A Combined Process for Char Activation and Calcium Oxide Formation from Calcium Carbonate

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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Universiti Teknologi PETRONAS
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Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr. Noridah Binti Osman)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERITIFICATION OF ORGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NUR IZZATUL A’LIAH BINTI MOHD NOOR

ABSTRACT

In this study, the pattern of carbon dioxide generation from calcination of calcium carbonate are studied at different temperatures 600, 700 and 800^{o}C. Besides, the morphology of activated char from the combination process of pyrolysis and calcination of calcium carbonate are investigated as the part of the objectives in this project. This project mainly focuses on synthesizing the products of pyrolysis that is biochar and product of calcination that is calcium oxide to produce activated char. To perform this experiment, the limestone with 600 mesh are calcined together with RWS biochar from pyrolysis in a tube furnace at 600, 700 and 800^{o}C. The carbon dioxide released from the calcination of limestone are used by the biochar to convert itself into activated char. The properties of activated char are studied by performing Scanning Electron Microscopy (SEM) and Fourier Transformation Infrared (FTIR) analysis. From this project, it can be concluded from FTIR analysis that O–H stretch, H–bonded and C-H stretch is decreasing as the temperature increasing. From the SEM images generated that under extensive heating, particle size of the bio-char decreased due to breakage and shrinkage mechanisms. It can be seen that the carbon and nitrogen in the samples are decreasing with increasing of calcination temperature, while oxygen shows the opposite pattern.

ACKNOWLEDGEMENT

I am using this opportunity to express my gratitude to the following persons who have made this completion of Final Year Project possible. First of all, I would like to thank my parents, for giving me motivation in my ups and downs while doing this project.

Secondly, I would like to thank my supervisor, Dr. Noridah Osman for giving me guidance to in doing this project. Without her guidance, this project would be impossible. Also, thanks to my friends who are striving with me in making our final year project complete by giving motivation and helps.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Calcium oxide is a well-known material to be used in many industries worldwide. Heating the limestone to drive off carbon dioxide produces the calcium oxide. This process is known as calcination. The production of calcium oxide from limestone is one of the traditional chemical transformations [1]. Lime has various properties, which made it very useful. Today, lime is produced industrially on a vast scale. The most important role of lime is in steel production. Lime is also an important material in the manufacture of chemicals besides used as stack gas to remove sulfur dioxide from power plants.

Malaysia is one of the biggest producer of rubber in South East Asia. Rubber is one of the most important plantation crops in Malaysia. The biomass from rubber tree has widespread applications in almost all sectors of the wood products manufacturing sector. Despite its abundance, the exploitation of rubberwood biomass such as oil palm, risk husk, cocoa, sugarcane, coconut and other wood residues [2]. Rubber Wood Sawdust (RWS) the potential feedstock for biochar production by pyrolysis.

Pyrolysis is considered to be an emerging technology for liquid oil production among these three methods in thermochemical. Pyrolysis is a thermal degradation of biomass under moderate temperature in the absence of oxygen [3]. Pyrolysis products consist of bio-oil (condensable gas), synthetic gas (non-condensable gas), and char [4].

Activated carbon has been in use for many thousands of years. The Egyptians started to use activated carbon for medical purposes and as purifying agent around 1500 B.C. The Hindus also filtered their drinking water through charcoal.

In this study, it is expected to combine both char from palm kernel shell and calcium carbonate to form calcium oxide and utilize the carbon production.

1.2 Problem Statement

In this study, it is expected to find a new alternative by using both of the calcination and pyrolysis to form calcium oxide, together with a higher value of carbon. The new replacement is expected to lower the cost, as the usage of limestone in calcination will be reduced. This study also emphasizes the properties of the calcium oxide and carbon values in calcination reaction products.

1.3 Objectives

The primary goal of this project is:

i. To study the textural properties of RWS biochar formed from pyrolysis
ii. To study the textural properties of RWS biochar formed from the combination process of pyrolysis and calcination
iii. To measure the carbon dioxide released from calcination of calcium carbonate at different temperatures
iv. To study the pattern of carbon dioxide released from calcination of calcium carbonate at different temperatures

1.4 Scope of Study

This project mainly focuses on synthesizing the products of pyrolysis that is biochar to make it became activated char. Both of the biochar and calcium carbonate will be placed in an activator to activate the biochar. The morphology of the activated char will be analyzed.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Calcination of Calcium Carbonate

Calcium carbonate ($CaCO_3$) or its commercial name, limestone is one of the man's oldest and vital chemicals. Generally, limestone can be found in rock formation throughout the world. Calcium oxide (CaO) or quicklime and carbon dioxide (CO_2) is produced from the calcination reaction of calcium carbonate. The chemistry of the calcination process is simple, represented by the net reversible reaction [1]:

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g) \qquad \Delta H > 0$$

Calcination is generally defined as decomposition of a substance through heating of limestone to a high temperature ranging between 780^{o}C to 1340^{o}C [5] to convert calcium carbonate to calcium oxide and carbon dioxide. The calcination reaction is a highly endothermic reaction [5]. Based on the equation above, the reaction is favored by higher temperature. The reaction will proceed only if the partial pressure of CO_2 in the gas above the solid surface is less than the decomposition pressure of the $CaCO_3$ [6]. Calcination reaction is mainly used in industries such as cement industry and chemical industry. The reaction is relatively inexpensive, and both of the quicklime and limestones are abundant [1].

The product from calcination that is calcium oxide is a white crystalline solid with a melting point of 2572^{o}C. The production of calcium oxide from limestone is one of the oldest chemical transformations produced by man [1].

The traditional uses of lime utilize its ability to react with carbon dioxide to regenerate calcium carbonate. In construction industries, lime is mixed with water and sand and creates mortar, which is used to secure bricks, blocks, and stones together. The most famous modern use of lime also relies on its ability to form solutions with silicates. Nearly 45% of lime is used in the steel industry [1].

Based on the article “Chemical of the Week – Lime,” lime is also an important material in the manufacture of chemicals. Its principal use here is in the production of calcium carbide, CaC_2 by heating lime with coke.

$$2CaO(s) + 5C(s) \rightarrow 2\ CaC_2(s) + CO\ (g) \qquad (1)$$

After that, calcium carbide reacts with water, releasing acetylene, C_2H_2

$$CaC_2\ (s) + 2H_2O(l) \rightarrow C_2H_2\ (g) + Ca(OH)_2\ (aq) \qquad (2)$$

Acetylene is an important fuel for welding and is also a starting material for a range of organic compounds, including vinyl chloride, neoprene, and acrylonitrile, all of which are raw materials for polymers.

Lime also plays a significant role pollution control. To reduce sulfur dioxide emissions from power plants, lime is used in stack gas scrubbers. Sulfur dioxide reacts with lime to form solid calcium sulfite.

$$SO_2(g) + CaO(s) \rightarrow CaSO_3(s) \qquad (3)$$

Lime is also added to sewage to remove phosphates. It is also used in the pretreatment of water supplies. In this process, lime is used to decrease the acidity, to soften, and to clear drinking water.

There are many more other industrial processes make use of lime. Lime also is used as an opacifier in plastics. Lime is highly alkaline, so the paper industry uses it in pulping wood; because, it dissolves the lignin that binds the fibers together in wood. In the refining of sugar, lime causes coagulation of plant material, allowing it to be more easily separated from the sugar syrup [1].

2.2 Pyrolysis of Rubber Wood Sawdust (RWS)

Rubber-wood is one of the main plantation crops in South East Asia with an estimated plantation area of 1.82 million hectare in Malaysia, which accounts for 20% of global plantations. The rubber trees are cut after their latex yielding period of around 25 years and the wood could be utilized for many downstream processes [7]. Rubber Wood Sawdust (RWS) is one of such abundant agricultural wastes, which has extensive of uses.

Figure 2.1 Rubber Wood Sawdust (RWS)

Pyrolysis is thermal degradation with a limited supply or completely without the oxidizing agent, which the gasification does not occur. Normally, in pyrolysis the temperature used is relatively low, about 400°C to 800°C. The products of pyrolysis usually exist in three forms, gas, pyrolysis oil and char [8]. The maximum amount of biochar production is at a temperature range of 400°C to 500°C. The relative proportions of which depend very much on the pyrolysis method, the characteristics of the biomass and the reaction parameters.

One of the advantages of pyrolysis is that the byproducts are reusable. The solid char and pyrolysis oil can be used as a fuel, and the gas can be recycled back to the process for chemical feedstock.

2.3 Activated Carbon

Activated carbon is a solid, porous, carbonaceous material prepared by carbonizing and activating organic substances [9]. Activated carbon is a generic term for a family of highly porous carbonaceous materials, none of which can be characterized by a structural formula or by chemical analysis [10].

