

Production of Eco-Friendly Urea with Superior Parameters of Mechanical Strength, Anti-Caking, Slow Release and Heat Resistance

Authors

Saadat Motamedi¹, Mojtaba Gholamian¹, Azam Namdari¹, hossein Sabahi²

1 Pardis Petrochemical Company, Pars Special Economic Zone, Bushehr, Iran

2 Faculty of New Sciences and Technology, University of Tehran, Tehran, Iran

Abstract

The purpose of this project was to produce urea with higher mechanical strength and superior anti-caking properties compared to the current urea produced by formaldehyde in Pardis Petrochemical Company using completely environmentally friendly and eco-friendly materials and methods.

In petrochemical companies using formaldehyde, formaldehyde is stored in tanks before use, which can be released into the atmosphere and hurt the personnel. However, published articles have shown that the release of formaldehyde from urea fertilizer in storage can occur during transport as well as during field application[1].

Our results showed that the addition of innovative additives to formaldehyde (UF85) was able to significantly: Increase the anti-caking property along with mechanical strength of urea granules, decrease urea release in farm and reduce the release of formaldehyde into the atmosphere.

Due to these parameters that comes from addition of completely natural substances, we call this fertilizer, Environmentally Friendly or Eco-Friendly Urea

Production of eco-friendly urea with superior parameters of mechanical strength, anti-caking, slow release and heat resistance

Saadat Motamedi¹, Mojtaba Gholamian¹, Azam Namdari¹, hossein Sabahi²

¹ Pardis Petrochemical Company, Pars Special Economic Zone, Bushehr, Iran

² Faculty of New Sciences and Technology, University of Tehran, Tehran, Iran

Abstract

The purpose of this project was to produce urea with higher mechanical strength and superior anti caking properties compared to the current urea produced by formaldehyde in Pardis Petrochemical Company using completely environmentally friendly and eco-friendly materials and methods. In petrochemical companies using formaldehyde, formaldehyde is stored in tanks before use, which can be released into the atmosphere and hurt the personnel. However, published articles have shown that the release of formaldehyde from urea fertilizer in storage can occur during transport as well as during field application [1]. Our results showed that the addition of innovative additives to Formaldehyde (UF85) was able to significantly: increase the anti-caking property along with mechanical strength of urea granules, decrease urea release in farm and reduce the release of formaldehyde into the atmosphere. Due to these parameters that comes from addition of completely natural substances, we called this fertilizer, environmentally friendly or Eco-friend urea.

1. Introduction

1.1 Necessity of the project

In some petrochemical companies such as Pardis Petrochemical Company, 0.8% of UF85 formaldehyde is added directly to molten urea to give urea the anti-caking and slow release properties. However, this amount of anti-caking properties of urea granules is not sufficient for some ocean transportations. In addition, a new problem arising from the addition of formaldehyde is the release of formaldehyde as a carcinogen in storage [2] and during transportation [1] which can be harmful to health of petrochemical personnel and farmers.

Researchers has been suggested some ways to solve these problems by replacing of formaldehyde by another safer materials or by putting formaldehyde on nanoparticles. If formaldehyde can be put on nanoparticles, two other benefits can be gained beside of increasing of anti-caking properties. First, increasing of slower release properties that can improve the efficiency of fertilizer application in the field and second, increasing heat resistance that can reduce release of ammonia and formaldehyde to atmosphere. In this

regard, we were able to directly add surfaces of nanoparticles (from vegetable powder) to the formaldehyde-containing urea fertilizer and directly produce urea with the superior property of anti-caking, higher mechanical strength, higher heat resistance with slower release.

1.2 Urea caking mechanism

The most important factor in caking process is phase changes. This phase change usually occurs at a temperature of 30 °C to 40 °C. In storage when the fertilizer is stacked in large volumes and urea granules are pressed, the shape of the urea granules will change and as a result, their contact points increase. After this event, the urea granules are adhered due to the Crystalline Bridge and intervention of water. Researchers believe that the most important factor in caking process is this type of bonding, which is the result of internal chemical interactions of urea granules including dissolution, recrystallization process or temperature effects [3, 4].

The second type of bond is adhesive contact that known as capillary adhesion that are formed as a result of molecular attraction between the surfaces in contact. This type of contact is influenced by plasticity of particles and pressure exerted on fertilizer [3].

The third type of bonding is the binding of urea granules due to the presence of a thin film of water on their surface. This type of adhesive contact is known as sticking contact that is not strong. According to these three types of connections, the factors involved in caking include: additives to fertilizer (conditioner), hygroscopic water (internal water), amount of physical water (surface water), shape of granules, size, surface roughness and crystallinity [4].

