

Review: Synthesis of Urea in Several Methods

Asep Rizki Pradana *, Asep Royani, Kiki Zulfikri, Nabila Tuffahati, Rahma Zulfa Azzahra, Tasya Qori Amini and Asep Bayu Dani Nandiyanto

Dr. Setiabudi No.229, Bandung City, West Java, Department of Chemistry Education, Mathematics and Science Education Faculty, Universitas Pendidikan Indonesia, Indonesia

Abstract: Urea ($\text{CO}(\text{NH}_2)_2$) is one of the compositions in making fertilizer. Fertilizer is crucial, especially for plant growth (affecting plant fertility). If a plant had urea fertilizer on the soil, nitrogen in the fertilizer releases quickly, and it will cause environmental pollution. Therefore, many studies want to develop urea fertilizer to be more efficient to use. The purpose of this review is to find the most appropriate method for the efficient use of urea as seen from the material used, the technique used, and the results obtained. This review shows that the most appropriate method is the slow release method with NaOH and fly ash ingredients. Because this method can increase the effective utilization of urea, reduce environmental pollution, and be relatively more straightforward, the raw material is more affordable and spread widely in the market.

Keywords: Methods; Nitrogen; Slow Release.

1. Introduction

Nitrogen is an essential nutrient in plants that function in protein formation, chlorophyll synthesis, and metabolic processes ¹. Nitrogen is also one of the macronutrients required by plants. Urea is widely used as fertilizer due to its high nitrogen content ($\pm 46\%$). However, as much as 50-60% nitrogen is lost through leaching, decomposition, and evaporation of ammonia ². Although nitrogen losses can be reduced by re-fertilization in one planting season, this method is inefficient because farmers' production costs will be higher.

Urea is a polar, highly soluble in water, and charge-neutral molecule, with oxygen and two nitrogen atoms serving as hydrogen bond acceptors. Two amino functions provide a total of four hydrogen bonds for donation. The molecular formula is $\text{CO}(\text{NH}_2)_2$; the molecular mass is 60.06 g/mol ³.

Based on Dazmiri, MK et al., 2019, formaldehyde to urea has 3 initial molar ratios F/U of 1.9, 2.1, and 2.3 resin synthesis have been examined in this work ⁴. While in Dorieh A. et al., 2018 initial molar ratio formaldehyde F/U ~ 5 and 4.3 molar ratio ⁵.

Nitrogen in agricultural and plantation activities is met through a fertilization process, such as urea. Excess use of urea fertilizer in agricultural and plantation activities results in environmental pollution. Urea fertilizer only provides a small part of the nutrients that plants absorb, and the rest is wasted in the environment ⁶.

Based on the researches, $\text{CO}(\text{NH}_2)_2$ various methods can produce 2, such as slow-release fertilizer with multiple materials (chitosan matrix; fluidized bed; coal fly ash and NaOH; cooking oil and paraffin; PVA polymer; aldehyde with 3-4 atoms of carbon), gasification with the help of temperature regulation, nuclear cogeneration, the nuclear steam reforming process, spectrophotometry, and graphene preparation.

2. Urea Fertilizer Synthesis Methods

Based on the studies that have been done before, urea can be synthesized in several ways. Based on [Table 1](#) the materials, methods, and results of each method will be explained.

*Corresponding author: Asep Rizki Pradana
Email address: rizkiasep38@gmail.com
DOI: <http://dx.doi.org/10.13171/mjc02103121554arp>

Received October 18, 2020
Accepted December 29, 2020
Published February 12, 2021

Table 1. Materials, methods and synthesis of urea's results.

Raw Materials	Research Group	Method	Reference	Result
Aldehyde with 3 or 4 atoms of carbon	Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruining, Frankfurt am Main, a corporation of Germany	Condensation of urea with aldehydes	S. H. Karl, K. P. Wilhelm, 1964 ⁷ .	The substance enlarges from medium to high. The molecular weight becomes 5% from 0.2% of the final product.
Acrylic Acid and amyllum	Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro	Fluidized Bed Spraying Coating (FBSC)	A. H. Margi, T. Septiana S. Triwiningsih, Suherman, 2012 ⁸ .	Controlled Release Urea (CRU) with a starch coating has been successfully produced by the FBSC method.
Air and natural gas	Center for Nuclear Energy Development (PPEN) - BATAN	The steam reforming gas process	D. H. Salimy, 2012 ⁹ .	Urea fertilizer from the reaction of CO ₂ and ammonia.
Starch polymers and PVA.	Farbwerke Hoechst Aktiengesellschaft vormals Meister	Urea coating with polymers	K. Ivanky, W. R. Tri, S. Suherman, 2012 ¹⁰ .	Characteristics of polymer coating urea can be seen by the factor of temperature and the amount of starch.
Domestic waste	United State Patent Application Publication	Gasification with temperature selection	G. H. Kiss, 2013 ¹¹ .	NH ₃ and CO ₂ as material for preparation urea.
Air and water	Center for the Study of Nuclear Energy Systems (PKSEN) – BATAN	Uses nuclear cogeneration	D. H. Salimy, 2014 ¹² .	Urea fertilizer from CO ₂ conversion.
Chitosan, silica compound, and urea	Department of Chemistry FMIPA UNESA	Addition of a chemical compound	L. F. E. Wulan, 2017 ¹³ .	Matrix Chitosan-silica formed by producing fertilizer granules rose-colored.
Fly ash, NaOH, and urea	Department of Chemical Engineering, Politeknik Sriwijaya	Coating method with Fly Ash Coal and NaOH	M. Yerizam, I. Purnamasari, A. Hasan, R. Junaidi, 2017 ¹⁴ .	Solid and hard Slow Release Fertilizer.
Waste cooking oil, Paraffin, and urea	Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada Yogyakarta	Urea Fertilizer Coating Method with a Mixture of Waste Cooking Oil and Paraffin	N. M. Prakarsa, 2012 ¹⁵ .	Urea coated with waste cooking oil and paraffin.

Urea prill fertilizer	Department of Chemistry Universitas Sumatera Selatan North	Spectrophotometry	D. I. Muthawali, 2018 ¹⁶ .	Urea fertilizer with different biuret levels.
Chitosan and Humic Acid	Department of Chemistry, Faculty of Mathematics and Natural Sciences State Universitas Surabaya	Slow Release Fertilizer	P. M. Andika, D. K. Maharani, 2018 ¹⁷ .	Urea fertilizer with higher water absorption.
<i>Molecularly Imprinted Polymers (MIPs)</i> , grapefruit from graphite, and urea	Department of Chemistry, Universitas Sultan Ageng Tirtayasa	Graphene preparation	I. Irhamni, 2016 ¹⁸ .	Formation of urea with molecularly imprinted polymers (M.I.P.s).
Urea, glutaraldehyde, chitosan, organic compound solvent	Department of Chemical Engineering, Faculty of Engineering, Universitas Sultan Ageng Tirtayasa	Cross-linking	R. S. D. Lestari, 2020 ¹⁹ .	Microsphere chitosan.
Sulfur, Starch, PVA, POP, Molasses, Gelatin, and Paraffin Wax	Department of Chemical Engineering, Department of Agronomy, Research and Development Department, and Department of Environmental Sciences, Pakistan	Coating Use Organic and Inorganic	B. Beig, M. B. Niazi, Z. Jahan, E. Pervaiz, G. Abbas Shah, M. Ul Haq, M. I Zafar, M. Zia, 2020 ²⁰ .	Coating of urea prills C-1 improved N release pattern with an efficiency of 6.87%, which was four times higher than other coated fertilizers.

