

Urea synthesis

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DOI: 10.1002/cite.201400064

The history of urea synthesis is followed by a description of the fundamental thermodynamics underlying urea production. The basic chemistry, side reactions and physical chemistry are summarized, after which the way these fundamentals logically result in a number of constraints to urea production processes is explained. Challenges in urea production process design are highlighted. Finally, using a number of recent urea processes as examples, it is shown how these challenges are addressed in the industrial urea production processes currently offered by the main urea process licensors.

Keywords: Licensors, Production-process, Thermodynamics, Urea

Received: April 28, 2014; *accepted:* August 28, 2014

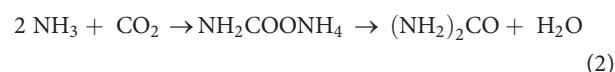
1 History

It was in 1828, at a time when alchemy was undergoing a transformation into chemistry that the German chemist Friedrich Wöhler [1] obtained from the reaction of silver cyanate with ammonium chloride a compound that he rightly recognized as urea:



That was the first time that a substance that was known to be produced in the body of living organisms (urea) was artificially synthesized starting from entirely inorganic materials. Wohler's discovery is therefore considered by many as the birth of organic chemistry.

Some 40 years later, the Russian chemist A. Basarov [2] working in Germany, obtained a small yield of urea from ammonium carbamate ($\text{NH}_2\text{COONH}_4$) after heating it for hours under pressure in a sealed tube.



In the succeeding years, the conditions for this Basarov reaction were further studied and optimized. Today, the Basarov reaction is the basis for all large-scale commercial urea production.

2 Basic Chemistry

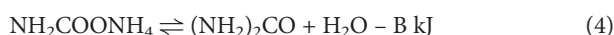
The Basarov reaction can be split into two parts:

(1) Ammonium carbamate is formed from ammonia and carbon dioxide:



This is a fast, strongly exothermic reaction. It runs practically to completion if the reaction heat is removed and the pressure is high enough to force the NH_3 and CO_2 into the liquid phase.

(2) Ammonium carbamate dehydrates to form urea and water:



This second reaction is slow and slightly endothermic. It is also a typical equilibrium reaction, the yield of urea being limited by the underlying reaction thermodynamics. The reaction only runs in the liquid phase, and there is no known catalyst to speed it up.

As $\text{A} \gg \text{B}$, the overall reaction of formation of urea from ammonia and carbon dioxide is exothermic.

These reaction characteristics impose some constraints on any process that uses the Basarov chemistry:

1. To speed up reaction (4) to a reasonable rate, elevated temperature is required.
2. It is also necessary to run at an elevated temperature because the reactions only run in the liquid phase and the melting point of pure ammonium carbamate is 153°C .
3. Elevated pressure is needed to force the normally gaseous feed materials NH_3 and CO_2 into the liquid phase at this elevated temperature.

In practice, the typical conditions for the endpoint of the synthesis step in all commercial processes are in the range of $170 - 220^\circ\text{C}$ and $125 - 250$ bar.

2.1 Side Reactions: Biuret Formation

Under certain conditions, two molecules of urea can react with each other, losing a molecule of ammonia to form biuret.



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The structural chemical formulae for urea and biuret clearly show their relationship:

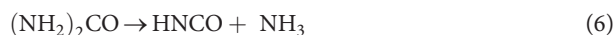
Urea: $\text{NH}_2\text{-CO-NH}_2$

Biuret: $\text{NH}_2\text{-CO-NH-CO-NH}_2$

Although the properties of biuret and urea are in many respects quite similar, in most applications of urea biuret is considered to be an unwanted contaminant. Reaction (5), like reaction (4), is relatively slow, so the formation of biuret can be minimized by restricting residence time and temperature at those places in the process where conditions would be favorable for biuret formation. From Eq. (5), it can also be seen that biuret formation can be suppressed by maintaining an excess of ammonia, forcing the reaction to the urea side.

2.2 Side Reactions: Isocyanic Acid

Urea can decompose into isocyanic acid according to:



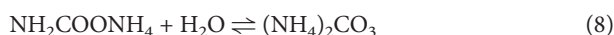
As in the case of biuret formation, the formation of isocyanic acid is suppressed by the presence of ammonia.

2.3 Carbamate Chemistry

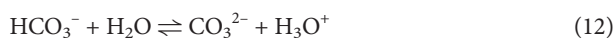
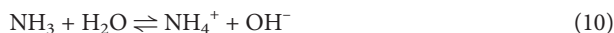
Ammonium carbamate is the ammonium salt of carbamic acid:



As shown by Eq. (4), ammonium carbamate can dehydrate to form urea and water. But it can also hydrate to form ammonium carbonate, which in turn may split off ammonia to form ammonium bicarbonate:



Finally, in the presence of water, the acidic and basic components (carbon dioxide and ammonia) exist in equilibrium with any of these species.



So, upon mixing the pure components NH_3 , CO_2 and H_2O , a mixture is obtained that contains all of the above-mentioned species, including the ionic forms of the salts involved. The exact composition of such a mixture will depend on the initial amounts of NH_3 , CO_2 and H_2O , on temperature and, to some extent, on residence time. In urea technology

it is customary to call such an aqueous mixture carbamate solution, and that indeed is how it is referred to in this article. But it should be noted that it is not strictly correct from a purely scientific point of view as such a carbamate solution contains many more species than just carbamate.

