*Kirk-Othmer Encyclopedia of Chemical Technology.*

# UREA

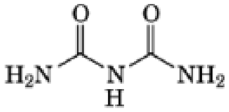
Urea [57-13-6] was discovered in urine by Rouelle in 1773 and first synthesized from ammonia (qv) and cyanic acid by Woehler in 1828. This was the first synthesis of an organic compound from an inorganic compound, and it dealt a deathblow to the vital-force theory. In 1870, urea was produced by heating ammonium carbamate in a sealed tube.

## 1. Properties

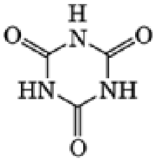
Urea can be considered the amide of carbamic acid, $NH_2COOH$, or the diamide of carbonic acid, $CO(OH)_2$. At room temperature, urea is colorless, odorless, and tasteless. Properties are shown in Tables 1, 2, 3, 4. Dissolved in water, it hydrolyzes very slowly to ammonium carbamate (1) and eventually decomposes to ammonia and carbon dioxide (qv). This reaction is the basis for the use of urea as fertilizer (qv).

Commercially, urea is produced by the direct dehydration of ammonium carbamate, $NH_2COONH_4$, at elevated temperature and pressure. Ammonium carbamate is obtained by direct reaction of ammonia and carbon dioxide. The two reactions are usually carried out simultaneously in a high pressure reactor. Recently, urea has been used commercially as a cattle-feed supplement (see Feeds and feed additives). Other important applications are the manufacture of resins (see Amino resins and plastics), glues, solvents, and some medicinals. Urea is classified as a nontoxic compound.

At atmospheric pressure and at its melting point, urea decomposes to ammonia, biuret (**1**), cyanuric acid (qv) (**2**), ammelide (**3**), and triuret (**4**). Biuret is the main and least desirable by-product present in commercial urea. An excessive amount $(>\text{wt}\%)$ of biuret in fertilizer-grade urea is detrimental to plant growth.



**(1)**
biuret



**(2)**
cyanuric acid

**Table 1. Properties of Urea**

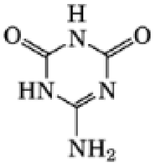
| Property | Value |
|---|---|
| melting point, °C | 135 |
| index of refraction, $n^{20}{}_D$ | 1.484, 1.602 |
| density, $d^{20}{}_4$, g/cm$^3$ | 1.3230 |
| crystalline form and habit | tetragonal, needles or prisms |
| free energy of formation, at 25°C, J/mol[a] | −197.150 |
| heat of fusion, J/g[a] | 251[b] |
| heat of solution in water, J/g[a] | 243[b] |
| heat of crystallization, 70% aqueous urea solution, J/g[a] | 460[b] |
| bulk density, g/cm$^3$ | 0.74 |
| specific heat, J/(kg·K)[a] | |
| at 0°C | 1.439 |
| 50 | 1.661 |
| 100 | 1.887 |
| 150[c] | 2.109 |

[a] To convert J to cal, divide by 4.184.
[b] Endothermic.
[c] Exothermic.

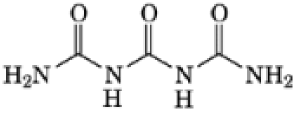
**Table 2. Properties of Saturated Aqueous Solutions of Urea**

| Temperature, °C | Solubilityin water, g/100 g solution | Density, g/cm$^3$ | Viscosity mPa·s(=cP) | $H_2O$ vapor pressure, kPa[a] |
|---|---|---|---|---|
| 0 | 41.0 | 1.120 | 2.63 | 0.53 |
| 20 | 51.6 | 1.147 | 1.96 | 1.73 |
| 40 | 62.2 | 1.167 | 1.72 | 5.33 |
| 60 | 72.2 | 1.184 | 1.72 | 12.00 |
| 80 | 80.6 | 1.198 | 1.93 | 21.33 |
| 100 | 88.3 | 1.210 | 2.35 | 29.33 |
| 120 | 95.5 | 1.221 | 2.93 | 18.00 |
| 130 | 99.2 | 1.226 | 3.25 | 0.93 |

[a] To convert kPa to mm Hg, multiply by 7.5.



