35th
Syngas I Ammonia I Urea I Nitrates I Methanol I GTL I Hydrogen
CRU Nitrogen + Syngas 2022
International Conference & Exhibition

The efficiency of Methylene-Urea

MASSIMO GORI – SVET VALKOV

Desmet Ballestra S.p.A.

Milano, Italy

The fertilizer industry as we know it is set for a change, and we already see it happening.

The name of the game is improving fertilizer efficiency and increasing product value without changing existing plants and renewing investment. The commonly available solutions came from outside fertilizer's fences. Exotic polymer coatings and urease inhibitors are the widely accepted solutions to make current fertilizers compatible with the world's issues. None of them is a product of the fertilizer industry, and both are poised to eat up the margins of our industry.

What if the tool to achieve fertilizer efficiency was a product already available within the industry? Methylene Urea is already there, limited by the relatively small size of the UF resin industry, which first discovered it. Ballestra is working to scale up the technology to fully-fledged fertilizer dimensions.

THE NEED TO INCREASE FERTILIZER EFFICIENCY

The Fertilizer industry is used to a comforting equation. Arable land is limited, and the population is growing. Hence, we need to pour more fertilizer per hectare to feed more people. That reasoning can spark huge investments but shows its weaknesses when applied to reality. The capability of crops to absorb nutrients is limited. All that crops cannot absorb is leached away by rain and end up in rivers and seas as ammonia, nitrates, phosphates, potassium. Figure 1 shows that a dramatic quantity of nitrogen fertilizers is sent to the oceans. Even worse, it refers to the situation of 2014, eight years ago.

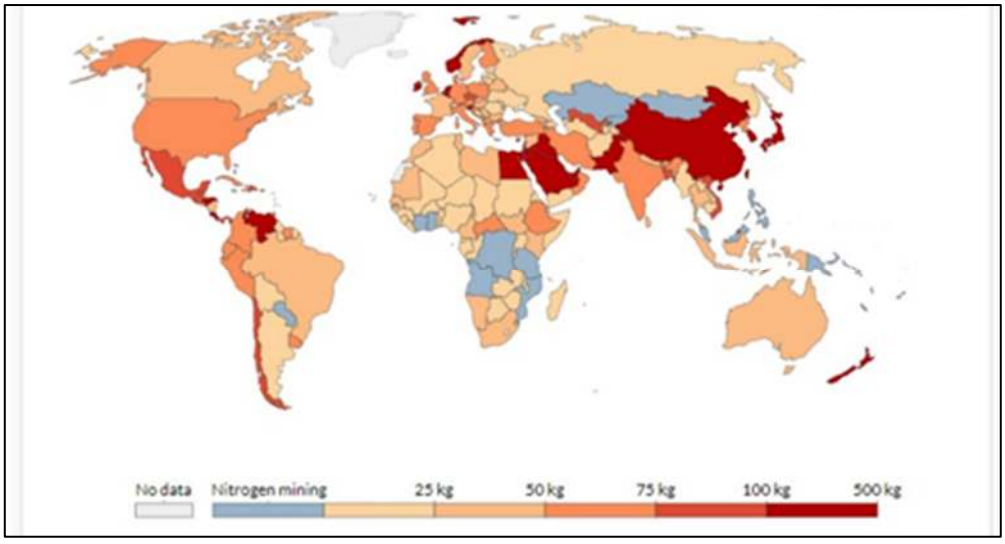

Fig. 1 – Excess nitrogen per hectare of cropland – ourworldindata.org

Let's be provocative: the fertilizer industry is more and more a business that burns methane to produce CO2 and increase the concentration of fertilizers in the sea. Policymakers started questioning the sustainability of the mainstream fertilizer business.

So, fertilizers had to start learning how to become lean and efficient. It all boils down to making nutrients available right when the crops need it and enhancing fertilizer resistance to leaching from rainwater or irrigation.

Lots of options available from outside the fertilizer market

Lots of different solutions quickly populated the market to give the crops time to absorb the nutrients, avoid or reduce leaching by rain or irrigations, and ultimately maximize the efficiency of the fertilizers. For Nitrogen-based fertilizers, three different strategies emerged:

a) Urease inhibitors - Block or slow down the decomposition of urea into NH_4^+;
b) Nitrification inhibitors - Block or slow down the conversion from NH_4^+ to nitrate;
c) Coatings – The entire surface of a fertilizer granule is covered by a substance that delays contact with water;
d) Formulations – Same as above, with substances intimately mixed with the mass of the fertilizer granule.

