



CHAPTER IV

RESULTS AND DISCUSSIONS

Released urea from urea fertilizer coated with cardanol was analyzed by using all methods which described in the chapter III. The results have been shown and discussed in each part of this chapter, respectively.

4.1 Polymerization of polymer

4.1.1 Preparation of polycardanol

In the $^1\text{H-NMR}$ spectrum of Figure 4.1 (A) and (B), the characteristic peaks for the $\text{CH}=\text{CH}$ protons were observed at chemical shift 5.8, 5.4, and 5.0 (peak a, b, and c, respectively) (Figure 4.1 (A)) which showed that the unsaturated group was not reacted during the polymerization. All of the peaks of Figure 4.1 (B) became broader than those of Figure 4.1 (A) which confirmed the polymerization of cardanol by Fe-salen and H_2O_2 .

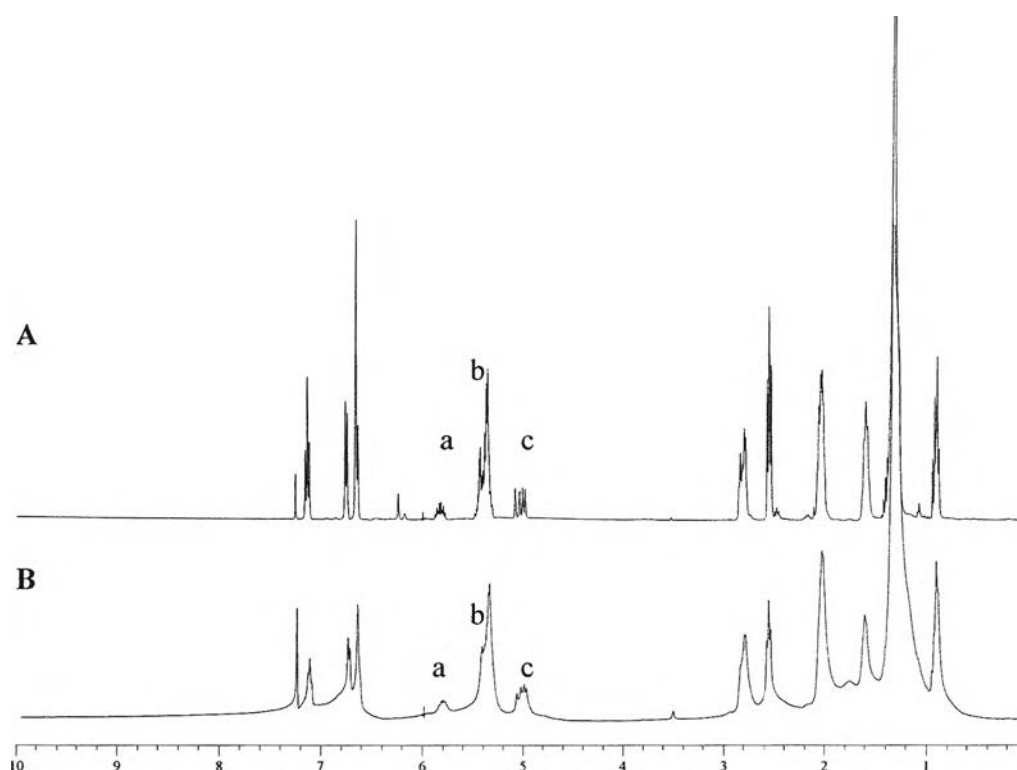


Figure 4.1 $^1\text{H-NMR}$ spectra of (A) cardanol and of (B) polycardanol synthesized using Fe-salen (in CDCl_3)

FT-IR spectra confirmed a structure of the polymer synthesized by Fe-salen and H_2O_2 . Figure 4.2, showed the FT-IR spectra of (A) cardanol and of (B) polycardanol formed by Fe-salen. Figure 4.2 (B), the broad peak at 3396 cm^{-1} was due to the stretching of the O-H linkage of phenolic group, and three characteristic peaks were also observed at 1241 , 1191 , 1154 cm^{-1} , respectively, which were ascribed to the vibrations of the $\text{C}(\text{Ar})\text{-O-C}(\text{Ar})$ and/or $\text{C}(\text{Ar})\text{-OH}$ linkages because of the polymerization of cardanol. These results reveal that polycardanol formed by Fe-salen and H_2O_2 consisted of a mixture of phenylene and oxyphenylene units. Although cardanol has two groups subject to polymerization (the phenolic moiety and the unsaturated hydrocarbon group), only the phenolic moiety was polymerized. Figure 4.2 (A), the spectrum of cardanol showed a characteristic peak at 3009 cm^{-1} due to C-H vibration of the unsaturated hydrocarbon moiety. As shown in the FT-IR spectra of

Figure 4.2 (B), the peak at 3008 cm^{-1} remained almost unchanged, indicating no reaction of the unsaturated groups during the Fe-salen catalyzed polymerization.

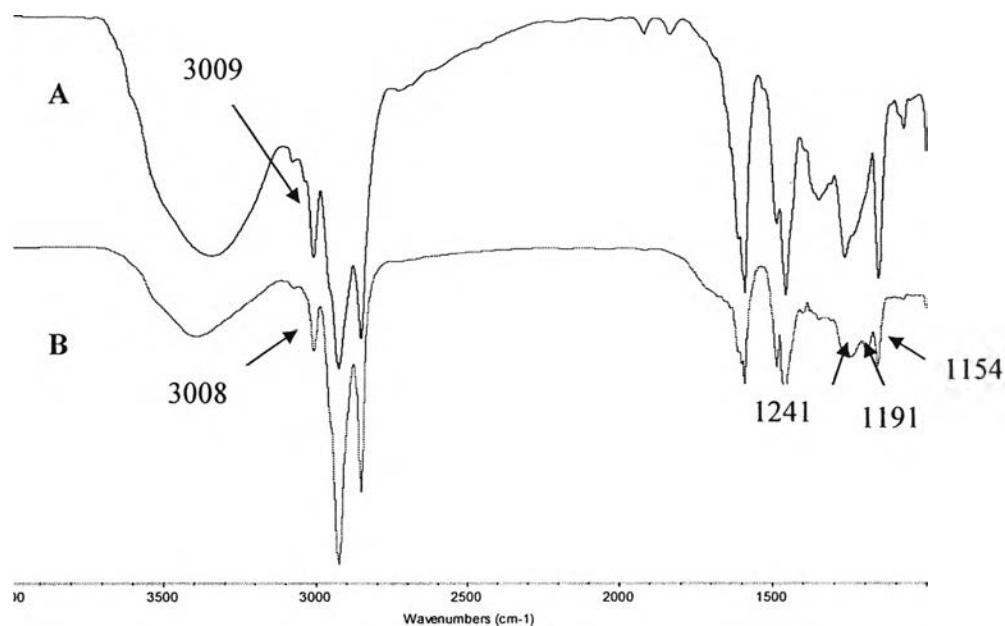


Figure 4.2 FT-IR spectra of (A) cardanol and of (B) polycardanol synthesized using Fe-salen

Table 4.1 The IR absorption bands assignment of cardanol and polycardanol synthesized using Fe-salen.