2.1. Urea Condensation Method with Aldehyde and Result

The researchers found that the aldehyde condensation method is challenging because it usually produces much dust in high enough quantities.

The process of preparation granular fertilizer by condensing urea with an aldehyde contains 3-4 carbon

atoms. Substances are added to the starting product before condensation to increase the molecular weight, such as modified cellulose, methylcellulose or carboxymethyl cellulose. Modified polyacrylonitrile, like polyacrylamide, polyvinyl alcohol, or substances of medium to high molecular weight, having similar properties in the amount range, 0.2 to 5%, especially 0.3 to 1%, is calculated on the final product ⁷.

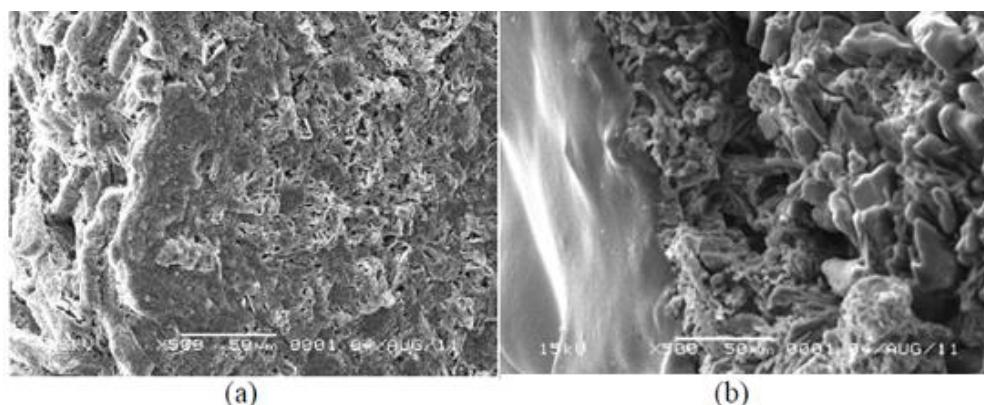


Figure 1. The result of urea with coating without coating (a) and (b) with coating Figure taken from Margie Agami Haq (2012) ⁸

Two results were obtained with different concentrations. In experiment one, 92% of the granules of the product had a particle size of 0.2 to 3 mm. The product also contains 32.2% nitrogen, including 45% soluble in water, 54% difficult to dissolve in water, and 1% insoluble in water. The second experiment produces a urea product with fine-grained and does not create dust. Nitrogen in the second experimental product is 30% with 33% soluble in water, 66% is difficult to dissolve in water, and 1% is insoluble ⁷.

2.2. Fluidized Bed Spraying Coating (FBSC)

Methods and Results

Figure 1 is obtained from the SEM test results. Figure 1 (a) shows that urea only consists of one layer, but in Figure 1 (b), it can be seen that there are two layers, consist of urea and coating. The purpose of

SEM testing is to determine the microscopic image of the product surface obtained. The coating spread equally on the surface of urea expected in the process. Observation of the appearance and shape of the surface was carried out before and after coating. The image is shot at 500x magnification ⁸.

Controlled Release Urea (CRU) with a starch coating has been successfully produced by the FBSC method. The greater the bed temperature used, the dissolution rate will increase. However, the speed of the dissolution rate will decrease as the starch concentration increases. A dustiness will increase with elevating bed temperature and the concentration of starch used. The coating efficiency decreases with an increase in bed temperature and vice versa ⁸.

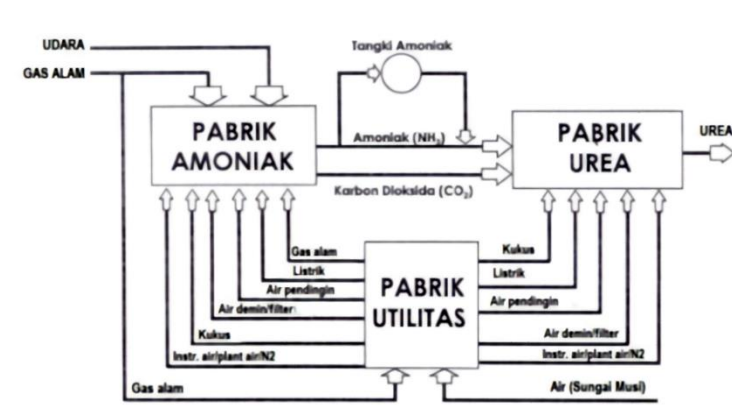
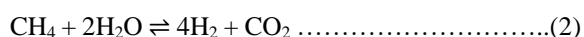


Figure 2. Block Diagram of Urea Fertilizer Manufacturing. Figure taken from PT. Pupuk Sriwijaya (2011) ²¹

2.3. Steam Reforming Gas Method

Based on Figure 2 about block diagram of urea fertilizer manufacturing, the preparation of urea fertilizer on a factory scale can be started by mixing natural gas and air into the ammonia factory, processing it, and the results further processed with the urea factory.

The ammonia plant unit serves to produce ammonia and the reverse process that requires the most energy. In the conventional method, natural gas raw materials are used with steam reforming process at high temperatures (~800°C) to produce synthesis gas (a mixture of H₂ and CO₂) as follows ²²:



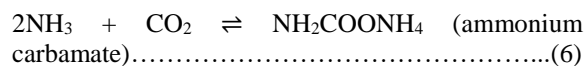
Furthermore, the CO formed in reaction (1) is re-reacted with water to form the CO₂ needed to produce urea.



The hydrogen produced in reactions (1) and (2), is reacted with nitrogen from the air to form ammonia gas following the reaction equation:

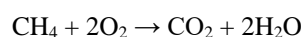


In the urea plant unit, ammonia is reacted with CO₂ obtained at the ammonia plant unit, which through a two-step reaction is produced urea.



In the production of urea, the emission levels of CO₂ obtained from natural gas use as fuel. The utilization of a high-temperature nuclear reactor can meet all the factory's thermal energy so that natural gas is only needed as a raw material.

Reaction:



Molecular weight of CH₄ = 16 and molecular weight of CO₂ = 44.

Natural gas of 12,307,057.75 MMBTU per year is equivalent to 261162331.65 kg/year. So that the

potential for reducing CO₂ emissions is = $44/16 \times 261162331.65 = 718,196.42$ tons/year.

It can be seen from the calculation results that the application of high-temperature nuclear reactor heat energy can save the depletion of natural gas fossil energy resources, which directly impacts the potential to reduce the rate of greenhouse gas emissions ¹².

2.4. Method of coating urea fertilizer with polymer (starch and PVA) and result

Recently, researchers have increased their efforts to use polymers in combination with starch as a coating material. Starch is a polysaccharide polymer that is available in vast quantities. Starch is blended with synthetic polyvinyl alcohol (PVA) polymer as a biodegradable polymer ²³.

According to the research, urea is served with a starch polymer from tapioca flour and polyvinyl alcohol (PVA) by spraying it on a fluid mount. The variables discussed were temperature and starch amount on coating efficiency, dissolution rate, and dust. The research was conducted by filtering the urea with a shaker and then serving it every 100 g ¹⁰.

The results of coating urea with starch can be seen by Scanning Electron Microscopy (SEM). In Figure 3. (a) pure urea enlargement before the coating is carried out up to 500x, and it can be seen that there is more cavity or free space. Meanwhile, in Figure 3. (b), polymer-coated urea looks solid and not hollow when the urea has been coated with starch and PVA ¹⁰.