There are many uses of activated carbon such as in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air [11] and many other applications. Some others application of activated carbon are:

i. ‘Tar’ filtration from smoking herbs
ii. Metal finishing field
    a. Purification of electroplating solutions
iii. Environment – removing pollutant from air or water
iv. Medical - treat poisonings and overdoses following oral ingestion

The general preparation of activated carbon is by either physical reactivation or chemical reactivation. The physical reactivation process precursor is developed into activated carbons using gases. This is generally done by using one or a combination of the carbonization and activation or oxidation processes. In carbonization process the material heating of the source material-as lumps or pre-sized material, or in molded form – in an inert atmosphere such as flue gas to a temperature that must not exceed 700°C so that dehydration and devolatilization of many of the carbon atoms can occur in a controlled manner [12]. In activation/Oxidation process the raw material or carbonized material is exposed to oxidizing atmospheres (carbon monoxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range of 600–1200 °C [11].

On the other hand, in chemical activation process the raw material can be impregnated with certain chemicals before carbonization. The chemical needs to be typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, zinc chloride, respectively). After impregnation, the raw material needs to be carbonized at lower temperatures (450–900 °C). It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material [11].

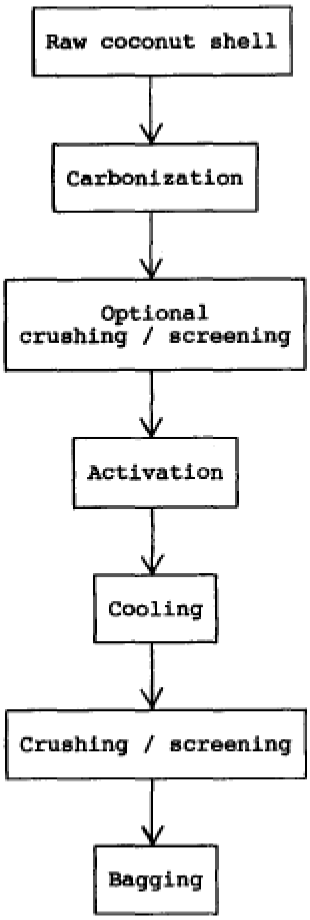

Figure 2.2 Flowsheet for the manufacture of activated carbon from coconut-shell char [12, 13]

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Materials

3.1.1 Calcium Carbonate Powder

Calcium carbonate laboratory standard powder with 600 mesh was obtained from the supplier. Before starting any experiment, the powder is dried in the oven at 110^{o}C for 30 minutes to ensure that there are no moisture present.

3.1.2 Rubber Wood Sawdust (RWS) Bio-Char

Rubber wood sawdust (RWS) bio-char was obtained from Centre for Biofuel and Biochemical Research (CBBR), Universiti Teknologi PETRONAS. The RWS was pyrolyzed using a fixed bed drop type pyrolyzer at 500^{o}C. The duration of the experiment was approximately 10 minutes.

3.2 Experiment Methodology

3.2.1 Carbon Dioxide Capture from Calcination of Calcium Carbonate

Calcination of calcium carbonate, $CaCO_3$ is carried out in a tube furnace at a desired temperature (600, 700, 800^{o}C) where the calcination reaction is favored. 10 grams of calcium carbonate powder in cubicle is weight and placed inside the tube furnace. The outlet plastic tube from the tube furnace was submerged in water inside a conical flask. Before the experiment begins, the weight of flask containing water is measured by using the mass balance and recorded. The calcination time is 3 hours. After that, the final weight of the flask is recorded. The difference of weight of the flask is determined. Lastly, the graph of Carbon Intensity and Temperature is plotted by using the data collected.

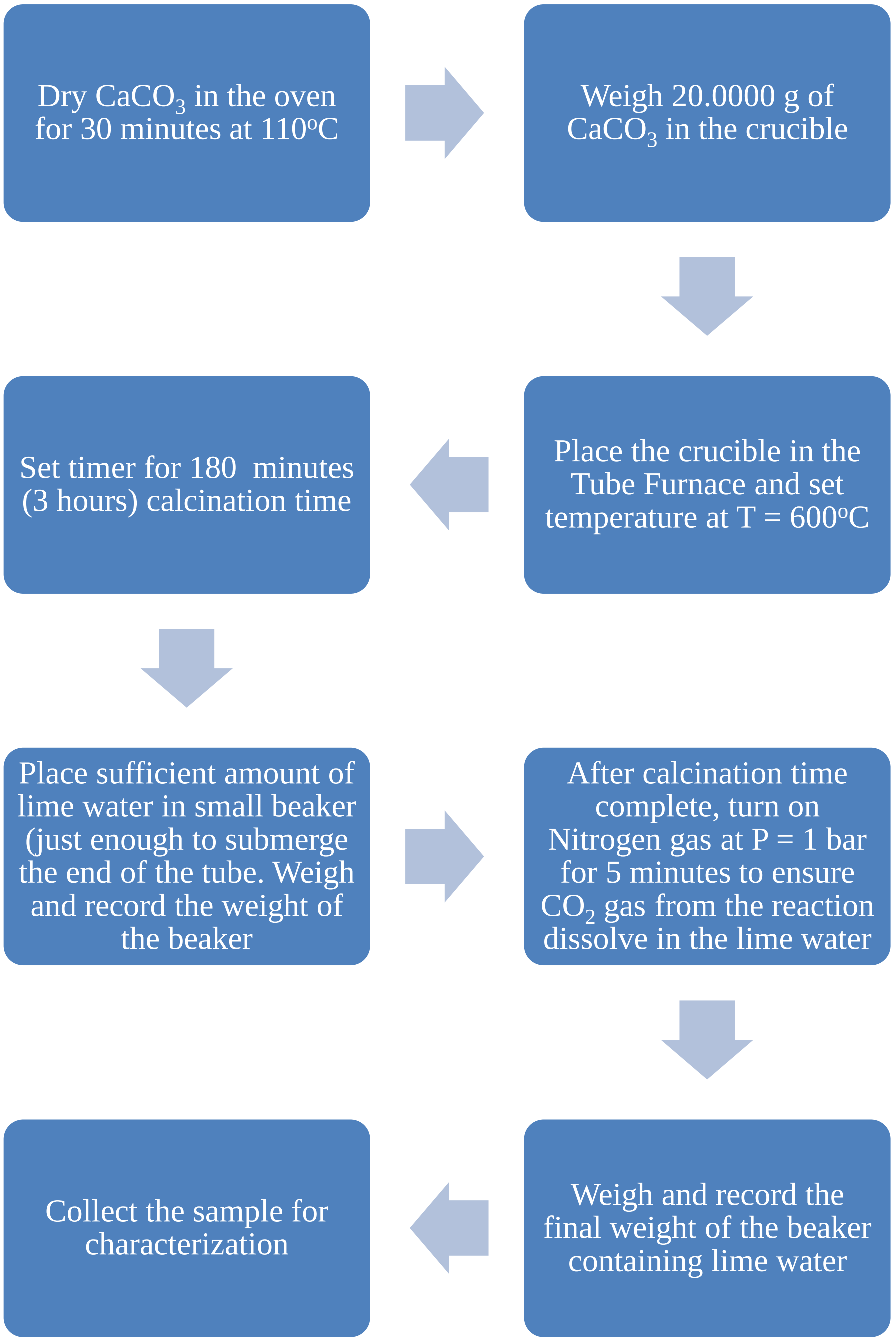

Figure 3.1 Flowchart for Carbon Dioxide Capture from Calcination of Calcium Carbonate

3.2.2 Rubber Wood Sawdust (RWS) Bio-Char Activation

In char activation process, both of the feedstock which are RWS bio-char from pyrolysis and calcium carbonate will be placed in the activator. The temperature of the tube furnace will be set at the desired temperature (600, 700, 800°C). The carbon dioxide gas released from the calcination of calcium carbonate will simultaneously activate the RWS biochar.

