Function and Properties of Formaldehyde in Urea Granulation

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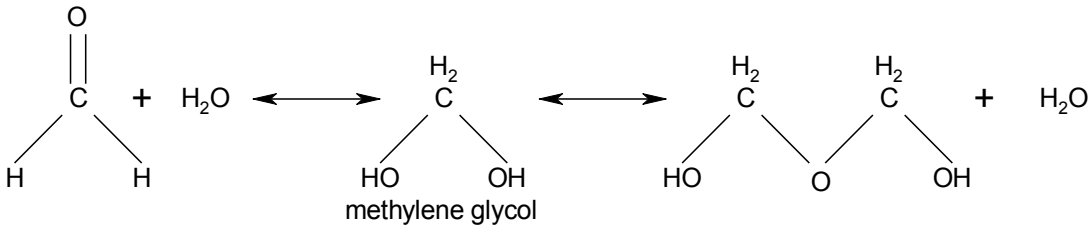
Formaldehyde is commonly used in urea granulation or prilling in order to improve the physical strength of the product and serves as an anti-caking agent for the products.
In urea granulation, formaldehyde also has a function as granulating aid to improve the product build up and reducing the dust formation during spraying of the urea solution in the granulator.

The formaldehyde is mostly added to the urea melt as formaline or as UF condensate depending on availability. Also para-formaldehyde or even hexamethylenetetramine may serve as a possible formaldehyde source.

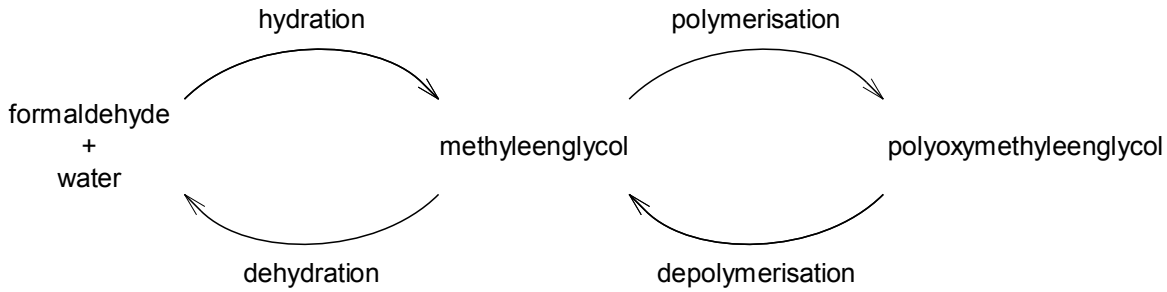
The UF condensate (mostly UF80 or UF85) contains 57-60% formaldehyde and 23-24% urea, while the rest is water. This low water content is a big advantage during transportation and has the advantage that the urea melt concentration hardly changes when adding the UF. The pH of UF condensate is practically neutral, pH 6-7 and the product can be stored for a long time without particular precautions. The formaldehyde in UF is present as a mixture of mono-, di- and trimethylol ureas.

Formaline is a different story. The formaldehyde content is only 37-42%, while the rest is water with eventually some methanol. The formaldehyde gas is not simply dissolved in water like NaCl, but is actually reacting with water in the form of methylene glycol. Those methylene glycols will polymerize, splitting off water again and form poly-methylene glycols (also called paraformaldehyde from a certain degree of polymerization on).



The degree of polymerization is determined by temperature and formaldehyde concentration. The polymerization can be inhibited by raising the temperature during storage or by adding an amount of methanol. If methanol is added, the methanol will evaporate during prilling or granulating and end up in the stack. The polymers can be hydrated again to produce free formaldehyde that can react with

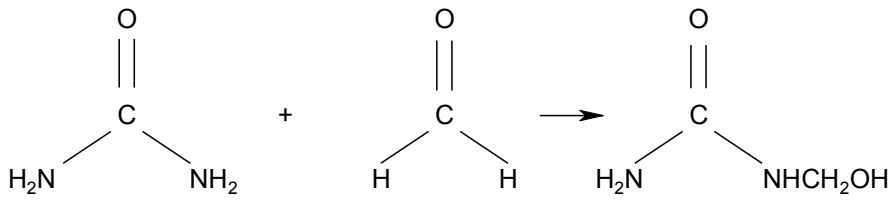
amines (for example with urea). This hydration reaction is catalyzed by high pH and by high temperatures.



