Parameters Affecting Coating Uniformity for Geopolymer Coated Fertilizer

by

Nik Muhammad Harris Bin Nik Azharuddeen
16846

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

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Malaysia

CERTIFICATION OF APPROVAL

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Approved by,

(AP Dr. Ku Zilati Binti Ku Shaari)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
May 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.

NIK MUHAMMAD HARRIS BIN NIK AZHARUDDEEN

ABSTRACT

The establishment of Control Release Fertilizers (CRF) in agriculture industry has given great significant outcome towards the development of economy while preserving the environment. As it is developed through coating process, it is not only help to increase fertilizer's efficiency, but also minimize the loss of nutrients into soil and environmental pollution. There are many types of coating materials that have been used and studied extensively in everyday life such as in road construction and corrosion control of steel structures like offshore platforms. For this research, the geopolymer composite material has been developed and is introduced as the main coating material for the CRF. Geopolymer material is much more environmental friendly compared to sulphur and polymer based. However, the combination of fly ash-based powder, sodium hydroxide (NaOH) solution, and distilled water producing this geopolymer material needs further research to ensure it is clearly suitable to be used as coating material. Coating uniformity of urea fertilizer is critical to allow urea to be released at controllable time with steady rate. It will also affects the rate of which the nutrients will be released. Better wettability properties of a geopolymer droplet from its solution promotes thin-film formation on urea fertilizers surface. Therefore, certifies the uniformity in coating process. Three parameters have been studied for this research to identify its effect towards the coating uniformity of geopolymer material on the surface of urea granules. They are inlet air pressure, rate of spraying and dry holding time. A method has been implemented by spraying the urea sample with geopolymer slurry with respect to its variability of inlet pressure, spraying rate and drying time. The spraying process is repeated for 25 times before the sample is put curing. Low pressure and low spraying rate has been identified to produce optimal size of coated sample with average thickness of 200 μm all over the granule. Air inlet pressure at 0.3 bar, spraying rate at 30 rpm and 3 minutes of dry holding time have been identified to be the most ideal parameters that is used to produce coated urea with coating uniformity.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

A century old application, agriculture is infrequently been questioned its necessity for feeding the world's population [1]. Agriculture has always been a vital contributor towards sustaining human life since years ago. With ever rising of human culture and civilization throughout times, farming has seen new turns with its inextricable and an integral part with human daily activities. Change of lifestyle, technology, and especially industrial revolution have played a crucial role in changing the shape of modern agriculture values.

The introduction of agricultural fertilizers have marked the new cultivation revolution with its variety of types and its function to promote and enhance the productivity of commercial crops such as paddy and palm oil. One of the popular fertilizer that is used widely today is urea. As a nitrogen fertilizer, its property of high solubility in water makes it useful for liquid application, and is much lower risk of causing fertilizer burn than other chemicals such as calcium cyanide or ammonium nitrate. But it also causes the nutrients to be absorbed into the soil rapidly and excessively during early plant growth stage. This is due to its vulnerability from volatilization and leaching when applied to crops [2]. Moreover, the denitrification process also happen as the fertilizer nutrient is loss to the atmosphere in the form of nitrogen gas (N_2).

A technique known as control release fertilizer (CRF) has been introduced to counter this problem by using the thin-film technology. This technique works by

controlling the amount of nutrients release from urea fertilizer. It is believed to boost crop yield

while reducing the environmental pollution caused by the hazardous emission such as NH_3, N_2O and etc. from current fertilizer practices [3]. Researchers had been investigating and developing this new technology prior optimizing the absorption of nutrient but at the same time minimizing the impact towards environment. Control release fertilizer (CRF) is granule coated with a mixture of various materials which will reduce the releasing period of nutrients and control the amount of nutrients released to plant subsequently. Figure 1.1 below shows the mechanism of controlled release urea [4]. Low solubility of the chemical compounds determines the slowness of the release in the soil mixture. The coating will ensure the release of fertilizer nutrient is controlled by diffusion.

There are many coating materials that can be used to control the release of urea. However, the geopolymer blends has been proposed to be used as the coating material for this research due to its biodegradable property and environmental friendly on nature. Several aspects need to be considered in conducting the coating process such as the compatibility of the coating material with the substrate and also the environmental aspect.

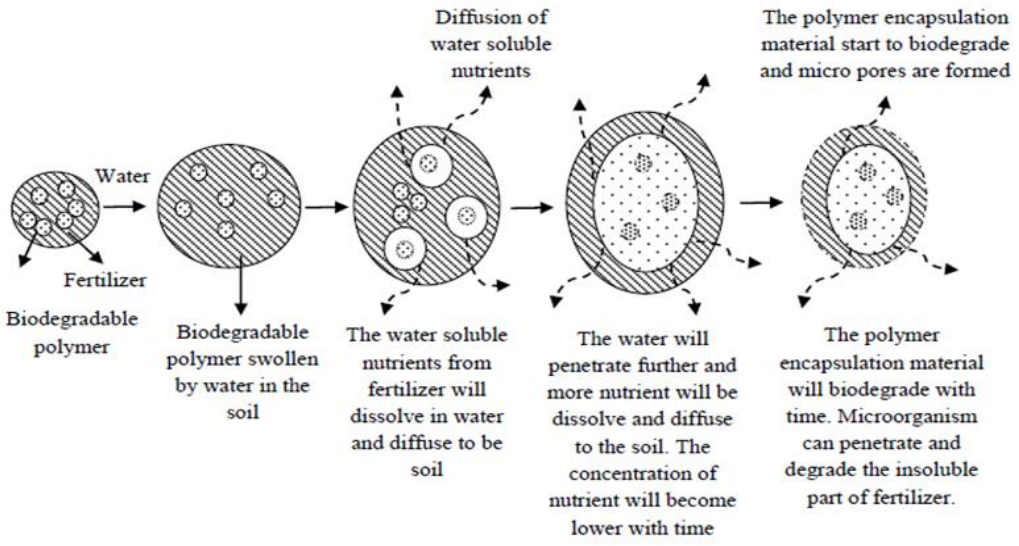


FIGURE 1.1 Mechanism of Controlled Release Fertilizer [4]

1.2 PROBLEM STATEMENT

Recent studies have found out that geopolymer can be developed as a coating material for fertilizer. Studies have proved that geopolymer based coating will make less impact to the environment as compared to the polymer based coating fertilizer. This is because the materials that is use to make the geopolymer itself are very environmental friendly. Rice husk and fly ash are some of the examples of the main materials that have been used to produce geopolymer. One of the important aspect in making coated fertilizer is the coating uniformity. Coating uniformity is crucial to have the urea fertilizer to be released at the specific required time. Therefore, in order to have better coating uniformity by the thin layer film technique, it is important to focus on the parameters that being set up during the experiment. This study will focus on the types of parameters which will affect the coating uniformity of a single granule geopolymer coated fertilizer.

1.3 OBJECTIVES

The aim of this project is to study the parameters that affect the coating uniformity of geopolymer coated urea fertilizer by using a pan coater. The parameters that are being studied are the inlet air pressure, spraying rate of the slurry and the temperature dry holding time.

1.4 SCOPE OF STUDY

The main materials for this project are the fly ash-based powder combined with sodium hydroxide (NaOH) solution and distilled water to make the geopolymer coating solution. As mention above, there are three types of parameters that are being studied namely inlet air pressure, rate of spraying and dry holding time. The scope of the research is to determine the physical properties of the geopolymer thin-film surface of the coated urea granules in which its coating uniformity can be measured based on the three studied parameters by using experimental tests such as hardness strength, and coating thickness.

CHAPTER 2

LITERATURE REVIEW

2.1 Significant of Control Release Fertilizer (CRF)

The world crop yields has been attributed about half of it to natural or synthetic fertilizers [5]. In the early days, controlled release fertilizers are considered too expensive to be used in a small area of production. But the recent development of lower-cost polymer coated urea products has led to consideration of their use in a wide range especially in agriculture sectors [6]. Controlled release fertilizer (CRF) is a purposely designed manure which releases fertilizing nutrients in a controlled, delayed manner in line with the sequential needs of plants for nutrients, thus providing enhanced nutrient use efficiency along with enhance yields [3]. An ideal controlled release fertilizer is the one that coated with a natural or semi-natural, environmentally friendly macromolecule that decelerates fertilizer release to such a slow rate that a single application to the soil can meet nutrient requirements for model crop growth [7].

More than 90% of world production of urea is used as the nitrogen-release fertilizer due to the highest nitrogen content in urea [8]. Since one of the characteristic of urea is high solubility in water, the nutrients can easily escape to the environment. Urea has the highest nitrogen content and not all nutrients are being absorbed by the plant due to vaporization, surface runoff and leaching [9]. Apart from that, the usage of commercial granular soluble fertilizer will cause the hazardous excess release of nitrogen during the beginning of plant growth and deficiency of nutrient towards the

end of growing season. Consequently, the control release urea technology has been initiate to give a steady release of nutrients for the optimum urea availability during growing season [10].

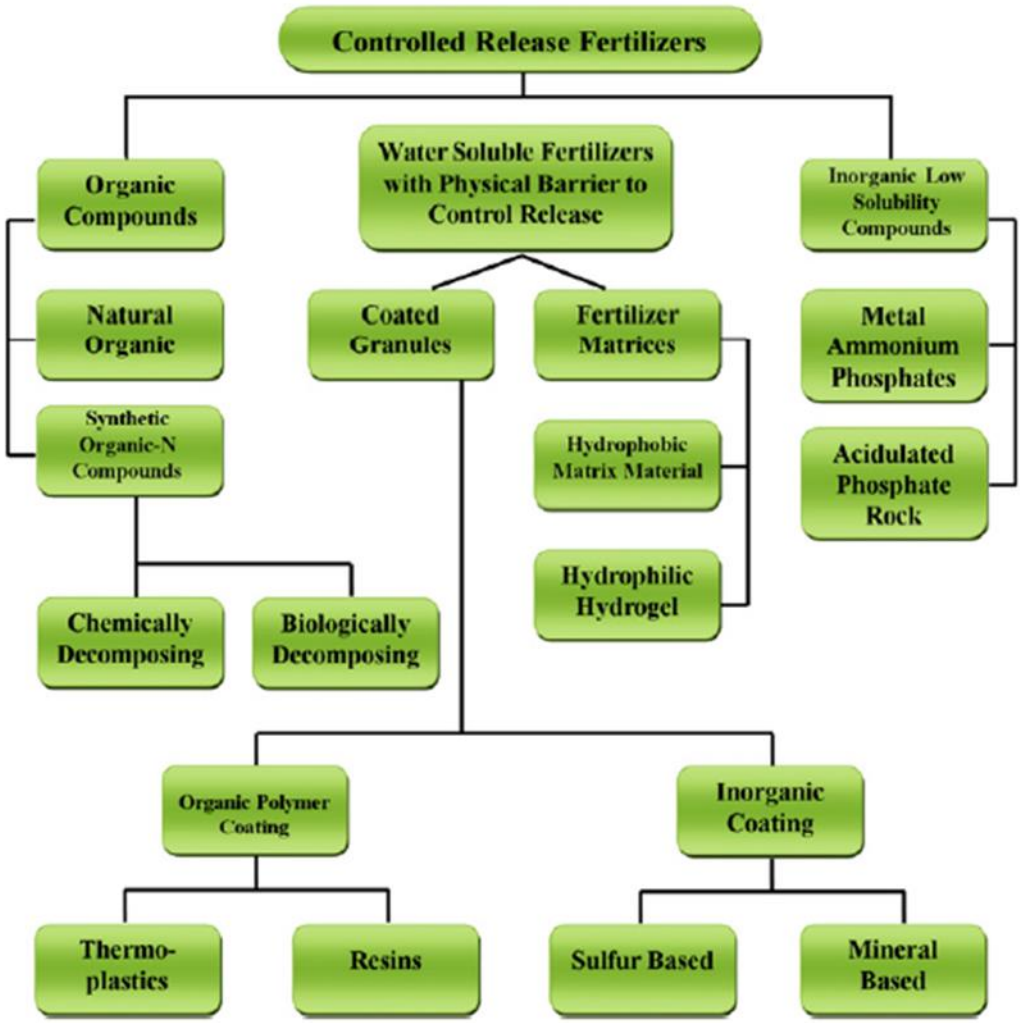


FIGURE 2.1 Classification of Controlled Release Fertilizers [10]

Furthermore, the use of control release urea (CRU) not only minimize the loss of nutrients from the urea but could also expand the crops yield. Kiran et al. [11], has proven this as the rice yields produced from the plant treated with CRU is substantial and performs significantly compared to granular urea. Roughly 40% to 70% of nitrogen in normal fertilizers vaporized to the environment which can give huge impact on economic and the loss of resource as well as environmental pollution [12]. Diagram below in Figure 2.2 shows the diffusion mechanism of controlled release fertilizer. In picture (a) shows fertilizer core with polymer coating while in picture (b) shows water

penetrates into the coating and core granule. Next is the picture (c) showing the fertilizer dissolution and development of osmotic pressure and lastly, picture (d) displayed the controlled release nutrient diffuse out through swollen coating membrane.