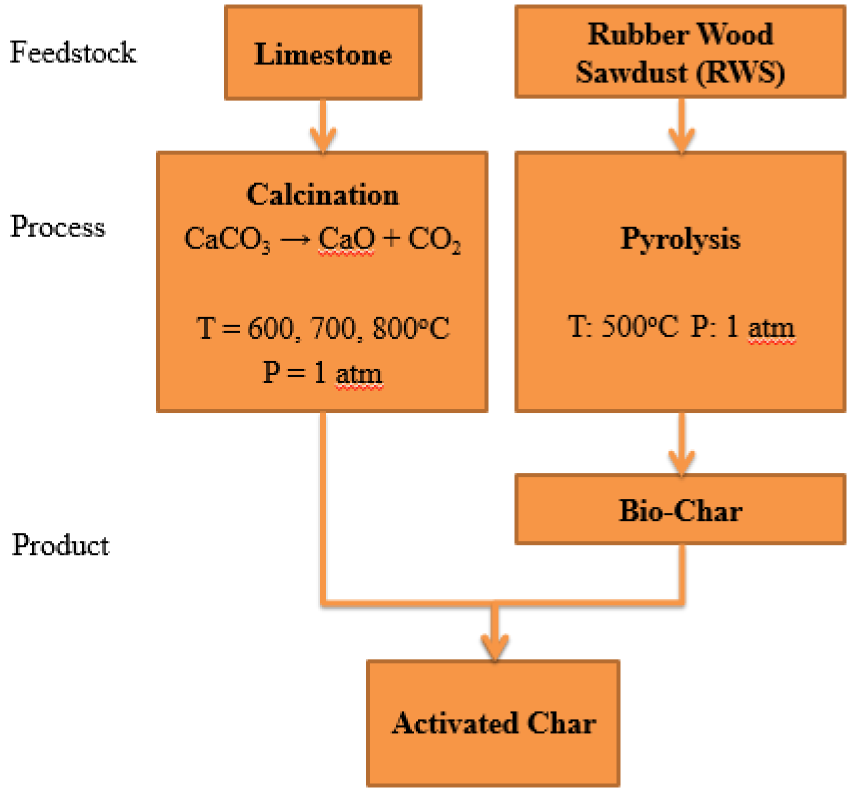

Figure 3.2 Flow Chart for Char Activation

3.2.4 Making Lime Water Solution

10 grams of $Ca(OH)_2$ is dissolved in 500 mL of distilled water. The solution is left for 24 hours. Lime water is a saturated solution. Therefore, there will be extra solute which is calcium hydroxide powder will not dissolve. After that, the solution is pour over a filter paper to get the clear solution, which is the lime water. The limewater is stored in a bottle to avoid the CO_2 from the air to dissolve in it.

3.3 Experiment Analysis

3.3.1 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) measures weight changes in the sample as the function of temperature or time under controlled atmosphere. The principal uses is to measure the thermal stability and composition of the sample.

TGA equipment, Perkin Elmer Model PYRIS 1 is used in this TGA analysis. Thermal characteristics of the powder is analyzed using a computerized TGA. The experiments is carried out with the following conditions; about 5 mg of sample us heated at a rate of 5^{o}C/min from 30-800^{o}C. Oxygen-free nitrogen gas is used as the carrier.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) is the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission.

FTIR equipment used in this project is Shidmadzu brand, model: 8400S. The following shows the table of characteristic of IR absorptions.

frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Figure 3.3 Characteristic of IR absorptions

3.3.3 Scanning Electron Microscopy (SEM) Analysis

The purpose of running Scanning Electron Microscopy (SEM) in this study is to investigate the surface morphology of the calcium carbonate, calcium oxide and activated char samples. SEM is useful for giving a three-dimensional image of the surface of the sample. The SEM scans the focused electron beams over the surface of the sample and then produce signals that can be used to obtain information about the surface topography and composition.

The sample preparation will be carried out in an inert atmosphere chamber to avoid the hydration of the calcium oxide. The samples will be put on top of a resin sample holder, embedded in a drop of epoxy-resin. Then, left overnight, introduced in liquid nitrogen and then fractured to obtain a fresh surface in which well-preserved particle cross-sections could be observed. The samples will be cleaned with air to avoid the possible water condensation at the surface and then introduced into a desiccator. A cut must be made to the sample holder in a direction crossing the hardened resin drop (but not reaching it) ensured that the fracture affected the region containing the sample. The backscattered electron signal provided sufficient phase contrast between sample and resin for the recognition and image processing of particle cross-sections [14].

3.4 Key Milestones

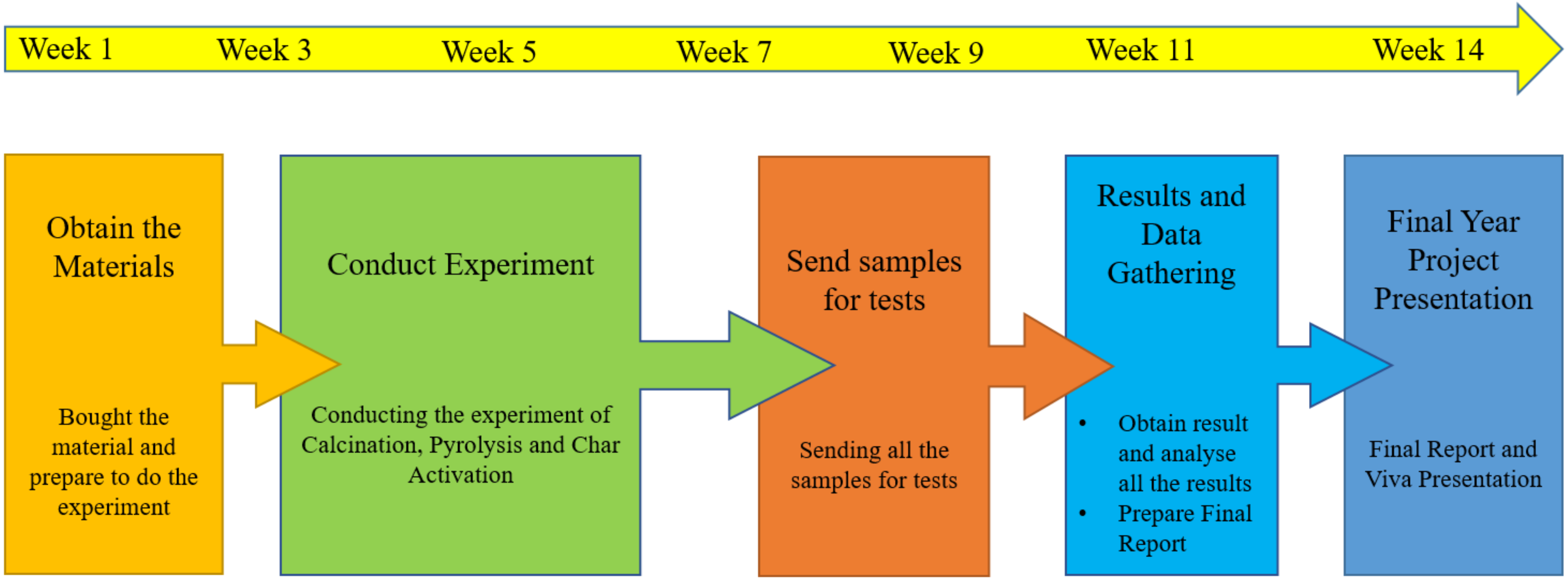

Figure 3.3 Project Key Milestones

3.5 Gantt-Chart

Table 3.1 Project Gantt Chart

Activities	FYP 1														FYP 2													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Project Topic Selection	🟦																											
Research Work		🟦	🟦	🟦	🟦	🟦																						
Extended Proposal Submission							🟦	🟦																				
Proposal Defence									🟦																			
Buy Material										🟦	🟦																	
Interim Draft Report Submission												🟦																
Tube Furnace Training													🟦	🟦														
Conduct Calcination														🟦	🟦	🟦	🟦	🟦										
Conduct Pyrolysis														🟦	🟦	🟦	🟦	🟦										
Conduct Char Activation Experiment																	🟦	🟦	🟦	🟦	🟦	🟦	🟦					
Analysis of the Products																						🟦	🟦	🟦	🟦			
Data Gathering and Analysis																						🟦	🟦					
Writing Report																								🟦	🟦	🟦	🟦	
Softbound Submission																										🟦		
Project Presentation (17th Dec 2015)																											🟦	
Hardbound Submission (12th Jan 2016)																												🟦

CHAPTER 4

RESULT AND DISCUSSION

4.1 Calcination of Calcium Carbonate

Before the experiment was conducted, the $CaCO_3$ powder was sent to TGA analysis. The following is the graph obtained from TGA analysis.

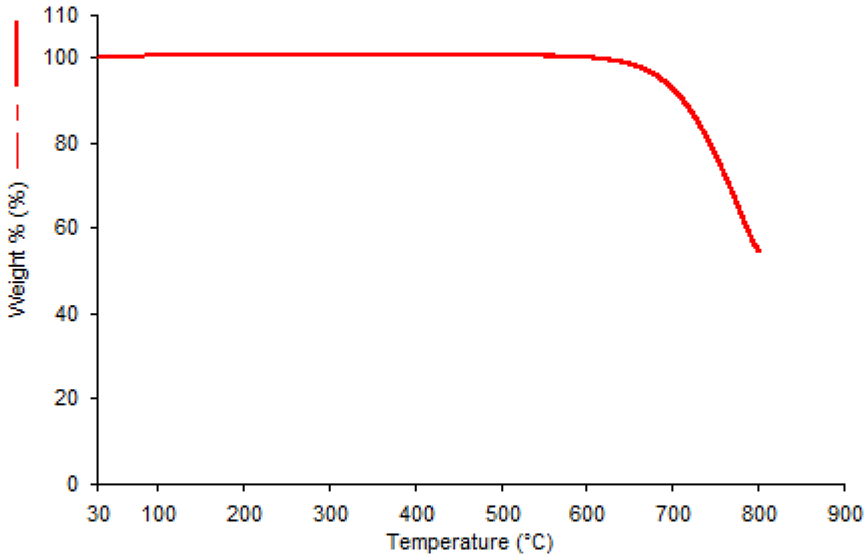

Figure 4.1 TGA Analysis for the standard sample of Calcium Carbonate

The graph shows that the weight loss starting from 600 degree Celsius. This explains that the suitable calcination temperature for calcium carbonate is starting from 600 degree Celcius.

