การห่อหุ้มปุ๋ยยูเรียด้วยน้ำมันชักแห้งจากเมล็ดแมงลัก *Ocimum canum*

นางสาวพิมพ์มาดา บุตรี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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ENCAPSULATION OF UREA FERTILIZERS WITH DRYING OIL FROM *Ocimum canum* SEEDS

Miss Pimmada Buttree

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Field of study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Nattaya Ngamrojanavanich, Ph.D.
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พิมพ์มาดา บุตรี : การห่อหุ้มปุ๋ยยูเรียด้วยน้ำมันชักแห้งจากเมล็ดแมงลัก *Ocimum canum* (ENCAPSULATION OF UREA FERTILIZERS WITH DRYING OIL FROM *Ocimum canum* SEEDS) อ. ที่ปรึกษา: รศ. ดร. นาตยา งามโรจนวณิชย์, อ. ที่ปรึกษาร่วม: รศ. ดร. อมร เพชรสม, 99 หน้า.

ได้ทำการศึกษาสมบัติการแห้งตัวของน้ำมันชักแห้งที่ได้จากน้ำมันเมล็ดแมงลักและใช้เตรียมเป็นสารห่อหุ้มปุ๋ยยูเรียเพื่อควบคุมการปลดปล่อยธาตุอาหารโดยใช้การเคลือบในหม้อเคลือบ และได้ทำการทดลองโดยศึกษาเปรียบเทียบกับน้ำมันลินสีด และน้ำมันถั่วเหลือง ซึ่งมีสมบัติในการแห้งตัวคล้ายคลึงกันและเป็นน้ำมันชักแห้งที่มีจำหน่ายในท้องตลาด ปริมาณของน้ำมันที่เหมาะสมในการเคลือบคือ ร้อยละ 6 ของน้ำหนักปุ๋ย และใช้โคบอลต์แนฟทีเนตร้อยละ 2 ของน้ำหนักน้ำมัน เป็นตัวเร่งปฏิกิริยาโดยใช้อุณหภูมิในการเคลือบคือ 60 องศาเซลเซียส จากการศึกษาพบว่าน้ำมันที่นำไปให้ความร้อนที่อุณหภูมิ 150 องศาเซลเซียส เป็นเวลา 2 ชั่วโมงก่อนนำมาใช้ห่อหุ้มปุ๋ยสามารถลดเวลาในการเคลือบได้ โดยพบว่าเมื่อใช้น้ำมันจากเมล็ดแมงลักและน้ำมันลินสีด ใช้เวลาในการห่อหุ้มปุ๋ยลดลงจาก 10 นาที และ 50 นาที เป็น 2 นาที และ 10 นาที ตามลำดับ ปุ๋ยที่ได้มีลักษณะผิวเรียบ แข็งเงา และไม่ละลายน้ำ การปลดปล่อยยูเรียสามารถยืดออกไปได้ถึง 2 เดือน ซึ่งเมื่อทำการห่อหุ้มจำนวนชั้นมากขึ้นปุ๋ยจะมีความแข็งแรงมากขึ้นด้วย น้ำมันจากเมล็ดแมงลักจะให้ความหนาของฟิล์มน้อยกว่าน้ำมันลินสีดที่จำนวนชั้นฟิล์มเคลือบเท่ากัน จากการศึกษาการปลดปล่อยของธาตุอาหารของปุ๋ยยูเรียด้วยเทคนิคยูวี วิสิเบิล สเปกโตรโฟโตเมตรี พบว่าปุ๋ยยูเรียที่เคลือบด้วยฟิล์มจากน้ำมันเมล็ดแมงลักและน้ำมันลินสีดทีมีความหนาของฟิล์มเท่ากันจะมีอัตราการปลดปล่อยยูเรียเท่ากัน และปุ๋ยยูเรียที่เคลือบด้วยฟิล์มที่มีความหนามากขึ้นจะควบคุมการปลดปล่อยได้นานขึ้น ซึ่งเมื่อศึกษาในภาวะที่อุณหภูมิสูงและภาวะที่ความเป็นกรดสูงปุ๋ยจะมีอัตราการปลดปล่อยยูเรียเพิ่มขึ้น

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต......................................

ปีการศึกษา.................2550.........................ลายมือชื่ออาจารย์ที่ปรึกษา.........................

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.......................

4872263423 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: DRYING OIL, AUTOOXIDATION, *Ocimum canum* SEEDS OIL, LINSEED OIL, SLOW-RELEASE, UREA FERTILIZER, PAN COATING

PIMMADA BUTTREE: ENCAPSULATION OF UREA FERTILIZERS WITH DRYING OIL FROM *Ocimum canum* SEEDS. THESIS ADVISOR: ASSOC. PROF. NATTAYA NGAMROJANAVANICH, Ph.D, THESIS COADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., 99 pp.

The drying oil from *O. canum* seed was investigated for its drying properties on controlled-released urea fertilizers by pan coating method. Linseed and soybean oil were used as coating materials for comparison with *O. canum* seed oil because of their drying properties and availability in the market. It was observed that the optimum amount of drying oils for coating process was 6% and using 2% cobalt naphthenate as catalyst at 60ºC. In coating process, *O. canum* seed and linseed oils pre-cured by heating at 150ºC for 2 hours could reduce coating time from 10 and 50 minutes to 2 and 10 minutes, respectively. The products obtained from this method were smooth, compact, glossy and water resistant. The releasing of urea could be prolonged for two months. In addition, it was observed that in the case of multiple coating the polymer layer was thicker and more compact. However, *O. canum* seed oil gave film thickness less than that from linseed oil at the same number of layers. The UV-Visible spectrophotometric method was used to determine the urea released from encapsulated urea fertilizer. It was observed that encapsulated urea fertilizer with drying oil from *O. canum* seed and linseed oil at the same average thickness had the same releasing rate of urea. The higher coating thickness showed the longer release time of urea. Furthermore, higher temperature and lower pH enhance releasing rate.

Field of study…Petrochemistry and Polymer Science… Student's signature……………
Academic year ……...2007……………………………. Advisor's signature……………
Co-advisor's signature……….....

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LIST OF ABBREVIATIONS

g	Gram
ºC	Degree Celsius
ml	Milliliter
min	Minute
SEM	Scanning Electron Microscope
ASTM	American Society for Testing and Materials
%	Percent
% wt	Percent by weight
wt	Weight
µm	micrometer
N	Normality
L	Liter
rpm	rounds per minute
O. canum	*Ocimum canum*
α	Alpha
UV	Ultraviolet
KOH	Potassium hydroxide
NaOH	Sodium hydroxide

CHAPTER I

INTRODUCTION

1.1 Introduction

Fertilizers and water are the important factors that limit the production of agriculture. It is very important to improve the utilization of water sources and fertilizer nutrients. However, about 40-70% of nitrogen of the applied normal fertilizers is lost to the environment and cannot be absorbed by crops, which causes not only large economic and resource losses but also very serious environmental pollution [1].

Nitrogen is the most vital nutrient for crops. Urea is considered one of the world's leading nitrogen fertilizers due to its high nitrogen content (46%), comparatively low cost of production [2], and commercial availability. However, urea fertilizer is very easy dissolution in water and rapid hydrolysis. This causes high nitrogen losses through ammonia volatilization [3]. Plant uptake of urea is generally below 50%.

One method of improving the utilization of fertilizers involves the use of slow or controlled-release fertilizers. Encapsulation fertilizers are physically prepared from granules of conventional fertilizers encapsulated with materials that reduce their dissolution rate. The materials applied most frequently as coating are inorganic materials, such as sulfur, phosphates and silicates: synthetic organic materials, for example, dicyclopentadiene polymers (Osmocote^{TM}), polyethylene, and ureic resin: and natural organic materials, including resin, rubber and wax [4]. Recently the use of slow release fertilizers is new trend to save fertilizers consumption and to minimize environmental pollution. The slow-release materials are generally too costly for cultivation on a large scale.

Drying oils are natural fatty oils, largely composed of mixtures of triglycerides. The drying power of oils is directly related to the chemical reactivity conferred on the triglyceride molecules by the double bonds of the unsaturated acids, which allows them to react with the oxygen of air and with one another to form rigid polymeric network within a reasonable time [5].

Studies on the encapsulation of the commercial urea granular fertilizers, 46-0-0, with drying oil as a coating material were performed. Coating used for this purpose must have two additional properties: they must be biodegradable in soil and not leave toxic substances behind which will effect crops [6], in order to improve duration of efficiency, reduced toxicity for plants, reduced nutrients loss and environmental loading and reduced application costs [7]. The experiment were carried out on rotating drum (pan coater) device which was used extensively in various industrial processes such as pharmaceutical industries, cosmetics [8], controlled-release fertilizers both continuous in line processes and batch processes.

1.2 Objectives of the research

1. To prepare controlled released fertilizers encapsulated with drying oil.
2. To investigate influences on release rate of encapsulated urea granular fertilizers.

1.3 Scopes of the research

1. Preparation of controlled-release urea fertilizers using various drying oil by pan coating method.
2. Investigation and optimization of coating process.
3. Investigation on controlled-release fertilizers morphology by Scanning Electron Microscope (SEM).
4. Characterization of the outer coating material of drying oil film by Fourier Transform Infrared Spectroscopy (FT-IR).
5. Determination of release characteristic of controlled-release urea fertilizers by spectrophotometric method.
6. Determination of influences on the nutrient release behaviors for example pH, temperature and coating thickness.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Plant nutrition [9]

Plant nutrients fall into 2 categories: macronutrients and micronutrients.

(*i*) Macronutrients are those elements that are needed in relatively large amounts. They include nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca) and magnesium (Mg).

(*ii*) Micronutrients are those elements that plants need in small amounts (sometimes trace amounts), like iron (Fe), boron (B), manganese (Mn), zinc (Zn), copper (Cu) and molybdenum (Mo). Both macro and micronutrients are naturally obtained by the roots from the soil.

2.1.1 Plant nutrients and deficiency symptoms

Plants will usually display definite deficiencies if required nutrients are not present in adequate concentrations. The following symptoms may occur if the level of one mineral nutrient is not high enough to be within the range needed for best plant growth. A plant may exhibit a particular symptom for reasons other than a nutrient deficiency. However, if one of the deficiency symptoms occurs, a lack of the proper nutrient may be suspected, and the amount of that nutrient should be increased.

2.1.2 Common nutrients deficiency symptoms

2.1.2.1. Nitrogen (N)

Nitrogen is an essential nutrient in most plant functions; it is the key constituent in proteins and in chlorophyll and thus is especially important for healthy growth of leaves and other green parts of plants. Good leaf growth is essential for good yields.

Deficiency symptoms: Plant turns pale green, then yellow. It begins at the tip of leaves at the bottom of plant especially older ones and works its way in the direction of the main stem. Yellowing gradually spreads up the plant to the top.

2.1.2.2 Phosphorus (P)

Phosphorus, normally expressed as phosphorus pentoxide (P_2O_5) on the label, is important for many plant functions, particularly healthy root growth. It also plays a significant role in encouraging good germination of seeds, seedling development and fruit ripening.

Deficiency symptoms: dead leaf tissue can occur when deficiency is severe. Leaves are reduced in size. Older leaves are the first to be affected and may drop prematurely. Early in the deficiency, plants look almost too healthy. Growth is normal but undersized. Plants become dark green frequently changing to purple, especially the undersides of leaves.

2.1.2.3 Potassium or potash (K)

Potassium, expressed as potassium oxide (K_2O) on the label, plays a major role in ensuring high quality and abundant fruit and flowers.

Deficiency symptoms: older leaves become mottled or spotted, edges become dry and scorched. Dead spots begin to appear, stems are weak, root systems are poor and fruit ripens unevenly. Plants show reduced disease resistance, poor storage qualities.

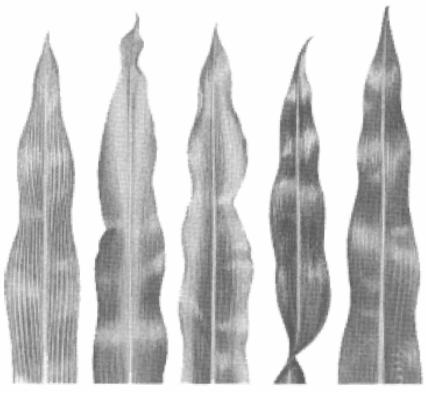


Figure 2.1 Plant nutrient symptoms.

2.2 Fertilizers [10]

The term "fertilizers" means a commercial fertilizer containing one or more of the recognized plant nutrients, which is used primarily for its plant nutrient content. Fertilizers are derived from a wide variety of natural and manufactured materials and are sold in solid, liquid and gaseous form (anhydrous ammonia). These materials are designed for use or claimed to have value in promoting plant growth or increasing plant available nutrient levels in soils.

2.2.1 Types of fertilizers

(*i*) Granular fertilizers is the most common form of fertilizer. It is usually packed in a bag, and can be applied with a drop spreader, spin spreader or hydro seeder. One of the advantages of this type of fertilizer is that they can be made to release the nutrients into the soil over a period of time. Another advantage is low cost.

(*ii*) Water soluble fertilizer is designed to dissolve in water. These often are a blue powder. These fertilizers are often a little more expensive than granular fertilizer, and usually are not a time release fertilizer. Manufacturers of these fertilizers claim that when used with a hydro seeding system the nutrients will enter the outer layer of the seed and will speed up germination.

(*iii*) Liquid fertilizer offers much of the same advantages and disadvantages as water soluble fertilizers. The difference is that it is already in a liquid form and to use it you dilute it with water.

(*iv*) Organic fertilizers are made from natural products such as bone meal, manure, dried blood, kelp and seaweed. They are popular with organic gardeners who want to avoid man made chemicals and their effects on the body. Organic fertilizers are usually expensive and do not have a high level of nutrients.

2.2.2 Urea fertilizer

Urea, white crystalline solid containing 46% nitrogen, is a low cost nitrogen fertilizer form. This is because of its high nitrogen composition and consequent low transport and storage costs. Urea may be the fertilizer of choice when only nitrogen is needed in a soil fertility program. Urea converts to ammonium bicarbonate within about 48 hours after field application. Nitrogen in this form will tend to volatilize to the air as ammonia gas. This lost fertilizer investment risk can be minimized or eliminated by assuring that the urea gets into the soil and does not merely remain on the surface of the soil or crop foliage. This can be accomplished by irrigating in the urea by plow down soon after surface broadcast application or by banding or injecting the urea directly into the soil.

The three primary plant nutrients: nitrogen, phosphorus and potassium, nitrogen is lost most easily from soil. Generally, nitrogen fertilizer efficiency in flooded rice fields is low. Upland crops usually use 40-60% of the applied N, whereas flooded rice crops typically use 20-40%.

2.3 Pathways for nitrogen loss [10]

Nitrogen in soil is subject to volatilization, immobilization, denitrification and leaching. Ammonium (NH_4) and ammonia (NH_3) producing N sources, such urea, are readily lost by NH_3 volatilization losses increase when left on the soil surface. Volatilization losses increase with factors that increase evaporation, such as high air and soil temperatures and wind speed. Applying NH_4 based fertilizers when temperature are cool, winds are light and there is good likelihood of receiving rain after N application would help to reduce volatilization losses. Both NH_4 and NH_3 sources of N are subject to immobilization or tie up by microorganisms during their growth and reproduction. Immobilization increases with the presence of substrate with a high C: N ratio.

Denitrification, conversion of nitrate to gaseous forms of N, occurs when oxygen availability in soil is limited. This mainly occurs when the soil is flooded or severely compacted. However, even when soil is not completely flooded, there will be microsites where oxygen availability is limited and denitrification can occur. The NO_3 form of N is more subject to leaching loss than ammonium (NH_4), as NH_4 -N is normally bound to soil particles and so protected from leaching losses, whereas NO_3 –N is mobile in the soil solution.

The potential for N losses via these pathways depends on soil type and environmental conditions. In order to minimize N losses and maximize fertilizer use efficiency, combinations of nitrogen source, timing and placement should, therefore, be selected considering the soil and environmental condition. The reaction representing this process is as follows:

$$H_2NCONH_2\ \text{(urea)} + H_2O \xrightarrow{\textit{Bacteria aerobic or anaerobic}} 2NH_3 + CO_2$$

$$2NH_3 + 3O_2 \xrightarrow{\textit{Nitrosomonas}} 2NO^-_2\ \text{(Nitrite)} + 2H^+ + 2\,H_2O$$

$$2NO^-_2 + O_2 \xrightarrow{\textit{Nitrobacter}} 2NO^-_3\ \text{(Nitrate)}$$

2.4 Slow or controlled release fertilizers

Controlled release technology in agriculture includes the controlled delivery of plant nutrients such as fertilizers to a target in a manner which maximizes its use efficiency, minimizes potential negative effects associated with over dosages, thereby mitigating environmental pollution and leading to the development of sustainable agriculture. Furthermore, use of coating materials may result in high production costs and even soil contamination after their release into soil. To solve these problem, some research have recently developed new uncoated slow/controlled release organic-inorganic compound fertilizers, such as the fertilizers prepared using plastic-starch and clay-polyester as cementing agents [11].

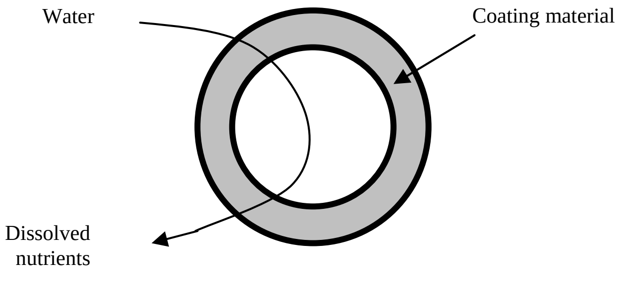


Figure 2.2 Mechanism of nutrients release from encapsulated fertilizer granules.

2.4.1 Slow – release nitrogen fertilizers

Less than optimum rates of recovery by plants of applied nitrogen have been recognized for years. Results of studies have shown 50-70% or less of fertilizer nitrogen applied is recovered by crop plants. Reasons for the poor nitrogen recovery relate to problems with ammonia volatilization, leaching and denitrification of nitrate. Rapid dissolution of the nitrogen products supplied allows the possibility of rapid uptake by plants. Large amounts of available nitrogen at one period in time may lead to luxury nitrogen consumption by plants which represent absorption without increased growth.

The problem of slowing nitrogen release from various compounds has been approached by altering the solubility of materials or to develop compounds that have low water solubility. Methods of altering the release of nitrogen from soluble materials has been to coat water-soluble compounds with materials that are less water soluble thus retarding entry of water into the particle and the movement of nitrogen out. Coating applied to soluble nitrogen materials generally have been of three types:

(*i*) Fertilizers whose components have been turned to give difficulty soluble or difficulty decomposable properties through a chemical way.

(*ii*) Fertilizers which are turned into difficulty soluble form by some method for example incorporation of inorganic substances such as cements or the like or organic substance such as wax or the like.

(*iii*) Fertilizers are coated with water-resistance substances [12].

2.4.1.1 Sulfur-coated urea (SCU)

Sulfur-coated urea has been developed in recent years as a product with the characteristics of slow nitrogen release. This material is basically urea with a coating of elemental sulfur including binding agent and a sealant. Elemental sulfur was chosen as a coating agent because of its relatively low cost and ease of handing. Nitrogen release rates can be varied by controlling the thickness of the sulfur coating. The nitrogen content of SCU ranges from about 10-37% depending on the thickness of sulfur coating. Nitrogen release is calculated as the amount of the nitrogen that will solubilize in 7 days. Characteristics of SCU that have been examined by the Tennessee Valley Authority include material ranging from 10% nitrogen solubilized in the first 7 days up to 40% nitrogen solubilized in the first 7 days. These forms of SCU are noted as SCU-10 and SCU-40, respectively.

Agronomic evaluations of SCU have indicated some possible improvement in nitrogen efficiency, particularly with crops with very large demands for nitrogen throughout an extended growing season.

Uncoated organic compounds of low water solubility have been studied as sources of nutrients for over 50 years. Intensive studies during the last 25 to 30 years have resulted in the production of certain urea-derived compounds that have a characteristic of slow nitrogen solubility in water. Typical of these types of compounds are those produced by the reaction of urea and formaldehyde to produce condensation products know generally as urea-formaldehyde or urea-form.

2.4.1.2 Urea formaldehyde (UF)

Urea reacts with formaldehyde in the presence of a catalyst to form a mixture of compounds that are classified under the general name of urea-form. These materials are white, odorless compounds that contain varying amounts of nitrogen but averaging around 38%. A basic component of urea-forms is methylene-urea polymers varying in chain length and in degree of cross-linking between chains. Basically, as the compound links are extended, the water solubility of these materials declines.

Although the urea-forms have been examined agronomically in the United States, they have not received wide attention except as nitrogen sources for very high value crops, turf, and ornamentals. More attention has been given to these compounds in Europe and in Japan.

2.4.1.3 Isobutylidenediurea (ISBU)

Isobutylidenediurea is a reaction product of urea and isobutyraldehyde. The reaction has been utilized to produce a compound containing approximately 32% nitrogen and having low water solubility. This compound also has the ability to be granulated with soluble nutrient sources of phosphorus and potassium to supply mixed fertilizer formulations with slow nitrogen release.

