Introduction

Urea Reactor High Efficiency trays target to increase the urea conversion in the reactor. A higher urea conversion can be translated into a higher plant capacity (in case there are no other bottlenecks) and/or a lower energy consumption.

Description

In a urea reactor the relatively slow and endothermic equilibrium reaction ammonium-carbamate $\leftrightarrow$ urea and water takes place. The required reaction heat is created by the condensation of gas forming ammonium-carbamate, which reaction creates a lot of heat. Ideally the reactor is a bubbling liquid column operating at its boiling point. In that case is the temperature at a certain location depending on the composition of the liquid, the total pressure in the reactor and the inert pressure. More urea and water will increase the boiling temperature and the delta-temperature over the reactor is a good indication for the urea conversion.

Most urea reactors are a cylindrical vertical vessel operating at a pressure in the range of typically 140-200 bars, in which upwards liquid and gas flows in a co-current manner. The vessel is divided into compartments by perforated plates.

The purpose of this configuration is to avoid the excessive mixing of the entire liquid phase contained in the reactor, which would tend to turn it into a complete mixing reactor, thus reducing the urea yield. By dividing the reactor into several stages by means of plates the amount of mixing of the total liquid volume is reduced, and the behavior of the liquid phase is brought closer to the behavior of a plug flow reactor, which is notoriously the most favorable for keeping the urea yield relatively high. This is based on the chemical engineering principle that a plug flow reactor can be modeled as infinitely many Continuous Stirred Tank Reactors (CSTR) in series. In practice a urea reactors has some 10-14 trays.

By dividing the reactor into stages by means of perforated trays, it is also possible to redistribute the gas, flowing upwards along the column, intermittently in smaller bubbles which are more suitable for increasing heat and mass exchange between the two phases. In effect, the rising showers of bubbles are subjected to coalescence phenomena which progressively increase the size of the bubbles, thus reducing the exchange surface between phases: this negative phenomenon is partly compensated by the redistribution brought about by the perforated trays. As going from the bottom to the top the amount of gas decreases one will see less gas holes in the trays going from bottom to the top.
High Efficiency trays typically create a continuous mixing of gas and liquid streams. CASALE is the urea licensor, which first introduced High Efficiency trays in the market. CASALE’s design is based on an invention from Mr. Mario Dente.

Currently nearly all urea licensors have developed their own patented designs. Refer to Figure 1.

![Various types of High Efficiency Trays](image)

Figure 1: Various types of High Efficiency Trays

**Urea Synthesis Reaction System: Chemical and Physical Aspects**

The urea synthesis reactor is a vapor-liquid heterogeneous reaction system. All along the reactor, both the vapor and the liquid phases are present. The vapor phase contains free CO2, NH3, some water, and inerts. The liquid phase mainly contains NH3, ammonium carbamate, bicarbonate, urea, and water. The reactants are progressively transferred from the vapor to the liquid phase, where CO2 reacts with NH3, producing carbamate, urea and water.

In the once through processes the gaseous CO2 feed is introduced into the reactor together with pure liquid NH3 (in excess over the stoichiometric ratio). No recycle is present. In the so-called NH3 stripping or conventional total recycle processes, CO2 feed is present at reactor inlet in the vapor phase, while all the NH3 (recycled and stoichiometric), as well as the recycled CO2 and H2O, are introduced by the liquid phase. In the CO2 stripping process, the CO2 and NH3 feeds, after mixing with the recycle stream, are partially transformed into
carbamate before entering the reactor. Therefore, at the reactor inlet the vapor phase is already containing CO2, NH3 (and some H2O).

