# Adsorption Capacity of CO<sub>2</sub> for Postcombustion Process Using Cockle Shells

by

## Muhammad Mustaqim bin Razak

# Dissertation submitted in partial fulfilment of the requirements for the Bachelor of Engineering (Hons) (Chemical Engineering)

SEPTEMBER 2011

Ì

Universiti Teknologi PETRONAS Bandar Seri Iskandar 31750 Tronoh Perak Darul Ridzuan

# Adsorption Capacity of CO<sub>2</sub> for Postcombustion Process Using Cockle Shells

by

Muhammad Mustaqim bin Razak

A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved b (Ap. Dr. Suzana Yusup)

UNIVERSITI TEKNOLOGI PETRONAS TRONOH, PERAK SEPTEMBER 2011

ABSTRACT .		v
LIST OF TAI	BLES	8
LIST OF FIG	URES	9
CHAPTER 1:	INTRODUCTION	10
	1.1Background of Study	11
	1.2 Problem Statement	12
	1.3 Objectives	13
	1.4 Scope of Study	13
	1.5 Project Relevancy	14
	1.6 Project Feasibility	14
CHAPTER 2:	LITERATURE REVIEW	16
	2.1 Natural Adsorbent Selection	16
	2.2 Calcination and Carbonation	18
	2.3 Calcination Duration	20
	2.4 Particle Sizes Selection	20
	2.5 Carbon Dioxide Capture	22
CHAPTER 3:	METHODOLOGY	24
	3.1 Overview	24
	3.2 Raw Materials	24
	3.3 Material Preparation	24
	3.4 Material Characterization	26
	3.5 Equipments	27
	3.6 Effect of Calcination Condition on Carbonation Conversion	27
	3.7 Gantt Chart	29
CHAPTER 4:	RESULTS AND DISCUSSIONS	30
	4.1 Carbonation Behaviour Under Various Calcination Conditions	31
	4.2 Comparison of Carbonation Performance	36
	4.2.1 Effect of Calcination Temperature	36
	4.2.2 Effect of Particle Sizes	
	4.2.3 Effect of Calcination Duration and Ramp Rate	
	4.3 Overall Comparison Performance of Adsorbent	39

# **Table of Contents**

CHAPTER 5: CONCLUSION	40
REFERENCES	42
APPENDICES A	46
APPENDICES B	64

### ABSTRACT

Carbon dioxide is the major contributor of greenhouse gases (GHG) emission thus become one of the most important environmental issues around the globe. Reducing the GHG impact has become critical to sequester  $CO_2$  from fossil fuel power plants which cover one third of all anthropogenic  $CO_2$  emissions (Herzog et al.,2004). This realization has raised some questions on the responsible use of the fossil fuels of the emerging from the reaction that critically need for  $CO_2$  management strategy and technology to reduce projected global warming as well its impacts. As  $CO_2$  emissions have been unequivocally linked to global warming and climate change (IPCC,2007), mitigation measures are a matter of urgency (Mercedes et al.,2010).

Calcium oxide (CaO) known to has capability as carbon dioxide (CO<sub>2</sub>) adsorbent. CaO present with precursor and can be produced via thermal decomposition known as calcination; CaCO<sub>3</sub> (s)  $\rightarrow$  CaO(s) + CO<sub>2</sub> (g). The popular natural calcium carbonate (CaCO3) sources such as dolomite, limestone, and seashell because of high percentage of calcium (Ca) present. The cockle shell is present abundantly in Malaysia and thus provide a profitable value if the resources being develop as an alternatives in CO<sub>2</sub> adsorbent. As a matter of fact over many study, thermal decomposition of CaCO<sub>3</sub> relies on several factors that can affect the process of adsorption capacity and reversibility. Thus, the objective of this study is to investigate the presence of CaCO<sub>3</sub> in cockle shell and to demonstrate the effect of particle sizes, calcination temperature, calcination duration and ramp rate on its adsorption capacity. The effect has been studied with three different particle sizes (less than 0.125mm, 0.355-0.710 mm, 1-2 mm), three different calcination temperature (800°C, 850°C, 950°C), three different calcination duration (20min, 30min, 40min), and three different ramp rate (10 °C/min, 15 °C/min, 20 °C/min).

### ACKNOWLEDGEMENTS

Alhamdulillah praises to The Almighty Allah for guiding me with the strength and health towards completing this Final Year Project. It is a pleasure to thank the many people who made this project possible.

First and foremost, I would like to say a million of thankfulness to my supervisor, Assoc. Prof. Dr. Suzana Yusup who has been very supportive from the beginning to the end of the project. Her guidance, attention and advice are very much appreciated. My heartfelt gratitude also goes out to the lecturers of Chemical Engineering Department for the advices and knowledge sharing. Their suggestions, enthusiastic support, knowledge and constructive criticisms helped me greatly in understanding the project.

I also wanted to acknowledge UTP Bio-Hydrogen Research Group, Universiti Teknologi PETRONAS (UTP) and the postgraduate office staffs for providing the facilities and guidelines to ensure successful of each project.

My utmost appreciation goes to my family and friends who inspired, encouraged with never ending prayers and fully supported me for every trial that come in my way. Their advices will always be remembered and become the motivation in continuing the journey of my life. The love, support and precious time together has made this journey more meaningful.

# **DEDICATION**

To Razak Abu Saman & Asmani Mohd Taha

To my family

To my supervisor

To my friends

## LIST OF TABLES

Table 2-1: Percentage of Chemical analysis (dry wt%) for different type of shell and
limestone (Y;i et al., 2009)
Table 2-2: Chemical analysis of cockle shells by XRF (Mustakimah et al., 2010)17
Table 2-3: Flue Gas R&D Pathways (Herzog et al., 2009)
Table 2-4: Time taken vs particle size for particular sizes of Goynuk limestone on the
calcination duration (Irfan et al.,2001)
Table 2-5 :Comparison of each CO <sub>2</sub> separation and capturing technology22
Table 3-1: Experimental condition to study the effect of calcination conditions on
carbonation conversion
Table 3-2: Equipment related and purpose
Table 4-1: Chemical analysis of cockle shells
Table 4-2: Taguchi Analysis level (Temperature, Diameter, Duration and Ramp
rate)
Table 4-3: Summary of experiment result
Table 4-4: Response Table for Signal to Noise Ratios
Table 4-5: Response Table for Mean (Carbonation Conversion)
Table 4-6: Optimum value for each parameter using S/N ratios

## LIST OF FIGURES

Figure 1-1: Global average abundance of CO <sub>21</sub>
Figure 2-1: Carbonation conversions of CaO adopted from (A) Bhatia et al, 198
and (B) Gupta et al., 20021
Figure 2-2: Time(min) taken vs conversion of Goynuk limestone to CaO (Irfan
al.,2001)2
Figure 3-1: Thermal Gravimetric Analyzer2
Figure 3-2: Preparation of cockle shell powder for research purposes
Figure 3-3: wt% moisture vs time (min) for drying process in oven at 105 <sup>o</sup> C2
Figure 4-1 : Temperature and weight% of cockle shell sample vs time attained from
Pyris manager software. (Calcination T; 950°C; Carbonation T: 650°C
Heating rate: 15°C /min; Particle size: < 0.125mm, Calcined duration: 2
min)
Figure 4-2: Carbonation Conversion over Number of Experimental Run3
Figure 4-3 : Effect of temperature and diameter to adsorption capacity at 40 mi
calcination duration and 15 °C/min ramp rate
Figure 4-4: Effect of calcination duration and ramp rate to adsorption capacity a
950 °C calcination temperature and <0.125 mm particl
diameter
Figure 4-5: Carrying capacity after number of cycles in a bed sand

### **CHAPTER 1**

#### **INTRODUCTION**

### **1. INTRODUCTION**

The problem of global warming caused by CO<sub>2</sub> emission has raised serious concerns since the CO<sub>2</sub> concentration in the atmosphere has increased rapidly due to the industrial revolution era. United Nations predicting world population growth from 6.6 billion in 2007 to 8.2 billion by 2030, thus energy demand must be increased substantially over that period (WNA,2011) which increase the need of energy efficiency. Fossil fuels will continue to be major source of energy for the next few decades as the non-carbon energy sources still expensive and limited. This situation open a critical need of studies over the effect of the continuity usage of the energy source.

Increment capacity of the energy demands especially fossil fuels along with a heightened awareness of human effect on the global climate change, in particular the production of greenhouse gases (GHG) cause the risen responsibilities to develop alternative sources of energy and chemicals. Others also taken futher step in addressing energy security to protect the environment from futher being affected from these threats. The recovery of carbon dioxide from large emission sources needed a scientific challenge and high engineering studies which also received numbers attention for years. A great figure of engineering studies has been dedicated to the restriction of GHG emissions, which remains the huge challenge of global warming scenario. In example, the growth rate of  $CO_2$  has averaged about 1.68 ppm per year over the past 30 years (J.H. Butler, 2011).



Figure 1-1: Global average abundance of CO<sub>2</sub>.

Most of these emission comes from the heavy industries that account the involvement of oil and gas industries. The IPCC (International Panel on Climate Change) stated "Globally, and in most countries,  $CO_2$  accounts for more than 90% of  $CO_2$ -eq GHG emissions from the industrial sector (Price *et al.*, 2006; US EPA, 2006b)" (Metz et al., 2007). It is therefore to develop cost-effective  $CO_2$  management schemes to curb its emission. The process to develop the new oxide surface is to find the solution of the current temperature constraint of the conventional carbon dioxide removal such as amine and zeolites.

#### 1.1. Background of Study

The main purpose of the study is to find and develop the best adsorbent condition for the carbon dioxide capability in uptake capacity. The background of study include the selection of adsorbent to be used, the suitable morphological properties of the selected adsorbent, how the reaction takes place on the surface of the adsorbent. The study in details include to find the fit variable of temperature in the TGA for the best setting condition in adsorbing carbon dioxide throughout the reaction cycles.

CaO (solid) + CO<sub>2</sub>(gas) 
$$\leq >$$
 CaCO<sub>3</sub>(solid) (1)  
 $\Delta H^{O}_{873.15} = -171.2 \text{ kJ mol}^{-1}$  (carbonation)

The integration of contionuous Calcium looping scheme, exploiting the reversible reaction between CaO and CO<sub>2</sub>, offer potential for reducing the cost of carbon capture in future clean energy system (Abanadez et al.,2007). Carbonation of CaO followed by recarbonation of CaCO<sub>3</sub> provide a way in developing the new adsorbent not only be able to do multiple cycles but also to withstand the high temperature of any gasification unit. However, discovery of this new oxide capability has disadvantegous as the potential is limited by the observed decay in CO<sub>2</sub> capture capacity of CaO through capture and release cycles (Silaban et al.,1995; Abanadez et al.,2003).

#### **1.2. Problem statement**

The current commercial operation for  $CO_2$  capture used a chemical absorption method. Monoethanol Amine (MEA) as the absorbent has been recognized as the most matured process (A.B.Rao,2002) to remove  $CO_2$  from gas streams in several areas of oil and gas industry and have been for over sixty years (John et al.,2011,p121). This proven type of amine for  $CO_2$  removal at low pressure, MEA will partially degraded when reacted with  $CO_2$ . The drawback of MEA is the absorbent is highly corrosive leading to the use of costly absorber packing and column materials. the impurities and minor components in the flue gas including  $SO_2$ ,  $NO_2$  and  $O_2$  need to be removed or separated before enters the absorber in order to prevent the degradation of the MEA solution.

The pretreatment processes before entering the absorber affect much on the processing cost. The flue gasses of commercial plant required cooling stage prior to capture carbon dioxide in the reactive solvent practice (Silaban et al., 1995). The sudden refrigeration system to meet temperature condition for the amine absorber system will cause shot up on overall power plant cost. These several pretreatment processes leads to high capture costs estimated at around \$59.1/tonnes (A.B.Rao,2002). There are many current studies that leads to low cost and high efficiency CO<sub>2</sub> removal. The studies include development of new absorbent to increase CO<sub>2</sub> absorption and broaden the focuses on solid adsorber which can sustain in high temperature environment. The example of reactive solid as calcium carbonate precursor is in the current development. Study has proven calcium oxide based

adsorbent is an effective method of capturing  $CO_2$  (H.Lu et al.,2009). The present technology of  $CO_2$  adsorbent like using amine-based adsorbent, activated carbon, and molecular sieve only withstand low-temperature process between 40-160<sup>o</sup>C (H.Lu et al.,2009). The adsorbent able to prevent the release of  $CO_2$  to atmosphere, in addition able to resist high temperature process 550 <sup>o</sup>C-950 <sup>o</sup>C (H.Lu et al.,2009).

The seashells have been proven as one of alternative reactive solid in adsorption process (Y.Li et al, 2009). The abundance capacity of cockle shells should be further being exploited in the adsorption process.

#### 1.3. Objective

The objective of the research is to find the new adsorbent that has optimum energy usage throughout the carbon dioxide adsorption. Adsorbent which is calcium carbonate precursor specifically obtain from natural resource of cockle shell. The objective of the critical literature review and methodology setup is to find the optimum condition of the cockle shell for the adsorption study. Comparison of the study result is presented with the past research range from the adsorber obtain neither from natural adsorber and commercial adsorber.

#### 1.4. Scope of study

The study specificaly focus into comparative study on adsorption capacity using cockle shells as calcium carbonate precursor and the characterization of this type of natural adsorber resource with the commercial adsorber. The study done at post combustion adsorption condition using 15% CO<sub>2</sub> mixture (Eric Favre, 2007). The parameters setting include adsorbent diameter, calcination temperature, calcination duration and ramping rate. The combination of run design using Taguchi method from Design Expert 8.0. The results of the postcombustion are analyzed using minitab 16 software.

#### 1.5. The Relevency of the Project

The carbon dioxide release shown increment and majoring from human activities (IPCC,2007). These number of figure shows the responsibility to find the new way to adsord the GHG to protect the mother earth. One of the method is use the calcium oxide. The simultaneous capability of the oxide to adsorb carbon dioxide open up the new path in recent research to find the perfect adsorption material with low cost. The enormous availability of calcium oxide from nature extracted from limestone and dolomite in the form of calcium carbonate compound also the commercial sources proove the reliability purpose of calcium oxide.

On the recent years, there have been many research conducted towards the function of calcium oxide as carbon dioxide adsorbent. The current aim is to find the perfect condition for reaction of carbon dioxide adsorption or synthesizing the calcium oxide itself in order to increase the uptake capacity for adsorption. The conventional way of using reactive solvent which is amine in practical case cannot withstand high temperature. The typical temperature condition for adsorption is between 30 to 70°C (Umberto et.al. 1999). In the developing calcium oxide, the adsorbent can withstand a very high temperature and act in solid form. As the melting point of a pure calcium oxide is 2572°C, the material can withstand more than thousand in temperature degree celcius and this can accomodate all the temperature point set in all reactor in gasification unit.

#### 1.6. Feasiblity of the Project

The project research is divided into 2 semester. For the first semester, the related literature research study is completed and the literature review is wrapped up to brief on the scope of the project. Then, from the study research, the right methodology is developed to ensure all equipments are available for the work execution as well as to obtain the feasible time frame for research.

The second semester is followed by completion of the developed experimental work. The work execution is done based on the developed methodology to ensure the good

work flow. The complete report of the work is attached with the result analysis and related documents are attached.

