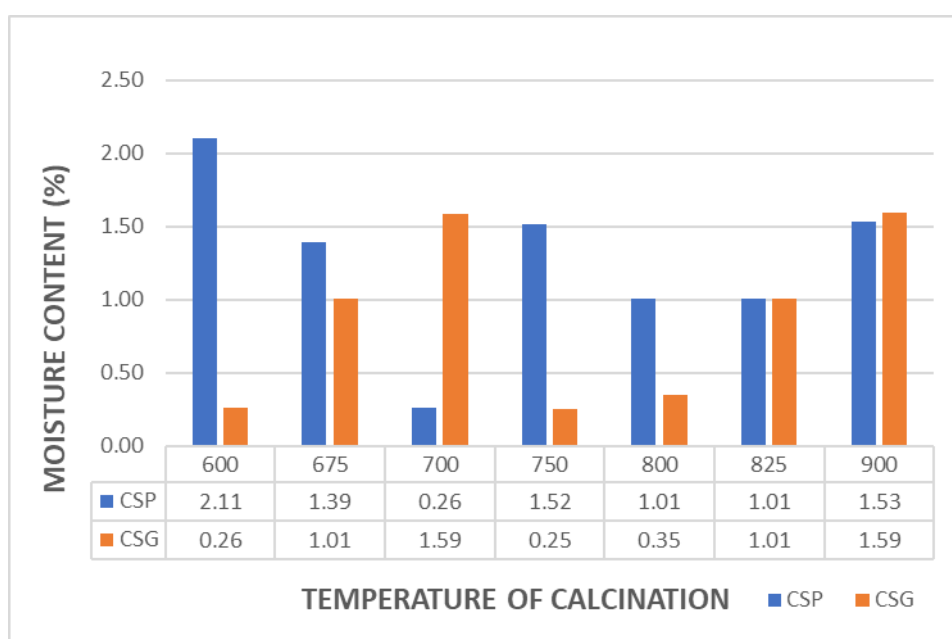
Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	7	27.2965	3.89951	172.69	0.000
Error	8	0.1806	0.02258		
Total	15	27.4772			

Based on analysis of variance data, the F-value for CSG is bigger than the value from the F distribution table, which is 172.69. This shows that the temperature significantly affects the pH of CSG.

## 4.5 PROXIMATE ANALYSIS

### 4.5.1 MOISTURE CONTENT

Moisture content was calculated to determine the amount of water still contained in the calcined cockle shell. It was obtained by heating the calcined sample for about 4 hours at 105°C by using a drying oven, and the difference in the mass before and after drying was calculated. The results are shown in Figure 4.8.



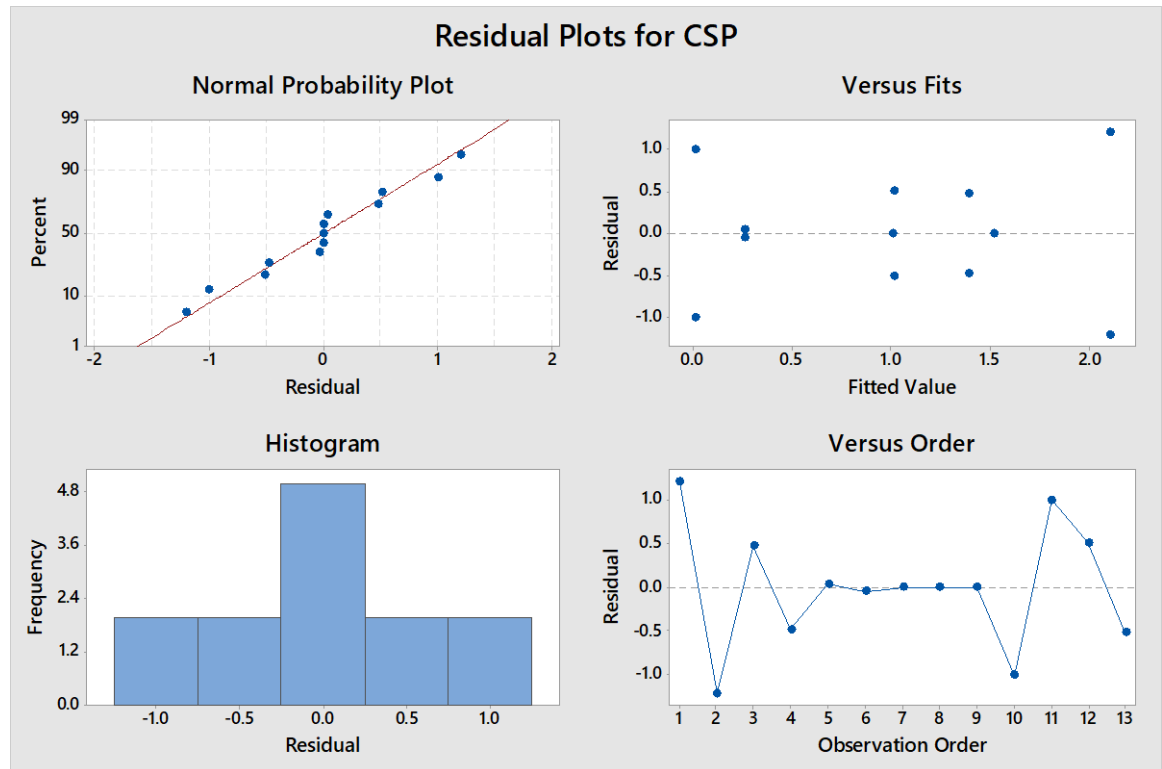
**Figure 4.8** The moisture content in CSP and CSG for difference temperature of calcination.

Based on Figure 4.8, the percentage of moisture content from the calcined cockle shell is less than 3%, which is very small. This proves that only a small presence of H<sub>2</sub>O or substance absorbed H<sub>2</sub>O in the calcined sample. However, the moisture content for the CSP at temperature 600°C has the highest percentage of moisture content, which is 2.11%. Powder form for uncalcined and some calcined samples has higher moisture content percent than granule. This is because the granules have better flow qualities and are more porous.

The moisture content for the raw cockle shell was calculated based on the TGA graph. The first step was the initial process, which started with a very small weight loss of 0.5% due to the moisture content in the samples. According to Baba et al. (2013), using the same procedure, the moisture content of pulverized raw egg-shell is

estimated to be 1.1 percent. Based on Suteu et al. (2011), cockle shells contain up to 95% CaCO<sub>3</sub>, which the other 5% of the shell is made up of other components that may include H<sub>2</sub>O or compounds that absorb H<sub>2</sub>O.

Then, one-way ANOVA was done to find the effect of temperature on the moisture content for calcined CSP and CSG.



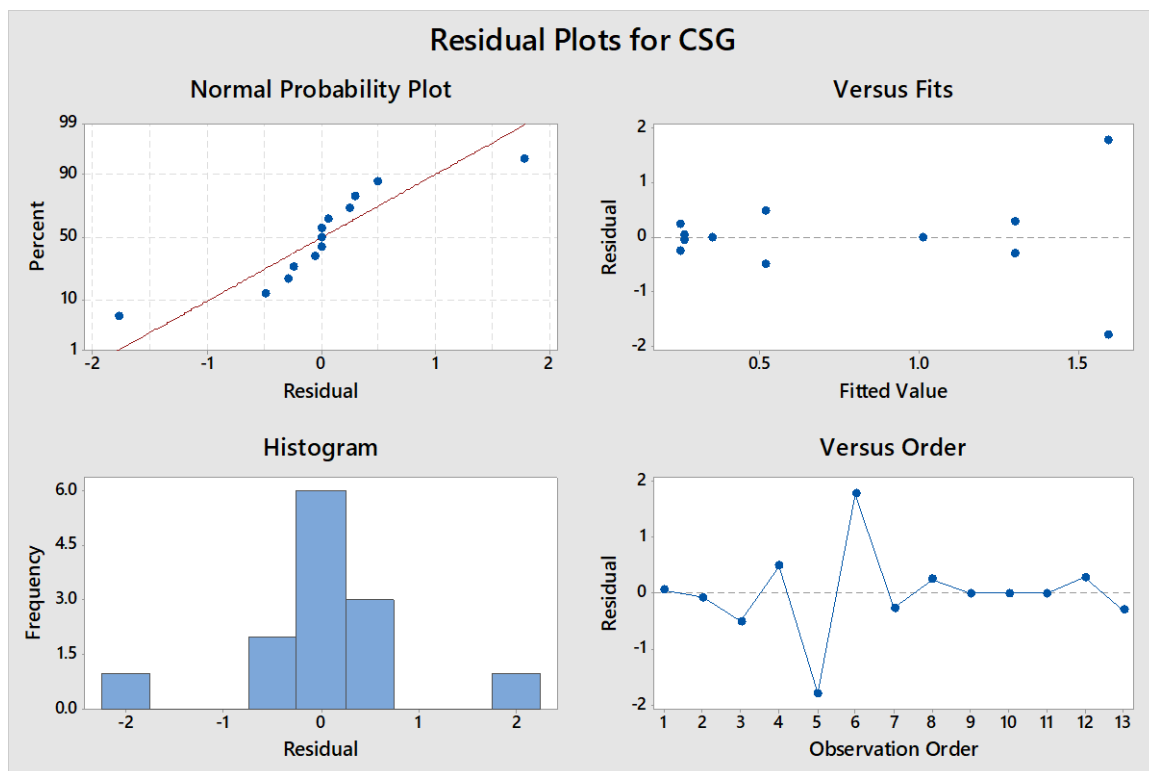
**Figure 4.9** Residual plots of moisture content data for CSP

The histogram from Figure 4.9 shows that the results for calcined CSP were almost normally distributed. The P-value shown in table 4.5 was 0.468, which is higher than the significant level at 0.05. Hence, the indicated data accept the null hypothesis that each moisture content was statistically equal. This stated that the means of moisture content affected by the difference in temperature were equal.

**Table 4.5** The analysis of variance for moisture content of CSP

Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	6	6.314	1.0524	1.07	0.468
Error	6	5.898	0.9831		
Total	12	12.213			

The F-value for CSP is 1.07, while F-value from the F distribution table is 3.05455. Thus, this shows that the temperature is not significant for the moisture content of CSP.



**Figure 4.10** Residual plots of moisture content data for CSG

The histogram from Figure 4.10 shows that the results for calcined CSG were almost normally distributed. The P-value shown in table 4.6 was 0.806, higher than the significant level at 0.05. Hence, the indicated data accept the null hypothesis that each moisture content was statistically equal. This stated that the means of moisture content affected by the difference in temperature were equal.