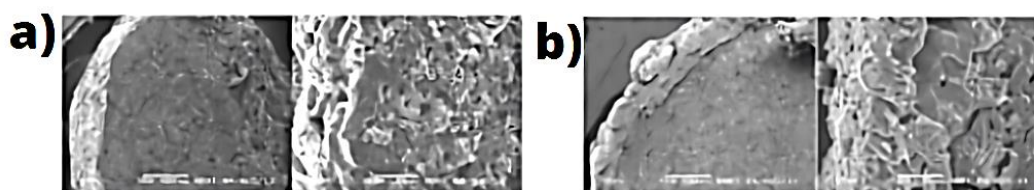


Figure 3. Cross-sectional Urea (a) Pure and (b) Polymer Coated. S.E.M. analysis of cross-sectional urea in 50x and 500x magnifications. Figure taken from Ivanky, K. Tri, WR. (2012) ¹⁰

2.5. Thermoselect Method

All the process used for the synthesis of ammonia is development with Haber-Bosch process in Germany. This process involves hydrogen and nitrogen reaction

under high temperature and pressure with an iron catalyst based and requires great energy ²⁴.

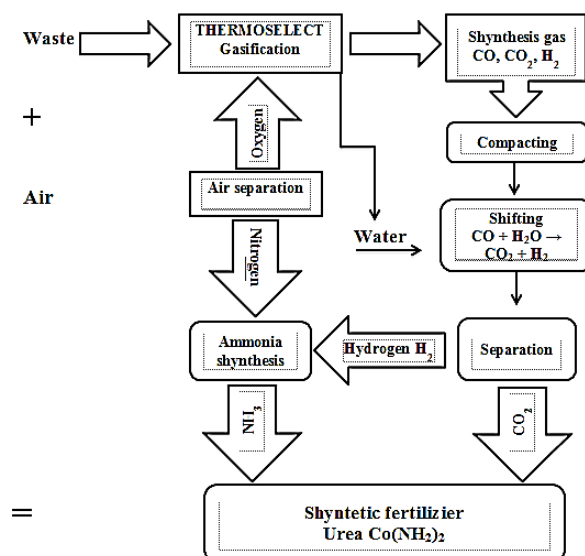


Figure 4. Scheme Steps Preparation of Thermoselect Method. Scheme taken from Locarno (2013) ¹¹

According to Figure 4 about scheme steps preparation of thermoselect method, the experiment was done by Locarno (2013). The first step is CO₂, CO, and H₂ gas synthesis of gasification in high temperature as a by-product of pure use oxygen selection temperature. Therefore, CO contained in a gas will be changed to CO₂ and H₂ in H₂O vapor. Then, H₂ gas formed from

CO₂ and H₂ converted into NH₃ and N₂ as a by-product. The final result of this method is NH₃ and CO₂ as material for preparation urea. The benefit of this method is not producing gas emissions. All substances formed can be used, so this is a low-cost process needed ¹¹.

2.6. Nuclear Cogeneration Method

Nuclear cogeneration is a method that can be used in the manufacture of urea fertilizer. Nuclear cogeneration has the advantage of saving natural gas reserves. Besides that, it will also have implications for reducing the rate of CO₂ emissions to be more environmentally friendly and reduce the impact of global warming due to emissions from CO₂¹².

Based on Figure 5 about flow charts of the nuclear urea fertilizer production process, nuclear cogeneration for water decomposition is the thermochemical process of breaking down water molecules into hydrogen and oxygen by utilizing nuclear thermal energy to carry out the process. This process is an important candidate for high-temperature nuclear reactor applications for producing hydrogen from water.

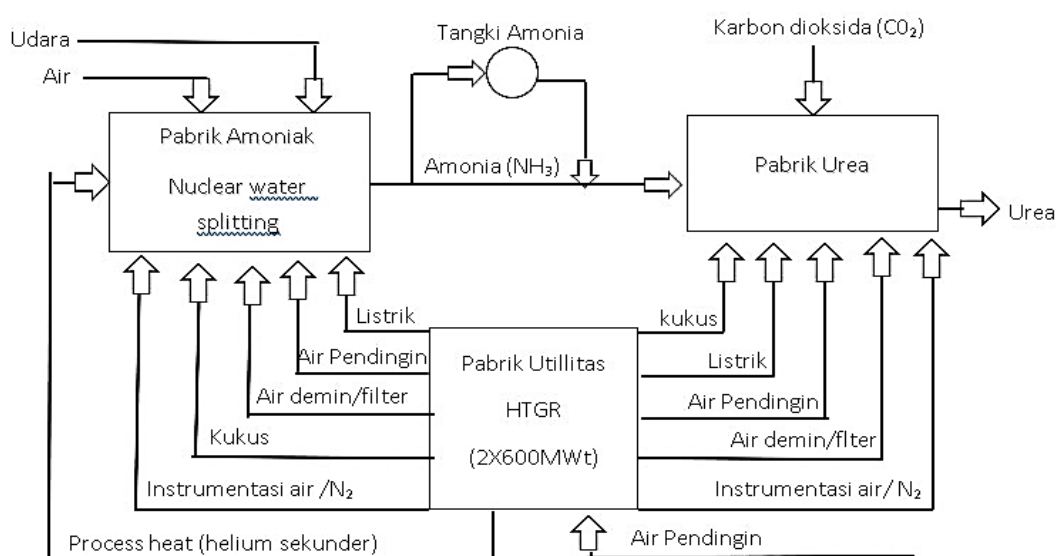
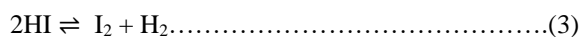
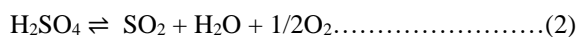


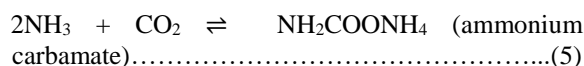
Figure 5. Flow Chart of Nuclear Urea Fertilizer Production Process. Figure taken from Salimy, Djati H. (2012)⁹

The main units in a urea fertilizer plant include an ammonia factory, urea factory, and utility factory. In the ammonia plant, by utilizing nuclear cogeneration technology for water decomposition, the process that is replaced forms hydrogen in the ammonia plant unit process. The reaction of hydrogen formation by the thermochemistry process of the iodine-sulfur cycle with nuclear heat is used to replace the natural gas steam reforming process. The reaction for the formation of hydrogen is as follows:



In contrast to the natural gas steam reforming reaction that produces CO₂, this reaction does not produce CO₂ needed in the urea plant unit's urea formation process. Because of that, CO₂ must be supplied from outside the system. The reactions that occur in the urea plant units are the same as those in conventional processes, and only the source of CO₂ is different. In the traditional method, CO₂ is obtained from the steam reforming reaction of natural gas, while in nuclear

cogeneration applications, CO₂ is obtained from outside the system¹².



High-temperature atomic reactors constitute a significant component of utility plants. The needs of all types of energy (heat, steam, and electricity) are fully supplied using high-temperature nuclear reactors. Process heat energy is met by utilizing secondary helium to carry out the nuclear cogeneration process. Simultaneously, steam and electricity requirements are obtained by converting some of the secondary helium's heat energy into steam and electricity¹².

2.7. Slow Release With Matrix Chitosan-Silica Method and Result

Chitosan is composed of poly (2-deoxy-2-acetyl-amino-2-glucose) and poly (2-deoxy-2-amino glucose) that binds (1-4) β-glycosidic. Characteristics of chitosan are non-toxic, biodegradable and biocompatible²⁵.

