Conceptual Production Plant of Calcium Chloride from Waste Cockle Shell.

By

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Dissertation submitted in partial fulfilment of the requirements for the
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CERTIFICATION OF APPROVAL

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APPROVED BY,

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BANDAR SERI ISKANDAR, PERAK

JAN 2015

CERTIFICATION OF ORIGINALITY

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.

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IBRAHIM FIKRI BIN MOHD SAID

ABSTRACT

Due to the environmental hazard that had been contributed from limestone mining activity to the surrounding area, waste cockle shell has been identified as a visible alternative for replacing limestone as source of calcium carbonate. Instead of escalating the potential risk of depleting of hills to excavate calcium carbonate, waste cockle shell is much more sustainable due to the annual production of the aquatic species that is recorded to be more than 40,000 metric ton per year. This study will focus on idea of conceptual production plant with a main objective to produce calcium chloride from waste cockle shell. Several designs are proposed with feasibility study conducted accordingly. To conclude, cockle shell is one of the best alternatives to limestone in producing calcium chloride. Cockle shell does not cause any environmental impact and it help to reduce solid waste produce from domestic waste, in particular cockle shell waste.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 Background

Anadara Granosa also known as blood cockle is a shellfish that could be found around muddy area specifically at mangrove swamp. It is quite famous among Malaysians because often they are used in local dishes. There are lots of shell waste produce by cockle, and research had been done on the composition of cockle shell. It is found that 98% of cockle shell is made up from calcium and researcher has begun to synthesize calcium from cockle shell for many purposes. In Malaysia cockle cultivation areas are numerous, especially on the west coast of the peninsular like Perak, Penang and Selangor. According to the annual fisheries statistic, Malaysia has been producing more than 40,000 metric tons of cockles every year for the past 5 years. The vast amounts of cockle produced suggested that there will be a huge amount of cockle shell discarded to the surroundings. This study will help to explore the possibilities to exploit waste cockle shell in producing calcium chloride, which is one of the most useful inorganic salts that have many uses and function. Some of the industries that required calcium chloride are oil and gas, construction and food industries. Calcium chloride normally being produced by three different process route which is through natural brine process, Solvay process and limestone-hydrochloric acid process. Both Solvay process and limestone-hydrochloric acid process need limestone as raw material to produce calcium chloride. Cockle shell has been identified as an alternative to replace limestone in calcium chloride production, and is chosen due to the high calcium content contained within.

1.2 Problem Statement

Traditionally, calcium chloride is produced from limestone where it is a preferred raw material due to its high composition of calcium carbonate. In order to obtain the supply and fulfill huge demand of calcium chloride, more limestone mining are done extensively until it has caused great impact to the environment. Therefore, limestone mining need to be reduced and other alternative methods are needed to be explored to provide the source of the raw material. Cockle shell has been identified as one of the alternative as it contain high amount of calcium and there are abundant amount of waste seashell produced.

In Malaysia cockle shell are recognized as good raw material source as there are tons of waste cockle shell could be found in the country. Most Malaysian consume cockle in their daily local dishes, where the shell are disposed as waste. By using waste cockle shell as main raw material, it could help to reduce domestic waste produce from cockle shell and at the same time help to replace limestone as raw material in producing calcium chloride. This indirectly will help to reduce limestone mining activity and save the environment.

1.3 Objective

The purpose of this study is to conceptually design a pilot plant for calcium chloride production by utilizing waste cockle shell as raw material. Feasibility study will be conducted based on the designed pilot plant for calcium chloride production. The production would fulfill a process with a better yield, an optimum energy requirement and high economic potential.

1.4 Scope of Study

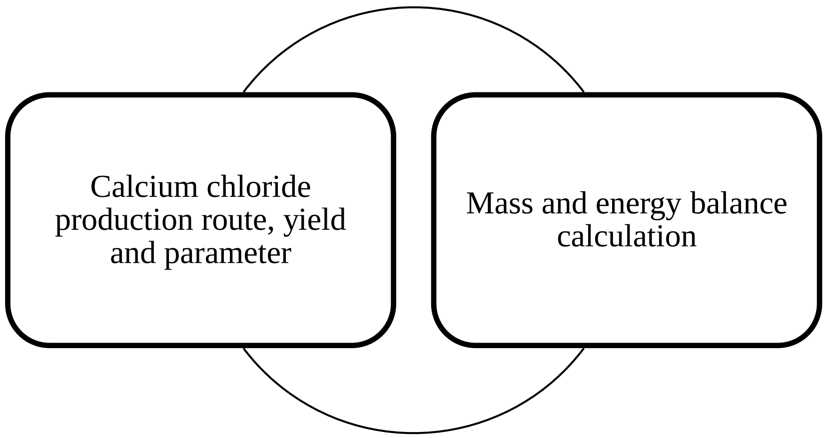

Figure 1: Scope of study

The scope of study for this project will cover on the calcium chloride production route, yield and parameter. This is because to design a pilot plant for calcium chloride production a study on existing process route must be known. Besides, the yield and the operating parameters must be investigated to ensure optimization in calcium chloride production could be achieved. In addition, mass and energy balance calculation must also be carried out to ensure the functional of the plant as well as to predict the optimum yield and cost effectiveness.

CHAPTER 2

LITERATURE REVIEW

2.1 Calcium carbonate

Limestone has been identified as one of the raw material with the highest content of calcium carbonate. According to the Ministry of Natural Resources and Environmental of Malaysia, from 2007 until 2010 the numbers of limestone production recorded are more than 32,000 metric tons each year. With the given statistic, the extensive limestone mining process has caused great environmental impact. Deforestation, soil erosion and pollution are some of the results of limestone mining activities, not to mention it could also disturb the equilibrium balance of an ecosystem. As reported by Ritchie (2004) the effect of limestone mining already could be seen around Kinta Valley area in Ipoh. By using cockle shell as an alternative, this can help to reduce limestone mining activities in the effort to obtain calcium carbonate which thus reduces environmental impact caused by the quarry mining activities. Furthermore, utilizing cockle shell would indirectly help to reduce shell waste discarded by the people that are resulted from the daily food consumption.

According to Barros et al. (2009) 95-99% of seashell contain calcium carbonate. This is further confirmed by Awang-Hazmi et al. (2007) who studied the composition of cockle shell obtained from three areas in Malaysia, which is Malacca, Kuala Selangor and Penang also obtained similar result. From the studies the authors found that the composition of calcium carbonate inside the cockle shell obtained from these three areas is up to 98%; that is later supported by Mohamed et al. (2012) in their findings. This proves that cockle shell is a good alternative to limestone in producing calcium chloride as far as calcium carbonate is concerned. The table below shows a comparison on cockle shell compositions obtain by the three researches.

TABLE 1: Comparison of cockle shell composition

Cockle shell composition	Barros, Bello et el.	Awang-Hazmi et el.	Mohamed, Yousuf et el.
Calcium Carbonate	95%	98%	98.99%
Sodium chloride	0.1%	0.9%	-
Silicon	0.1%	0.0183%	0.078%
Potassium Chloride	0.1%	0.03	-
Other	4.4%	0.7817%	0.422%

In other part of the world various kind of seashell had been used for many purposes. According to Barros et al. (2009), in United States mussels shell are used as soil conditioner while in Spain it has been used as animal feed additives and fertilizer. In Malaysia there are lots of suitable places that can be uses as cockle cultivation area, where most of them are located at mangrove swamp zone. Currently mangrove swamps in Malaysia that are used for these purposes are located at Kuala Selangor, Kuala Sepetang, Juru, Merbok, Muar and several other places. According to Malaysia Annual Fisheries Statistic, for the past five years Malaysia had managed to produce more than 40,000 metric tons of cockles. This proves that with large area of cultivation and vast amount of cockle production every year the sustainability of cockle is not an issue. Included below is table below that show production of cockle shell from year 2009 until 2013 which has been obtain from Malaysia Annual Fisheries Statistic.