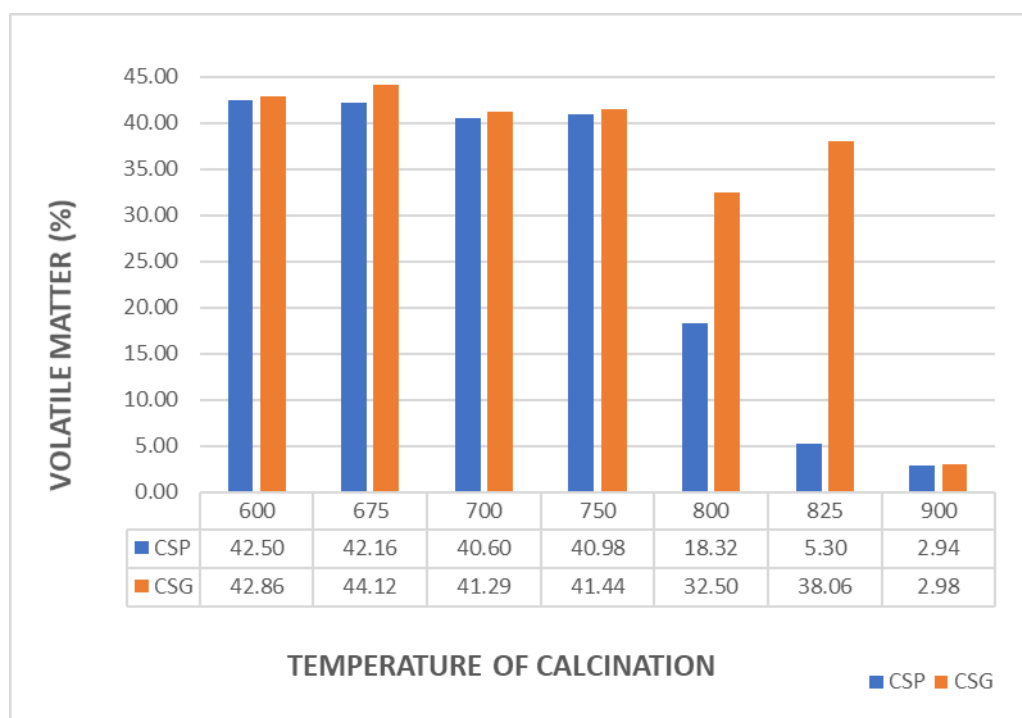
**Table 4.6** The analysis of variance for moisture content of CSG

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Temperature	6	3.386	0.5644	0.48	0.806
Error	6	7.127	1.1879		
Total	12	10.514			

The F-value for CSG is 0.48, lower than F-value from F distribution, 3.05455. Thus, this shows that the temperature is not significant for the moisture content of CSG.

#### 4.5.2 VOLATILE MATTER

In general, the samples' volatile matter measured the non-water gases produced from the calcined cockle shell sample during heating. It is calculated as the percentage weight of gas emissions from the cockleshell sample emitted in an oxygen-free atmosphere during heating to 950°C, except for humidity at a standardized temperature.



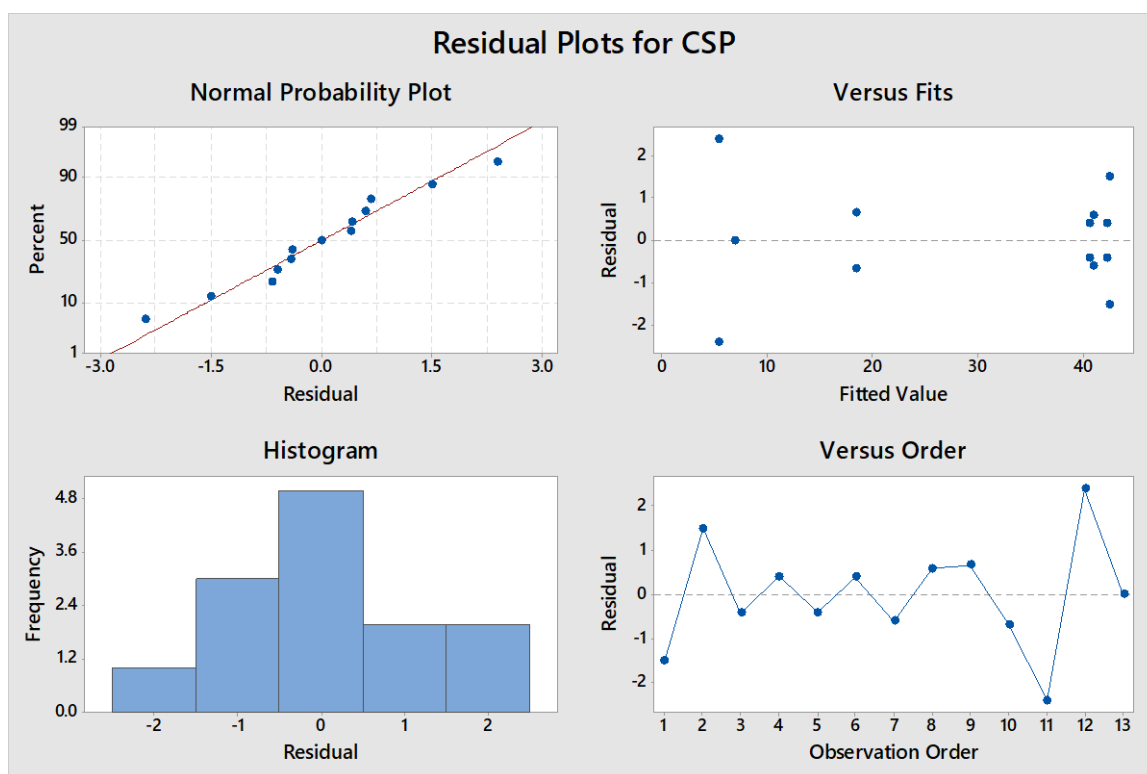
**Figure 4.11** The volatile matter (%) for CSP and CSG for difference temperature of calcination.

Based on Figure 4.11, the volatile matter for CSP and CSG at temperature 600°C to 750°C is above 40% while decreasing after that. However, the volatile matter percentage for CSP 900 and CSG 900 is almost equal, 2.94% and 2.98%. They have been exposed to a higher calcination temperature than other CSP and CSG. Moreover, it shows that CSP 900 and CSG 900 have a lesser hazardous material that rapidly transitions to another state or vaporizes compared to other CSP and CSG.

Aside from that, Figure 4.11 shows that the powder sample has less volatile materials than the granules.

The volatile matter for the raw cockle shell was calculated based on the TGA graph. The continuous change of weight loss from 200 to 1000°C were observed; in this temperature range, the percentage of weight loss is 45.5%. This is because the volatile minerals in the sample began to decompose, thereby releasing CO<sub>2</sub>. This result indicates the total decomposition of calcium carbonate to CaO and the release of CO<sub>2</sub>.

Then, one-way ANOVA was done to find the effect of temperature towards the volatile matter for calcined CSP and CSG.



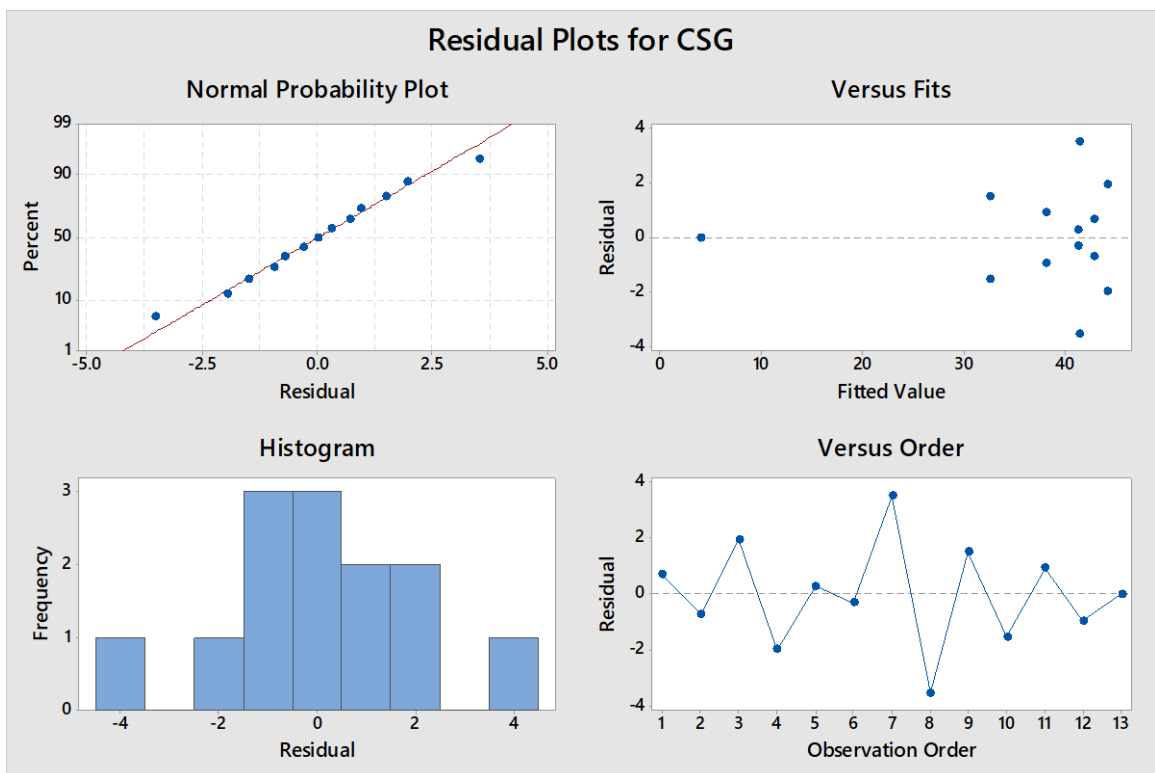
**Figure 4.12** Residual plots of volatile matter data for CSP

The histogram from Figure 4.12 shows that the results for calcined CSP were normally distributed. The P-value shown in Table 4.7 was approximately 0, lower than the significant level at 0.05. Hence, the indicated data reject the null hypothesis that each volatile matter was statistically equal. This stated that the means of volatile matter affected by the difference in temperature were not equal.

**Table 4.7** The analysis of variance for the volatile matter of CSP

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Temperature	6	3101.65	516.942	170.42	0.000
Error	6	18.20	3.033		
Total	12	3119.85			

The F-value for CSP is 170.42, which is higher compared to F-value from F distribution, 3.05455. Thus, this shows that the temperature is significant for the volatile matter of CSP.



**Figure 4.13** Residual plots of volatile matter data for CSG

The histogram from Figure 4.13 shows that the results for calcined CSG were almost normally distributed. The P-value shown in Table 4.8 was approximately 0, lower than the significant level at 0.05. Hence, the indicated data reject the null hypothesis that each volatile matter was statistically equal. This stated that the means of volatile matter affected by the difference in temperature were not equal.

**Table 4.8** The analysis of variance for the volatile matter of CSG

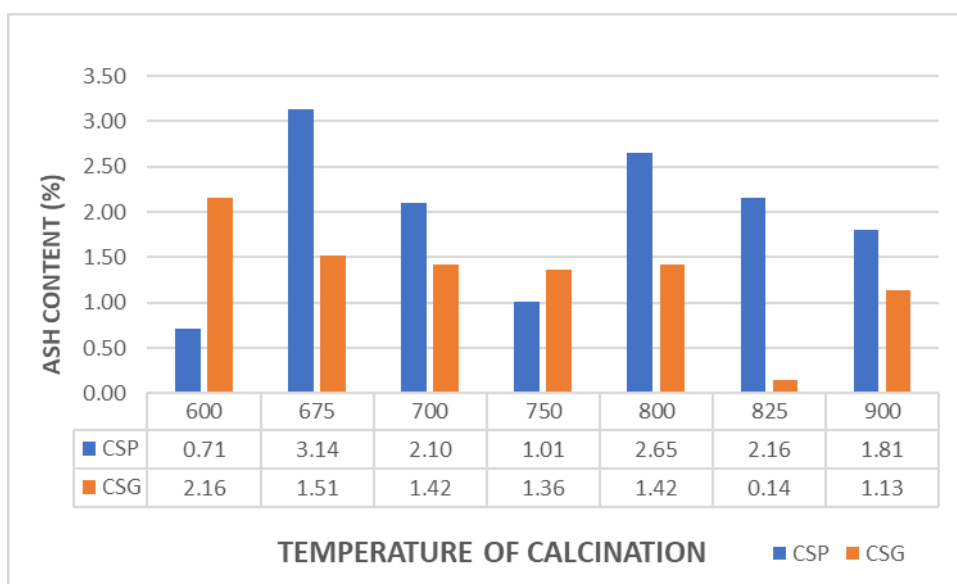
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Temperature	6	3101.65	516.942	170.42	0.000
Error	6	18.20	3.033		
Total	12	3119.85			

temperature	6	1377.07	229.512	34.64	0.000
Error	6	39.76	6.626		
Total	12	1416.83			

The F-value for CSG is 36.64, which is higher compared to F-value from F distribution, 3.05455. Thus, this shows that the temperature is significant for the volatile matter of CSG.