The experiment was conducted in a tube furnace with temperature of 600, 700 and 800°C.

Figure 4.2 Experiment for Calcination at 600° C

The CO_2 released from the reaction was captured at the end of the outlet tube of the tube furnace.

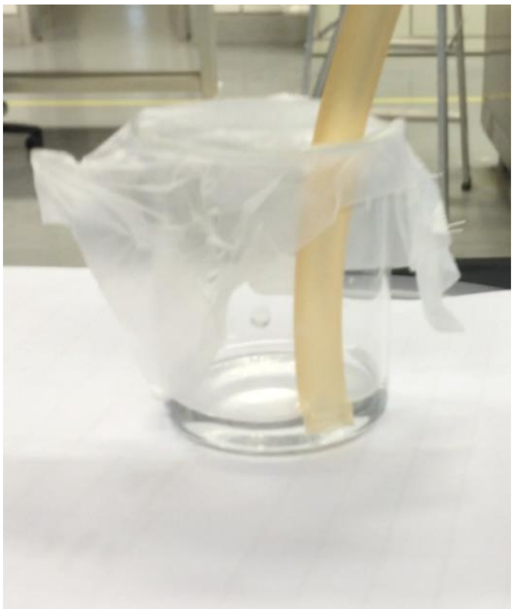

Figure 4.3 Capturing Carbon Dioxide from the reaction

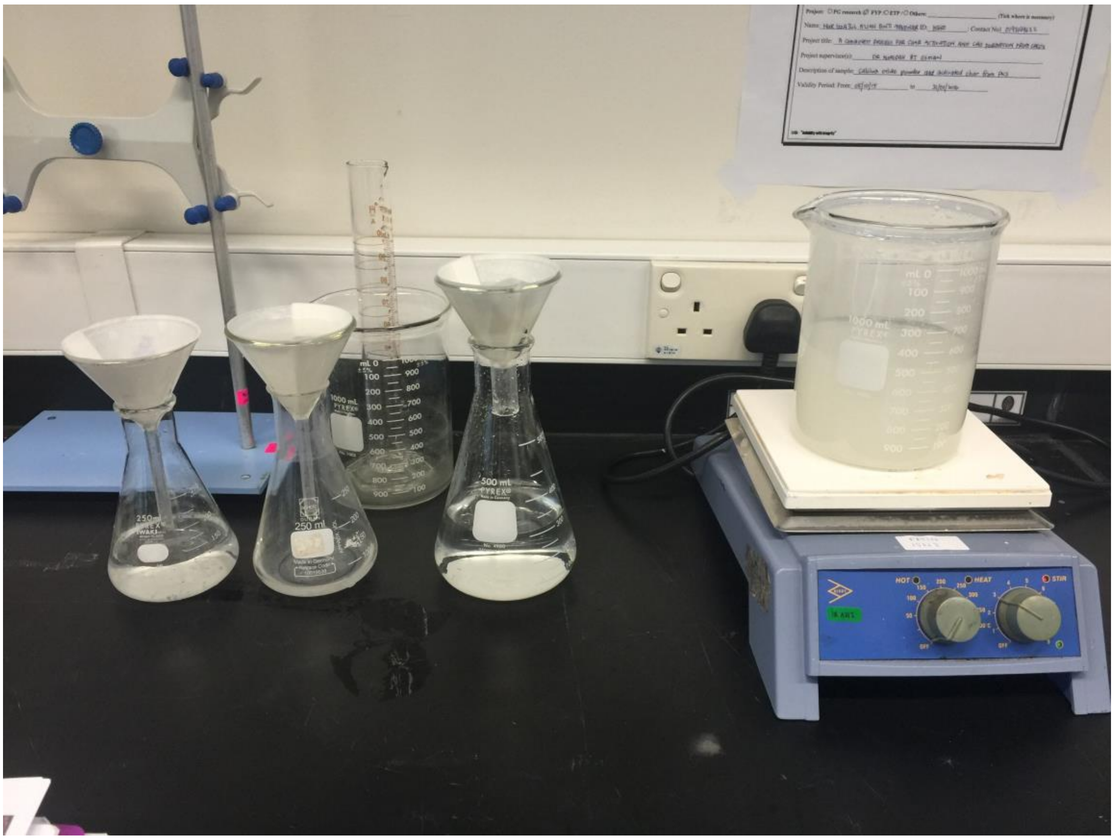

Figure 4.4   Filtration of Calcium Hydroxide solution to produce Limewater

Mass of Calcium Carbonate: **20.00 g**

Table 4.1 Data recorded from calcination experiment

Temperature (°C)	**Initial Mass (g)**	**Final Mass (g)**	**Total Change of Mass (g)**
600	45.1439	45.0281	0.1158
700	42.2891	41.9269	0.3622
800	44.1489	43.6457	0.5032