3 Basic Physical Chemistry

In urea technology, vapour-liquid equilibria (VLE) are of particular importance. VLE in the systems of concern are rather complex for the following reasons:

1. Mixtures of the components NH_3 and CO_2 show a strong azeotropic behavior.
2. The synthesis pressures as usually applied in commercial processes (125 – 250 bar) are higher than the critical pressures of both NH_3 ($P_{\text{crit}} = 113$ bar) and CO_2 ($P_{\text{crit}} = 74$ bar).
3. Although NH_3 and CO_2 under urea synthesis conditions are clearly supercritical, there can be a VLE between these components in this supercritical phase and a liquid phase, where the liquid phase contains a suitable solvent. Potential solvents are water, urea or carbamate solution. Note that these solvents are in varying degree chemically produced from the starting materials (NH_3 and CO_2) themselves.
4. A considerable number of chemical reactions and chemical species have to be taken into account in order to make a reliable and accurate description of the actual liquid phase compositions involved.
5. A number of the chemical reactions (notably reactions (4) – (6)) are relatively slow, so reaction kinetics and residence time have to be considered.

It is impossible to present a full quantitative description of the physical chemistry involved in one magazine article. The following is a brief explanation of its main practical influences on urea process design:

3.1 Choice of NH_3/CO_2 Ratio

As would be expected, from two components that show a strong chemical affinity towards each other, the system $\text{NH}_3\text{-CO}_2$ is characterized by a strong positive azeotrope. This azeotropic property continues to be significant in systems where there is solvent comprising one or more of the substances listed above, as shown by the minimum in the curve relating vapour pressure to the NH_3/CO_2 ratio for the system in a state of chemical equilibrium (Fig. 1).

The chemical equilibrium used in Fig. 1 comprehends all chemical reactions (3) to (12), including urea and biuret formation reactions (4) and (5), which are assumed to be at equilibrium at the specified temperature.

Fig. 1 indicates that the azeotropic NH_3/CO_2 mole ratio is approximately 3. From Eqs. (3) and (4) it can be seen that the stoichiometric NH_3/CO_2 mole ratio for urea formation is 2. But, as can be seen from Fig. 1, the pressure rise at the carbon dioxide-rich side of the azeotrope is much steeper in comparison with that at the ammonia-rich side, and in fact,

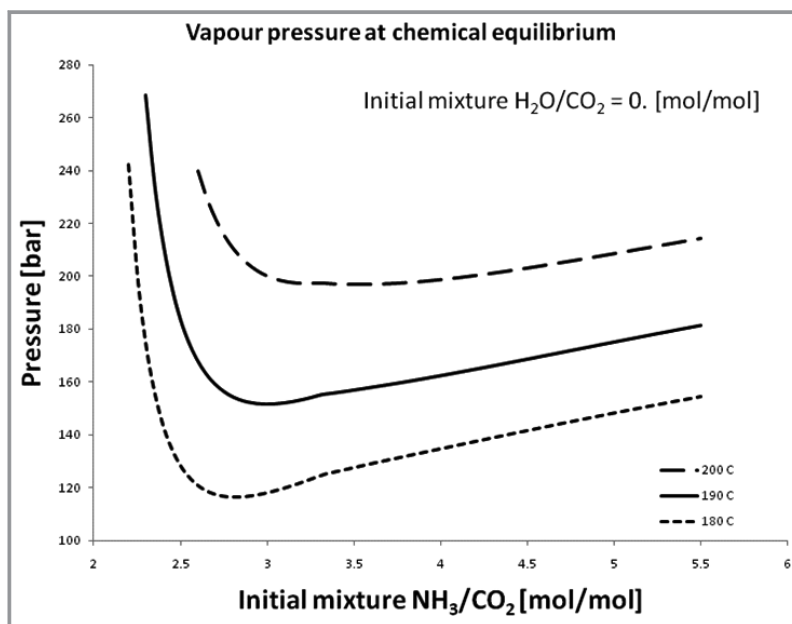


Figure 1. Vapour pressure at chemical equilibrium as a function of NH_3/CO_2 ratio of the initial mixture.

at the stoichiometric ratio (2 mol mol^{-1}) the vapour pressure is unpractically high. Avoiding such unpractical high pressures is the main reason why all commercial processes operate at a higher than stoichiometric NH_3/CO_2 ratio in the synthesis step.

The reason why the azeotropic point occurs at a stoichiometric excess of NH_3 is that the fugacity of NH_3 in these aqueous solutions is lower than that of CO_2 . In other words, in aqueous solutions ammonia is more soluble than carbon dioxide.

Fig. 2 shows the urea yield per pass. It can clearly be seen that the urea concentration in the mixture at chemical equilibrium as a function of NH_3/CO_2 ratio goes through a maximum. Upon combining Figs. 1 and 2, it now follows that this maximum achievable urea concentration occurs at an NH_3/CO_2 ratio that coincides with the azeotropic ratio.