Absorption bands (cm^{-1})			Functionality
Cardanol	Polycardanol synthesized using Fe-salen	Literature value [38]	
3340	3396	3640-3160	O-H stretching of phenols
	1241, 1191, 1154	1260-1000	C-O-C bending of alcohols group
3009	3008	3080-3020	C-H stretching of alkenes

The Mn, Mw, and polydispersity of polycardanol are 5882 Daltons, 8974 Daltons and 1.52, respectively. The viscosity of cardanol and polycardanol are 4, 290 poise, respectively. Table 4.2, viscosity increase was directly proportional to increase in apparent molecular weight and the degree of polymerization.

Table 4.2 Viscosity characteristic of materials

Types of material	Viscosity (poise)
Cardanol	4
Polycardanol	290
Tung oil	2.5
Heated tung oil	15
Linseed oil	1.4
Heated linseed oil	9.5

4.1.2 Polymerization of drying oil such as tung oil and linseed oil

Table 4.1, the viscosity of tung oil and heated tung oil is 2.5, 15 poise, respectively. While the viscosity of linseed oil and heated linseed oil is 1.4, 9.5 poise, respectively. The viscosity increase was directly proportional to increase in the degree of polymerization as same as cardanol and polycardanol.

4.1.3 Preparation of cardanol-formaldehyde resin

In the $^1\text{H-NMR}$ spectra of cardanol-formaldehyde resin, the peak at chemical shift 6.60–7.20 is due to aryl protons of benzene nuclei, the peak around the region chemical shift 5.80 is due to the phenolic hydroxyl, the peak at chemical shift 4.90–5.40 is due to methylene ($\text{C}=\text{CH}_2$) proton of long alkyl side chain originally present in cardanol and the peak at chemical shift 1.20–2.70 is due to the long aliphatic side chain. The small peak at chemical shift 0.80 is due to terminal methyl group of the chain. The strong peak at chemical shift 1.60 is attributed to the long chain (more than five methylene groups) of the side chain (Figure 4.3).

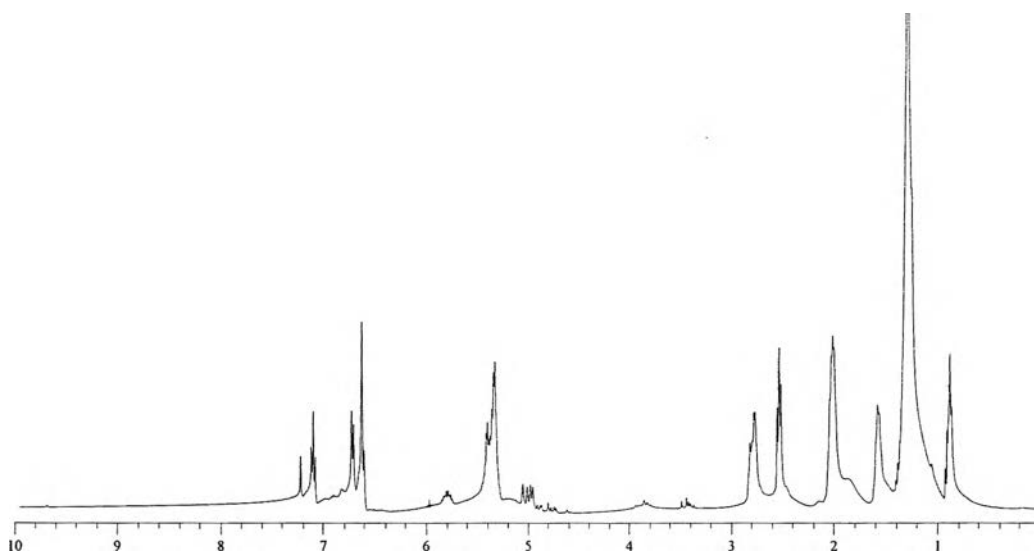


Figure 4.3 ^1H -NMR spectra of cardanol- formaldehyde resin (in CDCl_3)

4.1.4 Curing of polymer

Table 4.3 showed curing of cardanol, polycardanol, cardanol-tung oil, cardanol-linseed oil, and cardanol-formaldehyde which cardanol, polycardanol, cardanol-tung oil, and cardanol-linseed oil which were cured by catalyst such as Cobalt naphthenate or Cobalt naphthenate/*tert*-butylhydroperoxide while cardanol-formaldehyde was cured with catalyst such as hexamethylenetetramine. Table 4.3, cardanol was not cured with/without catalyst while polycardanol was not cured without catalyst such as Cobalt naphthenate. Polycardanol was rapidly cured when both Cobalt naphthenate and *tert*-butylhydroperoxide were added. Approximately amount of drying oil reduce drying time of polycardanol which tung oil the most reduce drying time. However, amount of drying oil was effect to property of film. Excess drying oil led to wrinkle of film which tung oil led to wrinkle of film than linseed oil. Cardanol-formaldehyde slowed curing because it had not free formaldehyde.

Table 4.3 Curing of cardanol matrix

Sample	Cobalt naphthenate (%w/w)	<i>t</i> -BuOOH ^a (%w/w)	drying time ^b (min.)	
Cardanol	-	-	-	
	2	-	-	
	2	2	-	
	2	4	-	
	4	2	-	
	4	4	-	
	6	6	-	
Polycardanol	2	-	>50	
	2	2	50	
	2	4	50	
	4	2	50	
	4	4	40	
	6	6	30	
Cardanol-tung oil	polycardanol: tung oil (9: 1)	2	-	50*
		2	2	30
		2	4	20
		4	2	20
		4	4	15
		6	6	10
	polycardanol: tung oil (8: 2)	2	-	40*
		2	2	25*
		2	4	25*
		4	2	20*
		4	4	10*
		6	6	10*

Sample	Cobalt naphthenate (%w/w)	<i>t</i> -BuOOH ^a (%w/w)	drying time ^b (min.)
polycardanol: tung oil (7: 3)	2	-	30*
	2	2	20*
	2	4	20*
	4	2	20*
	4	4	10*
	6	6	10*
polycardanol: tung oil (6: 4)	2	-	30*
	2	2	20*
	2	4	15*
	4	2	15*
	4	4	10*
	6	6	10*
polycardanol: tung oil (5: 5)	2	-	20*
	2	2	20*
	2	4	15*
	4	2	15*
	4	4	10*
	6	6	10*
Cardanol-linseed oil			
polycardanol: linseed oil (9: 1)	2	-	>50
	2	2	>50
	2	4	>50
	4	2	>50
	4	4	>50
	6	6	50

Sample	Cobalt naphthenate (%w/w)	<i>t</i> -BuOOH ^a (%w/w)	drying time ^b (min.)
polycardanol: linseed oil (8: 2)	2	-	>50
	2	2	>50
	2	4	>50
	4	2	>50
	4	4	60
	6	6	30
polycardanol: linseed oil (7: 3)	2	-	>50*
	2	2	>50*
	2	4	>50*
	4	2	>50*
	4	4	60*
	6	6	40*
polycardanol: linseed oil (6: 4)	2	-	>50*
	2	2	>50*
	2	4	>50*
	4	2	>50*
	4	4	60*
	6	6	40*
polycardanol: linseed oil (5: 5)	2	-	>50*
	2	2	>50*
	2	4	>50*
	4	2	>50*
	4	4	>50*
	6	6	50*

Sample	Cobalt naphthenate (%w/w)	<i>t</i> -BuOOH ^a (%w/w)	drying time ^b (min.)
Cardanol- formaldehyde ^c	-	-	> 3 h.

