The Effect of Milling Time in Production of Urea Compound by Ball Milling Technique

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Abstract— **The aim of the paper was to investigate the optimum milling time in production of urea compound through ball milling techniques by varying the time taken for the tendency of urea to avoid become hygroscopic in order to generate quality urea fertilizer that will not cause hydrate formation in the presence of water that will make the mixture wet and sticky. The effect of the milling time and mixture content was investigated. Physical observation showing that with prolonging the milling time, the mixture becoming from powder form to clumped. Through FTIR, the milling process of 2 minutes recorded moisture loss of 21.7% and 4.34 mg weight loss, while 4 minutes is at 24.01% with 4.80 mg, 6 minutes at 30.46% and 6.09 mg, 10 minutes is at 28.4% and 5.70 mg and 12 minutes at 25.28% and 5.06 mg of moisture loss and weight loss respectively for all of the samples that being milled. The ideal and optimum milling process for the urea calcium phosphate is to be suggested at 2 minutes with the lowest moisture and weight loss**.

Keywords— milling time, urea, calcium phosphate, milling techniques, FTIR, XRD, TGA

I. INTRODUCTION

Fertilizer production and consumption has increased in the past decade and there is sign that this will continue to grow and increase. Since the end of war, total production of phosphate fertilizers has already doubled [1]. Ever since the demand of fertilizer has been increased, the fertilizer production trends has rapidly changed since then as the competitiveness of producing fertilizers are tight. Several types of fertilizers are being used namely organic fertilizer and chemical fertilizer to expand the productivity of food crop in nation [2]. In Malaysia, mineral fertilizers represent more than 90 percent of manures utilized by a wide range of cultivating frameworks in Malaysia. There has been a comparing increment in manure use due to the rapid development in crop production, particularly of estate crops. Potassium fertilizers have demonstrated the biggest increment and exceptionally powerful for the yields.

The final production of urea fertilizer production operation is in either prilled or granular form. Both of the production form from urea melt requires the use of a large volume of cooling air which subsequently discharged to the atmosphere.

Pure urea when exposed to the air shows no tendency to absorb moisture, but it will become a remarkably hygroscopic substance if the humidity of the air is relatively at high level. It shows that different mixture of urea becomes hygroscopic at different humidity condition.

High energy ball milling (HEBM) is known as an monetary, straightforward, yet capable strategy for the creation of nanostructured and amorphous materials [3].

There are advantages in using this high energy ball milling technique which is one, it is greatly increased the density of the bulk fabricated. Secondly, the sintering temperature and dwell time are decreased greatly by this high energy ball milling technique due to the effective shortened length of diffusion paths [4]. The tensile and yield strength were also increased with increasing ball milling time and it has shown a significant increase in elongation as well [5]. Relentless state milling time was assessed by [6] in four diverse processing conditions with the same mill speed and charge ratio yet different ball sizes. Some other thought taken in to assess are the changes in shape, size, crystalline imperfections and orientation [6]. The aim of the paper was to investigate the optimum milling time in production of urea through ball milling techniques by varying the time taken for the tendency of urea to avoid become hygroscopic in order to generate quality urea fertilizer that will not cause hydrate formation in the presence of water that will make the mixture wet and sticky.

II. METHODOLOGY

A. Materials

The materials that being used in this study are urea $CO(NH_2)_2$ with a bulk density (700 – 800 kg/m^3 at 20 ºC), melting point at range 132 to 135 ºC which was supplied by R&M Chemicals and calcium phosphate $CaPO_4$, which supplied by R&M Chemicals with melting point of more than 450 ºC. These two chemicals were used as received. Mechanosynthesis is a dry preparation method where both raw materials of urea $CO(NH_2)_2$ and calcium phosphate $CaPO_4$ are used to obtain the $CaPO_4.4Co(NH_2)_2$ ionic co-crystal with reactant ratios of 1:2.

B. Preparation Stage

The preparation stage is done with 2grams total of urea (analytically pure) and calcium phosphate were weighted with the ratio of molar 1:2 (1 mole of calcium phosphate react with 2 mole of urea).

The mixture is loaded into a stainless steel jar where the stainless steel milling balls were sealed in and ground at 30 Hz speed in a Retsch MM400 mixer mill. Total mass of powder was 2 g. The weight ratio of ball to powder as kept at 10:1.Milling process is the process of milling mixture of urea and calcium phosphate to form the product by mechanomical reaction.

