Moisture Formation in Urea Compound via Ball Milling Technique

Ain Marseila Ahmad Isa, Atikah Kadri,

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract— **Moisture formation in urea calcium phosphate (UCP) fertilizer were synthesized by using ball milling technique. Prolonged milling time can cause moisture formation in the presence of moisture in air that makes the mixture wet and sticky. In this study is to find the best optimum milling time to avoid moisture formation of urea compound and to investigate the moisture formed in the compound during milling at 2 to 14 minutes. Physical observation and sample characterization were analyzed by X-Ray Diffraction (XRD), Thermal Gravimetric Analysis (TGA), and Fourier Transform Infrared (FT-IR) spectroscopy. It is observed that the product is in solid powder form at 2 minutes and become clumpier from 4 to 12 minutes. However, wet and sticky mixture was observed after milling for 14 minutes. The X-ray diffraction pattern of urea calcium phosphate shows the matching peaks with urea calcium hydrogen phosphate with a chemical formula of $Ca(H_2PO_4)_2.4CO(NH_2)_2$. TGA result shows that the moisture starts to develop at 4 minutes, become clumpier until 12 minutes and produce wet and sticky condition at 14 minutes. FTIR analysis shows that the moisture development in urea compound correspond to the reaction between urea and monocalcium phosphate monohydrate due to higher temperature in ball milling. From these results, the moisture formation in urea compound during ball milling was investigated and the optimum milling time to avoid moisture formation was determined.**

Keywords— **Ball milling, Fertilizer, Moisture formation, Urea**

I. INTRODUCTION

Fertilizers are materials containing the chemical elements that enhance growth and productivity of plants. Fertilizers plays an important role for preserving and improving agricultural output by way of retaining soil fertility, increasing yields and improving harvest satisfactory [7]. Urea (NH_2CONH_2), which act as nitrogen-rich fertilizer has become a great importance to the agriculture industry. In recent years, urea has turn out to be the primary source of nitrogen fertilizer in countries that highly develop [1, 2].

Nowadays, the production of urea in industrial sector is expensive as it cost the equipment used. Besides, current method of urea preparation requires longer time to produce the urea fertilizer. Therefore, ball milling is one of the efficient cost-effective grinding material to produce urea calcium phosphate fertilizer. It is capable technique in producing material with special properties. However, prolonged milling time can cause moisture formation in the presence of moisture in air that makes the mixture wet and sticky.

Mechanical alloying is a technique in processing of powder that allows production of homogeneous substances beginning from blending elemental powder mixtures. Increasing milling time will increase the milling efficiency as the particles getting smaller. Besides, a study has been reported that increase the milling time will increase the surface area of the particle which allow for uptake of a total amount of water in the particle [6]. Milling not only increases the surface area of solids. It is likely to increase the proportion of regions of high activity within the surface. It is also reported that the temperature rise when prolonged milling as the milling energy increase [8]. It had been reported that increasing vial speed and ball to powder weight ratio (BPR) could enhance the energy during milling as it can changes the resultant phases and boost up the formation of the products [12]. According to Sun et. al, increasing the rotation speed of the milling machine will reduce the ball milling time [13]. Abdellahi et al found that milling efficiency will reduce when the kinetic energy is decrease that resulted from the loss of weight of the powder. Second, the increase in the mill's degree of filling will results in the reduction of kinetic energy of the balls as the balls mobility becomes more difficult [14].

Urea is an applicable substance of mixed fertilizers, however caking may occur when urea form compounds which is hygroscopic when reacts with various fertilizer salts. Urea reacts with monocalcium phosphate monohydrate to form the adduct $Ca(H_2PO_4)_2.4CO(NH_2)_2$ [9]. It has been reported previously that $CaHPO_4$ and $CO(NH_2)_2.H_3PO_4$ products are form when urea reacts with monocalcium phosphate and attributed the poor physical properties of the mixture to the hygroscopicity of the $CO(NH_2)_2.H_3PO_4$ [3].

The adduct $Ca(H_2PO_4)_2.4CO(NH_2)_2$, is form in solid phase when urea reacts with the $Ca(H_2PO_4)_2.H_2O$, but then the hydrate water released from the $Ca(H_2PO_4)_2.H_2O$ wetted the product which results in wet and sticky condition of the mixture when milling for a longer time. Therefore, a further investigation and understanding is needed to observe the moisture development in urea compound during milling process.

In this study, the purpose is to investigate the moisture formation in urea during ball milling thus to determine the optimum milling time to avoid moisture formation in urea calcium phosphate.