۰.

### CHAPTER 2

### LITERATURE REVIEW

#### 2. LITERATURE REVIEW

In the country such as Malaysia, the abundant availability of cockle shells are an advantage because of a very low cost and many natural resources point (Utusan Malaysia., 2007). The availability of cockle shell is at peak in april and december. State goverment such as Selangor helps farmer to assist in boosting cockle shell farming as up to 1.5 to 2 tonnes of cockle can be produced per day in Kapar (Kapar, 2008). The percentage of calcium in cockle shell found in the state of Malysia is very high up to 98% (Zakaria et al.,2004). Others characteristic in building a good adsorbent is the porous media. CaO obtained from natural occurence precursors are to be classified as micro-porous and this will give better effect on adsorption of CO<sub>2</sub> (Gupta et al.,2002).

#### 2.1. Natural Adsorbent Selection

There are many type natural resources of adsorbent could be used and many of them categorized of shell and limestone as show in Table 2-1.

Table 2-1: Percentage of Chemical analysis (dry wt%) for different type of shell and limestone (Yi et al.,2009)

MV shell	97.63	0.41	0.21	0.13	1.62
					and a superior of the super-
	CaO ····	MgO	SiO	FeeOs	Others
Sample					In the Walter Street Street
			Dry we%		

Mussel shell	96:43	0.34	1.49	0.17	1.57
Scallop shell	96.62	0.48	0	0.07	2.83
MM limestone	85.62	8.42	4.84	0.49	0.63
JN limestone	86.9	4.39	7.28	0.88	0,55

The type of cockle shell that will be used in this post-combustion study recorded the chemical analysis as in Table 2-2. The XRF chemical analysis is take place after the drying process. This is to ensure no moisture present in the chemical composition.

Table 2-2: Chemical analysis of cockle shells by XRF (Mustakimah et al., 2010)

Oxide	(%wt)
CaO	97.93
MgO	0.85
SiO	0.17
Fe <sub>2</sub> O <sub>3</sub>	0.04
Others	<1.00

Carbon dioxide capture research and development progress is very wide. Many types of pathway are being studied in order to find the low energy usage and low cost carbon dioxide capture. The main reasons of the research are to attain cost reduction of the whole acid gas removal process and obtain the energy efficiency improvements in carbon dioxide capture system (Gemma et al.,2006). Among reactive solids that being researched in depth is calcium oxide (Table 2-3).

Table 2-3:	Flue	Gas	R&D	Pathways	(Herzog et	: <b>al</b> .,	2009)
------------	------	-----	-----	----------	------------	----------------	-------

	ABSORPTION	Reactive SOLIDS	ADSORPTION	MEMBRANES
	MEA, other	CaO	ZEOLITES 5A,	Gas/Liquid
A CONTRACTOR OF	alkanolamines.	Na <sub>2</sub> CO <sub>3</sub>	13X, MCM-41	Contactors

Blended	NaOH/CaO	CARBON, SILICA,	Permselective
alkanolamines.	Li <sub>2</sub> O/Li <sub>2</sub> ZrO <sub>3</sub>	ALUMINA Amine	and high-
Piperazine.	Li4SiO4	doped.	temperature
MEA/Piperazine.		Potassium salt-doped	Polymers.
K <sub>2</sub> CO <sub>3</sub> /Piperazine			
Less corrosive			
amines.			
Less degradable			
amines.			
Low $\Delta H_{rxn}$ amines.			
Chilled Ammonia.			
Nonaqueous			
solvents.			

### 2.2. Calcination and Carbonation

The carbonation of calcium oxide has been widely studied include related applications of CaO carbonation and calcination to the storage of energy. The current studies focusing on how to attain the best structure of CaO with high uptake capacity, good regeneration and long term stability and binding sorbent with other oxide for best desorbing condition (Philipp et al.,2011). Many commercial calcium oxide based adsorbent are studied in order to find the best properties or configuration for high capacity intake (Silaban et al. 1995; Abanadez et al.2003; Gupta et al.2002). The studied may varied in term of particle size, calcination duration, calcination temperature, carbonation temperature, and as well as the ramp or temperature increment rate for calcination.

The gas-solid CaO-CO<sub>2</sub> reaction proceeds through two rate-controlling regimes. The first regime involves a rapid, heterogeneous chemical reaction and the second regime, the reaction slows because of the formation of an impervious layer of CaCO<sub>3</sub> (Gupta et al., 2002). Through calcination process, the calcium carbonate solid compound is break into two compound which are calcium oxide and carbon dioxide.

Carbonation is the reaction of carbon dioxide and calcium oxide. The carbon dioxide will be adsorbed by the developed calcium-based adsorbents to capture CO<sub>2</sub> from

flue gases at high temperatures. The calcium carbonate formed from the reaction can be regenerated based on the reversibility of the reaction cycle (Silaban et al. 1995; Shimizu et al. 1999). The cycle involves two stages of reaction as it is reversible:

> Carbonation:  $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$ Calcination :  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

For the carbonation temperature selection, typically the temperature is over  $600^{\circ}$ C. CaO conversions at different temperature caused by kinetics rather than thermodynamics. This also means the different temperature provide different kinetics energy to the particle of CaO to react with CO<sub>2</sub> in adsorption phase. Postcombustion CO<sub>2</sub> capture using CaO requires a large scale circulating fluidized bed (CFB) reactor as CO<sub>2</sub> absorber, operating between 600-700 °C (Sanchez et al.,2011).



Figure 2-1: Carbonation conversions of CaO adopted from (A) Bhatia et al, 1983 and (B) Gupta et al., 2002.

Other study on carbonation temperature indicates that the gas flow containing diluted  $CO_2$  is put in contact with CaO at temperature typically over 600°C and carbonation takes place to form CaCO<sub>3</sub> (Abanades et al., 2002). Thus, from these observation, the temperature is decided to be fix at 650°C.

From the recent research throughout these years, calcium oxide is proven to be an effective sorbent to sequester carbon dioxide at high temperature of more than  $700^{\circ}$ C. In other study of higher temperature of calcination, condition higher than  $1000^{\circ}$ C will cause the metal carbonates have sintering effect and impose high energy penalties. So, the temperature between  $700-1000^{\circ}$ C is a possible range for good calcination process condition. Temperature of carbonation is typically 150-300K lower than calcination (Abanades et al., 2002). So, if the carbonation temperature is fix at 650 °C, the possible range of calcination temperature to takes place is between  $800-950^{\circ}$ C. Thus, in term of calcination, the temperature of this study on the cockle shell are varies at  $800^{\circ}$ C,  $850^{\circ}$ C and  $950^{\circ}$ C.

#### 2.3. Calcination Duration

For calcination duration, the presence of refractory silica, which is considered to reduce the effect of sintering and enhance durability, did not materially promote the overall performance of the undoped CaO. According to Hong Lu et al. "sintering effect not the main factor in decreasing carbonation performance" (Hong Lu et al.,2006). However, in other study state rapid loss of CO<sub>2</sub> capacity over many carbonation/decarbonation cycles is always observed because of severe adsorbent sintering that lead to structure damage to the adsorbent (Liyu et al.,2009). This unsimilarities may occur because of different type of precursor being used. So, variation in calcination duration is possible to give different results in term of adsorption capacity.

#### 2.4. Particle Sizes Selection

The particle size variation affected the calcination rate. From figure x, time taken for full conversion of Goynuk limestone were varied based on the particle sizes. The bigger particle size takes longer time to attain full colcination compared to the smaller particle. The particles are tested at the following sizes (less than 0.125mm, 0.355-0.710 mm, 1-2 mm)



Figure 2-2: Time(min) taken vs conversion of Goynuk limestone to CaO (Irfan et al.,2001)

From figure 2-2, comparison with our research can be made for the particle range less tha 0.125 mm and 1-2mm. Following table is to show the details of calcination rate over time related to the research.

Table 2-4: Time taken vs particle size for particular sizes of Goynuk limestone on the calcination duration (Irfan et al., 2001)

Time(min)	Particle size,mm	Calcination conversion, X	Particle size,mm	Calcination conversion, X
25		0		0
30		0		0.03
35	0.1	0.12	1.295	0.1
40		0.96		0.76
43		1		1

The total mass losses independent of heating rate. The amount of heat evolved during the course of decomposition plays a direct role in the resultant porosity and thereby regulates the eventual  $CO_2$  capture capacity (Hong Lu et al., 2008).

From the studies, it showed the physical properties for a good sorbent; must have high pore volume and large surface area or BET surface area for  $CO_2$  capture. High durability of adsorbent such as can withstand high temperature is a main concern in industry. High pore volume show the availability of carbon dioxide to go through every layer of sorbent and increase the carbonation of CaO. The high surface area provide many points available for mass transfer. BET surface area analysis is a technique to determine the specific surface area of powders, solid or granules in meter square per gram. Large BET provide  $CO_2$  with vast surface area thus more likely to react faster and adsorb more gas compared to lower surface area. The durability of CaO is most likely its capability to be reactive even in higher temperature and higher pressure condition.

#### 2.5. Carbon Dioxide Capture

Technology option	System Requirement	Advantages.	Drawbacks
Absorption	Absorber and	Suitable for dilute CO <sub>2</sub>	Heat of solvent
(Chemical)	stripper sections	streams (typical flue gas	regeneration is very
	Chemical solvent	from power plants)	high.
	(e.g. MEA, HPC)	Operates at normal T&P	Significant solvent losses
		Commercially available, proven technology	due to acidic impurities in the gas stream.
Absorption	Absorber and	Less energy required.	Requires high operating
(Physical)	stripper sections.	Solvents are less	pressure.
	Physical solvent	susceptible to impurities	Works better with gas
	(e.g Selexol)	in the gas stream.	stream having high $CO_2$
			content.
Adsorption	Adsorber beds	Very high CO2 possible	Require high operating
		removal	pressure.

#### Table 2-5 :Comparison of each CO<sub>2</sub> separation and capturing technology [38]

			Costly.
Membranes	Membrane filter	Upcoming promising technology.	Require high operating pressure.
		Space efficiency	May need multiple units and recycling due to lower product purity.
			Very costly.

## CHAPTER 3

## **METHODOLOGY**

## **3. METHODOLOGY**

### 3.1. Overview

Methodology of overall research procedure covers from the preparation of CaO adsorbent of cockle shells. Further explanation on the procedure using thermal gravimetric analyzer (TGA).



Figure 3-1: Thermal Gravimetric Analyzer

#### 3.2. Raw Material

Chemical used in this research include cockle shell powder of less than 0.125mm, 0.355-710mm and 1-2mm particle size range (~97% purity). Cockle shells were bought at stall in market originated from the cultivation center in Perak. The gas involve in TGA study are inert Nitrogen (N<sub>2</sub>) gas with purity of 99.999% and Carbon Dioxide mixture with 15% CO<sub>2</sub>, and 85% N<sub>2</sub> supplied by MOX-Linde Gas Berhad.

### 3.3. Material Preparation

Cockle shells were washed with raw water to remove dirt and dried under the sun for 8 hours, followed by 3 hours 105°C drying. Shells were crushed and grind using Fritsch Power Cutting Mill provided by PRSB (Petronas Research Sdn. Bhd.). The shell powder was sieved into different particle size groups of less than 0.125mm, 0.355-0.710mm and 1-2mm.



Figure 3-2: Preparation of cockle shell powder for research purposes

Drying process of cockle shells take place of 3 hours duration after 8 hours drying under the sun.



Figure 3-3: wt% moisture vs time (min) for drying process in oven at 105°C

### 3.4. Material Characterization

The study of the effect of variation in calcination temperature, calcination duration, ramp rate and particle diameter executed using TGA. The model or research condition is designed using Design Expert 8.0.6. The Taguchi OA factorial type level 9 is chosen. Table 5 show the corresponding test executed using TGA.

Table 3-1: Experimental condition to study the effect of calcination conditions on carbonation conversion

Run	Std.	Temperature of	Calcination	Ramp rate	Particle CaCO <sub>3</sub>
		Calcination (°C)	Duration (min)	(°C/min)	diameter (mm)
1	7	950	40	15	<0.125
2	6	850	20	15	1.000-2.000
3	1	800	20	10	<0.125
4	5	850	40	10	0.355-0.710
5	3	800	40	20	1.000-2.000
6	8	950	20	20	0.355-0.710
7	4	850	30	20	<0.125
8	2	800	30	15	0.355-0.710
9	9	950	30	10	1.000-2.000

The CO<sub>2</sub> uptake is expressed as an adsorption efficiency  $\theta$ , in which the number of adsorbed CO<sub>2</sub> molecules is related to the number of CaO sites:

$$\theta = \frac{n(CO2, ads)}{n(CaO)} \times 100\%$$
$$\theta = \frac{(m - mo)/44gmol}{y \ load \times mo/56gmol} \times 100\%$$

Where m and mo are the masses of the CaO sorbent before and after  $CO_2$  uptake and y load is the CaO loading as expressed in weight percent. Comparison of carrying capacity or adsorption efficiency can be made with the corresponding graph.

#### 3.5. Equipments

Table 3-2: Equipment related and usage

Equipment	Purpose
EXSTAR TG-DTA 6300	To study the reactivity of the synthesizing process
(Thermogravimetric	and carbon dioxide adsorbent capturing capability.
Analyzer)	
XRF	To analyse the chemical composition in the sample

#### 3.6. Effect of calcination conditions on carbonation conversion

The study of calcination and carbonation was done using TGA. Small amount of sample ( $\sim 10 \pm 0.5$  mg) is used to possibly eliminate the effect of thermal resistance due to sample mass. Atmospheric gas can be distributed evenly and minimized temperature gradient between sample and the sample holder. In addition, heating process will be more linear although the exothermic process may cause inhomogeneities or irregularities (T. Hatakeyama et al, 1998).

Table summarizes the experimental conditions used to study the effect of each parameter. The selection of desired parameters to study are based on the literature reviews on the common factors that regularly been studied by previous researchers. Followings are the steps for calcination and carbonation that been used in this research which is generally applied in most of the related studies during previous work:

- 1. Initially, nitrogen gas was set to flow at 50 ml/min.
- 2. Then 10mg of cockle shell powder in desired particle size was placed in ceramic sample crucible.
- 3. N<sub>2</sub> flow was set to continuously flow until the concentration reading for all gas is 0%. This step is considered as purging step.
- 4. TGA was heated up at 110°C for 10 minutes to remove moisture content in the sample.
- The heating was proceed to desired calcination temperature and been hold for design period.
- 6. Then, the sample was cooled down to carbonation temperature.
- 7. Finally,  $CO_2$  gas was switched on while  $N_2$  gas was shut down for carbonation to occur.
- 8. The conditions were hold until no significant weight change was observed from the TG curves.
- 9. Then, the sample was cooled down to ambient temperature.