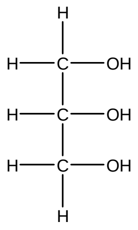
2.5 Drying oils [13]

Drying oils are natural fatty oils, largely composed of mixtures of triglyceride. These are esters formed between one molecule of glycerol and three molecules of various linear fatty acids. The most common fatty acids encountered in the composition of drying oils are saturated acids with 12, 14, 16 or 18 carbon atoms (lauric, myristic, palmitic and stearic acids respectively) and C_{18} polyunsaturated acids with 1, 2 or 3 double bonds (oleic, linoleic and linolenic acids, respectively) The drying power of such oils is directly related to the chemical reactivity conferred on the triglyceride molecules by the double bonds of the unsaturated acids, which allows them to react with the oxygen of air and with one another to form a polymeric network. Since the fifteenth century drying oils, were extensively used as a medium for paintings, owing to their capacity, after being spread out in a thin layer, to form a continuous film with good optical and mechanical properties within a reasonable time.

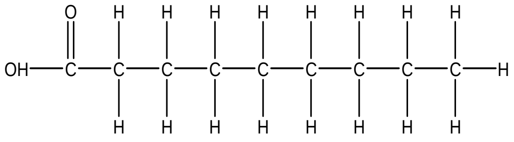
Agricultural raw materials precede petrochemicals in non-food applications. Vegetable oils, for instance, have been used for illumination and lubricating purposes as well as for coating and paints for many countries before and abundant and cheap supply of oil became available for a wide range of product [14].

2.5.1 Oil composition [14]

Triglycerides have the following composition:

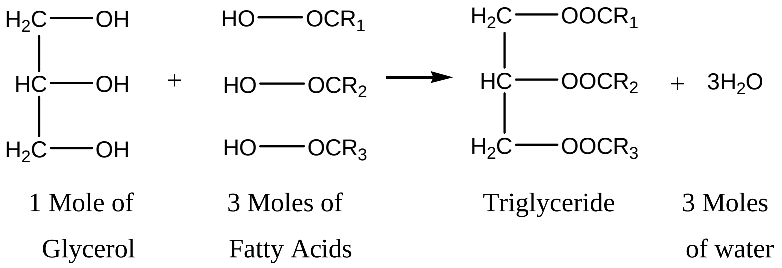


Glycerol



Fatty Acid

Fatty acid chain length can vary from C_9 to C_{22}.



In the formulas show above, R_1, R_2 and R_3 stand for fatty acid chains. If R_1, R_2 and R_3 are the same, a simple triglyceride results. If they are not the same, the triglyceride is mixed. Triglycerides occurring in nature are usually of this type. This is a reversible reaction so that if we hydrolyze and oil we obtain glycerine and fatty oils.

2.5.2 Fatty acids

The nature of the fatty acid present in oil determines its characteristics. The fatty acid consists of a carboxyl group attached to a hydrocarbon chain. Saturated fatty acids have hydrocarbon chains containing no double bonds, each carbon having a least two hydrogen atoms. Fatty acids with chains containing double bonds are termed *unsaturated*. They may have one, two, three or more double bonds, whose position in the chain may vary. Two double bonds separated by a single bond are called *conjugated*.

The double bonds in unsaturated fatty acids are chemically reactive sites. The reaction of oxygen with the oil molecule at the double bond results in drying; usually the greater the unsaturation, the better is the drying. Saturated fatty acids are nondrying. Fatty acids with three double bonds dry the most rapidly. However, in addition to the number of double bonds, the position of the double bond is important. Conjugated double bonds polymerize and dry more rapidly than isolated double bonds.

Table 2.1 Common fatty acids found in drying oils [15]

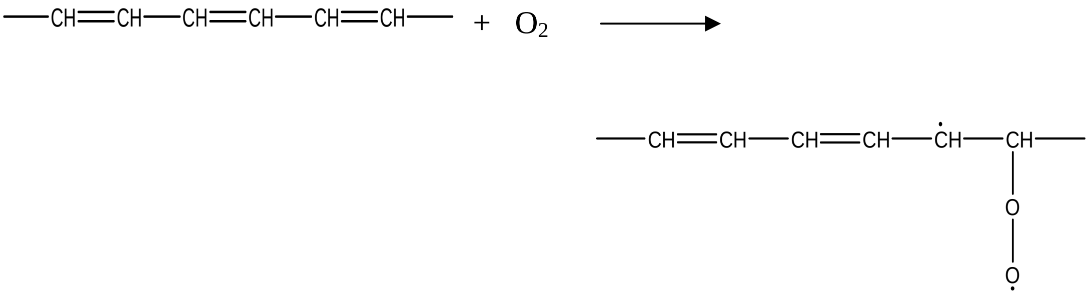
Common names	Formulas
Myristic acid	$CH_3(CH_2)_{12}CO_2H$
Palmitic acid	$CH_3(CH_2)_{14}CO_2H$
Stearic acid	$CH_3(CH_2)_{16}CO_2H$
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$
Linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$
Linolenic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$
Pinolenic acid	$CH_3(CH_2)_4CH{=}CHCH_2C{=}CHCH_2CH{=}CH(CH_2)_3CO_2H$
Ricinoleic acid	$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7CO_2H$
α-Eleostearic acid	$CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7CO_2H$

2.6 Drying mechanisms [16]

The drying mechanisms must be consistent with the facts. In particular different mechanisms are required for conjugated and non-conjugated oils.

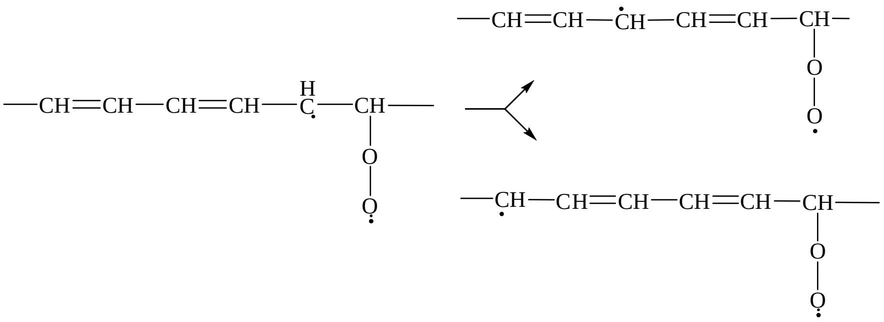
2.6.1. Conjugated oils

Oxygen attacks conjugated double bonds by direct addition, to form free radicals with two unsatisfied valencies (diradicals).

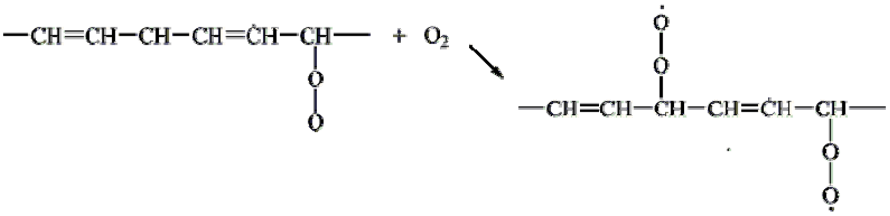


$$-CH{=}CH-CH{=}CH-CH{=}CH- \; + \; O_2 \longrightarrow -CH{=}CH-CH{=}CH-\dot{C}H-CH(-O-\dot{O})-$$

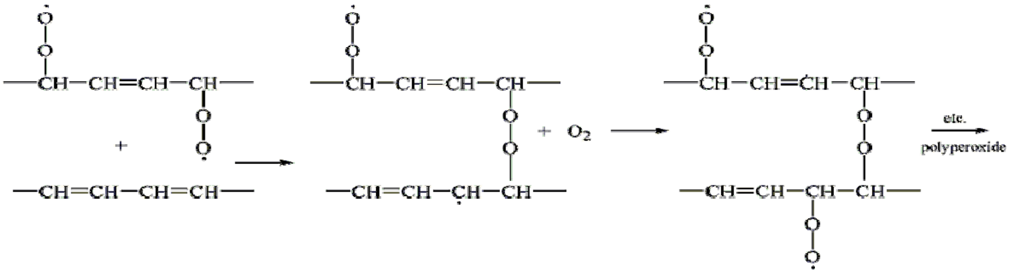
Rearrangement of double bonds can take place to give radical sites in the 1, 4 and 1, 6 positions as well.

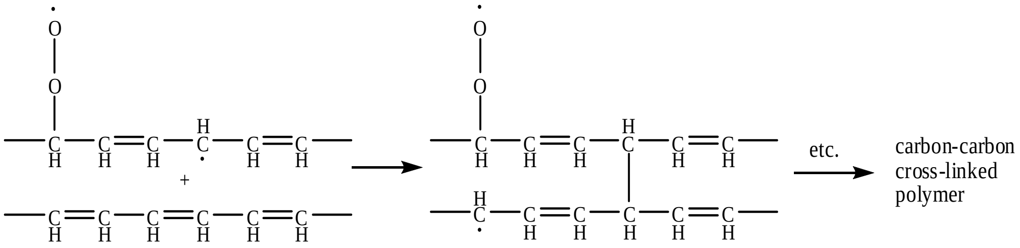


Such rearrangements involve only the redistribution of electrons in the molecule and occur frequently in unsaturated free radicals. Oxygen may react with free carbon valencies to convert them to peroxy radicals.



Cross-linking occurs when the diradicals attack double bonds in other oil molecules. The peroxy radicals produce polyperoxides.





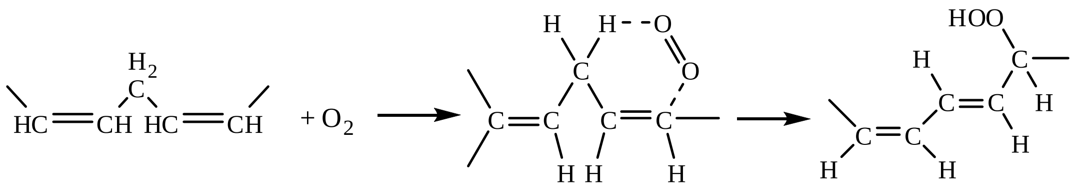
The cross-linking polymerization ceases when the two ends of the growing diradical combine with one another. Polyperoxides are exceptionally stable peroxides, but are decomposed by heat and light to alkoxy radicals (RC-O•), which will in turn react with double bonds to form ether linkages (RC-O-CR).

If 1, 4 diradicals are formed from triple unsaturation, the remaining double bonds are non-conjugated and hydroperoxide formation can occur in the manner show in the next section.

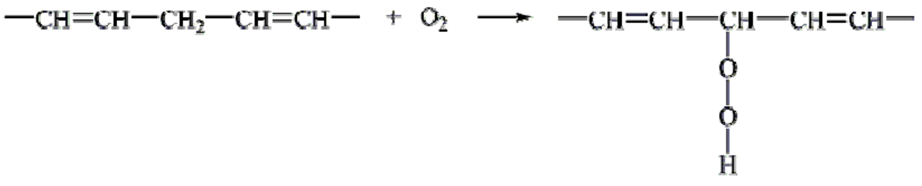
If 1, 2 or 1, 6 diradicals are formed, the remaining double bonds are conjugated and one will react with oxygen. Since each reaction produces two free valencies, the maximum functionality of eleostearic acid is four and that of the triglyceride twelve.

2.6.2 Non-conjugated oils

The essential difference is that reactions between oxygen (or free radicals) and non-conjugated oils occur without loss of unsaturation. One school of thought states that oxygen does attack the double bond, but that hydroperoxide formation and rearrangement of bonds occur simultaneously, so that no unsaturation is lost.



The alternative opinion is that the methylene group between two double bonds is particularly prone to direct oxidation. With oxygen, a hydroperoxide is formed.

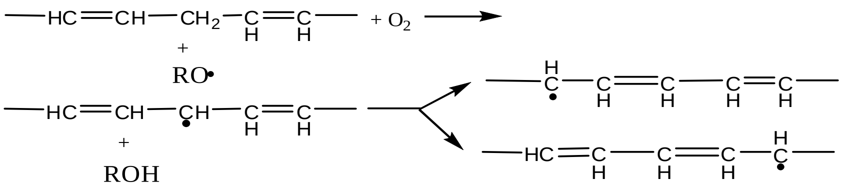


$$-CH=CH-CH_2-CH=CH- + O_2 \longrightarrow -CH=CH-\underset{\substack{| \\ O \\ | \\ O \\ | \\ H}}{CH}-CH=CH-$$

The decomposition of hydroperoxides by driers is described in the section on driers. Free radicals are also obtained when hydroperoxides are decomposed by heat and light.

$$\mathrm{RC{-}O{-}O{-}H \longrightarrow RC{-}O\cdot + \cdot O{-}H}$$

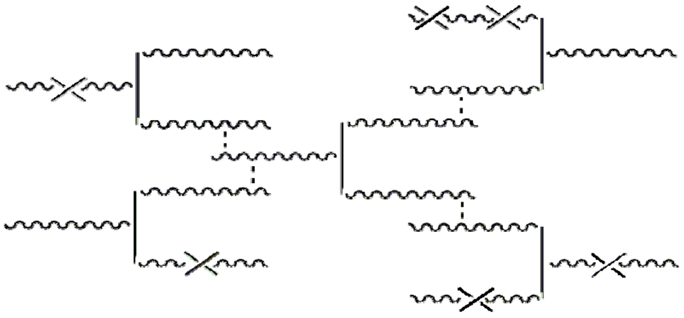
A free radical will readily remove a hydrogen atom from the active methylene group between double bonds, transferring its free radical nature to the attacked carbon atom. The new free radical may then rearrange to a conjugated form.



Oxygen can convert these free radicals to peroxy radicals, which in turn may abstract hydrogen form methylene groups to form hydroperoxides.

Whichever route is correct, it is generally agreed that hydroperoxide is formed and a substantial amount of isomerization to conjugated forms occurs.

During the initial stages of drying, the chief method of cross-linking is by direct combination of free radical sites on different oil molecules. Peroxy, ether and carbon-carbon links can be formed.



$$\left.\begin{array}{l}\mathrm{CR{-}O\cdot + \cdot O{-}CR \longrightarrow RC{-}O{-}O{-}CR}\\ \mathrm{CR\ \ O\ \ O\cdot + \cdot CR \longrightarrow RC{-}O{-}O{-}CR}\\ \mathrm{CR{-}O{-}O\cdot + \cdot O{-}O{-}CR \longrightarrow RC{-}O{-}O{-}CR + O_2}\end{array}\right\}\ \text{peroxy linkage}$$

$$\mathrm{CR{-}O\cdot + \cdot CR \longrightarrow RC{-}O{-}CR}\qquad \text{ether linkage}$$

$$\mathrm{RC\cdot + \cdot CR \longrightarrow RC{-}CR}\qquad \text{C-C linkage}$$

Figure 2.3 The cross-linking of oil molecules.

2.7 Modified drying oils [14]

Heat-polymerized oils, or bodied oils or stand oils are used in the manufacture of vanishes, paints and enamels. Drying oils with added metal salt of organic acids are termed “boiled oils”. Boiled oil is obtained by heated unmodified oil was with catalyst, with or without bubbling of air through the oil. In this process the double bonds of the unsaturated fatty acids in the oil are oxidized and to some extent polymerized. This leads to an increase in the viscosity of the oil and decrease in drying time. Boiled oil may be accomplished in several ways, each with its specific applications [17].

2.8 Vegetable oils

2.8.1 *Ocimum canum* seed oil [18]

Figure 2.4 *Ocimum canum* seeds.

Ocimum canum is a well-known spice in Africa and in Asia, where the aerial plant parts are used. *O. canum* oil is not commonly used as edible oil in most country in the world. This is because the *ocimum* plant is cultivated mainly for its essential oils that might be responsible for medicinal properties. *O. canum* seeds, which is a popular supplement used in drinks and desserts in Thailand. The seed is small, black, and oval and contains dietary fiber. *O. canum* seeds are soaked in water causing a gelatinous coat to form. Making *O. canum* seeds is alternative as a supplement in Thailand [19].

The composition of basil seed oil suggests that the oil would be suitable for industrial purposes, much in the same way as linseed oil is used. The highly of unsaturated oil such as linolenic acid oil that found in *O. canum* seeds could be used in the paint, varnish and ink industries, and as a source of linolenic acid. Techniques and conditions for basil cultivation are well known, as the plant has been grown as a culinary herb and source of essential oil for many years. Seed and oil content yields could be increased by plant selection.

2.8.2 Linseed oil [14]

Figure 2.5 Flax seeds.

Linseed oil is obtained from the seeds of the common flax (*Linum usitatissimum, L.*) plant, which is one of the oldest of cultivated plants. Two main varieties of flax are cultivated, the one for the production of linen fibre, and the other for the production of linseed oil. Flax seed has an average oil content of 35%. In order to obtain the best fibre the plant must be cropped before the stems become woody, and at this stage the seeds are not ripe, while of the seeds are allowed to ripen the stem is too woody to yield good linen fibre, It has not yet been found possible to produce strains of plant serving both purposes.

Linseed oil consists of a mixture of triglycerides of mainly palmitic, stearic, oleic, linloleic and linolenic acids. The drying of linseed oil is an oxidation and polymerization process, during which the triglycerides undergo cross-linking [20]. Linseed oil, historically, has been the most important oil in the coatings industry. Although its use has decreased because of other material, linseed oil still leads in volume in the coating industry. Linseed oil has a moderate drying rate. Because of its high linolenic acid content, linseed oil yellow on aging. It is used as the principal vehicle in house paints and also as the drying oil in some alkyds.

2.8.3 Soybean oil [14]

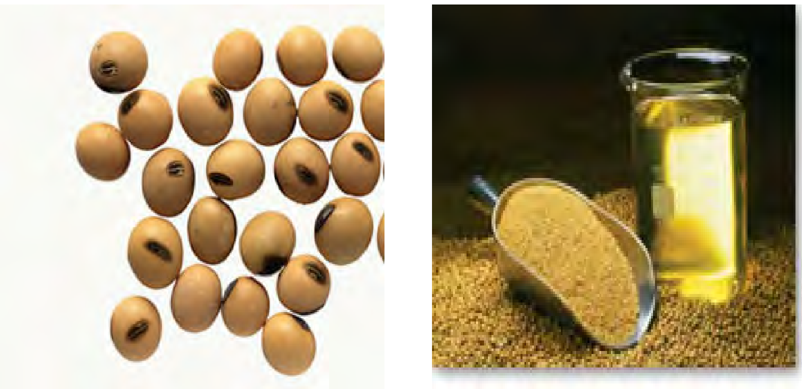


Figure 2.6 Seeds of *Soya max.*

Soybean oil, obtained from the seeds (oil content 20%, average, dry basis) of the legume *Soja max*, is the highest volume vegetable oil produced in the world. The main uses of the oil after refining, bleaching and deodorization, and partial hydrogenation are in the manufacture of margarine and shortenings. The un-hydrogenated oil is also used in blends with other oils, but its tendency to revert when exposed to air or high temperatures limits its use. Soybean oil is also used extensively in the manufacture of drying oil products.

The average iodine number of the soybean oil is in the 125-130 range, although iodine numbers as high as 151 and as low as 103 have been reported. Other average characteristics are approximately as follow:

Specific gravity at 25^0 C	0.917 - 0.921
Iodine number (wijs)	120 – 141
Saponification number	189 – 195
Unsaponifiable matter	Not over 1.5%
Refractive index at 25^0 C	1.470 – 1.476

Fatty acid composition of soybean oils of widely varying iodine numbers usually contains 5-9% of linolenic acid and generally 43-56% of linoleic acid. The saturated fatty content of soybean ranges from 11 to 26% and is almost independent of the iodine number of the oil; variation of iodine number reflects chiefly a variation in the oleic:linoleic ratio.

2.9 Driers [21]

Driers are materials that promote or accelerate the curing or hardening of film formers containing oxidizable or drying oil components. Air drying is the formation of a solid film at ambient temperature by oxidization process from an applied liquid coating. Such coatings are convertible coatings in that the film, after drying, does not re-dissolve in the original carrier solvent. The air-drying process can described as autooxidation, as it takes place automatically after the coating has been spread. Autooxidation is a chemical process that is greatly affected by temperature and the presence of catalysts.

The autooxidation of unsaturated drying and semi-drying oils does not proceed rapidly enough to be commercially acceptable; for instance, linseed oil, non-yellowing oil with conjugated unsaturation requires more than 24 hours to become non-tacky. The conversion of these oils into higher molecular weight polymers (alkyds) with greater propensity to oxidize still does not give commercially acceptable drying times unless autooxidation catalysts are added.

A major advance in drier technology occurred in the 1920s with the preparation of the metal naphthenates. The naphthenic acid is not of precise composition, but is a mixture of acid of the same general structure. As the mixture would vary, so would the acid number, or combining equivalent of the acid, so that the metal content of the drier was not always the same from batch to batch. The next major advance in technology was the preparation of solvent solutions of these metal naphthenates, which not only gave materials that were easy to handle but allowed the metal content to be standardized. Naphthenates soon became the standard for the industry.

2.9.1 Drier metals

The metals are divided into two major categories, active and auxiliary. These groupings, however, should only be considered arbitrary as a considerable amount of overlap exists between them. Active driers promote oxygen uptake, peroxide formation and peroxide decomposition. At elevated temperatures several other metals, such as bismuth, display this catalytic activity themselves, but appear to enhance the activity of the active drier metals. It has been suggested that the auxiliary drier improves the solubility of the active drier metal, can alter the redox potential of the metal, or most likely functions through the formation of complexs with the primary drier.