(**3**)
ammelide



(**4**)
triuret

**Table 3. Properties of Saturated Solutions in Urea in Ammonia**[a]

| Temperature, °C | Urea in solution, wt % | Vapor pressure of solution, kPa[b] |
|---|---|---|
| 0 | 36 | 405 |
| 20 | 49 | 709 |
| 40 | 68 | 952 |
| 60 | 79 | 1094 |
| 80 | 84 | 1348 |
| 100 | 90 | 1267 |
| 120 | 96 | 507 |

[a] Ref. 2.

[b] To convert kPa to atm, divide by 101.3.

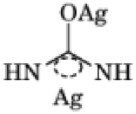
**Table 4. Properties of Saturated Solutions of Urea in Methanol and Ethanol**[a]

| | Methanol | | Ethanol | |
|---|---|---|---|---|
| Temperature, °C | Urea, wt % | Density, g/cm$^3$ | Urea, wt % | Density, g/cm$^3$ |
| 20 | 22 | 0.869 | 5.4 | 0.804 |
| 40 | 35 | 0.890 | 9.3 | 0.804 |
| 60 | 63 | 0.930 | 15.0 | 0.805 |

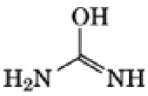
[a] Ref. 3.

Urea acts as a monobasic substance and forms salts with acids (4). With nitric acid, it forms urea nitrate, $CO(NH_2)_2{\cdot}HNO_3$, which decomposes explosively when heated. Solid urea is stable at room temperature and atmospheric pressure. Heated under vacuum at its melting point, it sublimes without change. At 180–190°C under vacuum, urea sublimes and is converted to ammonium cyanate, $NH_4OCN$ (5). When solid urea is rapidly heated in a stream of gaseous ammonia at elevated temperature and at a pressure of several hundred kPa (several atm), it sublimes completely and decomposes partially to cyanic acid, HNCO, and ammonium cyanate. Solid urea dissolves in liquid ammonia and forms the unstable compound urea–ammonia, $CO(NH_2)_2NH_3$, which decomposes above 45°C (2). Urea–ammonia forms salts with alkali metals, eg, $NH_2CONHM$ or $CO(NHM)_2$. The conversion of urea is biuret is promoted by low pressure, high temperature, and prolonged heating. At 10–20 MPa (100–200 atm), biuret gives urea when heated with ammonia (6, 7).

Urea reacts with silver nitrate, $AgNO_3$, in the presence of sodium hydroxide, NaOH, and forms a diargentic derivative (**5**) of a pale-yellow color. Sodium hydroxide promotes the change of urea into the imidol form (**6**):



(**5**)



(**6**)

which then reacts with silver nitrate. Oxidizing agents in the presence of sodium hydroxide convert urea to nitrogen and carbon dioxide. The latter reacts with sodium hydroxide to form sodium carbonate (8):

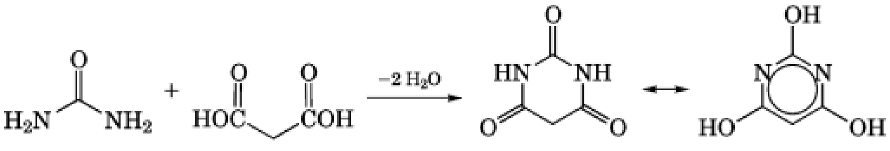
$$NH_2CONH_2 + 2\ NaOH + 3\ NaOBr \longrightarrow N_2 + 3\ NaBr + Na_2CO_3 + 3\ H_2O$$

The reaction of urea with alcohols yields carbamic acid esters, commonly called urethanes (see Urethane polymers):

$$NH_2\overset{\overset{O}{\|}}{C}NH_2 + ROH \longrightarrow NH_2\overset{\overset{O}{\|}}{C}OR + NH_3$$

Urea reacts with formaldehyde compounds such as monomethylolurea, $NH_2CONHCH_2OH$, dimethylolurea, $HOCH_2NHCONHCH_2OH$, and others, depending on the mol ratio of formaldehyde, to urea and upon the pH of the solution. Hydrogen peroxide and urea give a white crystalline powder, urea peroxide, $CO(NH_2)_2{\cdot}H_2O_2$, known under the trade name of Hypersol, an oxidizing agent.