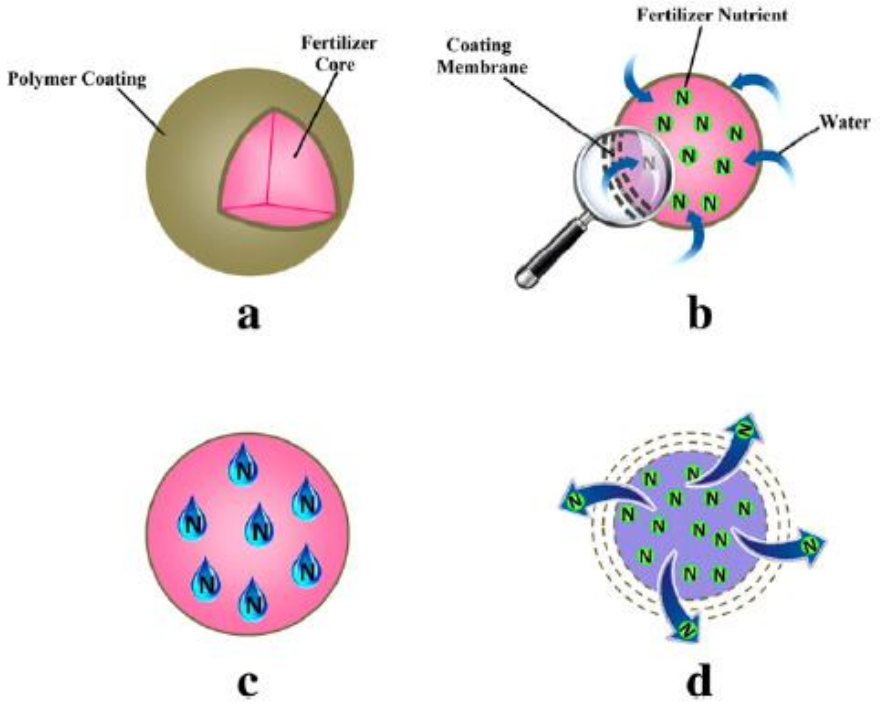


FIGURE 2.2 Diffusion Mechanism of Controlled Release [10]

The application of urea is needed to maintain the plant growth. It will be reduced with the use of CRU as it gives prolong nutrient supply. The reduced use of urea will subsequently reduce the environmental impact as the increase of nitrous oxide levels in the atmosphere is due to nitrogen-based fertilizer [13]. From the Figure 2.3 below, it shows that the agriculture soil management is the main responsible and the largest contributor of N_2O emission in the United States which is about 68% from the total Nitrous Oxide emission [14].

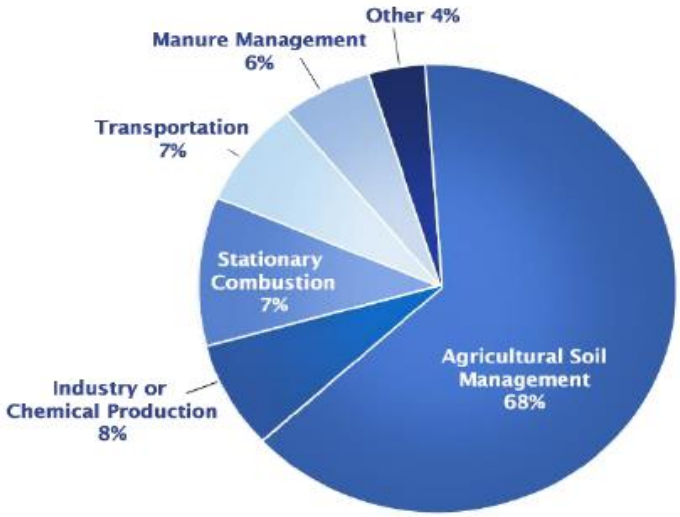


FIGURE 2.3 U.S Nitrous Oxide Emission [15]

2.2 Thin-film Coating Technology

One of the crucial aspect in the process of producing the controlled release urea is a technology known as a thin-film coating. It is used where a thin layer ranging from nanometers to several micrometers in thickness is formed by the coating material [9]. Several techniques are known in performing the thin-film coating. Different techniques have been studied by many researches for the coating process such as fluidized bed, spouted bed, rotating drum, with various coating materials like resin, sulphur, and polymers [16]. During the coating process, the sprayed liquid will mix with the solid bed material [17]. When the coating droplets in contact with the particles' surface, the droplets of liquid will spread over and the solid particle is coated partially. The repeated movement of particles through the spray zone will continuously coat all over the solid material. This resulted to smooth and uniform coating. Diagram below of Figure 2.4 shows the mechanism of fluid bed coating whereby each step of a process starting from spraying, wetting, and recrystallization to finally becomes coated particle.

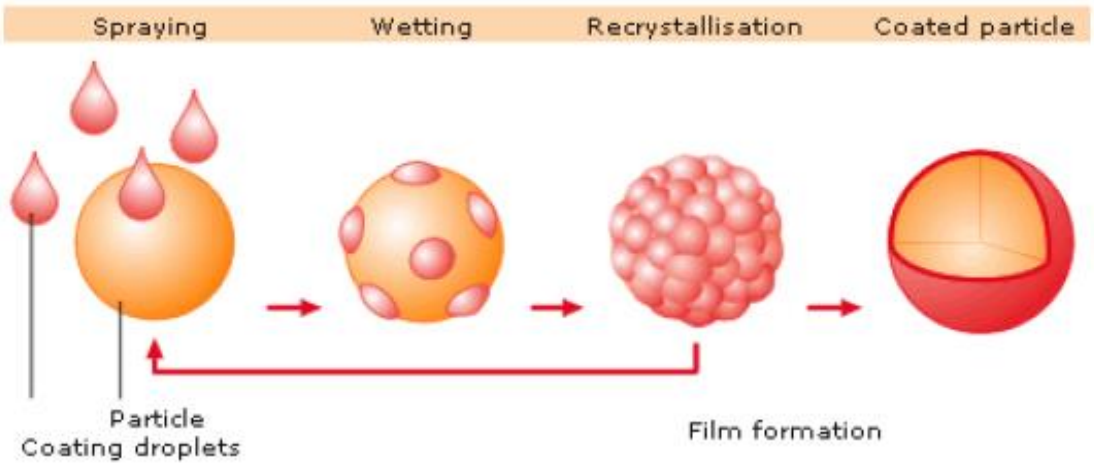


FIGURE 2.4 Fluid Bed Coating Mechanism

2.3 Geopolymer Used for Coating Material

The term "geopolymer" was first used by a man named Davidovits [18, 19] to describe a family of mineral binders which is closely related to artificial zeolites. These structures made up of polymeric Si-O-Al framework, similar to that found in zeolites. The major difference to zeolite structures is that geopolymers are amorphous to X-rays, although the exact nature of this amorphicity is still not completely quantified. As it is generically used to describe the amorphous to crystalline reaction products from synthesis of alkali hydroxide/ alkali silicate solution, geopolymeric gels and composites are also commonly referred to as 'low-temperature aluminosilicate glass', 'alkali-activated cement', 'geocement', 'alkali-bonded ceramic', 'inorganic polymer concrete', and 'hydroceramic' [20]. Geopolymer have been used and applied commercially in construction, fire protection, thermal insulation, etc. From the environmental point of view, CO_2 emission is less produced and the consumption of energy is low when geopolymer is used. As a result, the effect of global warming can be reduced and therefore help to save the Mother-nature.

Figure 2.5 below shows a highly simplified reaction mechanism for geopolymerization. The reaction mechanism outlines the key processes occurring in the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate. The figure also describes the activation reaction as an outcome of two successive and controlling stages. The first one is the nucleation, or the dissolution of

the aluminosilicate material and another one is the formation of polymeric species. This reaction is highly dependent on thermodynamic and kinetic parameters [20].

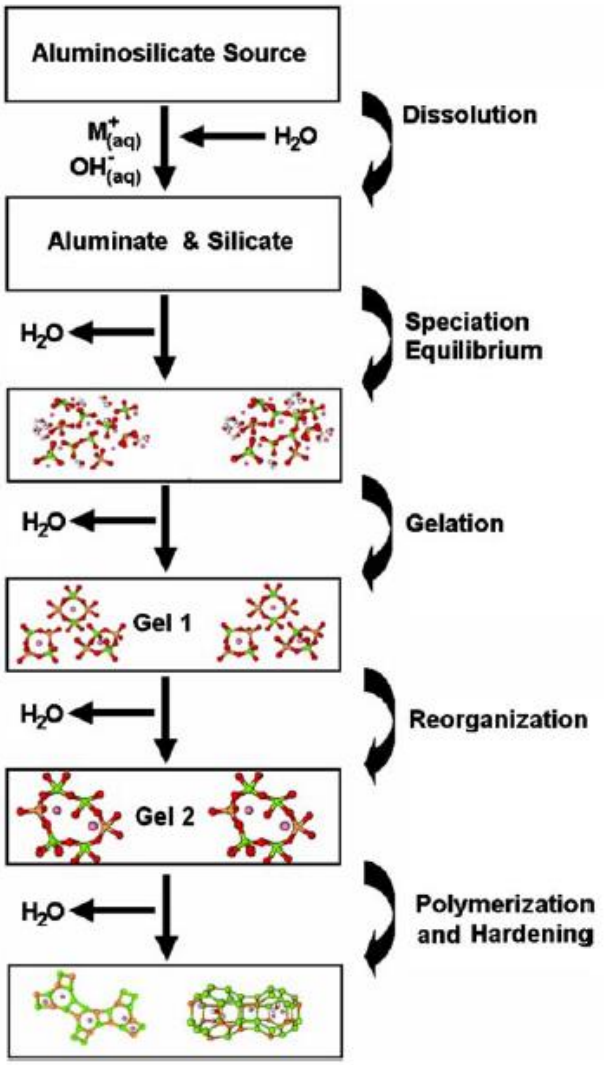


FIGURE 2.5 Conceptual Model for Geopolymerization [20]

2.4 Coating Parameters

Coating is applied for a number of reasons including masking unpleasant taste or odor of the ingredients, enhancing the appearance of the product, modifying its dissolution rate and to add active drug molecules to the tablet [21]. Meeting strict quality control standards for every batch of coated tablets is very tricky. Usually there are an unexpected batch failures that are hard to explain specially due to a lack of

process understanding. Moreover, there is a complex interplay between multiple parameters and device-specific factors within the process itself.

The relative effect of droplet size, impact and frequency, liquid spreading, drying and the ensuing solid-state transformations determine the morphology and quality of the coating [22, 23]. Operational parameters can be divided into two groups during the process of pan-coating. They are pan-and-tablet-related and spray-related [24, 25].

Important pan and tablet parameters are [26]:

- Pan diameter and depth
- Pan speed
- Pan load
- Core shape, size, and mass
- Baffle setup
- Number of spray nozzles
- Pan perforation
- Mechanic tablet properties (e.g. hardness, friability, friction coefficient)

Important spray-related parameters are [26]:

- Spray rate
- Inlet air flow rate
- Inlet/ outlet flow rate
- Inlet/ outlet air humidity
- Atomizing air
- Solution properties
- Nozzle-to-bed distance
- Coating time

Thus, it is crucial to identify these parameters and understand their effect on the product quality. The coating pan's speed of rotation, loading level of the pan, type of spray pattern and the efficiency of nozzles are some of the list of parameters that are being concerned in this study. This study is limited only to the study using a coating pan for the coating process.

2.4.1 Inlet Air Temperature

According to Subramonian S., 2014, temperature is the main key parameter in granulation process at primary alignment as reliability achievement in order bed humidity can be controlled [27]. Not only limited to that, it is crucial for the efficiency of coating [28], enhancing the generation of polymer film [29], coating quality, spreading droplets [30], and particle growth [31]. The solution to tablet coating is to get the film coating dried as fast as it can after it touches the tablet and layer after layer are builds on the tablet surface from time to time.

2.4.2 Rate of spraying

Economics of coating process [32], moisture content [32, 33], film characteristics [34] and particle agglomeration and layering [35, 36] are examples of effects causes by spraying rate parameter. The flow rate rises as the amount of droplets is sprayed onto the tablet rises over time and increase the droplet size [37]. Another one would be an increment to the surface roughness [38].

2.4.3 Pan Rotational Speed

According to Dubey A. et al., 2011, higher bed RPM in which apply more mixing action per unit time will resulted in achieving more uniform application of coating. Higher speed diminished the difference between the 5-circle and 5-ellipse patterns but full and band sprays were not affected [21]. The rotational speed of pan coater influences the motion of the particles affecting the time spent under spray zone [39]. The higher the speed resulted to the breakage of the particles and also reduce the time needed for drying process. On the other hand, low speed might cause the wetting of particle mass to be constrained which leads to agglomeration. Figure 2.6 below shows the effect of rotational speed on coating variability (CV) at a spray rate of 2.316 ml/min.