Driers containing transition metals with several oxidation states are called primary driers. They act as catalysts of hydroperoxide decomposition in a redox reaction called Haber and Weiss mechanism can be illustrated as follow:

$$M^{n+} + ROOH \longrightarrow M^{(n+1)+} + RO^{\bullet} + OH^{-}$$

$$M^{(n+1)+} + ROOH \longrightarrow M^{n+} + ROO^{\bullet} + H^{+}$$

2.9.2 Cobalt

Cobalt is the most important and most widely used drying metal. It is primarily an oxidation catalyst and as such acts as a surface or top drier. Used alone, it may have a tendency to cause surface wrinkling and poor through-dry. Therefore, to provide uniform drying, cobalt is generally used in combination with other metals, such as manganese, zirconium, lead, calcium and combinations of these metals.

Cobalt drier has a strong red-violet color, which contributes a little color to a clear a clear varnish. However, if cobalt drier is mixed with gum terpentine, dipentene, or similar solvents prone to take up oxygen on storage, a strong green color develops. This color usually disappears from the dried coating, but will be more persistent if calcium is used with cobalt.

Cobalt is a transition metal, which can exist in two valence states, and is known for its ability to form coordination complexes. If cobalt drier is added to some undiluted resins, profound changes in viscosity may occur, although this does not happen when cobalt drier is added to the pre-diluted resin. This is usually restricted to resins containing high molecular weight fractions, such as very high viscosity alkyds and copolymers. A similar effect occurs with calcium and zinc drier. The wrinkling effect with cobalt is turned to advantage in the production of alkyd-based baking wrinkling enamels.

2.9.3 Manganese

Manganese is also an active drier, though generally less active than cobalt. As an accelerator of polymerization in baking finishes, it is usually more effective than cobalt. Cobalt and manganese primarily improve the surface drying of the paint film. Manganese gives better low-temperature drying performance than cobalt, and films containing manganese do not suffer from wrinkling under high-humidity conditions, as do films with cobalt alone. It is generally preferred to formulate white enamels with no manganese or very low manganese content; a pink or pink-yellow color develops if high manganese contents are used.

Manganese also has the advantage that it does not cause baked films to brittle, as is the case if cobalt alone is used. Additionally, in systems prone to skinning, such as urethane oils, manganese can be used with good results. Manganese drier is seldom used alone; cobalt is the usually primary drier with manganese a very useful modifier.

2.9.4 Lead

Lead functions as a drier by promoting polymerization of drying oils to hard, insoluble films. In contrast to cobalt and other top driers, lead causes the film to dry through its entire thickness and is therefore known as a through-drier. Lead also improves flexibility, toughness and durability of the film. In addition to its function as a through-drier, lead improves the water resistance and salt spray resistance of a film, making it particularly desirable in rust-preventive coatings. It also serves as a pigment-dispersing and wetting agent, thereby assisting in the dispersion of the formulation. Lead driers are seldom used alone, but rather are used in combination with cobalt or manganese. Calcium, too, is often added to prevent lead precipitation.

Limitations to the use of lead are in aluminium paint vehicles, where it destroys the leafing characteristics of the pigment, and in films that will be subject to sulfur fumes if discolouration is to be avoided. Because of increased awareness of environmental pollution the incorporation of lead driers in paints is limited.

2.10 Equipment for coating process [22]

Coating materials can be applied to a wide variety of substrates ranging from micron particle to very large objects to improve its appearance. The coating of pharmaceutical, agricultural and food products has been practiced for hundred of years using techniques as diverse as applying coating by hand to individual tablets to the application of millions of tablets using rotating drum coating device.

Rotating drum (Pan coater)

Figure 2.7 Pan coater.

In general, rotating drums or perforated pans are currently used primarily to coat tablets. Figure 2.6 illustrates the basic elements of a rotating drum coating device. As the drum is rotated, solids cascade down the moving top surface of the bed. A dual-fluid nozzle distributes the coating material (solute and solvent) onto the moving particles. Simultaneously, hot air is drawn through the bed of solids to facilitate evaporation of the solvent. The repeated coating and drying cycle causes a coherent film of coating to be built up on the surface of the solids. The tumbling action of the solids is less abrasive than the circulating movement in a fluid bed coater, especially for large tablets that would require high air velocities that lead to high erosion and breakage in a fluid bed coater. However, heat and mass transfer are poorer in a rotating drum and the coating process tends to take significantly longer. In addition, the variability (tablet-to-tablet variation) tends to be higher for rotating drums compared to fluid beds. Thus, if active ingredients are contained in the coating material then it is more difficult to obtain the desired uniformity in a rotating drum coater than a fluid bed unit.

2.11 Literature reviews

In 1996 Garcia et al [6] prepared controlled-release fertilizer using the kraft pine lignin in formulations. Pine lignin obtained by the Kraft process was used. It was insoluble in water for all pH values that may occur in soil, this product was employed for coating pelleted urea. The physical and chemical evaluation of fertilizers showed that the most efficient are those whose coating embodies a mixture of dimerized, esterified and natural rosins, as well as lignin. It was also demonstrated that the efficiency of products noticeably increase by adding linseed oil as sealing agent.

In 2000 Hanafi et al [23] prepared controlled release compound fertilizer using granulation machine and was coated using polyvinyl chloride (PVC), polyacrylamide (PA), natural rubber (NR) and polylactic acid (PLA). Thermal-oxidative stability, as determined at 300ºC, decreased in the order: NR > PLA > PVC > PA. In contrast, the thickness of the coating layer on the compound fertilizer granules, determined by SEM, gave PVC compound coated fertilizer the highest value of 3.04 microns, and the lowest was obtained by PA (2.04 microns).

In 2002 Devassine et al [24] studied fertilizers coating method using polylactic acid as coating material. Compared the different techniques such as fluidized bed and pan coating, it was found that the best technique is fluidized bed method. The total release is reached in about 26 days. The fertilizers granules coated with the same polymer, using the coating pan present a quicker release about 45 hours.

In 2002 Hanpichanchai [25] prepared controlled-release NPK fertilizer using chitosan polymer. The fertilizers were coated with chitosan solution in a coating drum and dried at 75ºC for 24 hours. The results showed that the releasing rate depends on concentration of chitosan solution and degree of deacetylation. The fertilizers coated with high concentration of chitosan solution has low release rate while fertilizers coated with chitosan having low degree of deacetylation also has low release rate.

In 2003 Kiatkanarat [26] prepared prepolymer film for coating NPK fertilizers by reaction of epoxidized vegetable oils with amine compound, and cross-linking of vegetable oils using metallic salt as catalyst. The results showed that the most suitable oils preparing the prepolymer film were tung oil and 1:1 tung oil/soybean oil mixture in the presence of 0.5% cobalt naphthenate as catalyst.

In 2004 Saengrith [27] prepared controlled-release fertilizer coated with drying oil i.e. linseed oil, soybean oil and tung oil. The fluidized bed and pan coating were used for coating process. It was observed that pan coating was appropriate for the preparation of controlled-release fertilizers. Linseed oil and soybean oil were appropriate to be used as coating material but tung oil was not suitable. The optimum amount of linseed oil and soybean oil for coating by pan coating method was 10% and took 45, 120 minutes for drying.

In 2005 Ibrahim and Jibrilprepared [28] prepared controlled-release fertilizers with paraffin wax or a mixture of paraffin wax and rosin and study release profiles of KCl, NH_4NO_3, KNO_3, $(NH_4)_2SO_4$, and K_2SO_4 as fertilizers substrate. When the fertilizers were coated with wax/rosin or wax only, the rate of dissolution showed a higher decrease for wax/rosin samples than for wax-coated samples.

In 2005 Dutta et al [29] studied structural analysis and the performance of film for surface coating of heated and unheated Nahar seed oil. The film from heated oil showed shorter drying time over the film from unheated oil. However, the film from heated oil did not show significant improvement of coating performance. There is only marginal improvement of hardness and acid resistance on the film from heated oil compared to unheated oil.

In 2006 Tomaszewska and Jarosiewicz [7] prepared the encapsulated mineral fertilizer by polysulfone using a spraying method. Studies on the possibility of combining two techniques, inversion phase with spraying method in the fertilizer coating preparation. It was observed that the porosity and thickness of coating decreased about 30% compared with the reference coating that prepared by the inversion phase technique, wet method.

In 2006 Liang and Liu [4] prepared double-coated slow release urea fertilizers by cross-linked poly(acrylic acid) containing urea (PAAU) (outer coating), polystylene (PS) (inner coating), and urea granule (the core). It was found that PS coating percentage, temperature, water absorbency had a significant influence on the release of nitrogen. The results showed that the product had a good slow release property and excellent water-retention capacity.

In 2006 Handy et al [30] prepared controlled-release fertilizers using bitumen as a coating material. NPK fertilizer was coated with modified bitumen emulsion (50% active material) from commercial and 50% of emulsifier (polyvinyl acetate butyl acrylate). The releasing rate in deionized water for different periods was up to 120 days. Coating thickness influences the release rate.

In 2007 Wu and Liu [31] prepared a new type chitosan coated NPK compound fertilizer with three layer structure of chitosan and poly(acrylic acid-co-acrylamide) (P(AA-co-AM)). Its core was NPK fertilizer granular, the inner coating was chitosan, and the outer coating was (P(AA-co-AM)) superabsorbent polymer. This product gave good controlled-release and water-retention capacity, being degradable in soil and environment friendly.

In 2007 Chen et al [2] prepared slow-released membrane-encapsulated urea fertilizers with starch-*g*-poly (L-lactide) as biodegradable carrier materials. By solution-casting and washing rapidly with water the urea was individually encapsulated within the starch matrix modified by graft-copolymerization. The release behaviors of urea encapsulated in the film were achieved: (1) poly (L-lactide) reduced the swellability of starch matrix and decreased the release rate of urea (2) the urea release rate could be controlled from several hours to 1 day by adjusting the graft efficiency (3) the urea encapsulated in the modified starch film released through a diffusion mechanism.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1 Chemicals

1. Urea fertilizers 46-0-0; commercial grade
2. *O. canum* seed oil
3. Commercial linseed oil
4. Urea standard; Carlo Erba
5. Cobaltnapthenate; Fluka
6. *p*- dimethylaminobenzaldehyde; analytical grade, Riedel
7. Ethanol; Merck
8. Hydrochloric acid; Merck
9. Potassium hydroxide; Merck
10. Cyclohexane; Merck
11. Sodium thiosulfate; Fluka
12. Wijs solution, Merck
13. Isopropyl alcohol; Merck
14. Phenolphthalein indicator; Caplo
15. Potassium dichromate; Riedel
16. Potassium iodide
17. Starch (cassava); commercial grade
18. Methyl orange.

3.1.2 Equipments

1. Scanning Electron Microscope (SEM); JSM-5410LV, Japan
2. UV-VIS Spectrophotometer; spectronic 21
3. Fourier Transform Infrared Spectrophotometer (FT-IR); Nicolet Impact 410
4. GC-FID; Agilent 7890A GC
5. Pan coater
6. Film applicator
7. Automatic scratch test apparatus
8. Specular glossmeter
9. Hotplate stirrer with magnetic stirrer set
10. Thermometer
11. pH- meter
12. Water bath

3.2 Analysis of drying oils

The various physical properties of drying oils such as were intended to determining acid value, iodine value, saponification value and specific gravity were determined by the standard methods. The chemical compositions of drying oil were analyzed using GC-FID.

3.2.1 Acid value (ASTM D974)

Acid value is a numerical measure of the quantity of free acids in oils. It is a quoted as the number of milligrams of potassium hydroxide which are required to neutralize the free acids in 1 g of the oils.

Reagents

Titration solvent was prepared by mixing toluene, water and anhydrous isopropyl alcohol in the ratio of 100:1:99. Methyl orange indicator solution was prepared by dissolving 0.1 g of methyl orange in 100 ml of water. KOH 0.1 N standardized with potassium hydrogen phthalate (KHP).

Procedure

The oil sample (20 g) was added into the Erlenmeyer flask. Then, titration solvent and 0.5 ml of the indicator solution were added into the Erlenmeyer flask. Without delay, the solution was titrated with 0.1 N of KOH until the color change to green color. The calculation was showed in Appendix A.

3.2.2 Saponification value (ASTM D5558)

Saponification value is a numerical measure of the content of saponifiable compounds in oils. It is given as the number of milligrams of potassium hydroxide required to neutralize the free acids and saponify the esters and other saponifiable compounds present in 1 g of the oils.

Reagents

Hydrochloric acid solution, 0.5 N HCl. Alcoholic potassium hydroxide was prepared by dissolving 40 g of KOH in 1 L of the distilled alcohol, keeping the temperature below 15.5ºC while the alkali is being dissolved. This solution should remain clear.

Procedure

The oil sample (2 g) was added into Erlenmeyer flask and added 25 ml of alcoholic KOH with a pipette. The air condenser was connected to the flask and boiled the solution gently until the sample was completely saponified (approximately 1 h). After the flask and condenser have cooled, then disconnected the flask, added approximately 1 ml of indicator, and titrated the solution with 0.5 N HCl until the pink color has just disappeared. The calculation was showed in Appendix A.

3.2.3 Iodine value (ASTM D1959)

Iodine value is a numerical measure of the unsaturation of oils and fatty acids and is expressed as the quantity of halogen, in terms of the number of centigrams of iodine per gram of sample (weight percent of absorbed iodine).

Reagents

Cyclohexane, starch indicator solution, Wijs solution, 0.1 N sodium thiosulfate standard solution was prepared by dissolving 24.8 g of sodium thiosulfate in water and dilute to 1 L. The calculation was showed in Appendix A.

Procedure

The oil sample (2 g) was placed in a 500 ml of flask and added 20 ml of solvent. Then, 25 ml of Wijs solution was added into the flask containing specimen. The flask was stored in a dark place for 1 h. The flask was removed from storage and added 20 ml of KI solution and 100 ml of water and titrated with sodium thiosulfate solution until the yellow color had almost disappeared. Starch indicator solution 1 ml was added and continued the titration until the blue color has just disappeared.

3.3 Film performance

3.3.1 Film preparation

The coating performance of the cured film was evaluated by determining drying time, hardness, glossy, adhesion, water resistance, chemical resistance using the standard test method.

Apply the drying oils to be tested on clean glass. Cast the test film with film applicator provided film thickness 60 microns.

Figure 3.1 Film applicator.

3.3.2 Dry-hard time test (ASTM D1640)

The end of the thumb resting on the tested film and forefinger supporting on test panel, exert a minimum downward pressure of the thumb on the film. Lightly polish the contacted area with a soft cloth. The film was considered dry-hard when any mark left by the thumb was completely removed by the polishing operation.

3.3.3 Hardness [32]

Hardness property was usually defined as the resistance to deformation caused by attempted penetration of another body. Film hardness was tested by an automatic scratch test. This is represented by the force (g) which applied to the film.

Figure 3.2 Automatic scratch test apparatus.

3.3.4 Gloss (ASTM D523)

Gloss was measured by using a gloss meter also known as a glossmeter which directs a light at a specific angle to the test surface. Gloss was measured by shining a known amount of light at a surface and quantifying the reflectance. The angle of the light and the method by which the reflectance is measured are determined by the surface. The measurement results in % reflection of the illuminated light.

Figure 3.3 Specular glossmeter.

3.3.5 Adhesion (ASTM D3359)

Adhesion test was determined by a very simple method which found widespread use in coating is the grid method. The method consist in making five to ten parallel cuts though the film to the substrates at distance of 1 mm apart, followed by repeating the cuts across those already made and at right angle to them. This gives a grid of squares of 1 mm^2. The adhesion is judged to be good if the squares all sit fast and are not easily removed by stroking with the finger tip. In order to obtain a numerical result, a piece of pressure adhesive tape is applied to the grid and then jerked away. The number of squares which are not removed from the substrate is a measure of the adhesion. (Appendix B1)

3.4 Preparation of encapsulated urea fertilizers [26]

The experiments were carried out on an industrial pan coater used to produce encapsulation urea fertilizers by spraying drying oils onto granular fertilizers. The purpose of this study was to investigate and quantify the effect of (1) temperature (2) amount of drying oil (3) types of drying oil (4) amount of catalyst (5) types of drying oil (6) optimization of coating process.

3.4.1 Pan coating process [25]

In this study, granular fertilizers are coated with drying oil and drier solution, which acts as a hydrophobic barrier. The apparatus used for coating of fertilizer is shown in Figures 3.4 and 3.5. Procedure of fertilizer coating method was described below.

Figure 3.4 Pan coater.

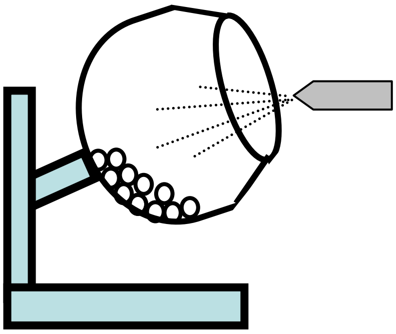


Figure 3.5 Schematic of coating fertilizer granules.

3.4.1.1 Method 1. Encapsulation of urea fertilizers with raw oils

(*i*) Fertilizers were dried in the oven at 80ºC 24 hours to remove moisture from granular fertilizers, and then kept in desiccator.

(*ii*) Approximately 100 g of granular fertilizers and drying oil solution were placed into the coating drum, which was rotated at 15 rpm.

(iii) Approximately 10 ml cobalt naphthenate solution as catalyst was placed in spray gun and was sprayed on the granular fertilizers

(iv) While drying oil and catalyst were spraying, hot air was allowed into coating drum in order to dry the fertilizers.

(v) The encapsulated fertilizer was placed in the oven at 80ºC for 24 hours period to allow the coated layer dried.

3.4.1.2 Method 2. Encapsulation of urea fertilizers with pre-cured oils

A measured amount of oil with cobalt naphthenate as catalyst was poured into a three necked round bottom flask fitted with a mechanical stirrer, thermometer. Air is blown continuously through the oils. One neck of which was kept open to facilitate the removal of volatiles produced during heating and to expose the oil to open air [29]. Then heat at two difference temperature (150ºC, 250ºC) with constant stirring up to 10 hours. The bulk viscosity of heated oil was measured at every hour of heating for both every temperature. Encapsulating fertilizer was prepared by pan coating process as described in method 1.

3.5 Morphological analysis

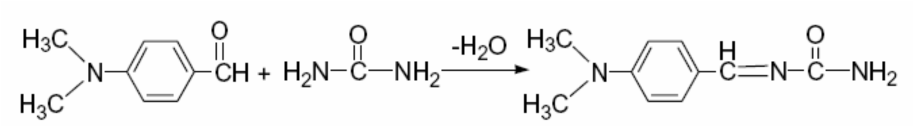
Sample of encapsulated urea fertilizers were examined for the film thickness of the coating materials using Scanning Electron Microscope (SEM). Initially, the samples were split into two halves. They were coated with a layer of gold sputtered using a coating machine and observed in JSM-5410LV SEM.

3.6 Characterization of the drying oil films

The outer coating material of encapsulated urea fertilizers, drying oil film was characterized by a Fourier Transform Infrared (FT-IR) spectrophotometer. The IR spectra of the samples were recorded on a Nicolet Impact 410 FT-IR spectrophotometer. Pellets were prepared using potassium bromide (KBr). Scanning was carried out between 4000 and 400 cm^{-1} wavelength.

3.7 Analytical method of urea release [33]

Urea release from encapsulated fertilizer in this experiment was determined by using colorimetric method or DMAB method. According to Ehrlich reaction, urea could react with *p*-dimethylaminobenzaldehyde in dilute HCl solution to produce a colour complex, lemon Kelly which would absorb visible light at 440 nm for spectrophotometric measurement.



DMAB Urea lemon Kelly

3.7.1 Calibration of spectrophotometer

Procedure

(*i*) *p*-dimethylaminobenzaldehyde (DMAB) 16.00 g was dissolved in 1000 ml 95% ethyl alcohol and added 100 ml concentrated HCl. The solution was stable for 1 month.

(*ii*) Reagent grade urea 5.000 g was dissolved in water and dilute to 1000 ml. Pipet 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 ml into 250 ml volumetric flasks and dilute to volume. These volumes contain a total of 0.0002, 0.0004, 0.0006, 0.0008, 0.0010, 0.0012, 0.0014, 0.0018, 0.0020 g urea in each 5 ml aliquot.

(*iii*) Standard urea solution 5 ml was pipett into 5 ml DMAB solution in 25 ml test tube, and allowed to stand for 10 minutes.

(*iv*) Reagent blank was prepared by diluting 5 ml DMAB solution in a test tube with 5 ml distilled water.

(*v*) Read the absorbance at 440 nm, using the reagent blank to set the spectrophotometer to 100% transmittance.

(*vi*) Plot on regular graph paper. Data should give a straight line.

3.7.2 Determination

(*i*) 0.5 g of encapsulated fertilizer was placed in a flask containing 100 ml of distilled water.