TABLE 2: Annual cockle shell production in Malaysia

Livestock	2009	2010	2011	2012	2013
Cockle	64,938.51	78,024.70	57,544.40	42,132.03	40,172.21

2.2 Calcium Chloride

Calcium chloride is an inorganic salt which are commonly used by many industries for various purposes. In food industries calcium chloride are mainly utilized to reduce post-harvest decay process and help to increase calcium content of food and vegetables. According to Ferguson (2001) by maximizing the calcium content on apple it can help to reduce risk of disorder and help in maintaining firmness of the apple. Another example is the studies done by Goncalves et al. (2000) which conducted research on pineapple. He had reported that, by using calcium chloride the decay rate of pineapple can be decrease significantly by doing post-harvest treatment method to the pineapple. Mahmud et al. (2008) had conducted a studies on how the presence of calcium chloride can effect storage life of a papaya and concluded that by using calcium chloride the storage life of papaya can be extended up to 25.9 days which is done by using vacuum infiltrations method. In construction industries, hygroscopic properties of calcium chloride has been manipulated, to help accelerate cement hydration process which result in faster cement final set time. Other than that, calcium chloride also release vast amount of exothermic energy release when react water. This properties had been identified and being use to help melt the snow and prevent any ice formation on the road during winter seasons which is proven to be effective. In waste treatment plant calcium chloride is used to absorb any heavy metal such as fluorine, phosphate and chromium in plant waste. Other than being used to remove heavy metal elements, calcium chloride also could be used to balance pH value of wastewater in the treatment plant. In oil and gas industries calcium chloride are mixed with other substance to form drilling mud. Drilling mud is use in any oil and gas exploration to help with the drilling and well completion process. In one project, drilling fluid alone cost about 15-18% of total well drilling cost and calcium chloride alone contributes about 25% of total drilling fluid composition. Book published by Caenn et al. (2011) states that shale control mud are one of drilling fluid that required calcium chloride in order to maintain and stabilize shale through presence of calcium ion.

Most of calcium chloride plants use calcium carbonate and hydrochloric acid as raw material to produce calcium chloride. Chemical reaction between calcium carbonate with hydrochloric acid will produce calcium chloride. As the reaction is very straightforward the yield of calcium chloride could be predicted easily. However, there might be some of site reaction that is occurring during the process upon utilizing waste cockle shell as the raw material since. The shell is made up of 95-98% calcium carbonate and another 5-2% of other element such as silicon, potassium, sodium and other minerals which could form other inorganic salt when reacted with hydrochloric acid. However, due to the trace amount of other element present the side reaction could be ignored as it will have little effect on final yield of calcium chloride. Equation shown below explained the reaction between calcium chloride and hydrochloric acid:

$$CaCO_{3(s)} + 2HCl_{(l)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \quad (1)$$

2.3 Synthesizing Calcium Chloride

As shown in the above chemical equation, there are two by-product that are synthesized along with calcium chloride which are carbon dioxide and water. In order to obtain pure calcium chloride, carbon dioxide and water must be removed. Carbon dioxide and calcium chloride can be separated easily as both of the components exist in different phase under room temperature and atmospheric pressure. However to obtain anhydrous calcium chloride it will required some heating at certain temperature to achieve the final result. There are several calcium chloride reactor patents which are available online. Each of these patents is used for different purposes. James (1994) had invented a patent and explained on how granules calcium chloride could be produce from calcium chloride solution by using his patent. Bowden and Terry (1967) also has patented a design that able to produce fine anhydrous calcium chloride, fine hydrated calcium chloride and granular calcium chloride by spraying calcium chloride in dry gas stream at some higher temperature. Other than that, Teyssier and Lepant (1981) had patented a design that are capable in producing calcium chloride solution by introducing calcium carbonate and hydrochloric acid at top of reactor. As the reaction occur calcium chloride solution and carbon dioxide will automatically separate due to the gravitational force and density. Calcium chloride solution will exit at the bottom of the reactor while carbon dioxide will exit through top of reactor. Table below summarizes all findings related to the patents:

TABLE 3: Patent findings

Patent inventor	Publication Year	Final Product	Findings
John H Bowden, Clifford T Terry	1967	Powder and Granular	• Dilute calcium chloride could be spray and dried to become anhydrous or hydrated products • Powder or granular calcium chloride with moisture percentage ranging from 25-1% could be produced from this patent. • To produce hydrated and anhydrous calcium chloride the entering gas temperature must be between 204^oC to760^oC. Above 760^oC the calcium chloride might undergo decomposition process. • To produce anhydrous calcium chloride the weight percentage of calcium chloride greater than 50% is preferable.
Gerard Teyssier, Marcel Lepant	1981	Aqueous solution	• Calcium carbonate is introduced from top of reactor and fall onto a filtration sieve. • Hydrochloric acid is introduced from top of the sieve and sprinkle on top of calcium carbonate. • Reaction will occur and any calcium chloride produced will fall from the filtration sieve and will be collected at the bottom of the reactor. • Carbon dioxide produce from the reaction will rise to the top of reactor and release to the atmosphere.
Lucas James	1994	granules	• Solution of calcium chloride is feed from the top portion of drying chamber through a

	ring shaped sprinkler. • The size of hole on sprinkler determines the size of granule produced. • Hot air is introduced at the lower portion of drying chamber and recycles back through the top. • Granules produced are removed from the bottom of chamber by using conveyor belt.

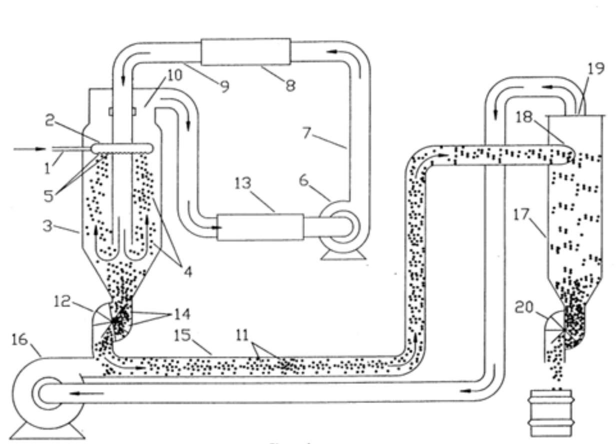

FIGURE 2: Patent by James (1993).

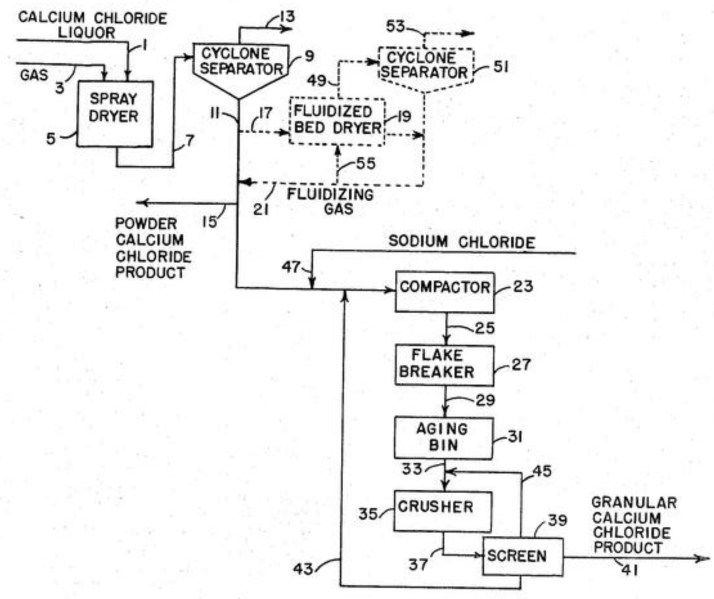

FIGURE 3: Patent by Bowden and Terry (1967)