Fig. 2 also tells us something else: if the curves for different $\text{H}_2\text{O}/\text{CO}_2$ ratios are

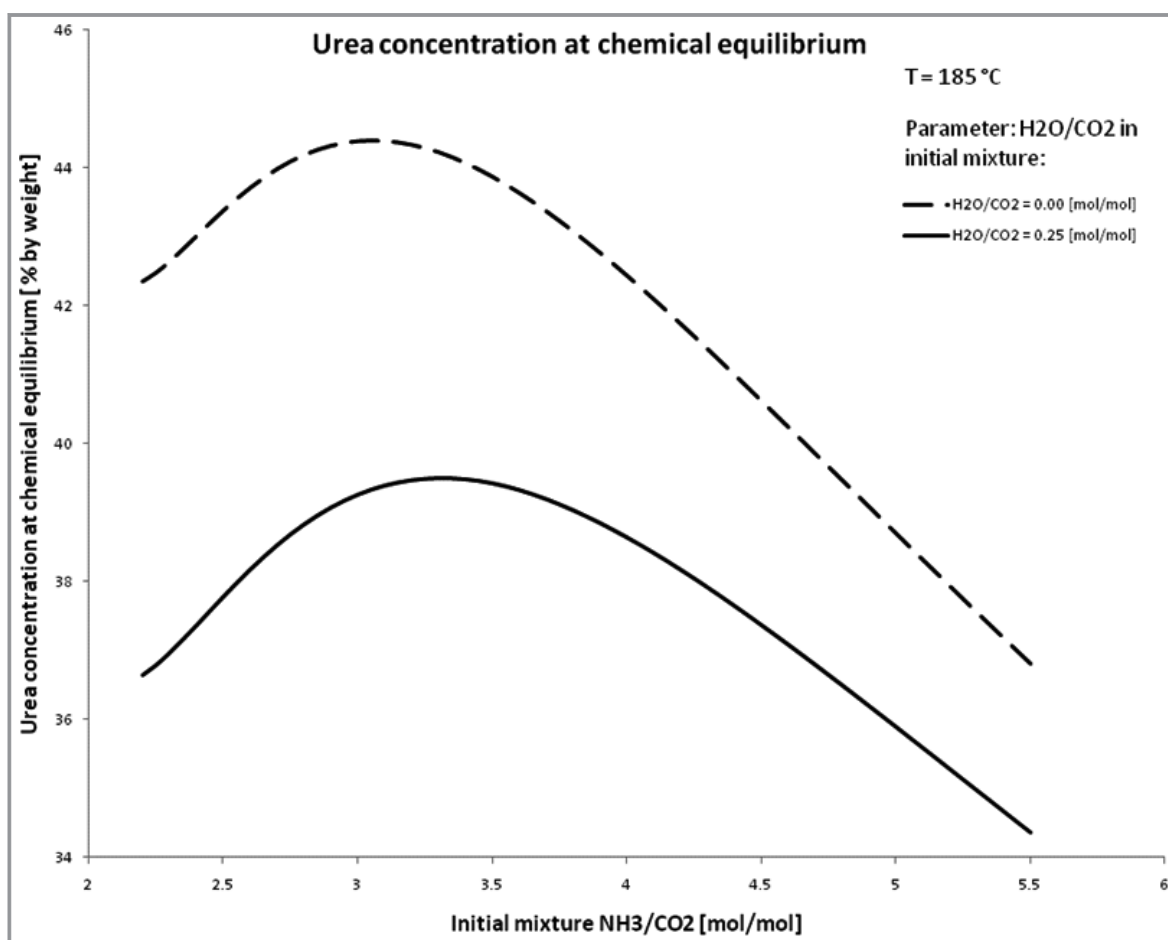


Figure 2. Urea concentration at chemical equilibrium as a function of NH_3/CO_2 ratio in the initial mixture. Parameter: $\text{H}_2\text{O}/\text{CO}_2$ ratio in the initial mixture.

compared, it is immediately apparent that surplus water has a highly detrimental effect on the maximum achievable urea yield per pass. It is because of this effect that so much emphasis has to be put on minimizing any water recycle to the synthesis section of a urea plant.

4 Challenges in Urea Technology

The constraints, outlined above, originating from the thermodynamics on the Basarov reactions lead to some fundamental challenges in urea technology.

Since the urea yield per pass is limited, the only way it is possible to achieve full conversion of the feed materials (ammonia and carbon dioxide) to urea is to recycle unconverted material. If different commercial processes are compared, it is found that these processes all use the same basic chemistry (Basarov), but they mainly differ in the choice of synthesis conditions and in the way unconverted material is recycled. The main challenge that must be overcome to arrive at a successful process design is to find the process conditions that fulfill all the requirements that process operators may reasonably expect from a mature technology: high feed material conversion, low energy consumption, low environmental footprint, low initial investment, high operating reliability and high product quality must be combined into a single process concept.

A special challenge in urea technology arises from the fact that the intermediate product, ammonium carbamate, is highly corrosive towards steel, especially in the parts of the plant operating at the highest temperatures and carbamate concentrations. To achieve high operating reliability, it is necessary to select a combination of process conditions and materials of construction that will prolong the service life of equipment items handling such ammonium carbamate-rich solutions and thus allow long, uninterrupted production runs.