### 4.5.3 ASH CONTENT

The ash content is the amount of inorganic waste material contained in the samples. Figure A below shows the identified ash content of the cockleshell samples.

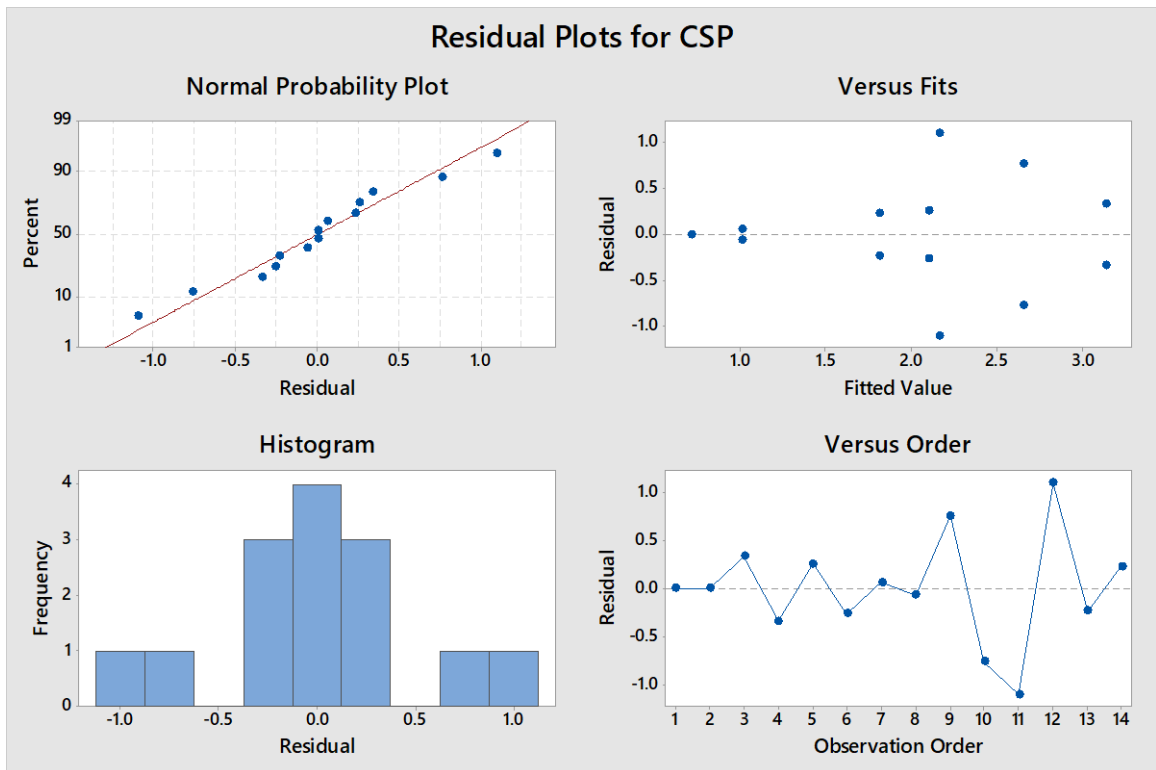


**Figure 4.14** The ash content (%) for CSP and CSG for difference temperature of calcination.

Based on Figure 4.14, the ash content of the calcined sample was less than 4%, with CSG 825 having the lowest ash content, which is only 0.14%. The percentages are very small because the inorganic residue or minerals in the cockleshells are completely oxidized after heating at a high temperature.

Then, one-way ANOVA was done to find the effect of temperature on the ash content for calcined CSP and CSG.





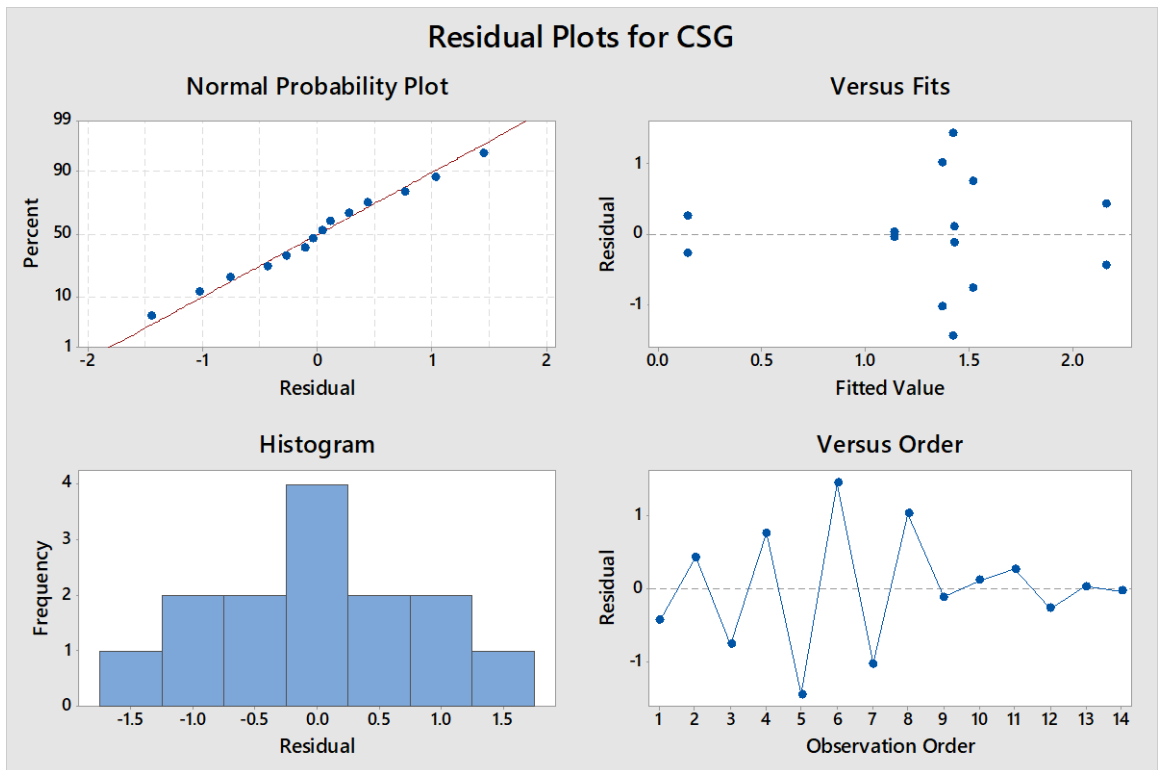
**Figure 4.15** Residual plots of ash content data for CSP

The histogram from Figure 4.15 shows that the results for calcined CSP were almost normally distributed. The P-value shown in Table 4.9 was 0.124, higher than the significant level at 0.05. Hence, the indicated data accept the null hypothesis that each ash content was statistically equal. This stated that the means of ash content affected by the difference in temperature were equal.

**Table 4.9** The analysis of variance for ash content of CSP

Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	6	8.858	1.4764	2.54	0.124
Error	7	4.071	0.5816		
Total	13	12.930			

The F-value for CSG is 2.54, which is lower compared to F-value from F distribution, 2.82739. Thus, this shows that the temperature is a significant factor for the ash content of CSP.



**Figure 4.16** Residual plots of ash content data for CSG

The histogram from Figure 4.16 shows that raw and calcined CSG results were almost normally distributed. The P-value shown in Table 4.10 was 0.697, higher than the significant level at 0.05. Hence, the indicated data accept the null hypothesis that each ash content was statistically equal. This stated that the means of ash content affected by the difference in temperature were equal.

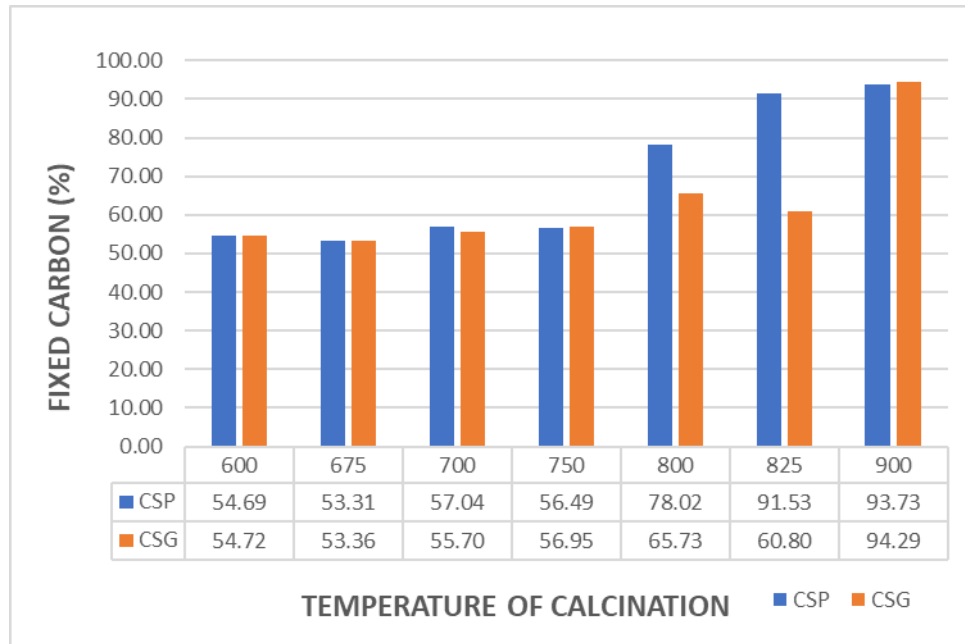
**Table 4.10** The analysis of variance for ash content of CSG

Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	6	4.385	0.7308	0.64	0.697
Error	7	7.963	1.1376		
Total	13	12.348			

The F-value for CSG is 0.64, which is lower compared to F-value from F distribution, 2.82739. Thus, this shows that the temperature is not significant for the ash content of CSG.

#### 4.5.4 FIXED CARBON

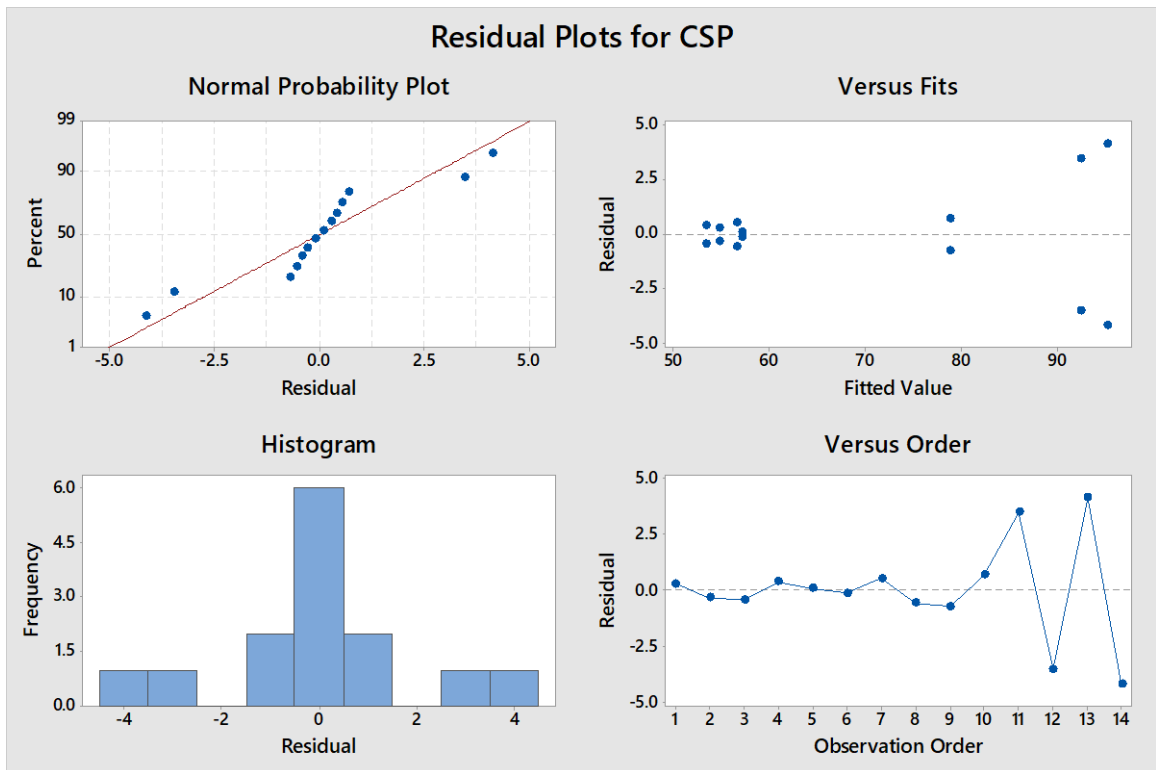
Fixed carbon was used to calculate the non-volatile carbon remaining in the cockleshell sample.