2. Method of implementation

In this process, no chemicals or even chemical solvents have been used to produce this additive. Consumption additives included vegetable powder, which was prepared from very cheap agricultural waste, and another additive was mineral nanoparticles derived from nature.

To achieve mentioned urea, this research was conducted directly on the urea production line in Pardis Petrochemical Company. In this way, innovative additives (20% innovative additives, 80% UF85) was added to the newly installed UF85 tank, then a completely homogeneous composition was obtained by stirring. Other process parameters like temperature, flow rate, pressure and ...were as a usual routine.

3. Results

3.1 X-Ray Diffraction (XRD) analysis

Figure 1 clearly shows that composite urea has a stronger and sharper peak in the 9° region, which is related to the crystalline property of urea. This increase in the crystalline property of urea can improve its anti-caking properties. Silverberge et al. [5] also found that the use of conditioners such as kaolin in the production of fertilizer could improve the crystalline properties of the fertilizer and thus prevent the growth of the crystalline bridge between the granules. Another result in this experiment was that the surface of the granules containing conditioner are much finer grained, more inter grown and more densely packed. Addo et al. [6] also found that the addition of an antifungal agent to jojoba fruit powder was able to enhance the XRD analysis peak and thus improved the crystalline property. According to Figure 1, there is not any effect of mineral nanoparticles peak in the region of about 7 degrees, which is characteristic of the interlayer distance of 12\AA of these nanoparticles [7] that proves there is a complete exfoliation and dispersion of this surface nanoparticle among the urea matrix that can improve mechanical strength of urea granules [8].

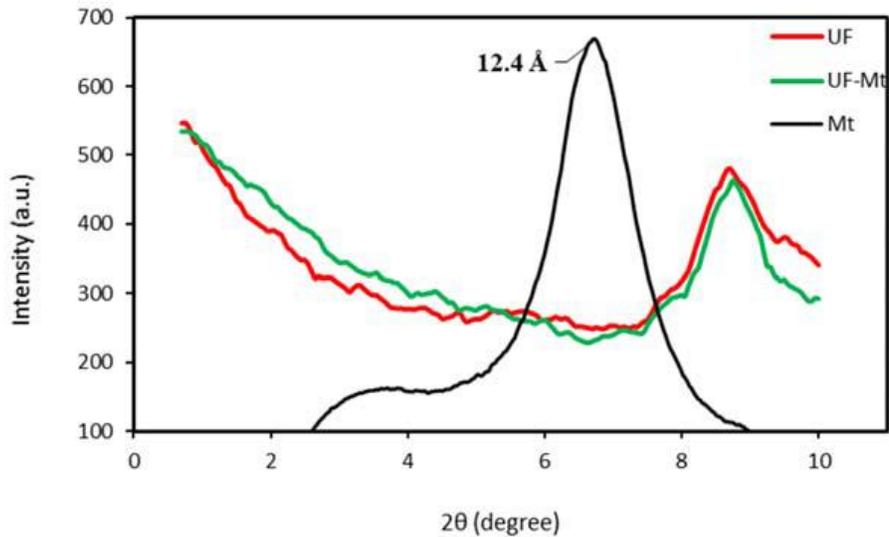


Figure 1: XRD analysis (UF: conventional urea, UF-Mt: composite urea, Mt: surfaces of nanoparticles)

3.2 Mechanical Strength (Strain / Force)

Mechanical strength was significantly increased in composite urea compared to conventional urea. Figures 2 and 3 show that the required force has been increased from 52 N in conventional urea granules to 60 N in composite urea, which shows a 15.4% increase in force.