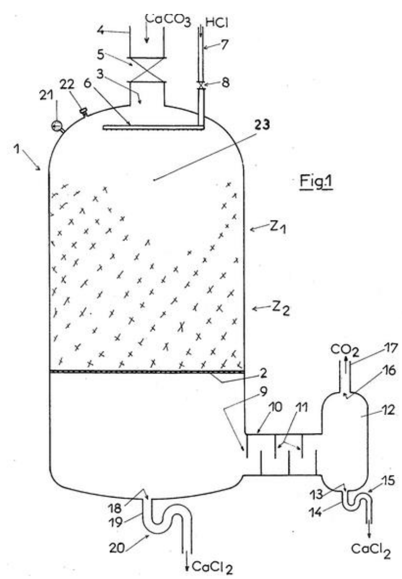

FIGURE 4: Patent by Teyssier and Lepant (1981)

However, through the reaction (1) shown there is some amount of CO_2 that are being produced. Stoichiometrically, if 100kg of calcium carbonate is reacted with hydrochloric acid, 44kg of carbon dioxide will be generated. Due to the amount of carbon dioxide released, environmental hazard could be expected as CO_2 is a greenhouse gas. In order to ensure the safety of the environment, carbon dioxide released must be treated prior release. There are several techniques that can be used to treat carbon dioxide. One of it is through conversion into other useful value-added product such as sodium bicarbonate. A study by Yoo et al. (2013) suggested the possibilities of dissolving CO_2 with sodium hydroxide. Several reactions might occur in the process , as illustrated in equation (2) to (4)

The main reaction:

$$NaOH_{(aq)} + CO_{2(g)} \rightarrow NaHCO_{3(aq)} \quad (2)$$

However there are two other side process that are occurring which is as below:

$$2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \quad (3)$$

$$3Na_3CO_{(s)}+CO_{2(g)}+5H_2O_{(g)} \leftrightarrow 2(Na_2CO_{3..}NaHCO\ .2H_2O) \text{ also known as trona} \quad (4)$$

From the paper published, it is reported that the mass ratio of CO_2 absorbed for production of Na_2CO_3, $NaHCO_3$, and trona to be 20:17:1. This process route is considered as one of the route to treat carbon dioxide because the abundant amount of sodium hydroxide available. Sodium hydroxide is identified as the main raw material needed in this process. Therefore it is essential to ensure the availability of sodium hydroxide to ensure the treatment method is effective.

CHAPTER 3
METHODOLOGY AND GANTT CHART

3.1 Methodology

For this study, the methodology can be separated into three sections which are process selection, final product desired and carbon dioxide treatment.

3.1.1 Process Selection

a) <u>Possible Route Utilizing Calcium Carbonate</u>

Calcium carbonate can be reacted with many different chemical to get the desired final product. Here are some of the most common reaction is the thermal decomposition of calcium carbonate to calcium oxide which can be described by the chemical equation below:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad (5)$$

Based on experiment conduct by Mohamed et al. (2012) calcium carbonate will decompose at temperature of 850^{o}C. There are many usage of calcium oxide in industries. For example, in agriculture sector calcium oxide is used as fertilizer to balance the acidic soil and provide nutrient to plant. Other than that, calcium oxide also is being used as an alkali in production of biodiesel.

Another reaction that could be done with calcium carbonate is to solute it with water containing concentrated carbon dioxide. This reaction usually could be observed occurring at limestone hill which are exposed to rain water saturated with carbon dioxide. The reaction will result in formation of calcium bicarbonate which could be used for many purposes. In document archiving process, papers are washed with calcium bicarbonate solution to neutralize acid in paper which helps to protect paper from future damages. The reaction could be described by the following chemical equation:

$$CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)} \rightarrow Ca(HCO_3)_{2(aq)} \quad (6)$$

Lastly, calcium carbonate also can be reacted with hydrochloric acid to produce calcium chloride. As explained in the previous section, this method is known as the most common method being used to produce calcium chloride. The reaction is very simple and straightforward with wide range of possible final product to be produced depending on the demand and market value. Other than that, availability to obtain hydrochloric acid made the reaction is more favorable. Due to all of the advantage stated, this reaction is highly preferred over the other method.

b) Alternative Routes of Producing Calcium Chloride

In industries calcium chloride can be produced from several routes. One way to produce calcium chloride is by reacting ammonium chloride with calcium hydroxide which will produce calcium chloride, ammonia and water. This process usually being used in one of the step in Solvay process. Solvay process is one of the reaction routes being used to produce sodium carbonate with calcium chloride as the side product. The following chemical equation explained the reaction:

$$2NH_4Cl_{(aq)} + Ca(OH)_{2(aq)} \rightarrow CaCl_{2(aq)} + 2NH_{3(g)} + 2H_2O_{(l)} \quad (7)$$

Other ways that could be used to obtain calcium chloride is by pumping calcium chloride from natural brine source that contain large amount of calcium chloride. The brine usually is obtained in form of solution which contains some impurities from other chloride salt such as sodium chloride.

Lastly, the most conventional route to produce calcium chloride is through reaction of calcium carbonate with hydrochloric acid which the process already been explained in the last section.

Based on the objective of this study which is to produce calcium chloride from waste cockle shells, thus reaction of calcium carbonate with hydrochloric acid process route is selected as the other process route did not have either calcium carbonate as the raw material or calcium chloride as final product. Other than that, reaction of calcium carbonate with calcium chloride is the most common route being used by many manufacturing plant in producing calcium chloride.

3.1.2 Final Product Desired

The type of final product synthesized is significant in attracting buyers to buy calcium chloride produced by this plant. One of the main properties that play an important role is the final form of calcium chloride which could either be the calcium chloride solution, solid calcium chloride or anhydrous calcium chloride. The description below illustrates the differences:

a) Calcium Chloride Solution

Calcium chloride solution is the easiest final product to be produced, this is because calcium chloride manufactured from the reaction of calcium carbonate and hydrochloric acid is already in solution form. However, the concentration of the calcium chloride is different according to the ratio of water and calcium chloride. Thus, the physical properties such as boiling point and melting will also be different. According to the material safety data sheet release by Occidental Chemical Corporation (OxyChem), the composition of calcium chloride solution is as followed:

TABLE 4 : Composition of calcium chloride solution

Component	Mass percentage (%)
Water	53-72
Calcium chloride	28-42
Sodium chloride	1- 2
Potassium chloride	2- 3

a) Solid calcium chloride

Granule, flake or powder calcium chloride could be produced through drying process. However, the technique and equipment use will determine which final product is generated. For example, to get powder calcium chloride the solution must be dried first and follow up with crushing process before the powder could be obtained while to obtain granule calcium chloride the solution only need to undergo drying process. Regardless the final product shape and size, the composition of calcium chloride should be the same at same purity. In terms of composition, according to product information sheet from OxyChem normal solid calcium chloride contain purity ranging from 77-87%. Table below shows the composition of granules calcium chloride composition:

TABLE 5 : **Composition of solid calcium chloride**

Component	Mass percentage (%)
Water	8-14
Calcium chloride	83-87
Sodium chloride	1- 2
Potassium chloride	2- 3

b) Anhydrous calcium chloride

The process of producing anhydrous calcium chloride is almost similar to process producing solid calcium chloride. Both of the process required to undergo drying process to obtain solid form of calcium chloride. However, the difference between anhydrous calcium chloride with solid calcium chloride is the purity of calcium chloride. Solid calcium chloride has purity of 83-87% while anhydrous calcium chloride has purity ranging from 94-97%. Table below shows composition of anhydrous calcium chloride:

TABLE 6 : Composition of anhydrous calcium chloride

Component	Mass percentage (%)
Water	less than 1
Calcium chloride	94-97
Sodium chloride	1- 2
Potassium chloride	2- 3

The composition of calcium chloride coming out from reactor will be crucial factor in determining the outcome of final product. If the composition below than 50%, then it is easier to produce calcium chloride in solution forms rather than solid or anhydrous. However, if the composition is calcium chloride composition is greater than 83% then it is feasible to produce solid or anhydrous calcium chloride. It is preferable to get the final product in solid phase over aqueous phase due to several reasons. The advantages of having solid phase over aqueous is that solid phase are easier to be handle and packing compare to solution. Other than that, solid calcium chloride can be easily dissolves with water whenever calcium chloride solution is required. In term of economics, usually the higher the purity of the component the higher the price of material. Thus, it is expected the price of anhydrous calcium chloride to be highest than other type of calcium chloride produced.