**Figure 4.17** The fixed carbon (%) for CSP and CSG for difference temperature of calcination.

Based on Figure 4.17, the fixed carbon in the calcined cockle shell is the lowest for CSP 675 and CSG 675, 53.31% and 53.36%. On the other hand, CSP 900 and CSG 900 have the highest fixed carbon, 93.73%, and 94.29%. In general, the fixed carbon is the fraction of cockle shell that remains as residue after the volatile matter has been removed, and the total of the coal's moisture and ash content has been deducted. Therefore, in general, the higher the percentage of fixed carbon of the calcined cockle shell sample, the higher the CaO production and CO<sub>2</sub> emission from the calcination process.

Then, one-way ANOVA was done to find the effect of temperature towards the fixed carbon for calcined CSP and CSG.



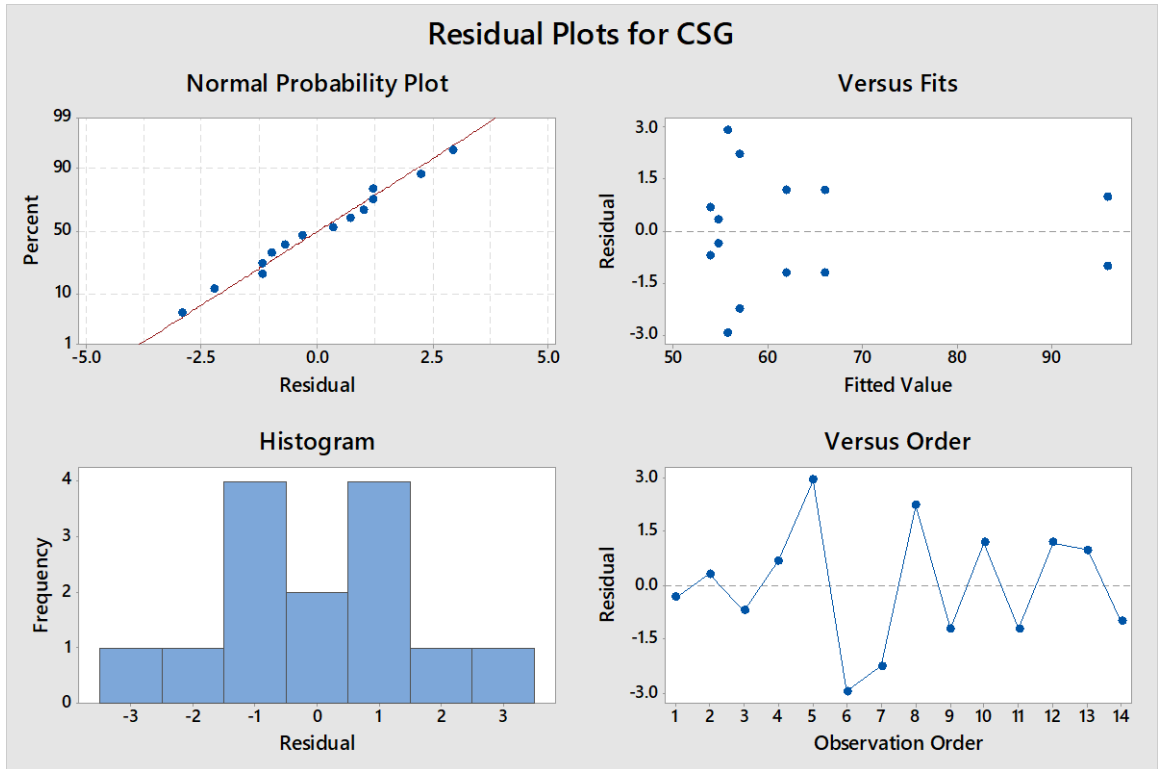
**Figure 4.18** Residual plots of fixed carbon data for CSP

The histogram from Figure 4.18 shows that the results for calcined CSP were normally distributed. The P-value shown in Table 4.11 was approximately 0, higher than the significant level at 0.05. Hence, the indicated data reject the null hypothesis that each fixed carbon was statistically equal. This stated that the means of fixed carbon affected by the difference in temperature were not equal.

**Table 4.11** The analysis of variance for fixed carbon of CSP

Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	6	4170.44	695.073	79.80	0.000
Error	7	60.97	8.710		
Total	13	4231.41			

The F-value for CSP is 79.80, higher than F-value from F distribution, 2.82739. Thus, this shows that the temperature is significant for fixed carbon of CSP.



**Figure 4.19** Residual plots of fixed carbon data for CSG

The histogram from Figure 4.19 shows that the results for calcined CSG were not normally distributed. The P-value shown in Table 4.12 was approximately 0, lower than the significant level at 0.05. Hence, the indicated data reject the null hypothesis that each fixed carbon was statistically equal. This stated that the means of fixed carbon affected by the difference in temperature were not equal.

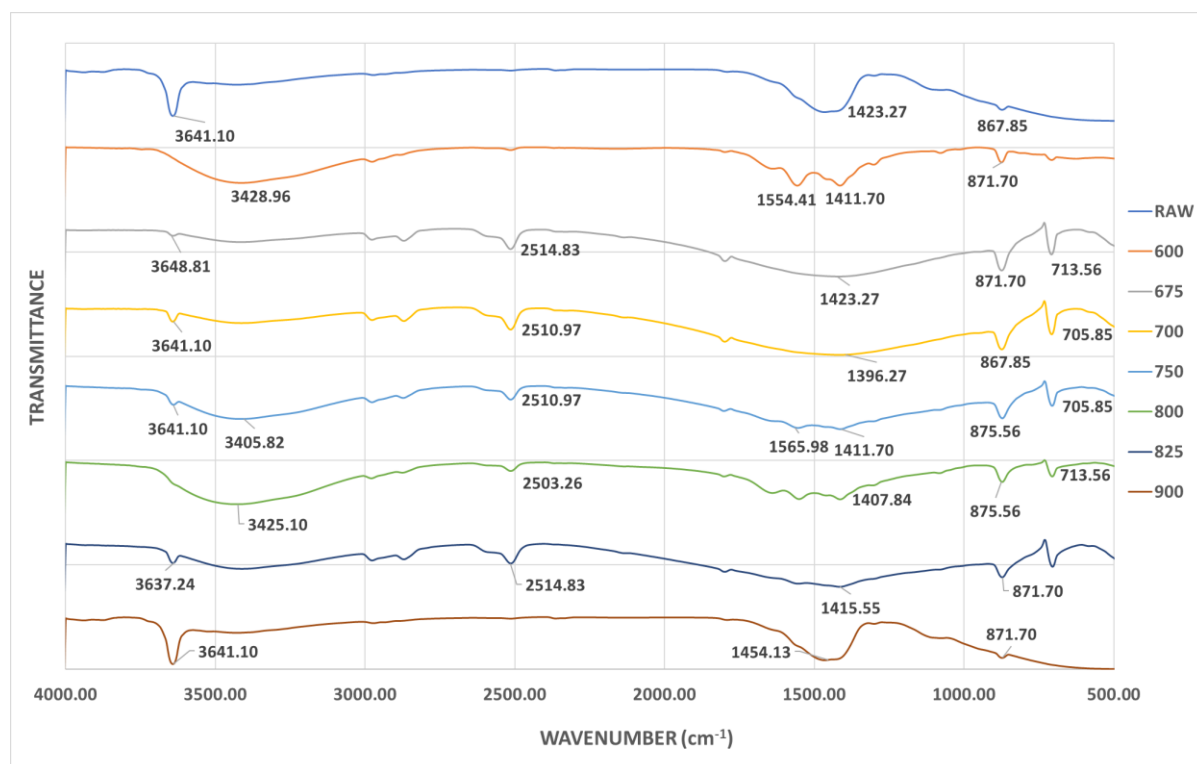
**Table 4.12** The analysis of variance for fixed carbon of CSG

Source	DF	Adj SS	Adj MS	F-Value	P-Value
temperature	6	2662.61	443.768	86.15	0.000
Error	7	36.06	5.151		
Total	13	2698.67			

The F-value for CSG is 86.15, higher than F-value from F distribution, 2.82739. Thus, this shows that the temperature is significant for fixed carbon of CSG.

## 4.6 FTIR

The raw and calcined cockleshells' FTIR spectra were collected at room temperature using the KBr technique, and the spectra were recorded at 400-4000  $\text{cm}^{-1}$ . The FTIR analysis spectrum for calcined CSP samples under different temperatures is shown in the figure below.



**Figure 4.20** The FTIR analysis spectrum for calcined CSP sample under different temperatures in  $^{\circ}\text{C}$ .

Based on Figure 4.20, the IR spectrum of cockleshell powder before and after calcined at various temperatures showed different transmittance and functional group. Several different peaks appeared, disappeared, or changed after calcination. For example, all of the CSP samples shown in the pictures have peaked around  $870\text{cm}^{-1}$ , indicating the existence of carbonate out-of-plane bending. According to Iram (2019), the bands associated with calcium carbonate have peaks of  $1430\text{ cm}^{-1}$ ,  $875\text{ cm}^{-1}$ , and  $715\text{ cm}^{-1}$ . The presence of carbonate ions implies that not all of the samples were converted fully to CaO, lowering the purity of the CaO generated.

Besides that, the IR spectrum in the raw cockleshell powder shows a sharp peak at the wavenumber of  $1423.27\text{ cm}^{-1}$ . In contrast, the peaks around that

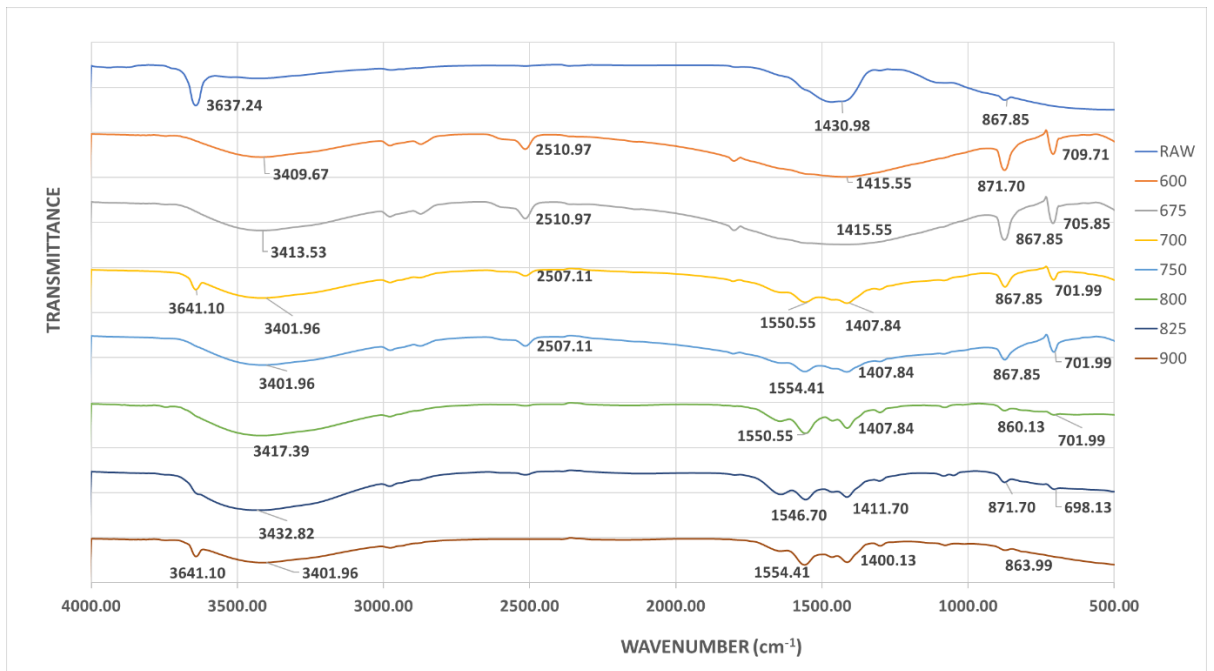
wavenumber are started to widen after calcination at various temperatures. This wavenumber belongs to the C-O vibration in the carbonate functional group of  $\text{CaCO}_3$ . Thus, the broader peaks indicate the lesser presence of  $\text{CaCO}_3$  in the calcined sample. However, a sharp peak appeared in the CSP 900 at  $1454.13\text{cm}^{-1}$ .

