Effect of Cu and Palm Stearin Coatings on the Thermal Behavior and Ammonia Volatilization Loss of Urea

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Abstract: Problem statement: Cu coated urea with palm stearin will be beneficial for plant nutrition and environment which can be beneficial for plant physiology and growth. Due to coating layer of natural materials, the nitrogen will be available to plants for a long period after a single application of coated urea. On the other hand, it will be slow down hydrolyses process of Cu coated urea by inhibiting the activity of urease enzymes. This combination can decrease the ammonia volatilization losses. Temperature is the one another important factor which reduces urea use efficiency of crops. Coating of urea with palm stearin and Cu can increase the thermal stability of urea. Approach: hundred grams of urea was coated by seven grams of palm stearin and 5µg of Cu by fluidized bed coating machine. After coating the coated urea was dried in vacuum desiccators for 48 hours. The urea and Cu- and palm stearin- coated urea were analyzed for TGA (thermo gravimetrical analysis) and DSC (diffraction scanning calorimetric).as well as the coated urea was evaluated for the ammonia volatilization losses till six weeks to compare the effect of coated urea with uncoated urea in selected soil series. Results: The analysis showed that there is a scope to increase thermal stability of urea to reduce ammonia volatilization losses by using coating of some natural material. As well as the combination Cu and palm stearin coated urea can reduce 50% ammonia loss from soils. Conclusion: This study has potential to develop a environmental friendly coating to reduce urea losses.

Key words: Thermo gravimetric analysis, Diffraction scanning calorimetric analysis, fluidized bed coating machine

INTRODUCTION

Application of Urea under high temperature caused ammonia volatilization losses which reduces the N fertilizer use efficiency by crops as well as caused environmental pollution. Stangle^[7]stated that urea as Nitrogen fertilizer is consumed 80% by the world. Despite of the importance of this fertilizer, its efficiency has been reported as low by Mikkelsen et al., [5], Fillery et al., [2], to substantial N lost to the atmosphere through volatilization, Urease activity in soils is influenced by many factors especially by temperature. Temperature can affect the rate of dissolution of a urea granule in water. Urea hydrolysis is accelerated by increasing temperature. The increase in temperature also caused increase in microorganism growth and urease enzyme production. Khanif et al., [4] reported that amount of urea remaining in soil after 12 hour incubation was 64% at 10°C and 27% at 35°C. The rate of urea hydrolysis is related to rate of ammonia loss. Polacco^[6] studied that urease enzymes present in plant and soils are responsible for the hydrolyses of urea in soil. The activity of these

enzymes become fast at high temperature and moisture. Bremner and Douglas^[1] investigated that Cu is effective as urease inhibitor to reduce hydrolyses rate of urea. On the other hand, Cu is very important for plant health and physiological process as micronutrient. Hanafi et al., ^[3] reported that use of various coatings would be utilized in producing controlled release fertilizers. The addition of palm stearin as coating incorporated with urease inhibitors allows the inhibitors to be at the urea micro site while enhancing the thickness and stability of urea. The present work is concerned about the study of the effects of palm stearin and urease inhibitor's coating on urea's thermal behavior and oxidative stability.

MATERIALS AND METHODS

Preparation of Cu and Palm Stearin Coated Urea:

Hundred grams of granule urea was coated by 7g of Palm stearin manually. Palm stearin coated urea was recoated again by $5\mu g$ of Cu dissolved in 10ml of distilled water. The Cu solution was applied by

fluidized bed coating machine. The coated fertilizer was kept in desiccators for 48 hours to be dry.

Granule urea and palm stearin coated urea were analyzed for the study of thermal behavior by TGA (thermo gravimetric analysis) and DSC (diffraction scanning colorimetric) in polymer laboratory of science faculty, Universiti Putra Malaysia.

Differential Scanning Calorimetric: About 2.5-5.0mg of the sample was weighed and differential scanning calorimetric thermograms were obtained using polymer laboratory –DSC. Thermal behavior for the samples was observed between 30° C and 500 °C.