It can now be discussed how several process licensors have approached the combination of these challenges. To better understand the logic behind the present modern urea processes, a short introduction in the history of commercial urea production will be useful.

5 Historical Perspective of Urea Processes

5.1 Conventional (Total-Recycle) Processes

Although the history of industrial urea production is almost as old as that of the nitrogen industry as a whole, it was the generation of urea processes developed in the 1940s –

1960s, nowadays called conventional urea processes, that paved the way to economical large-scale urea production in self-contained plants that did not depend on ancillary downstream processes to utilize unreacted ammonia. A typical flowsheet of such a conventional process is given in Fig. 3.

The urea reactor (c) provided sufficient residence time to allow reaction (4) (the slow step) to closely approach equilibrium. The mixture leaving this reactor contained a mixture of the reaction products urea and water, together with unconverted ammonium carbamate, surplus ammonia and a small amount of carbon dioxide. The process conditions at the reactor outlet were typically 200 – 250 bar and 190 – 220 °C. It was quite usual to maintain an excessive surplus of ammonia in the urea reactor (the NH_3/CO_2 ratio in the initial mixture might be in the range of 4.0 – 6.0).

Downstream of the urea reactor, the pressure of the urea synthesis solution was reduced and it was passed to the medium-pressure decomposer (d). This was a steam-heated heat exchanger in which the residual ammonium carbamate content of the urea synthesis solution decomposed into ammonia and carbon dioxide. Under the reduced pressure, the ammonia and carbon dioxide flashed off from the solution in vapor form. The off-gases from this decomposer were sent to the ammonia-carbamate separation column (e). Here, a distillation process was carried out, resulting in a liquid bottom product consisting of an ammonium carbamate solution in water and a vapor top product containing pure ammonia. This was achieved by using pure liquid ammonia as reflux fluid in the top of the column. The vapor top product (pure ammonia) was condensed in ammonia condensers. To allow normal industrial cooling water to be used to condense this ammonia, the pressure in this condenser had to be at least 18 – 21 bar. This requirement set the lower limit on the operating pressure of the entire MP section in these processes.

The condensed ammonia was recycled to the reactor, along with the fresh supply of ammonia from battery limits,

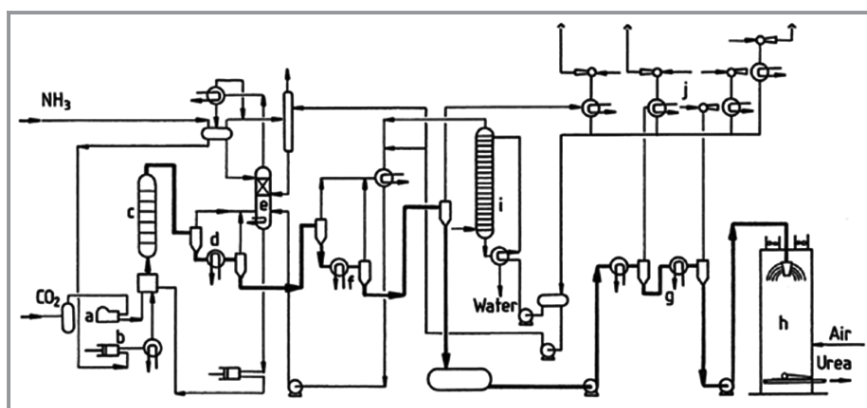


Figure 3. Conventional urea process. (a) CO_2 compressor; (b) high-pressure ammonia pump; (c) urea reactor; (d) medium-pressure decomposer; (e) ammonia-carbamate separation column; (f) low-pressure decomposer; (g) evaporator; (h) prilling; (i) desorber (wastewater stripper); (j) vacuum condensation section.

In the various commercial urea processes the NH_3 and CO_2 feed streams may be supplied to any of these process steps. Either one, as mentioned, may be used as the stripping agent. Additionally, in some processes the liquid ammonia feed drives a liquid-liquid ejector.

The main difference between stripping processes and conventional processes is that the main recycle is conducted under the full synthesis pressure and via the gaseous phase, which means that this main recycle now is (virtually) free of water. Only a minor part of the unconverted ammonium carbamate and surplus ammonia is recycled as aqueous solution from the MP and LP recirculation stages. As a result of the low water recycle, stripping processes attain a high urea yield per pass through the synthesis section.

Another advantage of the stripping processes is that because the bulk of carbamate condensation takes place under substantially higher pressure than in the conventional process, the heat liberated is at a sufficiently high temperature to be utilized in the downstream sections of the plant. Usually, as mentioned, this heat is used to produce LP steam, which is reused in the downstream sections of the plant such as LP carbamate decomposition, urea solution evaporation and waste water treatment – all functions which in conventional processes would run on imported steam. So the introduction of stripping processes made it possible to reduce the energy consumption of urea production quite significantly.

Several stripping processes are available on the licensing market. The differences between them stem from the type of stripping agent used, the mode of introduction of the feed and recycle streams into the synthesis loop, the design of the equipment items, the layout of the synthesis section and the integration of the basic process steps.