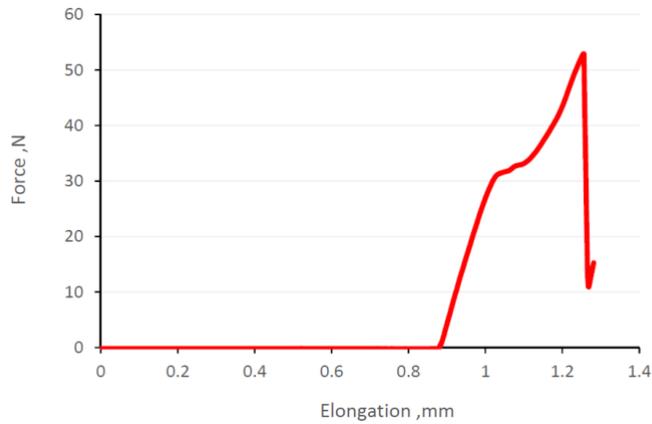


Figure2: Mechanical strength analysis of conventional urea

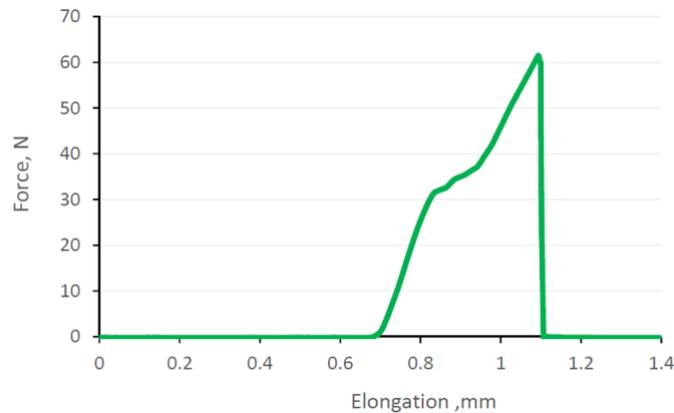


Figure3: Mechanical strength analysis of composite urea

Researchers have shown that low mechanical strength leads to more crushing of pressurized urea granules in storage and transportation, hence by increasing the amount of crushed and powder urea, the contact points between urea granules will significantly increase [3] and the anti-caking property will decrease.

3.3 Thermogravimetric Analysis (TGA)

Figure4A and B show the results of Thermogravimetric Analysis (TGA). In these figures the rate of weight loss in conventional urea and composite urea up to 800 °C is shown.

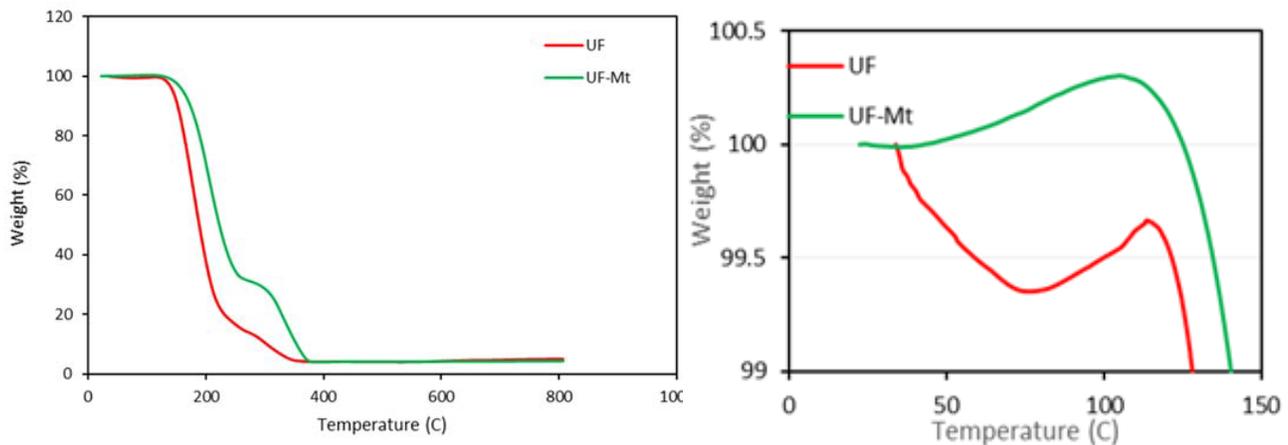


Figure4A: temperature range up to 800°C Figure4B: temperature range up to 150°C

Figure: Thermogravimetric Analysis (UF: conventional urea, UF-Mt: composite urea)

A very interesting result in TGA analysis is that, in conventional urea the rate of weight loss in the range of 50 to 100 °C is about 0.6% and in composite urea is 0% (Figure 4B). This weight loss is due to the evaporation of internal hygroscopic water of urea [7]. Indeed, addition of surfaces of innovative materials to urea matrix as a conditioner has decreased the hygroscopic water and since these water-absorbing nanoparticles are not placed only on the external surfaces of urea granules (as a coating), so its water cannot easily be released at room temperature and its ant-caking property increases[9]. The reason for this claim is the results of DTA and DTG analysis (Figures 5 and 6) which show that increasing the temperature to 100 °C could not cause it to evaporate.