There is also a broad peak for CSP 600, CSP 750 and CSP 800 at  $3428.96$ ,  $3405.82$  and  $3425.1\text{cm}^{-1}$ . Due to the formation of the O-H group connected to the calcium atom from CaO, these wavenumbers around  $3400\text{cm}^{-1}$  correspond to the O-H group vibrational absorption bands from  $\text{Ca(OH)}_2$  (Suryaputra et al., 2013). O-H bonds might be caused by a mistake in sample storage, as the sample has already absorbed moisture from the surrounding environment.

Moreover, CaO was detected at the absorption band of around  $2510\text{cm}^{-1}$  for CSP 675 to CSP 825. This wavelength is a characteristic of the peak for the C-H functional group. The samples that have CaO showed the C-H stretching vibrations.

The emergence of an absorption band at wavelengths  $713.56$ ,  $705.85$ ,  $705.85$ ,  $713.56$ , and  $701.99\text{cm}^{-1}$  confirmed the existence of CaO at CSP 675 till CSP 825. Aragonite polymorphs were believed to be present in these peaks. According to Raizada et al., these absorption bands represent a fingerprint that confirms the presence of the CaO bond (2017).

In general, the FTIR data revealed that the IR spectrum changed when the calcination temperature was raised. The temperature change was significant enough to influence the IR spectrum results, as seen by widening the spectrum peaks when the calcination temperature was raised (Brites et al., 2018). This indicates that  $\text{CaCO}_3$  has been converted to CaO due to the heating procedure.



**Figure 4.21** The FTIR analysis spectrum for calcined CSG sample under different temperature

Based on Figure 4.21, all of the CSG samples shown in the pictures have peaked from 860 to 875 $\text{cm}^{-1}$ , indicating the existence of carbonate out-of-plane bending. According to Iram (2019), the peaks at 875  $\text{cm}^{-1}$  indicate the band associated with calcium carbonate. The presence of carbonate ions implied that not all of the samples were converted fully to CaO.

Besides that, the IR spectrum in the raw cockleshell powder shows a sharp peak at the wavenumber of 1430.98  $\text{cm}^{-1}$ . In contrast, the peaks around that wavenumber are started to widen for CSG 600 and CSG 675. The peaks became crooked at the CSG 700 until CSG 900. This wavenumber belongs to the C-O vibration in the carbonate functional group of  $\text{CaCO}_3$ . Thus, the broader peaks indicate the lesser presence of  $\text{CaCO}_3$  in the calcined sample.

There is also a sharp peak for RAW, CSG 700, and CSG 900 at 3637.24, 3641.1, and 3641.1 $\text{cm}^{-1}$ , while there are broad peaks for CSG 600 until CSG 900 around 3400  $\text{cm}^{-1}$ . These indicate the presence of the O-H bond in the sample. The O-H bonds, especially in the raw sample, might be caused by an error in sample storage, as the sample has already absorbed moisture from the surrounding environment. Due to the formation of the O-H group connected to the calcium atom from CaO, these wavenumbers around 3400  $\text{cm}^{-1}$  correspond to the O-H group vibrational absorption bands from  $\text{Ca(OH)}_2$  (Suryaputra et al., 2013).



Moreover, CaO was detected at the absorption band of around  $2510\text{cm}^{-1}$  for CSG 600 to CSG 750. This wavelength is a characteristic of the peak for the C-H functional group. The samples that have CaO showed the C-H stretching vibrations.

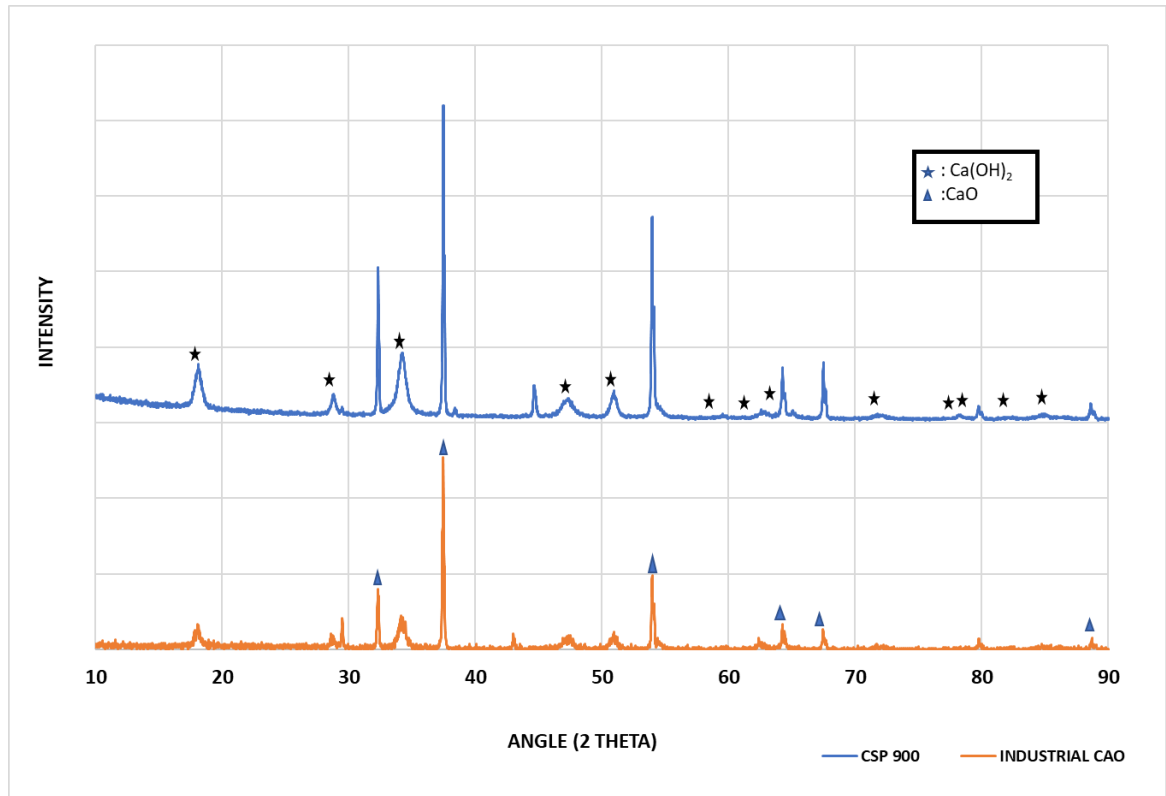
The emergence of the absorption band at wavelengths of 709.71, 705.85, 701.99, 701.99, 701.99, and  $698.13\text{cm}^{-1}$  confirmed the existence of CaO at CSG 675 till CSG 825. Aragonite polymorphs were believed to be present in these peaks. According to Raizada et al., these absorption bands represent a fingerprint that confirms the presence of the CaO bond (2017).

In general, the FTIR data revealed that the IR spectrum changed when the calcination temperature of CSG was raised. The temperature change was significant enough to influence the IR spectrum results, as seen by widening the spectrum peaks when the calcination temperature was raised (Brites et al., 2018). This indicates that  $\text{CaCO}_3$  has been converted to CaO due to the calcination procedure.

Besides, there is not much difference in peak from the FTIR analysis for the CSP and CSG. This proves that particle size did not become very significant in the calcination process.

## 4.7 XRD

The XRD analysis was done to determine the phase of the calcined cockle shell at 900°C, compared to the phase of the industrial CaO.



**Figure 4.22** XRD of calcined CSP at 900°C and industrial CaO.

The XRD patterns of the calcined cockle shell at 900°C and the industrial CaO are shown in Figure 4.22 above. Based on the XRD pattern for CSP 900 shown in the figure above, some peaks of  $\text{Ca(OH)}_2$  have appeared at  $2\theta$  of 18.18°, 28.70°, 34.29°, 47.31° and 50.94°. The presence of  $\text{Ca(OH)}_2$  peaks indicates the presence of CaO in the CSP 900. The formation of  $\text{Ca(OH)}_2$  is due to the reaction between CaO with  $\text{H}_2\text{O}$  in the air. This is because CaO is a highly reactive compound in the presence of water vapour. The sample's CaO could also absorb the moisture or water from the surrounding atmosphere (Khiri et al., 2017). The CaO was obtained because several  $\text{CaCO}_3$  compounds have changed phase after the calcination process (Berent et al., 2019).

The XRD pattern for CSP 900 was compared to the XRD pattern for industrial CaO. Based on figure 29 above, peaks of CaO were shown at  $2\theta$  of 32.33°, 37.45°, 53.97°, 64.24°, 67.47°, 79.79° and 88.66°. These CaO peaks from industrial CaO XRD

analysis also appeared in the peak for CSP 900. Thus, it proved the presence of CaO in the CSP 900.



## 4.8 CALCINATION




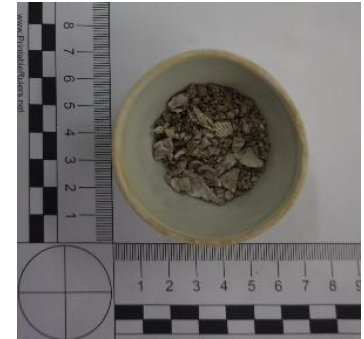


The calcination process on the raw cockleshell was based on the temperature and particle size parameters. As a result, the cockle shells will convert to pure CaO and produce carbon dioxide. The factors' effect was studied by calculating the percentage of mass loss after calcination and the percentage of CaO.

### 4.8.1 PHYSICAL OBSERVATION

After the cockleshell have been calcined for 4 hours, the physical of the CSG and CSP could be changed. Table 4.13 below shows the physical observation of the granulated sample. Based on the table below, the granulated calcined sample at 600°C has a darker colour and appears greyish. However, the calcined sample at 900°C appeared whiter.