5.2.1 Stamicarbon Stripping Processes

Stamicarbon, a company established in the Netherlands, was the first company to introduce a stripping process in the 1960s. In the Stamicarbon stripping process, the CO_2 required for the production of urea is introduced as a stripping agent to the stripper. The first generation of this CO_2 stripping process also had the following characteristic features.

1. Condensation in the HP section was split between two equipment items: the HP carbamate condenser and the HP scrubber, which purifies off-gas from the main reactor.
2. Gravity flow was used as the driving force for the recycle in the synthesis loop.
3. Falling-film condensation was used in the HP carbamate condenser.
4. On account of the high carbamate removal efficiency achieved by using CO_2 as the stripping agent in the HP stripper, no MP recirculation stage was provided and only a small LP recirculation stage downstream of the stripper was required.

5. For the same reason, no separate ammonia recycle was required.

Approaching the turn of the millennium, Stamicarbon introduced a second-generation CO_2 stripping process under the name Urea 2000plus[®]. The process comes in two variants, called the pool condenser concept and the pool reactor concept, respectively.

In the Pool Condenser concept (Fig. 5), the vertical shell-and-tube HP carbamate condenser of the original process has been replaced by a liquid-filled horizontal vessel with a U-tube cooling bundle. Pool condensation is a technology where the liquid phase is the continuous phase. Gases from the stripper, comprising the CO_2 feed and the off-gases from the decomposition of ammonium carbamate, are dispersed as bubbles into a bath of liquid, which is a mixture of carbamate liquor and the liquid ammonia feed, with which the incoming CO_2 instantly reacts to form fresh ammonium carbamate.

Pool condensation offers some advantages over falling film condensation:

1. In general, it can be noted that pool condensation results in enhanced heat transfer in comparison with film condensation. The introduction of bubbles into the liquid phase creates quite some turbulence. As is well known from the theory on boundary layers in heat transfer, turbulence is the key factor in obtaining a high heat transfer coefficient. What that means in practical terms is that it is possible to either reduce the heat-exchanging surface, which reduces initial investment costs, or to produce the LP steam at a higher pressure, which reduces energy consumption, or a bit of both.
2. Whereas the improved heat-transfer is a general advantage of pool condensation, specifically for urea technology there is an additional advantage: Maintaining a body of liquid in the condenser means that the ammonium carbamate is retained there for long enough for a significant proportion of it to react to urea and water (reaction (4)). These are less volatile than the feed materials, allowing the pool condenser to be operated at a higher temperature on the process side. And that allows further reduction of the required heat exchanging area and/or a further increase of the pressure of the LP steam.

In the pool reactor version of the Stamicarbon Urea 2000plus[®] process (Fig. 6), the main reactor and pool condenser are integrated into a single horizontal vessel: the pool reactor. Besides the advantages of pool condensation mentioned above, the integration of two major equipment items offers a further reduction in the initial investment required.

It should be noted that in both concepts, the main synthesis loop equipment (reactor, stripper and condenser) is arranged in such a way that circulation between them is promoted by gravity so no pumps or compressors are needed in the loop. This reduces not only the initial investment but also the maintenance requirement and energy consumption.