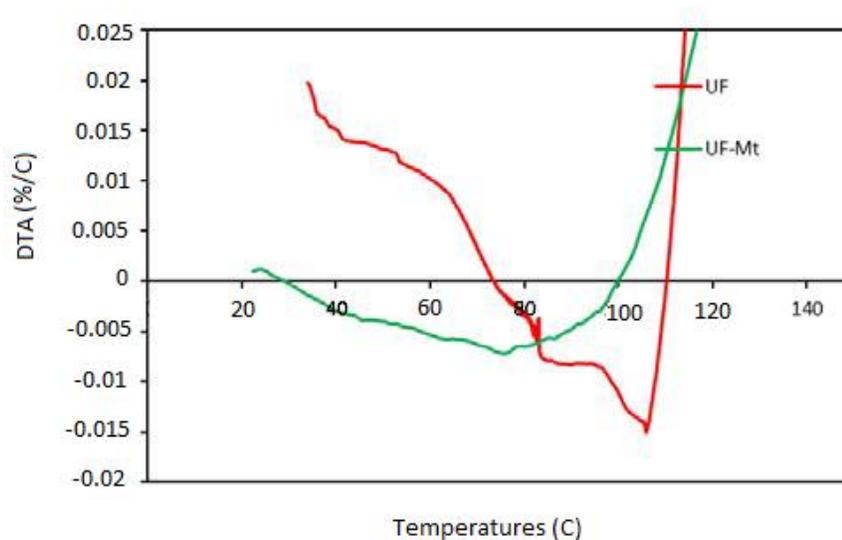


Figure5: results of DTA (UF: conventional urea, UF-Mt: composite urea)

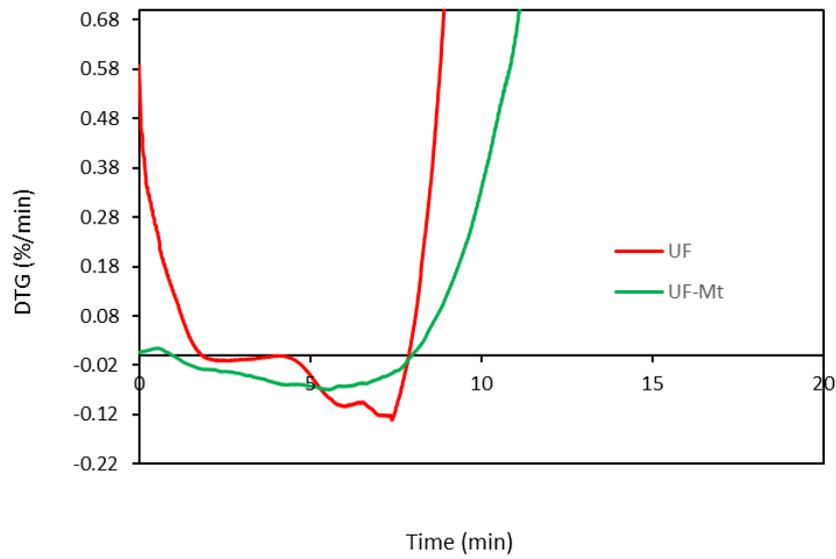


Figure6: Results of DTG (UF: conventional urea, UF-Mt: composite urea)

3.4 (DSC) Differential scanning calorimetry

DSC analysis (Figure7, 8 and 9) shows that conventional urea has 3 isothermal peaks in the region of 139.7 °C, 188 °C and 240 °C that the first is related to the melting point and the second and the third is related to its decomposition point into biuret and cyanuric acid [10].

Comparison of Figures8 and 9 clearly shows that, after the addition of the innovative materials, the first decomposition temperature of urea increased from 188 °C to 225 °C and the second decomposition point increased from 240 °C to 353 °C that are significant increase in urea heat resistance.

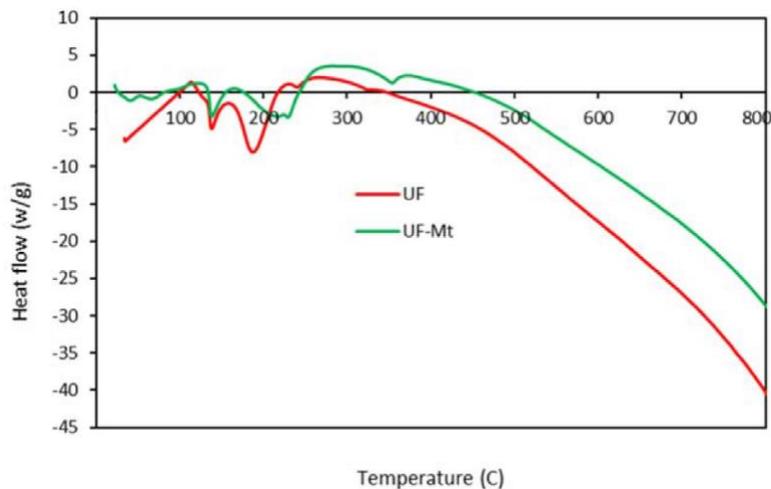


Figure7: Results of DSC (UF: conventional urea, UF-Mt: composite urea)