II. METHODOLOGY

A. *Materials*

Urea and calcium phosphate that was supplied by R&M Chemicals. Ethanol that was supplied was used to rinse the mill jar after the milling process.

B. *Experimental Details*

In this experiment, a total of 2g calcium phosphate and urea that are analytically pure were mixed with the molar ratio of 1:2 which means 1 mole of monocalcium phosphate monohydrate react with 2 mole of urea [5] in order to maximize the volume of powder half of the milling jar. Stainless steel/WC milling jar was used to seal the stainless steel/WC milling balls and the mixed powders. The ball to powder weight ratio that being used was 20:1 which means 20 gram of ball mill for every 1 gram of mixture powder (ball to powder ratio).

According to Zakeri et al, it is more preferable using high ball to powder ratio to enhance the milling performance and hence reducing the milling time for the formation of the product [10]. The ball- milling assembly consisted of milling jar bearing 10 balls of 10 mm diameter each. The mixtures was ground for 2 min at 30 Hz in a Retsch MM400 mixer mill. The milling process was repeated at 4, 6, 8, 10, 12 and 14 minutes. The milling process was conducted at room temperature.

C. *Characterization*

Compound identification was analyzed by X-ray diffractometry (XRD). The XRD measurements were carried out at the room temperature. The scanning rate that has been used is 2θ degree per minute and the range of angle being used is 10° to 90°. X-ray diffraction that was supplied by the faculty is Rigaku X-Ray Diffraction.

Identification of functional group present in the sample was analyzed by by Fourier Transform Infrared (FT-IR) spectroscopy. The sample was scanned and the results obtained were recorded in the range of 4000-500 cm^{-1}. The model that being used is ASTM D3403.

Thermal stability and moisture degradation was assessed using Thermal Gravimetric Analysis (TGA). In this experiment, nitrogen gas was used as the carrier gas. The heating rate that being used is 10°C per minute and the maximum temperature of thermal stability up to 700°C.

III. RESULTS AND DISCUSSION

A. *Physical analysis of urea compound after milling process*

Fig. 1 below shows the condition of urea compound after milling at various time. Physical changes of urea compound was observed after milling at 2, 4, 6, 8, 10, 12 and 14 minutes. After milling for 2 minutes, it is observed that the product is in solid phase and powder mixture form. As the milling time increase, the urea compound condition was observed to become clumpier from 4 to 12 minutes. However, wet and sticky mixture was observe at after milling for 14 minutes.

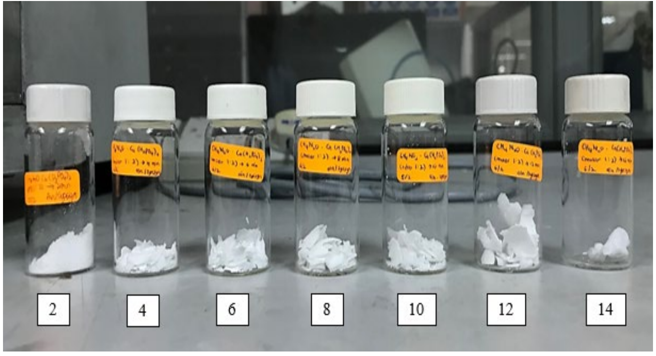

Fig. 1 Urea compound after milling at 2, 4, 6, 8, 10, 12 and 14 minutes

The clumpy and wet sticky condition of the mixture are cause by the hydrate water released from monocalcium phosphate monohydrate in the reaction when milling for a longer time. Besides, moisture formation in urea compound is due to the prolonged milling that may increases the surface area of solids which allow for uptake of a total amount of water in the reaction and produce poor physical condition of mixtures of urea compound [6]. It is also may be due to more energy transfer to the powder and boost up the chemical reaction between the milled materials.

B. *X-ray diffractometry (XRD) Analysis*

Fig. 2 shows the X- ray diffractograms (XRD) of urea calcium phosphate for 2 minutes and 14 minutes milling time. The X-ray diffraction peak of urea calcium phosphate was compared with the raw material which is urea and monocalcium phosphate monohydrate at 2 minutes and 14 minutes milling time.