					Ι	FINAL	YEAR	PROJE	ECT 2/	WEEK	NUM	BER			<u></u>	
Activities	1	2	3	4	5	6	7	M	8	9	10	11	12	13	14	15
Sample preparation (drying,																
grinding, sieving)																
Execute adsorption experiment																
using TGA		*														
Morphology study on CaO																
surface over cycle	:							AK								
Submission of Progress Report								BRE								
Data Analysis and Report								EM		a de la composition de la comp						
Pre-SEDEX																
Submission of Draft Report						1										
Submission of Dissertation and						ł										
Technical Paper										:						
Oral presentation															andra Cayra Silai Alba Balaa	
Submission of Project																
Dissertation (Hardbound)							· · · · ·									

# 3.7. Gantt Chart (Final Year Project II

# CHAPTER 4 RESULT AND DISCUSSION

#### 4. RESULT AND DISCUSSION

The cockle shells is first examine through the chemical components using X-ray Fluorescence (XRF). The Table 4-1 shows that chemical components are mostly the same as other type of sea shells as shown in Table 2-1.

Table 4-1: Chemical analysis of cockle shells

Oxide	(%wt)
CaO	97.93
MgO	0.85
SiO	0.17
Fe <sub>2</sub> O <sub>3</sub>	0.04
Others	<1.00

This chapter elaborates the finding of the experiment and define every single result. It is divided into two main sections which are carbonation behavior under various calcination conditions and comparison of carbonation performance among cockle shells and commercial adsorbent. The two reaction steps involve which are calcination; a process of synthesizing calcium oxide (CaO) from cockle shell and carbonation; a process of  $CO_2$  capturing reaction using the synthesized CaO.

Behavior of cockle shell during calcination and carbonation under various calcination conditions is demonstrated using TGA. TG and dTG curves record weight change in the sample with respect to time and temperature, which enable the demonstration of phase transitions of the sample throughout the reaction. For instance, calcination is indicated by weight lost and carbonation is denoted based on weight gain.

The results are also compared with the commercial adsorbent and other natural calcium based adsorbent. Table 4-2 show the level of every parameter tested in the carbonation conversion experiment.

Table 4-2: Taguchi Analysis level (Temperature, Diameter, Duration and Ramp rate)

Lovel	Temperatur	re Diameter	Duration	Ramp rate
1	800°C	<0.125mm	20 min	10°C/min
2	850°C	0.355-0.710 mm	30 min	15°C/min
3	950°C	1.000-2.000 mm	40 min	20°C/min

### 4.1. Carbonation Behavior Under Various Calcination Conditions

The two reaction step involves at different temperature range. Calcination can only be proceeding in inert atmosphere. First, the known sample mass is placed in the ceramic crucible and heated up to calcination specific temperature at certain heating rate in pure  $N_2$  condition. The sample is expected to reach full calcination conversion which all CaCO<sub>3</sub> particles is converted into CaO. Carbonation is then takes place by certain heating rate once the temperature reach specified temperature and the flow of CO<sub>2</sub> gas is switched on. Calcination and carbonation are conducted in pure  $N_2$  and 15% CO<sub>2</sub> 85%  $N_2$  atmosphere respectively in order to eliminate the potential of selectivity factor in reaction since the reaction is reversible.

The constant amount of sample (~10mg) is used for every run to eliminate or minimize the effect of mass and heat transfer to reaction. The flow rate of purge gas is 50ml/min for N<sub>2</sub> and 15ml/min for CO<sub>2</sub> mixture.



Figure 4-1 : Temperature and weight% of cockle shell sample vs time attained from Pyris manager software. (Calcination T; 950°C; Carbonation T: 650°C; Heating rate: 15°C /min; Particle size: < 0.125mm, Calcined duration: 20 min)

Overall, based on TG curves obtained, calcination of cockle shell took place in three phases as shown in Figure . The first phase was where a very small weight loss at temperature around 300-700°C occurred in which might be due to dissociation of volatile component in the sample. Then the mass was rapidly decreased once the temperature is above 700°C and finally became amost constant when the temperature reached 800°C. From figure 4-1, it indicates that cockle shell retained ~ 55% of its initial sample weight regardless the differences in particle sizes, heating rates, calcined duration and calcined temperature applied. The amount of weight loss represents the amount of CO<sub>2</sub> that been desorbed by carbonate contained in the shell and the remaining weight belongs to the amount of the product.

CaCO<sub>3</sub> started to attain full calcination into CaO at the temperature range of 700-900 °C [34] and at high temperature, CO<sub>2</sub> is released and CaO is formed (J.Khinast, 1996). The weight loss of the sample is wholly results of CaCO<sub>3</sub> decomposition since other compound is at negligible weight (I.Ar, 2001). From the review, it describe that synthesis of CaO from cockle shell can be obtained once the temperature is above 700 °C and the process is stable or complete after 800 °C as shown by constant weight, as indicated in Figure 4-1.

The first phase of weight loss (100-140 °C) is due to the moisture trap inside the material, once the temperature is increased (250-410 °C), the volatile organic material started to dissociate and release that occur at 500-540 °C, the resistance organic material also started to be released and finally at 700°C, the sample started to rapidly loss the weight as the sample started to disintegrate into CaO. No significant weight loss at the end of the process indicates the calcination was already complete.

The weight loss and retained weight achieved during calcination in this study is observed to meet the reaction stoichiometry as represents in Equation 2.1. Molecular weight of CaO, CO<sub>2</sub> and CaCO<sub>3</sub> are 56, 44, and 100 g/mol respectively. Therefore if the amount of weight retain, weight loss and initial weight is 55 -56%, 43-44% and 100% respectively, the amounts seemed to satisfy the stoichiometry balance of each species and the reaction equation itself.

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

Carbonation involved the reaction between synthesized CaO with  $CO_2$ . As illustrated, carbonation occurs in two regimes. The first regime involves a rapid weight gained experienced by the sample until it reached the second regime where the weight gained was slowed down until no significant weight change happened, as indicated by TG curve in Figure 4-14. Initially carbonation is controlled by chemical reaction where most of calcium oxide get reacted with carbon dioxide and producing the calcium carbonate. But then, as the time goes on, the product layer that build-up has introduced resistance to the reaction and cause the overall reaction to be controlled by  $CO_2$  gas. Due to product layer limitation and less pores available, the reaction is slower and insignificant.

In this study, carbonation was conducted at 650°C at 15°C/min in atmosphere of 15% carbon dioxide. The process was hold at certain carbonation temperature for 140 minutes to ensure carbonation became saturated and no significant weight change occur can be observed. Calcination was conducted before carbonation under certain conditions that been described previously to demonstrate the effects on carbonation. A number of calcination conditions were varied to understand this behavior. The figure 4-2 show the experimental run order and the carbonation conversion:



Figure 4-2: Carbonation Conversion over Number of Experimental Run

Sample no.	1	2	3	4	5	6	7	8	9
Temperature	800	800	800	850	850	850	950	950	950
Diameter	<0.125	0.355- 0.710	1.000- 2.000	<0.125	0.355- 0.710	1.000- 2.000	<0.125	0.355- 0.710	1.000- 2.000
Duration	20.0	30.0	40.0	30.0	40.0	20.0	40.0	20.0	30.0
Ramp rate	10.0	15.0	20.0	20.0	10.0	15.0	15.0	20.0	10.0
Initial Weight %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Decarbonation weight %	51.0	54.9	54.1	50.8	50.3	52.8	51.5	53.4	52.3
Recarbonation weight %	77.4	79.5	74.2	72.9	70.8	75.8	81.0	77.5	76.0
Carbonation conversion %	65.8	57.1	47.3	55.5	51.7	55.3	72.7	57.4	57.6
g CO2/kg CaO	516.8	448.7	371.4	436.1	406.4	434.3	571.2	450.8	452.6

Table 4-3: Summary of experiment result

Overall, synthesized CaO experienced carbonation rapidly in the temperature range of 650-700°C before become almost constant throughout the reaction. The time taken for rapid carbonation is around 30-60 minutes. This observation indicates that carbonation was favorable at the stated temperature and can be prolong for almost 60 minutes before becoming saturated. However, the ability relies on the calcination conditions. Other carbonation temperature also been tested to understand its capture capacity which has been portrayed by carbonation conversion and amount of CO<sub>2</sub> that been captured per kilogram of synthesized CaO utilized.

Level	Temperature	Diameter	Duration	Ramp rate
1	35.28	36.16	35.57	35.08
2	34.22	34.56	35.00	35.16
3	35.74	34.52	34.67	35.00
Delta	1.52	1.64	0.90	0.16
Rank	2	1	3	4

Table 4-4: Response Table for Signal to Noise Ratios

The table show the response of every parameter for signal to noise ratios. The larger the function of delta, the better or higher impact siven to the carbonation conversion. From the table, diameter of the sample rank at the first place followed by calcination temperature, duration and ramp rate. In maximizing the conversion of synthesize CaO, the parameter which higher value in delta is the most in affecting the conversion. In term of level or value of every single parameter chosen, the larger value is better.

Level	Temperature	Diameter	Duration	Ramp rate
1	58.37	64.66	60.67	57.23
2	51.50	53.52	56.72	57.59
3	61.69	53.39	54.17	56.74
Delta	10.19	11.27	6.50	0.85
Rank	2	1	3	4

Table 4-5: Response Table for Mean (Carbonation Conversion)

The result from the result analysis using S/N ratios from Minitab 16 and mean value from microsoft excel given the same result which can be summarized in the following table:

Tal	ble	<b>4-6</b> :	Optimum	value	for	each	parameter	using	S/N	ratios
-----	-----	--------------	---------	-------	-----	------	-----------	-------	-----	--------

Temperature	Diameter	Duration	Ramp rate
950°C (level 3)	<0.125mm (level 1)	20 min (level 1)	15 °C/min (level 2)

## 4.2. Comparison of Carbonation Performance 4.2.1. Effect of Calcination Temperature

From Table 4-5, the highest calcination temperature give high carbonation conversion. The kinetic movement of  $N_2$  at 950°C is higher compared to 850°C and 800°C. This kinetic movement of inert gas  $N_2$  aid in the calcination reaction. Thus, calcination be able to take place deep in the pore size of the adsorbent. Calcining the cockle shell at high temperature has many advantage in synthesizing CaO. A very high calcination temperature of more than 1100°C lead the particle to the sintering and attrition effect (B. R. Stanmore et al, 2005). The maximum temperature for calcination at 950°C is still in the range where the maximum carbonation conversion is attained without the negative impact on the structure. The synthesizing of CaO at higher temperature took longer time and it can lead to more effective regeneration process. This proves by the final weight gained during carbonation is the highest at 950°C. So, the diiferent calcination temperature did give impact in the final carbonation conversion.

#### 4.2.2. Effect of Particle Sizes

Sample weight loss indicates calcination reaction where calcium oxide being synthesized and weight gained represents the occurrence of carbonation reaction. In particles sizes parameter, the impact is refer to the pore sizes of CaO. Smaller particle diameter theoritically give better adsorption for carbonation to take place because of higher pore sizes or BET surface area. From the experiment results, for the different diameter, the smallest diameter which is <0.125 mm give the shortest time (<50 min) before no insignificant weight observed in calcination step but the

largest diameter which is 1-2 mm give the longest time which is more than 70 minutes.



Figure 4-3 : Effect of temperature and diameter to adsorption capacity at 40 min calcination duration and 15 °C/min ramp rate.

From figure 4-3, the fluctuation in adsorption capacity is very distinctive to the temperature of calcination and particle diameter of adsorbent. These two parameter are affected much on the adsorption capacity.



4.2.3. Effect of Calcination Duration and Ramp Rate

Figure 4-4: Effect of calcination duration and ramp rate to adsorption capacity at 950 C calcination temperature and <0.125 mm particle diameter.

From figure 4-4, the adsorption capacity not much fluctuated to the parameter of calcination duration and ramp rate of calcination. These two parameter not largely affected the adsorption capacity.

### 4.3. Overall comparison performance of adsorbent



Figure 4-5: Carrying capacity after number of cycles in a bed sand (0.355-0.435mm) at 750<sup>o</sup>C. Initial mass of eggshells, limestone, or mussel shells,  $m_0=2.00g$ ,  $Q_{N2}=80$  ml/s and  $Q_{CO2}=13.0$  ml/s (M Ives et al., 2008).

From the figure 4-5, the adsorbent capacity for first carbonation is 70% for eggshells, 75% for Purbeck limestone and 55% for Mussel shells. For the cockle shells, the adsorption capacity able to sustain at 73% (figure 4-1) for the first cycle. This indicates the potential of cockle shells be using as adsorbent.

#### **CHAPTER 5**

#### CONCLUSION

#### 5. CONCLUSION

Overall, this study is able to achieve its ultimate aim to synthesis CaO from waste cockle shell as potential material for  $CO_2$  adsorbent since the performance of this biomass is comparable to other! Ca based adsorbent. The synthesis process and  $CO_2$  adsorption reaction via calcination and carbonation also are able to be illustrated by using TGA. The potential or efficiency of synthesized CaO during carbonation is dependent on the condition of calcination and reaction conditions.

TGA managed to demonstrate the reactivity of cockle shell calcination and carbonation reaction. Loss of ~45-49% from its initial weight indicates  $CO_2$  is removed from the shells while the remaining ~51-55% of calcined shell can be considered as the synthesized CaO. However, various calcination conditions such as sample particle size, calcination temperature, calcination duration and heating rate are observed to have less influence on the stability of cockle shell calcination. The ability of synthesized CaO to capture  $CO_2$  during carbonation reaction proven to be affected by these factors.

The findings prove that sample with smallest particle size (<0.125 mm) provides the highest carbonation conversion and adsorption capacity compared to larger particles. In addition, cockle shell calcined at 950°C able to synthesize CaO with the highest carbonation compared to other lower temperature. The duration of calcination is found to be ideal at 20 minutes and and heating rate should remain at 15°C/min. The estimated amount of maximum CO<sub>2</sub> capture is at 0.570 kg for every kg of synthesized CaO.

Using the verified method, the objective of the research can be achieved. The calcium oxide based adsorbent using natural cockle shell as a resource is proven to be a good adsorbent. The corresponding tests are carried out to make sure the desired results are attained. Characterization of adsorbent using varies equipments are to ensure the capability of cockle shell to be used as industrial adsorbent for acid gas removal specifically  $CO_2$  in the future.

#### REFERENCES

- Abanades, J.C. 2002, "The maximum capture efficiency of CO<sub>2</sub> using a carbonation/calcination cycle of CaO/CaCO<sub>3</sub>," Chemical Engineering Journal 90(3), 303-306.
- Abanades, J.C., Alvarez, D. 2003, "Conversion limits in the reaction of CO2 with lime", Energy & Fuels, 17, 308-315.
- Abanades, J.C., Grasa, G., Alonso, M, Rodriguez, N, Anthony, E.J. and Romeo, L.M. 2007, "Cost structure of a postcombustion CO<sub>2</sub> capture system using CaO". *Environmental Science and Technology*, 41, 5523–5527.
- Ar, I. and Dogu, G. 2001, "Calcination kinetics of high purity limestones", Chemical Engineering Journal, 83(2), 131-137.
- Barros, M.C., Bello, P.M., Bao, M., Torrado, J.J. 2009, "From waste to commodity: transforming shells into high purity calcium carbonate", *Journal of Cleaner Production*, 17(3), 400-407.
- Bhatia, S.K. and Perlmutter. D.D. 1983, AIChE J., 29 (1), 79.
- Biezma, S., Ballesteros, J.C., Diaz, L., De Zárraga, E., Álvarez, F.J., López, J., Arias, B., Grasa, G., Abanades, J.C. 2011, Postcombustion CO<sub>2</sub> capture with CaO. Status of the technology and next steps towards large scale demonstration, Energy Procedia Volume 4, 852-859.
- Butler, J.H., 2011, The NOAA Annual Greenhouse Gas Index (AGGI), <a href="http://www.esrl.noaa.gov/gmd/aggi/>">http://www.esrl.noaa.gov/gmd/aggi/></a>.
- Carroll, J., Wu, Ying 2011, Carbon Dioxide Sequestration and Technologies. John Wiley and Sons, 121.
- Favre, E. 2007, "Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption", *Journal of Membrane Science* 294, 50–59.
- Gemma S. G., Abanades, J.C. (2006), CO<sub>2</sub> Capture Capacity of CaO in Long Series of Carbonation/Calcination Cycles, Ind. Eng. Chem. Res., 45 (26).
- Gruene, P., Anuta, Belova, G., Tuncel M. Y., Farrauto, R.J. and Castaldi, M.J.
  2011, "Dispersed Calcium Oxide as a Reversible and Efficient
  CO2 sorbent at Intermediate Temperature", *I&EC research*.