B. Characterization Stage

The product samples are analysed to see the thermal stability using Thermogravimetric Analysis (TGA) using nitrogen as carrier gas with heating rate of 10 c/min and heating range of 25 ºC to 700 ºC. The existing bond and wavelength were tested using Fourier Infrared Spectroscopy (FTIR) of standard test method ASTM D3403 and using X-Ray Diffraction (XRD, Rigaku X-Ray Diffraction) in determining the crystallographic structure and element of crystalline

material. Fig 1 showing the flow of the process of the milling process for urea calcium phosphate.

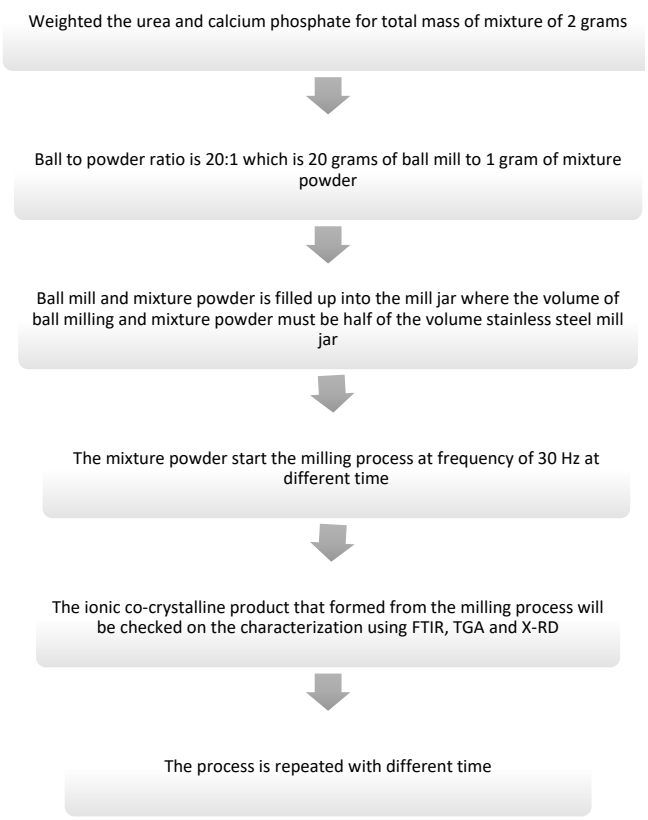

Fig 1: Flow process of the milling for urea calcium phosphate

III. RESULTS AND DISCUSSION

A. Physical Observation

The milling process for urea calcium phosphate has been done at different time at 2 minutes, 4 minutes, 6 minutes, 8 minutes, 10 minutes, 12 minutes and 14 minutes. Urea appearance form is solid white color while calcium phosphate is in crystalline white form before grinding and mixing them both into stainless steel jar where stainless steel milling balls were sealed in and ground at 30 Hz in a Retsch MM400 mixer mill.

Urea with bulk density of 700 to 800 kg/m^3 and melting point of 130 to 135 ºC has a molecular weight of 60.06 g/mol while calcium phosphate melting point of more than 450 ºC has a molecular weight of 252.08 g/mol, which both of the chemicals are supplied by R&M Chemicals. The molecular weight of urea and calcium phosphate is used to calculate the mass that needed for the milling process as shown in the calculation above so the mass of urea to calcium phosphate proportion is at exact weight of 2 g.

All the mixtures of urea and calcium phosphate of different time giving different appearance form. As shown in Figure 3, milling the mixture after 2 minutes gives the appearance of white powder, while 4 minutes appears to be in small white flakes. Milling for 6 minutes and 8 minutes showing white flakes as well but milling the mixture for 10 minutes gives the appearance of bigger white flakes. From the figure, after 14 minutes of milling, the mixture texture becomes clumpy, probably due to presence of moisture. As stated [7], grain size of powders increased by prolonging the milling time.

Fig 3: Urea calcium phosphate at different milling time

B. Fourier Transform Infrared Specstroscopy

Fourier transform infrared (FTIR) spectra of the prepared products were recorded with spectrometer ranging from 400 – 1500 cm^{-1}. Figure 4 shows the FTIR spectra for urea after milling for 2 min and 14 min. All the important absorption bands and their assignments for urea has been summarized in Table 1. The interaction between urea and calcium phosphate has been studied by FTIR.