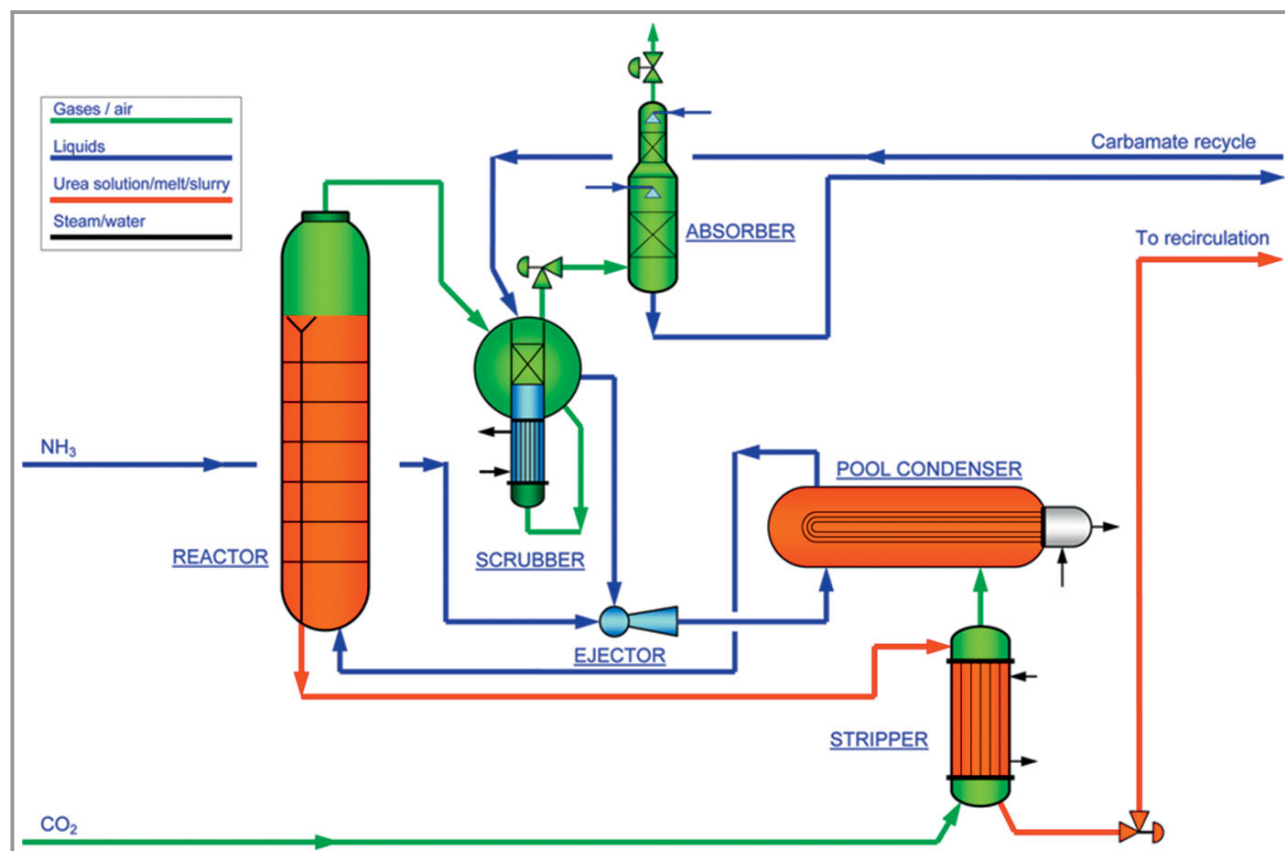


Figure 5. Stamicarbon Urea 2000plus[®] CO₂ stripping process: pool condenser concept.

In 2008 Stamicarbon introduced a further variant of its CO₂ stripping process under the name AVANCORE[®]. With the AVANCORE[®] CO₂ stripping process Stamicarbon introduced two new concepts: (i) an improved layout for the synthesis section and (ii) a superior material of construction for urea service: Safurex[®].

In the AVANCORE[®] layout the reactor is located at ground level, thus offering a further reduction in initial investment cost as well as simplified maintenance. In the layout chosen (Fig. 7), despite the low-level arrangement, gravity flow is maintained as the driving force for circulation in the synthesis recycle flow. The AVANCORE[®] process in this way combines the advantages of a low-level arrangement of the heavy synthesis equipment with the low energy requirement of gravity flow.

5.2.2 Combating Corrosion in the Stamicarbon Processes

In quite a number of projects embodying the Stamicarbon Urea 2000plus[®] concept, experience was built up on the use of a new material of construction, Safurex[®]. With the introduction of the AVANCORE[®] process Stamicarbon announced that this material of construction has proven its superiority over the older materials of construction, such

that Safurex[®] now is the standard material of construction for Stamicarbon urea plant synthesis sections.

As far back as the 1950s, a Stamicarbon researcher, Mr. van Waes, made an important discovery in urea technology: in a carbamate environment, addition of small amounts of an oxidizing agent (e.g., oxygen) greatly enhances the corrosion-resistance of stainless steels [3]. This discovery hugely increased equipment lifetimes and allowed the use of relatively simple stainless steels as materials of construction instead of the exotic and expensive alternatives that had been tried before. It served the industry well for more than half a century, during which austenitic stainless steels were used successfully in combination with the addition of a small amount of air to the CO₂ feed to the urea synthesis. Then a major new improvement in combating corrosion in urea service was announced: Safurex[®].

Safurex[®] is a duplex (austenitic/ferritic) stainless steel developed by Stamicarbon in collaboration with Sandvik Materials Technology. Its composition and microstructure have been optimized to combat carbamate-induced corrosion in urea service. The main advantage of Safurex[®] is its high corrosion-resistance at low oxygen concentration, allowing for a much lower air dosing to the urea plant. Moreover, Safurex[®] shows superior mechanical properties. As a result, Safurex[®] requires a lower investment compared