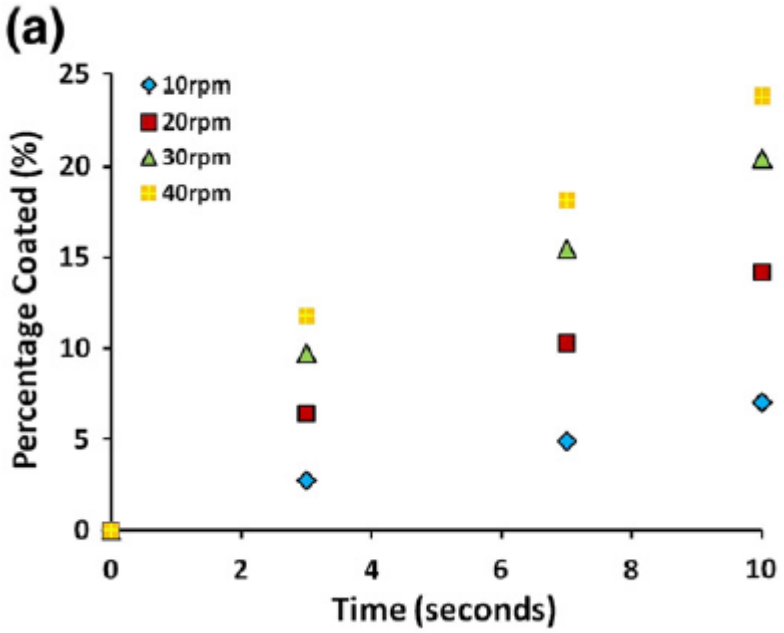


Figure 2.6: Effect of Rotational Speed On Coating Variability [40]

2.4.4 Inlet Air Pressure

Inlet air pressure onto the spray gun plays a crucial role in terms of affecting the spray pattern as well as the size of droplets of the geopolymer solution. At the moment, there has been no extensive studies regarding the effect of air pressure in the spray gun onto the coating uniformity of the coated urea tablets. Further study on this parameter is crucial in order to determine optimum pressure needed to coat the urea fertilizer.

2.5 Coating Uniformity

Tablet coating is a standard process for drug manufacturing [41]. Incorporating active pharmaceutical ingredients (APIs) into the coating layer allows the development of fixed dose combinations of a sustained release dose in the tablet core and an instant release dose in the coating layer [42]. There are two types of coating uniformity which are intra-tablet coating uniformity and the inter-tablet coating uniformity [43]. A successfully coated urea batch will have a prescribed coating thickness on each of urea tablet's surface with little inter- and intra- tablet variability [44]. Inter-tablet coating variability is the dissimilarity in the average coating mass from tablet to tablet [45].

On the other hand, intra-tablet coating variability is the disparity of an individual tablet in the coating thickness [45].

2.6 Pan Coater

Granular mixing is crucial but badly understood aspect of coating of pharmaceutical dosage preparations (tablets) [39]. Pharmaceutical coating of tablet or granular material is normally done in the rotating pan coaters. According to Sahni E. at al, 2011 during the coating, the coating solution is being introduced at distinct locations on the cascading region of the granular bed (as shown in Figure 6), and the liquid jet coats directly a small fraction of tablets only. From the figure below, the granular bed has two regimes in a rotary vessel. The first one is known as cascading layer composing of a thin layer of particles rotating as a fixed bed [46, 47]. The second one known as the quasi-static zone of rotating particles remained as a fixed bed [46, 47]. Coating solution are distributed from these spray locations (specific region (s) of cascading layer) towards remainder of the bed take place by mixing. The information and knowledge of particle flow and mixing in a pan coater is not only important for optimization of the design and operation of such equipment, but also achieving and maintaining uniformity, decreasing product variability, and improving process reliability.

Diagram below in Figure 2.7 shows the spray nozzle is used to spray the coating fluid on a specific portion of the cascading layer [39].

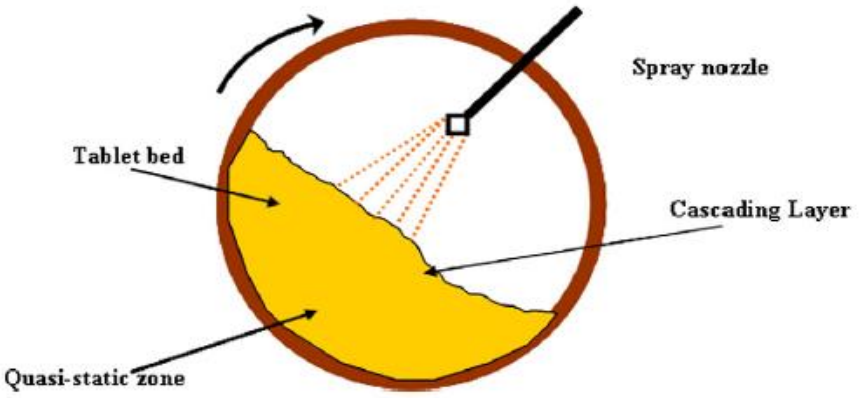


FIGURE 2.7 Sketch of A Granular Bed In A Rotating Pan Coater [39].

Another diagram from Figure 2.8 can be seen which shows a cycle (coating in the spray zone – transportation and drying – re-enter the spray) appears in the most types of coating process [48].

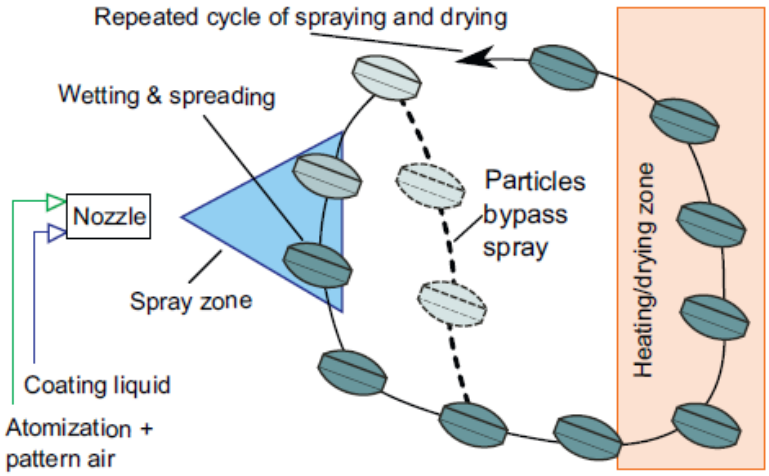


FIGURE 2.8 General Principle of A Particle Coating Process [48].

CHAPTER 3

METHODOLOGY

3.1 Research Methodology and Project Activities

In this chapter, the research methodology of this project will be discussed in details to ensure smooth running of research project activities. The project research is mainly focusing on experimental work. Since geopolymer is still considered as new material and it is first being used as coating material for fertilizers, the results from this research will be compared later with the literature results based on other related coating materials. The completion of literature review proceeded by experimental works. The experiment will be carried out thoroughly and extensively in order to achieve great results. Two important aspects are being focused for this project which is the parameters used for coating process namely inlet air pressure, rate of spraying and dry holding time. Another crucial aspect is the tests that will be carried out to find out which optimal level of these three parameters that would give the perfect coating uniformity of the fertilizer.

3.2 Experimental Procedures/ Approach

3.2.1 Materials Used

The urea granules used as particle cores for this experiment are taken from PETRONAS Chemicals Fertilizer Kedah, Malaysia (PCFK). The size of the urea granules diameter are varied ranging from 2.5 to 4 mm with the volume of 143.8 mm^3

for an average tablet. The granules are sieved in the beginning and are have an average weight of 0.045 gram per tablet. The composition of the urea granule is more than 97% of urea.

3.2.2 Coating Solution

The coating solution is prepared from the combination of fly ash-based powder, sodium hydroxide solution and deionized water. The preparation method and blending ratio for the coating solution is referred from Rosniza et al., 2015 [49] with a ratio of 3:1 of soda ash powder to sodium hydroxide. 600g of fly ash-based powder is used along with 200 gram of NaOH solution of 10M. The deionized water of 100 ml is heated for 30 minutes and followed by added fly ash-based powder and sodium hydroxide (NaOH). The mixture is stirred with magnetic stirrer hot plate for 10 minutes at 80ºC. **Table 3.1** below shows materials used for coating solution.

TABLE 3.1 List of Materials Used For Coating Solution

Materials	**Amount Used**
Fly-Ash powder	600 gram
Sodium Hydroxide (NaOH)	10M, 200 gram
Deionized water	100ml

3.2.3 Apparatus/ Equipment Used

TABLE 3.2 List of Apparatus/ Equipment Used

Apparatus/ Equipment	**Quantity**
Volumetric flask 1000mL	2
Mass Balance	1
Pan Coater	1
Oven	1
Beaker 500mL	3
Measuring Cylinder 100mL	1
Measuring Cylinder 1000mL	1

3.2.4 Procedure with Pan Coater

A pan coater is use to film-coat the urea granules with geopolymer substance. The conditions and settings inside the pan coater are measured and monitored throughout the process. In the control screen, the operation interface is used for controlling the process parameters. The amount of urea granules used as the starting material for this work is 150 gram. Firstly, the urea granules are preheated for 20 minutes. After that, comes the spraying process whereby it is executed for 50 minutes. When the spraying process is done, drying process is performed for 10 minutes.

3.2.5 Procedure without Pan Coater

Firstly, the urea granules are preheated for 5 minutes. After that, comes the spraying process whereby it is executed for about 180 minutes. When the spraying process is done, curing process is performed for 24 hour period. Each run/ experiment is conducted with 25 cycles.

Below is step by step procedures:

1. Geopolymer paste or solution consists of 3:1 ratio (S/L) ratio of fly ash and 10 M Sodium Hydroxide (NaOH) solution. 600 g of fly ash powder and 200 g of NaOH were mixed and diluted by 100 mL distilled water.
2. The mixture was then mixed uniformly at room temperature by a bake mixer for about 10 minutes until the solution is homogenous.
3. Next, urea granules were weighed for 150 g.
4. The spray gun, flow rate meter, pressure meter were assembled and connected to the beaker containing slurry, inlet pressure, and etc.
5. The geopolymer paste (slurry) inside the bake mixer bowl transferred to a beaker and is connected to the flow meter via a HDPE pipe and Polypro pipe to spray gun. For each cycle, the geopolymer paste is spray on top of the urea granules three times in a row from left to right motion. After that, the sprayed urea granules is quickly dried under a hair dryer for a set amount of time (holding time) with the hot air temperature blowing hot air around 55 °C.

6. The cycle is repeated for 25 times for each run until the urea granules are fully coated.
7. After coating process is finished, the coated sample is put in the oven for 24 hour at temperature of 60 °C.
8. The coated sample is then tested for hardness strength, thickness and dissolution.

➢ **Summary of Experimental Procedure**

FIGURE 3.1 Flow Chart of Experimental Procedure

3.2.6 Experimental Setup

Since the pan coater is unable to be used for this respective research project due to time constriction, manual experimental setup has been conducted in order for the experiment to go on as shown in Figure 3.2 (a) below.

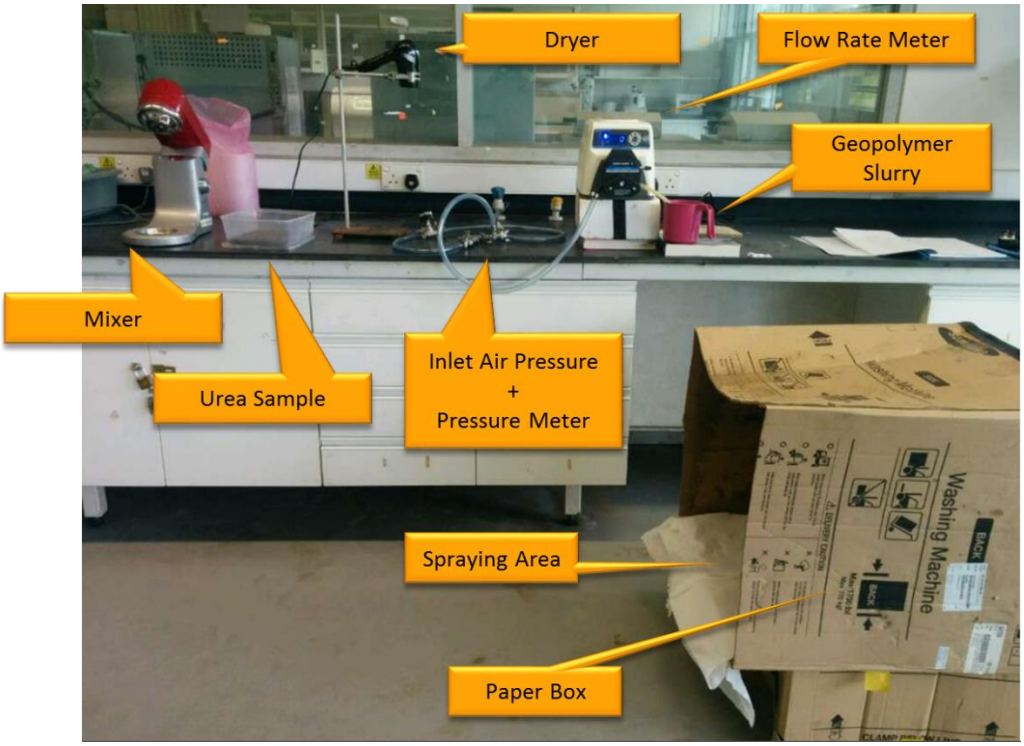


FIGURE 3.21 Manual Experimental Setup

As shown in the picture above, manual experimental setup consists of a bake mixer, a hairdryer, an unused box, a flow meter, pressure meter, and two sets of polyvinyl tube.