Thermo Gravimetric Analyses: Thermo gravimetric and differential thermo gravimetric analysis of the samples was examined. About 10-30mg of the sample was weighed and its weight loss was determined when it was heated from 30°C to 5000 °C.

Ammonia Volatilization Losses: The ammonia volatilization study was carried out on three soil series; Serdang series (Typic Paleudult), Rengam series (Typic Paleudult) and Holyrood series collected from experimental area of Serdang and undisturbed area of Johor at the depth of 0-15 cm depth. The sampled soil was analyzed for pH in water, total N content of soil by Auto Analyzer, Cu by mehlich-3 method, moisture content and texture.

Treatments T1 (urea) and T2 (coated Urea) were used to compare the Ammonia volatilization loss %. Ammonia Volatilization (NH3) was determined using force draft technique. The closed - dynamic (aerobic) air flow system is consist on an air exchange chamber (ground- glass Erlenmeyer 500ml) and trapping flask (ground- glass Erlenmeyer 250ml), both stopper and fitted with an inlet outlet facility. The inlet of the chamber was connected to a heavy duty air pump, while the outlet was connected by polyethylene tubing to the trapping flask fitted with a glass distribution rod immersed in trapping solution. The chamber was filled with 300gm of fresh soil. The soil % 25% was wetted to 25%moisture holding capacity and 400ug/g of fertilizer was added in each treatment the trapping flask contain 2% boric acid solution to capture NH₃. The green collected solution was titrated by 0.1 N hydrochloric acid solution on daily basis till 6 weeks to record ammonia volatilization % of each treatment urea and coated urea.

RESULTS AND DISCUSSION

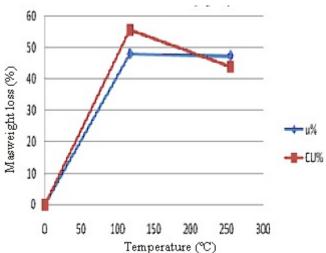
Thermo Gravimetric Analysis TGA: Coated urea was analyzed for observing the function of weight loss of coating in relation to temperature. It was observed that the temperature at the rate of maximum weight loss

occurred from 47% to 55.6 % during the first stage of decomposition and the DTG temperature ranged from 100 to 150°C. The weight loss% at first stage of decomposition described the water loss or solvent present in the coated urea. The range of temperature at maximum weight loss occurred as given in Table 1. Coated urea has less weight loss as compare to uncoated urea which was 43.8 and 47.3%, respectively at the second stage of decomposition with the maximum range of temperature from 150 to 300°C. The mass loss was found slightly higher for urea (3.8%) as compare to coated urea which is 3.4% as given in Table 1 at the 3rd stage of decomposition. Urea and coated urea showed a constant mass loss above 400 °C. However, as temperature was increased, the mass weight loss increased for both types of urea. The mass weight loss at 2nd and third stage of decomposition was due to inherent properties of coated material. The thermal oxidative stability of coating material is defined as the resistance of coating materials to chemical decomposition under the influence of temperature. The thermal stability of the coated and uncoated urea was determined by plotting of Weight mass loss versus temperature as shown in Fig 3.

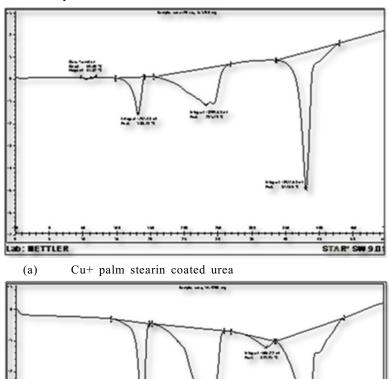
Differential Scanning Calorimetric: The pattern of DSC in urea and coated urea was similar with three peaks. The temperature ranged from 130 to 133 °C for the first endothermic stage, which was due to water or solvent present in the sample. The melting temperature was indicated by the second peak of endothermic reaction. The samples showed a difference between the peaks of urea at 230°C lower than the coated urea at 245°C. The degradation process as indicated by third stage of endothermic reaction. The degradation and melting temperature of urea is 374.3°C and 382°C for coated urea. The results showed that the coating is effective to increase the resistance of urea against high temperature.