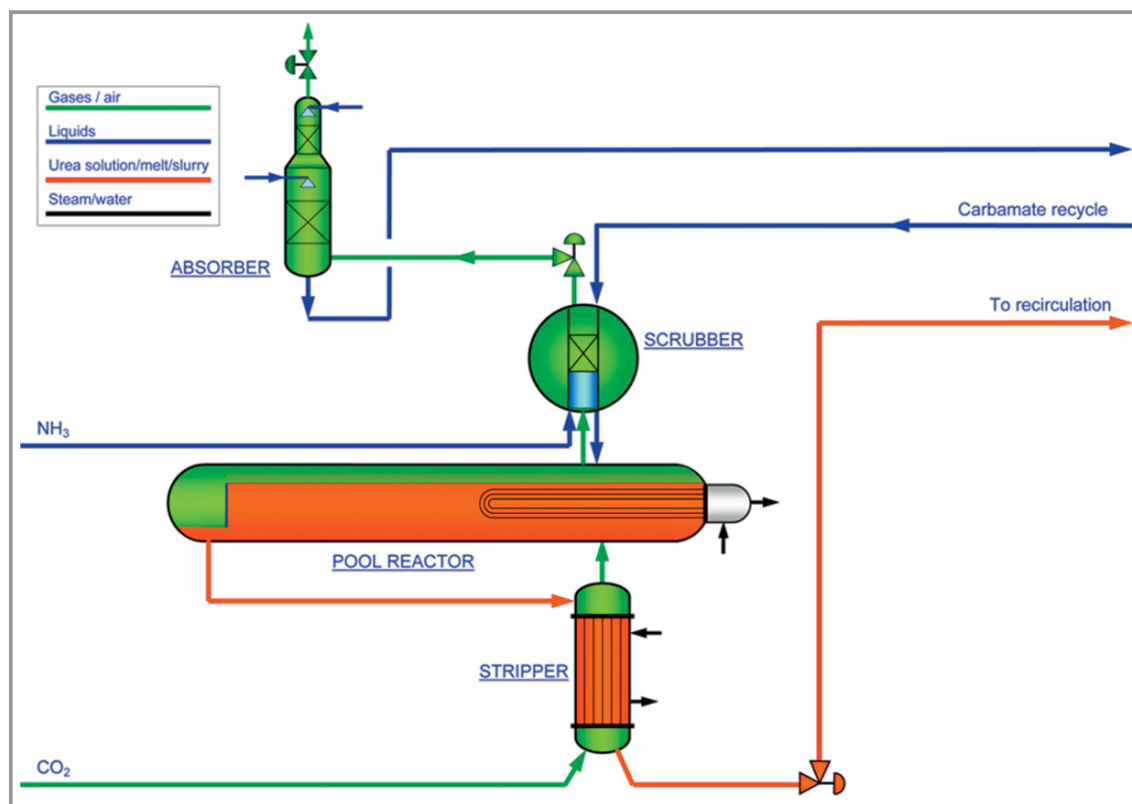


Figure 6. Stamicarbon Urea 2000plus® CO₂ stripping process: pool reactor concept.

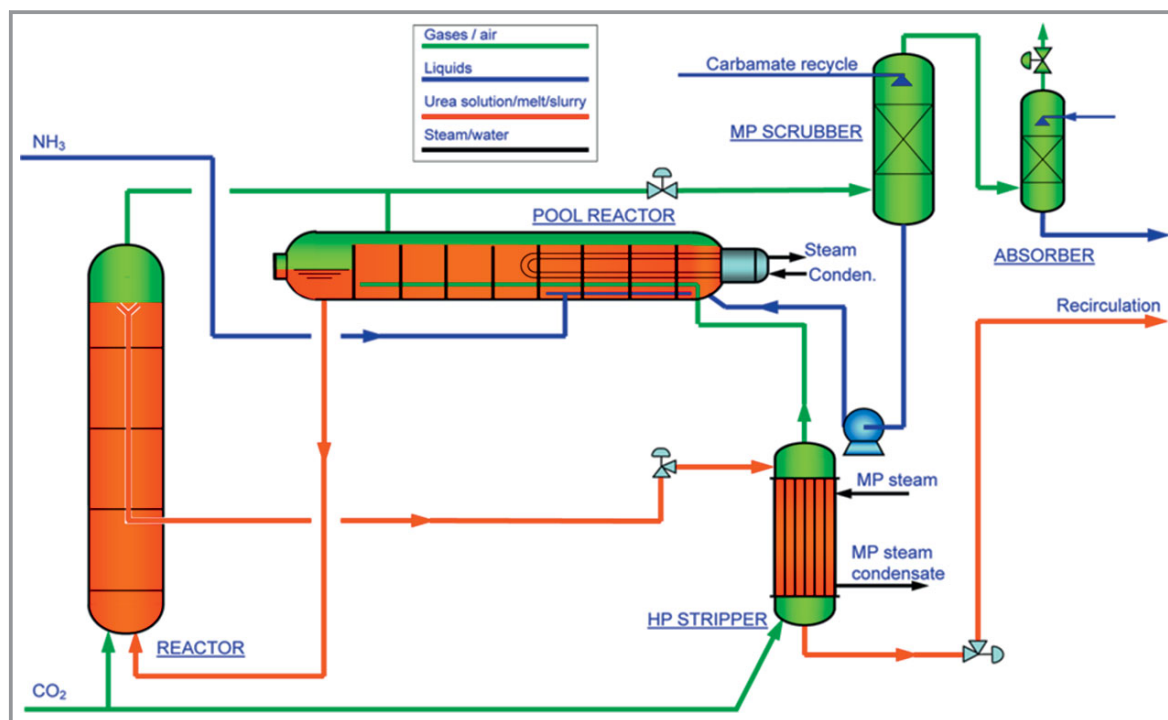


Figure 7. Stamicarbon AVANCORE® CO₂ stripping process.

to traditional materials of construction and offers a nearly maintenance-free urea plant with significant longer lifetime than any other commercially available urea process.

5.2.3 Snamprogetti Stripping Processes

The Snamprogetti stripping process (Fig. 8) [4] uses thermal stripping with no additional stripping agent on the tube side. That means that relatively high temperatures are required in the stripper. In comparison with CO₂ stripping, thermal stripping results in a higher efficiency of CO₂ removal from the urea synthesis solution. But on account of the higher temperatures needed in the stripper, the ammonia removal efficiency is limited, which makes it necessary to include an MP purification and recovery section in the process. To cope with the relatively high ammonia recycle from this MP section back to the synthesis loop, it is necessary to include an ammonia/carbamate separating distillation column (j) into the MP process section. It is claimed that this MP process section provides great plant flexibility, allowing operation over a wide range of NH₃/CO₂ ratios.