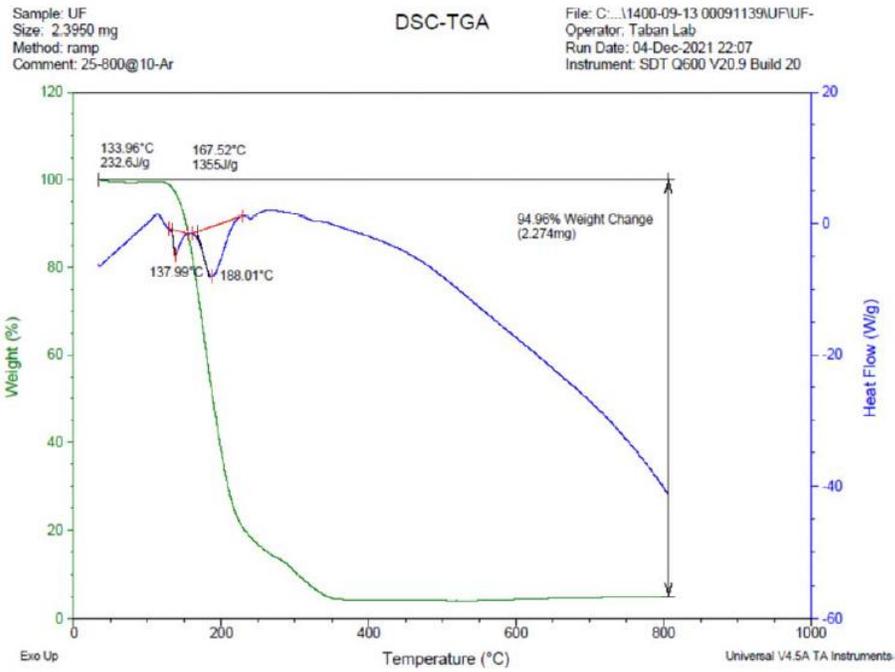


Figure8: Results of DSC of conventional urea

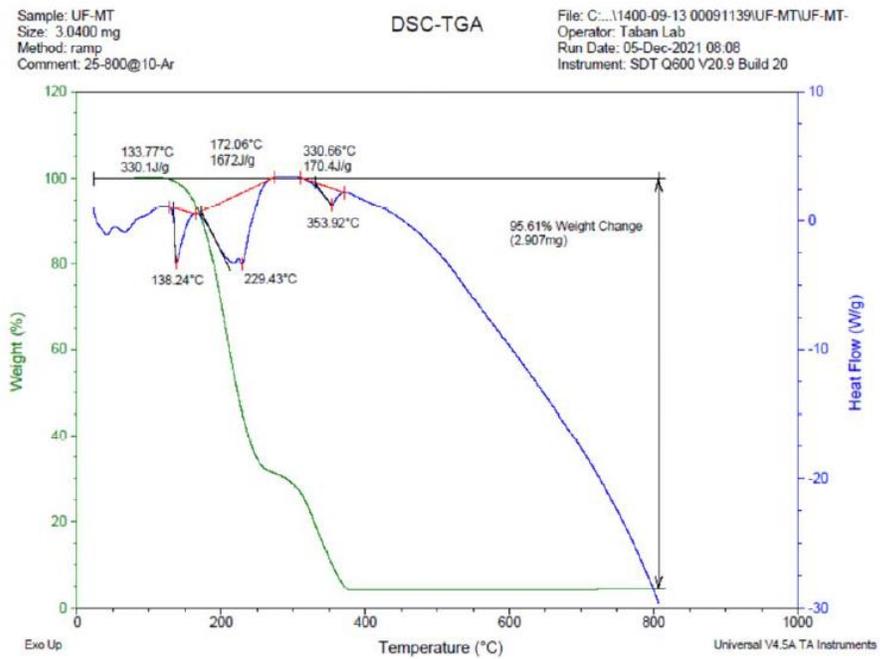


Figure9: Results of DSC of composite urea

Comparison of the data in Figures 8 and 9 shows that the heat required to melt conventional urea is 232.6 j/g which has increased to 333 j/g in composite urea. This indicates the higher heat required in the composite urea to convert urea from solid to liquid. Some researchers like Schaber [10] have shown that some biuret is produced at the melting temperature of, so this increase in energy required for melting can lead to a decrease in the percentage of biuret produced.