(*ii*) Everyday the sample were filtered and taken from the flask

(*iii*) Pipette 5 ml of the sample solution, added 5 ml DMAB solution and shake throughly. Allow to stand 10 minutes. Read absorbance at 440 nm against the reagent blank.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Analysis of drying oils by standard test method

Various physical properties such as acid value, iodine value, saponification value, density and specific gravity of drying oil are given in Table 4.1. From this Table, it was observed that the iodine value increased from soybean oil, linseed oil, *O. canum* seed oil, respectively. This is because *O. canum* seed oil has the highest unsaturated fatty acid content. Moreover, it has the highest acid value because *O. canum* seed oil that used in this experiment has been kept for a long period of time. The flash point values of three oils were greater than 150ºC. The density of soybean oil was the lowest compared to those of linseed and *O. canum* seed oil.

Table 4.1 Physical properties of drying oils

Type of oils	Iodine value	Saponification value	Acid value	Density (g/ml)	Specific gravity	Flash point (ºC)
Soybean oil	120	195	0.63	0.9274	0.9279	150
Linseed oil	164	198	1.59	0.9360	0.9635	150
O. canum seed oil	192	188	19.6	0.9286	0.9291	150

Table 4.2 Fatty acid compositions of drying oils (%wt)

Oil	Saturated	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)
O. canum seed	9.74	0.66	21.69	52.13
Linseed	9.76	0.71	16.14	45.49
Soybean	15.30	1.35	52.76	5.75

Table 4.2 showed the GC-FID analysis of fatty acid compositions of *O. canum* seed oil contains high percentage of linolenic acid (C18:3) (total about 52.13%) which was similar to that of linseed oil which contains 45.49%, while soybean oil contained only 5.75% and had high content of linoleic (C18:2) (total about 52.76%). (GC-FID chromatograms are shown in Figures A8 - A10 in Appendix A).

4.2 Film performance of drying oils cured films

The performance of coated films at 60 microns of thickness was tested by measurement of gloss, hardness, drying time, chemical resistance. Table 4.3 showed the coating performance of the cured films which were prepared from drying oil with catalyst. The films from *O. canum* seed oil showed the fastest drying time and hardness compared with the film from linseed and soybean oil. In addition, the film of soybean oil showed the highest gloss. The cured films from three oils showed excellent adhesion (grade 5B) to surface. (Table B1 in Appendix B)

Table 4.3 Performance characteristics of drying oil films

Type of oils	Drying time [a] (min)	Gloss (75^{o})	Hardness	Adhesion
O. canum seed oil	30	69	300	5B
Linseed oil	60	100	100	5B
Soybean oil	75	112	100	5B

[a] *Temperature for drying time : 80* °C.

The chemical resistance data of the films are shown in Table 4.4. The film of *O. canum* seed, linseed and soybean oil had high resistance to acid and distilled water but the alkali resistance was poor which could be due to the presence of significant amount of alkali hydrolysable ester groups in the polymer chain of these oils.

Table 4.4 Chemical resistance of drying oil cured films

Type of media	*O. canum* seed oil	Linseed oil	Soybean oil
Alkali	P	P	P
Acid	E	E	E
Distilled water	E	E	E

E: excellent; P: poor.

4.3 Structural analysis of drying oil film by FT-IR

The important FT-IR peaks are assigned in Table 4.5. The oil had strong absorbance at about 1744 cm^{-1} due to stretching vibration of the carbonyl group of the triglyceride esters. The film of oil had a new carbonyl absorbance which was observed at around 1711 cm^{-1}, resulted from the formation of aldehydic or ketonic functionalities. Peaks at around 1621 cm $^{-1}$ decreased due to decreasing concentration of unsaturation in the oil. Film drying promotes polymerization, thus in all spectra of film the concentration of double bonds were decreased. FT-IR spectra were showed in Figures A2-A7 in Appendix A.

Table 4.5 The main FT-IR peaks and the corresponding functional groups of oils

Bands (cm^{-1})	Assignments
3465	O-H stretching vibration
2852-2921	C-H stretching vibration
1744	C=O stretching vibration
1621	C=C stretching vibration
1465	C-H bending vibration
1152	C-O-C stretching vibration
721	methylene rocking vibration

4.4 Solubility of uncoated urea fertilizers

Commercial granular fertilizers used in this study were uncoated fertilizers available in the market. Figure 4.1 showed the photograph of uncoated urea fertilizers. Urea granules ranging from 3-5 mm in diameter were used in this experiment. Figures 4.2-4.4 showed the solubility of urea granules in 30ºC water which was obtained by placing them into deionized water. Then the granules were filtered from water solution as a function of time. The liquid part was used to determine urea concentration.

Figure 4.1 Uncoated granular urea fertilizers.

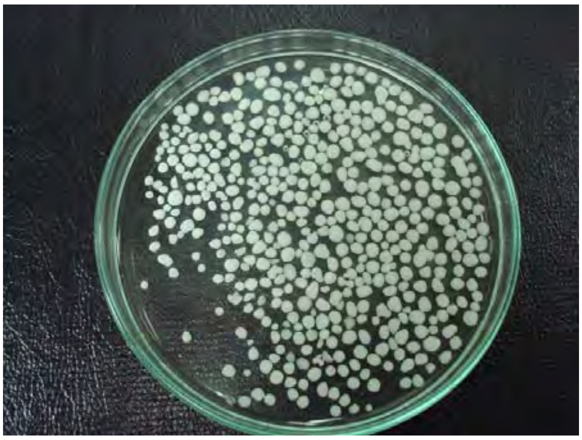


Figure 4.2 Uncoated urea fertilizers in DI water at 1 minute.

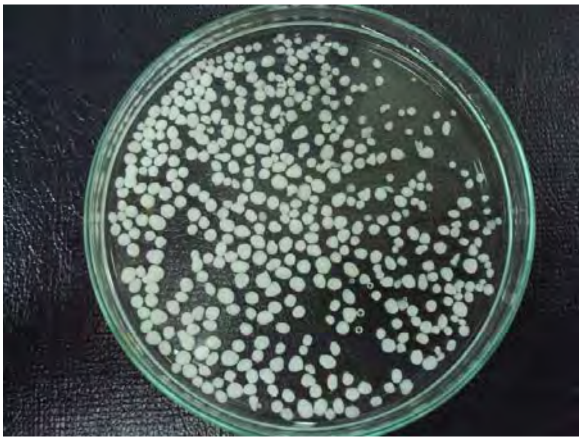


Figure 4.3 Uncoated urea fertilizers in DI water at 2 minutes.

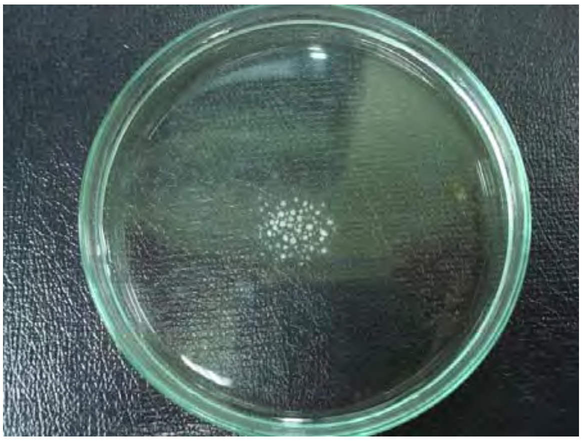


Figure 4.4 Uncoated urea fertilizers in DI water at 3 minutes.

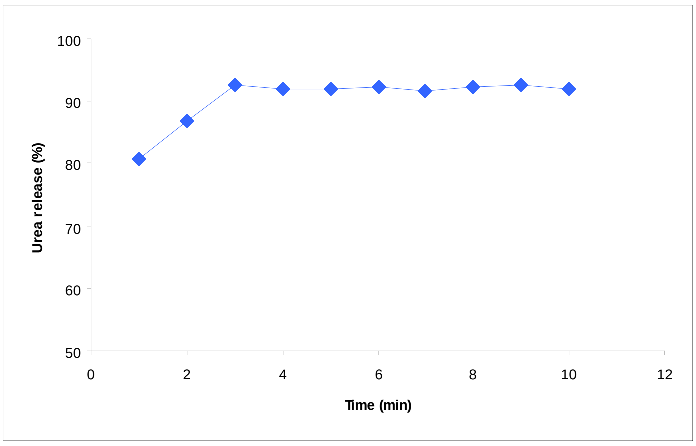


Figure 4.5 Dissolution profiles of uncoated urea fertilizers.

Figure 4.5 showed the solubility of uncoated urea fertilizer granules at 30ºC in distilled water which was found to dissolve completely within 3 minutes. According to its well-known character that urea is easily dissolved in water, so it will quickly dissolve in the field, and the nutrient will be quickly exhausted.

4.5 Preparation of encapsulated urea fertilizers by pan coating method

Coating of urea fertilizer granules were carried out in pan coater. The drum rotation rate was 15 rpm. At the same time, hot air was blown through the urea granules. The three parameters of greatest interest are (1) temperature, (2) amount of oil (3) amount of catalyst.

4.5.1 Encapsulation of urea fertilizers using raw oils

4.5.1.1 Optimization of amount of drying oils in coating process

The amount of drying oil was an important factor which influenced the coating process by pan coating. The amount of drying oil was varied from 4, 6, 8 and 10%. It was found that the urea fertilizers could be coated with 4% drying oil and it could be increased to 8%. The high amount of oil was not appropriate to coat urea fertilizers by pan coater because excess drying oil may cause polymerization on surface of coating pan instead of on fertilizers surface. Low amount of drying oil showed thin film coating. Thus in this research, was used 6% drying oil was used to encapsulate urea fertilizers.

4.5.1.2 Optimization of amount of catalyst in coating process

Table 4.6 showed the drying time of oils in coating process. At 1% concentration of catalyst the solution was loss into the air when spraying. Thus, the film coating was incompletely dried. At 2% of catalyst the film was completely dried (fully curing). Thus, in this study 2% amount of catalyst was selected for coating process in experiment.

4.5.1.3 Optimization of temperature in coating process

Influence of temperature had effect on encapsulated fertilizer in coating process because the polymer film of oils was thermal polymerization. At 60ºC temperature, the fertilizer granules were dried within 10, 50 and 120 minutes, respectively. In addition, drying time was decreased when the film layers were increased. However, increasing temperature too high over 100ºC caused the polymer film of linseed oil and soybean oil coated fertilizer to damage. The drying time of film from soybean oil was too long compared to those of *O. canum* seed oil and linseed oil. Therefore, fertilizers encapsulated with *O. canum* seed oil and linseed oil would be selected for further study.

Table 4.6 Drying properties of oils at different temperature and different amount of catalyst

Oil	Catalyst (%wt) (cobalt naphthenate)	Drying time (min)		
		60ºC	80ºC	100ºC
O. canum seed	1, 2, 3, 5, 10	10	10	10
Linseed	1, 2, 3, 5, 10	50	50	50
Soybean	1, 2, 3, 5, 10	120	120	120

4.5.2 Encapsulation of urea fertilizers using pre-cured oils

Encapsulation of urea fertilizers by pan coating process was carried out using *O. canum* seed and linseed oil, which heated separately at two different temperatures i.e., at 150ºC and 250ºC with bubbling of air through the oil. Coating conditions were described below.

Table 4.7 Thermal treatment of linseed oil with 1% cobalt naphthenate and various drying times of encapsulating process

Temperature (ºC)	Heating time (h)	Drying time (min)
150	2, 4, 6, 10	10, 10, 10, 10
250	2, 4, 6, 10	10, 10, 10, 10
kept heated oils at room temperature for 2 days.	2, 4, 6, 10	5, 5, 5, 5, 5

Table 4.8 Thermal treatment of *O. canum* seed oil with 1% cobalt naphthenate conditions and various drying times of encapsulating process

Temperature (ºC)	Heating time (hr)	Drying time (min)
150	2,4	2,2
250	2,4	2,2

Drying time in coating process using pre-cured linseed and *O. canum* seed oil in the present of 1% catalyst showed that the film from both oils were dried faster than untreated oils. This may be due to the heating at high temperature caused polymerization of double bond to form high molecular weight molecule as shown in Table 4.9. Therefore, Table 4.8 showed that the coating time of urea fertilizer encapsulate with *O. canum* seed and linseed pre-cured oil were reduced from 50 and 10 minutes to 10 and 2 minutes, respectively.

The curing characteristics of pre-cured oil had been shown that heating enhanced the drying ability of oil. In this experiment, two different temperatures were shown not to give significant difference of drying time for coating process.

From data in Table 4.9, *O. canum* seed and linseed pre-cured oil showed the high viscosity at 265.82 and 154.5 cST/s, while its unheated oil had 23.05, 30.07 cST/s, respectively. Viscosity increase was directly proportional to increase in apparent molecular weight and the degree of polymerization. Figure 4.6 showed that *O. canum* seed oil after heating more than 4 hours at 250°C became irreversible gelling. Although the iodine values of *O. canum* seed and linseed oil were similar, linseed oil with its greater oleic and low linoleic acid content required a longer reaction time to form gel.

Figure 4.6 Irreversible gelling of *O. canum* seed oil.

Table 4.9 Viscosity characteristic of raw oils and pre-cured oils by heating at 250°C for 2 hours

Types of oils	Viscosity at 40°C (cSt/s)
raw *O. canum* seed oil	23.05
boiled *O. canum* seed oil	265.82
raw linseed oil	30.07
boiled linseed oil	154.5

Figure 4.7 Urea fertilizers encapsulated with drying oil by pan coater.

Figure 4.8 Urea fertilizers encapsulated with pre-cured oil.

Figure 4.7 showed the photograph of urea fertilizers encapsulated by pan coating method. It was observed that urea encapsulated fertilizers had a good appearance and good characteristics of coating materials i.e. glossy, compactly, smooth, insoluble in water. In Figure 4.8, the encapsulation of urea fertilizers with pre-cured oil by pan coater showed that the drying oil film had the same appearance. However, its dried film was less glossy than coating film from raw oil. This may be due to the pre-cured oil film had larger polymeric network than untreated oil film.

4.6 Influence of drying oil types

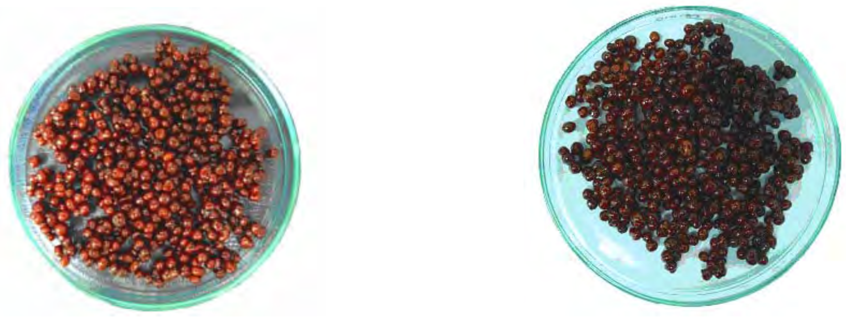
Encapsulated urea fertilizers were physically prepared from granules of conventional fertilizers encapsulated with materials that reduce their dissolution rate. The release and dissolution rates of water-soluble fertilizers depended on the coating materials. In this case, the selection of coating material was so important since it controlled almost all the qualities of the controlled-release fertilizer. Coating materials should not only be cheap but also have good coating properties. In addition, they should not contaminate the soil. In this study, vegetable oils were used as coating materials for the preparation of encapsulated urea fertilizer i.e. soybean oil, linseed oil, *O. canum* seed oil, mixture of linseed and soybean oil, mixture of *O. canum* seed and linseed oil, mixture of *O. canum* seed oil and soybean oil because these drying oils were extremely attractive due to its biodegradability, non toxicity and inexpensive. Therefore, the soluble urea fertilizers encapsulated by drying oils would be an ideal slow release formulation.

4.6.1 *Ocimum canum* seed oil encapsulated urea fertilizers

1 layer 2 layers

3 layers 6 layers

8 layers 10 layers



12 layers 14 layers

Figure 4.9 Comparison of the number of *O. canum* seed oil layers on encapsulated urea fertilizers.

4.6.2 Linseed oil encapsulated urea fertilizers

1 layer 2 layers

4 layers 6 layers

8 layers 10 layers

12 layers 14 layers

Figure 4.10 Comparison of the number of linseed oil layers on encapsulated urea fertilizers.

After the encapsulated fertilizer with oil was dried, the color of exterior surface of encapsulated fertilizer was yellow to dark brown instead of white which was original color of urea fertilizer. It was observed that the brown color of *O. canum* seed oil was darker than linseed oil.

In this experiment, *O. canum* seed oil was obtained from $ScCO_2$ extraction. The oil, essentially a mixture of triglycerides, was analyzed and found to contain more than 70% of unsaturated fatty acids such as oleic, linoleic, linolenic acid. This feature causes the oil to dry much faster than linseed oil and soybean oil. It could encapsulate urea fertilizer to have tough film coating properties. The coating materials based on *O. canum* seed oil had a high resistance against water penetration. Soybean oil contains predominantly linoleic and oleic acids (I.V. 125-140) and dried slower than those of *O. canum* seed oil and linseed oil under the same conditions. Fatty acid content of *O. canum* seed oil evaluated in this study was comparable to those of linseed and soybean oils. It was showed in Table 4.2.

4.7 Morphological analysis

The SEM of the cross-section of polymer film is shown in Figure 4.12, it could be seen that the coating film was smooth and dense. From Figure 4.13 it was observed that the coating film was coarse and porous, thus it could absorb water to form a swollen polymer network. The drying oil film of encapsulated fertilizer could not only absorb a large amount of water but also protect the fertilizer from damage.

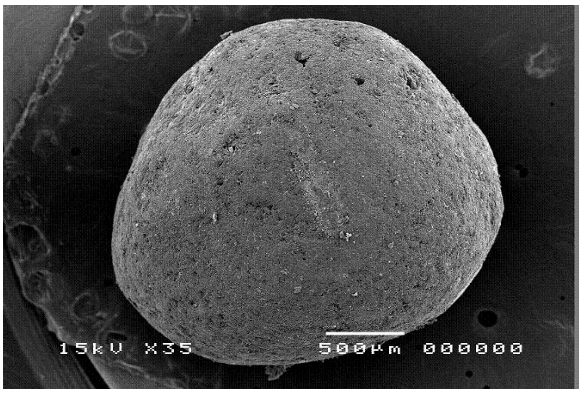


Figure 4.11 SEM image of the uncoated urea fertilizer surface.

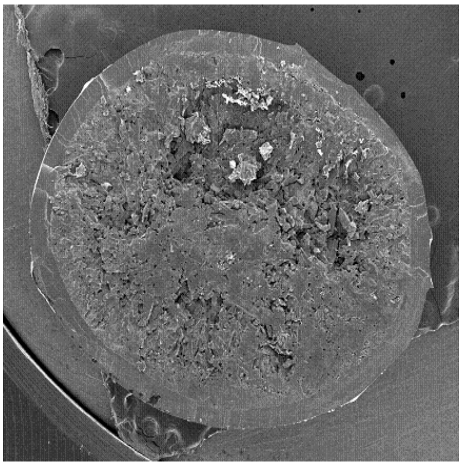


Figure 4.12 SEM of cross-section of the encapsulated urea fertilizer with drying oil film.

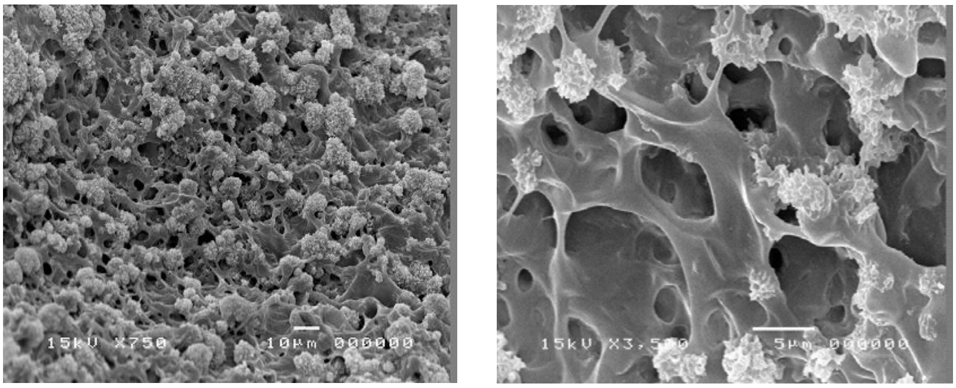


Figure 4.13 SEM images of porous of drying oil films coating after swollen in water.