^a *tert*-butylhydroperoxide

^b temperature for drying time 80 °C

^c cured by 15% hexamethylenetetramine (HMTA)

* wrinkling

The structure of curing of polymer was confirmed by FT-IR. Figure 4.4 (A), is shown the FT-IR spectra of polycardanol, with a characteristic peak at 3008 cm⁻¹ due to C–H vibration of the unsaturated hydrocarbon moiety. While the FT-IR spectra of figure 4.4 (C) showed almost disappeared peak at 3008 cm⁻¹, suggesting that tung oil reacted with polycardanol at unsaturated hydrocarbon. The polycardanol film and cardanol-linseed oil film were crosslink at unsaturated hydrocarbon as same as cardanol-tung oil.

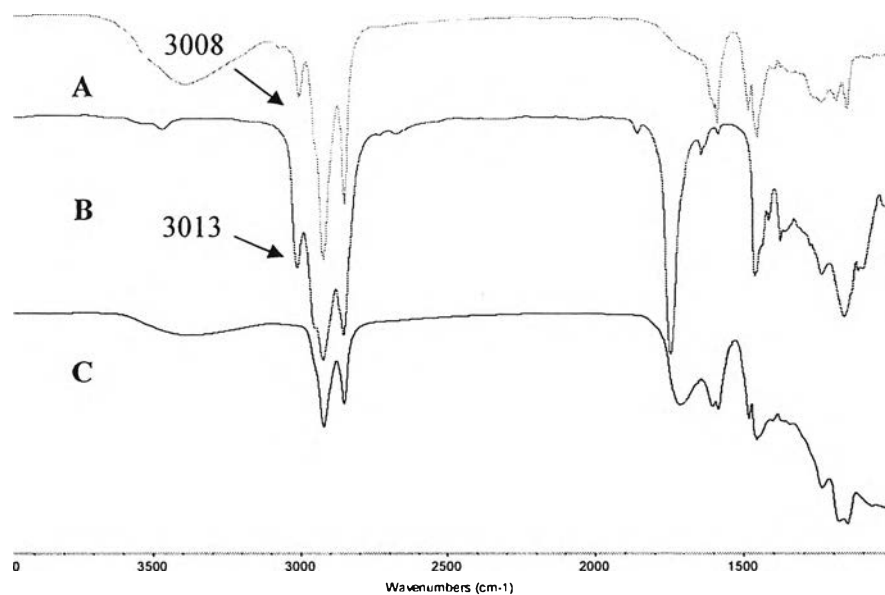


Figure 4.4 FT-IR spectra of (A) polycardanol synthesized using Fe-salen, (B) tung oil, and (C) cardanol-tung oil film

Table 4.4 The IR absorption bands assignment of polycardanol synthesized using Fe-salen, tung oil, and cardanol-tung oil film

Absorption bands (cm ⁻¹)				Functionality
Polycardanol synthesized using Fe-salen	Tung oil	cardanol-tung oil film	Literature value [38]	
3396		3374	3640-3160	O-H stretching of phenols
1241, 1191, 1154		1236, 1180, 1152	1260-1000	C-O-C bending alcohols group
3008	3013		3080-3020	C-H stretching of alkenes

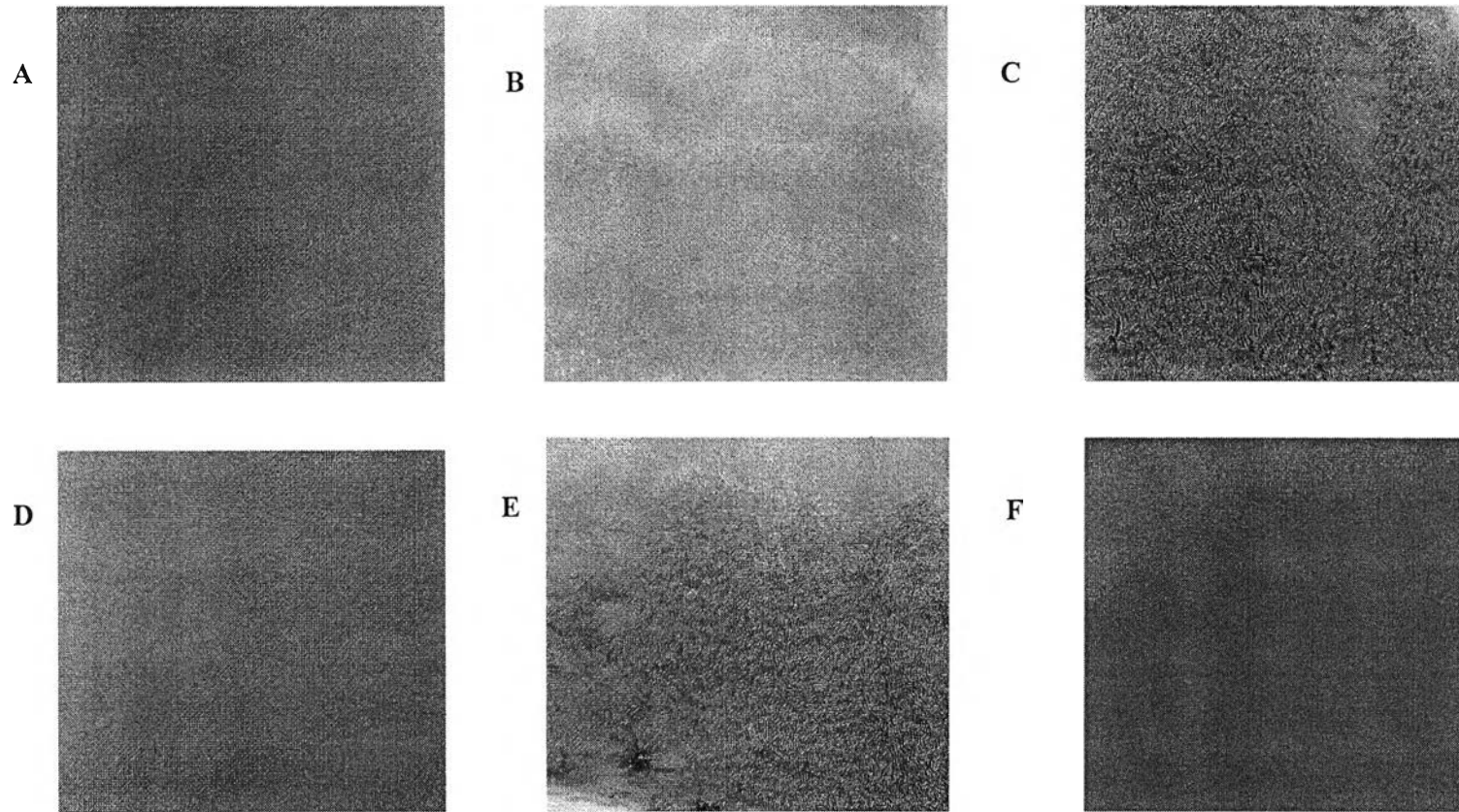


Figure 4.5 Characteristic of (A) polycardanol film, (B) cardanol-tung oil film (9: 1), (C) cardanol-tung oil film (8:2),

(D) cardanol-linseed oil film (8: 2), (E) cardanol-linseed oil film (7: 3), (F) cardanol- formaldehyde film

4.2 Film performance

The performance of coated films was tested by measurement of drying time, hardness, adhesion, gloss, water resistance, and acid-base resistance.