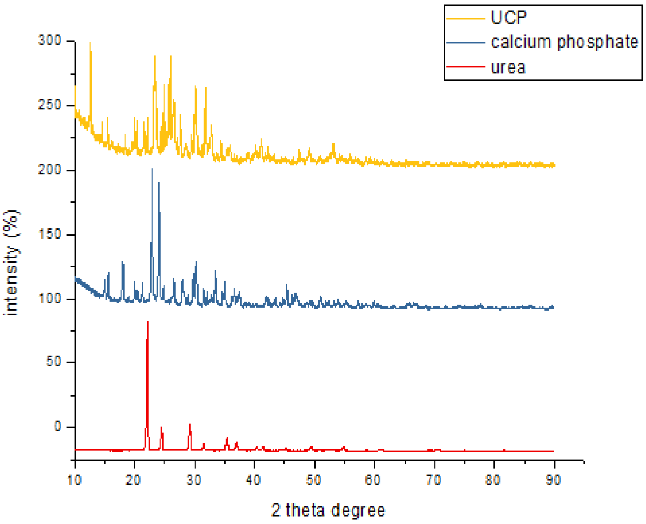

Fig. 2 XRD pattern for (a) urea calcium phosphate (b) monocalcium phosphate monohydrate, and (c) urea at 2 minutes milling time.

Based on Fig. 2 above, the XRD data given shows the matching peaks for the urea calcium phosphate agree well with the International Centre of Diffraction Database (ICDD). The similarities of X-ray diffraction peak pattern of urea on urea calcium phosphate peak at 2 minutes milling time was observed at 22.07°, 29.15°, 24.44° and 31.48° of 2 theta degree with relative intensity of 100%, 23.9%, 20.99% and 7.88% respectively. While the X-ray diffraction peak pattern of monocalcium phosphate monohydrate on urea calcium phosphate peak was observed at 23.0°, 30.2°, 24.1° and 31.5° of 2 theta degree with relative intensity of 100%, 30%, 90% and 12% respectively. From the figure above, the X-ray diffraction peak pattern at 2 minutes observed were matched with the peak of ICDD, which correspond to urea calcium hydrogen phosphate with a chemical formula of $Ca(H_2PO_4)_2.4CO(NH_2)_2$.

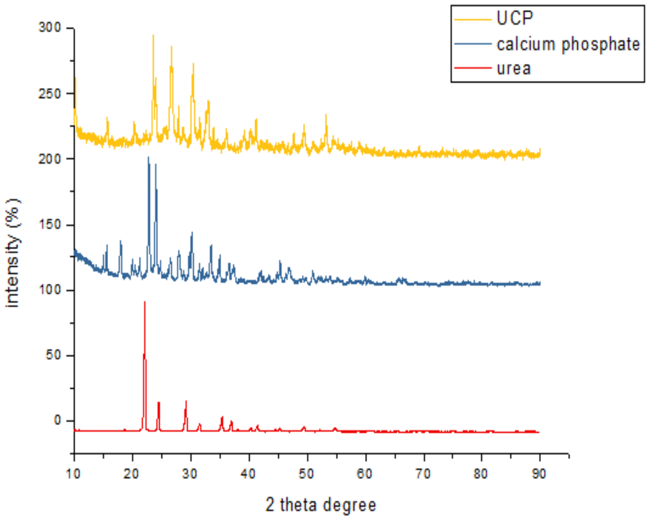

Fig. 3 XRD pattern for (a) urea calcium phosphate (b) monocalcium phosphate monohydrate, and (c) urea at 14 minutes milling time

For 14 minutes of milling time, the similarities of X-ray diffraction peak pattern of urea on urea calcium phosphate peak was observed at 22.15˚ and 35.5˚ of 2 theta degree with relative intensity of 100% and 12% as shown in Fig. 3. While the X-ray diffraction peak pattern of monocalcium phosphate monohydrate on urea calcium phosphate peak was observed at 23.0˚, 20.3˚, 26.6˚, 30.4˚, 32.8˚, 36.3˚ of 2 theta degree with relative intensity of 100%, 14%, 16%, 10% and 8% respectively.

From figure above, there are four sharp detected diffraction peaks corresponding to the urea calcium phosphate along with small urea peaks in XRD diffraction patterns of the compound. The fewer urea peaks and their lower intensity in the diffraction pattern might be attributed to the low content of the urea phase or the formation of amorphous phase. It is observed that calcium hydrogen phosphate hydrate peak was dominating in the compound. Although the XRD pattern was similar to the experimentally obtained and simulated by ICDD, they are not identical. Therefore, the possibility of the formation of monohydrate was very likely [11].

From the analysis data, the X-ray diffraction peak pattern at 14 minutes observed were matched with the peak of ICDD, which correspond to urea calcium hydrogen phosphate with a chemical formula of $Ca(H_2PO_4)_2.4CO(NH_2)_2$.

C. Thermal Gravimetric Analysis (TGA)

Fig. 4 below shows the thermal analysis of UCP from 2 to 14 minutes which was heated under nitrogen atmosphere. The TGA curves shows the weight loss between 32˚C until 700˚C.