A further characteristic of the Snamprogetti synthesis section is its horizontal layout, which means that an HP ejector (c) is needed to drive circulation in the reactor-stripper-condenser-reactor loop.

The relatively high temperature in the thermal stripper (h) precludes the use of stainless steels as materials of construction for the HP stripper tubes. Instead, Snamprogetti offers a number of alternatives for effectively combating corrosion. In the first industrial plants, Snamprogetti used titanium as the tube material. At the end of the 1980s titanium was replaced with bimetallic tubes, consisting of two coaxial tubes: an external tube made of 25-22-2 Cr-Ni-Mo, and an internal tube made of zirconium. Recently, new options have been developed and implemented for the Snamprogetti stripper design: (i) the full zirconium stripper, and (ii) the OMEGABOND® stripper.

In the full zirconium stripper, both lining and tubes are made of zirconium, which has proven to be perfectly re-

sistant to erosion and corrosion. The OMEGABOND® tubes (developed in collaboration with ATI Wah Chang, USA) take advantage of the long experience from the titanium stripper. The limitations resulting from erosion of the full titanium tubes are overcome by using tubes obtained from the extrusion of titanium (external) and zirconium (internal) billets, forming a metallurgical bond between the two materials.

5.2.4 TEC Stripping Processes

The Japanese company Toyo Engineering Corporation (TEC) licensed variants of the conventional urea process up to the 1980s, at which time TEC announced its own stripping technology, called the ACES process (Advanced process for Cost and Energy Saving) [5]. Recently, TEC announced the latest version of this stripping process called ACES21®.

The ACES processes apply CO₂ stripping in the synthesis section. In its latest version (ACES21®), in the synthesis section pool condensation is applied in a vertical submerged carbamate condenser (VSCC). The carbamate solution from this VSCC is propelled into the reactor by an ejector driven by HP liquid ammonia. The urea solution leaving the reactor is fed to a stripper, where unconverted ammonium carbamate is thermally decomposed and surplus ammonia and carbon dioxide are separated by CO₂ stripping. The stripped urea solution is sent to a MP decomposition stage for further purification. Using forced circulation in the urea synthesis loop allows TEC to use a low-level layout.

TEC is a pioneer in applying duplex stainless steels in urea plants. Its latest development in that area is a duplex stainless steel called DP28W™, a material developed in co-operation with Sumitomo Metal Industries Ltd. It is claimed that DP28W™ has greatly improved corrosion-resistance in comparison with conventional duplex steels. In addition, the material shows excellent passivation behavior in urea-carbamate solutions.

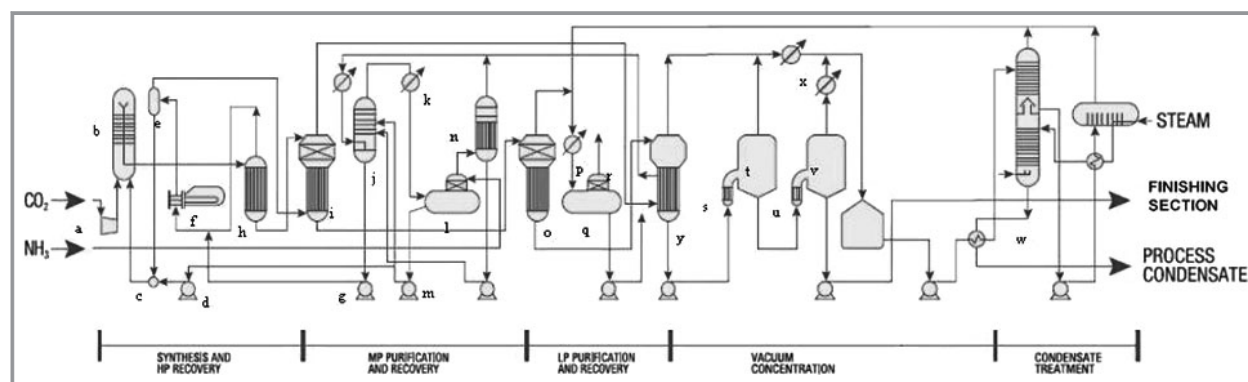


Figure 8. Snamprogetti urea process. (a) CO₂ compressor; (b) reactor; (c) ejector; (d) ammonia pump; (e) separator; (f) carbamate condenser; (g) carbamate pump; (h) stripper; (i) MP decomposer; (j) distillation column; (k) ammonia condenser; (l) ammonia buffer vessel; (m) ammonia reflux pump; (n) MP absorber; (o – r) LP recovery section; (s – v) Evaporation section; (w) condensate treatment section. Figure reproduced with permission of Saipem S.p.A.



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all over the world. At present he is principal engineer for the urea process within Stamicarbon. In this role, his key responsibilities include the integrity of projects realized under a Stamicarbon license, as well as new and innovative developments within the urea process.

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