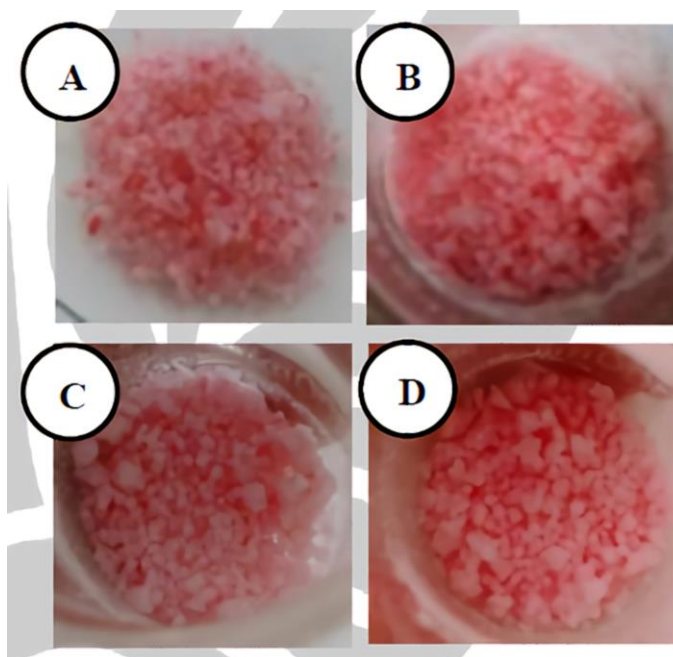


Figure 6. The Result of Slow Release with Matrix Chitosan-Silica Process Produce Matrix. Chitosan-silica formed by producing fertilizer granules rose-colored. Figure taken from Wulan and Maharani (2017) ¹³

Preparation of 0.2% chitosan solution is formed by dissolving 0.2 g of chitosan in 100 mL of 2% acetic acid solution. The silica sol made from TEOS precursor and HCl catalyst is hydrolyzed in ethanol for 24 hours. Furthermore, preparation of chitosan-silica matrix by stirring a mixture of chitosan solution and silica sol with various compositions. After all the materials are ready, matrix chitosan-silica mixed with urea fertilizers and stored for 4-5 days in a desiccator. The release of nitrogen testing uses a process spectrophotometer to prove release levels according to the ISO standard. Four times the release of nitrogen testing showed in Figure 6 that matrix chitosan and silica by comparison 1.5: 1.5 is about the release less than 15 % and the release of nutrients for 28 days almost 75%. Fertilizer slow release with matrix chitosan-silica formed by producing fertilizer granules rose-colored ¹³.

2.8. Coating method with Fly Ash Coal and NaOH and Result

Fly ash and NaOH are mixed with a specific ratio (in % volume) then stirred evenly. The urea that has been sifted in a certain amount (ratio based on volume% to FA) is stirred into the FA-NaOH mixture. Then the FA-NaOH urea was formed into pellets. The product is soluble in water, and the duration of release in the soil was observed ¹⁴.

Based on research conducted by Yerizam, Muhammad et al. (2017), modified urea is quite well-formed without heating during mixing. At the time of preparation, modified urea by heating it produces modified urea, which is very dilute because NaOH and urea are hygroscopic. So, modified urea is made without heating, and the product is produced in Figure 7 ¹⁴.



Figure 7. Modification Results on Products. Modified urea, the result of fly ash and NaOH method. Figure taken from Yerizam, Muhammad et al. (2017) ¹⁴

The solubility results of modified urea (based on Table 2) were compared with urea prills in water with the same weight; the following results are obtained. Based on Table 2 about long-time urea and modified urea dissolved in water are different. Urea dissolved

in water with 1 minute 10 seconds faster than modified urea. Because modified urea contains more components than urea, modified urea is slower dissolved in water than urea.

Table 2. Solubility Of Urea and Modified Urea in Water. Figure taken from Yerizam, Muhammad et al. (2017) ¹⁴.

Component	Long-Time Dissolved in water
Urea	15 minutes 10 seconds
Modified Urea	16 minutes 20 seconds

The test results on the soil release time consisting of five samples of urea prills and modified urea with

different ratios are shown in Figure 8.



Figure 8. Product Testing Results. The product in 12 hours after tested. Figure taken from Yerizam, Muhammad et al. (2017) ¹⁴

Based on the results, urea prills quickly release nitrogen more than modified urea. The relationship

between time release and the amount of urea released in the soil is illustrated in Figure 9.

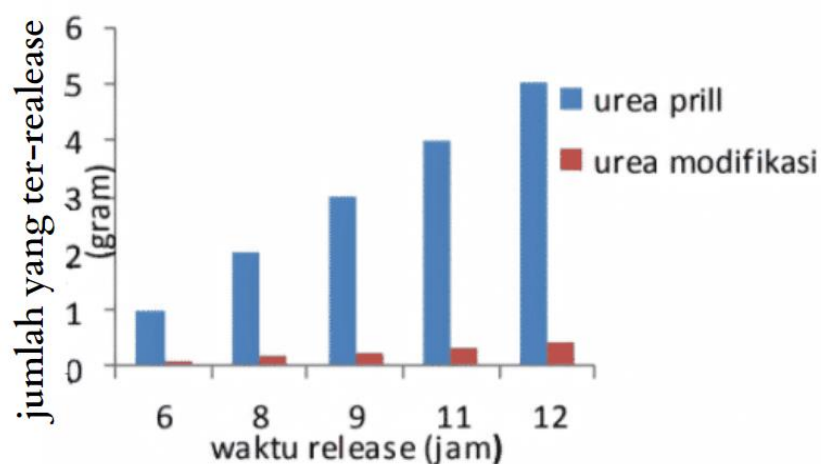


Figure 9. Effect of Release Time Graphic. The graphic shows in hours the number of releases. Figure taken from Yerizam, Muhammad et al. (2017) ¹⁴

Figure 9 about the effect of release time graphic between modified urea and urea prill indicates that the modified urea product is good enough to be used as a slow-release fertilizer. The resulting product is quite

dense and hard compared to ordinary urea prills so that it does not dissolve quickly from standard urea ¹⁴.

2.9. Urea Fertilizer Coating Method with a Mixture of Waste Cooking Oil and Paraffin and Result

Materials and tools needed for this method are urea prills, urea analytic with 99% purity, solid paraffin, and used cooking oil. This research using SpectroVis Plus Spectrophotometer.

Then dried at 100°C in an oven for 1 day and stored in a desiccator. Then prepare a beaker containing a mixture of 7 g of paraffin and used cooking oil. Place it on a hot plate at 70°C. When the paraffin mixture melts, then add the urea fertilizer gradually, then stir it so that the urea and paraffin mixture is evenly distributed. The resulting mixture was dried in a desiccator for 48 hours. The initial analysis used is to calculate the sample coating efficiency using the following equation ¹⁵.

$$\eta = \frac{(mf - mo)}{mo \times 100\%}$$

The first step to determine the amount of nitrogen released is to make a standard solution using distilled water. The solution was analyzed using a U.V./Vis spectrophotometer by looking for the maximum absorbance value produced; these results were used to determine the maximum wavelength (λ max) to be used in the urea coating sample test. The test sample was carried out using 25 g of sample urea coating, put in 250 mL of distilled water, and placed at room temperature. The amount of urea must match the urea concentration in the range of the calibration curve. Samples were allowed to stand for a variety of 2-5 days. The amount of nitrogen released was calculated from the urea concentration until nitrogen release reached 99%. This analysis was repeated 3 times to get accurate results ¹⁵.