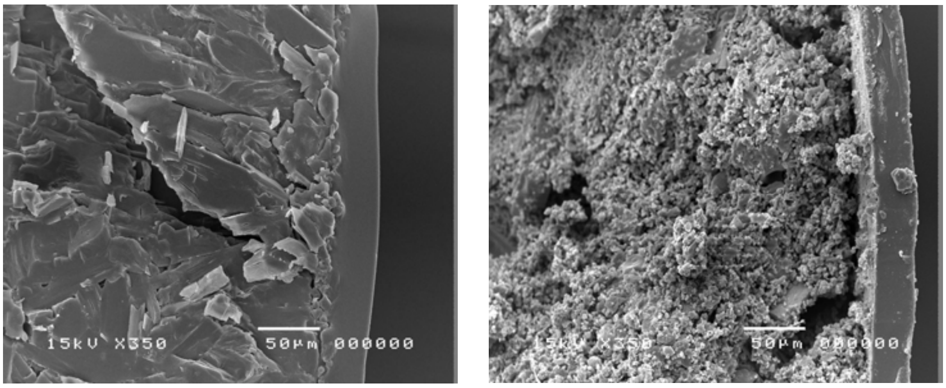
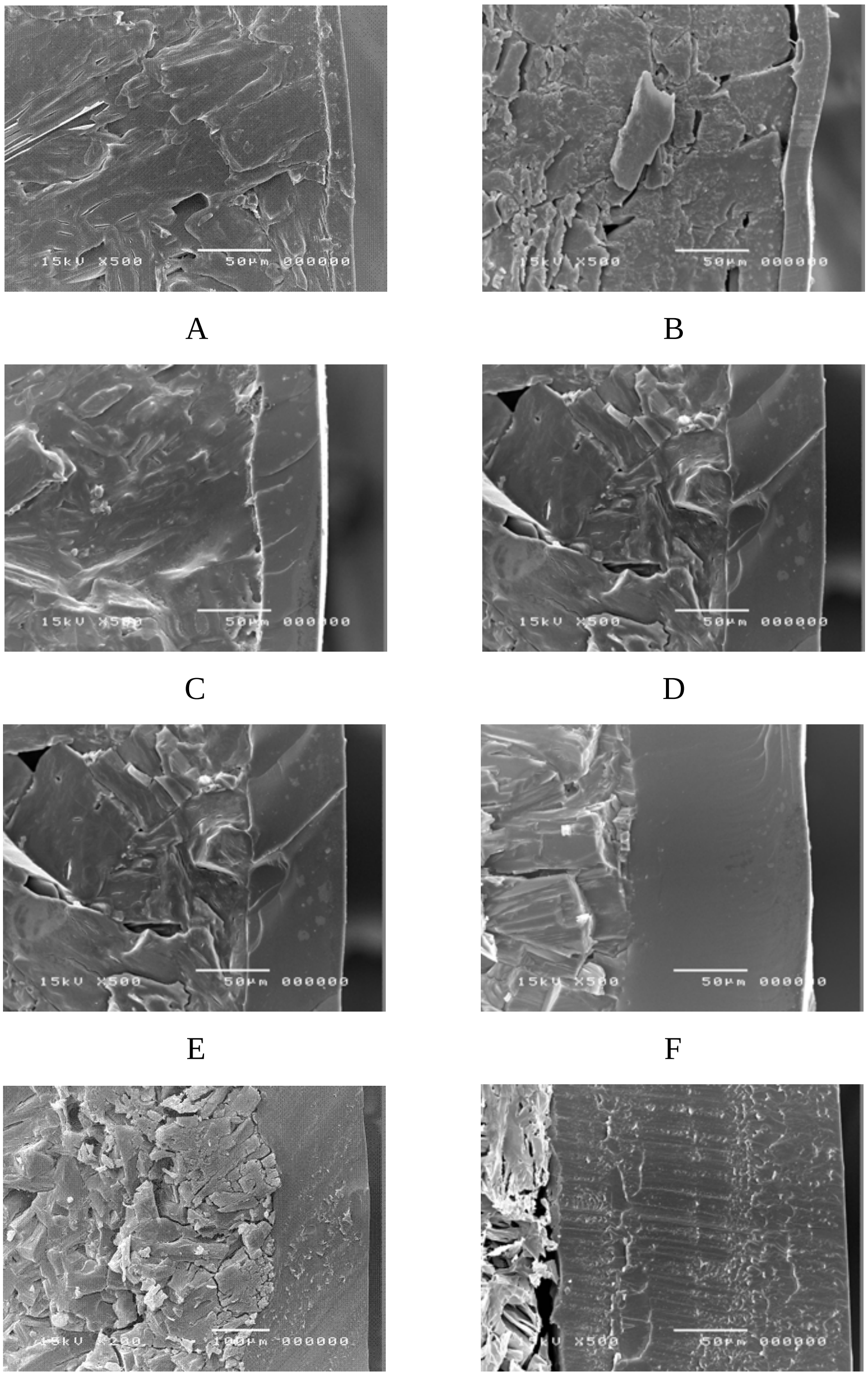


Figure 4.14 Comparison of films of encapsulated urea fertilizers and commercial controlled-release fertilizers (Osmocote^{TM}).

4.8 Influence of number of film layers or film thickness

The coating layer of the material used in this study was indicated by a smooth outer layer on the rough granule of the encapsulated fertilizers on SEM photographs (Figures 4.15, 4.16, 4.17 and 4.18). The thickness of the drying oil film, covering fertilizers granule, was estimated using SEM photograph and was determined by measuring the distance on the photograph and dividing with the scale of the instrument. The thickness of *O. canum* seed oil, linseed oil, *O. canum* seed oil mixed with linseed oil coatings on urea fertilizer granules varied widely (Table 4). Linseed oil mixed with *O. canum* seed oil gave the highest value (594 µm) while the lowest value (196 µm), at same number of layer was obtained with *O. canum* seed oil coating. The increase of the film thickness caused decrease of the releasing rate. Variation in the thickness of the encapsulating materials on fertilizers was possibly due to the polymerization in coating process during the coating of the fertilizers and also to the inherent properties and structure of each drying oil used in this study. Thus, variation in the thickness of the coating layer was expected to be effective in controlling the amounts of nutrient to distilled water. Moreover SEM images revealed that the multiple layers showed no border between each layers.



A B

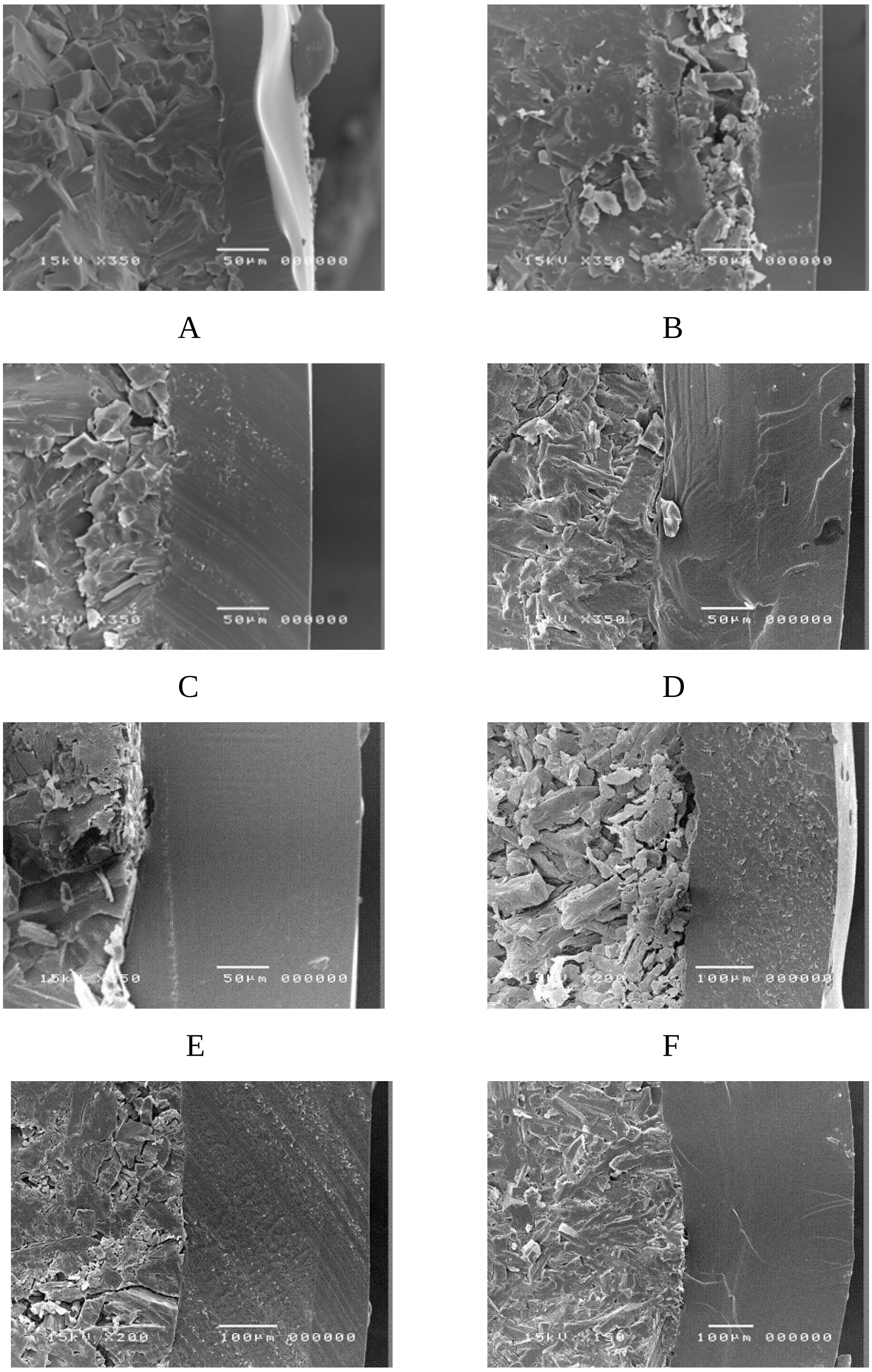
C D

E F

G H

Figure 4.15 SEM images of cross-section of encapsulated urea fertilizers with *O. canum* seed oil. Right: film layers.

A. 1 layer encapsulated B. 2 layers encapsulated
C. 4 layers encapsulated D. 6 layers encapsulated
E. 8 layers encapsulated F. 10 layers encapsulated
G. 12 layers encapsulated H. 14 layers encapsulate



A B

C D

E F

G H

Figure 4.16 SEM images of cross-section of encapsulated urea fertilizers with linseed oil. Right: film layers.

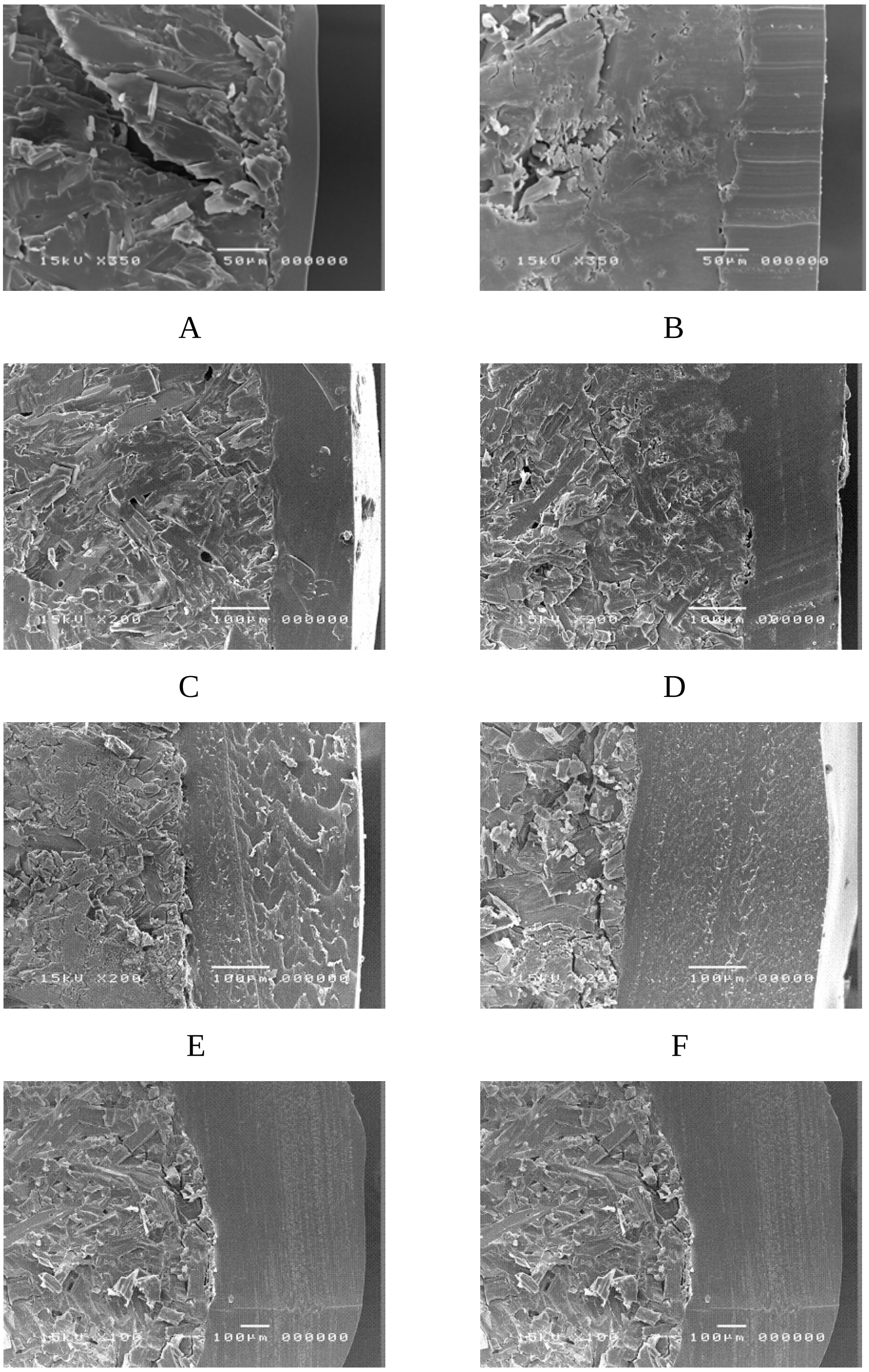
A. 1 layer encapsulated
B. 2 layers encapsulated
C. 4 layers encapsulated
D. 6 layers encapsulated
E. 8 layers encapsulated
F. 10 layers encapsulated
G. 12 layers encapsulated
H. 14 layers encapsulated

Table 4.10 The average thickness of *O. canum* seed oil film on the urea fertilizer granules using SEM

Number of layers encapsulated	Mean thickness of coating (micron)
1	16
2	23
4	40
6	65
8	120
10	150
12	180
14	196

Table 4.11 The average thickness of linseed oil film on the urea fertilizer granules using SEM

Number of layers encapsulated	Mean thickness of coating (micron)
1	45
2	70
4	142
6	172
8	205
10	256
12	315
14	393



A B C D E F G H

Figure 4.17 SEM images of cross-section of encapsulated urea fertilizers with *O. canum* seed oil:Linseed oil (1:1). Right: film layers.

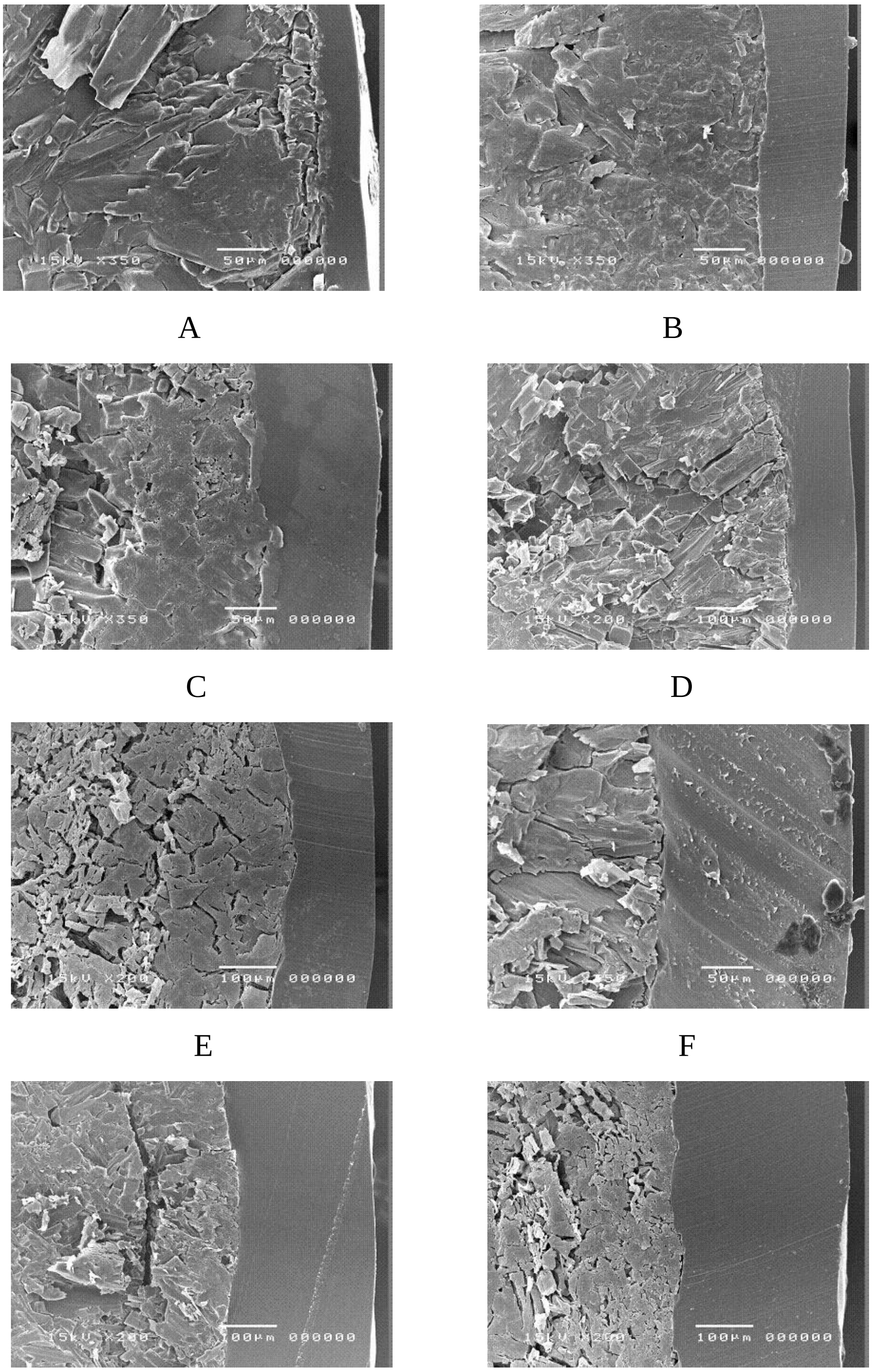
A.	1 layer encapsulated	B.	2 layers encapsulated
C.	4 layers encapsulated	D.	6 layers encapsulated
E.	8 layers encapsulated	F.	10 layers encapsulated
G.	12 layers encapsulated	H.	14 layers encapsulated

Table 4.12 The average thickness of mixture of *O. canum* seed oil and linseed oil (1:1) film on the urea fertilizer granules using SEM

Number of layers encapsulated	Mean thickness of coating (micron)
1	36
2	81
4	145
6	180
8	235
10	335
12	531
14	594

Table 4.13 The average thickness of mixture of *O. canum* seed oil and linseed oil (1:2) film on the urea fertilizer granules using SEM

Number of layers encapsulated	Mean thickness of coating (micron)
1	40
2	80
4	111
6	130
8	155
10	190
12	239
14	286



A B C D E F G H

Figure 4.18 SEM images of cross-section of encapsulated urea fertilizers with *O. canum* seed oil:Linseed oil (1:2). Right: film layers.

A. 1 layer encapsulated
B. 2 layers encapsulated
C. 4 layers encapsulated
D. 6 layers encapsulated
E. 8 layers encapsulated
F. 10 layers encapsulated
G. 12 layers encapsulated
H. 14 layers encapsulated

4.9 Determination of release rate of encapsulated urea fertilizers

4.9.1 Influence of film thickness on the controlled-release of encapsulated urea fertilizers

Urea release from drying oils encapsulated fertilizers was mainly controlled by diffusion mechanism. The coating thickness was the most important factor that influenced the diffusion coefficient. Figures 4.19, 4.20 and 4.21 showed the releasing rate of linseed and *O. canum* seed oil encapsulated urea fertilizers. It was revealed that the low film thickness or coating layers had higher urea release. Figure 4.20 showed release rate of linseed oil encapsulated urea fertilizers which was slower than that of *O. canum* seed oil encapsulated urea fertilizer because at the same number of coating layers, linseed oil gave higher film thickness than *O. canum* seed oil. It was found that two layer coating could not give controlled release of nutrient. Almost 100% of urea was released within 2 days.

Urea fertilizer encapsulated with mixture of *O. canum* seed oil and linseed oils gave release characteristic between using *O. canum* seed or linseed oil alone. In Figures 4.19, 4.20 and 4.21, it could be seen that 14 coated layers of *O. canum* seed oil gave urea released at 82.713% on 56th days, linseed mixed with *O. canum* seed oil (1:1) 54.01% and linseed oil, 66.15% on 56th days.