3.5 Fourier Transform Infrared (FTIR)

Figure 10 shows this spectrum is very similar in both conventional urea and composite urea and there is not significant change between them due to small amount of additives in the structure of composite urea. However, in most peaks, a 1-degree shift occurs that indicates hydrophilic interaction between nanoparticles and urea [8, 7].

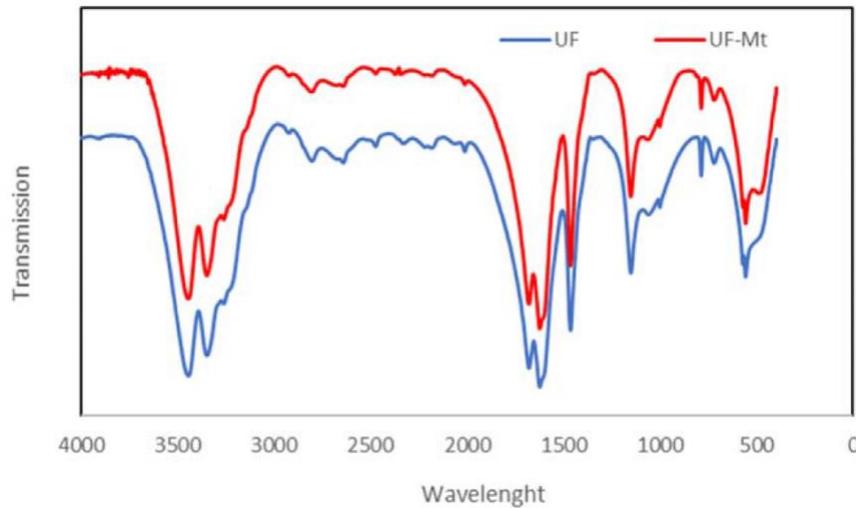


Figure 10: Results of FTIR (UF: conventional urea, UF-Mt: composite urea)

3.6 Urea release pattern and formaldehyde release

Figure 11 clearly shows that by adding innovative materials to urea, the release rate in composite urea has been significantly lower than conventional urea. The release of formaldehyde into the atmosphere from formaldehyde solution is also has a same pattern (Figure 12).

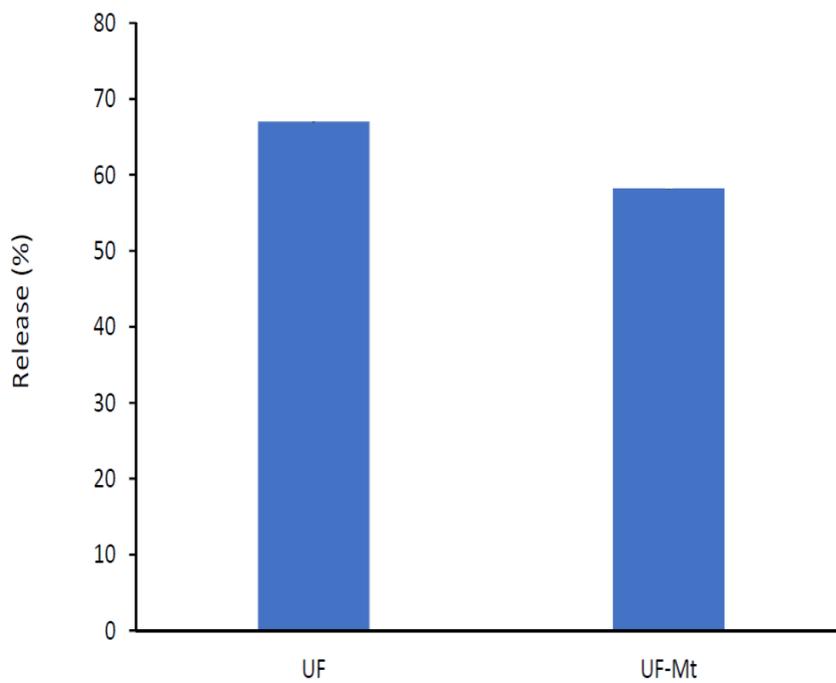


Figure 11: Results of urea release in pour water for 30 min
(UF: conventional urea, UF-Mt: composite urea)