Urea and malonic acid give barbituric acid (**7**), a key compound in medicinal chemistry (see also Hypnotics, sedatives, and anticonvulsants):



(**7**)
malonyl urea or
barbituric acid

## 2. Manufacture

Urea is produced from liquid $NH_3$ and gaseous $CO_2$ at high pressure and temperature; both reactants are obtained from an ammonia-synthesis plant. The latter is a by-product stream, vented from the $CO_2$ removal section of the ammonia-synthesis plant. The two feed components are delivered to the high pressure urea reactor, usually at a mol ratio >2.5 : 1. Depending on the feed mol ratio, more or less carbamate is converted to urea and water per pass through the reactor.

The formation of ammonium carbamate and the dehydration to urea take place simultaneously, for all practical purposes:

$$2\ NH_3 + CO_2 \rightleftharpoons NH_2\overset{\overset{O}{\|}}{C}ONH_4 \qquad (1)$$

ammonium
carbamate

$$NH_2\overset{\overset{O}{\|}}{C}ONH_4 \rightleftharpoons NH_2\overset{\overset{O}{\|}}{C}NH_2 + H_2O \qquad (2)$$

urea

**Table 5. Vapor Pressure of Pure Ammonium Carbamate at which Dissociation Begins**

| Temperature, °C | kPa[a] |
|---|---|
| 40 | 31 |
| 60 | 106 |
| 80 | 314 |
| 100 | 861 |
| 120 | 2,130 |
| 140 | 4,660 |
| 160 | 9,930 |
| 180 | 15,200; 19,300[b] |
| 200 | 20,300; 36,500[b] |

[a] To convert kPa to atm, divide by 101.3.

[b] The value has been extrapolated because, at temperatures above 170°C, the rate of reaction (**10**) rapidly increases and it is difficult to determine the carbamate vapor pressure owing to the formation of water and urea and the consequent lowering of the partial pressure of ammonium carbamate.

**Table 6. Specific Heat of Solid Ammonium Carbamate**

| Temperature, °C | J/(g·K)[a] |
|---|---|
| 20 | 1.67 |
| 60 | 1.92 |
| 100 | 2.18 |
| 140 | 2.43 |
| 180 | 2.59 |

[a] To convert J to cal, divide by 4.184.

Reaction **1** is highly exothermic. The heat of reaction at 25°C and 101.3 kPa (1 atm) is in the range of 159 kJ/mol (38 kcal/mol) of solid carbamate (9). The excess heat must be removed from the reaction. The rate and the equilibrium of reaction **1** depend greatly upon pressure and temperature, because large volume changes take place. This reaction may only occur at a pressure that is below the pressure of ammonium carbamate at which dissociation begins or, conversely, the operating pressure of the reactor must be maintained above the vapor pressure of ammonium carbamate. Reaction (**10**) is endothermic by ca 31.4 kJ/mol (7.5 kcal/mol) of urea formed. It takes place mainly in the liquid phase; the rate in the solid phase is much slower with minor variations in volume.

The dissociation pressure of pure carbamate has been investigated extensively (10–12) and the average values are shown in Table 5.