Firstly, the geopolymer solution is made by mixing the fly ash powder, ionized water and sodium hydroxide using a bake mixer. This equipment instead of a hand mixer due to large volume and constant mixing to achieve optimum viscosity of solution. After that, the geopolymer solution is transferred to a small beaker as is put near the flow meter. Diagram below shows the flow meter is being connected with a beaker containing geopolymer solution via a polyethylene tube.

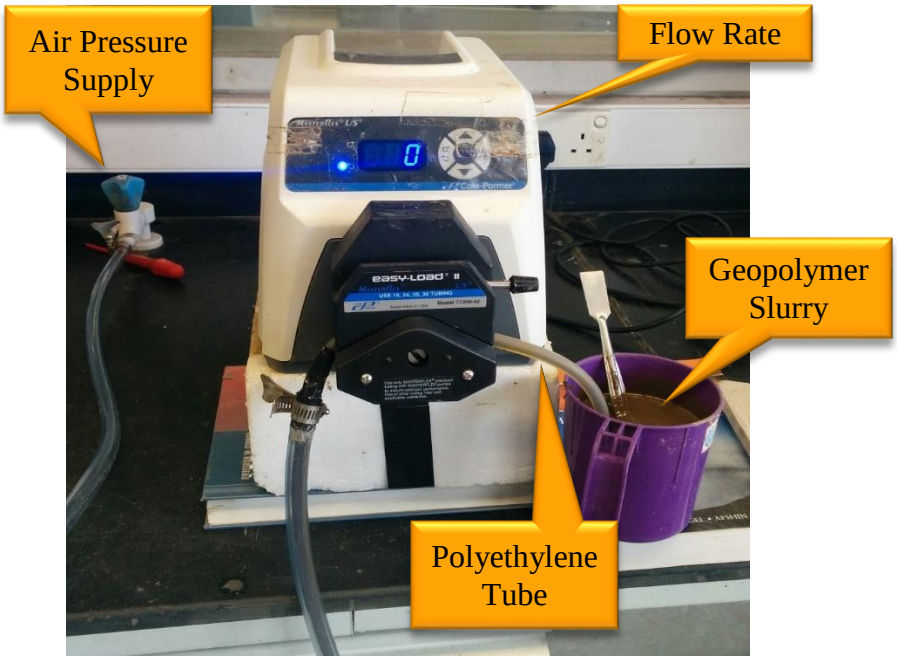


FIGURE 3.22 The Flow Meter Connected To Geopolymer Paste via A Tube

At the same time, a hairdryer is being equipped approximately 40 cm above the table desk using a stand. This hairdryer is used a source of inlet air temperature and also to measure drying holding time of the coated tablet per cycle. Below Figure 3.2 (c) shows the apparatus being setup.

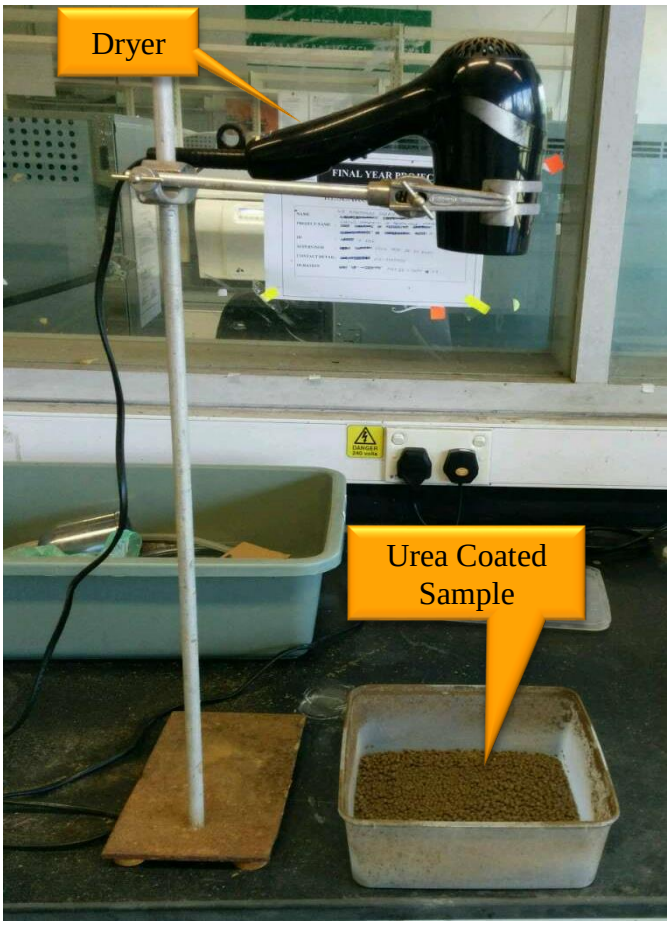


FIGURE 3.23 The Dryer Is Setup above The Coated Tablet

Unused paper/ wooden box is also important as a place for the spraying and shaking process to occur (spray zone). Since shaking, spraying and drying cannot be done simultaneously due to various limitations, the order of the process should be started with spraying, shaking and end with drying. Below is the picture showing a paper box being used as a place for spraying process in Figure 3.2 (d).

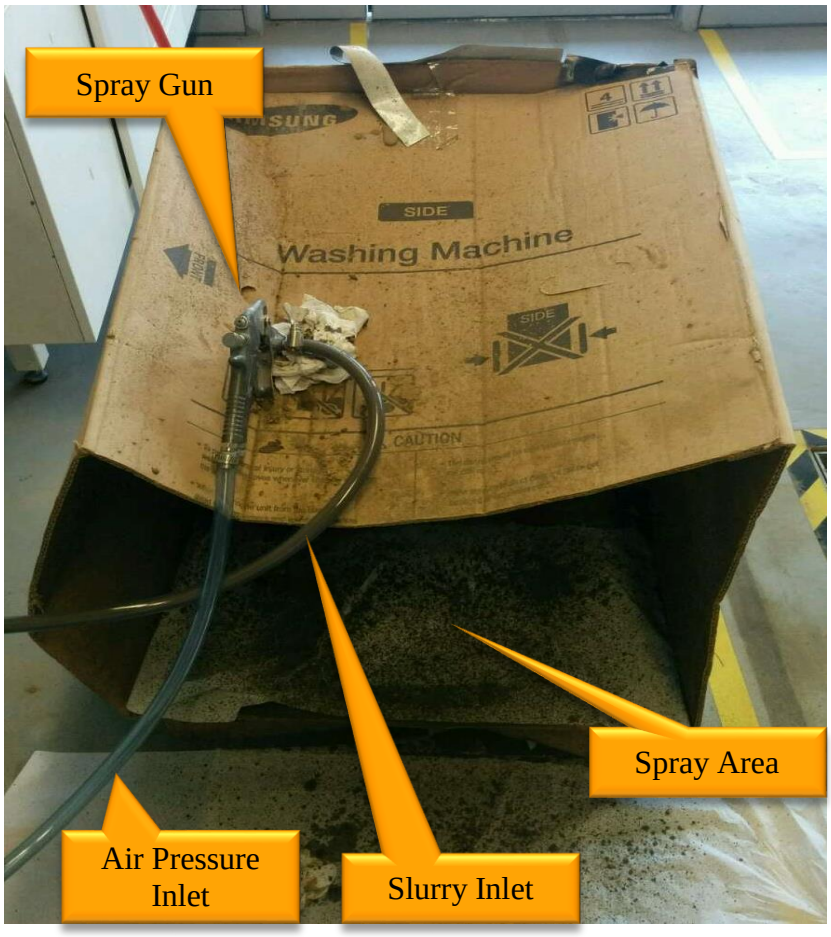


FIGURE 3.24 The Box Used As A Spraying Place

3.3 Evaluation of Coated Urea Granules

3.3.1 Coating Thickness

According to Hassan, from each experiment run, thirty coated urea granules are selected randomly. The coated urea granules are cut diametrically into halves using a sharp knife. Coated urea granules cross-sections are examined under an optical microscope (DM LM, Leica, Germany) (Figure 3.3) under 5x magnifications, with the cut surface facing up. Images are captured with a digital microscope camera with a c-mount interface (DFC 425, Leica, Germany.

FIGURE 3.3 Optical Microscope

3.3.2 Hardness Strength

In every experiment, a number of selected coated urea granules are tested for their hardness strength using Tablet Hardness Tester (Model TBH 325, ERWEKA Corporation, Germany) (Figure 3.4). The coated urea granules are being placed onto the sample support. As the driven force jaw moves towards the sample, it started to increase the force. The force continues to increase as the jaw touches the sample up to the point until the coated urea granule breaks. This resulted to the force values being shown at the display of the hardness tester. The total of 10 randomly selected coated urea granules are being tested after every experiment. Later, the average hardness in Newton (N) is calculated per experiment.

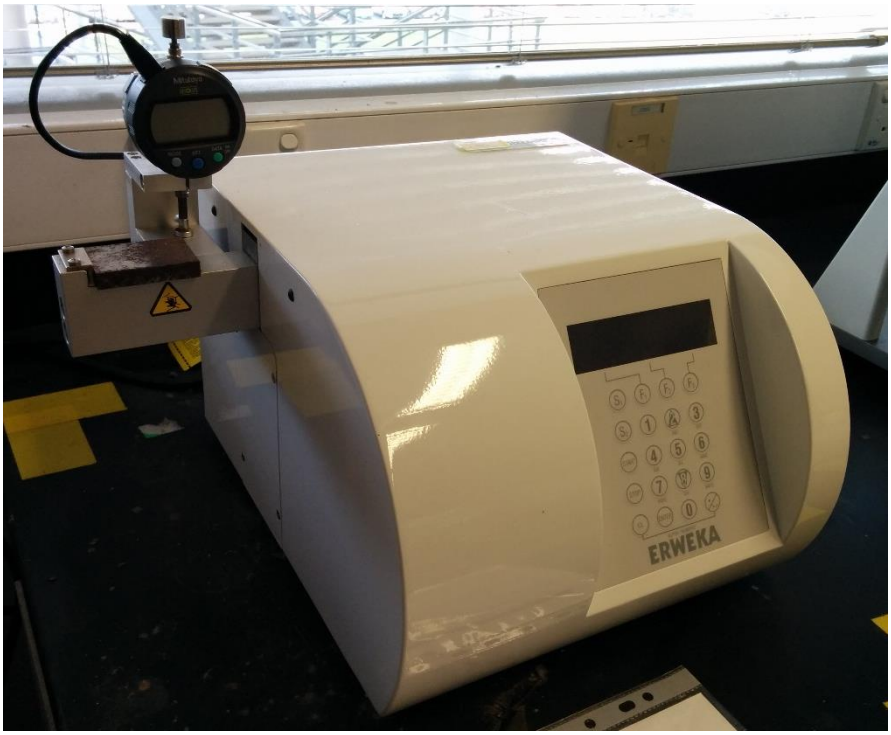


FIGURE 3.4 Tablet Hardness Tester

3.4 Design of Experiment (DOE)

3.4.1 Fractional Factorial Design

It is the most famously and often used types of design in industry. It is an orthogonal array design type that allows experimenters to research main effects and desired interaction effect in a minimum number of trials or experimental runs. According to Box et al., 1978 [50], the designs are normally represented in the form of $2^{(k-p)}$, where k is the number of factors and $1/2^{P}$ represents the fraction of the full factorial.

3.4.2 Two-level Full Factorial Design

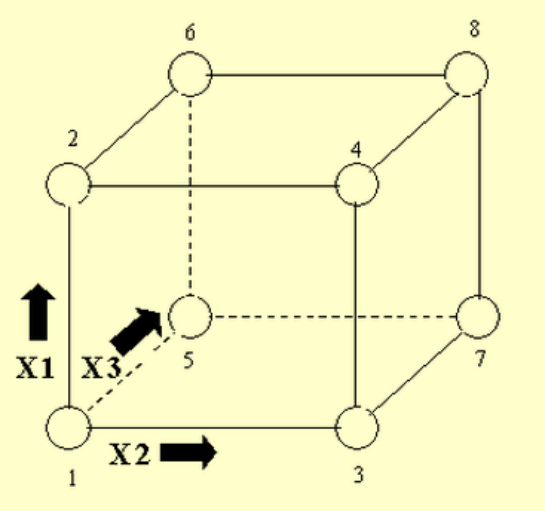


FIGURE 3.5 A 2^3 Two Level, Full Factorial Design

Figure 3.5 above shows the factors X1, X2 and X3 of which the arrows from these three factors pointing at the direction of increasing factors. Consider having a k factors, each run at two levels, therefore it will be 2^k different combination of the levels. In other words, when k = 3 and $2^3 = 8$.