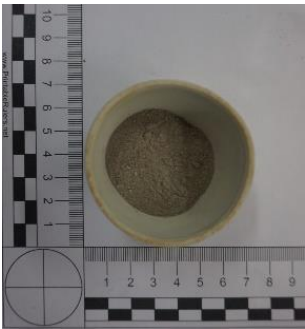
**Table 4.13** The physical observation of the granulated sample

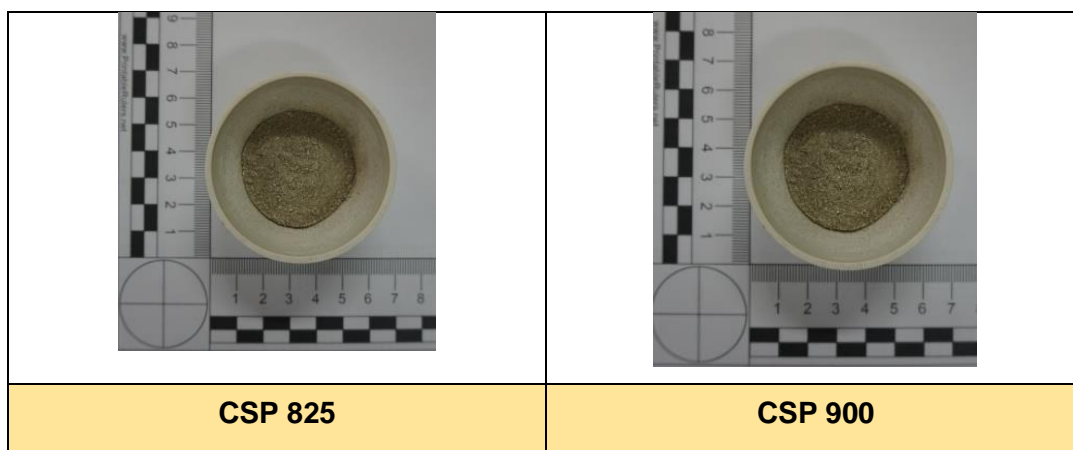
	
<b>RAW CSG</b>	<b>CSG 600</b>

	
<b>CSG 675</b>	<b>CSG 700</b>
	
<b>CSG 750</b>	<b>CSG 800</b>
	
<b>CSG 825</b>	<b>CSG 900</b>

Then, Table 4.14 below shows the physical observation of the powdered sample. Based on the table below, the powdered calcined sample at 600°C has a more greyish colour than the powdered calcined sample at 900°C.

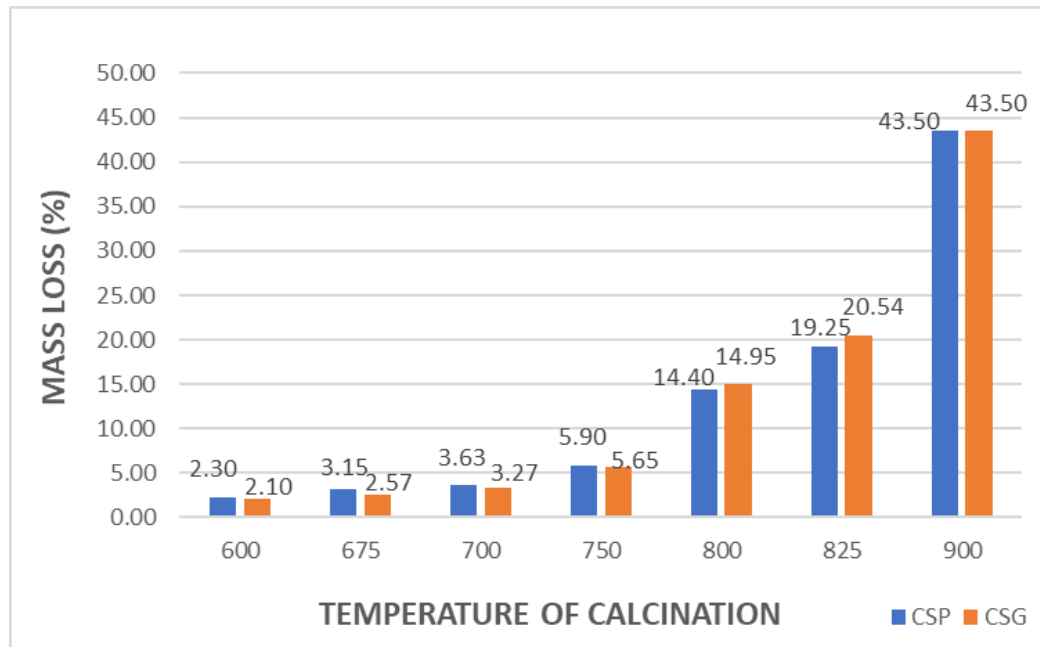
**Table 4.14** The physical observation of the powdered sample

	
<p><b>RAW CSP</b></p>	<p><b>CSP 600</b></p>
	
<p><b>CSP 675</b></p>	<p><b>CSP 700</b></p>
	
<p><b>CSP 750</b></p>	<p><b>CSP 800</b></p>



#### 4.8.2 MASS LOSS

The mass loss for CSP and CSG was recorded and compared after the calcination process at different temperatures. The temperature for calcination was varied from 600°C to 900°C while keeping constant the other parameters (weight and contact hour) to study the effect of calcination temperature on the mass loss of samples. The result of mass loss for the samples is as shown in Figure 4.23.



**Figure 4.23** The percentage of mass loss (%) of CSP and CSG for each calcination temperature.

The presentation of data in Figure 4.23 above shows that temperature increases will increase the mass loss of the sample. Based on the figure, the

calcination of the CSP and CSG at 900°C have the greatest mass loss, which is 43.5%, because most samples had been converted into their simplest form, CaO, when calcined at high temperature. This resulted in great mass loss. This result is tallied with the result obtained by Mohd Shuha (2019) which he obtained around 40% of mass loss for calcination at 900°C.

The lowest percentage of mass loss for CSP and CSG is when calcined at 600°C, which are 2.3% and 2.1%. The lowest mass loss happened because of the incomplete conversion of CaCO<sub>3</sub> to CaO, resulting in less mass loss. This can be proven by the change of colour of the sample before the calcination and after the calcination at 600°C. The white sample turns greyish. This also approved the statement by Yan (2016) that less volatilization of carbon occurred due to the thermal treatment at low, which was also approved by the study from Musa (2019).

Besides temperature, the effect of particle size on the mass loss of samples was studied. Based on data obtained, the mass loss for CSG is slightly lower than CSP for the calcination from temperature 600°C to 750°C, while the mass loss for CSG is slightly higher than CSP for the calcination between temperature 800°C and 825°C. The results show that particle size affected the heat distribution during the calcination process from temperature 600°C to 825°C.

However, there is no difference in the percentage mass loss for CSG and CSP, calcined at 900 °C. This shows that at 900°C, the particle size did not affect the percentage mass loss of the calcination.

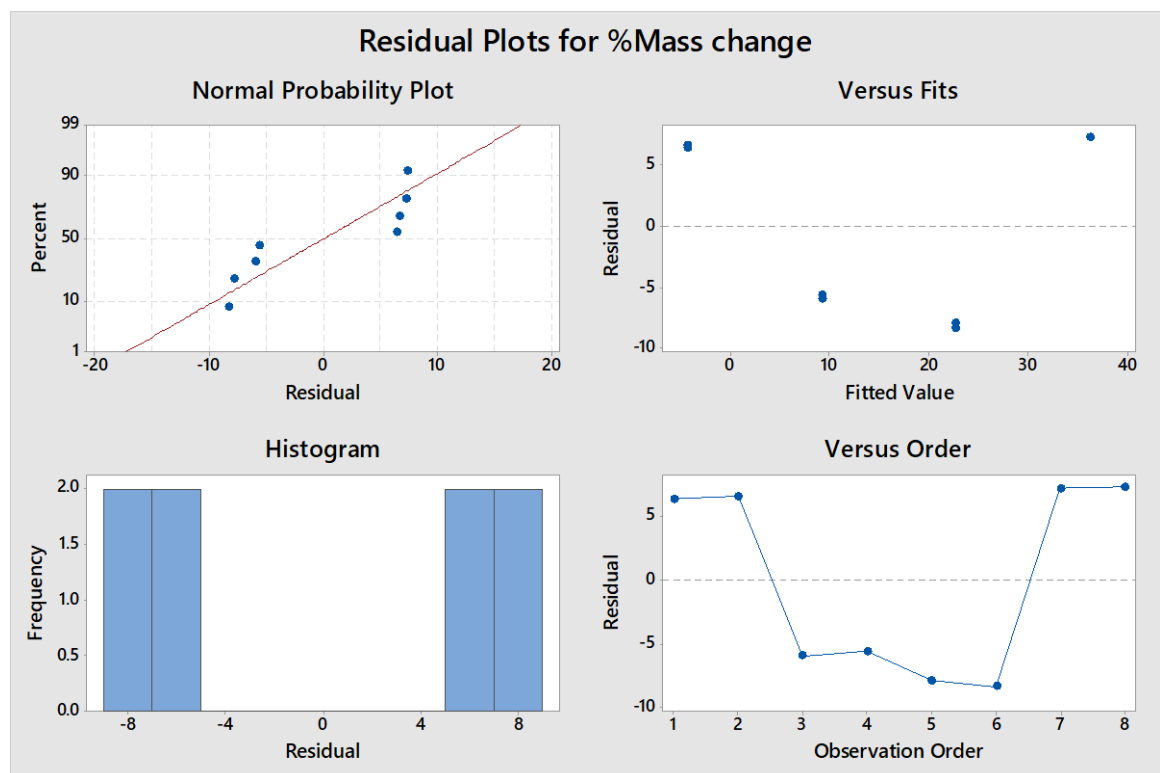
According to the results obtained, the CSG 800 and CSG 825 with a large surface area lose a higher mass percentage than the CSP 800 and CSP 825. CSP has a lesser mass reduction than CSG, which could be attributed to the powdered form converting to a fine particle after calcination at a high temperature. As a result, there was a lot of carbon volatilization and consequently a lot of mass loss in the samples. As heat distributes uniformly across a larger surface area, the heat distribution towards the sample with larger particle size is higher than the sample with a smaller particle size (McGraw Hill, 2008).

Nevertheless, the percentage of mass loss of CSG from temperature to 600°C to 750°C was slightly lower than the CSP. The The cockle shell's hard and thick shell

layer made it harder to decompose at these temperatures since the heat could not be distributed better onto the samples. The measured average thickness of the cockleshell was 1.812mm.

The uniformity of heating during the thermal treatment is important. Therefore, CSP samples that got more heat to penetrate uniformly across the sample lost most of their initial mass compared to CSG samples.

Henceforth, to show the significant difference in calcination temperature and particle size towards the mass loss between before and after the calcination, regression analysis was conducted. The graph and data obtained are from the regression analysis without the transformation for the percentage of mass change versus temperature and type of sample.



**Figure 4.24** The residual plots for the percentage of mass change of the regression without transformation

**Table 4.15** Analysis of variance of the regression without transformation.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	2	1827.15	913.57	11.75	0.013



Temperature	1	1827.15	1827.15	23.49	0.005
Type of sample	1	0.00	0.00	0.00	0.999
Error	5	388.89	77.78		

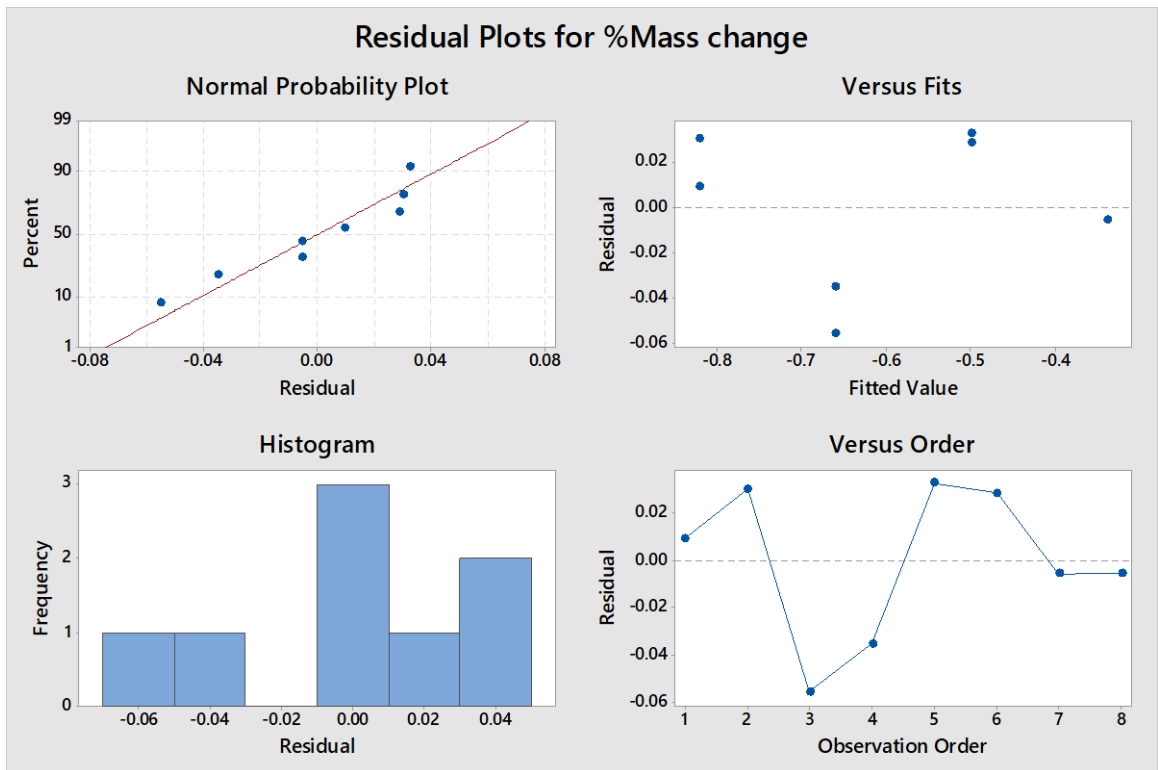
The histogram diagram indicated that this data was not normally distributed. The sample type was not significant in the percentage of the mass loss because the p-value is 0.999, which is larger than the significant level, 0.05. However, the p-value for the temperature factor is 0.005, which is lower than 0.05. Thus, the temperature is significant in the percentage of the mass loss.