Figure 5 shows the FTIR spectra for urea calcium phosphate after milling for 2 min and 14 min. All the important

Table 1: Assignment of FTIR spectra of Urea and Urea Calcium Phosphate

Samples	IR region of bonds (cm^{-1})	Band
Urea	3751.76	
	3431.28	Alcohol/Phenol O-H stretch
	3328.14	Alcohol/Phenol O-H stretch
	1676.68	Aromatic C=C bending
	1590.93	Aromatic C=C bending
	1458.53	Alkyl C-H stretch
	1150.19	C-O-C stretch
	1045.18	C-O-C stretch
	1002.91	C-O-C stretch
Urea calcium phosphate	3358.21	Alcohol stretch
	3214.56	Alcohol/Phenol stretch
	2368.01	
	1623.06	Aromatic C=C bonding
	1466.61	Alkyl C-H stretch
	1126.62	C-O-C stretch
	1061.99	C-O-C stretch

absorption bands and their assignments for urea calcium phosphate has also been summarized in Table 1.

The particles properties at different interval of time are shown in Figure 1. The transmittance (%) and wavelength number are plotted as a function of particles properties through this method. Raw urea with different interval time at 2 minutes and 14 minutes showing no difference in the peak as the milling time progressed. At wavenumber between 2000 and 1500, a small peak appears at urea 14 minutes.

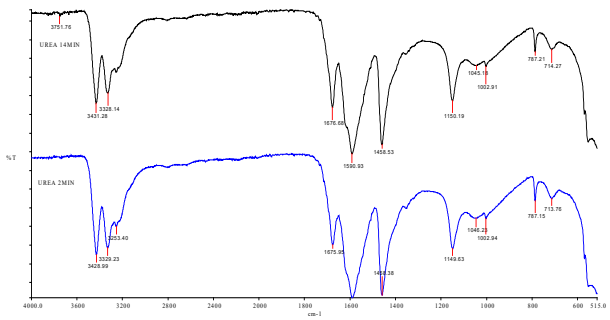

Fig 4: FTIR graph on milled urea of 2 min and 14 min

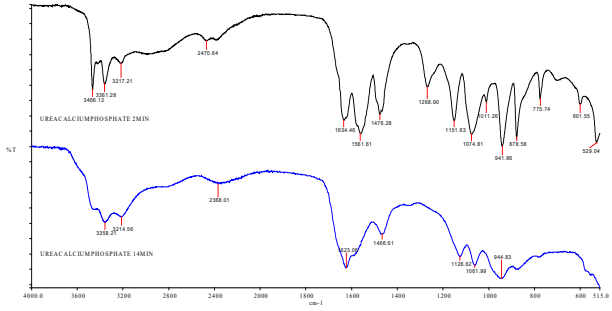

Fig 5: FTIR graph on milled urea calcium phosphate of 2 min and 14 min

C. *Thermogravimetric Analysis*

Thermogravimetric analysis (TGA) has been extensively applied to investigate the thermal stability of urea-calcium phosphate itself and the mixture of the urea and calcium phosphate composites. These studies showed that the thermal stability of the urea-calcium phosphate varies at different milling time.

Urea calcium phosphate thermogravimetric analysis showing that as the milling process increasing, the moisture and weight loss increasing, from 2 min to 8 min but milling process for 10 minutes onwards showing a decreasing value in moisture and weight loss. Milling process for urea calcium phosphate showing the least moisture and weight loss at 18.60% and 3.720 mg respectively. The highest loss has been recorded at 8 minutes of milling with 32% moisture loss and 6.4 mg weight loss.

Figure 6 showing urea calcium phosphate after milling process. The milling process of 2 minutes recorded moisture loss of 21.7% and 4.34 mg weight loss, while 4 minutes is at 24.01% with 4.80 mg, 6 minutes at 30.46% and 6.09 mg, 10 minutes is at 28.4% and 5.70 mg and 12 minutes at 25.28% and 5.06 mg of moisture loss and weight loss respectively for all of the samples that being milled. The ideal and optimum milling process for the urea calcium phosphate is to be suggested at 2 minutes with the lowest moisture and weight loss.