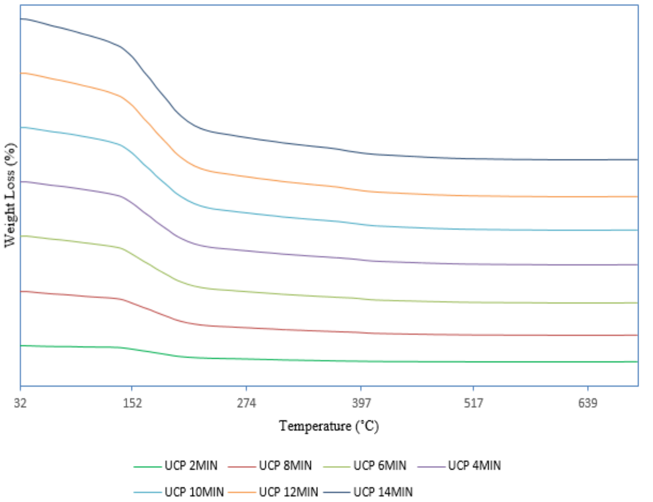

Fig. 4 TGA curve for UCP at 2 until 14 minutes.

Initial mass loss was observed in the temperature range of 54˚C until 100˚C which correspond to the moisture loss at an almost constant rate. A steady line was observed when milling UCP for 2 minutes in the temperature range of 54˚C until 100˚C indicating that no moisture loss from the compound. The rate of steepness was observed to be increase as milling time increase. A slightly steep curve was observed when milling for 4 minutes indicating that less moisture loss from the compound. This may be due to low rate of vaporization of water which attributed to low moisture content in the sample.

The distinct of the steepness observed indicates that the rate of moisture loss increase as the milling time increase. Water molecules were loss as urea compound was continuously heated [4]. The curve was observed to be very steep when milling at 14 minutes, which correspond to high rate of evaporation of the hydration water. The wet and sticky condition of the mixture is due to high moisture content in the urea compound.

From the TGA result it shows that the moisture starts to develop at 4 minutes and become clumpier until 12 minutes. Furthermore, the high moisture content results in wet and sticky condition of urea compound when milling at 14 minutes.

D. Fourier Transform Infrared (FT-IR) Analysis

The experimental IR spectra was compared between pure urea and monocalcium phosphate monohydrate at 2 minutes and 14 minutes, and also urea calcium phosphate at 2, 4 and 14 minutes. The important vibrational bands for pure urea, monocalcium phosphate monohydrate, and urea calcium phosphate at 2, 4 and 14 minutes are listed in Table 1. Fig. 5 below shows the FTIR spectra of urea monocalcium phosphate monohydrate at 2, 4 and 14minutes.