### 2.1. Ammonium Carbamate

Ammonium carbamate is a white crystalline solid which is soluble in water (2). It forms at room temperature by passing ammonia gas over dry ice. In an aqueous solution at room temperature, it is slowly converted to ammonium carbonate, $(NH_4)_2CO_3$, by the addition of one mol of water. Above 60°C, the ammonium carbonate solution reverts to carbamate solution, and at 100°C, only carbamate is present in the solution. Above 150°C, ammonium carbamate loses a mol of water and forms urea. The specific heat of solid ammonium carbamate is given in Table 6. Ammonium carbamate melts at ca 150°C, and has a heat of fusion of ca 16.74 kJ/mol (4.0 kcal/mol). The conversion of carbamate to urea begins at $\leq 100°C$. To obtain an appreciable amount of urea at 100°C requires 20–30 h. The rate of conversion increases with increasing temperature (13–15); at 185°C, ca 50% of the ammonium carbamate is converted to urea in ca 30 min.

**Table 7. Reaction Equilibrium Constant**[a]

| Temperature, °C | Reaction equilibrium constant, K |
|---|---|
| 140 | 0.695 |
| 150 | 0.850 |
| 160 | 1.075 |
| 170 | 1.375 |
| 180 | 1.800 |
| 190 | 2.380 |
| 200 | 3.180 |

[a] Ref. 16.

### 2.2. Conversion at Equilibrium

The maximum urea conversion at equilibrium attainable at 185°C is ca 53% at infinite heating time. The conversion at equilibrium can be increased either by raising the reactor temperature or by dehydrating ammonium carbamate in the presence of excess ammonia. Excess ammonia shifts the reaction to the right side of the overall equation:

$$2\,NH_3 + CO_2 \rightleftharpoons NH_2CONH_2 + H_2O$$

Water, however, has the opposite effect. Actual equilibrium constants at various temperatures are given in Table 7. A detailed study of the effect of pressure on urea conversion is given in Ref. 17.

## 3. Processing

At this time over 95% of all new urea plants are licensed by Snamprogetti, Stamicarbon, or Toyo Engineering. SNAM utilizes thermal stripping while STAC (Stamicarbon) and Toyo use $CO_2$ stripping. Only these three processes are, therefore, covered in detail. Process flow sheets are included for others at the end of this section.

As of the end of 1996, about 70 SNAM plants, 125 STAC, and 7 Toyo stripping plants have been built. Currently STAC will design plants for over 3000 MTD, SNAM about 2800 MTD, and Toyo about 2300 MTD as single train units.

STAC, with their current new design (pool reactor), feel the only size limitation will be vessel size. Unless both the vessel fabricator and the intended plant site are “on water”, a 4-m-diameter is the maximum that can be transported.

The urea produced is normally either prilled or granulated. In some countries there is a market for liquid urea–ammonium nitrate solutions (32% N). In this case, a partial-recycle stripping process is the best and cheapest system. The unconverted $NH_3$ coming from the stripped urea solution and the reactor off-gas is neutralized with nitric acid. The ammonium nitrate solution formed and the urea solution from the stripper bottom are mixed, resulting in a 32–35 wt % solution. This system drastically reduces investment costs as evaporation, finishing (prill or granulation), and wastewater treatment are not required.

### 3.1. Snamprogetti Thermal Stripping Process

The Snamprogetti process is outlined in Figure 1. Initially SNAM utilized $NH_3$ as the stripping agent. Owing to the high solubility of $NH_3$ in the synthesis liquid, an overload of $NH_3$ occurred in the downstream recirculation sections of the plant. At this time only heat is supplied to the stripper to remove unreacted $NH_3$ and $CO_2$. Because of the high $NH_3$ ratio, it is still necessary to have two recirculation sections.