Since cockle shell has 95-98% composition of calcium carbonate, it is expected that the final composition of calcium chloride produce with be greater than 80%. Therefore, anhydrous calcium chloride is chose as the final product desired. The calculation done in the next section will determine either this objective is feasible or not. If the objective is impossible to achieve, then solid calcium chloride is selected as final product.

3.1.3 Carbon Dioxide Treatment

The main problem when reacting calcium carbonate with hydrochloric acid is carbon dioxide being produce as a side product. There are several carbon dioxide treatments methods that already being identified to help reduce carbon dioxide release to atmosphere.

a) Dissolving Carbon Dioxide into water

Dissolving carbon dioxide into water is one of the most common ways being used to remove carbon dioxide. This method is mostly being use in producing soft drink. However the solubility of carbon dioxide inside water is very low and the operating pressure must be really high for carbon dioxide to start dissolve in water. This method is less commonly used in other industries because of the low solubility of carbon dioxide in water.

b) Absorption of Carbon Dioxide Using Sodium hydroxide

Absorption of carbon dioxide using water is relatively new technique that being study. According to Yoo et al. (2013) the amount of carbon dioxide being absorbed by sodium hydroxide is more compare to amount of carbon dioxide that could be absorbed by mono-ethanol-amine (MEA). Through the experiment they had conduct, the result obtained shows that it is possible to absorbed carbon dioxide with the highest amount of carbon dioxide capture capacity is $2.2134 \frac{\text{mg of total } CO_2 \text{ absorbed}}{\text{g of NaOH solution}}$. The chemical reaction that occurs between carbon dioxide and sodium hydroxide already has been explained in the previous section.

c) Releasing Carbon Dioxide to the atmosphere

The last step that could be taken in dealing with carbon dioxide is by releasing carbon dioxide to the environment. This step is not very environmental-friendly because by releasing carbon dioxide to the environment, this could increase the greenhouse gas inside the atmosphere. Due to the impact it could potentially cause to the environment, this step is considered as the last solution in dealing with carbon dioxide when other solution available is not effective.

After analyzing and study all the method available, it is decided that the carbon dioxide produce from the reaction between calcium carbonate and hydrochloric acid is to be release to the atmosphere without being treated. This is because, both of the treatment methods that are being study did not manage to treat most of the carbon dioxide being produce effectively. For example, the carbon dioxide absorption process by using sodium hydroxide. The stated method only manage to absorb 2.2134 mg of carbon dioxide per gram of sodium hydroxide which can be consider as very little and not very effective. Therefore, it is decided to release all carbon dioxide to the atmosphere without being treated until new and effective method is discovered.

3.2 Gantt Chart

FYP 1

Activities	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14
Briefing on FYP and project title														
Project title selection														
Project briefing by supervisor														
Findings and data gathering														
Extended proposal report writing														
Consultation and discussion with supervisor														
Proposal defense														
Interim report writing														
Mass balance and energy balance														
Selection of reactor, heat integration and utility requirement														
Compilation and interim report submission														

FYP 2

Activities	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14
Mass and energy balance														
Findings, data gathering and feasibility study on results obtain														
Correction and improvement on plant design.														
Consultation and discussion with supervisor														
Progress report writing														
Progress report submission														
Technical paper and project dissertation writing.														
Pre-SEDEX														
Submission of final report draft														
Submission of technical paper and soft bound														
Viva														
Submission of Hard bound														

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Selected Process Route

Based on studies and discussion done, the proposed flow diagram of the pilot plant will be as below.

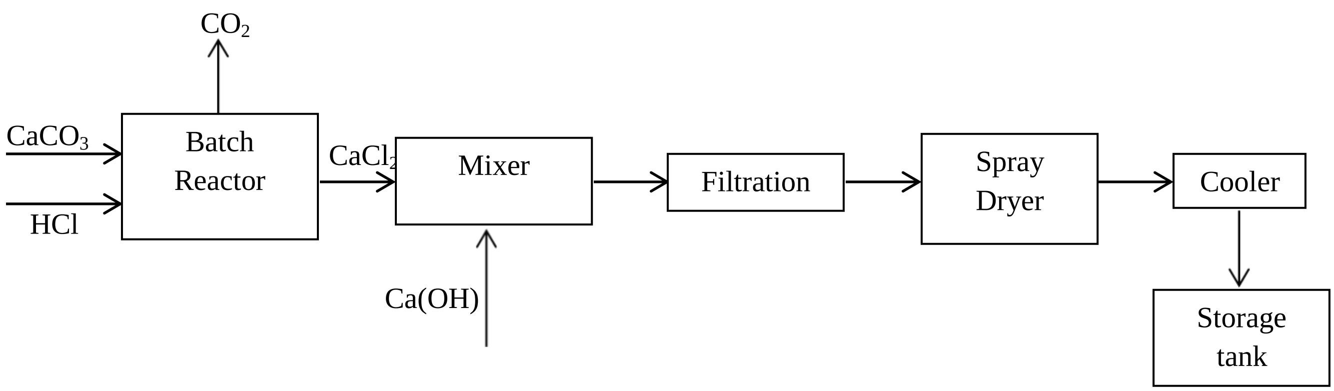

FIGURE 5 : Block diagram of calcium chloride production plant

Before cockle shell is fed into the batch reactor, it will be crushed into much smaller sizes by using pulverizer. Theoretically, increase in the surface area of the substrate will result in the increase of reaction rate; thus by crushing the raw material this factor will be ensured. The crushed cockle shell will enter the reactor along with hydrochloric acid. The reaction take place inside the reactor, as result carbon dioxide and calcium chloride solution will be produced. According to experiment conducted by Bukhari and Abdullah (2013) the reaction of powdered cockle shell with hydrochloric acid will produce calcium chloride solution with bubble of gas being produced, which is identified to be carbon dioxide. At atmospheric pressure carbon dioxide exists in gases phase will be release to atmosphere in gaseous phase. For this plant the calculated composition of calcium chloride in the solution would start from as low as 86% for cockle shell containing 98% calcium carbonate. As for the temperature of the exiting solution it is calculated to be at 68.24^{o}C.

The exiting calcium chloride solution from reactor will enter a mixer. Theoretically, there should be no unreacted hydrochloric acid exit from the reactor. However in case there is any runaway reaction or process upset occur which cause unreacted hydrochloric acid to exit from the reactor, a preventive measure must be taken to handle the unreacted acid. Introduction of calcium carbonate inside the mixer is one of the methods that could help to convert any unreacted hydrochloric acid exit from the reactor. The reaction of calcium hydroxide with hydrochloric acid should produce calcium chloride and water as shown in the equation below:

$$Ca(OH)_{2(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + 2H_2O_{(l)} \qquad (8)$$

After that the product will undergo filtration process where all unreacted calcium carbonate and calcium hydroxide will be filter from entering the next unit which is the drying unit. The drying process will take place by using spray dryer in order to obtain the final product in fine powder form. Then the product will be cooled down and store inside a storage tank. Since the calculated composition of calcium chloride in the solution to be at least 86%, therefore it is feasible to produce anhydrous calcium chloride as the final product. According to production information sheet produced by OxyChem, calcium chloride can be defined to be anhydrous when the composition of calcium chloride in the final product is between 94-97%. Therefore, the targeted composition for final product calcium chloride should be from 94-97%. According to the Material Safety Data Sheet for anhydrous calcium chloride 94-97% purity produce by OxyChem the melting point for anhydrous calcium chloride is 772^{o}C. With this information, the final product could be assumed in solid form.

Carbon dioxide that been produced during the reaction of hydrochloric acid and calcium carbonate will be released to atmosphere and will not be treated.