The manufacture of slow-release fertilizer (SRF) using a coating of 7 g of used cooking oil and paraffin on urea produce in a coating efficiency of 6.6%, while the UV/VIS analysis results using a standard solution in the Vernier SpectroVis Plus Spectrophotometer to find the maximum wavelength value at 424 nm. Whereas in the test for decreasing nitrogen concentration at various times (days), the maximum nitrogen release time was obtained on the 3rd day with a nitrogen release concentration of 33100 ppm ¹⁵.

2.10. Spectrophotometric Methods and Result

Spectrophotometry is an analytical method based on measuring monochromatic light absorption by a strip of colored solutions at a specific wavelength using a prism monochromator or diffraction grating with a phototube detector ²⁶.

Spectrophotometry is used to analyze the concentration of a substance in a solution based on the

absorbance of the solution's color at a particular wavelength. Simultaneously, the spectrophotometer is a tool for measuring the transmittance or absorbance of a sample as a wavelength function. In addition, a spectrophotometer can also use a bottom-up technique. The bottom-up process is a synthesis technique with a high enough particle homogeneity. To find out the results of urea-hydroxyapatite synthesis, it is necessary to perform Scanning Electron Microscopy (SEM) characterization to observe particle morphology, Energy Dispersive X-Ray Spectrometry (EDX) to observe elemental composition, Fourier Transform Infrared Spectrometer (FTIR) to observe the bonds between elements, and Particle Size Analyzer (PSA) to observe particle size distribution ²⁷.

Based on the urea prill as a sample from PT PUSRI analysis result, the biuret content in urea prill on average is 0.31%. Meanwhile, the urea prill fertilizer at PT PIM, the urea prill's biuret content on average, is 0.34%. The two fertilizers that have been studied show that the value of biuret content in good quality urea is in accordance with the value set by the Indonesian National Standard (SNI) 02-2801-1998 ¹⁶.

2.11. SFR (Slow-release Fertilizer) Method with Chitosan - Humate Acid Matrix

The main principle of SRF fertilizer is to create a barrier in molecular interactions so that the nutrients in the fertilizer do not easily escape into the environment ²⁸.

To prepare chitosan-humate acid slow-release fertilizer, it is necessary to prepare urea fertilizer for the grinding and sieving process with a 60 mesh sieve. Furthermore, the urea fertilizer produced by the sieve was mixed with Chitosan-humate acid composites with various concentrations and stirred using a magnetic stirrer for 2 hours. Moreover, the samples were dried in an oven at 60°C ¹⁷.

Testing of water absorption (swelling) can be done by weighing 0.5 g of the fertilizer sample placed on filter paper, where the filter paper is measured first. Furthermore, 2 mL of Aqua DM was added and left 24 hours at 25°C (room temperature). Then the measuring process and the calculation of the swelling power are carried out, which are as follows:

$$\% \text{ Swelling Power} = \frac{M - M_0}{M_0} \times 100\%$$

Description :

M = sample that has undergone splitting

M₀ = dry samples that have not yet undergone refinement ¹⁷.

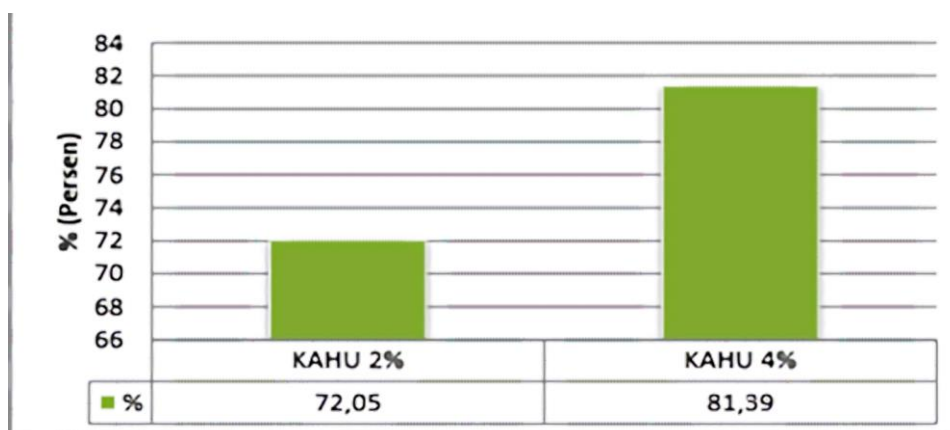


Figure 10. Graph of Fertilizer Swelling Power. The swelling power of the fertilizer is calculated over 24 hours. Figure taken from Andika, PMV. and Maharani, DK. (2018) ¹⁷

Based on Figure 10 about percent of the swelling test, it was found that the effect of humate acid in the fertilizer sample was quite large, so that the higher the concentration of the Chitosan-humate acid matrix, the greater the percentage of water absorption (swelling) in the fertilizer sample which can be seen in Figure 10. With the nature of humate acid like a sponge with a large surface area and a linear molecular structure when interacting with chitosan, it can absorb and hold large amounts of water ¹⁷. (Andika, P.M.V. And Maharani, KD. 2018)

2.12. Graphene Preparation Method and Result

Grapefruit preparation is a MIPs adsorption mechanism against urea which occurs through hydrogen bonds in the mold pores of MIPs compounds ²⁹.

The urea research began with the preparation of grapefruit from graphite. Molecularly Imprinted Polymers (MIPs) compound preparation to determine the optimal preparation conditions, chemical characterization, and surface morphology using IR, XRD, and SEM; then proceed with the characterization of the MIPs compound adsorption on

urea. Research on Molecularly Imprinted Polymers (MIPs) has experienced significant development, especially about its use as an adsorbent because of its high sensitivity and selectivity. Apart from that, its preparation is easy and cheap. Molecularly Imprinted Polymers (MIPs) have been successfully prepared using chitosan which is composited with graphene as the polymer, and urea as the template compound. The MIPs compound formed can be used as an adsorbent on urea. The adsorption ability of MIPs to urea gradually increased in proportion to the increase in concentration and interaction time with the analyte ¹⁸.

2.13. Cross-linking method and result

Based on research, microsphere chitosan containing urea fertilizer and cross-linking with glutaraldehyde. Changes in the concentration of a chitosan and glutaraldehyde solution can affect characterization microsphere chitosan filled fertilizer urea as particles' size. A change in temperature relating to the melting point, and identification in the crystalline phase, this study aims to determine characterization microsphere chitosan who cross-linked by glutaraldehyde as a matrix to the release of under control (a controlled release) urea fertilizer ¹⁹.

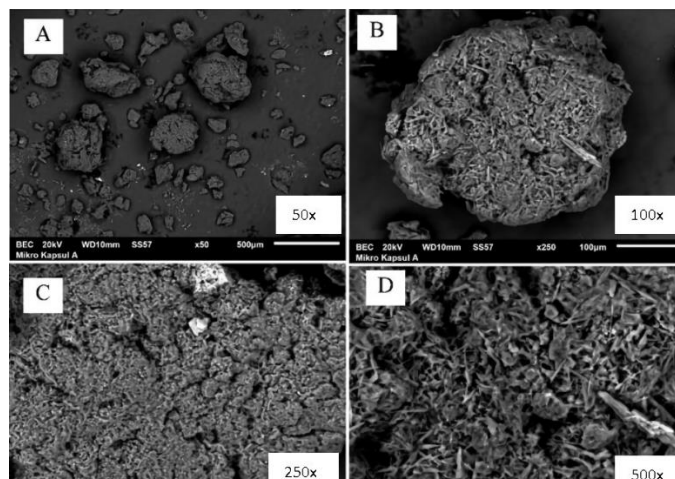


Figure 11. The Result of Cross-Linking Method with Glutaraldehyde. Morphological analysis of urea fertilizer microcapsules with magnification of (A) 50 X, (B) 100x, (C) 250 X, and(D) 500X. Figure taken from Lestari, RSD, et al. (2020) ¹⁹

The research materials used were urea, glutaraldehyde solution, toluene, chitosan, vegetable oil, glacial acetic acid, petroleum ether, n-hexane. All ingredients are mixed one by one and stirred for 2 hours until microsphere chitosan is formed. Then the microsphere chitosan that is created will be filtered, washed, and dried using an oven; the next stage of the microsphere chitosan will be characterized to determine the particle size, melting point, and shape of the crystalline phase.