Table 4.5 showed the coating performance of the cured films which was prepared from cardanol with catalyst. The films from cardanol-tung oil showed the fastest drying time because tung oil had conjugated double bonds in unsaturated fatty acids. They are chemically reactive sites which conjugated double bonds of tung oil were reacted with unsaturated hydrocarbon of polycardanol. Polymer structure was confirmed by FT-IR (Figure 4.4 (C)).

The films from polycardanol showed the hardness than the films from cardanol-tung oil, cardanol-linseed oil and cardanol-formaldehyde because main structure of polycardanol is aromatic, while cardanol-tung oil and cardanol-linseed oil had aliphatic hydrocarbon than polycardanol. The aliphatic hydrocarbon made reduce hardness. In addition, the cured films from cardanol were showed excellent gloss. The film of cardanol-formaldehyde showed the highest adhesion.

Table 4.5 Performance characteristics of cardanol matrix

Sample	Cardanol matrix	Drying time ^c (min.)	Hardness (g)	Adhesion	Gloss 75°
1	Polycardanol ^a	30	200	3B	149.9
2	Cardanol-tung oil (9:1) ^a	10	180	3B	139.3
3	Cardanol-linseed oil (8:2) ^a	30	170	3B	136.9
4	Cardanol-formaldehyde ^b	>3 h	20	5B	118.3

^a cured by 6% Cobalt naphthenate and 6% *tert*-butylhydroperoxide

^b cured by 15% hexamethylenetetramine (HMTA)

^c temperature for drying time 80°C

Resistance test of the resulting films toward acid (23% sulfuric acid) and basic (1 N NaOH) solution was carried out (Table 4.6). Almost of the films were wrinkled and peeled from the glass slide in the alkaline solution and peeling in the

acidic solution, only the film from cardanol-formaldehyde was wrinkled and discoloration from the glass slide in the alkaline solution and discoloration in the acidic solution. All of the films were no change in distilled water. The alkaline resistance was poor which could be due to the presence of significant amount of alkali hydrolysable ester groups in the polymer chain of aliphatic of cardanol and drying oil.

Table 4.6 Resistance test of cured film (sample was immersed in test solution for 24 h (distilled water or alkaline solution) or 96 h (acidic solution))

Sample	Distilled water	Acidic solution ^a	Alkaline solution ^b
1	No change	Peeling	Wrinkling, peeling
2	No change	Peeling	Wrinkling, peeling
3	No change	Peeling	Wrinkling, peeling
4	No change	Discoloration	Wrinkling, discoloration

^a 23% sulfuric acid

^b 1 N NaOH

4.3 Preparation of coated urea fertilizer

4.3.1 Pan coating process

From data above, the films from cardanol-tung oil showed the fastest drying time and water resistance which are an effective material for coating water-soluble fertilizer such as urea for slow release.

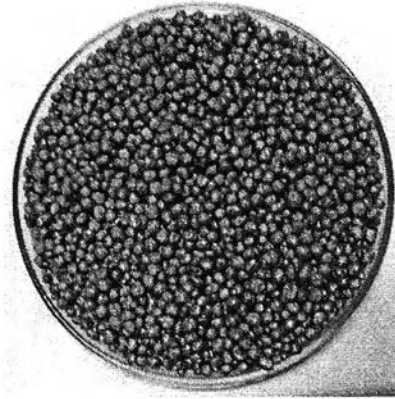
4.3.1.1 Effect of the amount of cardanol-tung oil

Amount of cardanol-tung oil is the factors which influence the coating process by pan coating. The amount of cardanol-tung oil was varied from 6, 10, and 15 part per hundred. Fertilizer used in this experiment was urea fertilizer, and cardanol-tung oil was used as coating material, while Cobalt naphthenate, and *tert*-butylhydroperoxide as catalyst.

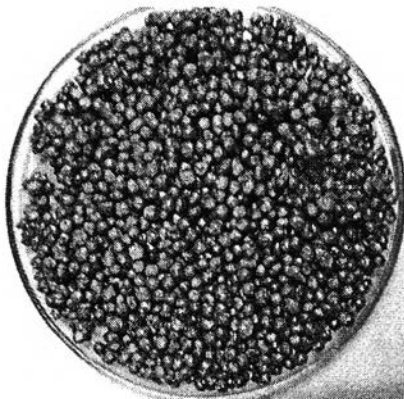
The influence of amount of cardanol-tung oil coating is shown in Figure 4.6, was found that 6 part per hundred cardanol-tung oil was appropriate to coat fertilizer by pan coating method while the higher amount of cardanol-tung oil was not

appropriate because excess cardanol- tung oil may cause polymerization on surface of coating pan instead of on fertilizer surface. Thus in this research 6 part per hundred cardanol-tung oil was used to coat fertilizer.

A



B



C



Figure 4.6 Urea fertilizers coated with cardanol-tung oil (A) 6%, (B) 10%, and (C) 15% of cardanol-tung oil.

4.3.1.2 Determination of coating percentage

The thickness of cardanol-tung oil of coated urea fertilizer was effect to amount of urea in urea fertilizer per 100 g which the thickness of cardanol-tung oil was determinate by coating percentage.