4.2 Reactor Mass Balance And Heat Balance

All mass balance done in the calculation below is based on chemical equation:

$$CaCO_{3(s)} + 2HCl_{(l)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \quad (1)$$

Assume 1000g of crushed cockle shell enter the reactor. From the literature review done, 95-98% of cockle shell is made up from calcium carbonate.

Therefore mass of calcium carbonate available in 1000g of cockle shell, vary from 950g to 980g

For calculation sample done below, assume mass of calcium carbonate entering the reactor to be 950g. Therefore molar of calcium carbonate:

$$= 950\ g\ CaCO3\ x\ \frac{1\ mol\ \ CaCO3}{100\ g\ CaCO3}$$

$$= 9.5 \text{ mol } CaCO_3$$

Stoichiometrically, 1 mol of calcium carbonate reacts with 2 mol of hydrochloric acid. Therefore total molar of hydrochloric acid required to react with 9.5 mol of calcium carbonate must be 19 mol. Total mass of hydrochloric acid need to react with 950 g of $CaCO_3$ is:

$$= 19\ mol\ of\ HCl\ x\ \frac{36.46\ g\ HCl}{1\ mol\ HCl}$$

$= 692.74\ g\ of\ HCl$

However since hydrochloric acid need to be provided in aqueous form the value need to be converted from mass to volume by using density of hydrochloric acid:

Density of HCl = 1.49 g/cm^3

$$Volume = \frac{Mass}{Density}$$

Therefore, volume of HCl needed = $\frac{692.74g}{1.49\ g/cm3}$

= 464.93 cm^3

Convert the value to Liter = 464.93 cm^3 $x\,\frac{0.001\ Liter}{1\ cm3}$

HCl needed = 0.465 L

By referring to stoichiometry chemical equation done, reacting 1 mol of calcium carbonate with 2 mol of hydrochloric acid will produce 1 mol of calcium chloride, 1 mol of water and 1 mol of carbon dioxide. Therefore the amount of calcium chloride, water and carbon dioxide produced from 9.5 mol calcium carbonate is calculated as below:

Mass of $CaCl_2$ produced = $9.5\ mol\ of\ CaCl_2\ x\,\frac{110\ g\ CaCl2}{1\ mol\ of\ CaCl2}$

= 1045 g $CaCl_2$

Mass of H_2O produced = $9.5\ mol\ of\ H_2O\ x\ \frac{18\ g\ H2O}{1\ mol\ of\ H2O}$

Mass of H_2O produced = 171 g of H_2O

Mass of CO_2 produced = $9.5\ mol\ of\ H_2O\ x\ \frac{44\ g\ CO2}{1\ mol\ of\ CO2}$

Mass of CO_2 produced = 418 g of CO_2

From calculation done above, total mass balance inside the reactor obtained when 950g calcium chloride reacted with hydrochloric acid:

950g $CaCO_3$ + 692.74g HCl → 1045g $CaCl_2$ + 418g CO_2 + 171g H_2O

For heat balance of the reaction, total heat being produced from the reaction can be calculated using Hess's Law of constant heat summation. Hess's law stated that the enthalpy change in chemical reaction is constant regardless of the step taken to complete the reaction. The following formula is used to calculate the enthalpy of reaction:

$$\Delta H\ of\ reaction = \sum n\Delta H\ formation\ in\ products - \sum n\Delta H\ formation\ in\ reactants \quad (9)$$

Where n = number of moles

Assuming that the reaction occurs in standard states, all information on enthalpy of formation are obtained from (Felder and Rousseau 2000). The obtained heat of formation is listed below:

ΔH for $CaCO_{3\,(s)}$ = - 1207 kJ/ mol

ΔH for $HCl_{\,(aq)}$ = -167.46 kJ/mol

ΔH for $CaCl_{2\,(aq)}$ = -877.3 kJ/mol

ΔH for $CO_{2\,(g)}$ = -393.51 kJ/mol

ΔH for $H_2O_{\,(aq)}$ = -285.8 kJ/mol

By using equation (6) and enthalpy of reaction obtained, the enthalpy of reaction could be calculated which is shown below:

$$\text{Enthalpy of reaction} = \sum[(9.5X(-877.3)) + \left(9.5X(-393.51)\right) + (9.5X(-285.8))] - \sum[(9.5X(-1207)) + (19X(-167.46))]$$

Enthalpy of reaction = -139.556 kJ/mol

The negative sign of the enthalpy of reaction signify that the reaction that occurring is exothermic reaction. From the enthalpy calculated, the final temperature of solution could be determined by using the following formula:

$$\Delta H\ of\ reaction = (mass\ flow\ rate)x\ (specific\ heat\ capacity\ of\ solution)x(change\ in\ temperature) \quad (10)$$

The specific heat capacity of solution is assume to be equal to specific heat capacity of calcium chloride. This is because the composition of calcium chloride in solution is larger than composition of water. Thus, it is safe to assume the specific heat capacity of solution is almost same to specific heat capacity of calcium chloride which is found to be 3.06 kJ/kg.K.

We also assume that the initial temperature of reaction to be 25^{o}C since the feed entering the reactor is at standard temperature and pressure. For the solution obtained from previous calculation, the temperature of the solution is calculated as below:

$139.556\ \text{kJ/mol} = (1.0545\ \text{kg})(3.06\ \text{kJ/kg.K})(T_F – 298.15)$

$139.556 = 3.231T_F – 962.06$

$139.556 + 962.06 = 3.23T_F$

$1101.62 = 3.23\ T_F$

$1101.62 /3.23 = T_F$

$341.8\ \text{K} = T_F$

$68.65^{o}\text{C} = T_F$

By using the same calculation method as shown above, table below summarize the mass of hydrochloric acid required, mass of carbon dioxide produced, mass of water produced, mass of calcium chloride produced and heat of reaction when the composition of calcium carbonate entering the reactor differ between 950-980g.

TABLE 7 : Summary of mass balance in reactor

% of $CaCO_3$	gram of $CaCO_3$	mol of $CaCO_3$	gram of HCl required	mol of HCl	gram $CaCl_2$ produced	gram CO_2 produced	gram H_2O produced	Temperature of solution (^oC)	delta H (kJ/mol)
95%	950	9.5	692.74	19	1054.5	418	171	68.65	-139.556
96%	960	9.6	700.03	19.2	1065.6	422.4	172.8	68.65	-141.024
97%	970	9.7	707.32	19.4	1076.7	426.8	174.6	68.65	-142.493
98%	980	9.8	714.61	19.6	1087.8	431.2	176.4	68.65	-143.960

All of the data in the above table are translated into graph according to the feed, product produce and enthalpy of reaction as shown below.

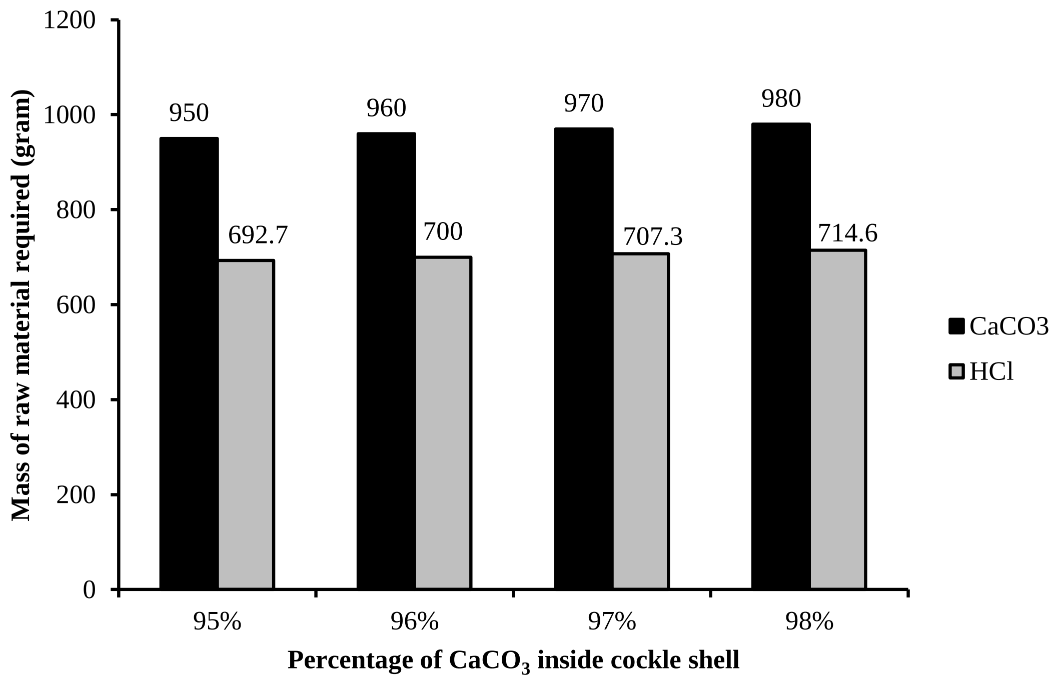

FIGURE 6 : Mass of raw material required for various $CaCO_3$ composition in waste cockle shell.