3.4.3 Three-level Full Factorial Design

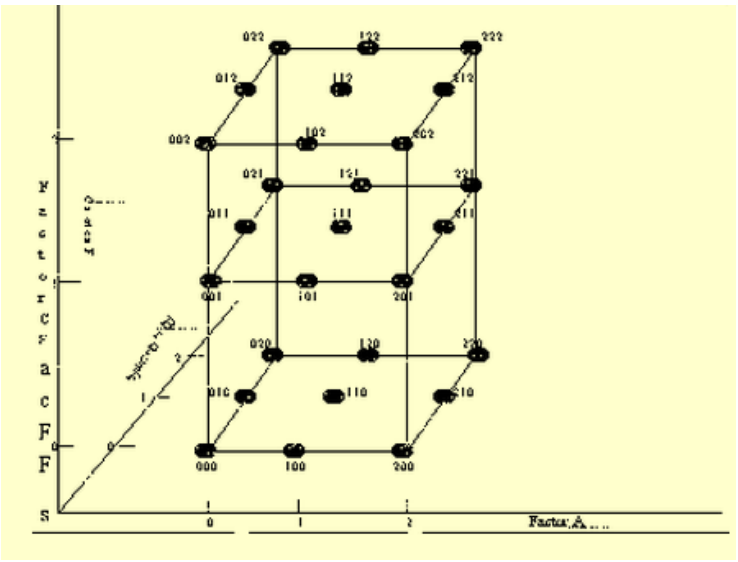


FIGURE 3.6 A 3^3 Design Schematic

Figure 3.6 above shows the design being represented pictorially. Three-level full factorial design is a design that consists of three factors, each at three levels. It can also be expressed as a 3 x 3 x 3 = 3^3 design.

3.5 Experimental Matrix

3.5.1 Preliminary Experimental Matrix (2-Level)

Based on the Table 3.3 below, an experimental layout is designed to find out which from these two-level values for each process parameters that have the most optimum response which they are closes to. The purpose of preliminary experimental procedure is to reduce the error and improve the results by finding the mean values for each process parameters between the highest level and the lowest level. Thus, three level of experimental design can be planned. This will ensure for the final experimental procedure, the experiment will only be conducted within the nearest optimum level of each process parameters. High efficiency of experimental procedure can be achieved.

TABLE 3.3 List of Process Parameters & Their Respective Levels

Process Parameters	**Labels**	**Low Level**	**High Level**
Dry Holding Time (ºC)	**t**	***3 min.***	***7 min.***
Inlet Air Pressure (bar)	**P**	***0.3 bar***	***0.7 bar***
Spraying Rate (rpm)	**R**	***10rpm***	***50rpm***

Below is Table 3.4 which has been designed using Fractional Factorial Design of 2^3. It consists of two level of process parameters.

Table 3.4 Experimental Layout with Response Values

Trial/ Runs	**P (bar)**	**R (rpm)**	**t (minute)**	**Response**	
				R1 (%)	**R2 (%)**
1	**0.3**	**10**	**3**	***r11***	***r12***
2	**0.7**	**10**	**3**	***r21***	***r22***
3	**0.3**	**50**	**3**	***r31***	***r32***
4	**0.7**	**50**	**3**	***r41***	***r42***
5	**0.3**	**10**	**7**	***r51***	***r52***
6	**0.7**	**10**	**7**	***r61***	***r62***
7	**0.3**	**50**	**7**	***r71***	***r72***
8	**0.7**	**50**	**7**	***r81***	***r82***

3.5.2 Final Experimental Matrix (3-Level)

Based on the above two-level design of experiment, an experimental layout Table 3.5, is designed to find out which of these three process parameters based on selected three level design for each process parameters which will give the highest efficiency of perfect coating uniformity.

TABLE 3.5 The 3^3 Design

Trial/ Runs	P (bar)	R (rpm)	t (minute)		
			-1	0	+1
1	-1	-1	-1-1-1	0-1-1	+1-1-1
2	-1	0	-1-10	0-10	+1-10
3	-1	+1	-1-1+1	0-1+1	+1-1+1
4	0	-1	-1+1-1	00-1	+10-1
5	0	0	-100	000	+100
6	0	+1	-10+1	00+1	+10+1
7	+1	-1	-1+1-1	0+1-1	+1+1-1
8	+1	0	-1+10	0+10	+1+10
9	+1	+1	-1+1+1	0+1+1	+1+1+1

3.5.3 Overall Experimental Matrix

TABLE 3.6 Overall Experimental Matrix

Trial/ Runs	Process Parameters					Response		
	B (bar)	C (rpm)	A (minute)					
			-1 ABC	0 ABC	+1 ABC	R1 (%)	R2 (%)	R3 (%)
1	-1	-1	-1-1-1	0-1-1	+1-1-1	*r1*	*r2*	*r3*
2	-1	0	-1-10	0-10	+1-10	*r4*	*r5*	*r6*
3	-1	+1	-1-1+1	0-1+1	+1-1+1	*r7*	*r8*	*r9*
4	0	-1	-1+1-1	00-1	+10-1	*r10*	*r11*	*r12*
5	0	0	-100	000	+100	*r13*	*r14*	*r15*
6	0	+1	-10+1	00+1	+10+1	*r16*	*r17*	*r18*
7	+1	-1	-1+1-1	0+1-1	+1+1-1	*r19*	*r20*	*r21*
8	+1	0	-1+10	0+10	+1+10	*r22*	*r23*	*r23*
9	+1	+1	-1+1+1	0+1+1	+1+1+1	r25	r26	r27

Notation:

Sign	P (bar)	R (rpm)	T (minute)
-1	0.3	10	3
0	0.5	30	5
+1	0.7	50	7

Legends:

Notation	A (minute)	B (bar)	R (rpm)
Meaning	Holding Drying Time	Inlet Air Pressure	Spraying Rate

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Agglomeration of the Coated Sample

Figure 4.1, Figure 4.2 and Figure 4.3 show a distinct difference between three coated urea samples that have gone through same coating process but with different set of levels for parameters. It should be noted that in Figure 4.1, agglomeration has occurred with some of the samples are sticking to each other. There are many factors that can be considered which leads to this situation. Most notably is in terms of the spraying rate.

FIGURE 4.1 Agglomeration Process Occurs At Coated Samples

In Figure 4.2, the spraying rate that is used to create the coated sample is 50 rpm. The agglomeration happens due to wettability of the solution on the surface of the tablets of which it is not dried completely before being applied with the second coating. Besides that, with spraying rate as high as 50 rpm, the amount of droplets that come out from the nozzle of the spray gun is high and has larger size compared with lower spraying rate.

On the other hand, for Figure 4.2, there has been minimum presence of agglomeration of coated tablets as seen in the diagram below.

FIGURE 4.2 Minimum Agglomeration Process Occurs At Coated Samples

The reason is due to the level used for parameter of spraying rate which is 30 rpm. The amount of solution in the form of droplets are sprayed out with less amount than the rate at 50 rpm. Besides that, the size of the droplets is also smaller compared to the one using 50 rpm. Therefore, the wettability of the solution on the surface of the tablet is lesser compared to in Figure 4.1. This causes the agglomeration process to still occur but with minimum presence.

FIGURE 4.3 Zero Presence of Agglomeration Of Coated Samples

Diagram above shows coated tablets with zero presence of agglomeration process which means there is no inter-coated tablets as well as intra-coated tablets occurred. The reason is due to the amount of solution that has been sprayed towards urea samples which is very little since the spraying rate is just 10 rpm compared to 30 rpm and 50 rpm spraying rates that are being used as shown in both figures above. Since the amount of solution that comes out in the form of droplets is low, and the size of the droplets also small, there is little to no chance for the existing or occurring of agglomeration of the coated tablets. It is because the thin-film of geopolymer solution on the surface of the tablet is dried before the new coating is being applied. The thin-film is easily dried compared to using rates of 30 rpm and 50 rpm is because the amount is small. But, the downside of using less spraying rate is that is takes longer for the tablets to be fully coated.

4.2 Analyzation of Coating Thickness

Testing for coating thickness was carried out in order to determine the physical properties of the geopolymer coated sample. This is to ensure that the objective of this project which is find the right coating uniformity is comply with the parameters that have been set up.

Figure below shows pictures of selected coated samples chosen only for dry holding time parameter at t = 3 min. The coating thickness is determined by cutting a granule into half. For each sample, two readings are taken on the cross section of the surface area of half granule. The measured two sides are chosen of which it is diagonally to each other.

FIGURE 4.41 Sample 1 for R=10 rpm & Sample 2 for R=30 rpm at P=0.3 bar

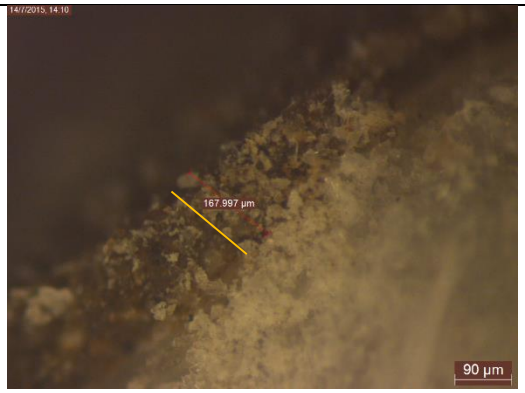
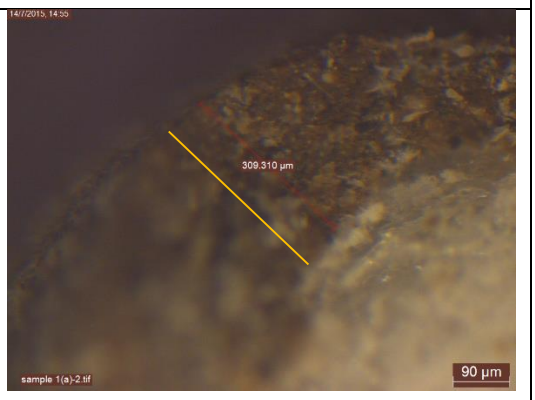
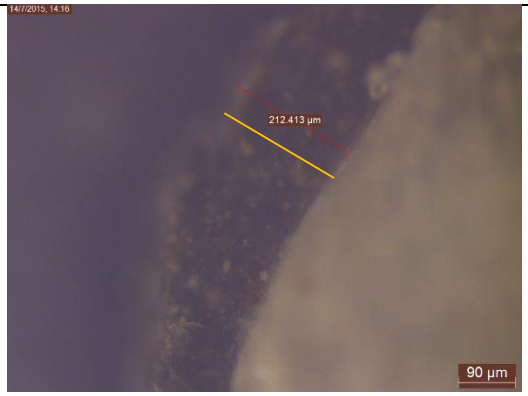
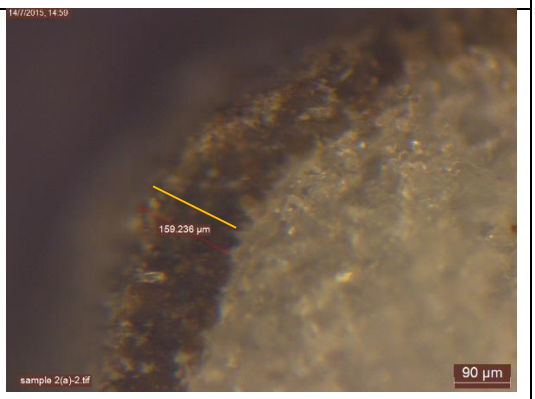
No.	Sample Pictures	
1	 Sample 1(a) – i (top left side) T = 3 min, P = 0.3 bar, R = 10 rpm	 Sample 1(b) – ii (bottom right side) T = 3 min, P = 0.3 bar, R = 10 rpm
2	 Sample 2(a) – i (top left side) T = 3 min, P = 0.3 bar, R = 30 rpm	 Sample 2(b) – ii (bottom right side) T = 3 min, P = 0.3 bar, R = 30 rpm

FIGURE 4.42 Sample 3 for R=50 rpm, P=0.3 bar; Sample 4 for R=10 rpm & Sample 5 for R=50 rpm at P=0.5 bar