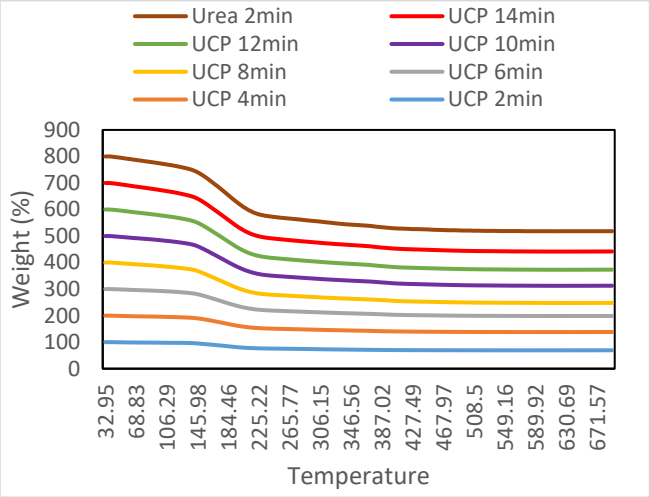

Fig 6: Comparison graph of urea calcium phosphate at different milling time

D. X-ray diffraction Analysis

The milled samples of the mixture urea calcium phosphate were investigated by X-ray diffraction. The crystal properties of the milled sample were investigated using X-ray diffraction from the Faculty of Applied Science, UiTM.

Powder XRD of the 2min milling urea calcium phosphate was performed, as shown in Figure 7. Figure showing the XRD pattern of the milled urea calcium sample at room temperature of 25°C.

Figure below showing comparison between urea calcium phosphate, calcium phosphate and urea of 2 mins milling. Comparison of the graph showing there is a peak exist in the urea calcium phosphate between 10 to 15 theta degree, that does not presence in both calcium phosphate and urea. This perhaps showing the peak of the product itself as both graph of calcium phosphate and urea showing none of it.

The comparison of urea calcium phosphate graph at different milling time, where it shows urea calcium phosphate at 14 mins milling showing the highest intensity while 2 mins milling has the lowest intensity following by 4 mins, 6 mins, 8 mins, 10 mins and 12 mins.

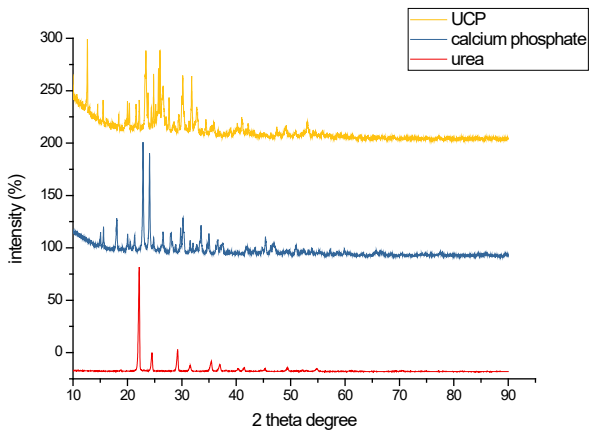

Fig 7: Comparison graph of urea calcium phosphate, calcium phosphate and urea at 2 mins milling

IV. Conclusion

Urea calcium phosphate were fabricated using the ball milling method. The structure of the mixtures were examined through FTIR, XRD and TGA. The results showing with prolonging the milling time, the urea calcium phosphate becoming sticky and clumpy. The coarser particles have been formed after milling for 2 min where at 2 min the urea calcium phosphate is in powdery formed but prolonging the milling, the particles has been coarser and forming into white flakes.

Through TGA, the influence of milling time and the content on the thermal stability of urea calcium phosphate has been investigated. The TGA analysis showing that weight loss increasing with increasing milling time up to 8 min, but showing weight loss starting from 10 min onwards. Weight loss showing the least at 2 mins milling time.

Through all the above characterizations of FTIR, XRD and TGA that has been made on milled urea calcium phosphate, optimum milling time in production of urea through ball milling techniques to avoid urea from becoming hygroscopic in order to generate quality urea fertilizer that will not cause hydrate formation in the presence of water that will make the mixture wet and sticky is at 2 mins of milling.

Acknowledgment

Thank you to my supervisor, Dr. Atikah Kadri for her constance guidance and advice played a vital role in helping me completing my research project. and Universiti Teknologi Mara. It is an honor for me to acknowledgement to all these who contributed significantly towards the completion of this research project.

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