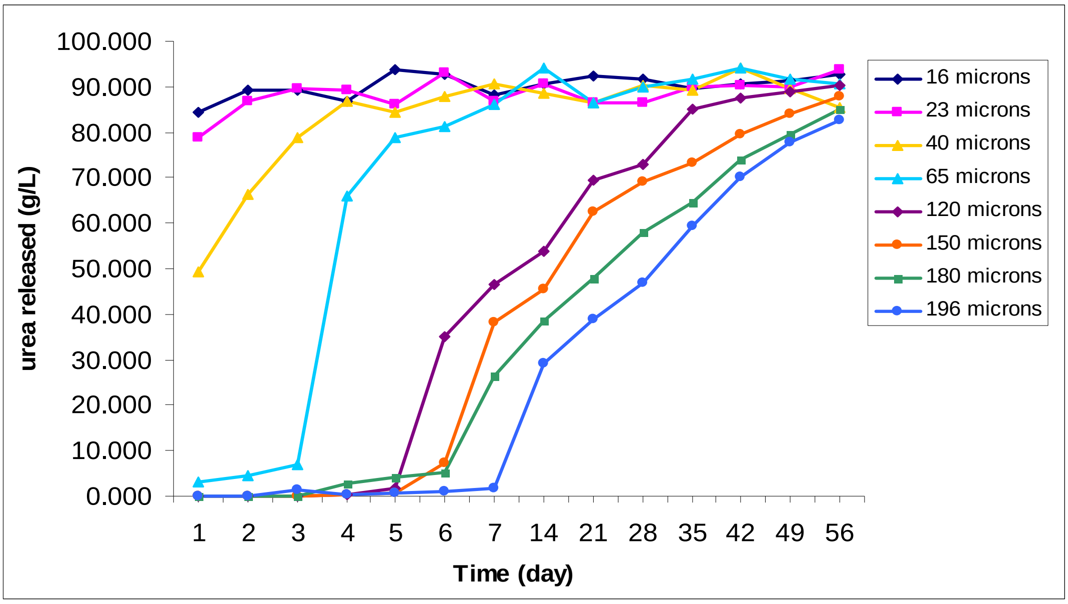


Figure 4.19 Release behavior of *O. canum* seed oil encapsulated urea fertilizers with various thickness.

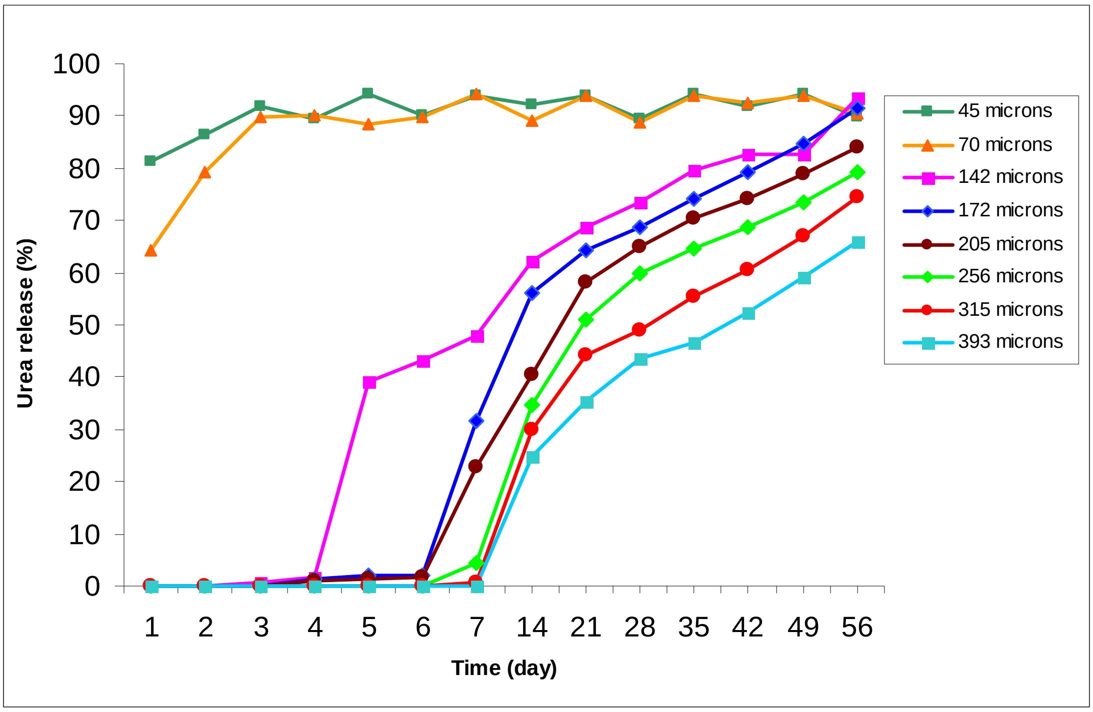


Figure 4.20 Release behavior of linseed oil encapsulated urea fertilizers with various thickness.

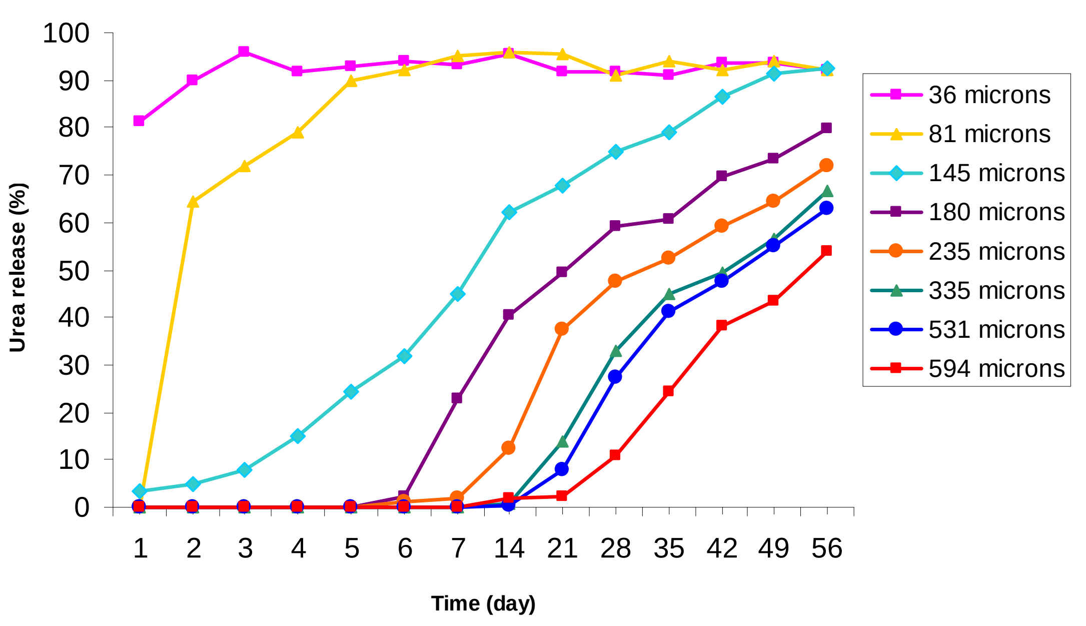


Figure 4.21 Release behavior of *O. canum* seed oil:linseed oil (1:1) encapsulated urea fertilizers with various thickness.

From the above urea releasing profiles the controlled-release period of nutrient could be designed by using urea fertilizers encapsulated with different film thickness depending on plant age and stage of plant growth. At lower average film thickness urea will be released more quickly and at higher film thickness they will be available over a longer period of time. Thus, one bag of encapsulated fertilizer might comprise uncoated urea fertilizer and multiple layer coated fertilizer to exhibit the linear or Gaussian release curves which were appropriate nutrient for a wide range of plants.

4.9.2 Influence of drying oil types on the controlled-release of encapsulated urea fertilizers

Although, the urea fertilizer encapsulated with *O. canum* seed oil might increase the cross-linked of film because linolenic acid had three double bonds. This would make it more difficult for the network to be penetrated by water than linseed oil film. On the other hand, the experiment result found that the drying oil type had not significant effect the releasing rate. However, the same thickness of coating film of encapsulated urea fertilizer had the same urea releasing rate.

4.9.3 Influence of temperature on the controlled-release of encapsulated urea fertilizers

Figure 4.22 showed the urea releasing behaviors of encapsulated urea fertilizers with six layers of *O. canum* seed oil in distilled water at temperatures of 20, 25, 30, 35 and 40ºC. From Figure 4.22, it was observed that all of the curves gave similar trend and that the temperature had a considerable effect on the urea release rate. The higher temperature, the higher urea release rate was. The dependence of the urea release on the temperature was mainly due to the increased diffusion rate as the temperature increased. When the temperature increased, the exchange of free water between polymer film and solution would be accelerated.

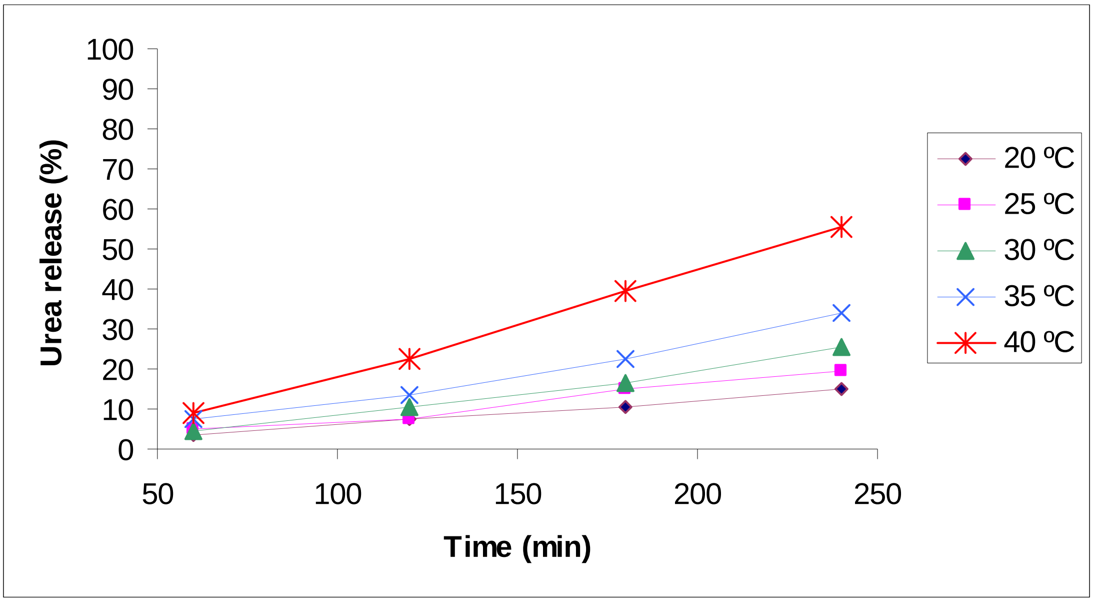


Figure 4.22 Influence of temperature on urea release behaviors in distilled water using 65 microns encapsulated urea fertilizers.

4.9.4 Influence of pH on the controlled-release of encapsulated urea fertilizers

Figure 4.23 showed the curves of urea releasing behavior at various pH. To match the pH of most soils, this study chose pH value, 5, 6, 7, 8, 9 and10 as the experimental conditions. 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.

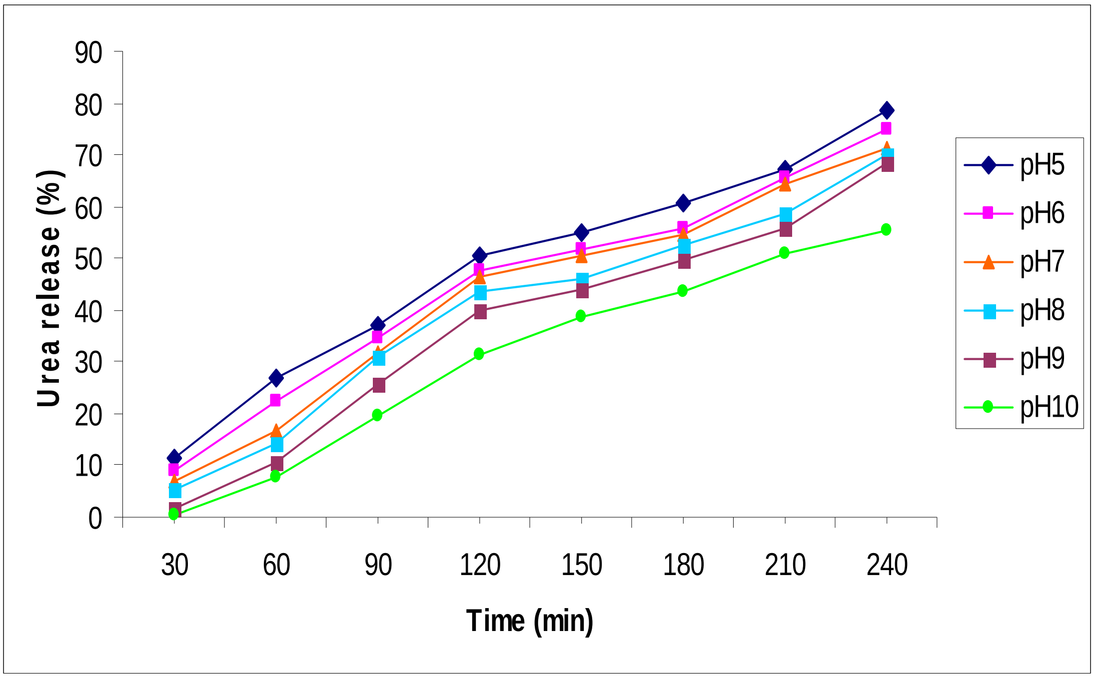


Figure 4.23 Influence of pH on urea release behaviors in distilled water using 65 microns encapsulated urea fertilizers.

4.9.5 Comparison of urea fertilizers encapsulated with drying oils and commercial controlled-release fertilizers (osmocote™)

It was interesting to compare drying oil encapsulated urea fertilizers with the commercial fertilizers. Figure 4.24 and 4.25 showed the coatings of drying oil film encapsulated urea fertilizers and commercial NPK fertilizers coated with dicyclopentadiene (osmocote™) remained in water after completely undergoing nutrients released. Figure 4.26 indicated that the releasing rate of urea fertilizer which was coated at 196, 393 and 594 µm, respectively was faster than that of commercial fertilizers but it had analogous trend of controlled-release with osmocote™.

The calculated cost of encapsulated urea fertilizers with drying oil was compared with the commercial fertilizers (osmocote™) (Appendix A4). The price of commercial fertilizer (osmocote™) available in Thailand was about 150 baht/kg. Cost of encapsulated urea fertilizers with drying oil was about 15 baht/kg less than that of commercial fertilizers.

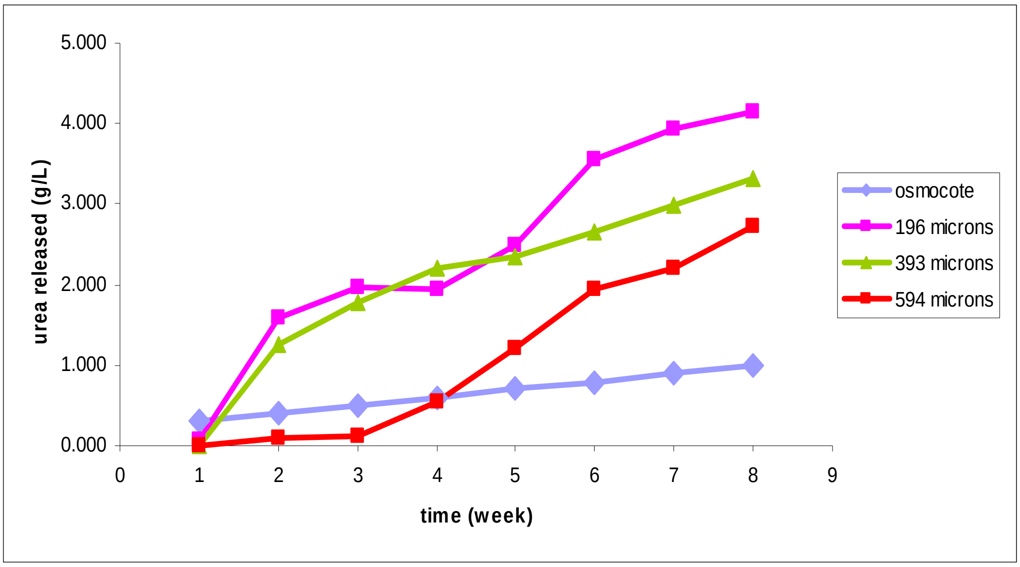


Figure 4.24 Comparison of the releasing rates of drying oil encapsulated fertilizers with osmocote™.

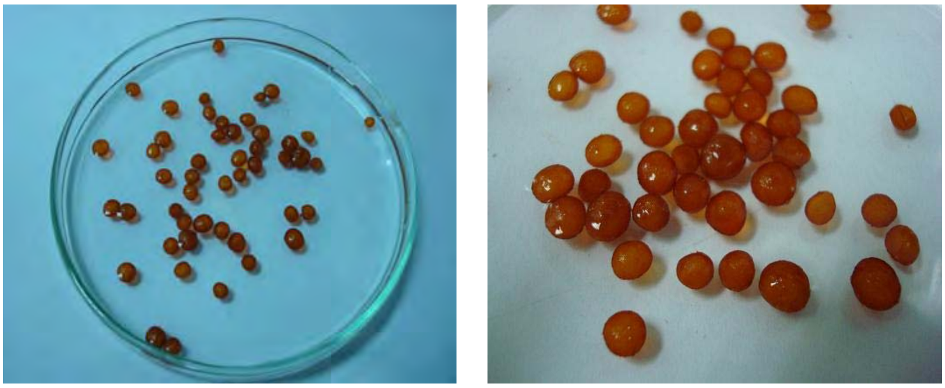


Figure 4.25 Encapsulated urea fertilizers with drying oil after completely urea released in water.

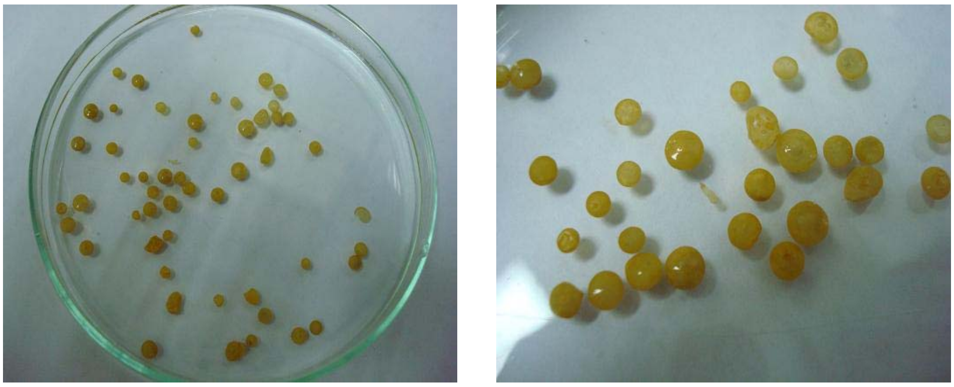


Figure 4.26 Commercial NPK fertilizers after completely nutrient released.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

This research focused on the study of encapsulated urea fertilizers using drying oil from *O. canum* seeds as a new coating material by pan coater.

The parameters for optimization on encapsulating process by pan coating method were studied. It was found that pre-polymerized drying oil by heating at 150ºC and 250ºC for 2 hours could reduce the drying time faster than untreated oil. The linseed oil film was dried within 5 minutes instead of 50 minutes and *O. canum* seed oil film was dried within 2 minutes instead of 10 minutes. The pre-polymerized drying oil gave significantly energy saving of coating process. The influence of parameters on encapsulated urea releasing rate were the following:

1. The releasing rate of encapsulated urea fertilizer was slower than that of commercial uncoated urea fertilizer. The releasing of urea could be prolonged for two months.
2. The urea encapsulated with drying oil film from *O. canum* seeds indicated faster releasing rate than that of linseed oil encapsulated urea fertilizers. At the same number of layers, the thickness of coating was thinner than linseed oil film.
3. The study on influence of the amount of drying oils indicated that *O. canum* seed and linseed oil at 6 %wt of oil per weight of fertilizer was suitable for pan coating method.
4. Investigation on the amount of catalyst for coating process indicated that 2% cobalt naphthenate was appropriate to be used for spraying in this coating process.
5. The increase of pH caused the decrease of releasing rate of urea.
6. The temperature also had significant effect on releasing rate. The increase of temperature caused increasing rate of urea released.
7. If the film thickness was increased the releasing rate decreased.

5.2 Suggestions for future work

1. Experiment in field test should be performed in order to investigate the effectiveness of the slow-release urea.
2. Different method of coating and materials such as UV-curing method should be continued to develop in order to save time and energy.

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APPENDICES

APPENDIX A

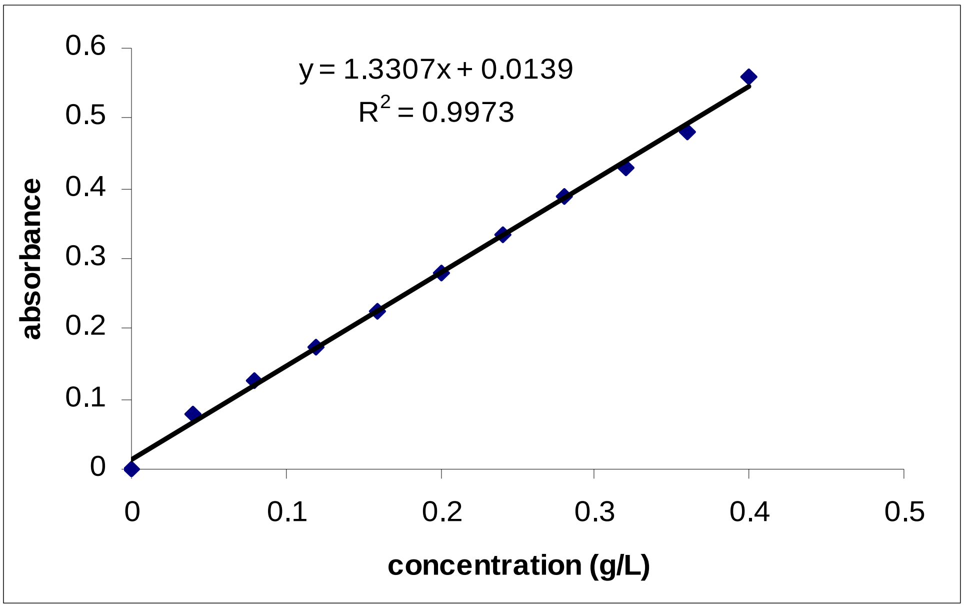


Figure A1 Calibration curve of standard urea solution.