- Gupta, H, Fan, L.S. 2002, "Carbonation-calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas", *Industrial Chemical Engineering Resources*, **41(16)**, 4035-4042.
- Hatakeyama, T., Liu, Z. 1998 Handbook of thermal analysis, John Wiley and Sons, England.
- Herzog, H., Meldon J., Hatton A. 2009, "Advanced Post-Combustion CO<sub>2</sub> Capture", Clean Air Task Force under a grant from the Doris Duke Foundation.
- Herzog, H., Gollomb, D., Encyclopedia of Energy; Elsevier Science Inc.: New York, 277-287.
- Ives, M., Mundy, R.C., Fennell, P.S., Davidson, J., Dennis, J.S. and Hayhurst, A.N. 2008, "Comparison of Different Natural Sorbents for Removing CO2 from Combustion Gases, as Studied in a Bench-Scale Fluidized Bed", *Energy & Fuels*, 22, 3852–3857.
- Kerajaan sasar hasil 130000 tan metric kerang, Utusan Malaysia 15 December 2007, <a href="http://www.seafdec.org.my">http://www.seafdec.org.my</a> (accessed: 4th Ogos 2011).
- Khinast, J., Krammer, G.F., Brunner, C., Staudinger, G.1996, "Decomposition of limestone:the influence of CO<sub>2</sub> and particle size on the reaction rate", *Chemical Engineering Science*, 51(4), 623-634.
- Li, L., David L., Zimin Nie and Howard, Chris. 2009, "Magnesia-Stabilized Calcium Oxide Absorbents with Improved Durability for High Temperature CO<sub>2</sub> Capture", Ind. Eng. Chem. Res., 48 (23), 10604–10613.
- Li, Y., Zhou, C., Chen, H., Duan, L., Chen, X. 2009, "CO<sub>2</sub> capture behavior of shell during calcination/ carbonation cycles", *Chemical Engineering Technology* 32(8), 1176-1182.
- Lu, H., Khan Ataullah and Smirniotis P.G. 2008, "Relationship between Structural Properties and CO<sub>2</sub> Capture Performance of CaO-Based Sorbents Obtained from Different Organometallic Precursors", Ind. Eng. Chem. Res., 47(16), 6216–6220.
- Lu, H., Reddy, E.P. and Smirniotis P.G. 2006, "Calcium Oxide Based Sorbents for Capture of Carbon Dioxide at High Temperatures", Ind. Eng. Chem. Res., 45 (11), 3944–3949.

- Lu, H., Smirniotis, P.G., Ernst, F.O., Pratsinis O. 2009, "Nanostructured Ca-based sorbents with high CO<sub>2</sub> uptake efficiency", *Chemical Engineering Science*, 64(9), 1936-1943.
- Mercedes M., Valer, M. 2010, Development and Innovation in CO<sub>2</sub> capture and storage technology: CO<sub>2</sub> storage and utilisation; Woodhead Publishing Limited.: Cambridge, 2-3.
- Metz, B., Davidson, O.R., Bosch, P.R., Dave R., Meyer L.A. 2007, Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. Chapter 7: Industry, Mitigation of Climate Change.
- Mustakimah M., Suzana Y., Saikat M 2010, Decomposition Study of Calcium Carbonate in Cockle Shell, Chemical Engineering Department, Universiti Teknologi PETRONAS, Malaysia.
- Perasmian Projek Ternakan Kerang Kg. Tok Muda, Kapar, 4 Jun 2008, <a href="http://www.mpkapar.com/manikavasagam/posts/perasmian-projek-ternakan-kerang-kg-tok-muda-kapar/">http://www.mpkapar.com/manikavasagam/posts/perasmian-projek-ternakan-kerang-kg-tok-muda-kapar/> (accessed: 2<sup>nd</sup> November 2011).</a>
- Rao, A.B. and Rubin, E.S., 2002, "A technical, economic, and environmental assessment of amine-based CO<sub>2</sub> capture technology for power plant greenhouse gas control." *Environ. Sci. Technol.*, 36, 4467–4475.
- Rubin, E.S., Rao, A.B. 2002, "A technical, economic, and environmental assessment of amine-based CO<sub>2</sub> capture technology for power plant greenhouse gas control", Carnegie Mellon University, Pittsburgh.
- Stanmore, B.R., Gilot, P. 2005, "Review- calcination and carbonation of limestone during thermal cycling for CO<sub>2</sub> sequestration", *Fuel Processing Technology*, 86(16), 1707-1743.
- Shimizu, T., Hirama, T., Hosoda, H., Kitano, K., Inagaki, M., Tejima, K 1999. Trans. Inst. Chem. Eng., 77A, 62-68.
- Silaban, A., Harrison, D. P. 1995, "High-temperature capture of carbon dioxide: characteristics of the reversible reaction between CaO(s) and CO<sub>2</sub>(g)." Chem. Eng. Commun., 137, 177.
- World Nuclear Association (WNA), 2011.<http://www.worldnuclear.org/info/inf16.html> (accessed 07.05.11).

Zakaria A.B., Zakaria, N., Kasim, Z. (2004), "Mineral composition of the cockle (Anadara granosa) shells, hard clamp (Meretrix meretrix) shells and corals (Porites spp.): A comparative study", *Journal of Animal and Veterinary Advances*, vol. 3, no. 7, 445-447.

# APPENDICES A: TGA reading for cockle shell calcined at 950°C for 40 minutes using heating rate of 15°C/min and particle sizes of less 0.125mm

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
0.00	29.15	100.00	63.00	957.54	52.20
1.00	29.73	99.99	64.00	957.48	52.18
2.00	34.99	99.95	65.00	957.04	52.17
3.00	44.55	99.87	66.00	957.46	52.14
4.00	56.75	99.77	67.00	957.79	52.13
5.00	70.64	99.67	68.00	957.02	52.12
6.00	85.45	99.59	69.00	957.22	52.10
7.00	100.80	99.54	70.00	957.37	52.09
8.00	116.64	99.50	71.00	957.54	52.07
9.00	132.70	99.46	72.00	957.64	52.05
10.00	149.04	99,44	73.00	957.73	52.05
11.00	103.50	99.42	74.00	937.76	52.04
12.00	102.00	99.30	75.00	957.85	52.02
14.00	215.04	99.16	77.00	937.91	52.00
14.00	213.44	98.04	78.00	957.03	51.00
16.00	748.91	98.63	79.00	957.04	51.97
17.00	265.70	98.21	80.00	957.06	51.96
18.00	282.44	97.68	81.00	957.11	51.95
19.00	299.21	97.09	82.00	957.12	51.94
20.00	315.98	96.50	83.00	957.16	51.93
21.00	332.70	95.99	84.00	957.15	51.92
22.00	349.31	95.59	85.00	957.14	51.91
23.00	365.79	95.28	86.00	957.18	51.90
24.00	381.94	95.03	87.00	957.18	51.89
25.00	398.04	94.81	88.00	957.21	51.88
26.00	414.07	94.61	89.00	957.24	51.87
27.00	430.14	94.41	90.00	957.22	51.85
28.00	446.15	94.19	91.00	957.20	51.84
29.00	462.28	93.95	92.00	957.20	51.84
30.00	478.19	93.66	93.00	957.20	51.83
31.00	494.20	93.38	94.00	957.21	51.82
32.00	509.83	93.09	95.00	957.21	51.81
33.00	525.30	92.82	96.00	957.21	51.80
34,00	540.91	92.00	97.00	957.20	51.79
35.00	571.68	97.41	99.00	957.21	51.70
37.00	586.97	92.06	100.00	957.20	51.77
38.00	602.46	91.86	101.00	957.22	51.76
39.00	617.86	91.68	102.00	957.16	51.75
40.00	633.13	91.30	103.00	957.33	51.73
41.00	648.43	90.64	104.00	950.56	51.72
42.00	663.67	89.63	105.00	944.54	51.71
43.00	678.96	88.14	105.00	928.53	51.70
44.00	694.30	86.02	107.00	912.56	51.69
45.00	709.66	83.10	108.00	896.69	51.68
46.00	724.98	79.15	109.00	880.86	51.67
47.00	740.36	73.92	110.00	865.08	51.67
48.00	755.99	67.19	111.00	849.37	51.66
49.00	771.82	59.20	112.00	833.52	51.65
50.00	/89.92	52./9	115,00	817.97	51.64
52.00	873.07	57.55	114.00	707.30	51.04
53.00	840 11	52.45	115.00	707.22	51.05
54.00	856.29	52.35	117.00	7756 70	51.02
55.00	872.67	52.32	118.00	741.45	51.61
56.00	889.13	52.30	119.00	726.31	51.61
57.00	905.74	52.29	120.00	711.27	51.60
58.00	922.57	52.27	121.00	696.18	51.61
59.00	936.54	52.26	122.00	681.18	51.61
60,00	949,62	52.24	123.00	669,76	51.57
61.00	957.84	52.23	124.00	656.19	51,59
62.00	957.22	52.21	125.00	655.08	51.69
1	1		······································		

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
126.00	655.07	53.20	189.00	654.25	71.39
127.00	655.07	54.55	190.00	654.25	71.57
128,00	655.06	55.11	191.00	654.20	71.75
129.00	655.04	55.60	192.00	654.17	71.93
130.00	655.04	56.05	193.00	654.14	72.10
131.00	655.04	56.46	194.00	654,14	72.27
132.00	655.03	56.86	195.00	654.12	72.44
133.00	655.00	57.23	196.00	654.16	72.61
134.00	654.99	57.59	197.00	654.16	72.78
135.00	654.97	57.95	198.00	654.11	72.95
136.00	654.94	58,29	199.00	654.16	73.11
137.00	654.92	58,63	200.00	654.15	73.28
138.00	654.93	58.96	201.00	654.13	73.44
139.00	654.92	59.29	202.00	654.08	73.60
140.00	654.92	59.61	203.00	654.07	73.77
141.00	654.91	59.92	204.00	654.10	73.92
142.00	654.90	60.24	205.00	654.17	74.08
143.00	654.89	60.54	206.00	654.23	74.24
144.00	654.74	60.85	207.00	654.27	74.40
145.00	654.82	61.15	208.00	654.25	74.54
146.00	654.94	61.44	209.00	654.25	74.69
147.00	654.94	61.74	210.00	654.20	74.88
148.00	654.57	62,03	211.00	654.17	75.05
149.00	654.32	62.32	212.00	654.14	75.21
150.00	654.19	62.60	213.00	654.14	75.38
151.00	654.07	62.87	214.00	654.11	75.54
152.00	654.02	63.14	215.00	654.16	75.70
153.00	654.00	63.41	216.00	654.15	75.87
154.00	654.03	63,68	217.00	654.13	76.04
155.00	654.05	63.95	218.00	054.08	76,21
156.00	004.11	64.21	219.00	654.05	76.37
157.00	004.10	64.72	220.00	654.03	/0.54
158.00	034.13	64.02	221,00	654.07	76.71
159,00	654.09	65.22	222.00	654.10	/0.8/
161.00	654.05	65.48	223,00	654.22	77.01
162.00	654.03	65 77	224.00	654.23	77.10
163.00	654.07	65.96	225.00	654.25	77,50
164.00	654.10	66.20	220.00	654.23	77.43
165.00	654.17	66.43	227,00	654.27	AF FF
166.00	654.23	66.66	220,00	654.25	77.14
167.00	654 27	66.89	230.00	654.25	78.02
168.00	654.25	67 12	231.00	654.20	78.15
169.00	654.25	67.35	232.00	654 17	78.13
170.00	654.20	67.57	233.00	654.14	78.47
171.00	654.17	67.80	234.00	654.14	78.56
172.00	654.14	68.01	235.00	654.11	78.72
173.00	654.14	68.23	236.00	654.16	78.91
174.00	654.12	68.44	237.00	654.15	79.04
175.00	654.16	68.64	238.00	654.14	79.18
176,00	654.16	68.86	239,00	654.12	79.31
177.00	654.11	69.06	240.00	654.16	79.45
178,00	654.16	69.26	241.00	654.16	79.58
179.00	654.15	69.47	242.00	654.11	79.70
180.00	654.13	69.67	243.00	654.16	79.85
181.00	654.08	69.87	244.00	654.15	80.00
182.00	654.05	70.07	245.00	654.13	80.13
183.00	654.03	70.27	246.00	654.08	80.27
184.00	654.07	70.46	247.00	654.07	80.41
185,00	654.10	70.65	248.00	654.10	80.55
186.00	654.17	70.84	249.00	654.17	80.69
187.00	654.23	71.03	250.00	654.23	80.83
188.00	654.27	71.21	251.00	654.14	80.96