The formaline, when not pH stabilized, contains some free acid (pH 3,0-3,5) because of the cannizaro reaction where two formaldehyde molecules are converted in one formic acid molecule and one methanol molecule. In case of formaline, the high water content of the formaline has to be taken into account in order to maintain proper concentration of the final urea melt.

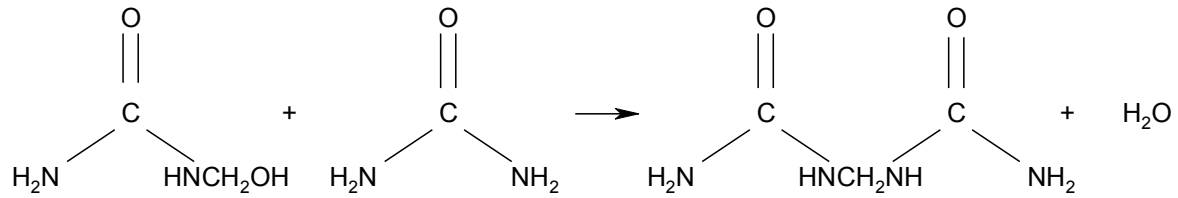
In urea prilling or granulation the formaldehyde is added to the hot concentrated urea melt, where it chemically reacts with urea. The reaction takes place in 2 steps:

Step 1: methylol formation: one formaldehyde molecule reacting with one urea molecule.



This is a fairly fast reaction, but one needs to remember that, in case of formaline, the polymethyleneglycol molecules have to split off free formaldehyde for the reaction with urea. In case of UF condensate, the di- and trimethylol urea molecules also have to split off their excess formaldehyde to convert all into mono methylol urea. In both cases the high temperature of the urea melt speeds up these reactions. Once added to the urea melt, no di- and trimethylol must be considered because of the very low ratio formaldehyde/urea in both urea prilling and granulation.

Step 2: methylenediurea formation (MDU): condensation of one monomethylolurea molecule with another urea molecule and splitting off one water molecule.



This is a slower reaction.

Both reactions are pH and temperature sensitive: methylol formation prefers a "high" pH while methylene formation accepts lower pH. This "high" and "lower" pH is very relative. For example, in urea formaldehyde glue production (where the molar ratio formaldehyde /urea is much higher than in urea fertilizer production) "high" pH means 6,2-6,5 and "low" means 5,5-5,7.

Especially in urea granulation, it is important to control the progress of both reactions in such a way that a good balance between methylol and methylene is obtained in the end product. This balance can sometimes be upset because of the pH sensitivity of both reactions and/or the need for residence time of the formaldehyde in the urea melt stream.

Methylol urea is a typical anti caking agent for urea and is sometimes used in the form of UF condensates for coating the final urea as an anti caking treatment.

In China, where UF condensate is hardly available, all plants work with formaline. Several Chinese urea granulation units have the option to first convert the formaline into a lean UF condensate. The need to do this is not always very clear but, at least in one case, all the formaldehyde from the formaline was converted into MDU. The granulation process itself worked completely normal but the product had a strong caking tendency, even at low moisture contents. This problem was completely solved by adding the lean UF preparation unit leaving more methylol urea in the granules.

On the other hand, extremely short residence time of the formaldehyde (not enough time for MDU formation) is known to have caused high dust formation in the granulator while the caking behavior of the product remained normal. Extending the residence time solved this problem.

References:

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