Most approaches work pretty well, allowing crops to grow similar or even better than regular fertilizers, reducing the quantity required. For classification releases, inhibitor-treated fertilized generally belong to the "controlled release" category, while coated fertilizers and formulations belong to the "slow-release" fertilizers.

All such solutions are made possible by substances like polylactic acid, polyurethane, N-(n-butyl) thiophosphoric triamide, Dicyandiamide, Sulfur, 2-chloro-6 (trichloromethyl) pyridine, 2-chloro-6 (trichloromethyl) pyridine, Malic+ itaconic acid copolymer, etc. Just by reading such names, it is evident that none of them is coming from within the methane to N-fertilizers value chain. As an implication, the fertilizer industry has to pay a third-party fee to achieve fertilizer efficiency. That erodes, sometimes significantly, the margin from the added value of controlled and slow-release fertilizers.

Methylene-urea

The nitrogen industry is used to urea-formaldehyde concentrate (UFC). It is the essential additive to impart mechanical resistance and hardness to the urea granules. In addition, formaldehyde is the product of the partial oxidation of methanol, one of the strictest relatives of ammonia in terms of chemical processes.

Strictly speaking, methylene urea results from condensing one molecule of urea and one formaldehyde molecule. If the condensation proceeds further, di-methylene-urea is formed. With the chain length increase, the name changes to "ureaform." Proceeding with polymerization, we get to UF resins, featuring longer reticulated chains.

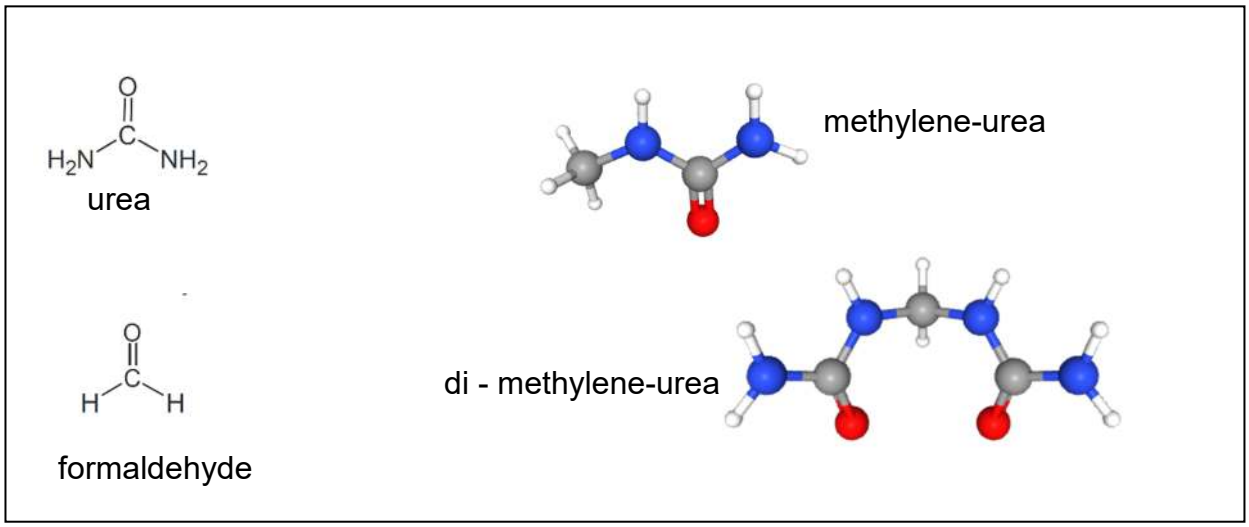

Fig. 2 – chemical structures

Urea is very soluble in water. UF resins – think at the laminates of the furniture – are absolutely insoluble. Methylene urea (Me-urea), di-methylene urea, and ureaform sit in between, and the longer the polymer chain, the more insoluble the chemical compound is. On the other hand, they all are clearly perfect carriers of nitrogen. That is nitrogen fertilizers. Starting from urea (very soluble) and arriving at UF resins, the longer the polymer chain is, the more the substance can resist water leaching. Consequently, methylene-urea chains can be precisely engineered to dissolve and make

nitrogen available to crops within days, weeks, or months, depending on the different cultivations' nitrogen intake requirement.

Methylene urea and longer urea form (UF fertilizers) are available in liquid and granular form and are demonstrably safe for the body and the environment. The liquid form can also be used for foliar application and is proven to be 4-5 times more efficient than non-slow-release counterparts (i.e.to get the same effect as 1 kg of Me-urea, 4-5 kg of urea are needed). Granular Me-urea has similar efficiency advantages and wide application in golf courses and edible crops. Both liquid and granular forms feature very low salinity and no nitrate, hence no burns in the crops.