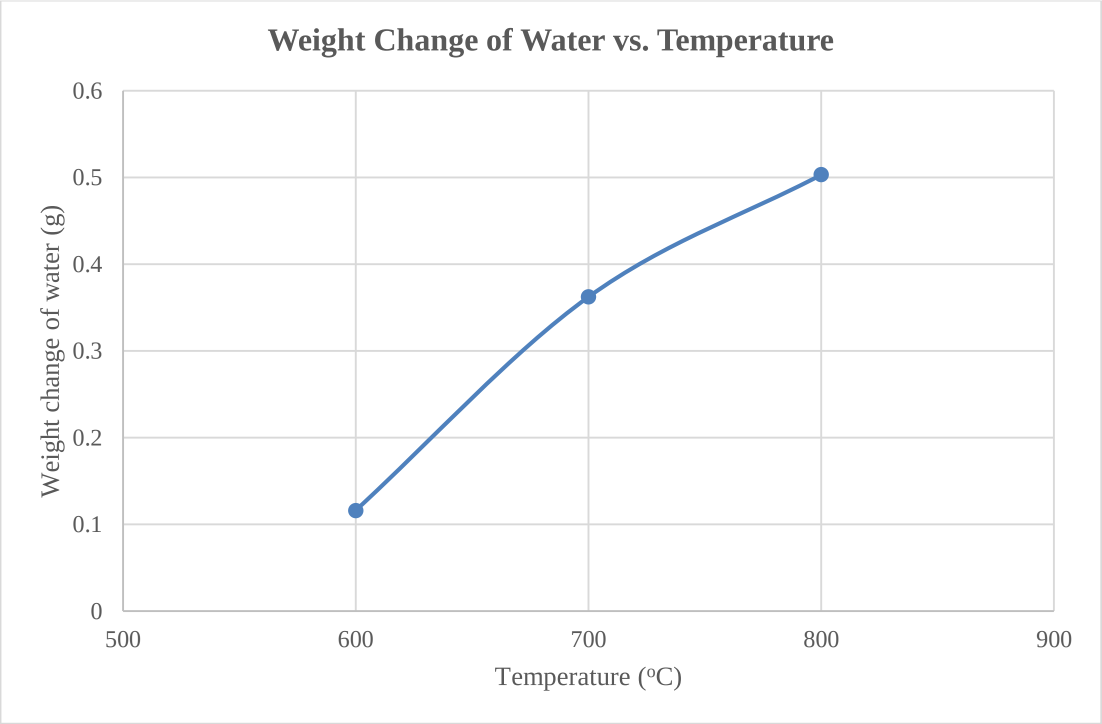

Figure 4.5 Graph of weight change of water vs. temperature

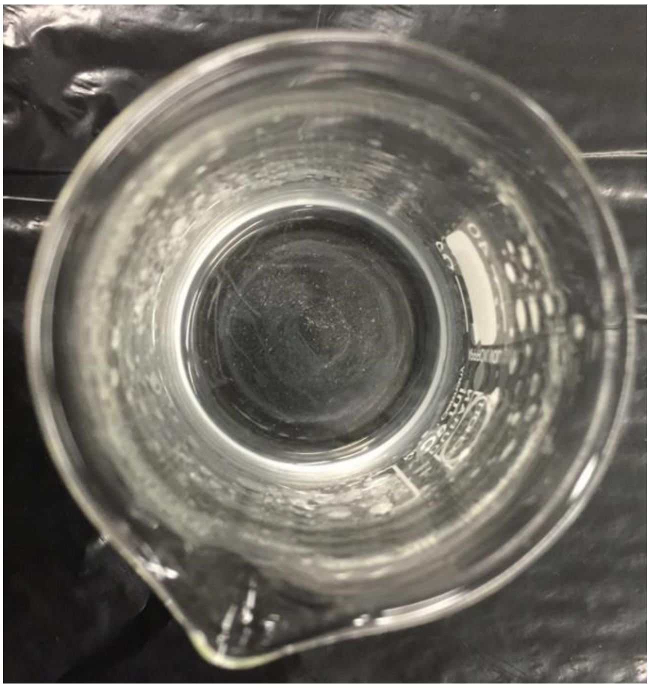

Figure 4.6 Limewater after calcination at 600 degree Celcius

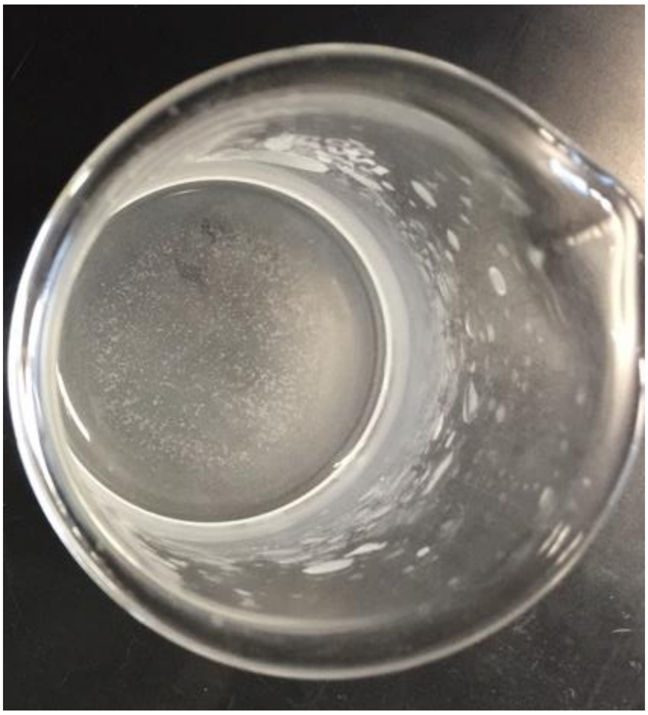

Figure 4.7 Limewater after calcination at 700 degree Celcius

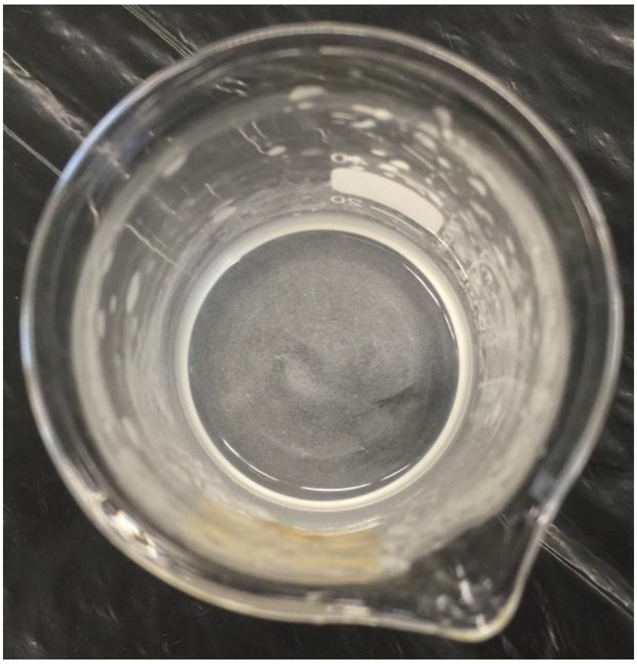

Figure 4.8 Limewater after calcination at 800 degree Celcius

From the figures above, the graph shows increasing trend of weight loss as the temperature increases from 600 to 800 degree Celsius. This is because of the higher the temperature, the cloudier the lime water, more CO_2 present.

4.2 Rubber Wood Sawdust (RWS) Activation

The RWS biochar were calcined together with calcium carbonate at desired temperature (600, 700, 800^{o}C). The after product of biochar were sent to FTIR and SEM analysis.

4.2.1 FTIR Analysis

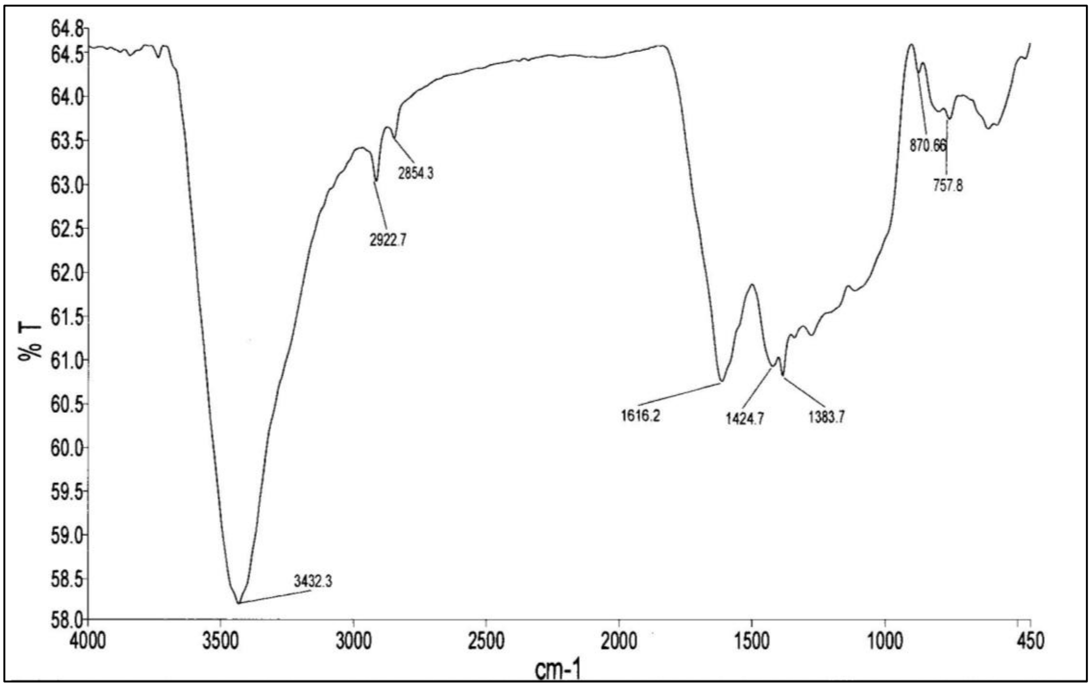

Figure 4.9 RWS biochar before calcined with $CaCO_3$

Table 4.2 Functional group present at each peak

Frequency (cm^{-1})	Bond	Functional Group	%T
3432.3	O–H stretch, H–bonded	alcohols, phenols	58.3
2922.7	O–H stretch, C-H stretch	carboxylic acids, alkanes	63.0
2854.3	C-H stretch	alkanes	63.5
1616.2	C=C stretch	α,β-unsaturated ketone	60.8
1424.7	C-H bending	alkane	61.0
1383.7	C-H bending	aldehyde	60.9
870.66	C-H bending	1,4-disubstituted or 1,2,3,4-tetrasubstituted	64.3

From the table above, it can be seen that the functional group present are mostly O-H, C-H, H and C=C at the raw RWS bio char.

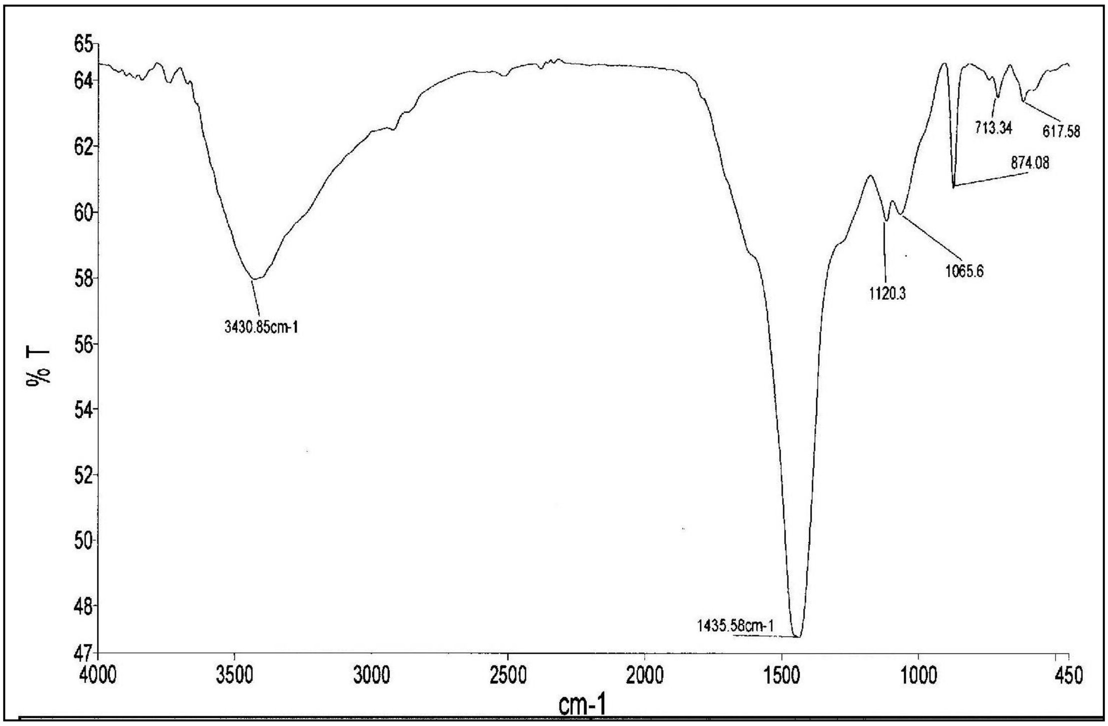

Figure 4.10 RWS Activated Char at 600°C

Table 4.3 Functional group present at each peak at 600 °C

Frequency (cm^{-1})	**Bond**	**Functional Group**	**%T**
3430..85	O–H stretch, H–bonded	alcohols, phenols	57.8
1435.58	C-C stretch	aromatics	47.5
1120.3	C-O stretch	Secondary alcohol	60.2
1065.6	C-O stretch	Primary alcohol	60.5
874.08	C-H bending	1,4-disubstituted or 1,2,3,4-tetrasubstituted	60.8
713.34	C-H bending	1,3-disubstituted	64.0
617.58	-C≡C-H: C-H bending	alkynes	63.8