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
0.00	28.09	100.00	63.00	861.31	54.10
1.00	29.46	100.00	64.00	861.45	54.09
2.00	35.36	100.00	65.00	861.69	54.08
3.00	45.15	99.99	66.00	861.70	54.07
4.00	57.46	99.99	67.00	861.56	54.04
5.00	71.29	99.99	68.00	861.72	54.03
6.00	86.09	99.99	69.00	861.96	54.04
7.00	101.35	99.99	70.00	862.06	54.04
8.00	117.04	99.99	71.00	862.21	54.03
9.00	133.00	99.99	72.00	862.11	54.00
10.00	149.25	99.99	73.00	862.08	53.86
11.00	165.64	99,99	74.00	862.06	53.74
12.00	182.20	99.99	/5.00	861.11	53.55
13.00	198.98	99.99	76.00	860.81	53.35
14.00	215.62	99.99	77.00	941 17	52.54
15.00	252.52	33.30	78.00	091.17	52.50
17.00	245.11	00 93	75.00	<u> </u>	52.00
17.00	203.03	99.03	91.00	705 20	52.05
10.00	202.30	99.09	01.00	755.20	52.05
19.00	230.50	99.00	82.00	760.13	52.04
20.00	332.45	98.75	83.00	763.07	52.04
27.00	348.92	98.67	85.00	730.04	52.04
22.00	365 30	98.65	85.00	734.50	57.94
24.00	381.60	98.62	87.00	705.00	57.85
25.00	397.81	98.60	88.00	682.94	52.05
26.00	413.95	98.58	89.00	667.02	52.85
27.00	430.03	98.56	90.00	656.17	52.81
28.00	445.93	98.53	91.00	655.16	53.00
29.00	461.95	98.51	92.00	655.60	54.09
30.00	477.84	98.49	93.00	655.28	54.12
31.00	493.65	98.47	94.00	655.08	55.15
32.00	509.54	98.45	95.00	655.06	56.33
33.00	525.32	98.45	96.00	655.18	56.91
34.00	541.01	98.44	97.00	655.19	57.78
35.00	556.60	98.43	98.00	654.98	58.61
36.00	572.21	98.42	99.00	654.60	58.96
37.00	587.87	98.43	100.00	654.45	59.19
38.00	603.57	98.43	101.00	654.33	59.42
39.00	619.17	98.44	102.00	654.26	59.63
40.00	634.83	98.44	103.00	654.20	59.85
41.00	650.37	98.45	104.00	654.20	60.05
42.00	665.92	98.45	105.00	654.22	60.26
43.00	681.54	98.45	106.00	654.27	60.46
44.00	697.20	98.45	107.00	654.29	60.66
45.00	712,91	98.45	108.00	654.29	60.85
46.00	728.83	98.43	109.00	654.26	61.04
47.00	744.71	98.03	110.00	654.23	61.22
48.00	/50.18	96.48	111.00	654.20	61.40
49.00	7/5./2	93./6	112.00	654.15	61.58
50.00	/91.19	89.04 03.07	113.00	054.15	61.75
52.00	921.93	76 41	114.00	654.15	61.92
52.00	821.02 837.72	57 60	115.00	004.18 657 72	62.09
53.00	\$45.07	59 34	117.00	65/ 37	02.20 £3.43
55.00	849.01	54.20	118.00	654.20	62.43 62.43
56.00	853.14	54.18	119.00	654 33	67.76
57.00	857.48	54.14	120.00	654.36	62.93
58.00	860.18	54.17	121.00	654.36	63.09
59.00	860.46	54.13	122.00	654,34	63.25
60.00	860.80	54.14	123.00	654.30	63.41
61.00	860.95	54.12	124.00	654.28	63.57
62.00	861.12	54.10	125.00	654.19	63.72
			·····		

# TGA reading for cockle shell calcined at 850°C for 20 minutes using heating rate of 15°C/min and particle sizes between 1.00-2.00 mm

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
126.00	653.99	63.88	178.00	654.25	71.22
127.00	653.94	64.05	179.00	654.26	71.34
128.00	653.94	64.21	180.00	654.22	71.45
129.00	653.94	64.37	181.00	654.18	71.56
130.00	654.01	64.53	182.00	654.19	71.67
131.00	654.05	64.69	183.00	654.16	71.78
132.00	654.11	64.85	184.00	654.17	71.89
133.00	654.15	65.02	185.00	654.16	72.00
134.00	654.16	65.17	186.00	654.13	72.10
135.00	654.16	65.33	187.00	654.12	72.21
136.00	654.16	65.49	188.00	654.07	72.30
137.00	654.15	65.65	189.00	654.24	72.40
138.00	654.10	65.80	190.00	654.25	72.50
139.00	654.07	65.95	191.00	654.25	72.57
140.00	654.05	66.11	192.00	654.26	72.66
141.00	654.01	65.26	193.00	654.22	72 75
142.00	654.01	66.41	194.00	654.18	72.83
143.00	654.04	66.56	195.00	654.19	77.93
144.00	654.08	66.71	196.00	654.16	73.06
145.00	654.12	66.86	197.00	654 17	73.00
146.00	654.13	67.01	198.00	654.16	73.23
147.00	654.15	67.15	199.00	654.13	73.22
149.00	654.17	67.30	200.00	654.12	73.32
140.00	654.21	67.50	200.00	654.02	73.41
149.00	12.400	67.60	201.00	654.07	73.31
150.00	654.24	67.74	202.00	654.25	73.01
151.00	654.24	67.09	205.00	654.23	73.70
152.00	654.20	69.02	204.00	654.10	73.77
153.00	654.2J	60.02	205.00	654.22	73.00
154.00	034.24	60.17	208.00	654.23	/3.93
155.00	654.20	00.51	207.00	654.23	74.03
158.00	004.20 654.15	00.44 60 E0	208.00	034.23 [	74.12
157.00	034,13 CEA 12	00,30 ¢0,71	209.00	034.23 654.24	74.21
158.00	034.13	00.71 C0.05	210.00	034.24	74.30
159.00	034.09	C0.60	211.00	034.23	74.39
160.00	004.00	08.98	212.00	054.25	74.46
161.00	004.00	69.12	213.00	054.25	/4.54
162.00	654.07	69.25	214.00	654.26	/4.62
163.00	654.98	69.38	215.00		/4./0
164.00	654.08	69.51	216.00		74.80
165.00	654.08	69.64	217.00	654.19	/4.88
166.00	654.09	69.76	218.00	654.16	74.97
167.00	654.11	69.89	219.00		75.04
168.00	654.12	70.02	220.00	654.16	75.12
169.00	654.21	70.14	221.00	654.13	75.20
170.00	654.19	70.27	222.00	654.12	75.30
171.00	654.23	70.39	223.00	654.07	75.37
172.00	654.23	70.51	224.00	654.24	75.45
173.00	654.23	70.63	225.00	654.25	75.53
174.00	654.23	70.75	226.00	654.25	75.62
175.00	654.24	70.87	227.00	654.26	75.70
176.00	654.25	70.99	228.00	654.22	75.79
177.00	654.25	71.11			

.

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
0.00	30.62	98.31	63.00	671.36	91.12
1.00	31.31	98.29	64.00	681.66	91.10
2.00	34.31	98.27	65.00	692.01	91.06
3.00	40.14	98.24	66.00	702.18	90.81
4.00	47.78	98.18	67.00	712.28	89.85
5.00	56.56	98.11	68.00	722.39	88.01
6.00	66.06	98.06	69.00	732.56	85.25
7.00	75.91	98.01	70.00	742.83	81.40
8.00	86.05	97.97	71.00	753.35	76.32
9.00	96.31	97.94	72.00	763.64	69.90
10.00	106.80	97.92	73,00	774.03	62.24
11.00	117.31	97.90	74.00	785.09	54.32
12.00	127.90	97.89	75.00	799.16	51.45
13.00	138.70	97.88	76.00	810.13	51.40
14.00	149.49	97.87	77.00	820.71	51.36
15.00	160.36	97.86	78.00	826.97	51.32
16.00	171.28	97.84	79.00	828.45	51.29
17.00	182.22	97.82	80.00	828.91	51.27
18.00	193.29	97.76	81.00	829.11	51.24
19.00	204.37	97.68	82.00	829.25	51.23
20.00	215.32	97.56	83.00	829.41	51.21
21.00	226.39	97.40	84.00	829.53	51.20
22.00	237.35	97.20	85.00	829.62	51.18
23.00	248.44	96.97	86.00	829.69	51.17
24.00	259.53	96.69	87.00	829.76	51.16
25.00	270.60	96.36	88.00	829.80	51.15
26.00	281.62	95.99	89.00	829.83	51.15
27.00	292.66	95.59	90.00	829.86	51.14
28.00	303.71	95.19	91.00	829.88	51.13
29.00	314.73	94.79	92.00	829.91	51.12
30,00	325.71	94.44	93.00	829.91	51.11
31.00	336.70	94.15	94.00	829.92	51.10
32.00	347.60	93.92	95.00	829.92	51.09
33.00	358.46	93.73	96.00	829.94	51.09
34.00	369.23	93.57	97.00	829.96	51.09
35.00	379.87	93.43	98.00	823.36	51.07
36.00	390.56	93.31	99.00	810.14	51.07
37.00	401.18	93.18	100.00	795.53	51.06
38.00	411.77	93.07	101.00	780.65	51.06
39.00	422.44	92.97	102.00	765.70	51.05
40.00	432.97	92.87	103.00	750.73	51.05
41.00	443.55	92.77	104.00	735.71	51.05
42.00	454.06	92.67	105.00	720.77	51.05
43.00	464.66	92.55	106.00	705,77	51.06
44.00	475.22	92.44	107.00	690.71	51.06
45.00	485.72	92.31	108.00	670.68	51.08
46.00	496.25	92.17	109.00	657.77	51.00
47.00	506.73	92.03	110.00	655.00	51.03
48.00	516.99	91.89	111.00	655.62	51,10
49.00	527.38	91.75	112.00	655.37	51.17
50.00	537.80	91.63	113.00	655.15	51.22
51.00	548.09	91.53	114.00	655.05	51.26
52.00	558.34	91.43	115.00	655.00	51.39
53.00	568.57	91.35	116.00	655.14	51.87
54.00	578.85	91.30	117.00	655.26	52.82
55.00	589.12	91.26	118.00	655.27	54.13
56.00	599.50	91.24	119.00	655.06	55.49
57.00	609.79	91.22	120.00	655.50	56.16
58.00	620.00	91.21	121.00	655.29	56.47
59.00	630.32	91.19	122.00	655.21	56.75
60.00	640.54	91.18	123.00	655.17	57.03
61.00	650.82	91.16	124.00	655.16	57.30
62.00	661.09	91.14	125.00	655.16	57.57

# TGA reading for cockle shell calcined at 800°C for 20 minutes using heating rate of $10^{\circ}$ C/min and particle sizes of less <0.125 mm

	Temperature			Temperature			Temperature	
TIME (min)	(°C)	Weight %	Time(min)	("C}	Weight %	Time (min)	(°C)	Weight %
126.00	655.18	57.83	174.00	655.58	67.08	222.00	656.16	73.0
127.00	655.22	58.09	175.00	655.60	67.23	223.00	656.19	73.1
128.00	655.24	58.34	176.00	655.59	67.38	224.00	656.19	73.2
129.00	655.27	58.59	177.00	655.58	67.53	225.00	656.18	73.3
130.00	655.28	58.83	178.00	655.58	67.67	226.00	656.17	73.4
131.00	655.30	59.08	179.00	655.61	67.82	227.00	656.15	73.5
132.00	655.30	59.31	180.00	655.62	67.96	228.00	656.12	73.6
133.00	655.28	59.54	181.00	655.60	68.10	229.00	656.09	73.7
134.00	655.24	59.78	182.00	655.58	68.25	230.00	656.10	73.8
135.00	655.22	60.00	183.00	655.58	68.39	231.00	656.11	73.9
136.00	655.19	60.22	184.00	655.57	68.53	232.00	656.11	74.0
137.00	655.17	60.44	185.00	655.56	68.67	233.00	656.10	74.1
138.00	655.16	60.66	186.00	655.55	68.81	234.00	656.12	74.2
139.00	655.16	60.87	187.00	655.56	68.94	235.00	656.16	74.3
140.00	655.18	61.08	188.00	655.57	69.07	236.00	656.18	74.4
141.00	655.18	61.28	189.00	655.57	69.21	237.00	656.16	74.5
142.00	655.21	61.49	190.00	655.58	69.34	238.00	656.19	74.6
143.00	655.24	61.69	191.00	655.58	69.48	239.00	656.19	74.7
144.00	655.28	61.89	192.00	655.61	69.61	240.00	656.18	74.8
145.00	655.33	62.09	193.00	655.61	69.73	241.00	655.17	74.9
146.00	655.37	62.29	194.00	655.61	69.86	242.00	655.16	75.0
147.00	655.41	62.48	195.00	655.61	69.99	243.00	655.16	75.1
148.00	655.44	62.67	196.00	655.65	70.12	244.00	655.18	75.2
149.00	655.43	62.86	197.00	655.67	70.24	245.00	655.18	75.3
150.00	655.43	63.05	198.00	655.68	70.37	246.00	655.21	75.4
151.00	655.42	63.24	199.00	655.69	70.49	247.00	655.24	75.5
152.00	655.44	63.42	200.00	655.70	70.61	248.00	656.16	75.6
153.00	655.43	63.60	201.00	655.70	70.74	249.00	656.18	75.7
154.00	655.41	63.78	202.00	655.73	70.85	250.00	656.16	75.8
155.00	655.40	63.96	203.00	655.78	70.98	251.00	656.19	75.9
156.00	655.38	64.14	204.00	655.81	71.10	252.00	656.19	76.0
157.00	655.38	64.31	205.00	655.83	71.21	253.00	656.18	76.1
158.00	655.34	64.48	206.00	656.11	71.34	254.00	656.17	76.2
159.00	655.35	64.65	207.00	656.18	71.46	255.00	656.15	76.3
160.00	655.36	64.82	208.00	656.21	71.57	256.00	656.12	76.4
161.00	655.36	64.99	209.00	656,20	71.69	257.00	655.16	76.5
162.00	655.37	65.16	210.00	656.18	71.80	258.00	655.16	76.6
163.00	655.39	65.33	211.00	656.17	71.91	259.00	655.18	76.7
164.00	655.43	65.49	212.00	656.15	72.02	260.00	655.18	76.8
165.00	655.45	65.66	213.00	656.12	72.13	261.00	655.21	76.8
166.00	655.47	65.82	214.00	656.09	72.24	262.00	656.18	76.9
167.00	655.51	65.98	215.00	656.10	72.34	263.00	656.16	77.0
168.00	655.52	66.14	216.00	656.11	72.45	264.00	656.19	77.1
169.00	655.54	66.30	217.00	656.11	72.55	265.00	656.19	77.2
170.00	655.58	65.46	218.00	656,10	72.66	266.00	656.18	77.3
171.00	655.59	65.62	219.00	656.12	72.76			
172.00	655.58	66.77	220.00	656.16	72.87			
173.00	655.57	66.92	221.00	656.18	72.97			