Based on Figure 11, the result morphological analysis urea microcapsules have already formed with the surface coarse and aggregates shape.

Based on the urea microcapsule release results, the higher the concentration of glutaraldehyde and chitosan, the lower the urea fertilizer's cumulative release. Glutaraldehyde, as a cross-linking agent function, binds the amine groups of chitosan. The presence of these bonds causes an increase in

viscosity and causes the chitosan matrix's hydrophobic properties to increase, and causes a decrease in the mobility of the macromolecular chains³⁰.

2.14. Coating Use Organic and Inorganic Method and Result

For the synthesis of spray coating solutions, 10 g of starch was mixed with 100 mL of deionized water at a constant temperature of 80°C for 30 min. Then, purposed quantities of polyvinyl alcohol, sulfur, and Paraffin wax were added to the starch-based deionized water solution while maintaining the solution temperature at 80°C. Thus, the final solution was ready for its application as a coating material over urea prills. Due to the smaller particle size, the handling of urea prills was complicated during the coating process. A similar methodology was adopted to synthesize all fertilizer formulations, as mentioned in Table 3²⁰.

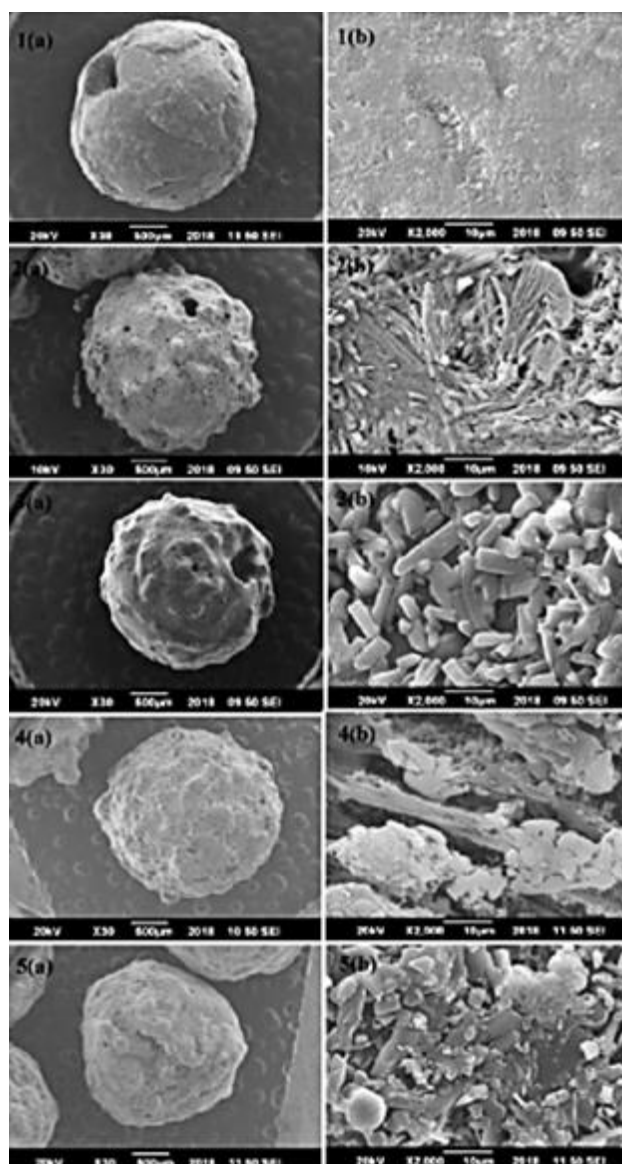


Figure 12. SEM Micrographs of Uncoated and Coated Urea. (1: uncoated urea, 2: C-1 coated, 3: C-2 coated, 4: C-3 and 5: C-4 coated) (a = at 30 magnification and b = at 2000). Figure taken from Beig, B. et al. (2020)²⁰

Table 3. Composition of Coating solutions used in the study.

Treatment Code	Sulfur	Starch	PVA *	POP **	Molasses	Gelatin	Paraffin Wax
	(g (100 g of urea) ⁻¹)						
C-1	5	-	5	10	-	-	2
C-2	5	10	5	-	-	-	2
C-3	5	-	-	10	-	5	2
C-4	5	10	5	-	2.5	-	2.5

* PVA = Poly Vinyl Alcohol, ** POP = Plaster of Paris

Based on Figure 12, the uncoated urea's surface in Figure 12 (b1) looked softer, but the surface has some spot on it. After urea was coated, which was found in Figure (b2, b3, b4, and b5), the surface looked rougher, but the spot was covered with some materials used for spray coating solutions. The surface on each different material used for coating shows that the

difference of each urea coated. The surface can be rougher, or it seems that the surface has some spots too. But if only by SEM analysis, it will not be enough to know which one of 4 coated urea is more efficient. To be more specific, which coated urea is more efficient for slow-release urea can be shown in Figure 13.

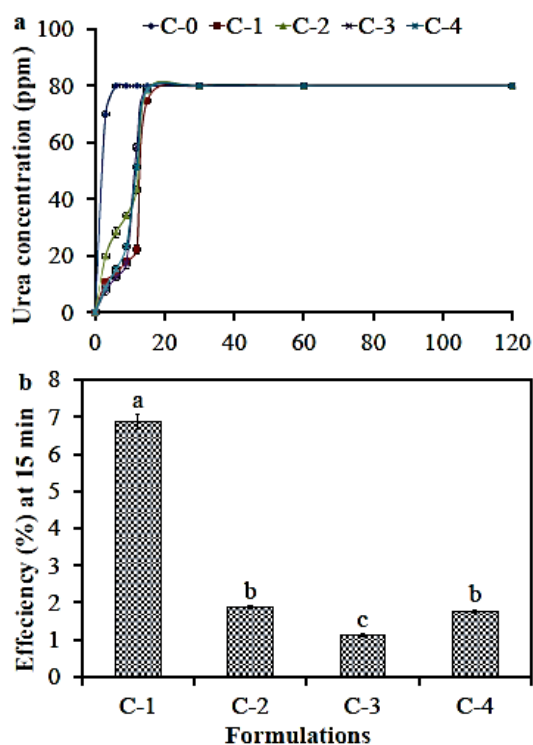


Figure 13. Effect and Efficiency Of Coated Urea. (a) Effect of coating on release rate and (b) efficiency of coated urea formulations. Error bars represent the standard error of the means. Different small letters above bars show significant differences among treatments at 5% probability level. Figure taken from Beig, B. et al.²⁰

Based on Figure 13, POP, PVA, and sulfur combinations with Paraffin wax (C-1) depicted an efficiency of 6.87%. POP's binding ability with wax was stronger and compatible, ultimately resulting in a reliable coating, as shown in SEM Figure 12 (a2,b2). The SEM micrograph of C-3 coated urea also supported this release, probably because of insufficient coating, which looked like a fibrous rod-like structure formed because of POP and para_n wax,

which possessed poor compatibility against each other. The samples composed of POP depicted better efficiency than different formulations, probably due to the sparingly soluble property of POP²⁰.