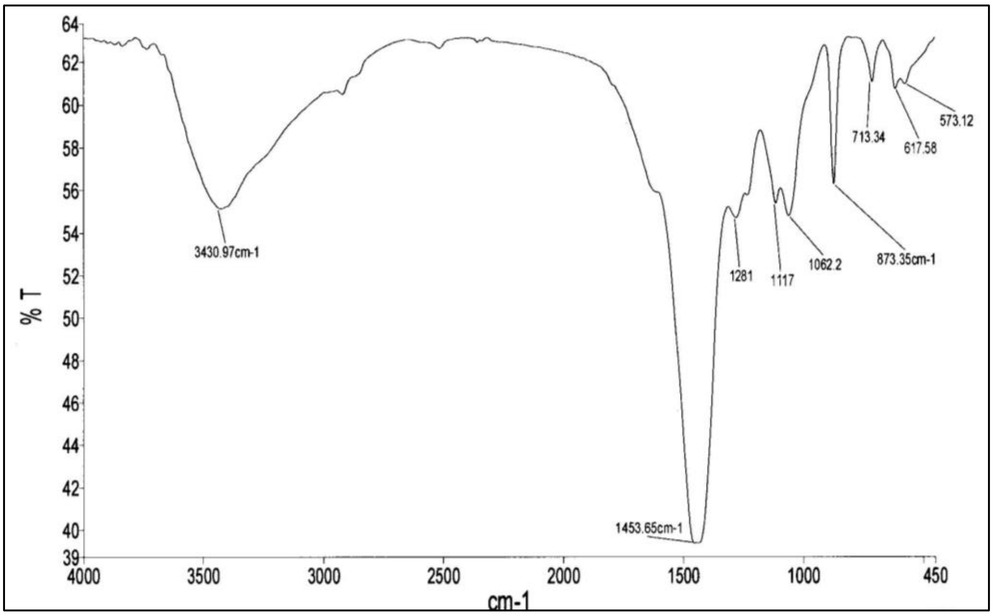

Figure 4.11 RWS Activated Char at 700^{o}C

Table 4.4 Functional group present at each peak at 700 ^{o}C

Frequency (cm^{-1})	**Bond**	**Functional Group**	**%T**
3430.97	O–H stretch, H–bonded	alcohols, phenols	55.0
1453.65	C-H stretch	alkanes	39.5
1281.0	C-O stretch	Aromatic ester	55.6
1117.0	C-O stretch	Primary alcohol	56.4
1062.2	C-O stretch	Secondary alcohol	56.2

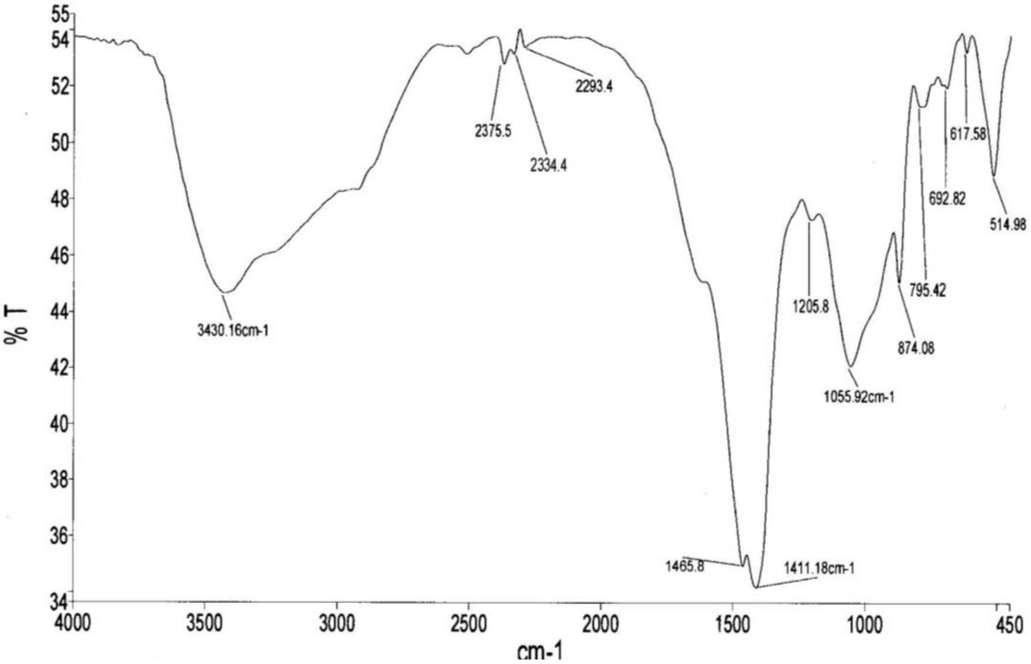

Figure 4.12 RWS Activated Char at 800^{o}C

Table 4.5 Functional group present at each peak at 800 ^{o}C

Frequency (cm^{-1})	**Bond**	**Functional Group**	**%T**
3430.16	O–H stretch, H–bonded	alcohols, phenols	44.8
2375.5	O=C=O stretch	Carbon dioxide	53.0
2334.4	O=C=O stretch	Carbon dioxide	53.5
2293.4	O=C=O stretch	Carbon dioxide	54.0
1465.8	C-H bending	alkane	35.0
1411.18	O-H bending	alcohol	34.2

From the FTIR analysis it can be seen that O–H stretch, H–bonded percentage of transmission decreases as the calcination temperature increases compared to the raw RWS biochar. From table 4.5, there are carbon dioxide functional group present at calcination temperature of 800^{o}C.