· · · · · · · · · · · · · · · · · · ·			·	r	······
Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
0.00	29.73	100.00	63.00	810,39	54.97
1.00	24.00	100.00	64.00	810.41	54.07
1.00		100.00	64.00	810.41	54.97
2.00	44.55	100.01	65.00	810.42	54.96
3.00	56.75	100.01	66.00	810.42	54.95
3.00		100.01	00.00	010.43	54.35
4.00	70.64	100.02	67.00	810.45	54.95
5.00	85.45	100.02	68.00	810.45	54.94
5.00	402.00	400.02			
6.00	100.80	100.02	69.00	810.43	54.94
l 7.00 l	116.64	100.02	70.00	810.44	54,94
e 00	132 70	100.02	71.00	910.46	EA 04
8.00	152.70	100.02	71.00	810.40	54.54
9.00	149.04	100.02	72.00	810.48	54,87
10.00	165.50	100.02	73.00	810.48	55.00
11.00	102.05	100.03	74.00	010 70	CC 44
11.00	102.00	100.03	/4.00	00.010	33,11
12.00	198.84	100.03	75.00	810.50	55.20
13.00	215 44	100.03	76.00	810.49	55 17
13.00		100.00		010.45	
14.00	232.14	100.04	//.00	810.49	55,16
15.00	248.91	100.03	78.00	810.46	55.15
16.00	265.70	100.02	70.00	810.00	EE 14
10.00	205.70	100.02	79.00	010.03	55.14
17.00	282.44	99.98	80.00	810.67	55.13
18.00	299.21	99.92	81.00	795.99	55.12
10.00	205121	40.00	01.00	735.55	
19.00	315.98	99.83	82.00	/81.04	55,11
20.00	332.70	99.73	83.00	766.08	55.10
21.00	240.21	00.62	84.00	751 13	55.00
21.00	343.51	33.02	04.00	/31.12	33.09
22.00	365.79	99.52	85.00	736.10	55.09
23.00	381.94	99.34	86.00	721.17	55.08
24.00	200.04	00.16	07.00	700 45	Cr of
24.00	596.04	33.10	87.00	700.15	55.07
25.00	414.07	<del>9</del> 8.97	88.00	691.06	55.07
26.00	430.14	98.85	00.68	679 24	55.06
27.00	400124	00.70	00.00	075124	
27.00	446.15	98.78	90.00	668.50	55.06
28.00	462.28	<del>9</del> 8.73	91.00	657.60	55.05
20.00	479 10	02 60	02.00	62710	EE 04
23.00	4/0.13	50.05	52,00	1057.10	55,04
30.00	494.20	98.66	. 93.00	656.95	55.04
31.00	509.83	98.64	94.00	656.78	55.03
22.00	505.00	00.64	05.00		55.00
32.00	525.30	98.61	95.00	656.66	55.03
33.00	540.91	98.59	96.00	656.49	55.02
24.00	556 33	02 52	97.00	656 22	55.02
34.00			37.00		JJ.V2
35.00	571.68	98.56	98.00	656.19	55.01
36.00	586.97	98.55	99.00	656.03	55.00
17.00	602.46	00 53	100.00	CEE 00	55.11
37.00	002.46	98.33	100.00	000.88	\$5.11
38.00	617.86	95.78	101.00	655.81	55.21
39.00	633 13	92,53	102.00	655 76	55.28
	-1	~~.~~	102.00	000.70	55.20
40.00	648.43	87.02	103.00	655.73	55.32
41.00	663.67	79.65	104.00	655.78	55.34
42.00	679.06	77 25	105.00	50 223	55 36
42.00	0/0.30	14.33	103.00		
43.00	694.30	66.00	105.00	656.08	55.38
44.00	709.66	60.72	107.00	656.18	55.40
AE 00	734 00	55 00	100 00	CC 333	
45.00	/ 24.98	30.69	100.00	030.23	JJ.4J
46.00	740.36	55.07	109.00	656.27	55.66
47.00	755.99	55.06	110.00	656.17	56.09
40.00	771 01		111.00	LEE 70	EE 7F
40.00	//1.04	00.00	111.00	035.78	30,73
49.00	789.92	55.05	112.00	655.63	57.61
50.00	807.89	55.04	113.00	655.57	58.61
E1 00	75 000	EE 04	114.00		E0 63
21.00	26,600	33.04	114.00	053.36	33.03
52.00	809.58	55.03	115.00	655.56	60.25
53.00	809.74	55.03	116.00	655.58	60.51
51 AA	000.00	EE 02	447.00	CFF C-	CO 7C
54.00	809.86	55.02	117.00	055.61	6U.76
55.00	810.00	55.02	118.00	655.66	61.01
56.00	810.09	55.01	119.00	655.69	61.26
	010 4F	55.02	420.00	CEF 34	C4 F0
57.00	810.15	55.00	120.00	655./4	01.50
58.00	810.23	55.00	121.00	655.74	61.74
50.00	£10.75	5A 00	122.00	£55 72	£1 00
33.00	010.20	533	122.00	033.72	01.33
60.00	810.31	54.99	123.00	655.72	62.23
61.00	810.33	54.98	124.00	655.71	62.47
	010.37	E4.00	100 00	CEE 70	07.02
02.00	010.3/	34.98	172.00	000.70	02.70

# TGA reading for cockle shell calcined at 800°C for 30 minutes using heating rate of 15°C/min and particle sizes of less 0.355-0.710 mm

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
126.00	655.67	62.93	178.00	655.89	72.21
127.00	655.64	63.16	179.00	655.90	72.36
128.00	655.62	63.39	180.00	655.89	72.51
129.00	655.63	63.61	181.00	655.88	72.65
130.00	655.63	63.82	182.00	655.89	72.80
131.00	655.62	64.03	183.00	655.84	72.95
132.00	655.59	64.25	184.00	655.82	73.10
133.00	655.59	64.45	185.00	655.82	73.24
134.00	655.64	64.66	186.00	655.81	73.39
135.00	655.66	64.86	187.00	655.79	73.53
136.00	655.70	65.06	188.00	655.80	73.67
137.00	655.73	65.25	189.00	655.83	73.82
138.00	655.79	65.45	190.00	655.85	73.95
139.00	655.80	65.64	191.00	655.87	74.10
140.00	655.83	65.83	192.00	655.90	74.26
141.00	655.85	66.02	193.00	655.89	74.43
142.00	655.87	66.21	194.00	655.90	74.60
143.00	655.90	66.39	195.00	655.89	74.76
144.00	655.89	66.58	196.00	655.88	74.94
145.00	655.90	66.76	197.00	655.89	75.09
146.00	655.89	66.94	198.00	655.84	75.24
147.00	655.88	67.12	199.00	655.82	75.40
148.00	655.89	67.30	200.00	655.82	75 55
149.00	655.84	67.48	201.00	655.81	75.70
150.00	655.82	67.65	202.00	655.74	75.85
151.00	655.82	67.83	203.00	655.74	76.03
152.00	655.81	68.00	204.00	655.72	76.15
153.00	655.79	68.17	205.00	655.72	76.30
154.00	655.74	68.34	206.00	655.71	76.44
155.00	655.74	68.51	207.00	655.73	76 58
156.00	655.72	68.68	208.00	655.79	76.33
157.00	655.72	68.85	209.00	655.80	76.87
158.00	655.71	69.02	210.00	655.83	77.01
159.00	655.70	69 18	211.00	655.85	77.16
160.00	655 67	69 35	212.00	655.87	77.30
161.00	655.64	69.51	213.00	655.90	77.45
162.00	655.62	69.68	214.00	655.89	77 59
163.00	655.63	69.84	215.00	655.90	77.74
164.00	655.63	70.01	216.00	655.89	77.88
165.00	655.62	70.17	217.00	655.87	78.02
166.00	655.59	70.33	218.00	655.90	78.17
167.00	655.59	70.49	219.00	655.89	78.31
168.00	655.64	70.65	220.00	655.90	78.45
169.00	655.66	70.81	221 00	655.89	78.60
170.00	655.70	70.97	222.00	655.89	78 74
171.00	655.73	71.13	273.00	655.84	78.89
172.00	655.79	71.28	274.00	655.87	79.00
173.00	655.80	71.44	225.00	655.82	79.12
174.00	655,83	71.60	226.00	655.81	79.25
175.00	655.85	71.75	227.00	655.79	79.37
176.00	655.87	71.90	228.00	655.74	79.50
177.00	655.90	72.05			

Time (min)	Tomporature (%)	Mainh+ 9/	Time (mia)	Temporatura / ??	Moight 9/
Line (inen)	remperature ( C)	weight %	(ADE (HID)	remperature ("C)	weight 70
U.00	<u>30.15</u>	100.00	62.00	11.608	54.30
1.00	31.27	99.99	63.00	809.15	54.29
2.00	38.23	99.98	64.00	809.17	54.28
3.00	50.80	99.95	65.00	809.18	54.28
4.00	67.19	99.91	66.00	809.17	54.27
5.00	85.92	99.82	67.00	809.19	54.26
6.00	105.04	00.74	69.00	900 28	54.25
7.00	103.34	33.74	00.00	009.20	34.23
7.00	126.87	99.70	69.00	809.40	54.24
8.00	148.61	99,68	70.00	809.48	54.23
9.00	170.63	99.67	71.00	809.50	54.22
10.00	193.04	99.64	72.00	809.50	54.21
11.00	215.58	99.58	73.00	809.48	54,21
12.00	238.08	99,39	74.00	809.50	54.20
12.00	260.72	00 14	75.00	01 009	54 19
14.00	200:75	00.90	75.00	00,40	54.10
14.00	283.27	98.00	78.00	005.50	54.10
15.00	305.47	98.06	77.00	809.48	54.18
16.00	328.15	97.73	78.00	809.50	54.17
17.00	350.49	97.66	79.00	807.59	54.16
18.00	372.57	97.61	80.00	806.53	54.15
19.00	394.47	97.56	81.00	802,23	54.15
20.00	416 32	97.52	82.00	787 34	54 14
20.00	427.01	07.46	93.00	707.01	E4 12
21.00	457.51	97,40	03.00	40 775	54.13
22.00	439,41	97,41	64.00	/5/,40	54.15
23.00	480.92	97.36	85.00	742.51	54.13
24.00	502.28	97.32	86.00	727.57	54.13
25.00	523.42	97,28	87.00	712.57	54.14
26.00	544.59	97.26	88.00	697.52	54.14
27.00	565.78	97.24	89.00	683.48	54.20
28.00	586 82	97.22	90.00	677.90	54.07
20.00	607.93	97.21	91.00	656 49	EA 10
23.00	507.05 679.79	07.20	91.00	030.45 CEE 04	34.13
30.00	628.78	97.20	92,00	033,34	54.55
31.00	649.73	97.18	93.00	655.64	54.40
32.00	670.67	97.16	94.00	655.47	54.44
33.00	691.75	97.14	95.00	655.45	54.57
34.00	713.11	97.12	96.00	655.58	55.09
35.00	734.52	97.11	97.00	655.60	55.92
36.00	755.77	97.04	98.00	655.30	56.58
27.00	775 39	05.79	00.00	655.05	56.55
37.00	770.30	33.70	35.00	033.05 CCA 05	50.82
38.00	/9/.00	92.55	100.00	654.95	57.04
39.00	798.13	87.02	101.00	654.86	57.24
40.00	801.03	79.65	102.00	654.80	57.44
41.00	802.77	72.35	103.00	654.76	57.64
42.00	803.88	66.00	104.00	654.72	57.83
43.00	804.87	60.72	105.00	654.71	58.02
44.00	805.98	56.89	106.00	654.76	58.21
45.00	807 16	54.93	107.00	654.79	59 20
45.00	909.05	EA 52	102.00	654.91	50.55
40.00	000.03	54,55	100.00	654.93	50.30
47.00	<u>808.27</u>	54.49	103.00	034.62	36.74
48.00	808.42	54,46	110.00	654.82	58.91
49.00	808.55	54.44	111.00	654.80	59.08
50.00	808.66	54.43	112.00	654.80	59.25
51.00	808.76	54,41	113.00	654.77	59.41
52.00	808.83	54,40	114.00	654.71	59.57
53.00	808.88	54.39	115.00	654.67	59.73
54.00	808.92	54.38	116.00	654.67	59.89
55.00	808.05	54 27	117.00	654.68	60.05
55.00	000.93	EA 36	110 00	CEA 70	<u> </u>
50.00	009.UI	24.30	115.00	034.70	00.21
57.00	809.04	54.35	119.00	654.70	60.37
58.00	809.08	54.34	120.00	654.73	60.53
59.00	809.10	54.33	121.00	654.74	60.69
60.00	809.09	54.32	122.00	654.80	60.85
61.00	809.12	54.31	123.00	654.83	61.01

# TGA reading for cockle shell calcined at 800°C for 40 minutes using heating rate of 20°C/min and particle sizes of less 1.00-2.00 mm

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
124.00	654.86	61.16	183.00	655.17	69.00
125.00	654.87	61.32	184.00	655.15	69.11
126.00	654.89	61.47	185.00	655.14	69.21
127.00	654.90	61.63	186.00	655.15	69.32
128.00	654.93	61.79	187.00	655.17	69.42
129.00	654.91	61.94	188.00	655.15	69.53
130.00	654.89	62.09	189.00	655.16	69.63
131.00	654.86	62.24	190.00	655.15	69.73
132.00	654.83	62.39	191.00	655.16	69.83
133.00	654.82	62.54	192.00	655.17	69.93
134.00	654.81	62.69	193.00	655.17	70.03
135.00	654.79	62.84	194.00	655.15	70.13
136.00	654.81	62,99	195.00	655.17	70.23
137.00	654.81	63.13	196.00	655.16	70.23
138.00	654.82	63.28	197.00	655.17	70.53
139.00	654.89	63.43	198.00	655.17	70.52
140.00	654.95	63.57	199.00	655.18	70.52
141.00	654.97	63.72	200.00	655.18	70.00
142.00	655.00	63.87	201.00	655.18	70.83
143.00	655.03	64.01	202.00	655.16	70.03
144.00	655.06	64.15	203.00	655.17	71.04
145.00	655.08	64.29	204.00	655 18	71 13
146.00	655.07	64.43	205.00	655.10	71.23
147.00	655.07	64.57	206.00	655.15	71 33
148.00	655.06	64.71	207.00	655 14	71,33
149.00	655.04	64,85	208.00	655 15	71.43
150.00	655.04	64.99	209.00	655.13	71.54
151.00	655.04	65 12	210.00	655.15	71 73
152.00	655.03	65.26	211.00	655.16	71,73
153.00	655.00	65.39	212.00	655.15	71.01
154.00	654.99	65.52	213.00	655.16	72.03
155.00	654.97	65.65	214.00	655.17	72.14
156.00	654.94	65.78	215.00	655.17	72.22
157.00	654.92	65.91	216.00	655.15	72.33
158.00	654.93	66.05	217.00	655.17	72.41
159.00	654.92	66.17	218.00	655.16	72.53
160.00	654.92	66.30	219.00	655.17	72.63
161.00	654.91	66.43	220.00	655.17	72.74
162.00	654.90	66.56	221.00	655.18	72.87
163.00	654.91	66.68	222.00	655.17	72.73
164.00	654.93	66.80	223.00	655.18	72.81
165.00	654.97	66.93	224.00	655.17	72.93
166.00	654.98	67.05	225.00	655.15	73.01
167.00	655.00	67.17	226.00	655.14	73.09
168.00	655.02	67.29	227.00	655.15	73.16
169.00	655.01	67.41	228.00	655.17	73.22
170.00	655.01	67.53	229.00	655.15	73.32
171.00	655.08	67.65	230.00	655.16	73.40
172.00	655.07	67.77	231.00	655.15	73.50
173.00	655.10	67.88	232.00	655.14	73.57
174.00	655.13	68.00	233.00	655.15	73.65
175.00	655.12	68.12	234.00	655.17	73.73
176.00	655.15	68.23	235.00	655.15	73.80
177.00	655.18	68.34	236.00	655.16	73.88
178.00	655.18	68.45	237.00	655.15	73.95
179.00	655.18	68.56	238.00	655.16	74.00
180.00	655.16	68.67	239.00	655.17	74.08
181.00	655.17	68.78	240.00	655.17	74.16
182.00	655.18	68.89			

.