Great expectations

Me-urea is told to be born out of the observation that leaks from an ureaform tank gave origin to greener and taller grass around it. The truth is that Me-urea comes from the UF resin industry, an industrial environment much smaller than fertilizers'. Consequently, Me-urea has been sold and used for decades, well known, and studied, but installed capacity is limited to a few hundred thousand metric tons per year. Yet it is a proven slow-release fertilizer that taps into the broader world market and gets premium prices. Interestingly, Me-urea is made from chemicals that belong to the fertilizer value chain and could solve the fertilizer efficiency issue from within the fertilizer industry without sharing added value and margins with third parties. Indeed, this paper aims to move Me-urea from resin manufacturing to the industry it belongs to: fertilizers.

Production

Me-urea shares the production process with the UF resin industry. The reactor is typically batch to allow easy change of recipes and get different product grades. UFC or formaldehyde are loaded with solid urea or urea solution into the reactor. The polymerization under acid or basic catalysis is performed under varying, but closely controlled cycles, till the required polymer length (or mix thereof) is obtained. The recipe is the core know-how behind Me-urea. The product can be stored as liquid N-fertilizer, can be sent to finishing, or mixed with fine nutrients and micronutrients to get precisely tailored liquid NPK fertilizers. The latest can also proceed to finishing.

As for all modern installations, the design of Desmet Ballestra guarantees a safe and durable system, with no volatile organic compounds emission and fully automatized. Add the recipe to the control system, and you are ready to go.

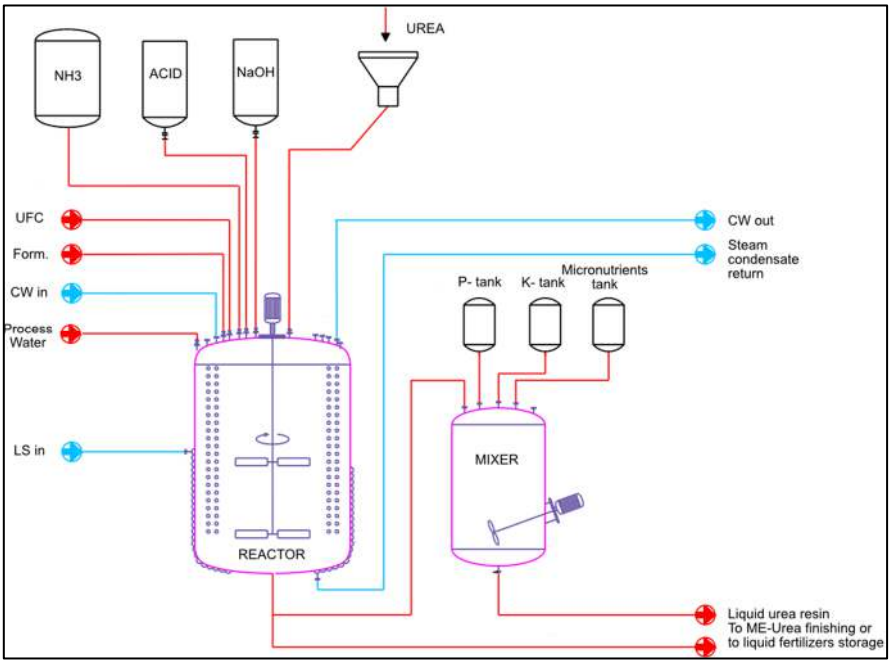

Fig. 3 – The methylene-urea reaction section

Finishing

While the technology for Me-urea production is well defined, finishing is where most existing plants come short. This is why the maximum capacity of a single Me-urea line is limited.

Me-urea is not a single product based on well-defined commercial specs but a family of different products. Each different recipe entails specific finishing parameters, and most of the available granulation technologies do not have the flexibility to cope with the range of Me-urea product grades.

Enter the Ballestra fluid drum granulator. The unit is basically a rotating drum with a fixed table of perforated metal sheet inside. The drum rotation lifts the granules to the table, where they are kept in fluid bed conditions by air flowing through the holes of the metal sheet. The perforated table is slightly inclined on a side, so those dry granules from the fluid bed fall back to the lower part of the rotating drum. While doing so, they pass through a spray of incoming fresh Me-urea, which creates a further layer of material.