Table 4.7 The coated percentage of cardanol-tung oil of coated urea fertilizer

layers	% coating
1	9.65
3	26.67
5	38.08
7	48.69
9	56.55

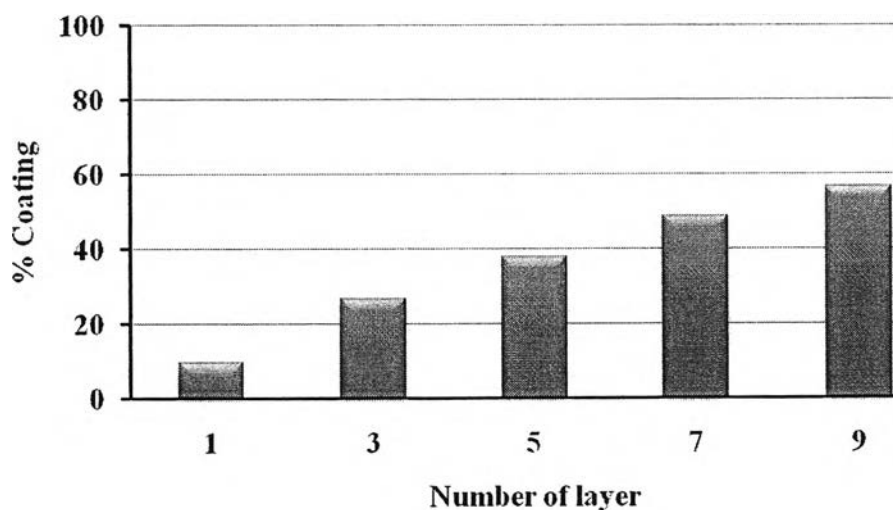
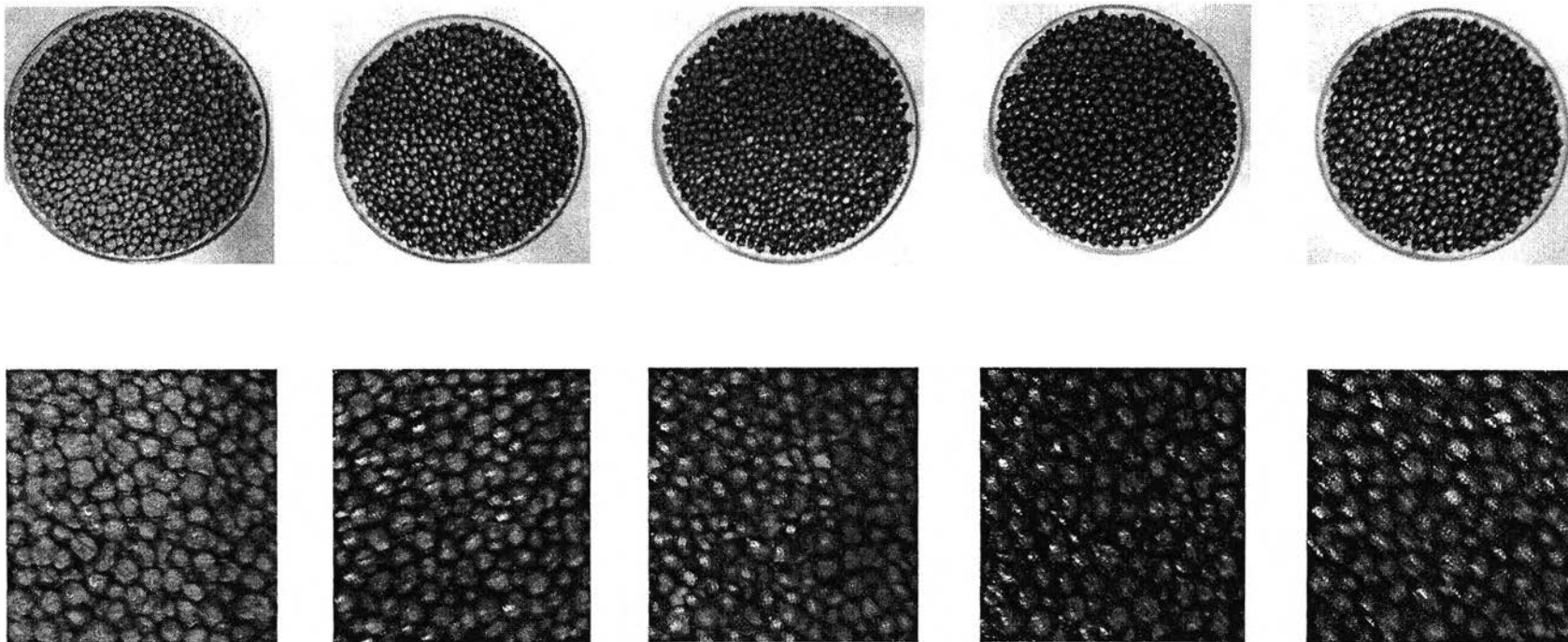


Figure 4.7 The percentage of coating

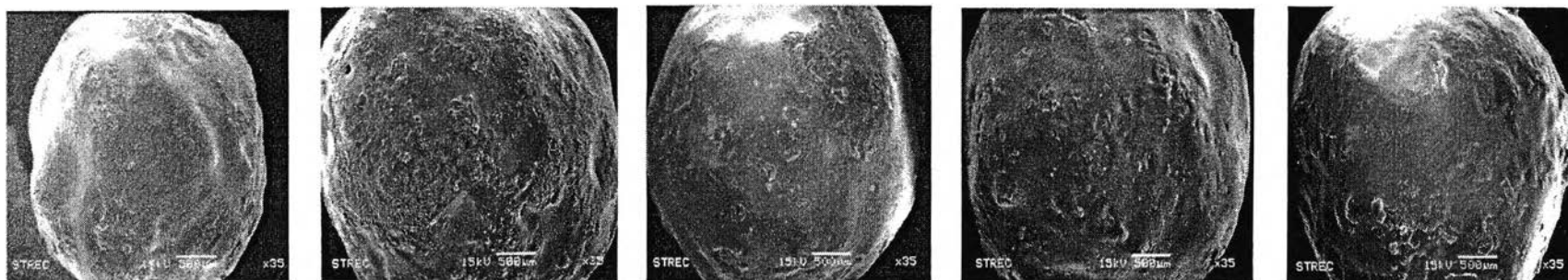
4.3.1.3 Morphological analysis

The microscopic structure of coated fertilizer was investigated by using scanning electron microscope (SEM). SEM micrographs in Figure 4.9 showed the increasing thickness when increased the number of coating. The coating layer was completely separated from the urea core.

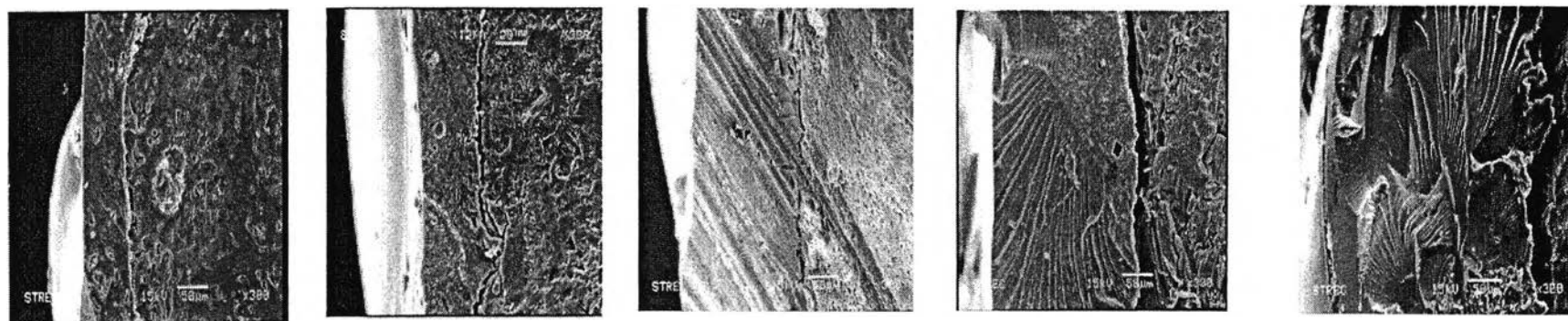


(A) 1 layer coated fertilizer (B) 3 layers coated fertilizer (C) 5 layers coated fertilizer (D) 7 layers coated fertilizer (E) 9 layers coated fertilizer

Figure 4.8 Cardanol-tung oil coated urea fertilizer.