Ammonia Volatilization losses: The soil series used in this study were acidic and low in total N and Cu content. As indicated in illustrated Fig 3 and Table 4 ammonia volatilization losses became 20 to 45% less in all soil series. The same results has been reported by khanif [7].

Discussion: According to the results of DSC and TGA, there is no any significant difference in thermal behavior of both treatments. But results in Table 1 and Table 2 showed a potential to increase resistance of urea against temperature by enhancing the coating layer. Addition of Cu as urease inhibitor is effective in reducing the ammonia losses. The texture



Temperature (°C) Fig. 1: Thermal oxidative stability of urea and coated urea



Lab: BETTLER STAR SW 9.01

Fig. 2: Differential scanning calorimetric curves of the coated and uncoated urea

(b)urea

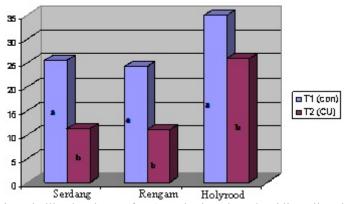


Fig. 3: Cumulative Ammonia volatilization losses for 6 weeks in selected acidic soil series.

Table 1: Temperature range and maximum peak temperature of the DTG curve and corresponded weight loss from TGA for urea and Cu+

palm stearin ur	ea.		
Treatment	DTG temperature		Weight loss from TGA
Urea	Range	Maximum peak	%
	100-150	117	47.9
	150-300	255	47.3
	300-500	454	3.8
Cu+ PS urea	100-150	123	55.6
	150-300	249	43.8
	300-600	449	3.4

Table 2: The endothermic peaks of the urea and coated urea using DSC

Fertilizer	•	Endothermic stages (°C)		
	First	second	third	
T1 (urea)	130.76	231	374.43	
T2(Cu.P.S.U)	133.31	242	382.65	

CU.P.S stands for Cu and palm stearin coated urea

Table 3: Soil characterization

Soils	Serdang	Rengam	Holy rood
Moisture content %	27	25	20
Texture	sandy clay	sandy clay	sandy
pH in water	4.5	4.7	5.1
total N mg/kg	0.11	0.19	0.08
Cu content mg/kg	0.05	0.05	0.02

Table 4: Total amounts of Ammonia volatilization loss over 6 weeks in soil series

Soil Series	Treatments	Total Ammonia volatilization loss (%)
Serdang	T1 (control)	25.61a
	T2(coated urea)	11.06b
Rengam	T1(control)	24.60a
	T2(coated urea)	11.00b
Holy rood	T1(control)	35.00a
	T2(coated urea)	26.70b

Different alphabets indicate significant difference between means using Tukey's test at P=0.05

of soil is seems as important factor in this study like Holyrood series has more ammonia volatilization then other soils because it has high content of sand. Urea has shown more losses than Coated urea in Serdang and Rengam soil series. The difference of ammonia volatilization can be observed easily by Fig 3 of bar graph. The highest loss was recorded at T1 (control) in Holyrood series which became 20% less in the same soil at T2 (coated urea).

Despite of this ammonia loss of urea in Rengam and Serdang soils became 50% less in soil which were treated by coated urea T2.

Conclusion: It is concluded that the thermal behavior of urea was affected by coating. The study results showed that the coating is effective to increase the urea thermal stability. Coating of urea can play an important role to enhance the efficiency of urea fertilizer. This development has potential to fulfill the requirement of plant nutrition by providing Cu and N by the same source of fertilizer. It is also concluded that further investigation will be beneficial to improve the coating thickness to increase it's resistance against temperature.

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