All those methods of synthesis of urea must have strengths and weaknesses. There are some weaknesses and strengths that are already discussed and mentioned in Table 4.

Table 4. Weaknesses and Strengths of Each Method.

Raw Material	Research Group	Reference	Method	Weaknesses	Strengths
Aldehydes with 3-4 carbons of atom	Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruining, Frankfurt am Main, a corporation of Germany	S. H. Karl, K. P. Wilhelm, 1964 ⁷ .	Condensation of urea with aldehydes	there are two steps of dry condensation which will take more time	<ul style="list-style-type: none"> Urea fertilizer will be larger in molecular weight so that it does not produce large amounts of dust. The product contains nitrogen soluble in water and nitrogen, which is difficult to dissolve in water.
Acrylic Acid and amyllum	Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro	A. H. Margi, T. Septiana S. Triwiningsih, Suherman, 2012 ⁸ .	Fluidized Bed Spraying Coating (FBSC)	<ul style="list-style-type: none"> The bonds that occur between urea and coating agents tend to be weak (easily detached), resulting in higher levels of pollution Increasing the bed temperature hurts the efficiency of the coating due to the loss of solutes due to increased drying 	<ul style="list-style-type: none"> Polymer coated urea has a function as a physical barrier to the release of urea into the environment. The more starch, the more physical obstructions on the surface of the urea, resulting in a longer release time and a lower dissolution rate. Starch as a coating agent for urea can increase coating efficiency from 0% wt starch (without starch) by 1.6% to 14.4% at a concentration of 2% wt starch. The use of acrylic can improve the coating function of urea
Air and Natural Gas	Center for Nuclear Energy Development (PPEN) - BATAN	D. H. Salimy, 2012 ⁹ .	The steam reforming gas process	The ammonia steam reforming process requires large amounts of high-temperature thermal energy.	Application of high-temperature nuclear reactor heat energy can save the depletion of natural gas fossil energy resources
Amyllum polymers and PVA.	Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro	K. Ivanky, W. R. Tri, S. Suherman, 2012 ¹⁰ .	Urea coating with polymers	The materials needed are quite a lot and a bit difficult to find	<ul style="list-style-type: none"> The analysis method used is Scanning Electron Microscopy (SEM). The magnification can be up to 500x The dissolution rate decreases as the temperature and concentration are increased

Domestic waste	United State Patent Application Publication	G. H. Kiss, 2013 ¹¹ .	Gasification with thermostelection	Needs high temperature (1000 - 2000°C)	<ul style="list-style-type: none"> • Not producing gas emissions • Low cost • Raw material from waste
Air and water	Center for the Study of Nuclear Energy Systems (PKSEN) – BATAN	D. H. Salimy, 2014 ¹² .	Uses nuclear cogeneration	It is necessary to be careful in processing nuclear energy resources.	The nuclear cogeneration method is beneficial in saving natural gas reserves, but it will also have implications for reducing CO ₂ emissions.
Chitosan, silica compound, and urea	Department Chemistry FMIPA UNESA	L. F. E. Wulan, 2017 ¹³ .	Addition of a chemical compound	Need a lot of ingredients	<ul style="list-style-type: none"> • Increase the quality of fertilizer • Needs low cost • Non-toxic and biodegradable
Fly ash, NaOH, and urea	Department of Chemical Engineering, Sriwijaya State Polytechnic	M. Yerizam, I. Purnamasari, A. Hasan, R. Junaidi, 2017 ¹⁴ .	Coating method with Fly Ash Coal and NaOH	Observation time is more than 15 hours	<ul style="list-style-type: none"> • Increase the effectiveness of urea use and reduce environmental pollution. • Increase the efficiency of fertilizer use
Waste cooking oil, Paraffin, and urea	Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada Yogyakarta	N. M. Prakarsa, 2012 ¹⁵ .	Urea Fertilizer Coating Method with a Mixture of Waste Cooking Oil and Paraffin	<ul style="list-style-type: none"> • It takes 48 hours to dry in the desiccator • To Samples must be allowed to stand for 2-5 days 	<ul style="list-style-type: none"> • Using low costs • Does not use any solvents • Using low temperatures • It does not require complicated equipment
Urea prill fertilizer	Department of Chemistry, Universitas Sulmatara Selatan	D. I. Muthawali, 2018 ¹⁶ .	Spectro photometry	It evaporates easily and dissolves easily so that nutrients are quickly lost	<ul style="list-style-type: none"> • Easy to find at KUD, fertilizer retailers, farmer stalls, other places, Farmers affordable prices. • Easy to apply. • It can be used for other purposes, such as fertilizing ponds, ration mixtures or animal feed, glue mixtures in the wood industry, and a variety of fabric processing materials in the clothing industry.

Chitosan and Humic Acid	Department of Chemistry, Faculty of Mathematics and Natural Sciences State, Universitas Surabaya	P. M. Andika, D. K. Maharani, 2018 ¹⁷ .	Slow Release Fertilizer	<ul style="list-style-type: none"> The manufacturing process is relatively complicate Many use chemicals 	<ul style="list-style-type: none"> Formed urea fertilizer which has a higher water absorption Chitosan - humic acid matrix can increase water absorption The element content contained in urea fertilizer is not easily lost
Molecularly Imprinted Polymers (MIPs), grapefruit from graphite, and urea	Department of Chemistry, Universitas Sultan Ageng Tirtayasa	I. Irhamni, 2016 ¹⁸ .	Graphene preparation	<ul style="list-style-type: none"> It takes a relatively long time. Difficult immobilization of bioreceptors and low bioreceptor stability. 	<ul style="list-style-type: none"> Easy and cheap preparation high sensitivity and selectivity.
Urea, glutaraldehyde, chitosan, organic compound solvent	Department of Chemical Engineering, Universitas Sultan Ageng Tirtayasa	R. S. D. Lestari, 2020 ¹⁹ .	Cross-linking	<ul style="list-style-type: none"> The materials used are dangerous The material used is only available in the laboratory 	<ul style="list-style-type: none"> It becomes more effective as a function of fertilizer Easy and cheap preparation
Sulfur, Starch, PVA, POP, Molasses, Gelatin, and Paraffin Wax	Department of Chemical Engineering, Department of Agronomy, Research and Development Departement, and Department of Evironmental Sciences, Pakistan	B. Beig, M. B. Niazi, Z. Jahan, E. Pervaiz, G. Abbas Shah, M. Ul Haq, M. I Zafar, M. Zia, 2020 ²⁰ .	Coating Use Organic and Inorganic	<ul style="list-style-type: none"> Because the SEM analysis results cannot determine whether coated urea is efficient or not, other tests are needed that use a lot of time not to be produced in a brief period. 	<ul style="list-style-type: none"> The coated urea is tested directly on plants such as spinach Materials that used for urea coating are measly so that it will save costs

3. Conclusion

Based on the methods mentioned, the urea fertilizer coating method with fly ash and NaOH was chosen to be the most effective than other methods. This method can increase the effective utilization of urea, reduce environmental pollution, relatively more straightforward, the raw material of this method more affordable and spread widely in the market. Also, fly ash has excellent potential in agriculture due to its efficacy in modifying soil health and crop performance. The release of modified urea is more extended than standard urea with the same weight. The time observed is 12 hours. 5 g of urea has been used up, while much-modified urea remains. This modified urea's release time is more than 15 hours with a weight of 1 g and the water release time reaches 16 minutes.