Time (min)	Temperature /°C	Weight %	Time (min)	Temperature (°C)	Meight %
	20 10	100.00	62 00	1011perature ( C)	67 CG 74
1.00	21.41	00.00	62.00	955.11 055 12	53.71
1.00	31.41	99.99	53.00	955.13	55.09
2.00	38.23	100.00	64.00	955.16	53.67
3.00	50,65	99.99	65.00	955.21	53.65
4.00	66.92	<u>99.99</u>	66,00	955.28	53.63
5.00	85.61	99.99	67.00	948.10	53.61
6.00	105.71	99.98	68.00	937.14	53.59
7.00	126.60	99.97	69.00	933.25	53.58
8.00	148.31	99.97	70.00	925.24	53.57
9.00	170.36	99.98	71.00	917.27	53.55
10.00	192.75	99.98	72.00	906.36	53.54
11.00	215.30	99.95	73.00	890.54	53.53
12.00	237.86	99.84	74.00	874.74	53.52
13.00	260.55	99.67	75.00	858.97	53 51
14.00	283.04	99.38	76.00	843.16	53 50
15.00	205.04	09.92	70,00	077 50	53.50
15.00	277.00	98.05	79.00	017 12	53.00
10.00	327.35	30.00	78.00	706 70	53.43
17.00	330.28	96.52	/9.00	/90./0	55.48
18.00	372.35	98.47	00.08	/81.30	53.48
19.00	394.29	98.43	81.00	766.07	53.47
20.00	416.10	98.39	82.00	750.90	53.47
21.00	437.73	98.35	83.00	735.69	53.47
22.00	459.26	98.31	84.00	720.53	53.46
23.00	480.73	98.28	85.00	705.32	53.46
24.00	502.04	98.26	86.00	685.17	53.45
25.00	523.18	98.24	87.00	672.88	53.44
26.00	544.35	98.22	88.00	664.96	53.35
27.00	565.49	98.22	89.00	656.02	53.40
28.00	586.54	98.21	90.00	655.52	53.41
29.00	607.60	98.21	91.00	655.14	53,44
30.00	628.56	98.20	92.00	654.89	53.47
31.00	649.50	98.19	93.00	654.74	53 51
32.00	670.41	98 19	94.00	654.82	53.82
22.00	691.42	08.19	95.00	654.04	53,52 EA EA
33.00	717 75	00 17	96.00	654.04	55.53
34.00	712.75		90.00	034.94 CEA E7	55.55
35.00	754.15	90.13	37.00	654.57	30.27
36.00	/34.65	97.20	.98.00	534.32	50.57
37.00	//5.0/	93.57	99.00	654.19	56.83
38.00	795.42	86.72	100.00	654.07	57.07
39.00	815.64	76.54	101.00	654.02	57.30
40.00	835.91	62.80	102.00	654.00	57.53
41.00	862.52	54.49	103.00	654.03	57.76
42.00	885.06	54.43	104.00	654.05	57.98
43.00	906.90	54.41	105.00	654.11	58.20
44.00	929.15	54.37	106.00	<u>654.16</u>	58.42
45.00	951.64	54.34	107.00	654.15	58.63
46.00	954.49	54.31	108.00	654.13	58.84
47.00	955.65	54.25	109.00	654.08	59.05
48.00	955.25	54.19	110.00	654.05	59.26
49.00	954.22	54.15	111.00	654.03	59.47
50.00	955.84	54.11	112.00	654.07	59.67
51.00	956.32	54.07	113.00	654.10	59.88
52.00	955.67	54.03	114.00	654.17	60.08
53.00	955.98	53.99	115.00	654.23	60.29
54.00	955.25	53.95	116.00	654.27	60.49
55.00	955.44	53.97	117.00	654.25	60.69
56.00	955.60	53.88	118.00	654.25	60,89
57.00	055.00	53.00	119.00	654.20	£1.00
50.00	055 97	53.03	120.00	£54 17	£1 70
50.00	055 00	53.02	101.00	11.400	C1 47
23.00	UC.CC	53.60	121.00	004.14	01.4/
60.00	900.99	33./8	122.00	004.14	01.0/
1 61.00	ı 955.07	53./4			

# TGA reading for cockle shell calcined at 950°C for 20 minutes using heating rate of 20°C/min and particle sizes between 0.355-0.710 mm

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
123.00	654.12	61.86	176.00	654.48	70.49
124.00	654.16	62.05	177.00	654.50	70.63
125.00	654.16	62.23	178.00	654.53	70.76
126.00	654.22	62.42	179.00	654.51	70.89
127.00	654.27	62.61	180.00	654.52	71.03
128.00	654.30	62.81	181.00	654.51	71.16
129.00	654.33	62.99	182.00	654.50	71.29
130.00	654.32	63.18	183.00	654.48	71.42
131.00	654.30	63.36	184.00	654.48	71.54
132.00	654.27	63.53	185.00	654.50	71.67
133.00	654.24	63.72	186.00	654.53	72.11
134.00	654.26	63.90	187.00	654.51	72.25
135.00	654.24	64.08	188.00	654.52	72.39
136.00	654.26	64.25	189.00	654.51	72.54
137.00	654.28	64.43	190.00	654,50	72.67
138.00	654.30	64.61	191.00	654.48	72.82
139.00	654.34	64.78	192.00	654.48	72.96
140.00	654.37	64.95	193.00	654.47	73.09
141.00	654.41	65.13	194.00	654.47	73.23
142.00	654.45	65.30	195.00	654.46	73.36
143.00	654.47	65.47	196.00	654.42	73.50
144.00	654.47	65.64	197.00	654.37	73.62
145.00	654.46	65.81	198.00	654.33	73,77
146.00	654.42	65.97	199.00	<u>654.38</u>	73.91
147.00	654.37	66.14	200.00	<u>654.37</u>	74.04
148.00	654.33	66.30	201.00	654.38	74.17
149.00	654.32	66.46	202.00	654.36	74.29
150.00	654.30	66.62	203.00	654.36	74.41
151.00	654.27	66.79	204.00	654.35	74.53
152.00	654.24	66.95	205.00	654.40	74.66
153.00	654.26	67.11	206.00	654.44	74.79
154.00	654.24	67.26	207.00	654.49	74.91
155.00	654.26	67.42	208.00	654.48	75.04
156.00	654.28	67.58	209.00	654.50	75.16
157.00	654.30	67.74	210.00	654.55	/5.28
158.00	654.34	67.89	211.00	654.51	/5.40
159.00	654.3/	68.04	212.00	654.50	/5.53
160.00	654.41	68.20	213.00	654.48	/5.66
161.00	654.45	08.35	214.00	654.48	/5./8
162.00	054.47	60.50	215.00	034.47 CE4 20	75.91
105.00	034.47 EEA AC	69.70	210.00	034.39	70.04
165.00	654.40	69.04	217.00	654.47	76.10
165.00	654.97	60.04	218.00	654.50	76.28
167.00	654.37	69.08	213,00	654.50 654.50	76.52
168.00	22 A2A	69.23 69.27	721.00	554.50 554.50	76.55
169.00	654 37	69.51	222.00	654.50	76.72
170.00	654.2R	69.66	222.00	654.50	76.01
171.00	654.36	08,63	274 00	654.48	77.02
172.00	654 35	69.94	225.00	654.48	77.12
173.00	654.40	70.08	226.00	654.47	77.25
174.00	654.44	70.22	227.00	654.39	77.36
175.00	654.49	70.35	228.00	654.43	77.47

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
0.00	31.06	98.81	61.00	882.68	50.98
1.00	37.86	98.69	62.00	882.69	50.97
2.00	43.45	98.62	63.00	882.71	50.95
3.00	53.80	98.53	64.00	882.74	50.95
4.00	68.66	98.43	65.00	882.79	50.95
5.00	86.54	98.34	66.00	882.82	50.94
6.00	106.23	<del>9</del> 8.26	67.00	882.85	50.93
7.00	126.94	98.21	68.00	882.87	50.92
8.00	148.52	98.18	69.00	882.88	50.91
9.00	170.55	98.15	70.00	882.87	50.91
10.00	192.94	98.09	71.00	882.88	50.90
11.00	215.46	97.94	72.00	875.90	50.88
12.00	238.02	97.66	73.00	862.14	50.86
13.00	260.71	97.16	74.00	847.00	50.86
14.00	283.51	96.49	75.00	831.90	50.85
15.00	306.27	95.68	76.00	816.70	50.84
16.00	328.98	94.87	77.00	801.42	50.83
17.00	351.56	94.26	78.00	786.18	50.82
18.00	373.78	93.84	79.00	771.03	50.82
19.00	395.69	93.53	80.00	755.92	50.81
20.00	417.14	93.27	81.00	740.80	50.81
21.00	438.72	93.04	82.00	725.77	50.81
22.00	460.35	92.83	83.00	710.67	50.81
23.00	481.89	92.57	84.00	695.53	50.81
24.00	503.48	92.27	85.00	676.63	50.82
25.00	524.76	91.97	86.00	668.03	50.80
26.00	545.75	91.70	87.00	656,99	50.76
27.00	566.43	91.50	88.00	656.53	50.80
28.00	586.96	91,39	89.00	656.20	50.84
29.00	607.75	91,33	90.00	655.92	50.88
30.00	628.68	91.28	91.00	655.77	51.04
31.00	649.62	91.25	92.00	655.78	51.58
32.00	670.49	91.22	93.00	655.81	52.53
33.00	691.41	91.17	94.00	655.75	53.71
34.00	712.38	91.10	95.00	655.55	54.78
35.00	733.12	90.32	96.00	655.21	55,28
36.00	753.41	86.88	97.00	655.12	55,59
37.00	773.42	79.93	98.00	655.07	55.87
38.00	793.48	69.03	99.00	655.00	56.12
39.00	814.83	55.91	100.00	654,94	56.37
40.00	841.76	51.51	101.00	654.83	56.61
41.00	863.64	51.43	102.00	654.71	56.83
42.00	876.07	51.36	103.00	654.65	57.05
43.00	878,95	51.30	104.00	654.63	57.27
44.00	879.85	51.26	105.00	654.67	57 49
45.00	880.43	51.24	105.00	654 70	57 69
46.00	880.83	51 71	107.00	654.73	57.89
47.00	881.19	51.19	108.00	654.74	58.09
48.00	881.49	51.17	109.00	654.79	58.29
49.00	881.71	51.15	110.00	654.82	58.48
50.00	881.87	51.13	111.00	654.81	58.68
51.00	882.05	51.11	112.00	654.81	58.86
52.00	882.18	51.10	113.00	654.80	59.05
53.00	882.27	51.08	114.00	654.79	59.24
54.00	882.35	51.07	115.00	654.78	59.42
55.00	882.43	51.05	116.00	654.77	59.60
56.00	882.47	51.04	117.00	654.76	59.77
57.00	882.50	51.03	118.00	654.74	59.95
58.00	882.58	51.02	119.00	654.74	60.13
59.00	882.62	51.01	120.00	654.75	60.30
60.00	882.66	50.99			

# TGA reading for cockle shell calcined at 850°C for 30 minutes using heating rate of 20°C/min and particle sizes of less <0.125 mm

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
121.00	654.79	60.47	171.00	655.54	67.70
122.00	654.86	60.65	172.00	655.54	67.82
123.00	654.86	60.82	173.00	655.55	67.93
124.00	654.90	60.99	174.00	655.59	68.05
125.00	654.96	61.16	175.00	655.59	68.17
126.00	654.99	61.32	176.00	655.61	68.28
127.00	654.99	61.49	177.00	655.60	68.40
128.00	654.99	61.65	178.00	655.62	68.51
129.00	654.99	61.82	179.00	655.66	68.63
130.00	655.02	61.98	180.00	655.66	68.74
131.00	655.02	62.14	181.00	655.69	68.85
132.00	654.99	62.30	182.00	655.71	68.96
133.00	654.97	62.45	183,00	655.73	69.07
134.00	654.98	62.61	184.00	655.71	69.18
135.00	654.97	62.77	185.00	655.78	69.29
136.00	654.94	62.92	186.00	655.81	69.40
137.00	654.92	63.07	187.00	655.75	69.51
138.00	654.93	63.22	188.00	655.55	69.62
139.00	654.92	63.37	189.00	655.21	69.74
140.00	654.92	63.52	190.00	655.12	69.84
141.00	654.91	63.67	191.00	655.07	69.96
142.00	654.90	63.82	192.00	655.00	70.07
143.00	654.91	63.97	193.00	654.94	70.18
144.00	654.93	64.12	194.00	654.83	70.28
145.00	654.83	64.26	195.00	654.71	70.39
146.00	654.71	64.41	196.00	654.65	70.50
147.00	654.65	64.55	197.00	654.63	70.60
148.00	654.63	64.70	198.00	654.67	70.71
149.00	654.67	64.84	199.00	654.70	70.81
150.00	654.70	<del>6</del> 4.98	200.00	654.73	70.92
151.00	654.73	65.12	201.00	654.74	71.02
152.00	654.74	65.26	202.00	654.82	71,13
153.00	654.79	65.39	203.00	654.81	71.23
154.00	654.82	65.53	204.00	654.81	71.33
155.00	654.81	65.67	205.00	654.80	71.43
156.00	654.81	65.80	206.00	654.79	71.54
157.00	654.80	65.93	207.00	654.78	71.64
158.00	654.79	66.07	208.00	654.77	71.74
159.00	654.78	66.20	209.00	654.76	71.85
160.00	654.77	66.33	210.00	654.74	71.95
161.00	654.76	66.46	211.00	654.79	72.04
162.00	654.74	66.58	212.00	654.82	72.14
163.00	654.79	66.71	213.00	654.81	72.24
164.00	654.82	<del>66</del> .84	214.00	654.81	72.33
165.00	654.81	66.96	215.00	654.80	72.43
166.00	654.81	67.09	216.00	654.79	72.52
167.00	654.80	67.21	217.00	654.71	72.61
168.00	654.79	67.33	218.00	654.65	72.71
169.00	654.78	67.46	219.00	654.63	72.81
170.00	654.77	67.58	220.00	654.67	72.90