(A) 1 layer coated fertilizer (B) 3 layers coated fertilizer (C) 5 layers coated fertilizer (D) 7 layers coated fertilizer (E) 9 layers coated fertilizer



(A) 1 layer cross section (B) 3 layers cross section (C) 5 layers cross section (D) 7 layers cross section (E) 9 layers cross section

Figure 4.9 SEM micrographs of urea fertilizer coated with cardanol-tung oil.

The thickness of coating was determined from SEM micrographs. Figure 4.9 showed the average of cardanol-tung oil that corresponded to the percent coating (Figure 4.7).

Table 4.8 The thickness of cardanol-tung oil of coated urea fertilizer

layers	Thickness (micron)
1	52.63
3	71.01
5	124.56
7	175.44
9	230.70

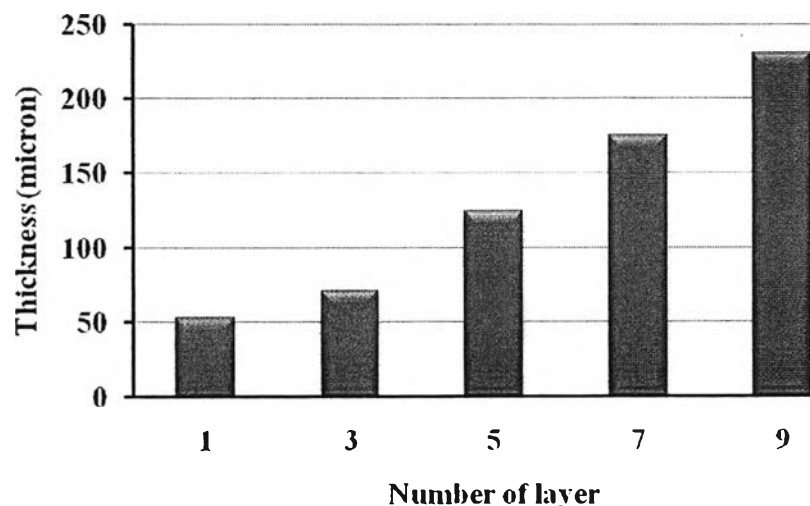


Figure 4.10 The average thickness of coating

4.4 The solubility of uncoated urea fertilizer

An appearance of commercial urea fertilizer is white solid (Figure 4.11). Its granule contains 46% of nitrogen. About only 23% of urea in uncoated fertilizer (Figure 4.10) could be detected from UV-Vis spectroscopy which correspond to the fertilizer formula 46-0-0. The uncoated urea fertilizer (0.5 g) completely dissolved in 100 ml deionized water within 6 minutes (Figure 4.13).

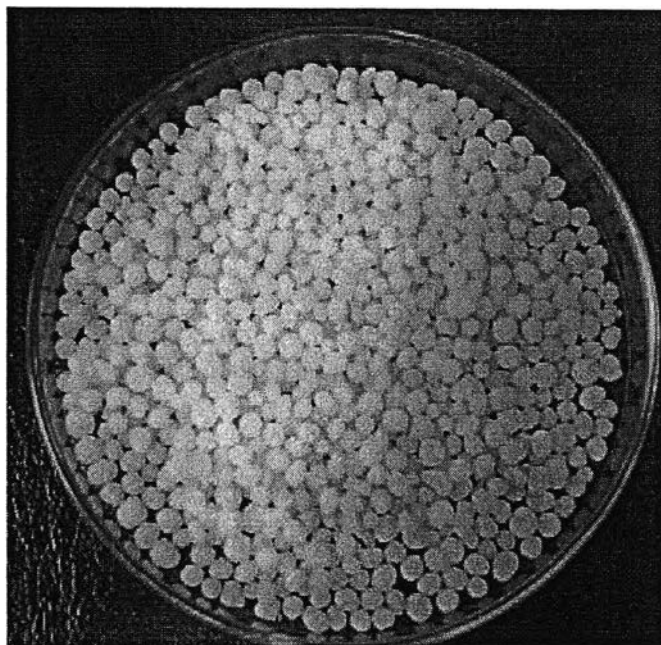


Figure 4.11 The uncoated urea fertilizer

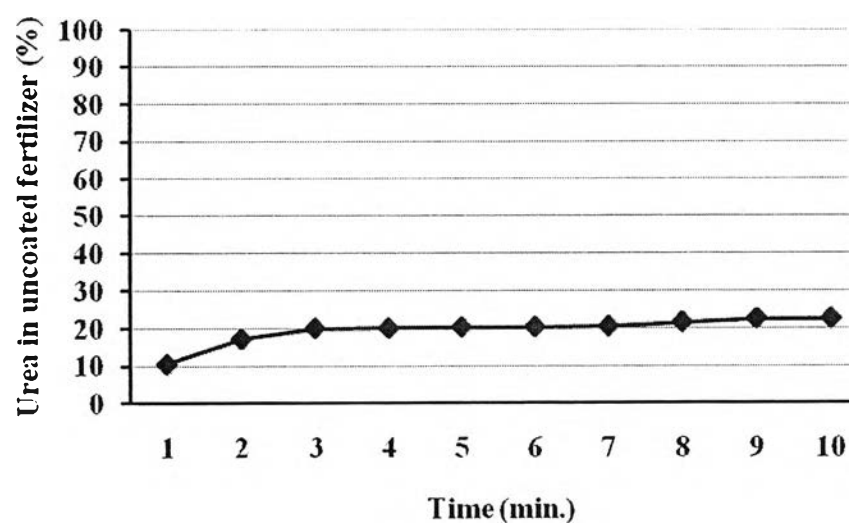


Figure 4.12 The urea content in the uncoated fertilizer

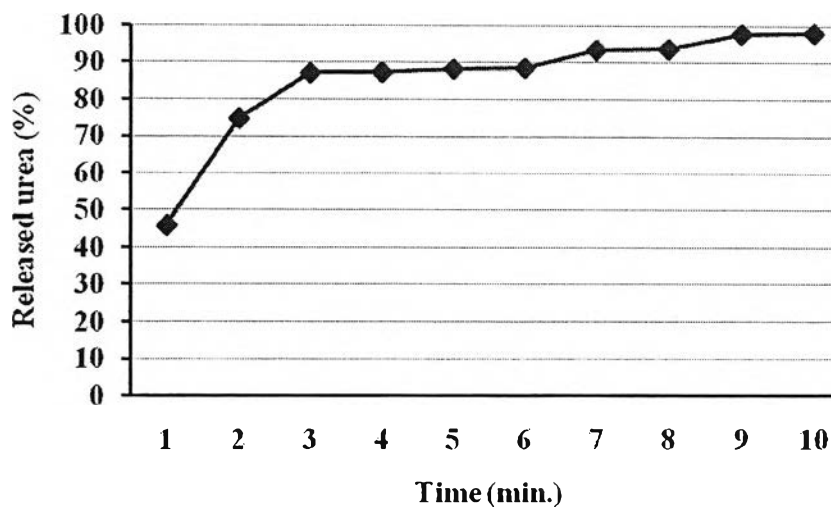


Figure 4.13 The solubility of uncoated urea fertilizer

4.5 Factors effecting of the controlled-release urea

4.5.1 Effect of film thickness on releasing of coated urea fertilizer

In this study, the effect of layer thickness of cardanol-tung oil to release rate of nutrient was investigated. Fertilizer granules were coated with cardanol-tung oil for 52.63, 71.05, 124.56, 175.44, and 230.70 micron.