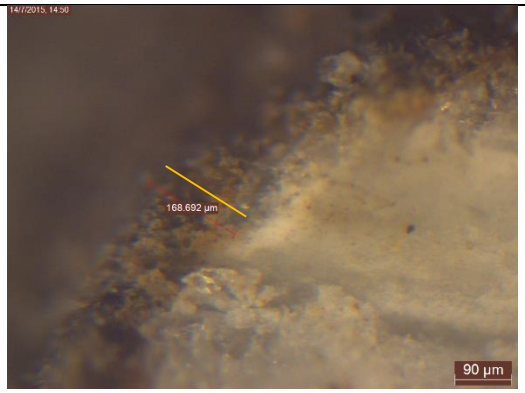
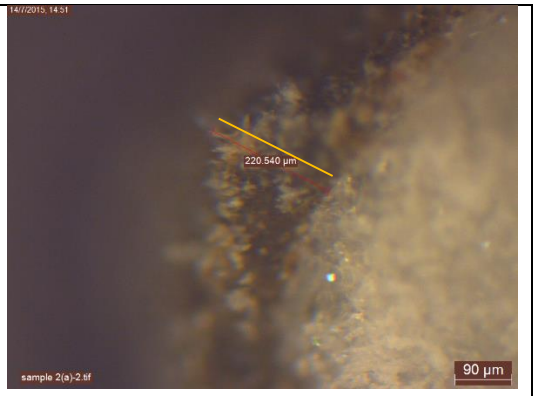
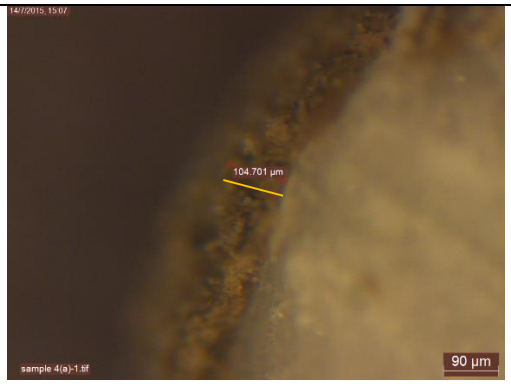
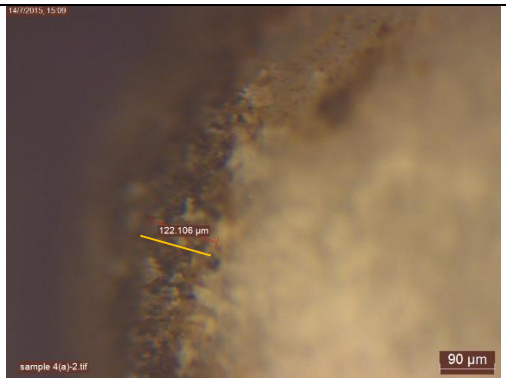
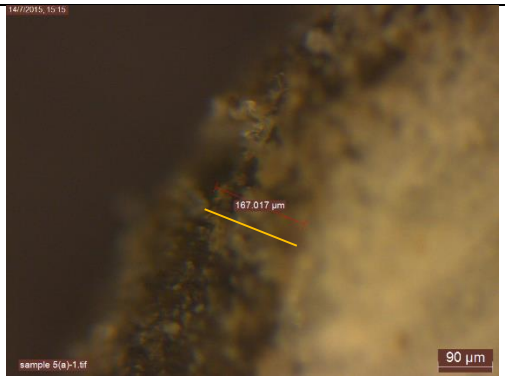
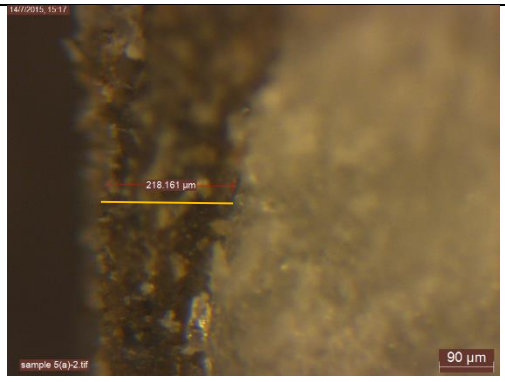
3	 Sample 3(a) – i (top left side) T = 3 min, P = 0.3 bar, R = 50 rpm	 Sample 3(b) – ii (bottom right side) T = 3 min, P = 0.3 bar, R = 50 rpm
4	 Sample 4(a) – i (top left side) T = 3 min, P = 0.5 bar, R = 10 rpm	 Sample 4(b) – ii (bottom right side) T = 3 min, P = 0.5 bar, R = 10 rpm
5	 Sample 5(a) – i (top left side) T = 3 min, P = 0.5 bar, R = 50 rpm	 Sample 5(b) – ii (bottom right side) T = 3 min, P = 0.3 bar, R = 50 rpm

FIGURE 4.43 Sample 6 for R=50 rpm, P=0.5 bar; Sample 7 for R=10 rpm & Sample 8 for R=30 rpm at P=0.7 bar

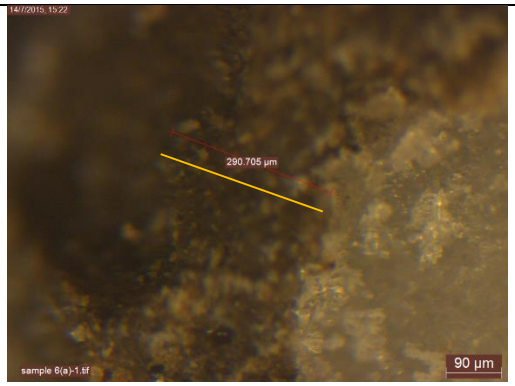
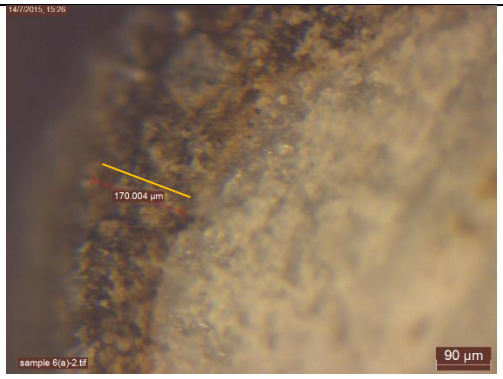
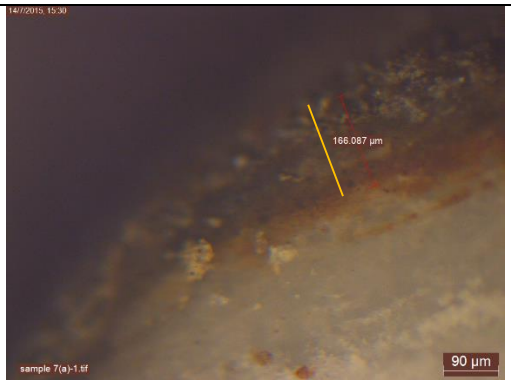
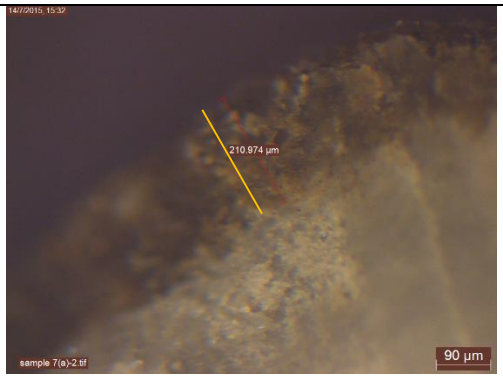
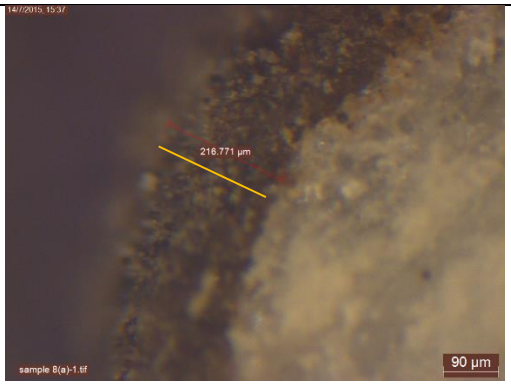
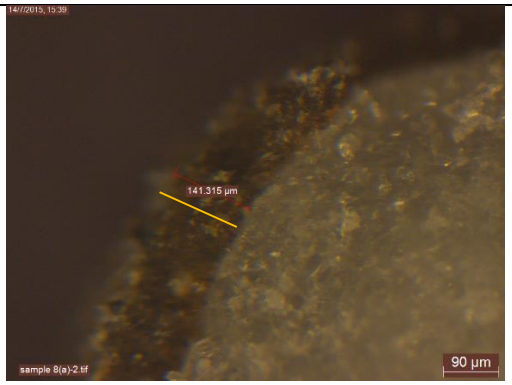
6	 Sample 6(a) – i (top left side) T = 3 min, P = 0.5 bar, R = 50 rpm	 Sample 6(b) – ii (bottom right side) T = 3 min, P = 0.5 bar, R = 50 rpm
7	 Sample 7(a) – i (top left side) T = 3 min, P = 0.7 bar, R = 10 rpm	 Sample 7(b) – ii (bottom right side) T = 3 min, P = 0.7 bar, R = 10 rpm
8	 Sample 8(a) – i (top left side) T = 3 min, P = 0.7 bar, R = 30 rpm	 Sample 8(b) – ii (bottom right side) T = 3 min, P = 0.7 bar, R = 30 rpm

FIGURE 4.44 Sample 9 for R=50 rpm at P=0.7 bar

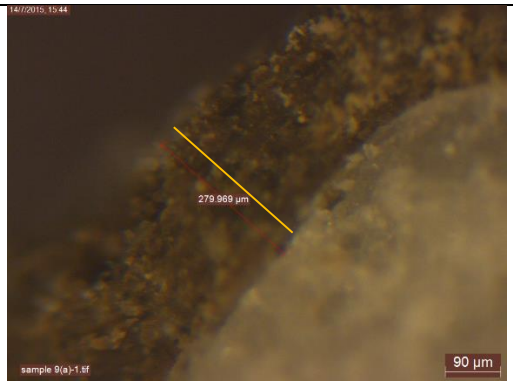
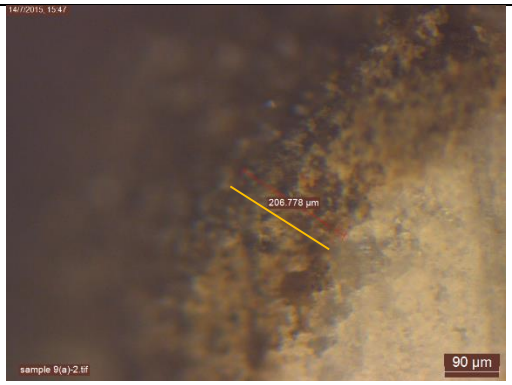
9	 Sample 9(a) – i (top left side) T = 3 min, P = 0.7 bar, R = 50 rpm	 Sample 9(b) – ii (bottom right side) T = 3 min, P = 0.7 bar, R = 50 rpm

Figure below shows an illustration of cross section of a granule and how readings are taken based on sides that diagonal to each other.

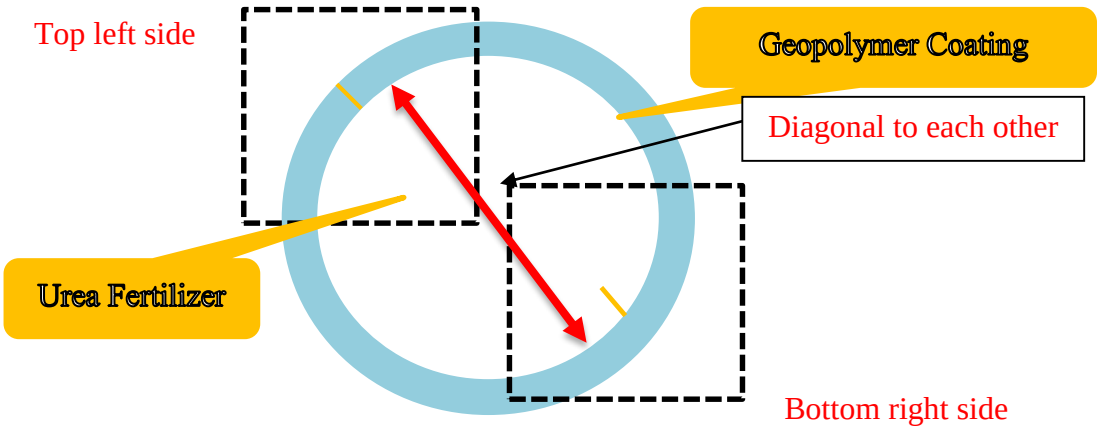


FIGURE 4.5 Illustration of A Coated Granule Measured for Thickness Coating

4.3 Hardness Test

Hardness test is conducted to find out how hard the coating can withstand when being pressurized by certain amount of force. This is important physical property as it effects the reliability of the coating uniformity of a coated granule. As mention earlier in the literature review, hardness of a coating material relates to the amount of slurry that being applied to the urea sample during coating process. Therefore, by knowing the hardness of a coated sample, valuable information regarding other factors such as

coating time, rate of rotation & shaking, and etc., can be predicted mostly by observation during experimental work.

4.3.1 Effect of Inlet Air Pressure

Air pressure is needed in order for the spray gun to be able to force the slurry out from the nozzle with compressed air. Air is being supplied through inlet air source via a tube and is monitored using meter pressure. Optimum level of pressure is not known during the initial experiment of the project. Therefore, the selected level of pressure used in the experiment is considered not accurate and further research is required.

Figure below shows a graph of inlet air pressure against hardness. Clearly from the result it shows that as inlet air pressure increases, the hardness strength increases. The decrement of the hardness when pressure applied is 0.7 bar can be concluded with respect to the effect from other external factors.