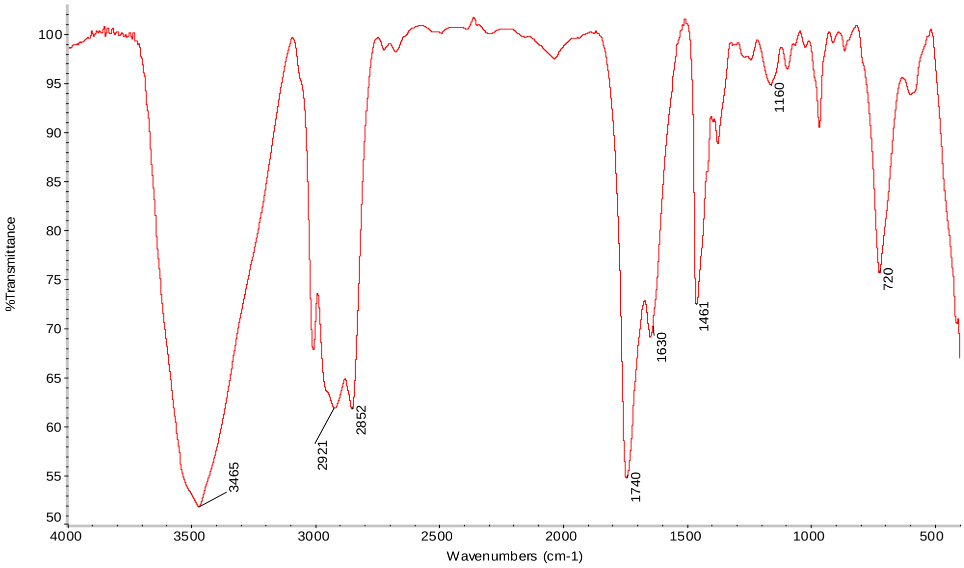


Figure A2 The FT-IR spectrum of *O. canum* seeds oil as a neat liquid on KBr plate.

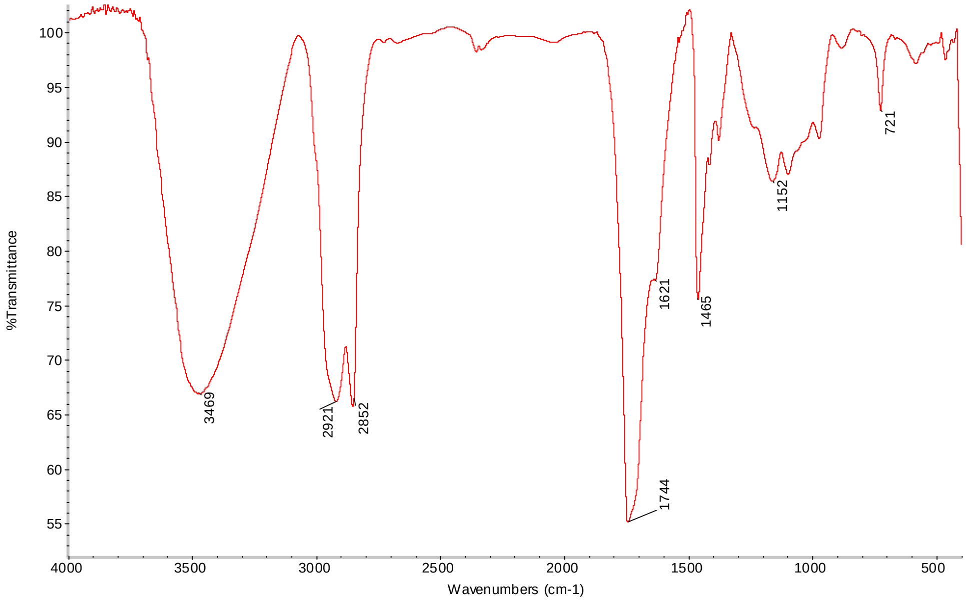


Figure A3 The FT-IR spectrum of *O. canum* seed oil cured film.

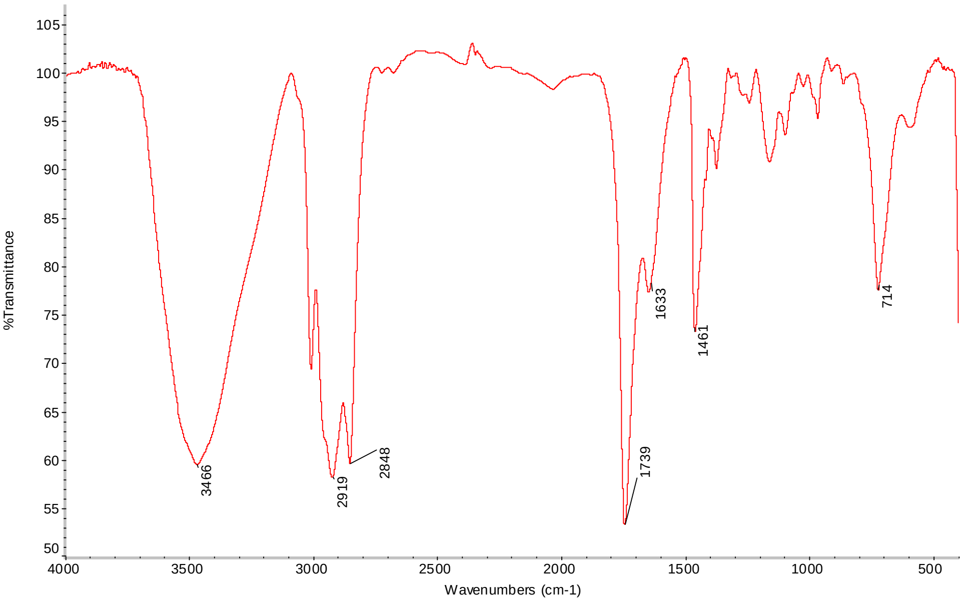


Figure A4 The FT-IR spectrum of linseed oil as a neat liquid on KBr plate.

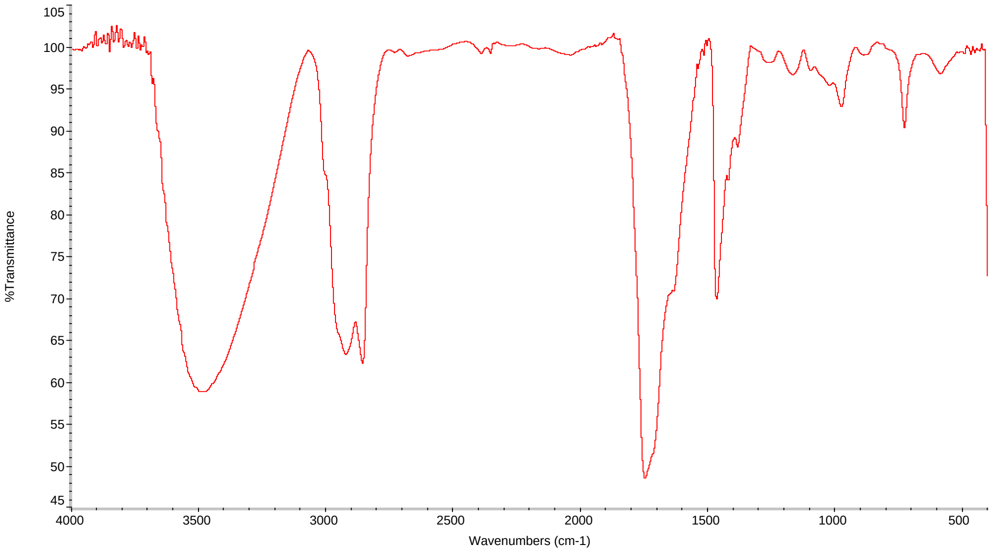


Figure A5 The FT-IR spectrum of linseed oil cured film.

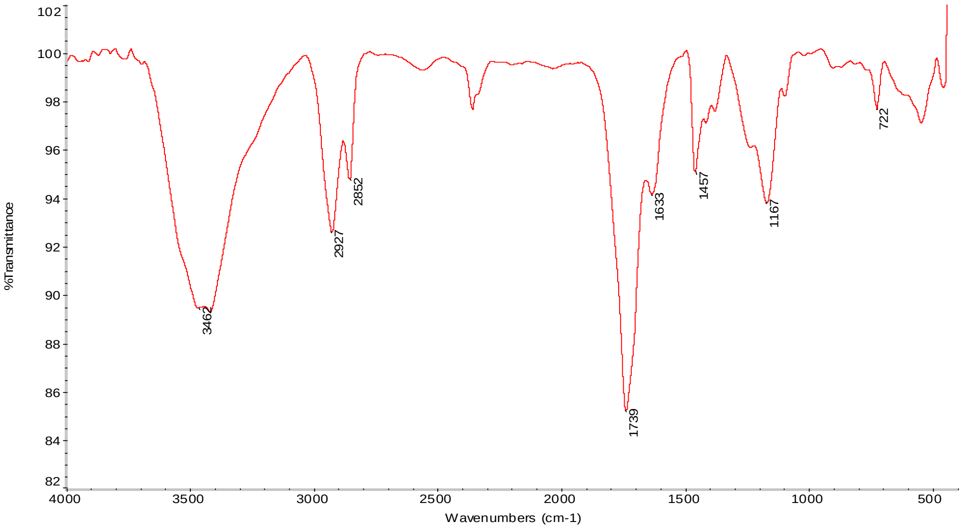


Figure A6 The FT-IR spectrum of soybean oil as a neat liquid on KBr plate.

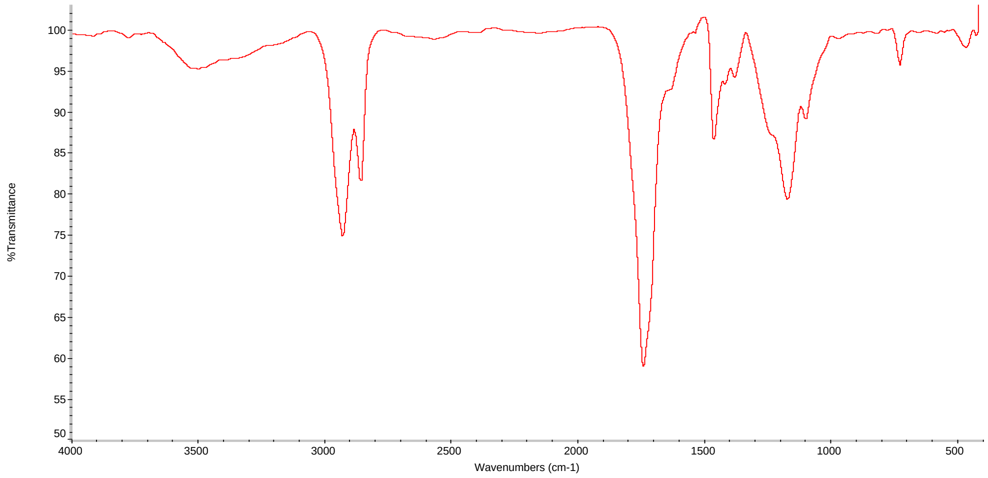


Figure A7 The FT-IR spectrum of soybean oil cured film.

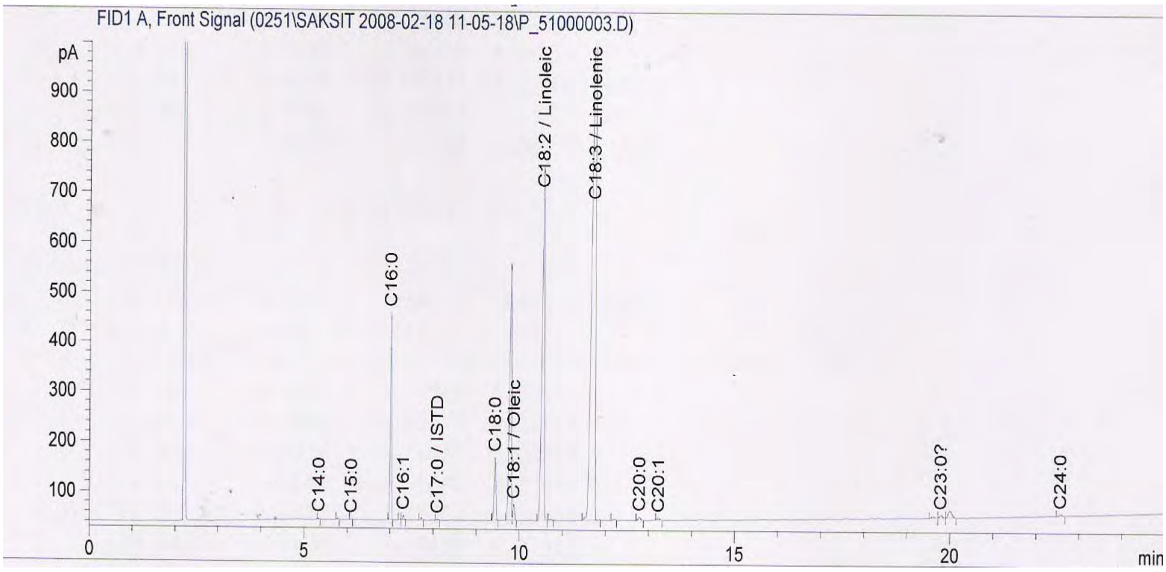


Figure A8 The GC-FID chromatogram of *O. canum* seed oil.

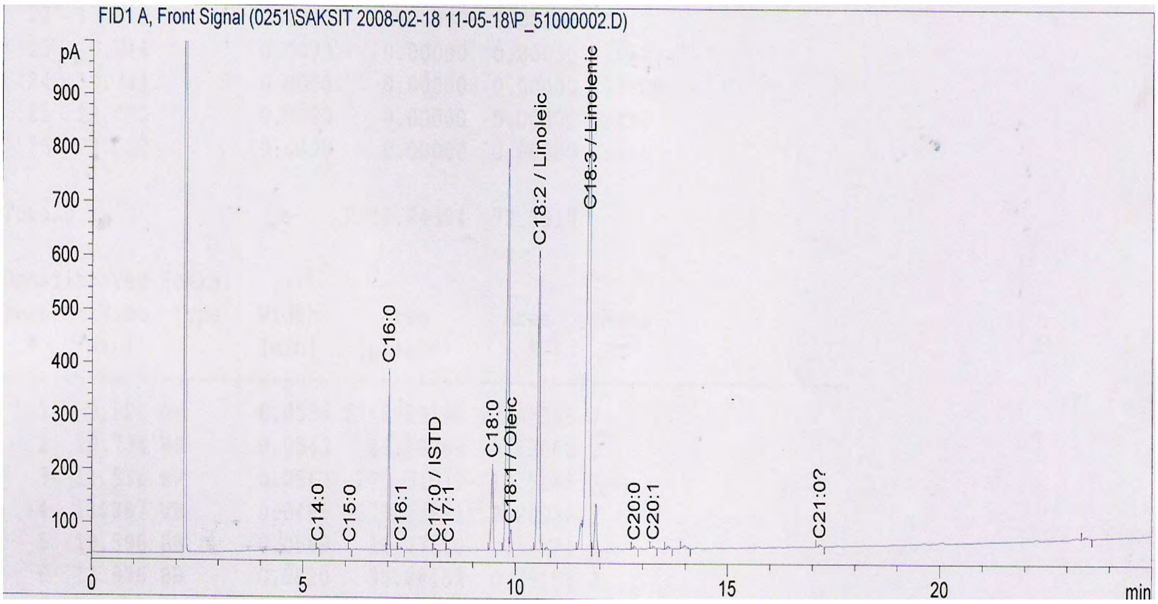


Figure A9 The GC-FID chromatogram of linseed oil.

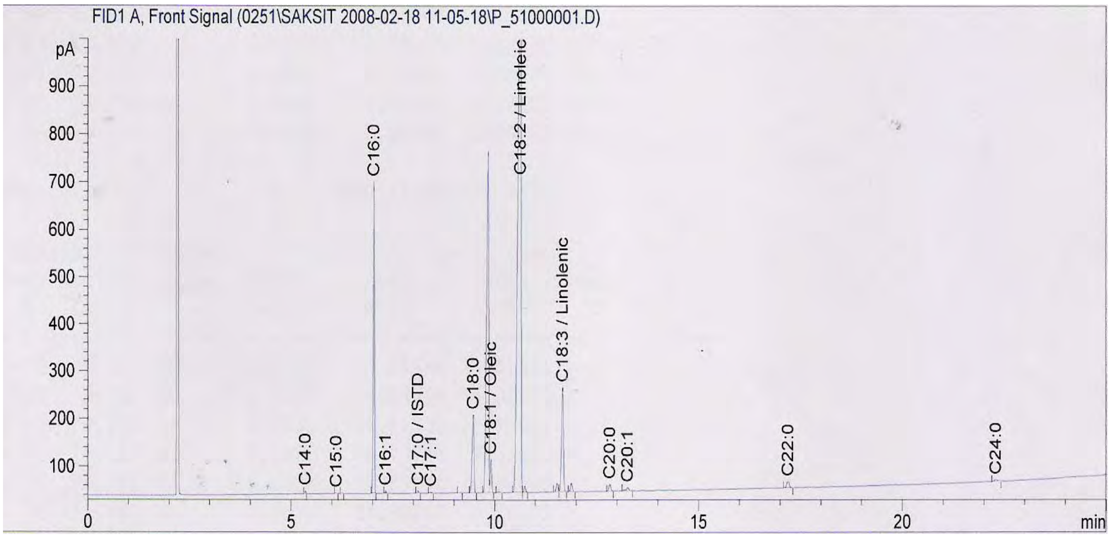


Figure A10 The GC-FID chromatogram of soybean oil.

CALCULATIONS

1. The calculation of iodine value

Calculated the iodine value, *I*, as follows:

$$I = [(B - V)\,N \times 12.69] / S$$

where:

V = $Na_2S_2O_3$ solution required for titration of the specimen, mL,

B = $Na_2S_2O_3$ solution required for titration of the blank, mL,

N = normality of the $Na_2S_2O_3$ solution, and

S = sample used, g.

2. The calculation of acid value

Calculated the acid number as follows:

$$\text{Acid number} = [(A - B)\,M \times 56.1] / W$$

where:

A = KOH solution required for titration of the sample, mL,

B = KOH solution required for titration of the blank, mL,

M = molarity of the KOH solution, and

W = sample used, g.

3. The calculation of saponification value

$$\text{Calculate the saponification value} = \frac{28.05\,(A - B)}{\text{Weight of sample}}$$

where:

A = titration of blank, and

B = titration of sample.

4. Calculation of the cost of drying oil encapsulated urea fertilizers product

It is interesting to note that the main components of the examined coating are locally available. Producing one ton of this coating (*O. canum* seed oil) cost ≃ 20,000 baht/ton (price on year 2008). This will be economically justified if compared with other types of commercial coatings.

Price of raw material

1. *O. canum* seed oil ≃ 20 baht/kg
2. Linseed oil ≃ 40 baht/kg
3. Catalyst ≃ 300 baht/kg
4. Urea fertilizers ≃ 10,000/ton

For example

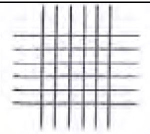
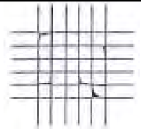
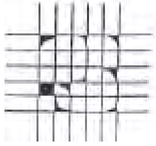
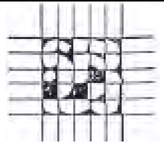
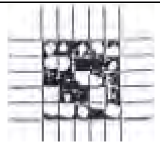
Coatings	1 layer of coating	2 layers of coating
	price (baht/kg)	price (baht/kg)
O. canum seed oil	11.38	12.76
Linseed oil	12.58	15.16

From the above Table the production cost of drying oil encapsulated urea fertilizer are shown. The relative price of controlled-release fertilizer in relation to uncoated urea granular will determine its commercialization potential for rice crop. A price of controlled-release fertilizer at about 25-50% higher than that of urea granular will be very attractive to farmers. However, the crop field required half dose for controlled-release fertilizers. Thus, the cost of fertilizer was reduced.