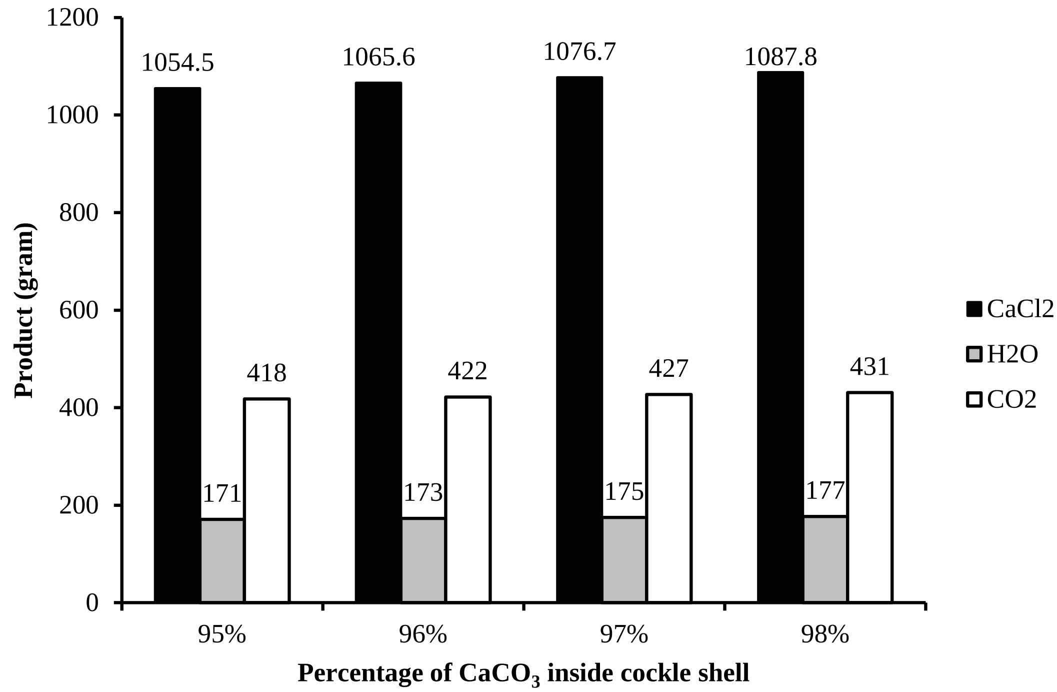

FIGURE 7 : Mass of product synthesized for various $CaCO_3$ composition in waste cockle shell.

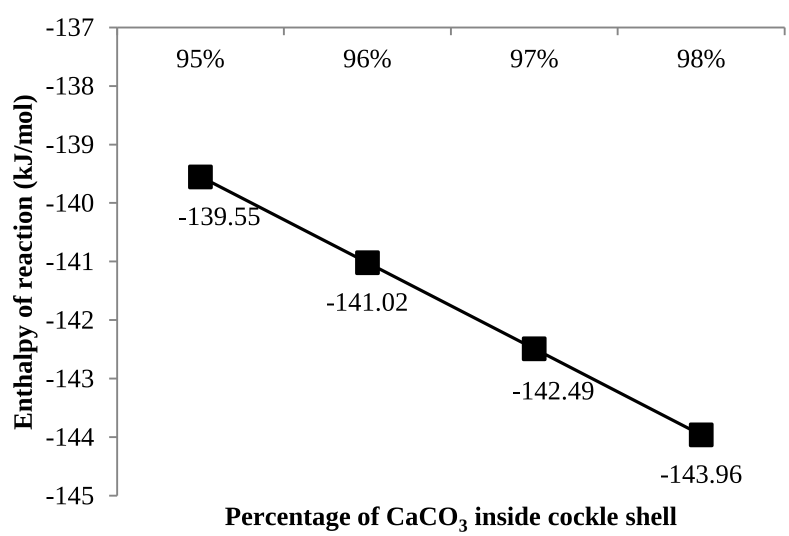

FIGURE 8 : Energy change for $CaCl_2$ synthesis for different percentage of $CaCO_3$ in waste cockle shell.

4.3 Spray Dryer Mass Balance And Heat Balance

To calculate mass balance and heat balance for spray dryer several assumptions must be made, all assumptions are as followed:

1. No heat loss to surrounding during the whole process.
2. No calcium chloride or water loss during the filtration process.
3. No unreacted hydrochloric acid or calcium carbonate entering the spray dryer.
4. All feed entering spray dryer are in aqueous phase.
5. The following calculations on spray dryer are continued from calculations done at reactor assuming that all previous calculations done are correct.
6. Assuming the plant to be built at industrial area around Ipoh.

The objective of doing spray dryer mass balance is to calculate amount of hot air required to remove water content from calcium chloride solution to the desired final composition. Since the composition of calcium chloride solution and final calcium chloride composition is already known the following mass balance formula could be used in determining mass of hot air required for the drying process.

$$L_sX_1 + G_sY_1 = L_sX_2 + G_sY_2 \qquad (11)$$

Where L_s = solution flow rate

X_1 = moisture content of entering solution

G_s = air flow rate

X_2 = moisture content of exit solid

Y_1 = humidity of entering air

Y_2 = humidity of exit air

The value of X_1 is the mass ratio of water content in entering solution to total mass of solution. Mass of water and calcium chloride entering the spray dryer can be obtained from table 7 which is 1054.5 gram for calcium chloride and 171 gram for water. Calculating the moisture content inside the solution the value of X_1 will be $(\frac{171\ g\ H2O}{1054.5\ g\ CaCl2+171\ g\ H2O})$ this value can be further simplified to $(0.1395\,\frac{kg\ H2O}{kg\ CaCl2})$

To obtained value of Y_1 which is the humidity of entering air, the average relative humidity and average temperature of Ipoh must be find from Malaysian Meteorological Department website. From the value of relative humidity and temperature the value of Y_1 can determined by using psychometric chart. On the psychometric chart the value of Y_1 is label as moisture content with unit kg H_2O/kg dry air. Based on the reading taken from Malaysia Meteorological Department website, the average temperature of Ipoh is 33^{o}C with relative humidity to be at 47%. By referring to psychometric chart, the value of moisture content obtained is $(0.0062\frac{kg\ H2O}{kg\ air})$