As soon as urea and H2O are formed, the amount of liquid phase increases, and by consequence, that of the vapor phase decreases; CO2, NH3, (and H2O) are continuously exchanged between the two phases. Urea is produced into the liquid phase according to the following reversible chemical reactions scheme:

\[
\begin{align*}
\text{CO}_2,\text{Liq} + 2\text{NH}_3,\text{Liq} & \rightleftharpoons \text{NH}_4^+ + \text{NH}_2\text{CO}_2^- \quad (1) \\
\text{NH}_4^+ + \text{NH}_2\text{CO}_2^- & \rightleftharpoons (\text{NH}_4\text{NH}_2\text{CO}_2) + \text{H}_2\text{O}_{\text{Liq}} \rightleftharpoons \text{Urea} \quad (2)
\end{align*}
\]

An important side reaction completes the system of main reactions, taking place in the liquid phase:

\[
\text{H}_2\text{O}_{\text{Liq}} + \text{NH}_2\text{CO}_2^- \rightleftharpoons \text{NH}_3,\text{Liq} + \text{HCO}_3^- \quad (3)
\]

Reaction 1 is strongly exothermic, while Reactions 2 and 3 are both endothermic. Reactions 1 and 3 involve ions: therefore, they are so fast in both the directions that may be considered at the equilibrium. Reaction 2 constitutes the chemical rate determining step.

At the vapor-liquid interface, phase equilibria are established:

\[
\begin{align*}
\text{CO}_2,\text{Gas} & \rightleftharpoons \text{CO}_2,\text{Liq}; \quad \text{NH}_3,\text{Gas} \rightleftharpoons \text{NH}_3,\text{Liq}; \quad \text{H}_2\text{O}_{\text{Gas}} \rightleftharpoons \text{H}_2\text{O}_{\text{Liq}}
\end{align*}
\]

It means that at the interface chemical activities of the local liquid phase free components CO2, NH3, and H2O are equal to those of the local gas phase.

Moreover, as the free liquid CO2 concentration in the liquid phase is extremely low, the formation of carbamate can be practically considered as directly occurring at the interface between gaseous CO2 and liquid free NH3. The overall rate of evolution for a gas-liquid reaction system, like the one described above, is complicated due to the interactions between chemical and physical processes.

It can be useful to introduce some schematic fluid dynamic aspects of the vapor and liquid streams, co-currently flowing between two subsequent reactor trays (like those typical of present most known technologies). Of course, the vapor phase contains bubbles. Their average size and spatial distribution (after the reactor entrance devices) mainly depends on the configuration of the trays. The size of the bubbles can depend also on the vapor holdup that also controls their coalescence rates. The interfacial surface among the population of bubbles and the surrounding liquid phase governs the first step of the transport between the two phases.

The vapor phase flow produces columns or intermittent swarms of bubbles (depending on the specific trays configuration). The liquid contained in the bubbles region, wherein the vapor is moving, can be referred to as the "liquid emulsion". Outside of the emulsion, there is a clean liquid phase. An ideal boundary separates the emulsion from the clean liquid (Figure 2).
Figure 2. An ideal boundary separates the emulsion from the clean liquid.

It is extremely complex to characterize the detailed fluid-dynamic behavior of mass bubbling. Nevertheless, at least a macroscopic important aspect of the dispersed vapor-phase movement is constituted by the generation of specific motions into the continuous liquid phase. The predominant mechanisms are essentially two. The first one depends on the lifting of liquid volumes adherent (particularly in their rear zone) to the rising bubbles. In the case of permanent emulsion columns, a further mechanism takes place.

In fact, the difference of the effective specific gravity between the clean liquid and the gas-liquid columns generates a draught that moves the former towards the latter. Both the mechanisms (when simultaneously operating) collect liquid from the down part of the stage over each tray, and progressively release it in approaching the next one where the bubbles coalesce. For the continuity of fluid flow, the released liquid turns back towards the down part of the stage.

Therefore, these liquid displacements provide a place to the eddies, the stream lines of which cross the columns of emulsion determining the convective mass and heat transport among the different fluid regions. This extra mechanism is absent in the case of intermittent swarms.

As a consequence, the global rate of exchange is dictated by several factors: average length of the streamlined path into the emulsion columns, extension of its boundary surfaces, total recirculated flow rates, and so on.

Due to the interaction among physical and chemical processes, the overall rate of transformation is controlled by factors that affect both the physical and chemical elementary processes, that is:

- Fluid dynamics and flow patterns of the two phases
- Surface areas of the interface and of the emulsion to clean liquid bounds.
- Geometry of reactor vessel and its internals (that is, trays).
• Chemical kinetics, and, of course, temperature and pressure.