Besides that, the F-value for temperature is 23.49, which is higher than F-value from F distribution, 4.06042. Thus, this shows that the temperature is significant for the percentage of mass loss. However, the F-value for the sample type is 0, which is lower than F-value from F distribution, 4.06042. Thus, this shows that the sample type is not significant for the percentage of mass loss.

Equation 8 below is the percentage of mass change for granule and powder samples. They have the same equation because the particle size is not critical for the calcination process.

$$\% \text{ Mass change} = -85.4 + 0.1352 \text{ Temperature} \quad (\text{Eq. 8})$$

Further study was done using Box-cox transformation with the stepwise selection of terms.



**Figure 4.25** Residuals plots for the percentage of mass change of Box-cox transformation

Based on Figure 4.25 above, the data is almost normally distributed because the histogram graph had a half bell-curved shape. The p-value of the temperature is 0. Thus, it indicated that the temperature is a significant factor in mass change.

Besides that, the F-value for temperature is 213.23, which is higher than F-value from the F distribution, 3.77595. Thus, this shows that the temperature is significant for the percentage of mass loss. The R-squared is 97.26% which is considerably high. So, the correlation between the percentage of mass change and the temperature was approved.

**Table 4.16** Analysis of Variance of mass change for Transformed Response

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	1	0.257641	0.257641	213.23	0.000
Temperature	1	0.257641	0.257641	213.23	0.000
Error	6	0.007250	0.001208		
Total	7	0.264890			

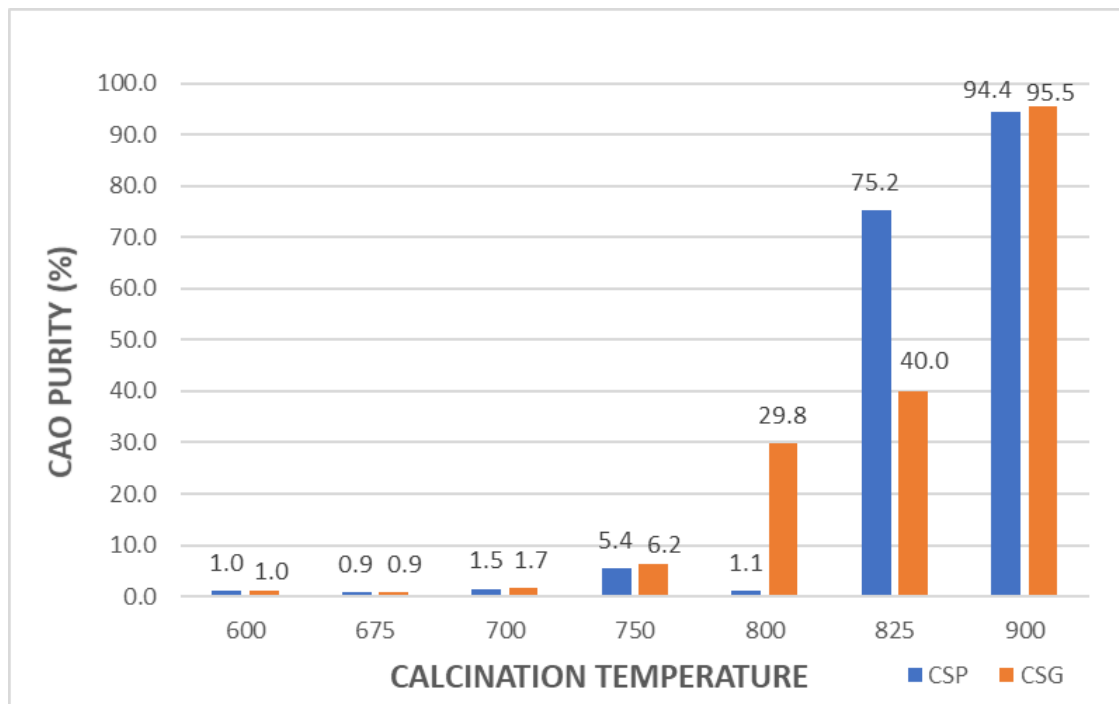
The regression equation after the transformation for the percentage of mass loss is shown below.

$$-\% \text{Mass change}^{-0.282357} = -1.7837 + 0.001605 \text{ Temperature} \quad (\text{Eq. 9})$$

The percentage of mass change regression equation would be used again with the regression equation of the percentage of CaO purity to find the optimal condition for the calcination process.

#### 4.8.3 CAO PURITY

The rapid sugar test (using sulphuric acid) was done to determine the available lime (CaO) contained in the calcined cockle shell sample. The calculated available lime contained in the calcined cockle shell is shown in the figure below.



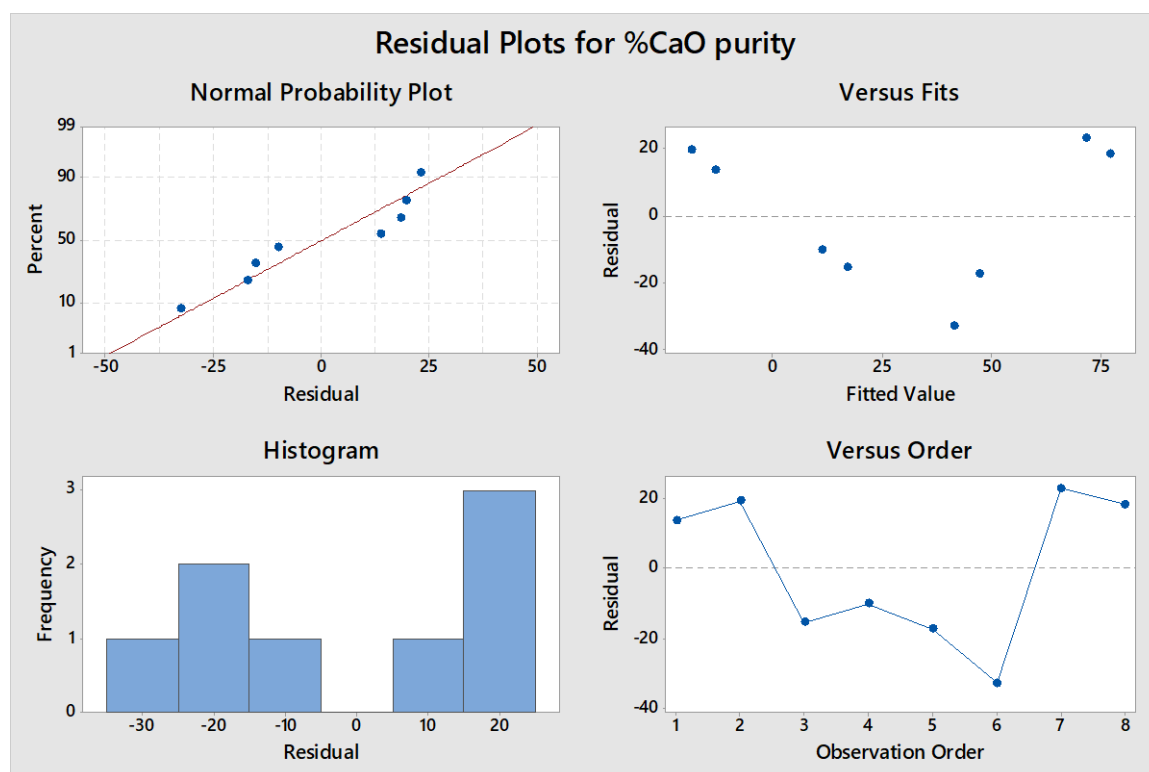
**Figure 4.26** The percentage of CaO purity for CSP and CSG for each temperature of calcination.

Based on Figure 4.26, the calcined CSP and CSG at 900°C have the highest percentage of available lime, 94.4%, and 95.5%. Therefore, it shows that almost all CaCO<sub>3</sub> has turned to CaO at 900°C.

The percentage of CaO purity in the CSP and CSG for temperature 600°C to 700°C is very small, less than 2%. Even the sample has lost mass after calcination at this temperature; however, the small CaO purity value indicates that only a small amount of CaCO<sub>3</sub> has been converted into CaO.

Based on the CaO purity test, the percentage of CaO in the CSG 825 is lower than that of CaO in the CSP 825. This shows that the particle size affects the calcination process at this temperature.

Henceforth, to show the significant difference in calcination temperature and particle size towards the percentage of CaO purity after the calcination, regression analysis is conducted.



**Figure 4.27** Residual plots for the percentage of CaO purity without transformation

**Table 4.17** Analysis of variance of the percentage of CaO purity

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	2	9029.1	4514.56	7.18	0.034
Temperature	1	8965.1	8965.08	14.26	0.013

Type of sample	1	64.0	64.04	0.10	0.762
Error	5	3143.2	628.64		
Total	7	12172.3			

The graph and data obtained are from the regression analysis without the transformation for CaO purity percentage versus temperature and sample type. The histogram diagram indicated that this data was not normally distributed. The sample type was not significant in the percentage of the CaO purity because the p-value is 0.762, which is larger than the significant level, 0.05. However, the P-value for the temperature factor is 0.005, lower than 0.05. Thus, the temperature is significant in the percentage of CaO purity.