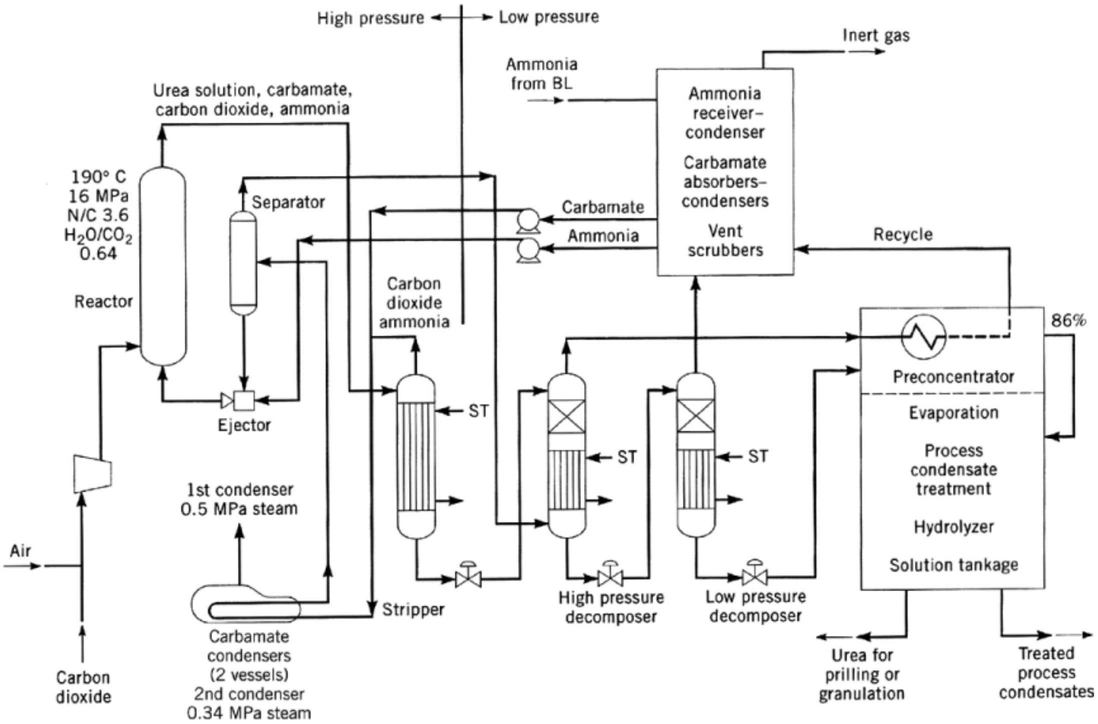


**Fig. 1.** Snamprogretti thermal stripping urea process. BL=battery limits.

The synthesis recycle loop has the stripped gas going to two high pressure carbamate condensers in series and to a high pressure separator and then back to the reactor. The flow is maintained by using an $NH_3$-driven liquid–liquid ejector. The reactor is operated at 15 MPa (150 bar) with a $NH_3$–$CO_2$ molar feed ratio of 3.5. The stripper is a falling-film type and since high temperatures (200–210°C) are required for efficient thermal stripping, stainless steel tubing is not suitable. Titanium was initially used, but it also was not satisfactory because of erosion near the bottom. At this time a bimetallic tube of zirconium and 25-22-2 stainless steel is used. The zirconium is corrosion-free and the only problem is the difficulty in getting proper welds and separation of the two layers at the bottom ends. Fabrication mistakes have been the only source of problems with this vessel to date.

The stripper off-gas going to the high pressure carbamate condensers also contains the carbamate recovered in the medium and low pressure recirculation sections. Both of these systems are similar to those shown in the total-recycle process.

The plant is designed with an excellent heat-exchange system to kee overall steam required to a minimum.

The plant wastewater containing $NH_3$ and urea is subjected to a desorption–hydrolysis operation to recover almost all the $NH_3$ and urea. In some plants, this water can then be used for boiler feedwater.

The urea solution is evaporated in a two-stage system (99.8%) if the final product is prills, and a single-stage system (+95%) if granules are to be provided.