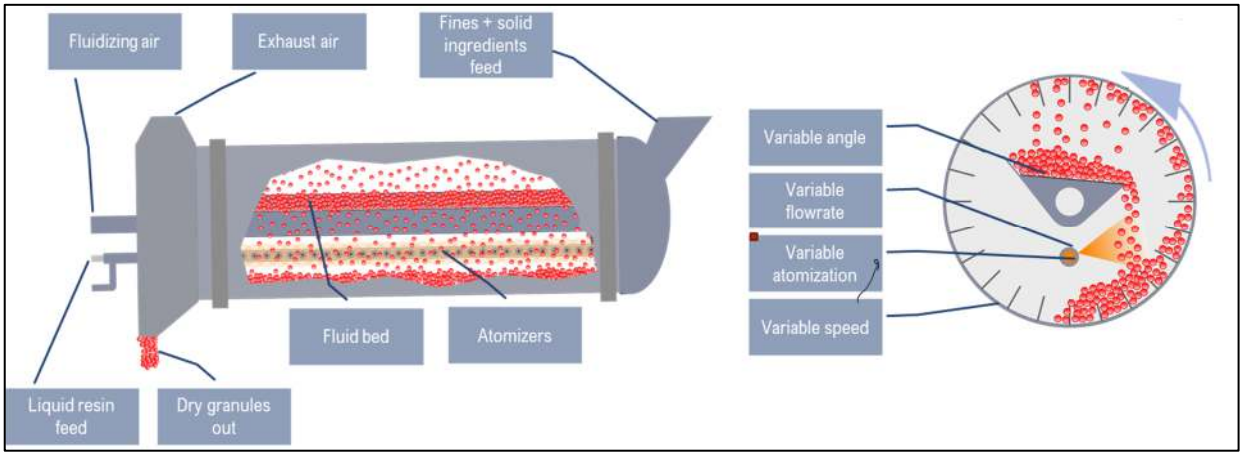

Fig. 4 – Schematics of the Ballestra fluid drum granulator

Everything in the design is about flexibility. Rotation speed, inclination of the fluid bed table, temperature of fluidizing air, flow, and temperature of the freshly sprayed liquid. Once the proper parameters for each recipe are defined, the result is a granule with a solid and resistant onion-like structure, vastly exceeding the hardness and mechanical resistance of urea granules. It is worth noting that the fresh solution is sprayed in an area away from the fluidizing air flow. So, the entrainment of droplets is limited compared to standard urea granulations, and the duty of the downstream air cleaning section is much smaller.

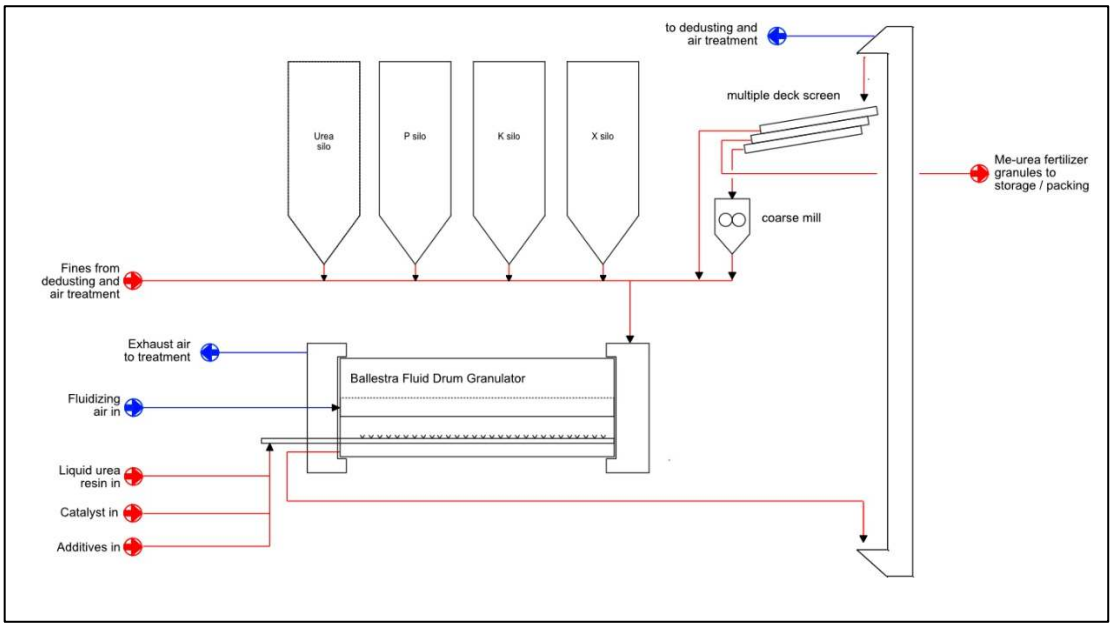

Fig. 5 – The methylene-urea finishing section

Besides such differences, the overall scheme of the finishing closely resembles a simplified urea fluid bed granulation.