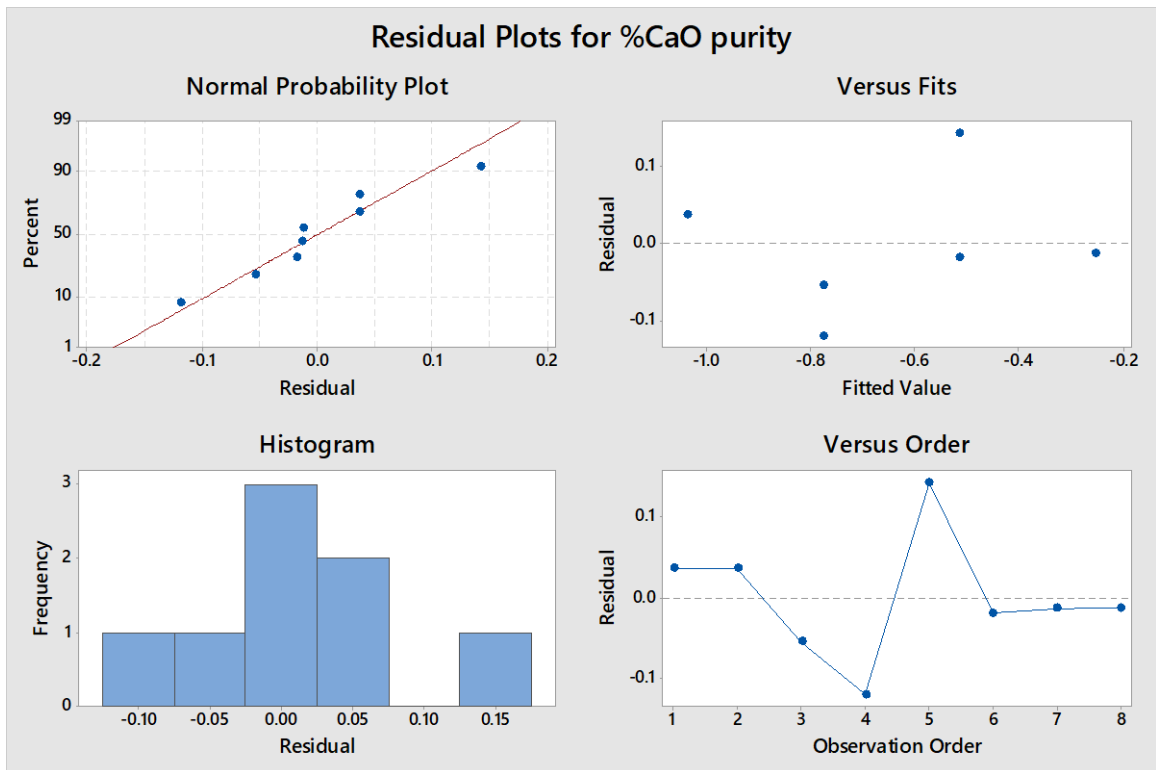
Besides that, the F-value for temperature is 14.26, which is higher than F-value from F distribution, 4.06042. Thus, this shows that the temperature is significant for the percentage of CaO purity. However, the F-value for the type of sample is 0.10. Therefore, this indicates that the sample type is not significant for the percentage of CaO purity.

Equations 10 and 11 below are the percentage of CaO purity for granule and powder samples.

$$\text{Granulated sample: \%CaO purity} = -192.5 + 0.2994 \text{ Temperature} \quad (\text{Eq. 10})$$

$$\text{Powdered sample: \%CaO purity} = -198.2 + 0.2994 \text{ Temperature} \quad (\text{Eq. 11})$$

Further study was done using Box-cox transformation with the stepwise selection of terms.



**Figure 4.28** Residual plots for the percentage of CaO purity with Box-cox transformation

Based on Figure 4.28 above, the data is almost normally distributed because the histogram graph had a bell-curved shape. In addition, the P-value of the temperature is 0. Thus, it indicated that temperature is a significant factor in CaO purity.

Besides that, the F-value for temperature is 100.67, which is higher compared to F-value from the F distribution, 3.77595. Thus, this shows that the temperature is significant for the percentage of CaO purity. The R-squared is 94.38% which is considerably high. So, it approved the correlation between the percentage of CaO purity and the temperature.

**Table 4.18** The analysis of variance for the percentage of CaO purity with Box-cox transformation.

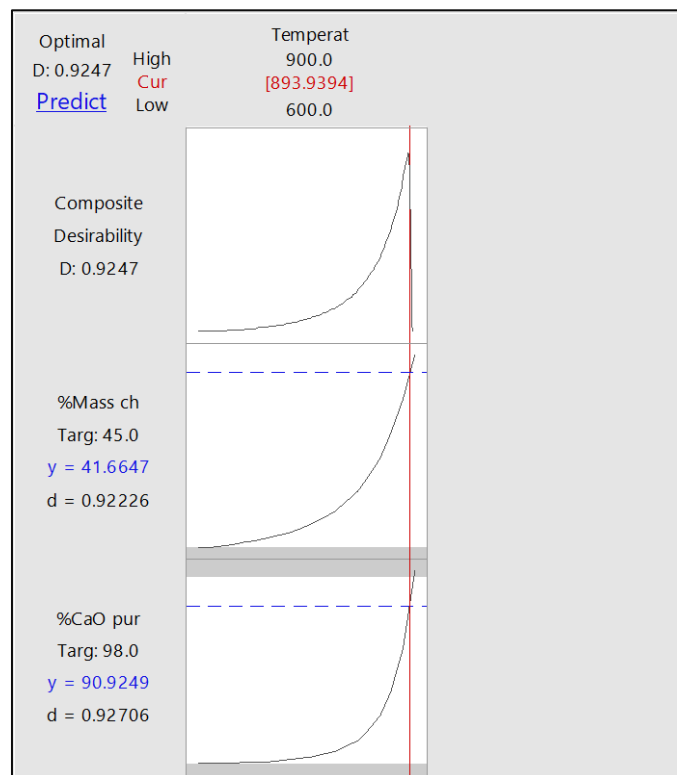
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	1	0.68224	0.682243	100.67	0.000
Temperature	1	0.68224	0.682243	100.67	0.000
Error	6	0.04066	0.006777		
Total	7	0.72290			

After the transformation for the percentage of CaO purity, the regression equation is shown below.

$$-\%CaO \text{ purity}^{-0.290946} = -2.604 + 0.002612 \text{ Temperature} \quad (\text{Eq. 12})$$

The response optimization was done based on final regression equations for mass loss and the percentage of CaO purity. The response optimization was done to find the optimal condition for the parameters. However, since the particle size was insignificant, the only temperature was the main parameter. Therefore, the targeted percentage of mass loss was 45%, and the percentage of CaO purity was 98% with the variable temperature range of 600°C to 900°C.

The obtained graphs from the response optimization are shown in Figure 4.29 below.



**Figure 4.29** The graphs for response optimization.

The obtained solution is shown in Table 4.19.

**Table 4.19** The solution for the response optimisation.

Solution	Temperature	%Mass change Fit	%CaO purity Fit	Composite Desirability
1	893.939	41.6647	90.9249	0.924655

Based on Table 4.19, the calcination temperature required to get 41.66% of mass change and 90.92% of CaO was 893.9°C with the composite desirability of 0.924655. The composite desirability is the weighted geometric mean of the individual desirabilities for the responses. Therefore, in this case, Minitab determines optimal settings for the temperature variables by maximizing the composite desirability.

**Table 4.20** Multiple response prediction

Response	Fit	95% CI	95% PI
%Mass change	41.6647	(26.1534, 71.234)	(17.3133, 134.3)
%CaO purity	90.9249	(26.5167, 632.313)	(10.7031, 85452.0)

Based on Table 4.20, the 95% confidence interval for the percentage of mass change was (26.1534, 71.234) while the 95% predicted interval was (17.3133, 134.3). On the other hand, the 95% confidence interval for the percentage of CaO purity was (26.5167, 632.313), while the 95% predicted interval was (10.7031, 85452.0).

#### **4.9 SUMMARY OF THE RESULT**

Some of the results obtained in this study were tabulated in the table to understand better. For example, the percentage of mass loss, CaO purity, pH, bulk density, and proximate analysis result of the granulated sample are shown below.



**Table 4.21** The percentage of mass loss, CaO purity, pH, bulk density, and proximate analysis result of CSG

SAMPLE	MASS LOSS (%)	CaO PURITY (%)	pH	BULK DENSITY (g/ml)	MOISTURE CONTENT (%)	VOLATILE MATTER (%)	ASH YIELD (%)	FIXED CARBON (%)
RAW	N/A	N/A	8.7	1.07	0.5	45.5	N/A	N/A
CSG 600	2.10	1.0	11.0	1.09	0.26	42.86	2.16	54.72
CSG 675	2.57	0.9	12.3	1.00	1.01	44.12	1.51	53.36
CSG 700	3.27	1.7	12.3	1.14	1.59	41.29	1.42	55.70
CSG 750	5.65	6.2	12.5	1.12	0.25	41.44	1.36	56.95
CSG 800	14.95	29.8	12.5	0.92	0.35	32.50	1.42	65.73
CSG 825	20.54	40.0	12.3	0.94	1.01	38.06	0.14	60.80
CSG 900	43.5	95.5	12.4	0.68	1.59	2.98	1.13	94.29

Table 4.21 shows that CSG 900 has the highest percentage mass loss with the highest percentage of CaO purity and fixed carbon. However, its pH is indifferent from other calcined CSG.

**Table 4.22** The percentage of mass loss, CaO purity, pH, bulk density, and proximate analysis result of CSP

SAMPLE	MASS LOSS (%)	CaO PURITY (%)	pH	BULK DENSITY (g/ml)	MOISTURE CONTENT (%)	VOLATILE MATTER (%)	ASH YIELD (%)	FIXED CARBON (%)
RAW	N/A	N/A	8.7	1.39	0.5	45.5	N/A	N/A
CSP 600	2.30	1.0	11.3	1.27	2.11	42.50	0.71	54.69
CSP 675	3.15	0.9	11.8	1.23	1.39	42.16	3.14	53.31
CSP 700	3.63	1.5	12.1	1.27	0.26	40.60	2.10	57.04
CSP 750	5.90	5.4	12.4	1.25	1.52	40.98	1.01	56.49
CSP 800	14.40	1.1	12.4	1.15	1.01	18.32	2.65	78.02
CSP 825	19.25	75.2	12.1	1.23	1.01	5.30	2.16	91.53
CSP 900	43.5	94.4	12.3	0.75	1.53	2.94	1.81	93.73

The percentage of mass loss, CaO purity, pH, bulk density, and proximate analysis result of the powdered sample are shown in Table 4.22. The table above shows that CSP 900 has the highest percentage mass loss with the highest percentage of CaO purity and fixed carbon. However, its pH is indifferent from other calcined CSP.

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 OVERALL DISCUSSION

The main objectives of this study were to formulate the ideal conditions with the parameters: particle size of cockleshell sample and temperature (°C) of the calcination process of cockle shells to synthesize calcium oxide (CaO). In this research, the important variables that significantly affect the formation of calcium oxide are temperature, as referred to in the analysis conducted. Therefore, these dependent variables should be associated with calcination in aiming for the optimum condition. Weight and contact hours were constant for this study, while particle size did not significantly affect the calcination process.

After being analyzed, the ideal temperature calcination process for the cockle shell is 893.9°C. Besides that, CSP 900 and CSG 900 have the highest percentage of CaO, 94.4%, and 95.5%. Therefore, it shows that almost all CaCO<sub>3</sub> has turned to CaO at 900°C.

The following objectives were to study the physicals and chemical characteristics of calcined and uncalcined cockle shells. It has been done through FTIR analysis, XRD, TGA, proximate analysis, bulk density, and pH. The emergence of an absorption band at wavelengths around 710 and 2510cm<sup>-1</sup> confirmed the existence of CaO. The XRD pattern for CSP 900 has shown some peaks at 2θ of 18.18°, 28.70°, 34.29°, 47.31° and 50.94°. It indicates the presence of Ca(OH)<sub>2</sub> in the sample and proves the presence of CaO in the CSP 900. Besides that, CSP 900 and CSG 900 have the highest fixed carbon, 93.73% and 94.29%

## 5.2 RECOMMENDATION

In order to improve the rapid sugar test method, the volumetric flask should be used during the dilution of the mixture of calcined sample and sugar solution to obtain a more exact value of the percentage of the purity of CaO.

Besides that, the granule sample in this experiment did not have a specific size. Therefore, it is much better to categorise the particle size into a few ranges of size to get better results.

Other than that, the mass of the sample used in the proximate analysis was very small. Thus, it might affect the value of the moisture content, volatile matter, and ash content negatively. Therefore, the enormous mass of samples to be used in further study was recommended.

Lastly, the research on various other shellfish should be studied to be added as an alternate source for CaCO<sub>3</sub>.

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