The releasing rate of all coated fertilizer decreased when increased the number of coating. Figure 4.14 indicated that the urea particle having a coating thickness equal to 52.63 and 71.05 micron, immediate and relatively rapid release of urea occurs, while for a coating thickness equal to or greater than 124.56 micron, there is an extended period of time with little or no release before a sudden and dramatic change in release rate takes place. The time required for the formation of hole(s) is plotted against the coating thickness of less than 71.05 micron, almost no time is needed before a rapid release of urea, indicating that there exist a few holes or many microscopic pores originally in the coating. The slowest releasing rate obtained from the 124.56, 175.44, and 230.70 micron and the approximate urea released at 84 days was 87.76%, 83.48%, and 76.68%, respectively.

The releasing rate of urea fertilizer coated with urea cardanol-tung oil is similar trend to other previous studies of urea fertilizer coated with drying oil from *Ocimum canum* seeds of Buttrees [30]. However, at thickness as same the urea fertilizer coated with urea cardanol-tung oil slow-release than urea fertilizer coated with drying oil from *Ocimum canum* seeds.

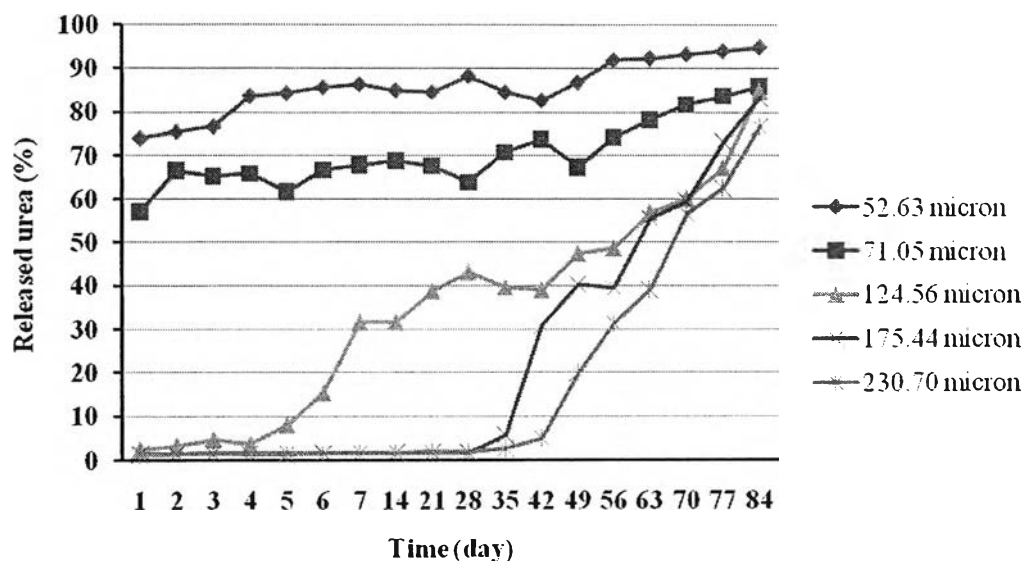


Figure 4.14 Influence of thickness on urea release behaviors in distilled water

4.5.2 Effect of temperature on releasing of coated urea fertilizer

The influence of temperature on the releasing rate of urea through cardanol-tung oil coating is present in Figure 4.15. The test was performed using 124.56 micron coated urea fertilizer. The temperatures were varied from 25, 30, 35, and 40°C. The results indicated that the temperature has an influence on the release of urea from coated urea. The higher temperature, the higher urea release rate was. Because of no bubbles or pore in the coating surface, the probable released mechanism was diffusion was controlled by the temperature. The dependence of the urea release on the temperature was mainly due to the increased diffusion rate as the temperature increased. If the temperature was raised, water molecule more penetrated to the coating to dissolve out the urea.

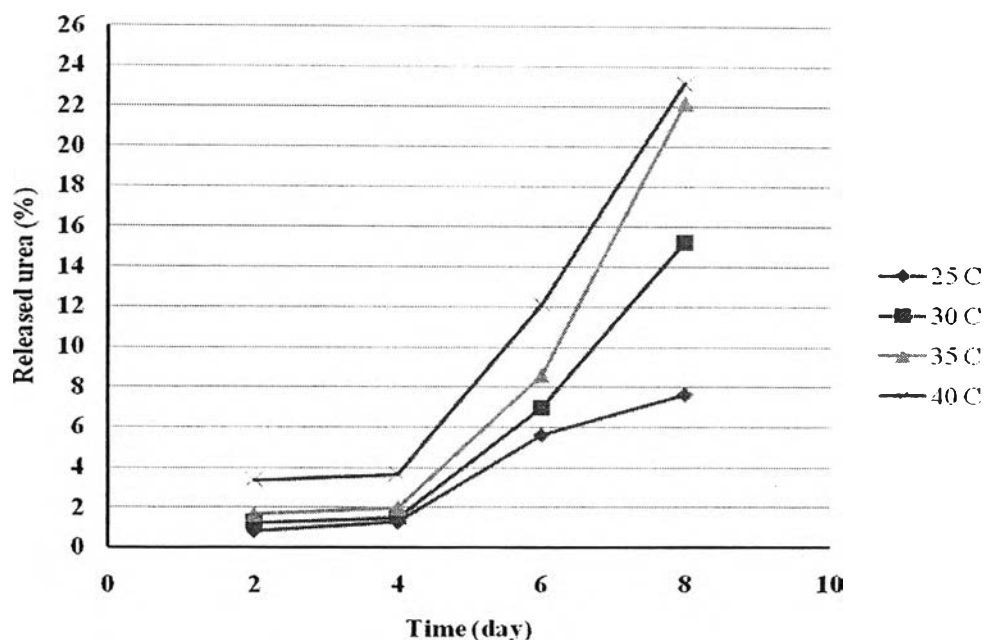


Figure 4.15 Influence of temperature on urea release behaviors in distilled water using 124.56 micron coated urea fertilizers

4.5.3 Effect of pH on releasing of coated urea fertilizer

The influence of pH on the releasing rate of urea through cardanol-tung oil coating is present in Figure 4.16. The test was performed using 124.56 micron coated urea fertilizer. The pH was varied from 5, 6, 7, and 8. It was observed that at low pH, releasing rate was higher than at high pH. Under acidic condition, the polymer coating film was more effectively hydrolyzed than that at basic condition which created more porosity for water to penetrate into core urea particle. The pH greater than 6.5 significantly increased the rate of urea conversion to ammonia gases [39].