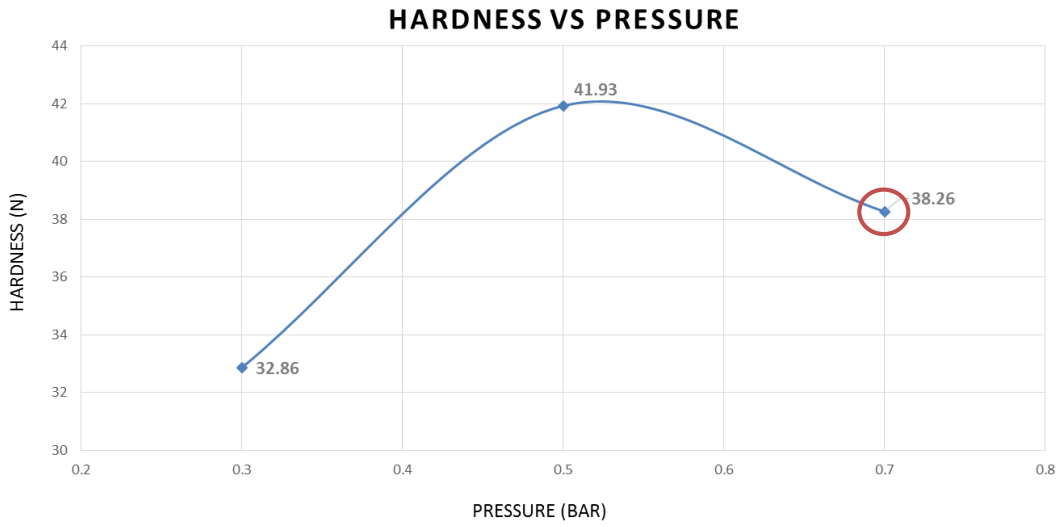


FIGURE 4.6 Hardness Vs Pressure Graph

At dry holding time of 3 minutes, the inlet air pressure is vary at 0.3 bar, 0.5 bar and 0.7 bar. The expected results should be an increment of hardness of a coated sample as pressure increase. The experimental error at pressure 0.7 bar which causes the hardness to reduce from 41.933 N to 38.267 N can be explained largely due to the

influence of inlet air pressure itself. Pressure causes the spraying pattern of slurry to change. As slurry is being sprayed out through nozzle, the pattern can come out in the form of wide, narrow, horizontal and even vertical. Even though horizontal and vertical pattern can be made set at the nozzle, but the force of pressure can somehow able to make the slurry come out in a disoriented pattern.

Same goes to another factor that also being influenced by the pressure which resulted to reduction of hardness of a coated sample that is the amount of slurry droplet. The slurry should sprayed out in the form of small size droplets. On rare occasion, the slurry can come out in the form of large amount at one time. This causes the urea sample to be damaged and messed the coating process. It is very difficult to avoid this circumstances as it can happen anytime at any spraying cycle. The best thing to do when this happen is to start up the coating process with new fresh urea sample.

4.3.2 Effect of Spraying Rate

During coating process, the spray nozzle that creates spray pattern is kept 7 in away from granular bed. The spraying rate is varied using the flow rate meter Masterflex Easy-Load II Model 77200 – 62. The equipment is basically a controller which connected to the peristaltic pump. The slurry is sprayed at three different level of spraying rate which is 10 rpm, 30 rpm and 50 rpm. Figure below shows the variation of the average hardness strength of the coated granules for different spraying rate of coating fluid. In usual case, the hardness strength increases with spraying rate, and the increment in hardness is observed to be directly proportional to coating thickness [39].

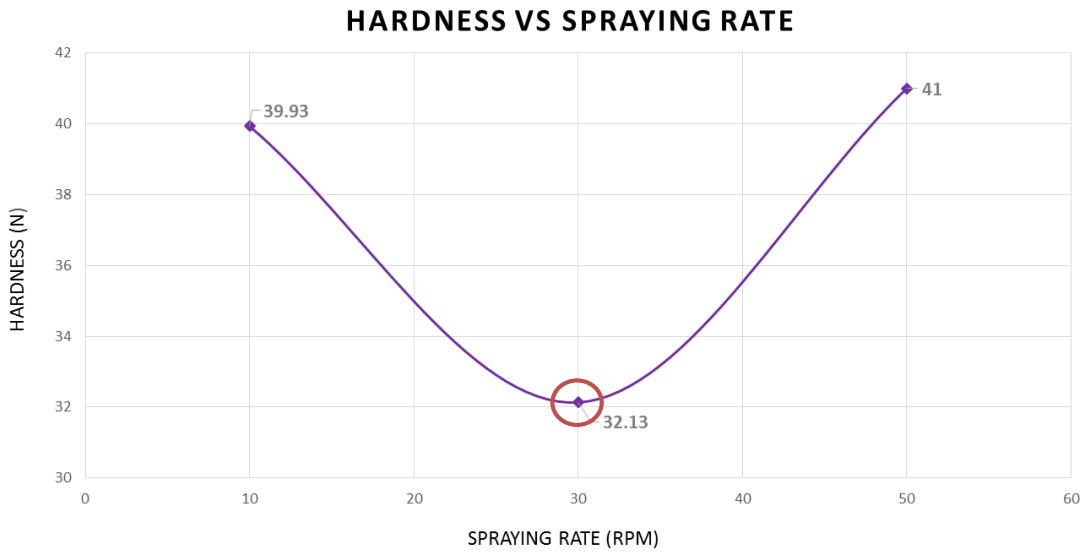


FIGURE 4.7 Hardness Vs Spraying Rate Graph

Based on Figure 4.7, at spray holding time of 3 minute, spraying rate at 10 rpm resulted to 39.933 N of hardness strength. The hardness reduce as spraying rate increase to 30 rpm which is 32.133 N. The hardness is then increased tremendously when spraying rate at 50 rpm is applied at hardness of 41 N. Based on the observation during the experiment, some of external factors have been identified which directly influence the result of the experiment. These identified factors are distance between nozzles and sample (spray zone), fill load and etc. Even though in the beginning of the experiment, the distance is set up to be 7 in between spray nozzle and spray zone, it is very hard maintain the distance as the majority of the experimental work relies upon human factors.

Besides that, fill load which is the amount of slurry being applied towards sample plays a major role in effecting coating uniformity of the tablet. The effect of fill load on the distribution of coating thickness among the tablets subsequently affects its hardness. Based on literature review, 67% fill load is found to be better than 100% fill load using pan coater [21]. In contrast to this research project, the amount of fill load being applied is near to impossible when it comes to measuring it due to the technique used which is thin-film coating and also the container used to put sample during coating process.

4.4 Thickness Test

The purpose of thickness test is to figure out the length of Geopolymer coating thickness of the coated sample. The reason thickness is being measured is find out the average coating thickness per tablet to ensure coating uniformity achievable. As coating uniformity is describe as having coating material to be equal in every angle and side of a granule. Inter-tablet and intra-tablet coating are the consequence that need to be avoided during coating process.

4.4.1 Inlet Air Pressure

Based on Figure 4.8 below, the graph of thickness versus inlet air pressure shows a parabola shape of which the coating thickness is higher when inlet air pressure is 0.3 bar and 0.7 bar compare to at 0.5 bar. The trending indicates that inlet air pressure plays a major role in determining the thickness of geopolymer coating of a sample.

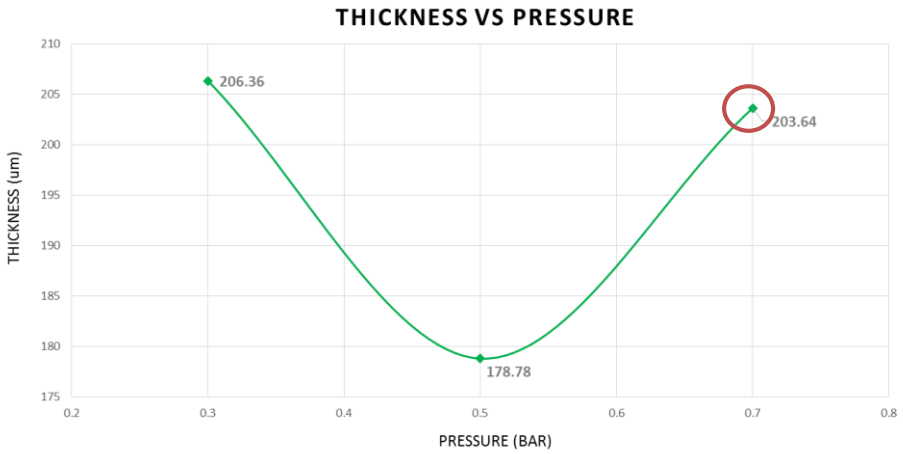


FIGURE 4.8 Thickness Vs Inlet Air Pressure

At dry holding time of 3 minutes, definite explanation based on experiment of which thickness at inlet air pressure 0.7 bar at 203.649 μm is higher than 0.5 bar at 178.782 μm is due to the different in rotational speed for each cycle, angle of tilting, and coating period. These three factors are some of the examples of external factors that cannot be controlled during the experimental set up. During the experiment, rotational speed must be constant and continuous throughout the 25 cycles for each

sample. Since the rotating and shaking motion is done manually by the author, it is very hard to actually maintain the speed due to fatigue and cramps of muscle. Same goes to the angle of tilting of the rotating container, which directly and indirectly affects the coating sample outcome. From the literature review, upon mixing as tilting of the container/ pan actually enhances axial mixing of the granular bed that resulted to better coating. Coating non-uniformity can happen when the variability increased as an effect of extreme high tilt [51]. Coating variability has been found out to be decreased as the tilt increased [51].

4.4.2 Spraying Rate

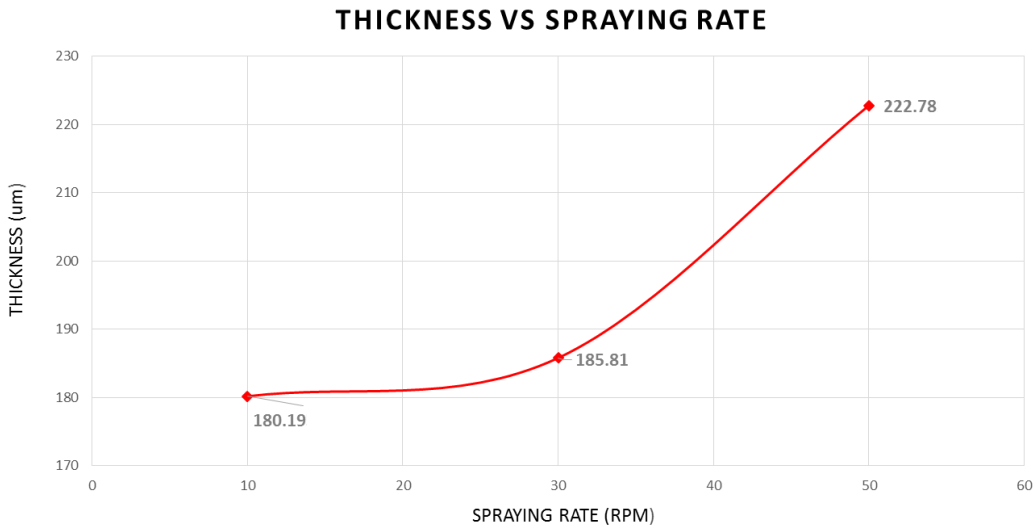


FIGURE 4.9 Thickness Vs Spraying Rate graph

According to above Figure 4.9, the higher the spraying rate, the higher the thickness. This is shows that spraying rate is one of the important factor in ensuring the thickness of the geopolymer coated sample can be controlled. The simple explanation of this case is that as spraying rate increases, more geopolymer slurry is being apply on top of the granule bed by layer after layer. There is also a downside to this method that is as the spraying rate goes higher, fill load is getting thicker on the top surface of the granule bed. Thus, making it harder to dry as preparation for the next coating layer. As the process run, number of urea sample stick to each other increasing. This phenomena is what we called inter and intra tablet coating. Agglomeration is the perfect example of the effect of this phenomena. In order to find the perfect coating

uniformity of urea sample, the selected parameters that are being used during the experiment must give the minimum amount of agglomerated of coated urea sample.

Large quantity of agglomeration of coated urea sample is a sign that the level of parameters used are not suitable. Coating uniformity will be unachievable if this process is to be let happen. Further research must be done to find the best optimal spraying rate that can give absolute perfect of coating thickness which led to great hardness strength and eventually produce a sample with coating uniformity.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The coating of urea is needed to avoid unnecessary nutrients loss through leaching, volatilization, and denitrification. Geopolymer is the future substance that should be used as coating material and further research must be made in order to find out the potential of this material towards other application in agriculture industry. An efficient control release fertilizer provides necessary nutrients for plant to grow at the right time with the right nutrients amount. From this study, it shows that the three selected parameters are highly important in ensuring the coating uniformity of the coated samples. Coating uniformity can only be achieved when the thickness of coating is consistent all over the granule. The targeting coating thickness is 200 μm all around the urea granule. Hardness test is also crucial as it relates on how thick the coating should be which reflect on how much the nutrients can be released on certain time. Based on this research, it can be concluded that low air inlet pressure of 0.3 bar, low spraying rate of 30 rpm and low dry holding time of 3 minute are the best parameters to be used to coat a perfect sample and attain an ideal coating uniformity. Even though based on experiment, it shows that higher spraying rate leads to higher coating thickness, but there is a downside of using too high spraying rate. High pressure and high spraying rate can cause agglomeration to the sample which can cause non-uniform coating. Further research of this project should be made using an equipment such as pan coater or fluidized bed in order to reduce human error. Other factors should also be considered when conducting the experiment such as fill load, angle of tilting, and spray patterns.

5.2 Recommendations

i. The measured values for thickness test should be increased for consistency and accuracy. For example, instead of taking 10 readings for each sample, make it 30 readings for high consistency and accuracy.

ii. The knife used to cut the coated urea sample must be very sharp so that it will not damage the coating part of the granules.

iii. For the preparation of slurry, reduce the ratio of fly ash powder to sodium hydroxide solution by half. Changing it from 600 g of fly ash to 300 g and from 200 g of sodium hydroxide solution to 100 g. This is because ratio of materials mixing in slurry affect the coating appearance as well as its ability to coat. Thus affect the coating uniformity of the sample.

iv. Air humidity should be controlled by running the experiment in a vacuum room. This is because air humidity can affect the surface of urea sample and the wettability of geopolymer slurry on the urea sample.

v. Geopolymer slurry cannot be left for too long without being stirred as it gets harden easily due to its cementing ability. Therefore, in the future experimentation while coated sample is being dried under the dryer, the slurry is put into a stirrer.

vi. The spray gun tends to shoot large amount of slurry and not in the form of droplets especially after one spraying process has done. Use high spec spray gun instead of cheaper one.