The global rates of mass and heat transfer involve the following series of steps, each one characterized by its own surface area: from the bulk of the bubbles to the interfacial surface through the diffusional penetration layer to the bulk of the emulsion and across the bulk of the emulsion regions; finally, through their limiting boundaries to the clean liquid phase. (Of course, the reaction to urea takes place both in the emulsion and the clean liquid-phase volumes.)

Moreover, the temperature of the gas-liquid interface compared with those of the surrounding regions can be quite higher because of the "instantaneous" carbamate formation, consequently reducing the local equilibrium concentration of the carbamate itself. The net result of all these physical phenomena that are in competition with the chemical reaction rate is to increase the resistance against the CO2 conversion to urea. The following main steps can be distinguished for urea formation:

- CO2 and NH3 are transported from the vapor into the liquid
- At the vapor-liquid interface, gaseous CO2 reacts with liquid free NH3 to form carbamate (and bicarbonate, the relative amount depending on interfacial water concentration). At the vapor-liquid interface, local equilibrium between the two phases is maintained. Reaction heat is generated and then the interface temperature increases.
- The carbamate (and the produced heat) is transported into the bulk of the liquid emulsion, and from there into the clean liquid-phase bulk. In these two, the slower carbamate to urea reaction takes place.

In this way a significant part of the total residence time into the reactor is justified by the necessity to reach the maximum amount, compatible with the operating conditions of vapors transported into the liquid phase. The optimum conversion to urea, in fact, could be obtained only on the basis of that condition.

**Casale**

Casale High Efficiency trays (see Figure 3) are made up of several inverted U beams with large perforations for liquid passage on the bottom wings, and small perforations for gas passage on the sloping and top sections. With this unique design, very small bubbles are generated, and, by consequence, a very high surface for the mass and heat transfer is obtained. This advantage is combined with a very high efficiency in the mixing between vapors and liquid.

The new trays are in fact designed so that:

- Separate and distributed paths through the tray are provided. They guarantee a steady-state flow of the two phases and a better approach of an even uniform flow of the two phases throughout the whole reactor.

![Figure 3: Principle of Casale High Efficiency trays](image-url)
• These separated paths through the tray are chosen so that a very high mixing efficiency between vapor and liquid is obtained. Consequently, a very high mass and heat transport within the liquid phase is realized.

• With an appropriate design, the diameter of the generated vapor bubbles is smaller than in any previous design. Consequently, the interfacial surface for mass and heat transfer is increased (see Figure 4).

A very much larger surface of exchange between emulsion and clean liquid is created.

The much shorter length of recirculation streamlined paths into the emulsion phase significantly decreases the transport resistances.

Being the first urea licensor with High Efficiency trays has resulted in numerous references starting from 1993. Casale claims CO₂ conversion improvements up to 64.%, steam consumption reduction figures up to 300 kg/mt and capacity increase figures up to 17% (although additional modifications in the urea plant were required).

Stamicarbon

While revamping a Stamicarbon Urea plant, in most of the cases, the specific reaction volume is decreased with the revamp. As a result the residence time of the urea solution in the reactor will decrease and thus the efficiency of the reactor will go down. However, by changing the internals of the reactor (using a different type of trays) the efficiency in the reactor can be improved. In the past two types of trays were used in Stamicarbon Urea plants: the conventional trays and the high efficiency trays. Since 2001 a new type of trays has been introduced, which improves the efficiency of the reactor and thus results in savings of the high-pressure steam consumption. These trays are called the Siphon Jet Pumps.

The principle of the siphon effect is not unknown to Stamicarbon. The flow deflector plates in the pool condenser operate at the same principle. Inside the flow deflector plates the gas sparger releases the gas and a circulation flow is induced by the difference in density. The Siphon Jet Pump consists of several parts. The tray itself is a normal tray and in the center gas holes are drilled. Around this hole area a support brim is located to lead the gas inside the skirt. Above the tray a skirt is installed which assures the rise of gas in the center of the compartment. A circulation will be aroused and the mixture is coming back through the space between the tray and the skirt.