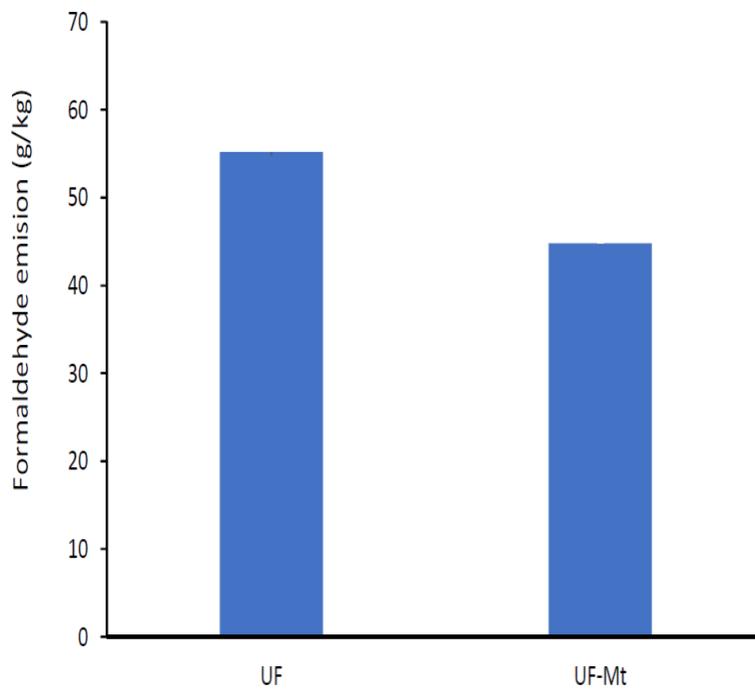


Figure 12: Results of formaldehyde in 48 hours at 35°C
(UF: conventional urea, UF-Mt: composite urea)

4. Conclusion

The results of using innovative materials showed that the mechanical strength of composite urea was 15% higher than normal urea. The results of XRD analysis also showed that composite urea fertilizer has higher crystalline properties than conventional urea. Another interesting result was about TGA analysis (Thermal Gravimetric Analysis) that showed in normal urea, the rate of weight loss in the range of 50 °C to 100 °C is about 0.6% and in composite urea is 0%.

DTA (Differential Thermal Analysis) and DTG (Derivative thermos gravimetry) also confirmed this result. This result clearly shows that the addition of innovative materials to urea as a conditioner has reduced the hygroscopic water to zero percent. The mechanism of this process, was that the additive was placed in the form of fully dispersed nanoplate (Exfoliation) inside the urea matrix and due to its high hydrophilicity (due to hydrogen bonds) it absorbed water molecules as its structural water. Some researchers [3, 5] used nanoparticles as a conditioner to reduce the moisture content in urea to increase the anti-caking properties of fertilizers. In this project, since water-absorbing nanoparticles are not placed only on the surface of urea granules as a coating, so this type of urea cannot release its water easily at room temperature and it can increase its anti-caking properties. This can be proven by results of DTA, TGA and DTG analysis that show increasing the temperature up to 100 °C could not cause this water to evaporate. Surprisingly, in the produced composite urea, the urea release rate was about 16% slower, the heat resistance increased from 37 °C to 113 °C, and the release of formaldehyde into the atmosphere was 22% lower than conventional urea. The results showed that the addition of these additives to urea, increased the energy required to melt and decompose urea by 43% and 23%, respectively, indicating an improvement in the heat resistance of urea.

Increasing the heat resistance can bring three important benefits to urea. First, it can reduce the percentage of biuret in the fertilizer production and also reduce the emission of ammonia from it to the atmosphere during use in the field [11]. Second advantage, because urea is widely used in the wood industry to make resin, urea adhesive and Formaldehyde, use of this type of urea in the production of wood adhesives can reduce the risk of formaldehyde emissions into the atmosphere [12].

Another use of urea is as a catalyst in the automotive industry. One of the harmful gases involved in global warming and climate change is N_2O , which is released from diesel engines. To solve this problem a solvent of urea and water (ad blue) is using to convert this harmful gas to N_2 [13, 14, 15]. Since in this process the temperature is higher than 200 °C, urea is converted to biuret and cyanuric acid, in addition to reducing its efficiency as a catalyst [16, 17]. Our DSC results showed that in the produced composite urea, the decomposition point of urea to biuret is changing from 188 °C to 225 °C and its decomposition point to cyanuric acid is changing from 240 °C to 353°C. By using of

produced composite urea, it can be expected that the efficiency of related catalyst can be increased significantly [18].