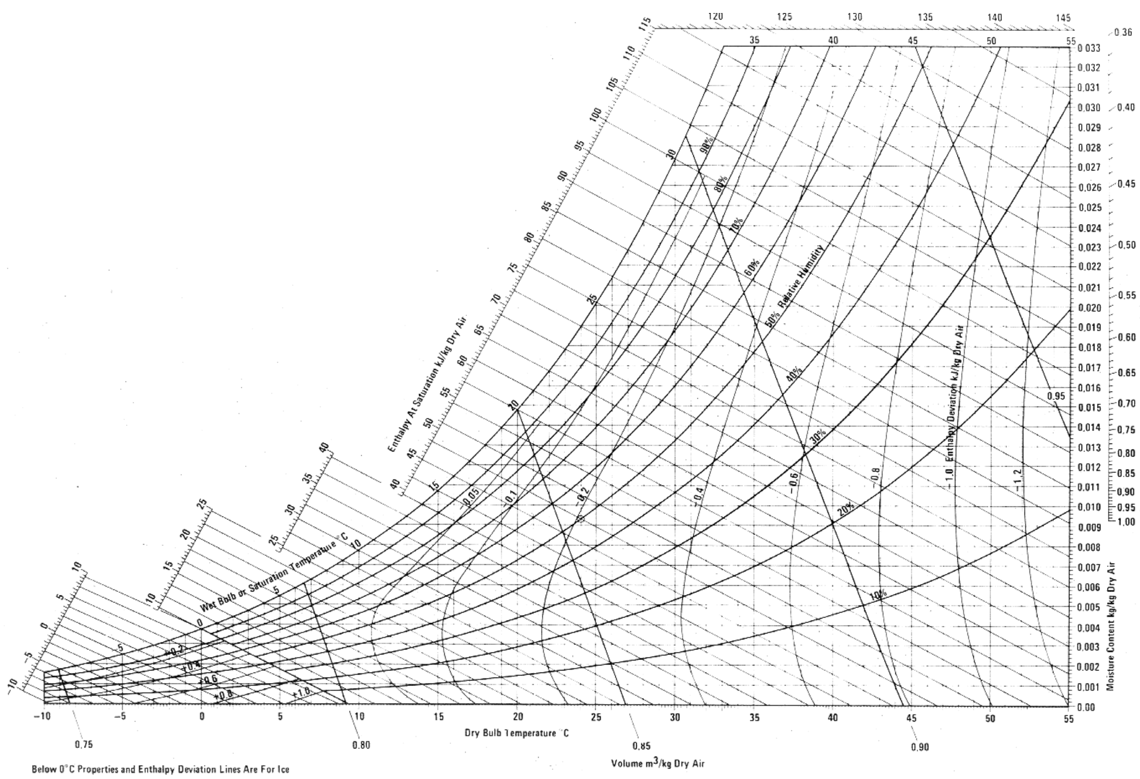

FIGURE 9 : Psychometric chart

From table 6 the composition of water in anhydrous calcium chloride is less than 1%. Therefore, moisture content needed to be removed from the entering solution and moisture content need to be remaining in final product must be known. Firstly, the concentration of $CaCl_2$ entering the spray dryer must be calculated.

Composition of water in feed solution = $\frac{171\ g\ H2O}{1054.5\ g\ CaCl2+171\ g\ H2O}\ x\ 100\%$ = 13.95%

Assuming that the final composition of water in final product = 1%

Thus, to find total mass of water left inside the solution when reduce to 1% it is calculated as below:

Mass fraction of water x 100 = 1% purity

Therefore, $\frac{\text{Mass of water exiting spray dryer}}{\text{Total mass of solution exiting spray dryer}}$ X 100% = 1%

It is known that total mass in the solution is equal to summation of mass of calcium chloride and mass of water. Therefore:

$\frac{Y}{1054.5\ g\ CaCl2+Y}\ X\ 100\%$ = 1%

$\frac{Y}{1054.5\ g\ CaCl2+Y}$ = 0.01%

1054.5 g $CaCl_2$ = (1054.5 g $CaCl_2$ + Y) 0.01%

Y = 10.545g $CaCl_2$ + 0.01Y

Y – 0.01Y = 10.545g $CaCl_2$

0.99Y = 10.545g $CaCl_2$

$\frac{10.545}{0.99}$ = Y

10.65 = Y

Unit for Y should be gram of water since all calculations done are based on gram.

10.65 g H_2O = Y

The amount of water left inside the solution can be expressed in term of X_2 which is moisture content in the exit solid by dividing mass of water content in solid exiting spray dryer with total mass of solid exiting spray dryer. Therefore value of X_2 = $\frac{10.65 \text{ g H2O}}{1054.5\ g\ CaCl2 + 10.65\ g\ H2O}$ which be simplified to ($0.01 \frac{\text{g H2O}}{g\ CaCl2}$). Formula shown below can be used to calculate amount of water needed to be removed:

$$Water\ content\ in\ entering\ solution - Water\ content\ in\ exiting\ solid = Water\ content\ needed\ to\ be\ removed \quad (12)$$

In this calculation the water content in entering solution is 171g whereas water content in exiting solid is 10.65g.Therefore, amount of water needed to be removed is:

171g H_2O – 10.65g H_2O = 160.35g H_2O

= 0.164 kg H_2O

From the calculation done above, the amount of Y_2 which is moisture in the outlet air could be determined. The amount of moisture in the outlet air is the summation of moisture of inlet air and moisture remove from calcium chloride solution. The sample calculation done is shown below:

$Y_2 = 0.0062 \frac{kg\ H2O}{kg\ air} + 0.1604 \frac{kg\ H2O}{kg\ air}$

$Y_2 = (0.1666\frac{kg\ H2O}{kg\ air})$

By substituting all value into equation (11) the value of air required to remove 160.35g moisture content could be obtain. The calculation to obtain the value of gas flow rate is shown below:

$$L_sX_1 + G_sY_1 = L_sX_2 + G_sY_2 \quad (11)$$

$$(1.0545\text{kg } CaCl_2)(0.1395\,\frac{kg\ H2O}{kg\ CaCl2}) + (G_s)(0.0062\,\frac{kg\ H2O}{kg\ air}) =$$

$$(1.0545\text{kg}CaCl_2)(\ 0.01\,\frac{kg\ H2O}{kg\ CaCl2}) + (G_s)(0.1667\,\frac{kg\ H2O}{kg\ air})$$

$$0.1471\text{g } H_2O - 0.0105\text{kg } H_2O = (G_s)(0.1667\,\frac{kg\ H2O}{kg\ air} - 0.0062\frac{kg\ H2O}{kg\ air})$$

$$0.1366\text{kg } H_2O = (G_S)(0.1605\,\frac{kg\ H2O}{kg\ air})$$

$G_S = 0.851090$ kg air.

Table below are developed based on calculation method sample shown above. The table produced summarize amount of moisture content in solution entering spray dryer, amount of moisture content of solid leaving spray dryer, amount of moisture needed to be remove and amount of air need for the process when the mass of calcium chloride entering the reactor differ ranging 1054.5 gram to 1087.8 gram. As discussed before, to obtain anhydrous calcium chloride water content in the final product should be less than 1%. Therefore, calculation done to remove moisture content up to 1% signify the minimum amount of air need to produce anhydrous calcium chloride. Hence, first table show the minimum amount of air required to achieve 1% moisture content in the final product. While the second table shows the amount of air required to remove all water content from the final product. This signifies the maximum amount of air required to obtain anhydrous calcium chloride.

TABLE 8 : summary of mass balance in spray dryer with 1% moisture content in final product

% of $CaCO_3$	Mass of $CaCl_2$ solution entering	Feed solution moisture content (gram)	Final Product moisture content (gram)	Moisture removed (gram)	Amount of air required (gram)
95%	1054.5	171	10.65	160.35	851.62
96%	1065.6	173	10.76	162.24	850.70
97%	1076.7	175	10.87	164.13	849.73
98%	1087.8	177	10.99	166.01	848.19

Table 9 : summary of mass balance in spray dryer with no moisture content in final product

% of $CaCO_3$	Mass of $CaCl_2$ solution entering	Feed solution moisture content (gram)	Final Product moisture content (gram)	Moisture removed (gram)	Amount of air required (gram)
95%	1054.5	171	0	177.2	860.25
96%	1065.6	173	0	179.2	859.26
97%	1076.7	175	0	181.2	858.28
98%	1087.8	177	0	183.2	857.33

Based on both table shown above, a graph has been plotted to determine the range of air feed that could be manipulated to produce anhydrous calcium chloride. As long the amount of air feed into spray dryer is within the area between both lines, the process should be in acceptable range. However, if the air feed falls below the lowest line then the air supplied is not sufficient and calcium chloride with moisture content more than 1% will be produced. If the air feed is above the highest line, then the amount of air feed is in excess which could lead to power wastage in pumping extra air into the spray dryer.