The first Siphon Jet Pump trays have been installed in the three urea plants of SKW Piesteritz in the years 2001, 2002 and 2003. Stamicarbon claims that installation of the three Siphon Jet Pumps at SKW Piesteritz resulted in: A capacity increase of 10 – 15 % together with a high pressure steam consumption of around 60 kg/ton urea.
The urea synthesis reactor can be divided into three operating zones (see Figure 6):

1. mixing zone;
2. carbamate formation zone;
3. urea formation zone.

For each zone NIIK has developed a set of highly efficient internal devices.

**MIXING AREA**
- Efficient filling of mixing zone
- Expanded surface of contact between the phases

**AREA OF UREA SYNTHESIS REACTION WITH CARBAMATE FORMATION**

**AREA OF UREA SYNTHESIS REACTION WITH UREA FORMATION**

**Figure 6: Principle and pictures of the NIIK high efficiency reactor internals**
**Mixing zone.**

In the mixing zone the gas is dispersed into the liquid resulting in the formation of a liquid-gas mixture. The area comprises the existing feeding nozzles and a mixing device, which is designed by the process licensor. The design of the mixing device is very important as the conversion rate of the original feedstock into ammonium carbamate directly depends on its efficiency. A mixer should have the following features: 1) it must fill up the volume of the reactor with a gas-liquid mixture as much as possible; 2) it must ensure the largest possible specific surface of media contact of components supplied to the reactor.

During its research into reactor design, NIIK carried out model trials of all types of conventional mixers applied in urea reactors in a specially designed scale-down laboratory urea reactor. Based on the tests it was concluded that no conventional mixers ensure the necessary mixing of the components. Gas in the form of large bubbles rises up reducing the specific surface of the media contact of gas and liquid. In this case the fill factor of the bottom part is low. This process results in an extension of the ammonium carbamate formation zone and further reduces the efficiency of the entire synthesis process. To ensure efficient mixing of feedstock in the reactor inlet NIIK offers a high efficiency vortex mixer (Figure 7). The working principle of the mixer is based on the effect of intensive dispersion of gas resulting from the breaking of a swirling gas-liquid jet with liquid at the nozzle outlet. Due to the unique design of the vortex mixer, the dispersion of the gas into the liquid is carried out more efficiently – the bubbles are much smaller than the ones produced in conventional mixers. In this case the specific surface of the media contact generated by the vortex mixer is two times higher.

![Image](image)

**Figure 7: Principle sketch of vortex mixer**

The location of the vortex mixer in the reactor and a special design of its outlet nozzle provide the largest mixing area in the same volume – up to 90% (compared to 30% for conventional mixers). In addition, installation of the vortex mixer eliminates dead zones in the bottom of the reactor which increases the useful volume for reaction. These two factors result in an increase of the CO₂ conversion rate in the synthesis reactor and reduce the energy consumption in the distillation sections. NIIK’s patented vortex mixer technology has been used since 2005. To date, many urea plants using Stamicarbon total liquid recycle, Saipem and Tecnimont technologies have been equipped with the vortex mixer. NIIK claims that in each case the installation of the vortex mixer has resulted in enhanced performance of the urea synthesis section. In some cases it has resulted in both an increase in unit capacity and a reduction of energy consumption. Installation of the vortex mixer gives: 0.5-1.0% increase of CO₂ conversion rate in the urea synthesis reactor depending on the process technology; steam saving from 15 to 40 kg/t depending on the process technology. In several plants also the Conversion Booster and trays have been installed. NIIK claims an increase of CO₂ conversion figures up to 2.5%.
**Saipem**

The fluid-dynamics of a urea reactor can be significantly improved by the introduction of the latest generation of internals recently invented and patented by Saipem. The proprietary Snamprogetti™ SuperCups drastically increase the mixing of the reactants phases, respectively ammonia / ammonium carbamate and carbon dioxide, thus optimizing the product conversion rate in the reactor.

The innovative concept of the Snamprogetti™ SuperCups lies in the realization of a confined reaction space within the reactor tray geometry, namely the cups. They perform as a number of mixing units where ammonia is contacted with the gaseous CO2 in small bubbles. Once the reactants have swirled inside the cups, the mixed solution of product and non-reacted components is uniformly distributed on the upper part of the tray by means of the upper cup distributor. The outlet flow pattern ensures a further mixing of the solution coming from all the cups. The peculiar behavior of the SuperCups is characterized by a triple fluid-dynamic effect – Gas Equalizer, Mixer Reactor and Gas Distributor – which are described here below.