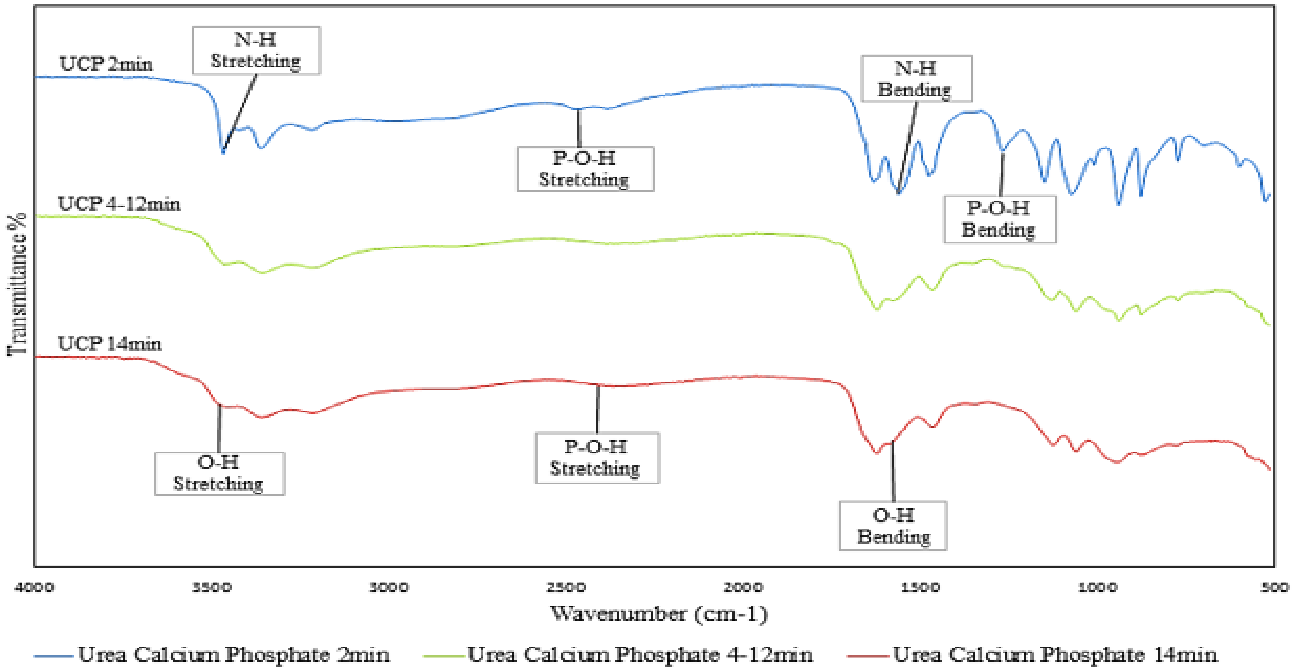

Fig. 5 FTIR spectra for urea calcium phosphate at 2, 4 and 14 minutes

Table 1: FT-IR assignment for urea calcium phosphate at 2, 4 and 14 minute

Time	Wavenumbers (cm^{-1})	Functional group
2 minutes	3466	N-H stretching modes of NH2 primary amine
	3361	N-H stretching modes of NH2 primary amine
	2470	P-O-H stretching mode
	1634	C=O stretching vibration mode
	1561	N-H bending mode
	1476	C-N stretching mode
	1268	P-O-H bending
	1074	P=O stretching mode of PO_2 bond
	957	P-O asymmetric stretching of $P(OH)_2$ bond
	878	HPO_4^{2-} ion
4 – 14 minutes	3200-3700	O-H stretching vibration of OH group
	3358	N-H stretching modes of NH_2 primary amine
	3214	N-H symmetric stretching vibration
	2368	P-O-H stretching mode
	1623	C=O stretching vibration mode
	1200-1600	O-H in-plane bending mode
	1466	C-N stretching mode
	1061	P=O stretching mode of PO_2 bond
	944	P-O asymmetric stretching of $P(OH)_2$ bond

For UCP at 2 minutes, the band observed at about 3466 cm^{-1} and 3361 cm^{-1} indicates the N-H stretching modes of NH_2 primary amine group as well as for UCP at 14 minutes which observed at 3358 cm^{-1}. A similar pattern and band was observed when milling from 4 to 12 minutes. However, as milling time increase to 14 minutes, the absorption band have become broadened as it indicates there is a reaction happen during the milling process that cause the peak become broadened. The broad absorption band of O-H stretching vibration of hydrogen bonded OH group was observed in the range of 3200-3700 cm^{-1}, together with the broad peak in the range of 1200-1600 cm^{-1} was assigned to O-H in-plane bending mode, are evidence of the presence of absorbed water in the urea compound when milling for 14 minutes that cause the wet and sticky condition of the mixture. Hydrogen bonding interaction occurred may lead to the broadening peak due to higher temperature when milling for a longer time that will lead to moisture formation in the reaction.

An absorption band of P-O-H stretching was observed at about 2470 cm^{-1} for UCP at 2 minutes. The band shift to lower wavenumber at 2368 cm^{-1} and become broadened as milling time increase to 14 minutes, indicates that less of that particular type of bond. From FTIR analysis it shows that the moisture development in urea compound correspond to the reaction between urea and monocalcium phosphate monohydrate that may be due to higher temperature in ball milling as milling time increase.

I. CONCLUSION

Solid powder phase was observed when milling for 2 minutes, while clumpy white flakes was observed when milling time increase from 4 to 12 minutes. However, wet and sticky condition of mixture was observed when it comes to 14 minutes. X-ray measurements confirmed the phases identified in both milling conditions which is urea calcium hydrogen phosphate with a chemical formula of Ca(H2PO4)2.4CO(NH2)2 as the peak was matched with International Centre of diffraction pattern (ICDD). This means that the targeted product had achieved for 2 until 14 minutes. Further investigation on moisture was analyzed by TGA. From TGA result, it shows that the moisture starts to develop at 4 minutes as the moisture loss increase with increasing milling time. To support the XRD and TGA result, FTIR analysis shows that the moisture development in urea compound correspond to the reaction happened between urea and monocalcium phosphate monohydrate in ball milling as the peak became broadened with increasing milling time. Therefore, the optimum milling time to avoid moisture formation in urea calcium phosphate via ball milling technique is 2 minutes.

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