MORE PRODUCTS WITH THE SAME PLANT

The presented units are not "simply limited" to the production of the entire range of Me-Urea, and ureaform. The finishing is so flexible that it could be used for a further profitable variation on slow-release fertilizers.

The first example is that Me-urea and ureaform before finishing are basically Urea Formaldehyde resins with shorter polymer chains. Indeed, a glue. Accordingly, particles and dust of other nutrients, even if non-homogeneous, can be fed to the Ballestra fluid drum granulator and embedded into the Me-urea granules' solid and hard matrix. Such granules of NPK and more fertilizer shall have the same slow-release properties as the Me-urea matrix, which holds true even if the granule is broken. In fact, the exposed part will still be the Me-urea matrix.

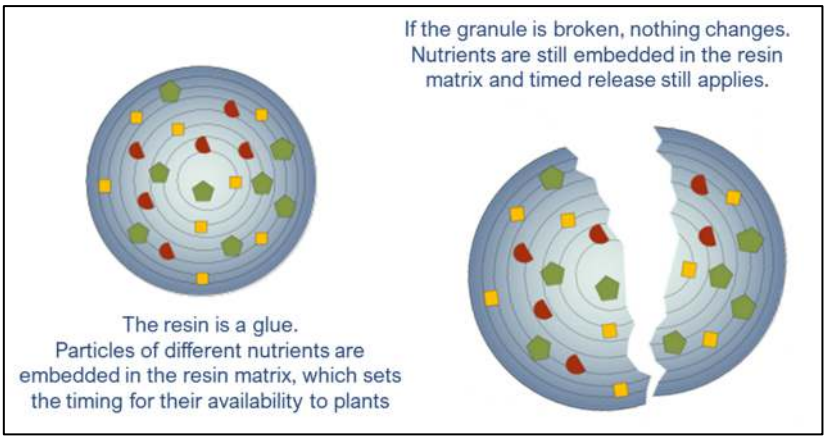

Fig. 6 – Methylene urea as a carrier matrix for complex fertilisers

The second example is a quick and economical way to impart timed-release properties, surface resistance, ad bulk flowability to urea granules and prills. Urea prills and granules are fed to the Ballestra fluid drum granulator and coated or even fattened with Me-urea. The pure urea at the core of the resulting granule shall be released to the soil only upon complete consumption of the Me-urea coating, which can be programmed by design. Imagine using Me-Urea coated urea right at crop seeding and having the boost of fertilization after a pre-set time when growing plants need it. Furthermore, mixing granules coated with different Me-urea grades will allow multiple fertilization boosts at different times. That's time-engineered delivery of nutrients.

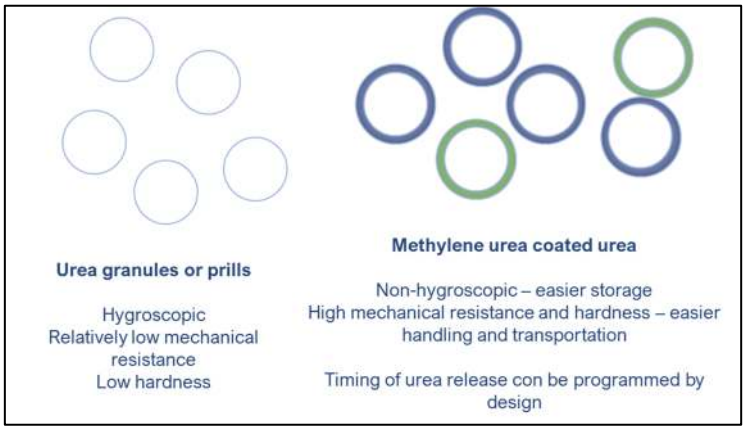

Fig. 7 – Methylene urea as a coating for urea granules or prills

A COMMON JOURNEY

Desmet Ballestra invites partners from the fertilizer industry to a joint journey to take Methilene Urea from the UF resins and laminates industry to the broader fertilizer industry, where it belongs, thus giving a significant contribution to the sustainability of our industry and the environment.

Desmet Ballestra will bring in robust and scalable reaction and finishing technologies, agronomical, marketing, and regulatory support, the expertise to consistently define new product recipes. With a partner with feedstock availability, marketing push, and spirit of innovation, we could follow a joint development path: industrial size pilot, definition of new products and applications, joint IP development, scaling up the technology to meet the actual demand. And ultimately decrease natural gas consumption, improve our world, and keep sustainable margins.