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
0.00	29.98	99.68	64.00	702.81	91.53
1.00	44.05	99.68	65.00	712.96	91.42
2.00	51.21	99,68	66.00	723.14	91.31
3.00	60.55	99.66	67.00	733.34	91.20
4.00	68.47	99.62	68.00	743.61	85.56
5.00	77.52	99.52	69.00	754.21	80.68
6.00	87.05	99.34	70.00	764.62	73.96
7.00	97.23	99.16	71.00	775.04	65.38
8.00	107.53	98.97	72.00	785.46	55.33
9.00	118.02	98.95	73.00	796 39	50.97
10.00	178.44	98.92	74.00	805.14	50.93
11.00	139.15	98.89	75.00	816.96	50.90
12.00	150.01	09.31	75.00	925 51	50.93
12.00	150.01	09.32	77.00	936.60	50.07
14.00	100.71	00.23	77.00	030.05 0AC 15	50.83
14.00	192.52	96.27	79.00	954.44	50.03
15.00	102.32	70.24	73.00	059.99	50.00
17.00	193.30	<u> </u>	80.00	050.70	50.00
10.00	204.38	<u> 90.11</u>	82.00	050.32	50.79
10.00	213.32	90.00	02.00	030.10	50.77
19.00	220.57	96.01	63.00	000.24	50.76
20.00	237.38	97.97	04.UU pe oo	606.30 000 47	50.74
21.00	246.09	97.94	0.00	050.47 050 54	50.73
22.00	209./2	97.92	07.00	858,54	50.72
23.00	270.71	97.90	87.00	00.00	50.70
24.00	201.00	97.09	30.00	030.00	50.69
25.00	292.00	97.00	89.00	030.72	50.08
20.00	303.08	97.87	90.00	636./3	50.67
27.00	314.07	97.80	91.00	05.000	50.65
28.00	323.38	97.84	92.00	63.63	50.64
29.00	330.31	97.82	93.00	85.66	50.63
30.00	347.34	97.76	94.00	858,69	50.62
31.00	350.13	97.00	95.00	959.02	50.01
32.00	300.90	97.30	90.00	070.93 950.05	50.59
33.00	379.39	97.40	97.00	00.90	50.58
34.00	390.37	97.20	98.00	658.94	50.57
35.00	401.02	90.97	99.00	838.90	50.55
36.00	411.0/	90.09	100.00	538.90	50.55
37.00	422.30	90.30	101.00	06.000	50.54
00.86	432.91	95.99	102.00	626.93	50.53
39.00	445.55	95.59	103.00	656.97	50.51
40.00	454.00	95.19	104.00	858.96	50.51
41.00	464.57	94.79	105.00	858.93	50.49
42.00	4/5.08	94.44	105.00	856.61	50.48
43.00	485.45	94.15	107.00	850.87	50.46
44.00	495,98	95.92	108.00	841.80	50.45
45.00	500,47	95./3	109.00	820.72	50.44
40.00	516./3	95.5/	111.00	811.63	50.44
47.00	527.19	95.45	111.00	790.48	50.43
48.00	057.08 EA9.00	93.51	112.00	751.30	50.42
49.00	246.UZ	50.50	115.00	751.00	50.42
50.00	520.50	95.0/	114.00	735.00	50.42 E0.44
51.00	20.000	54.3/	115.00	733.92	50.41 E0.44
52.00	5/9.JI E00 44	52.0/	110.00	720.01	50.41 En 40
53.00	505.41	52.77 02 67	117.50	/03./1 695.76	50.40
54.00	555.05 610.12	07.55	110.00	676 61	50.41
55.00	20.12	92.33	120.00	070.01 666 70	50.57
50.00	620.38	92.44	120.00	600.70 600.70	50.52
57.00	640 07	02.51	122.00	030.73 EEA 7A	50.40
50.00	CE1 22	92.19	122.00	004.74 657.03	50.52
53.00	661.60	52.00 01.09	123.00	20,4CU	20.37 En <i>En</i>
61.00	671.02	21.20	124.00	034.61 CE4.04	50.67
01.00	CO1.95	91.0/	125.00	004.61	51.00
02.00	602.23	91./5	120.00	U5.400	5U.LC
65.00	692.62	91.64	L127.00	654./9	51.95

# TGA reading for cockle shell calcined at 850°C for 40 minutes using heating rate of 10°C/min and particle sizes between 0.355-0.710 mm

Time (mis)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
128.00	654.78	53.03	192.00	654.32	63.98
129.00	654.77	53.52	193.00	654.30	64.10
130.00	654.76	53.78	194.00	654.27	64.23
131.00	654.74	54.02	195.00	654.24	64.35
132.00	654.79	54.26	196.00	654.26	64.48
133.00	654.82	54.49	197.00	654.24	64.60
134.00	654.81	54.72	198.00	654.26	64.72
135.00	654.81	54.95	199.00	654.28	64.84
136.00	654.80	55.17	200.00	654.30	64.96
137.00	654.79	55.39	201.00	654.34	65.08
138.00	654.94	55.60	202.00	654.37	65.19
139.00	654.94	55.80	203.00	654.41	65.31
140.00	654.57	56.00	204.00	654.45	65.43
141.00	654.32	56.20	205.00	654.47	65.54
142.00	654.19	56.39	206.00	654,47	65.65
143.00	654.07	56.58	207.00	654.46	65.77
144.00	654.02	56.77	208.00	654.42	65.88
145.00	654.00	56.96	209.00	654.37	66.00
146.00	654.03	57.14	210.00	654.33	66.11
147.00	654.05	57.32	211.00	654.38	66.22
148.00	654.11	57.50	212.00	654.37	66.33
149.00	654.10	57.0/	213.00	004.38	56.44
10.00	C1.400	57.65	214.00	004,50 664.35	CC.00
151.00	654.09	50.U2 EQ 10	215.00	654.00	66.76
152.00	654.05	59.25	210,00	654.40	66.97
154.00	654.03	58 52	217.00	654.49	66.98
155.00	654.07	58.69	210.00	654.48	67.09
156.00	654.10	58.85	220.00	654.50	67.19
157.00	654.17	59.02	221.00	654.53	67 30
158.00	654.23	59.18	222.00	654.51	67.41
159.00	654.27	59.34	223.00	654.52	67.52
160.00	654.25	59.50	224.00	654.51	67.63
161.00	654.25	59.65	225.00	654.50	67.73
162.00	654.20	59.81	226.00	654.48	67.84
163.00	654.17	59.96	227.00	654.48	67.95
164.00	654.14	60.12	228.00	654.50	68.05
165.00	654.14	60.27	229.00	654.53	68.17
166.00	654.12	60.42	230.00	654.51	68.27
167.00	654.16	60.57	231.00	654.52	68.37
168.00	654.16	60.71	232.00	654.51	68.48
169.00	654.22	60.86	233.00	654.50	68.58
170.00	654.27	61.01	234.00	654.48	68.68
171.00	654.30	61.15	235.00	654.48	68.78
172.00	654.33	61.30	236.00	654.47	68.89
173.00	654.32	61.44	237.00	654.47	68.99
174.00	654.30	61.59	238.00	654.46	69.09
175.00	654.27	61.73	239.00	654.42	69.20
176.00	654.24	61.87	240.00	654.37	69.30
177.00	554.26 554.26	62.01	241.00	654.33	69.40
1/8.00	C24.24	02.14 £7.7P	242.00	C74.58	60.50
1/5.00	034.20 657 JO	62.20 63 A1	243.00	CEA 20	60.00 60.70
191 00	654 30	62.41	247.00	65 <u>4</u> 26	69.70 69.70
182.00	654.34	67.68	245.00	654.36	09.79 69.89
183.00	654.37	62.82	247.00	654.35	69.99
184.00	654.41	62.95	248.00	654.40	70.09
185.00	654.45	63.08	249.00	654.44	70.19
186.00	654.47	63.21	250.00	654.49	70.29
187.00	654.47	63.34	251.00	654.48	70.39
188.00	654.46	63.47	252.00	654.50	70.48
189.00	654.42	63.60	253.00	654.53	70.58
190.00	654.37	63.73	254.00	654.51	70.68
191.00	654.33	63.85	255.00	654.50	70.77

Time (min)	Temperature (°C)	Weight %	Time (min)	Temperature (°C)	Weight %
0.00	29.79	99.97	63.00	681.66	90.64
1.00	34.31	99.98	64.00	692.01	89.63
2.00	40.14	99.98	65.00	702.18	88.14
3.00	47.78	99.97	66.00	712.28	86.02
4.00	56.56	99.96	67.00	722.39	83.10
5.00	66.06	99.96	68.00	732.56	79.15
6.00	75.91	99.96	69.00	742.83	73.92
7.00	86.05	99.95	70.00	753.35	67.19
8.00	96.31	99.95	71.00	763.64	59.20
9.00	106.80	99.87	72.00	774.03	57.11
10.00	117.31	<del>99</del> .77	73.00	785.09	55.23
11.00	127.90	99.67	74.00	799.16	54.20
12.00	138.70	99.59	75.00	810.13	54.18
13.00	149.49	99.54	76.00	820.71	54.14
14.00	160.36	99.50	77.00	830.75	54.17
15.00	171.28	99.46	78.00	839.97	54.13
16.00	182.22	99,44	79.00	850.06	54.14
17.00	193.29	99.42	80.00	861.16	54.12
18.00	204.37	99.38	81.00	872.43	54.10
19.00	215.32	99.30	82.00	881.89	54.10
20.00	226.39	99,16	83.00	897 54	54.10
21.00	237.35	98.94	84.00	901 17	54.09
22.00	248.44	98.77	85.00	911 24	54.08 54.07
23.00	259.53	98.60	86.00	921 20	54.04
24.00	270.60	98.42	87.00	931 37	54.03
25.00	281.62	98.24	88.00	940.43	54.03
26.00	292.66	98.07	89.00	947 34	54.04
27.00	303.71	97.91	90.00	953.75	54.03
28.00	314.73	97.73	91.00	956.88	54.00
29.00	325.71	97.55	92.00	957.64	53.86
30.00	336.70	97 38	93.00	957.04	53.00
31.00	347 60	97.20	94.00	957.78	53 59
32.00	358.46	97.03	95.00	957.14	53.25
33.00	369.23	96.85	96.00	957.14	52.04
34.00	379.87	96.67	97.00	957.18	57.96
35.00	390.56	96 51	98.00	957.10	52.90
36.00	401 18	96.35	99.00	057.21	52.51
37.00	411 77	96.18	100.00	057.00	57.83
38.00	477 44	96.02	101.00	957.91	52.05
39,00	422.44	95.85	102.00	957.38	52.02
40.00	443 55	95.69	102.00	957.12	52.78
41.00	454.06	95.53	104.00	057.15	52.74
42.00	464.66	95.36	105.00	957.03	52.69
A2 00	475 22	05 10	105.00	057.05 Q57.04	52.03
44.00	485.77	95.02	107.00	957.04	52.67
45.00	496.75	04 86	107.00	Q57 11	52.04
45.00	506 73	94 50	109.00	957.11 957.74	52.02
47.00	516,99	94.53	110.00	957.24	52.55
48.00	527.38	94.39	111.00	957 71	52.57
49.00	537.80	94.28	112.00	957.21	\$7 \$7
50.00	548.09	94.19	113.00	957.21	52.52
51.00	558.34	93.95	114.00	957.21	52.47
52.00	568.57	93.66	115.00	957.21	52.45
53.00	578.85	93.38	116.00	957,20	52.42
54.00	589.12	93.09	117.00	957.20	52.40
55.00	599.50	92.82	118.00	957.22	52.37
56.00	609.79	92.60	119.00	957.16	52.35
57.00	620.00	92.41	120.00	957.22	52.32
58.00	630.32	92.23	121.00	957.20	52.30
59.00	640.54	92.06	122.00	957.20	52.29
60.00	650.82	91.86	123.00	955.28	52.39
61.00	661.09	91.68	124.00	948.10	52.52
62.00	671.36	91.30	125.00	937.14	52.68

# TGA reading for cockle shell calcined at 950°C for 30 minutes using heating rate of 10°C/min and particle sizes of less 1.00-2.00 mm

Time	Temperatur		Time	Temperatur		Time	Temperatur	
(min)	€ (°C)	Weight %	(min)	e (°C)	Weight %	(min)	e (°C)	Weight %
126.00	933.25	52.77	178.00	655.18	64.21	230.00	655.61	71.45
127.00	925.24	52.87	179.00	655.21	64.37	231.00	655.61	71.56
128.00	917.27	52.96	180.00	655.24	64.53	232.00	655.61	71.67
129.00	906.36	53.06	181.00	655.21	64.69	233.00	655.65	71.78
130.00	890.54	53.15	182.00	656.18	64.85	234.00	655.67	71.89
131.00	874.74	53.25	183.00	656.16	65.02	235.00	655.68	72.00
132.00	858.97	53.34	184.00	656.19	65.17	236.00	655.69	72.10
133.00	843.16	53.44	185.00	656.19	65.33	237.00	655.70	72.21
134.00	827.59	53.58	186.00	656.18	65.49	238.00	655.70	72.30
135.00	812.13	53.73	187.00	655.26	65.65	239.00	655.73	72.40
136.00	796.70	53.88	188.00	655.35	65.80	240.00	655.78	72.50
137.00	781.36	54.03	189.00	655.44	65.95	241.00	655.81	72.57
138.00	766.07	54.17	190.00	655.43	66.11	242.00	655.83	72.66
139.00	750.90	54.32	191.00	655.41	66.26	243.00	656.11	72.75
140.00	735.69	54.47	192.00	655.40	66.41	244.00	656.18	72.83
141.00	720.53	54.67	193.00	655.38	66.56	245.00	656.17	72.93
142.00	705.32	54.87	194.00	655.38	66.71	246.00	656.15	73.06
143.00	685.17	55.00	195.00	655.34	66.86	247.00	656.12	73.13
144.00	672.88	55.15	196.00	655.35	67.01	248.00	656.17	73.22
145.00	664.96	56.33	197.00	655.36	67.15	249.00	656.15	73.32
146.00	657.77	56.91	198.00	655.36	67.30	250.00	656.12	73.41
147.00	655.00	57.78	199.00	655.37	67.45	251.00	656.09	73.51
148.00	655.62	58.61	200.00	655.39	67.59	252.00	656.10	73.61
149.00	655.37	58.96	201.00	655.43	67.74	253.00	656.11	73.70
150.00	655.15	59.19	202.00	655.45	67.88	254.00	656.11	73.77
151.00	655.05	59.42	203.00	655.47	68.02	255.00	656.10	73.86
152.00	655.00	59.63	204.00	655.51	68.17	256.00	656.12	73.95
153.00	655.14	59.85	205.00	655.52	68.31	257.00	656.16	74.03
154.00	655.26	60.05	206.00	655.54	68.44	258.00	656.18	74.12
155.00	655.27	60.26	207.00	655.58	68.58	259.00	656.16	74.21
156.00	655.06	60.46	208.00	655.59	68.71	260.00	656.19	74.30
157.00	655.50	60.66	209.00	655.58	68.85	261.00	656.19	74.39
158.00	656.16	60.85	210.00	655.57	68.98	262.00	656.18	74.46
159.00	655.21	61.04	211.00	655.58	69.12	263.00	656.17	74.54
160.00	655.17	61.22	212.00	655.60	69.25	264.00	656.15	74.62
161.00	655.16	61.40	213,00	655.59	69.38	265.00	656.12	74.70
162.00	656.18	61.58	214.00	655.58	69.51	266.00	656.09	74.80
163.00	655.18	61.75	215.00	655.58	69.64	267.00	656.10	74.88
164.00	655.22	61.92	216.00	655.61	69.76	268.00	656.11	74.97
165.00	656.19	62.09	217.00	655.62	69.89	269.00	656.11	75.05
166.00	655.27	62.26	218.00	655.60	70.02	270.00	656.10	75.13
167.00	656.19	62.43	219.00	655.58	70.14	271.00	656.12	75.21
168.00	656.18	62.60	220.00	655.58	70.27	272.00	656.16	75.28
169.00	655.30	62.76	221.00	655.57	70.39	273.00	656.18	75.35
170.00	655.28	62.93	222.00	655.56	70.51	274.00	656.16	75.43
171.00	655.16	63.09	223.00	655.55	70.63	275.00	655.18	75.50
172.00	655.22	63.25	224.00	655.56	70.75	276.00	656.19	75,57
173.00	655.19	63.41	225.00	655.57	70.87	277.00	656.18	75.63
174.00	655.16	63.57	226.00	655.57	70.99	278.00	655.17	75.70
175.00	655.18	63.72	227.00	655.58	71.11	279.00	655.16	75.76
176.00	655.16	63.88	228.00	655.58	71.22	280.00	655.16	75.83
177.00	655.18	64.05	229.00	655.61	71.34	281.00	655.18	75.89
						282.00	655.18	75.96

#### **APPENDICES B**

#### **INTERACTION PLOT**

#### EFFECT OF TEMPERATURE







#### EFFECT OF PARTICLE SIZE/DIAMETER







#### **EFFECT OF RESIDENCE TIME**







#### **EFFECT OF HEATING RATE**