Note : The price of controlled-release fertilizer available in Thailand.
(Osmocote^{TM}, 18-6-12) ≃ 120-150 baht/kg

APPENDIX B

Table B1 Qualification of adhesion test results (ASTM D3359)

Grade	Description	Surface
5B	The edges of the cuts are completely smooth: none of the squares of the lattice is detached	
4B	Small flakes of the coating are detached at intersections: less than 5% of the area is affected.	
3B	Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5-15% of the lattice.	
2B	The coating has flaked along the edges and on parts of the squares. The area affected is 15-35% of the lattice	
1B	The coating has flaked along the edges of cuts in large ribbons and whole square have detached. The area affected is 35-65% of the lattice.	
0B	Flaking and detachment worse than Grade 1.	Greater than 65%

Procedure

1. Brush the area before test
2. Make the grid in a different location
3. Place the center of the tape over the grid and in the area of the grid smooth into place by a finger. To ensure good contact with the film rub the tape with eraser on the end of a pencil.
4. Within 90 ± 30 seconds of application, remove the tape rapidly pulling it off at as close to and angle of 180° as possible.
5. Inspect the grid area for removal of coating from the substrate. Rate the adhesion in accordance with the following scale illustrated in Table 3.1.

Table B2 Results of calibration curve of standard urea solution

Amount of 5 g/L Urea solution (ml)	Concentration (g/L)	Absorbance
0	0.00	0.000
2	0.04	0.080
4	0.08	0.125
6	0.12	0.175
8	0.16	0.225
10	0.20	0.280
12	0.24	0.335
14	0.28	0.390
16	0.32	0.430
18	0.36	0.480
20	0.40	0.560

Table B3 Results of solubility of uncoated urea fertilizer

Time (min)	Absorbance	Urea fertilizer (g/L)	urea released (g/L)	Urea release (%)
1	0.120	5.028	3.987	79.288
2	0.128	5.028	4.268	84.893
3	0.138	5.030	4.644	92.329
4	0.135	5.051	4.550	90.086
5	0.140	5.044	4.738	93.945
6	0.140	5.040	4.738	94.010
7	0.140	5.019	4.738	94.403
8	0.140	5.033	4.738	94.141
9	0.140	5.027	4.738	94.263
10	0.140	5.059	4.738	93.666

Table B4 Release rate of *O. canum* seed oil encapsulated urea fertilizer for 56 days

Thickness (µm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
1 day				
16	0.128	5.056	4.362	84.423
23	0.120	5.047	3.987	78.990
40	0.080	5.050	2.484	49.181
65	0.218	5.165	0.155	2.963
120	0.000	5.066	0.000	0.000
150	0.000	5.074	0.000	0.000
180	0.000	5.028	0.000	0.000
196	0.000	5.092	0.000	0.000
2 days				
16	0.135	5.091	4.550	89.387
23	0.130	5.024	4.362	86.839
40	0.103	5.025	3.423	66.257
65	0.320	5.098	0.230	4.512
120	0.020	5.032	0.004	0.091
150	0.000	5.038	0.000	0.000
180	0.000	5.070	0.000	0.000
196	0.000	5.065	0.000	0.000
3 days				
16	0.135	5.091	4.550	89.282
23	0.135	5.084	4.550	89.501
40	0.120	5.060	3.987	78.795
65	0.475	5.081	0.365	6.820
120	0.025	5.032	0.010	0.166
150	0.025	5.035	0.008	0.166
180	0.025	5.020	0.006	0.166
196	0.110	5.041	0.005	1.433

4 days	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
16	0.130	5.034	4.362	86.667
23	0.135	5.093	4.550	89.340
40	0.130	5.031	4.362	86.710
65	0.103	5.059	3.325	65.812
120	0.033	5.051	0.016	0.277
150	0.035	5.050	0.016	0.314
180	0.190	5.058	0.132	2.617
196	0.043	5.127	0.023	0.419
5 days				
16	0.140	5.054	4.738	93.750
23	0.133	5.060	4.362	86.213
40	0.128	5.062	4.174	84.331
65	0.120	5.068	3.987	78.670
120	0.120	5.041	1.595	1.582
150	0.065	5.057	0.042	0.759
180	0.303	5.026	0.031	4.316
196	0.065	5.129	0.038	0.749
6 days				
16	0.138	5.018	4.550	92.550
23	0.140	5.100	4.738	92.913
40	0.133	5.075	4.362	87.818
65	0.125	5.129	4.174	81.390
120	0.133	5.075	1.745	35.127
150	0.500	5.035	0.365	7.256
180	0.358	5.048	0.038	5.115
196	0.075	5.092	0.050	0.902

1 week	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
16	0.133	5.054	4.362	88.174
23	0.135	5.021	4.362	86.891
40	0.135	5.026	4.550	90.543
65	0.130	5.060	4.738	86.213
120	0.170	5.035	2.346	46.596
150	0.143	5.082	1.895	38.036
180	0.103	5.032	1.557	26.463
196	0.120	5.060	0.080	1.576
2 weeks				
16	0.135	5.013	4.550	90.769
23	0.135	5.017	4.550	90.696
40	0.133	5.039	4.550	88.436
65	0.140	5.029	4.738	94.216
120	0.195	5.060	2.722	53.792
150	0.168	5.089	2.271	45.364
180	0.143	5.014	2.158	38.548
196	0.113	5.065	1.595	29.258
3 weeks				
16	0.138	5.023	4.550	92.458
23	0.130	5.046	4.362	86.461
40	0.130	5.045	4.362	86.478
65	0.130	5.055	4.926	86.298
120	0.250	5.115	3.549	69.381
150	0.225	5.080	3.173	62.456
180	0.175	5.065	2.609	47.809
196	0.145	5.058	1.970	38.960

4 weeks	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
16	0.138	5.064	4.738	91.710
23	0.133	5.043	4.362	86.503
40	0.135	5.039	4.550	90.309
65	0.135	5.069	4.738	89.766
120	0.260	5.080	3.699	72.811
150	0.245	5.025	3.473	69.122
180	0.210	5.096	3.135	57.842
196	0.173	5.077	1.954	46.956
5 weeks				
16	0.135	5.078	4.362	89.616
23	0.135	5.057	4.550	89.979
40	0.135	5.094	4.738	89.334
65	0.138	5.060	4.55	91.791
120	0.300	5.052	4.300	85.115
150	0.260	5.058	3.699	73.135
180	0.233	5.075	3.436	64.745
196	0.215	5.087	2.480	59.416
6 weeks				
16	0.135	5.027	4.550	90.516
23	0.138	5.048	4.550	90.148
40	0.140	5.028	4.738	94.234
65	0.140	5.042	4.738	93.973
120	0.310	5.078	4.450	87.639
150	0.280	5.041	3.999	79.345
180	0.263	5.058	3.887	73.871
196	0.250	5.062	3.549	70.101

7 weeks	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
16	0.138	5.094	4.550	91.169
23	0.138	5.059	4.550	89.943
40	0.135	5.073	4.362	89.704
65	0.138	5.059	4.738	91.809
120	0.135	5.114	4.555	88.976
150	0.300	5.117	4.300	84.042
180	0.280	5.028	4.187	79.550
196	0.275	5.052	3.924	77.685
8 weeks				
16	0.138	5.006	4.738	92.772
23	0.140	5.051	4.738	93.815
40	0.130	5.115	4.362	85.294
65	0.135	5.028	4.738	90.498
120	0.135	5.048	4.555	90.148
150	0.310	5.072	4.450	87.751
180	0.298	5.006	4.413	85.155
196	0.290	5.017	4.150	82.713

Table B5 Release rate of lineed oil encapsulated urea fertilizer for 56 days

Thickness (µm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
1 day				
16	0.123	5.027	4.081	81.18
23	0.100	5.031	3.235	64.31
40	0.000	5.061	0.000	0.00
65	0.000	5.092	0.000	0.00
120	0.000	5.092	0.000	0.00
150	0.000	5.0620	0.000	0.000
180	0.000	5.0475	0.000	0.000
196	0.000	5.0735	0.000	0.000
2 days				
16	0.130	5.045	4.362	86.47
23	0.120	5.026	3.987	79.33
40	0.000	5.036	0.000	0.00
65	0.000	5.045	0.000	0.00
120	0.000	5.045	0.000	0.00
150	0.000	5.0365	0.000	0.000
180	0.000	5.0575	0.000	0.000
196	0.000	5.0285	0.000	0.000
3 days				
16	0.138	5.056	4.644	91.86
23	0.135	5.073	4.550	89.70
40	0.050	5.066	0.027	0.54
65	0.000	5.052	0.000	0.00
120	0.000	5.052	0.000	0.00
150	0.000	5.0405	0.000	0.000
180	0.000	5.0445	0.000	0.000
196	0.000	5.0775	0.000	0.000

Thickness (µm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
4 day				
16	0.135	5.080	4.550	89.58
23	0.135	5.041	4.550	90.27
40	0.120	5.025	0.080	1.590
65	0.108	5.013	0.070	1.400
120	0.080	5.013	0.050	0.990
150	0.000	5.0410	0.000	0.000
180	0.000	5.0740	0.000	0.000
196	0.000	5.0300	0.000	0.000
5 days				
16	0.140	5.031	4.738	94.190
23	0.133	5.036	4.456	88.490
40	0.145	5.034	1.970	39.140
65	0.145	5.060	0.099	1.950
120	0.095	5.060	0.061	1.200
150	0.000	5.0335	0.000	0.000
180	0.000	5.0720	0.000	0.000
196	0.000	5.0570	0.000	0.000
6 days				
16	0.135	5.055	4.550	90.010
23	0.135	5.065	4.550	89.850
40	0.160	5.076	2.196	43.260
65	0.160	5.058	0.110	2.170
120	0.130	5.058	0.087	1.730
150	0.083	5.0220	0.000	0.000
180	0.000	5.0375	0.000	0.000
196	0.000	5.0485	0.000	0.000

Thickness (µm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
7 day				
16	0.140	5.043	4.738	93.950
23	0.140	5.025	4.738	94.290
40	0.175	5.062	2.421	47.840
65	0.120	5.026	1.595	31.730
120	0.090	5.026	1.144	22.760
150	0.320	5.072	0.230	4.536
180	0.070	5.054	0.042	0.834
196	0.000	5.045	0.000	0.000
2 weeks				
16	0.138	5.040	4.644	92.160
23	0.135	5.097	4.550	89.270
40	0.223	5.026	3.135	62.390
65	0.203	5.037	2.835	56.280
120	0.150	5.037	2.046	40.610
150	0.130	5.042	1.745	34.612
180	0.115	5.063	1.520	30.012
196	0.098	5.048	1.256	24.891
3 weeks				
16	0.140	5.053	4.738	93.780
23	0.140	5.045	4.738	93.930
40	0.245	5.066	3.473	68.570
65	0.230	5.053	3.248	64.280
120	0.210	5.053	2.947	58.330
150	0.185	5.030	2.572	51.120
180	0.163	5.058	2.233	44.156
196	0.133	5.034	1.783	35.413

Thickness (µm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
4 weeks				
16	0.135	5.078	4.550	89.610
23	0.133	5.013	4.456	88.890
40	0.260	5.033	3.699	73.490
65	0.245	5.054	3.473	68.720
120	0.233	5.054	3.285	65.010
150	0.215	5.039	3.022	59.987
180	0.180	5.094	2.496	49.012
196	0.160	5.062	2.196	43.383
5 weeks				
16	0.140	5.036	4.738	94.090
23	0.140	50.43	4.738	93.690
40	0.283	5.078	4.037	79.510
65	0.263	5.043	3.736	74.090
120	0.250	5.043	3.549	70.370
150	0.230	5.036	3.248	64.500
180	0.200	5.039	2.797	55.513
196	0.170	5.035	2.346	46.596
6 weeks				
16	0.138	5.057	4.644	91.840
23	0.138	5.025	4.644	92.430
40	0.290	5.027	4.150	82.560
65	0.280	5.051	3.999	79.190
120	0.263	5.051	3.736	73.980
150	0.245	5.061	3.473	68.630
180	0.218	5.052	3.060	60.571
196	0.190	5.042	2.647	52.499

Thickness (µm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
7 weeks				
16	0.140	5.025	4.738	94.300
23	0.140	5.053	4.738	93.780
40	0.125	5.049	4.174	82.680
65	0.300	5.068	4.300	84.850
120	0.280	5.068	3.999	78.910
150	0.260	5.044	3.699	73.338
180	0.240	5.079	3.398	66.907
196	0.213	5.052	2.985	59.083
8 weeks				
16	0.135	5.074	4.550	89.680
23	0.135	5.021	4.550	90.163
40	0.140	5.070	4.738	93.450
65	0.320	5.025	4.601	91.560
120	0.295	5.025	4.225	84.080
150	0.280	5.048	3.999	79.235
180	0.265	5.059	3.774	74.599
196	0.235	5.024	3.323	66.150

Table B6 Release rate of urea fertilizers encapsulated with *O. canum* seed oil and linseed oil (1:1) for 56 days

Thickness (μm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
1 day				
16	0.123	5.014	4.081	8.139
23	0.000	5.053	0.000	0.000
40	0.025	5.049	0.167	3.300
65	0.000	5.079	0.000	0.000
120	0.000	5.053	0.000	0.000
150	0.000	5.031	0.000	0.000
180	0.000	5.051	0.000	0.000
196	0.000	5.027	0.000	0.000
2 days				
16	0.135	5.061	4.550	89.910
23	0.100	5.026	3.235	64.370
40	0.030	5.049	0.242	4.790
65	0.000	5.024	0.000	0.000
120	0.000	5.026	0.000	0.000
150	0.000	5.051	0.000	0.000
180	0.000	5.025	0.000	0.000
196	0.000	5.040	0.000	0.000
3 days				
16	0.143	5.040	4.832	95.870
23	0.110	5.026	3.611	71.850
40	0.040	5.061	0.392	7.750
65	0.000	5.073	0.000	0.000
120	0.000	5.026	0.000	0.000
150	0.000	5.070	0.000	0.000
180	0.000	5.043	0.000	0.000
196	0.000	5.048	0.000	0.000

Thickness (µm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
4 day				
16	0.138	5.064	4.644	91.720
23	0.120	5.057	3.987	78.840
40	0.065	5.073	0.768	15.140
65	0.135	5.048	0.000	0.000
120	0.000	5.057	0.000	0.000
150	0.000	5.084	0.000	0.000
180	0.000	5.036	0.000	0.000
196	0.000	5.035	0.000	0.000
5 days				
16	0.140	5.098	4.738	92.950
23	0.135	5.053	4.550	90.050
40	0.095	5.044	1.219	24.170
65	0.150	5.039	0.000	0.000
120	0.000	5.053	0.000	0.000
150	0.000	5.027	0.000	0.000
180	0.000	5.067	0.000	0.000
196	0.000	5.018	0.000	0.000
6 days				
16	0.140	5.048	4.738	93.860
23	0.138	5.044	4.644	92.080
40	0.120	5.036	1.595	31.670
65	0.160	5.076	0.110	2.160
120	0.100	5.044	0.065	1.280
150	0.000	5.036	0.000	0.000
180	0.000	5.017	0.000	0.000
196	0.000	5.038	0.000	0.000

Thickness (μm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
7 day				
16	0.140	5.074	4.738	93.390
23	0.143	5.071	4.832	95.300
40	0.165	5.042	2.271	45.050
65	0.190	5.044	1.144	22.680
120	0.145	5.071	0.099	1.940
150	0.000	5.038	0.000	0.000
180	0.000	5.028	0.000	0.000
196	0.000	5.061	0.000	0.000
2 weeks				
16	0.143	5.058	4.832	95.532
23	0.143	5.034	4.832	96.000
40	0.223	5.043	3.135	92.170
65	0.150	5.076	2.046	40.300
120	0.055	5.034	0.618	12.270
150	0.060	5.085	0.035	0.680
180	0.045	5.045	0.023	0.460
196	0.130	5.044	0.087	1.730
3 weeks				
16	0.138	5.065	4.644	91.690
23	0.143	5.066	4.832	95.390
40	0.240	5.020	3.398	67.690
65	0.180	5.062	2.496	49.320
120	0.140	5.066	0.895	37.410
150	0.060	5.027	0.693	13.780
180	0.040	5.095	0.392	7.700
196	0.170	5.016	0.117	2.340

Thickness (μm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
4 weeks				
16	0.138	5.069	4.644	91.630
23	0.138	5.094	4.644	91.170
40	0.265	5.042	3.774	74.850
65	0.213	5.056	2.985	59.040
120	0.175	5.094	2.421	47.530
150	0.125	5.066	1.670	33.960
180	0.105	5.027	1.369	27.240
196	0.050	5.063	0.543	10.720
5 weeks				
16	0.135	5.009	4.550	90.850
23	0.140	5.043	4.738	93.950
40	0.280	5.056	3.999	79.100
65	0.220	5.107	3.098	60.650
120	0.190	5.043	2.647	52.480
150	0.165	5.032	2.271	45.130
180	0.153	5.053	2.083	41.230
196	0.190	5.025	1.219	24.260
6 weeks				
16	0.140	5.063	4.783	93.580
23	0.138	5.048	4.644	92.010
40	0.305	5.050	4.375	86.650
65	0.248	5.049	3.511	69.540
120	0.213	5.048	2.985	59.140
150	0.180	5.040	2.496	49.530
180	0.173	5.021	2.384	47.470
196	0.143	5.035	1.933	38.390

Thickness (µm)	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
7 weeks				
16	0.140	5.060	4.783	93.640
23	0.140	5.039	4.738	94.040
40	0.320	5.029	4.601	91.490
65	0.260	5.040	3.699	73.400
120	0.230	5.039	3.248	64.460
150	0.205	5.065	2.872	56.710
180	0.200	5.071	2.797	55.160
196	0.160	5.039	2.196	43.580
8 weeks				
16	0.138	5.032	4.644	92.290
23	0.138	5.032	4.644	92.300
40	0.323	5.015	4.638	92.490
65	0.283	5.055	4.037	79.860
120	0.255	5.032	3.624	72.020
150	0.240	5.10	3.398	66.510
180	0.225	5.047	3.173	62.860
196	0.195	5.040	2.722	54.010

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Table B7 Influence of pH on releasing rate of urea encapsulated fertilizer

pH5	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
Time (min)				
30	0.053	5.022	0.580	11.552
60	0.105	5.031	1.369	27.215
90	0.140	5.064	1.895	37.426
120	0.185	5.106	2.572	50.364
150	0.200	5.058	2.797	55.299
180	0.223	5.138	3.135	61.020
210	0.245	5.147	3.473	67.483
240	0.280	5.053	3.999	79.149
pH6				
Time				
30	0.045	5.117	0.467	9.136
60	0.090	5.115	1.144	22.363
90	0.133	5.155	1.783	34.578
120	0.173	5.014	2.384	47.541
150	0.190	5.109	2.647	51.805
180	0.205	5.142	2.872	55.857
210	0.238	5.125	3.361	65.580
240	0.270	5.123	3.849	75.134

pH7	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
Time				
30	0.038	5.056	0.355	7.015
60	0.070	5.066	0.843	16.644
90	0.123	5.087	1.632	32.086
120	0.170	5.056	2.346	46.403
150	0.183	5.170	2.543	49.014
180	0.200	5.089	2.797	54.968
210	0.233	5.085	3.285	64.611
240	0.255	5.077	3.624	71.374
pH8				
Time				
30	0.033	5.081	0.280	5.502
60	0.063	5.066	0.730	14.419
90	0.120	5.143	1.595	31.009
120	0.163	5.093	2.233	43.853
150	0.170	5.077	2.346	46.216
180	0.193	5.121	2.684	52.423
210	0.213	5.081	2.985	58.746
240	0.253	5.111	3.586	70.165

pH9	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
Time				
30	0.020	5.058	0.092	1.813
60	0.050	5.068	0.543	10.706
90	0.100	5.021	1.294	25.773
120	0.148	5.026	2.008	39.952
150	0.163	5.058	2.233	44.156
180	0.180	5.022	2.496	49.710
210	0.203	5.054	2.835	56.086
240	0.245	5.061	3.473	68.630
pH10				
Time				
30	0.015	5.057	0.017	0.327
60	0.040	5.048	0.392	7.771
90	0.080	5.029	0.993	19.755
120	0.123	5.091	1.632	32.061
150	0.143	5.061	1.933	38.190
180	0.155	5.025	2.121	42.203
210	0.183	5.046	2.534	50.218
240	0.200	5.031	2.797	55.596

Table B8 Influence of temperature on releasing rate of urea encapsulated fertilizer

Time	Absorbance	Urea fertilizer (g/L)	Urea release (g/L)	Urea release (%)
20^{0}C				
60	0.025	5.105	0.167	3.268
120	0.040	5.102	0.392	7.689
180	0.050	5.129	0.543	10.579
240	0.065	5.103	0.768	15.050
25^{0}C				
Time				
60	0.030	5.006	0.242	4.843
120	0.040	5.109	0.392	7.678
180	0.065	5.121	0.768	14.997
240	0.080	5.105	0.993	19.461
30^{0}C				
Time				
60	0.030	5.122	0.242	4.724
120	0.050	5.109	0.543	10.620
180	0.070	5.110	0.843	16.500
240	0.100	5.100	1.294	25.374
35^{0}C				
Time				
60	0.040	5.114	0.392	7.671
120	0.060	5.108	0.693	13.564
180	0.090	5.134	1.144	22.278
240	0.130	5.104	1.745	34.188
40^{0}C				
Time				
60	0.045	5.126	0.467	9.119
120	0.090	5.115	1.144	22.361
180	0.150	5.147	2.046	39.742
240	0.200	5.045	2.797	55.442

VITA

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