Gas Equalizer: The first effect of SuperCups is to uniformly distribute the concentration of the light phase reagent on the entire section of the tray. In this way, the gas-like bubbles moving upward “lose the memory” of the nonuniformity of the previous reaction stage and the non-reacted CO2 can be evenly fed to each cup of the tray.

![Figure 8: CFD showing CO2 volume fraction](image)

Mixer Reactor: The cups behave as a number of confined reaction volumes in which the multi-phase reagents – carbon dioxide and ammonia/carbamate – heavily swirl inside, thus reaching a high mixing degree. Each cup performs as a static mixer where the phases are strongly contacted (see Figure 9).

![Figure 9: Principle sketch of mixer reactor](image)

Gas distributor: The CO2 phase forming the gas-cushion below the tray can be partially streamed inside the cups to create a mixer-reactor and partially distributed on the upper stage by means of dedicated holes. This split range is one of the most critical design parameters since it allows to customize the residence time distribution (RTD) curve of each reactor stage and to increase (or decrease) the CSTR (perfect mixing) or PFR (plug flow) behavior according to the composition of each stage.

In 2014 the first SuperCups have been applied in two revamp cases, adding in one case two and in the other case replacing two trays by SuperCup trays in the existing reactors. Saipem claims that the CO2 conversion increases with some 0.5% and the steam consumption reduces with some 1-2%.
Performance evaluation

Important is how to evaluate the performance of High Efficiency trays. High Efficiency trays claim to increase the urea conversion in the reactor. But to measure the effect of High Efficiency trays on the CO\(_2\) conversion is not so easy as CO\(_2\) conversion depends also on several other factors. For example N/C and H/C ratio and total and inert pressure all also influence the urea conversion. Thus, when evaluating the performance of High Efficiency trays, one should target to keep all these parameters constant.

One can imagine that the more time is available to reach equilibrium of the urea formation reaction, the less impact High Efficiency trays will be able to have. Thus one can expect more benefits of High Efficiency trays in plants which operate at higher plant loads than these were designed for. Refer to Figure 5 which shows that more efficiency can be gained when the retention time in the urea reactor is low (high plant loads compared to design) than at high retention times.

F.A.E means Fraction Approach to Equilibrium

Figure 10: CO\(_2\) conversion versus retention time for three situations (a. No trays, b. Conventional trays and c. High efficiency trays)

What can one expect from installing High Efficiency trays?

Depending on the retention time, one may expect an increase in CO\(_2\) conversion from negligible up to a few percent translating into an increase of the potential plant load from negligible to some 5-10% and/or a reduction figures of the steam consumption on the High Pressure stripper from again negligible up to some 50-100 kg/mt. There are some positive exceptions described in the public literature, but we believe the above figures are realistic as what one can expect as typical figures.
Mechanical aspects

Like any other stainless steel applied in the high pressure synthesis section of a urea plant, also high efficiency trays will face several failure modes. One obvious one will be passive corrosion, which rates are for a significant part determined by the temperature. As the temperatures increase from bottom to top, also the corrosion rates of the trays increase from the bottom to the top, the corrosion rates of the top trays are some two times higher than of the bottom trays. Also note that trays corrode from two sides, so two times faster than for example a loose liner.

Also crevice corrosion could be an issue in case crevices are formed between the tray and the protective layer of the shell or between parts of the tray.

In time cross cut end attack can occur enlarging the hole diameter and reducing the process performance.

A critical failure modes are weld defects (e.g. pinholes) in the welds of the tray clip to the protective layer of the reactor vessel. Important is that the design of the clips allow an easy welding procedure and a proper corrosion inspection during turnarounds. Also the a proper quality of the clip welds should be assured and it is recommended to use higher alloy materials as welding material.

The process design of the trays should be such that no crevice corrosion, erosion corrosion or dead volumes will exist. These are further attention points during a regular corrosion inspection.

References

1) 1997, Zardi, Dente & Bozzano, Urea Reactor Trays to Increase Plant Capacity and Efficiency