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APPENDICES

6.1 Flow Chart of Research Activities

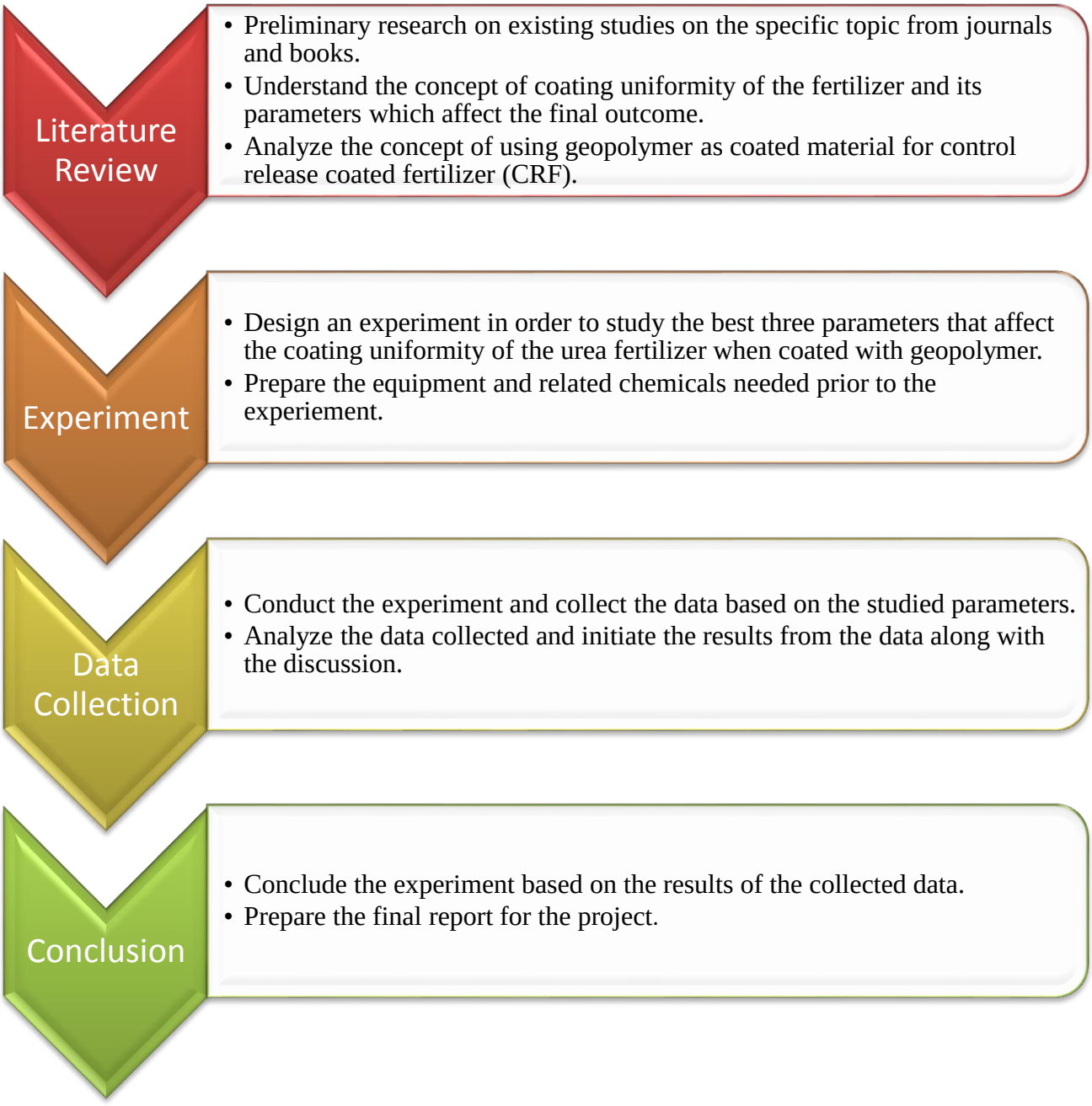


FIGURE 6.1 Flow Chart of Research Activities

6.2(a) Gantt Chart

	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic														
2	Preliminary Research Work														
3	Submission of Extended Proposal														
4	Proposal Defense														
5	Project Work Continues														
6	Submission of Interim Draft Report														
7	Submission of Interim Report														

TABLE 6.1 Project Timeline for FYP I

Process **Suggested Milestone**

6.2(b) Gantt Chart

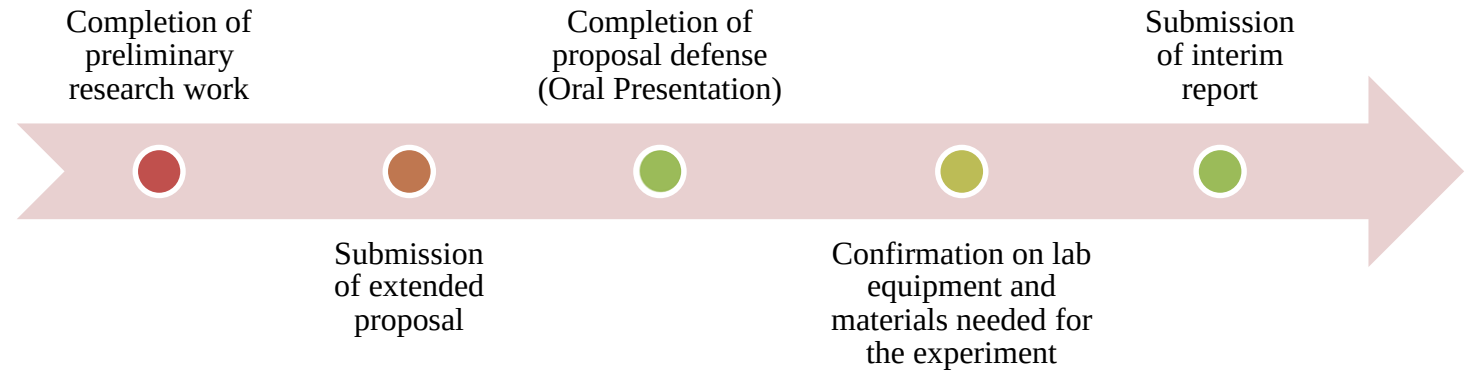
	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continues														
2	Submission of Progress Report														
3	Project Work Continues														
4	Pre-SEDEX														
5	Submission of Draft Final Report														
6	Submission of Dissertation (Soft Bound)														
7	Submission of Technical Paper														
8	Viva														
9	Submission of Project Dissertation (Hard Bound)														

TABLE 6.2 Project Timeline for FYP II

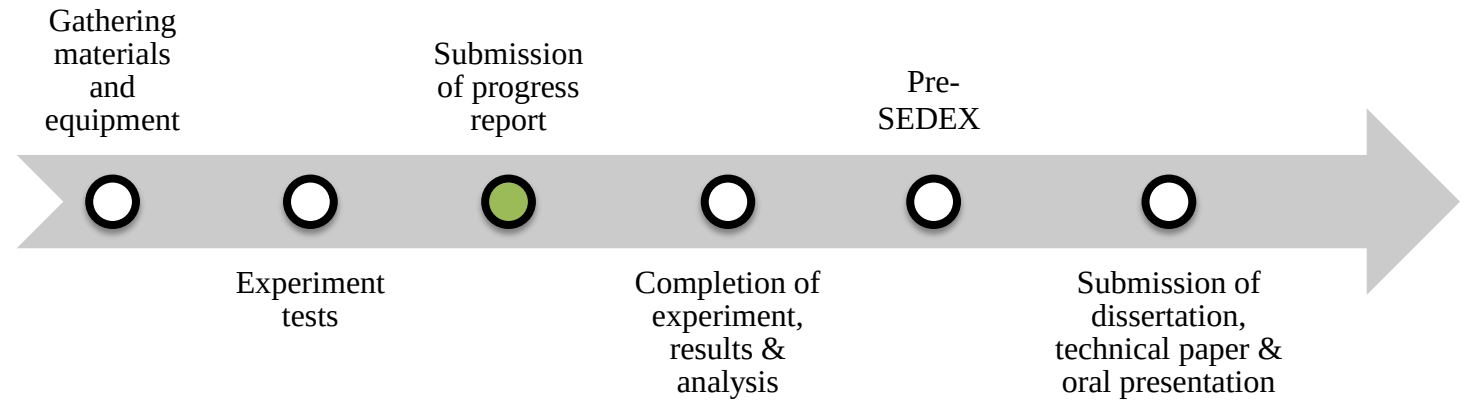
Process **Suggested Milestone**

6.3 Key Milestone for the Project

FYP I



FYP II



6.4 Pan Coater Design (Initial Concept)

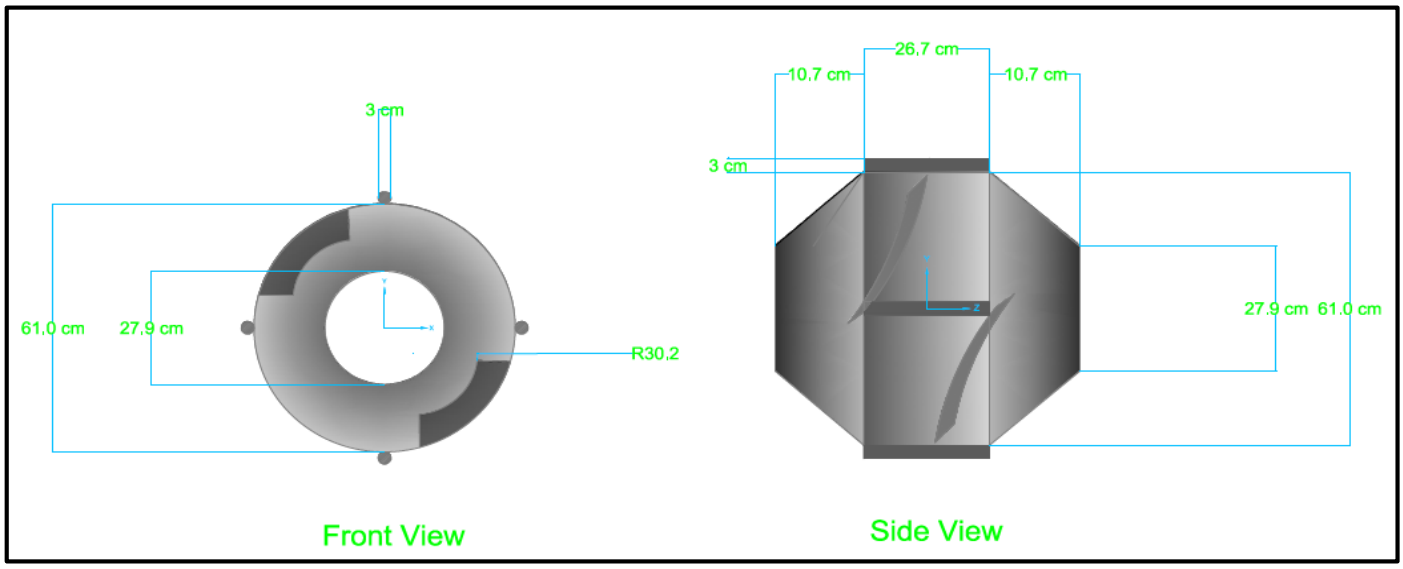


FIGURE 6.2 Schematic Diagram of Pan Coater Design

6.5 Coated Urea Fertilizer in Process

FIGURE 6.3 Coated Urea Fertilizer in Process

6.6 Finished Coated Urea Fertilizer

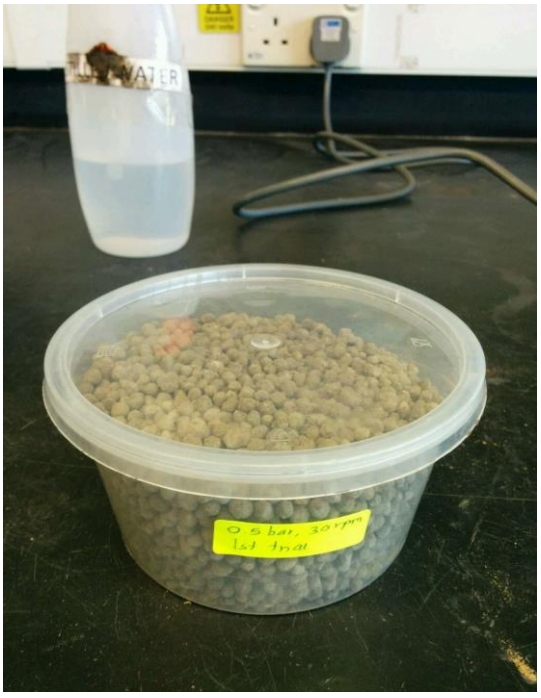


FIGURE 6.4 First Trial of Coated Urea Fertilizer

FIGURE 6.5 Second Trial of Coated Urea Fertilizer