References

- 1- J. Albari, Peranan Pupuk Nitrogen dan Fosfor pada Tanaman Kelapa Sawit (*Elaeis guineensis* Jacq.) Belum Menghasilkan Umur Tiga Tahun, *Buletin Agrohorti*, **2018**, 6(1), 42-49.
- 2- S. K. De Datta, Advances in Soil Fertility Research and Nitrogen fertilizer Management for Lowland Rice, *Providing Efficiency of Nitrogen*, **1987**, 27-41.
- 3- G. G. L. Gopar, M. A. L. Villanueva, D. E. R. García, Pueblos ferroviarios símbolos de la industrialización. Interpretación de vivencias para rescatar la historia. Caso El Parián Oaxaca, *Cuerpos Académicos de la Universidad Autónoma "Benito Juárez" de Oaxaca*, **2018**, 23.
- 4- M. K. Dazmiri, M. V. Kiamahalleh, A. Dorieh, A. Pizzi, Effect of initial F/U molar ratio in Urea-

- formaldehyde resins synthesis and its influence on the performance of medium density fiberboard bonded with them, *International Journal of Adhesion and Adhesives*, **2019**, 95, 102440.
- 5- A. Dorieh, N. O. Mahmoodi, M. Mamaghani, A. Pizzi, M. Mohammadi Zeydi, Effect Of Different Acid During The Synthesis of Urea-Formaldehyde Adhesives, *Journal of Applied Polymer Science*, **2018**, 136(14), 47256.
 - 6- T. Guru, R. Thatikunta, N. Reddy, S. N. Reddy, Crop Nutrition Management with Nano fertilizers, *International Journal of Environmental*, **2015**, 1(1), 4-6.
 - 7- S. H. Karl, K. P. Wilhelm, Process For The Manufacture Of Granular Urea-Aldehyde Fertilizer, Germany : Farbwerke Hoechst Aktiengesellschaft vormals Meister, Lucius & Bruining, Frankfurt am Main, a corporation of Germany, Patent No. 3,326,665, **1964**.
 - 8- A. H. Margie, T. Septian, Pembuatan Urea Pelepasan Lepas Lambat melalui Pelapisan Dengan Amilum-Acrylic, *Jurnal Teknologi Kimia dan Industri*, **2012**, 1, 229-236.
 - 9- D. H. Salimy, Aplikasi Energi Panas Nuklir Temperatur Tinggi Pada Pabrik Pupuk Urea, *Jurnal Pengembangan Energi Nuklir*, **2012**, 14, Doi: [10.17146/jpen.2012.14.1.1478](https://doi.org/10.17146/jpen.2012.14.1.1478).
 - 10- K. Ivanky, W. R. Tri, S. Suherman, Pembuatan Urea Pelepasan terkendali Melalui Pelapisan Dengan Amilum Menggunakan Teknologi Fluidized Bed Spray, *Jurnal Teknologi Kimia dan Industri*, **2012**, 1, 64-68.
 - 11- G. H. Kiss, Method of Manufacturing Urea From Refuse Preferably Domestic Waste of Any Composition. U.S. Patent No. 9,458,099, **2016**.
 - 12- D. H. Salimy, Aplikasi Kogenerasi Nuklir Untuk Dekomposisi Air Pada Konversi CO₂ Menjadi Pupuk Urea, *Jurnal Pengembangan Energi Nuklir*, **2014**, 16, 85-94.
 - 13- L. F. E. Wulan, Pemanfaatan Kitosan-Silika sebagai Matriks pada Pembuatan Pupuk Urea Slow Release, *UNESA Journal of Chemistry*, **2017**, 6.
 - 14- M. Yerizam, I. Purnamasari, A. Hasan, R. Junaidi, Modifikasi Urea Menjadi Pupuk Lepas Lambat Menggunakan Fly Ash Batubara dan NaOH Sebagai Binder, *Jurnal Teknik Kimia*, **2017**, 23, 226-229.
 - 15- N. M. Prakarsa, Pelepasan Pada Pupuk Urea Menggunakan Campuran Minyak Jelantah dan Parafin Dengan Metode Slow Release Fertilizer, *Yogyakarta : Universitas Gadjah Mada*, **2012**.
 - 16- D. I. Muthawali, Penetapan Kadar Biuret Dalam Pupuk Urea Prill dengan Metode Spektrofotometri, *Saintek ITM*, **2018**, 31.
 - 17- P. M. Andika, D. K. Maharani, Penentuan Daya Penyerapan Air (Swelling) Pupuk Urea (Slow Release Fertilizer) Dalam Matriks Kitosan-Asam Humatdetermination Swelling Of Urea Fertilizer (Slow Release Fertilizer) In The Matrix Of Chitosan-Humic Acid. *UNESA Journal of Chemistry*, **2018**, 7.
 - 18- I. Irhamni, Preparasi Moleculary Imprinted Polymers Sebagai Adsorben Untuk Urea dan Kreatinin, *EduChemia (Jurnal Kimia dan Pendidikan)*, **2016**, 1(2), 189-203.
 - 19- R. S. D. Lestari, J. Jayanudi, Preparasi dan Karakterisasi Kitosan Tertaut Silang Glutaraldehyda sebagai Matrik Pupuk Urea, *Jurnal Integrasi Proses*, **2020**, 9(2), 27-33.
 - 20- B. Beig, M. B. Niazi, Z. Jahan, E. Pervaiz, G. Abbas Shah, M. Ul Haq, M. I Zafar, M. Zia, Slow-Release Urea Prills Developed Using Organic and Inorganic Blends in Fluidized Bed Coater and Their Effect on Spinach Productivity, *Sustainability*, **2020**, 12, 5944.
 - 21- A.B.D. Nandiyanto, Kurnia, D. Sofiani, D. C. Kusuma, F. Fitriani, I. P. Rahayu, A. Rusli, A. Purnamasari, A. S. Wiryani, A. Rahim, Pengantar Kimia Industri: Penerapan Ilmu Kimia Menjadi Produk Kimia Skala Besar, *Bandung: UPI Press*, **2016**.
 - 22- E. R. Riegel, J. A. Kent, Handbook of Industrial Chemistry, *Springer*, **2007**.
 - 23- E. Chiellini, A. Corti, R. Solar, Biodegradation of poly (vinyl alcohol) based blow films under different environment conditions, *Polym. Degrad. Stability*, **1999**, 64(2), 305-312.
 - 24- I. Kroschwitz, M. Howe-Grant, Kirk-Othmer encyclopaedia of chemical technology, Vols. 3-10, *Angewandte Chemie-English Edition*, **1995**, 34(22), 2564-2564.
 - 25- A. Rosma, P. Laras, Industry Pharmaceuticals: Chitosan as an Alternative Replacement Gelatin Capsule on Shell, *Journal of Medical and Bioengineering*, **2016**, 5.
 - 26- A. L. Underwood, R.A. Day, JR. *Analisis Kimia Kuantitatif*. Jakarta : Erlangga, **2001**.
 - 27- J. Basset, Vogel: Buku Ajar Kimia Analisis Kuantitatif Anorganik, Jakarta : EGC Kedokteran, **1994**.
 - 28- A. Firdas, M. Dian, Pelepasan Nitrogen Pada Pupuk Slow Release Urea dengan Menggunakan Matriks Kitosan – Bentonit, *UNESA Journal of Chemistry*, **2017**, 6, 68-72.
 - 29- H. A. Tsai, M. J. Syu, Preparation of Imprinted Poly(tetraethoxysilanol) Sol-Gel for The Specific Uptake of Creatinine, *Chemical Engineering Journal*, **2011**, 168, 1369-1376.
 - 30- K. S. Patel, M. B. Patel, Preparation and Evaluation of Chitosan Microspheres Containing Nicorandil, *International journal of pharmaceutical investigation*, **2014**, 4(1), 32.