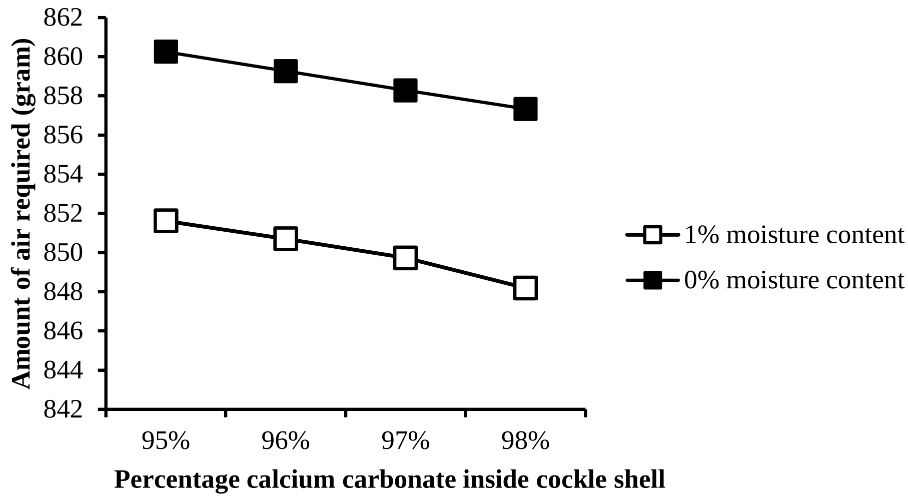

FIGURE 10 : Graph of air feed required at various composition of $CaCO_3$ in waste cockle shell.

For spray dryer heat balance, the objective is to calculate amount of heat energy required heat the air entering spray dryer to from the final product up to 1%. To calculate amount of heat required we must know how much heat energy required to raise the temperature of solid to 100^oC and how much lantern heat required in removing the water content. The following formula can be used to calculate the amount of heat required to remove moisture content:

Heat energy required = heat energy to raise temperature to 100^oC + latent heat to remove water

Heat energy required = (mass flow rate x specific heat capacity x temperature change) + (latent heat of vaporization of water x amount of moisture to be removed) *(13)*

The specific heat capacity of solution is assume to be equal to specific heat capacity of calcium chloride. As discussed before, the composition of calcium chloride in solid is larger than composition of water. Thus, it is safe to assume the specific heat capacity of solution is almost same to specific heat capacity of calcium chloride which is 3.06 kJ/Kg. K. The temperature change in this equation is referring to the incensement of temperature of solution to 100^{o}C. 100^{o}C is selected because at this temperature water starts to boil and evaporates. Thus, this show the minimum heat required to remove water from the anhydrous calcium chloride. Through previous calculation done, the temperature of solution is 68.24^{o}C. For the latent heat of vaporization the value can be found in (Felder and Rousseau 2000) which is 2257 kJ/kg. The following sample calculation is done to calculate the amount of heat required:

$$\text{Heat energy required} = (1.0545 \text{ kg x } 3.06 \text{ kJ/kg. K x } (373.15\text{- } 341.80 \text{ K})) + (2257 \text{ kJ/kg x } 0.1604 \text{ kg})$$

$$\text{Heat energy required} = 193.50 \text{ kJ} + 362.02 \text{ kJ}$$

$$\text{Heat energy required} = 463.18 \text{ kJ}$$

Table below summarize the amount of energy required to heat air entering spray dryer. The table is separated into two, the first table show the amount of heat required to remove moisture content until 1% is left while the second table show amount of heat required to remove all moisture content in the solid.

TABLE 10 : Summary of heat balance inside spray dryer with 1% moisture content in final product

% of $CaCO_3$	**Mass of $CaCl_2$ solution entering**	**Moisture removed (gram)**	**Heat energy required (kJ)**
95%	1054.5	160.35	463.18
96%	1065.6	162.24	468.40
97%	1076.7	164.13	473.73
98%	1087.8	166.01	479.04

TABLE 11 : Summary of heat balance inside spray dryer with no moisture content in final product

% of $CaCO_3$	Mass of $CaCl_2$ solution entering	Moisture removed (gram)	Heat energy required (kJ)
95%	1054.5	177.2	501.10
96%	1065.6	179.2	506.68
97%	1076.7	181.2	512.26
98%	1087.8	183.2	517.84

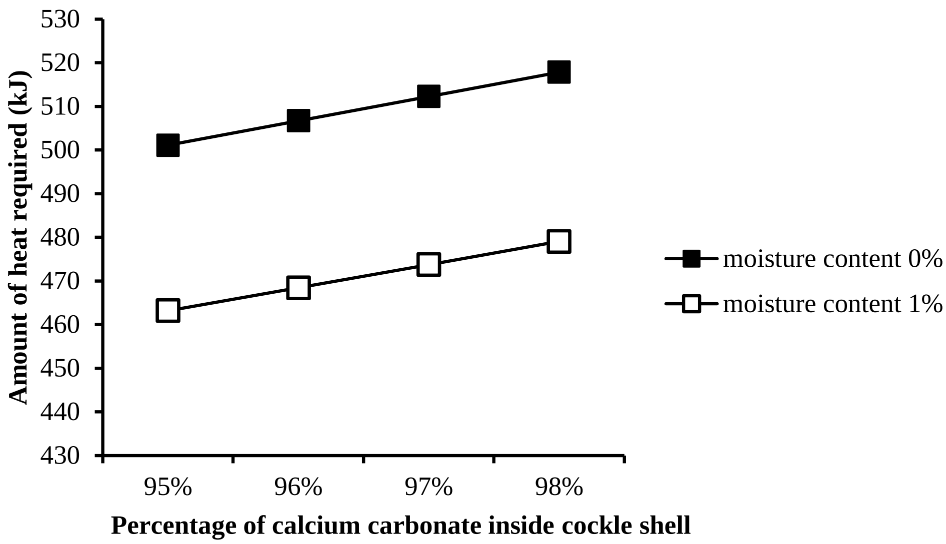

FIGURE 11 : Graph of air feed against calcium carbonate percentage

Graph plotted above is used to determine the range of heat required that could be manipulated to produce anhydrous calcium chloride. As long as the amount of heat supplied to the air entering the spray dryer is within the area between both lines, the process should be in acceptable range. However, if the heat supplied falls below the lowest line then the heat supplied is not sufficient and calcium chloride with moisture content more than 1% will be produced. If the heat supplied is above the highest line, then the amount of heat supplied is in excess which could lead to decomposition of calcium chloride if the temperature keeps increasing.

CHAPTER 5

CONCLUSION

5.1 Conclusion

In conclusion, cockle shell has been identified as possible alternative to limestone in producing calcium chloride. However there is no production plant that has been designed to produce calcium chloride production from cockle shell in a large scale. Therefore it is crucial to study on the feasibility of calcium chloride production plant by using cockle shell as raw material in providing alternative route for production of calcium chloride. Based on the mass balance and heat balance done, the production of calcium chloride from cockle shell is feasible. All the production calculated shows more than 1 kg of calcium chloride being produce with 1 kg of cockle shell being feed into the reactor. Cockle shell is chosen as raw material because of the low environmental effect with high sustainability.

5.2 Recommendation

However there is still lots room for improvement that could be made for this project. Firstly, type and dimension of reactor and spray dryer are not being specified. Thus, by determining the type and dimension of reactor and spray dryer it could produce more accurate calculation than that have been produced. Other than that, the carbon dioxide that being produced are not being treated and are release to environment. Thus, there are rooms for improvement to find a suitable and effective method in treating the carbon dioxide that are being produce as side product of the reaction. Lastly, the report does not cover on the economic part of the plant. Thus, a study on the economics of building a plant, running a plant and profit gain and payback period is highly recommended to be done. Because economics play an important factor in determining the feasibility of building and operating a plant.

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