5. Refrences

- [1] Salthammer, T., & Gunschera, J. (2021). Release of formaldehyde and other organic compounds from nitrogen fertilizers. *Chemosphere*, 263, 127913.
- [2] Pontel, L. B., Rosado, I. V., Burgos-Barragan, G., Garaycochea, J. I., Yu, R., Arends, M. J., ... & Patel, K. J.(2015). Endogenous formaldehyde is a hematopoietic stem cell genotoxin and metabolic carcinogen. *Molecular cell*, 60(1), 177-188.
- [3] Rutland, D. W. (1991). Fertilizer caking: mechanisms, influential factors, and methods of prevention. *Fertilizer research*, 30(1), 99-114.
- [4] Tyc, A., Nieweś, D., Pankalla, E., Huculak-Mączka, M., Hoffmann, K., & Hoffmann, J. (2021). Anti-Caking Coatings for Improving the Useful Properties of Ammonium Nitrate Fertilizers with Composition Modeling Using Box–Behnken Design. *Materials*, 14(19), 5761.
- [5] Silverberg, J., Lehr, J. R., & Hoffmeister Jr, G. (1958). Fertilizer caking, microscopic study of the mechanism of caking and its prevention in some granular fertilizers. *Journal of Agricultural and Food Chemistry*, 6(6), 442-448.
- [6] Addo, K. A., Bi, J., Chen, Q., Bhandari, B., Lyu, J., Wu, X., ... & Li, C. (2020). Assessment of Anticaking Agent on Caking Behavior of Jujube Amorphous Powder via Glass Transition and State Diagram. *Food and Bioprocess Technology*, 13(9), 1588-1599.
- [7] Golbashy, M., Sabahi, H., Allahdadi, I., Nazokdast, H., & Hosseini, M. (2017). Synthesis of highly intercalated urea-clay nanocomposite via domestic montmorillonite as eco-friendly slow-release fertilizer. *Archives of Agronomy and Soil Science*, 63(1), 84-95.
- [8] Pereira, E. I., Minussi, F. B., da Cruz, C. C., Bernardi, A. C., & Ribeiro, C. (2012). Urea–montmorillonite extruded nanocomposites: a novel slow-release material. *Journal of agricultural and food chemistry*, 60(21), 5267-5272.
- [9] Barneto A.G, & A. Carmona, J. (2007). Moisture profile determination in urea prill. II. Fertiliser caking implications. *Journal of the Science of Food and Agriculture*, 87(10), 1917-1924.
- [10] Schaber, P. M., Colson, J., Higgins, S., Thielen, D., Anspach, B., & Brauer, J. (2004). Thermal decomposition (pyrolysis) of urea in an open reaction vessel. *Thermochimica acta*, 424(1-2), 131-142.

- [11] Irina Klimova • Tiit Kaljuvee • Valdek Mikli • Andres Trikkel (2013), Influence of some lime-containing additives on the thermal behavior of urea, *Therm Anal Calorim* (2013) 111:253–258.
- [12] Yadav, S. M., Lubis, M. A. R., Wibowo, E. S., & Park, B. D. (2021). Effects of nanoclay modification with transition metal ion on the performance of urea–formaldehyde resin adhesives. *Polymer Bulletin*, 78(5), 2375-2388.
- [13] Börnhorst, M., & Deutschmann, O. (2021). Advances and challenges of ammonia delivery by urea-water sprays in SCR systems. *Progress in Energy and Combustion Science*, 87, 100949.
- [14] Demir, U., Kozan, A., & Özer, S. (2021). Experimental investigation of the effect of urea addition to fuel on engine performance and emissions in diesel engines. *Fuel*, 122578.
- [15] Jang, J., Na, S., Roh, H., Ahn, S., & Choi, G. (2021). Spraying and Mixing Characteristics of Urea in a Static Mixer Applied Marine SCR System. *Energies*, 14(18), 5788.
- [16] Lundström, A., Andersson, B., & Olsson, L. (2009). Urea thermolysis studied under flow reactor conditions using DSC and FT-IR. *Chemical Engineering Journal*, 150(2-3), 544-550.
- [17] Brack, W., Heine, B., Birkhold, F., Kruse, M., Schoch, G., Tischer, S., & Deutschmann, O. (2014). Kinetic modeling of urea decomposition based on systematic thermogravimetric analyses of urea and its most important by-products. *Chemical Engineering Science*, 106, 1-8.
- [18] Bernhard, A. M., Peitz, D., Elsener, M., Wokaun, A., & Kröcher, O. (2012). Hydrolysis and thermolysis of urea and its decomposition byproducts biuret, cyanuric acid and melamine over anatase TiO₂. *Applied Catalysis B: Environmental*, 115, 129-137.