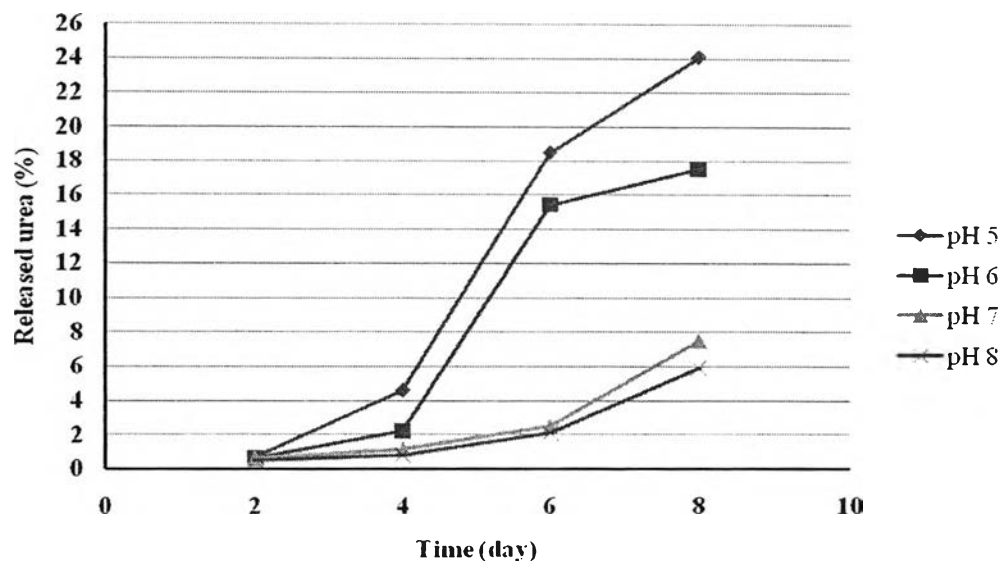


Figure 4.16 Influence of pH on urea release behaviors in distilled water using 124.56 micron coated urea fertilizers

4.5.4 Comparison of urea fertilizers (fertilizer 1 month for rice) coated with cardanol and commercial controlled-release fertilizers (osmocote™ 16-16-0; fertilizer 6 month for flower plant)

It was interesting to compare cardanol-tung oil coated urea fertilizers with the commercial fertilizers. Figure 4.17 showed the coatings of cardanol-tung oil film coated urea fertilizers and commercial NPK fertilizers coated with dicyclopentadiene (osmocote™) remained in water after completely undergoing nutrients released. Figure 4.18 indicated that the releasing rate of urea fertilizer which was coated at 52.63, 71.01, 124.56, 175.44, and 230.70 micron, respectively. Urea fertilizer coated with cardanol-tung oil was faster than that of commercial fertilizers. However, urea fertilizer coated with cardanol-tung oil at thickness 124.56 micron approximated for rice which was wanted nutrient within 1 month.

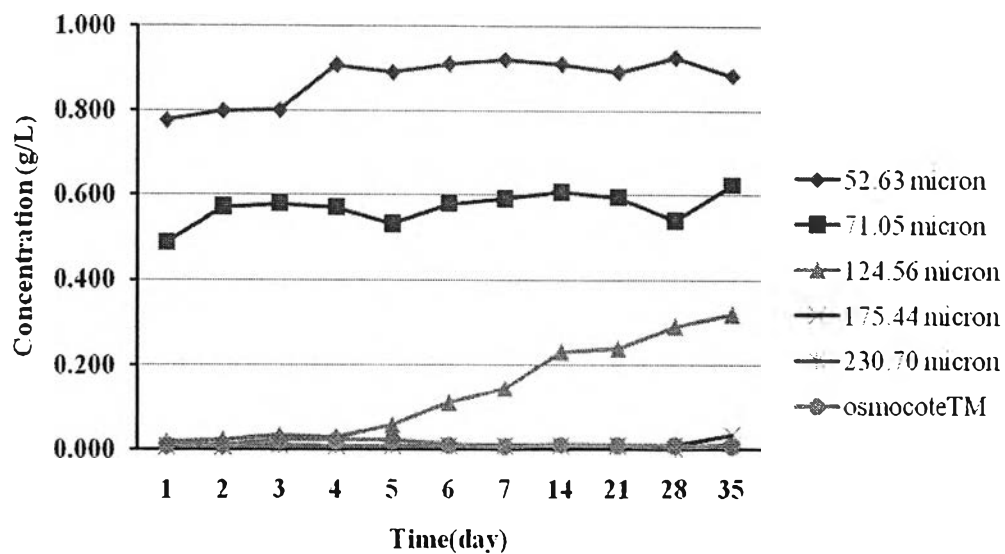


Figure 4.17 Comparison of the releasing rates of cardanol-tung oil coated fertilizers with osmocoteTM

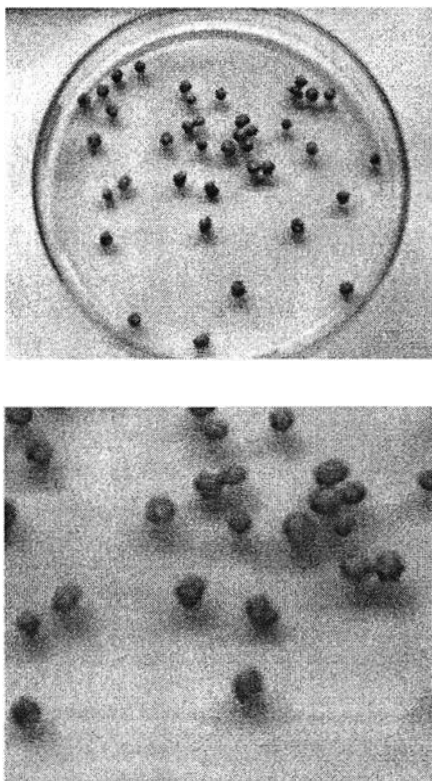


Figure 4.18 Coated urea fertilizers with cardanol-tung oil (9:1) after completely urea released in water

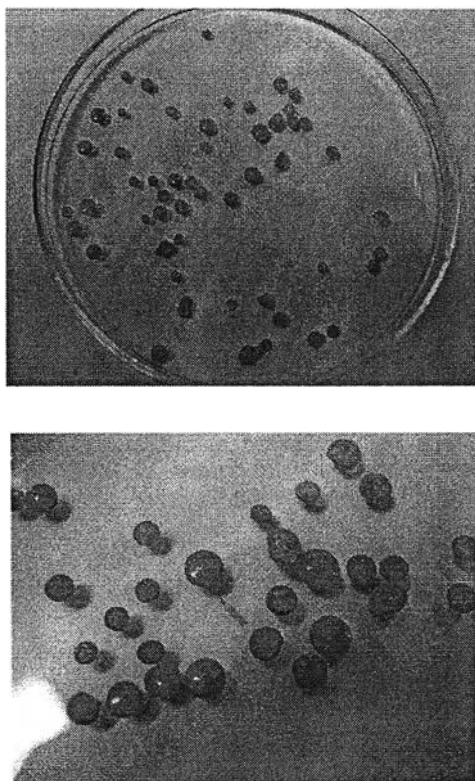


Figure 4.19 Commercial NPK fertilizers (osmocote™) after completely nutrient release