4.2.2 SEM Analysis

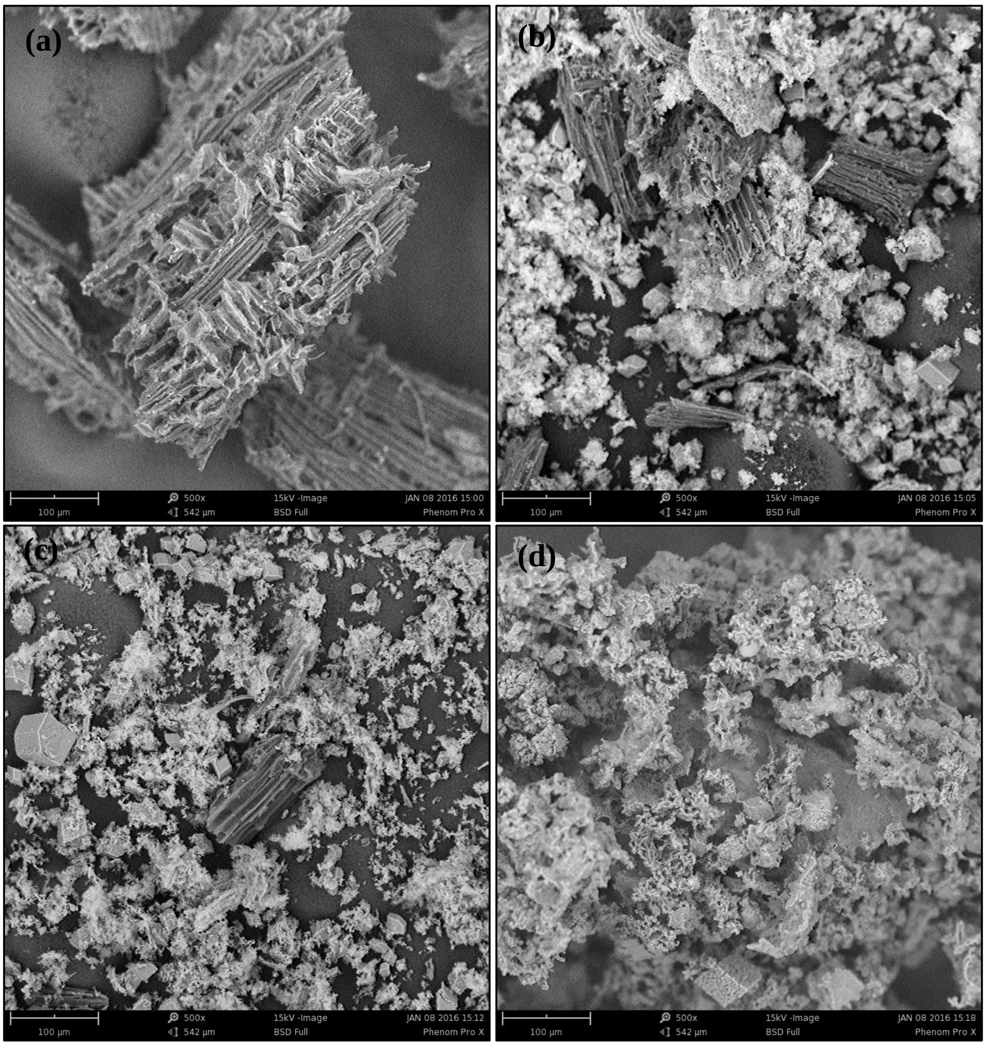

Figure 4.13 SEM Image produced (a) Bio-char before activated, (b) Activated Char at 600^{o}C, (c) Activated Char at 700^{o}C, and (d) Activated Char at 800^{o}C

Figure 4.13 exhibit the morphology comparison of the feedstock (RWS biochar before calcined) with the product generated after the RWS biochar being activated with calcination of calcium carbonate at 600, 700 and 800^{o}C. In this analysis, the composition of the samples were determined. Focusing closely through the SEM instrument at 100µm magnifications, the particle size of the RWS chars decreased as the temperature of calcination increased when compared to their raw feedstock, as shown in Figure 4.13 accordingly. Under extensive heating from the calcination reaction, the biomass particles undergo breaking and shrinking processes to form charred material.

4.2.3 Energy Dispersive X-ray Spectroscopy (EDS)

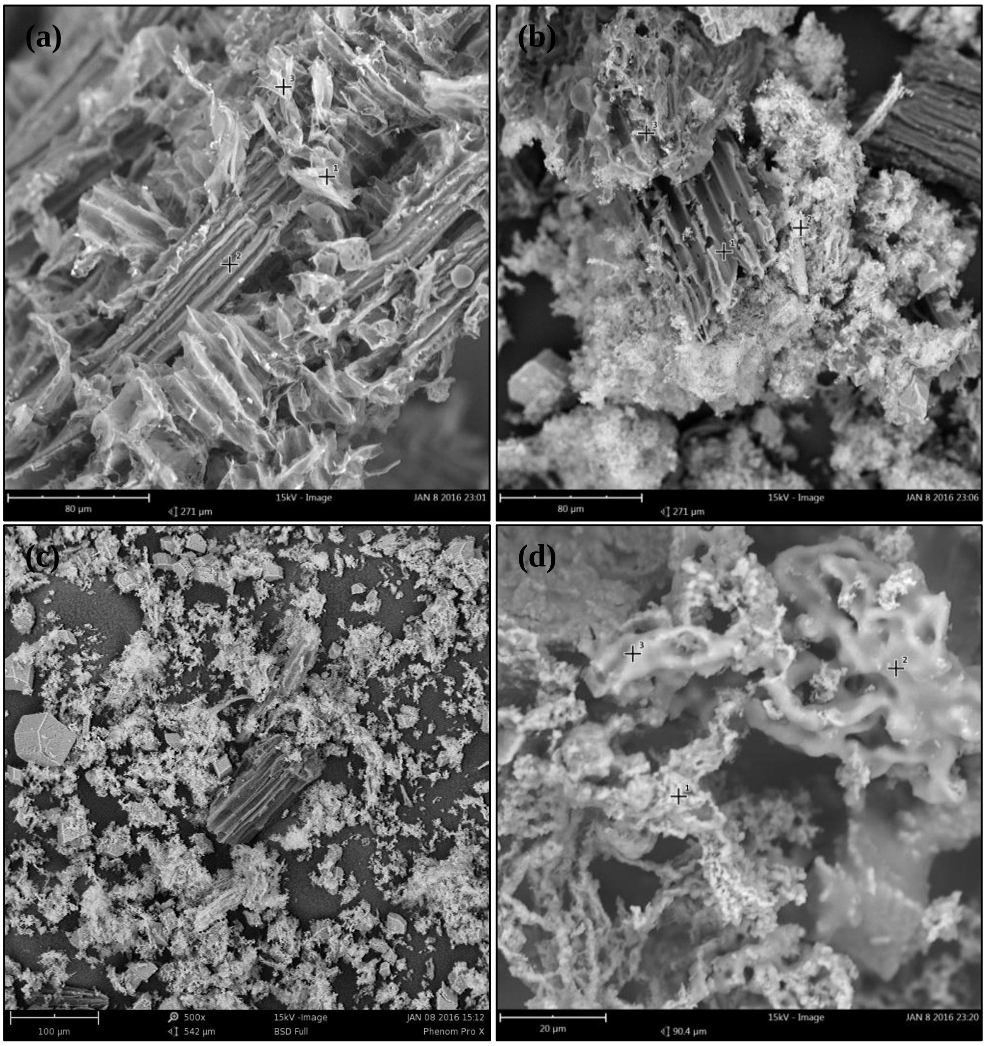

Figure 4.14 SEM Image produced and spots for EDS (a) Bio-char before activated, (b) Activated Char at 600°C, (c) Activated Char at 700°C, and (d) Activated Char at 800°C

Table 4.6 Presence of Carbon at respective spots and temperature

Composition	**Carbon**			
Temperature/Spot	**1**	**2**	**3**	**Average**
Standard	27.6	29.4	28.8	28.6
600	25.6	11.4	27.9	21.6
700	27.1	12.6	13.2	17.6
800	10.7	14.4	16.8	14.0

Table 4.7 Presence of Nitrogen at respective spots and temperature

Composition	**Nitrogen**			
Temperature/Spot	**1**	**2**	**3**	**Average**
Standard	60.1	61.9	57.1	59.7
600	53.4	15.3	53.4	40.7
700	53.1	16.0	13.3	27.5
800	12.9	17.0	17.9	16.0

Table 4.8 Presence of Nitrogen at respective spots and temperature

Composition	**Oxygen**			
Temperature/Spot	**1**	**2**	**3**	**Average**
Standard	12.3	8.7	14.1	35.1
600	21.0	73.3	18.8	37.7
700	19.8	71.4	73.5	54.9
800	76.4	68.6	65.2	70.1

From Table 4.6 and 4.7 it can be seen that the carbon and nitrogen weight concentration decreases as the temperature increases. On the other hand, the oxygen weight concentration increases as the calcination temperature increases.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

It is expected that this project could combine both of calcination of calcium carbonate and biochar from pyrolysis of palm kernel shell to produce calcium oxide with higher carbon content. This project is expected to analyze the morphology of the calcium oxide and biochar after the char activation.

From carbon dioxide capture experiment, the higher temperature of calcination, the higher carbon dioxide released. It is expected that calcination of calcium carbonate can activate biochar from pyrolysis of palm kernel shell. The experiment will be continued by doing the activation of biochar.

From the char activation experiment, there are carbon dioxide functional group present at calcination temperature of $800^{o}C$ as shown by FTIR analysis. From the SEM images generated, the particle size of the RWS chars decreased as the temperature of calcination increased when compared to their raw feedstock. This is because under extensive heating from the calcination reaction, the biomass particles undergo breaking and shrinking processes to form charred material. The decreasing of carbon and nitrogen weight concentration decreases as the temperature increases also can be observed. On the other hand, the oxygen weight concentration increases as the calcination temperature increases.

However, from the experiment, the surface area of the pores was not determined because of the unavailability of equipment and time constrain. It can be concluded that this project's objectives were achieved.

5.2 Recommendations

Although this research was carefully prepared, there are some limitations. First of all, the research for carbon dioxide released from calcination of calcium carbonate was a try and error experiments. This experiment took the longest time to complete as each run took 180 minutes to complete. Besides that, the carbon dioxide produced was too little to capture by the lime water. The author need to figure out some other ways to push out the gas out of the tube furnace by using nitrogen gas.

Furthermore, the unavailability of the equipment in the university also became of the limitation. There are many students doing research in the university and the number of equipment of analysis was not enough to cater all the students. There are some analysis equipment in maintenance and cannot be used.

Based on the observation made during this study, a few recommendations can be suggested for future work in this area.

1. Use carbon dioxide meter instead of bubbling the gas in lime water. By using a carbon dioxide meter, the exact amount of carbon dioxide can be detected. With lime water there are disturbance which is the carbon dioxide from the surrounding air can dissolve in the lime water.

2. Increase the parameter of interest in carbon dioxide capture. Some of other parameters, such as pH value of lime water before and after calcination should be taken into account for more accurate conclusion to be drawn, as well as the value of turbidity of lime water in Nephelometric Turbidity Unit (NTU).

3. Make more analysis. Analysis such as Brunauer-Emmett-Teller (BET) Surface Area Analysis which can measure the specific surface area of a material, and X-Ray Diffraction (XRD) Analysis to identify the various crystalline formed and also known as phase on the samples.

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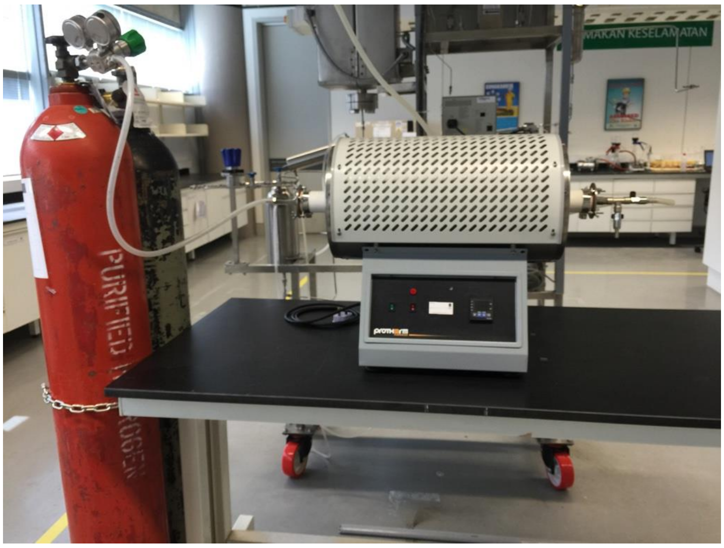
APPENDICES

Appendix 1: Pyrolyzer for PKS Pyrolysis

Appendix 2: Tube Furnace for Char Activation



Appendix 3: Material Data Sheet for Calcium Carbonate

Health	2
Fire	0
Reactivity	0
Personal Protection	E

Material Safety Data Sheet
Calcium carbonate MSDS

Section 1: Chemical Product and Company Identification

Product Name: Calcium carbonate

Catalog Codes: SLC1141, SLC4720, SLC4438, SLC1645

CAS#: 471-34-1

RTECS: FF9335000

TSCA: TSCA 8(b) inventory: Calcium carbonate

CI#: Not available.

Synonym:

Chemical Name: Calcium Carbonate

Chemical Formula: $CaCO_3$

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Calcium carbonate	471-34-1	100

Toxicological Data on Ingredients: Calcium carbonate: ORAL (LD50): Acute: 6450 mg/kg [Rat].

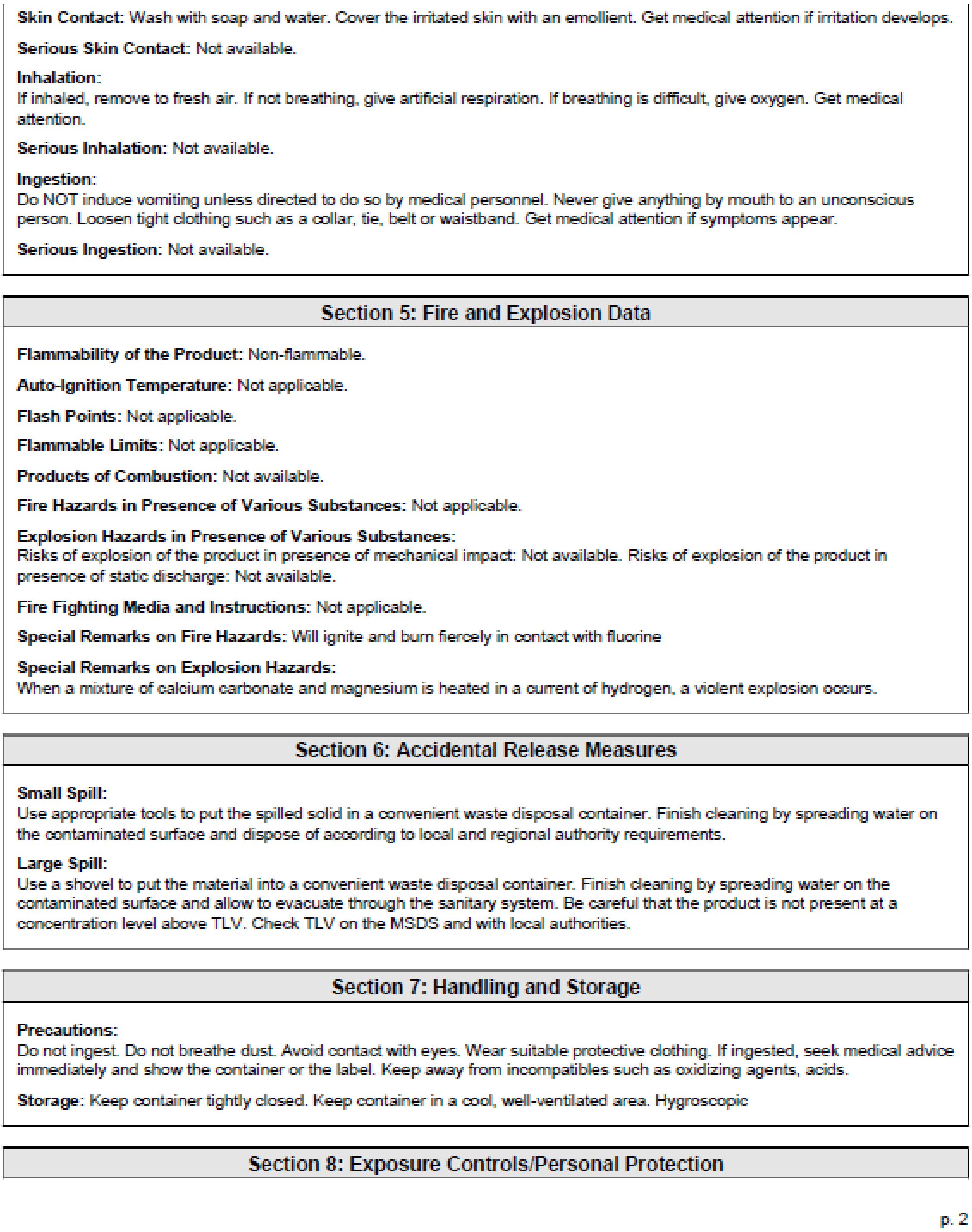
Section 3: Hazards Identification

Potential Acute Health Effects:
Hazardous in case of eye contact (irritant). Slightly hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to kidneys. Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. WARM water MUST be used. Get medical attention.



Skin Contact: Wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops.

Serious Skin Contact: Not available.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Not available.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Non-flammable.

Auto-Ignition Temperature: Not applicable.

Flash Points: Not applicable.

Flammable Limits: Not applicable.

Products of Combustion: Not available.

Fire Hazards in Presence of Various Substances: Not applicable.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions: Not applicable.

Special Remarks on Fire Hazards: Will ignite and burn fiercely in contact with fluorine

Special Remarks on Explosion Hazards:
When a mixture of calcium carbonate and magnesium is heated in a current of hydrogen, a violent explosion occurs.

Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:
Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:
Do not ingest. Do not breathe dust. Avoid contact with eyes. Wear suitable protective clothing. If ingested, seek medical advice immediately and show the container or the label. Keep away from incompatibles such as oxidizing agents, acids.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Hygroscopic

Section 8: Exposure Controls/Personal Protection

Incompatibility with various substances: Reactive with oxidizing agents, acids.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity:
Hygroscopic. Will ignite and burn fiercely in contact with fluorine. Incompatible with acids, alum, ammonium salts, mercury + hydrogen, aluminum and magnesium

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 6450 mg/kg [Rat].

Chronic Effects on Humans: May cause damage to the following organs: kidneys.

Other Toxic Effects on Humans: Slightly hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects: Skin: Causes skin irritation. Eyes: Dust causes eye irritation. Inhalation: Excessive inhalation causes respiratory tract and mucous membrane irritation. Low hazard for usual industrial handling. Ingestion: Ingestion of large amounts may cause gastrointestional tract disturbances with nausea and possibly constipation. Expected to be a low hazard for usual industrial handling. Chronic Potential Health Effects: Chronic ingestion may affect kidneys, and may cause hypercalcemia with alkalosis.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The product itself and its products of degradation are not toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations: TSCA 8(b) inventory: Calcium carbonate

Other Regulations: EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):
R36- Irritating to eyes. S2- Keep out of the reach of children. S46- If swallowed, seek medical advice immediately and show this container or label.

HMIS (U.S.A.):

Health Hazard: 2

Fire Hazard: 0

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 1

Flammability: 0

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

Created: 10/10/2005 08:15 PM

Last Updated: 05/21/2013 12:00 PM

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