### 3.2. Stamicarbon $CO_2$ Stripping Process

In the early 1960s, Stamicarbon introduced the first stripping process. One of the main improvements was the reduction of steam required pre ton or urea to 0.8–0.95 from the 1.8 ton required in the conventional

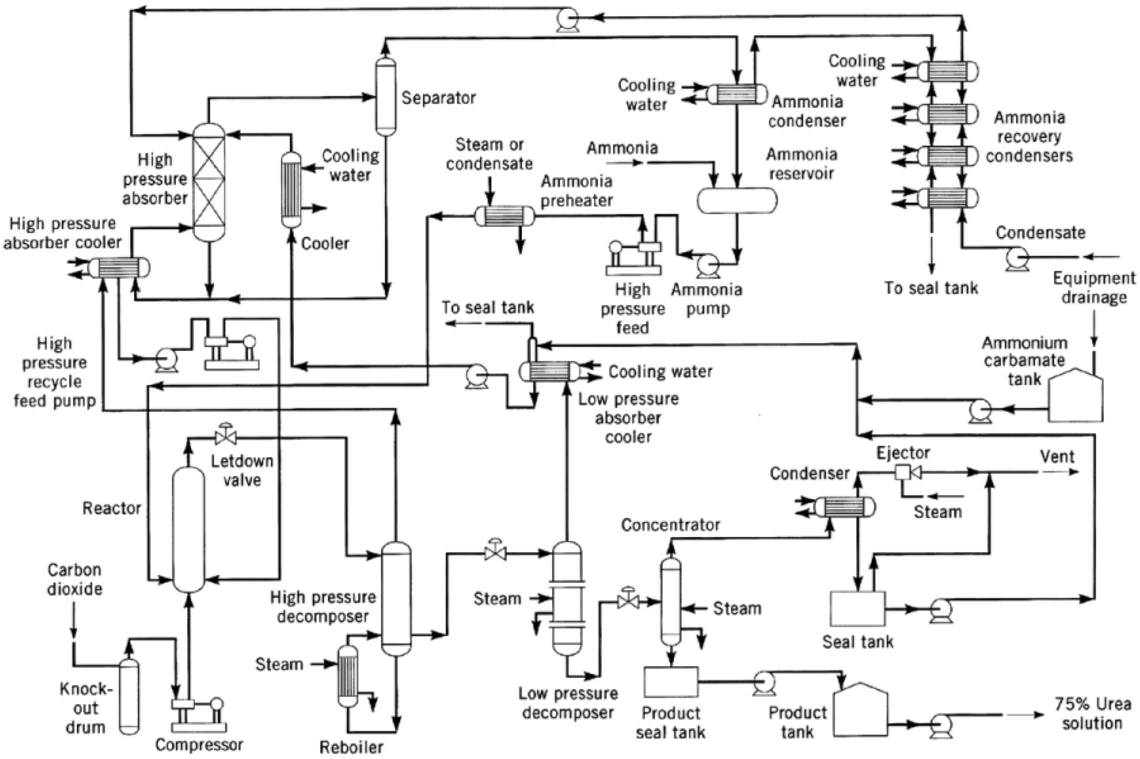


**Fig. 2.** Typical total-recycle urea process.

total-recycle process (Fig. 2). Steam usage and electric power required can be varied depending on the final design.

The Stamicarbon process is described in Figures 3, 4, 5, 6, 7. The synthesis section of the plant consists of the reactor, stripper, high pressure carbamate condenser, and a high pressure reactor off-gas scrubber. In order to obtain a maximum urea yield per pass through the reactor, a pressure of 14 MPa (140 bar) and a 2.95/1 $NH_3$–$CO_2$ molar ratio is maintained. The reactor effluent is distributed over the stripper tubes (falling-film type shell and tube exchanger) and contacted by the $CO_2$, countercurrently. This causes the partial $NH_3$ pressure to decrease and the carbamate to decompose.

The urea solution out of the stripper bottom flows to a single-stage low pressure recirculation section (0.4 MPa, 4 bar). The stripper off-gas is sent to the carbamate condenser.

In this condenser, part of the stripper off-gases are condensed (the heat of condensation is used to generate low pressure steam). The carbamate formed and noncondensed $NH_3$ and $CO_2$ are put into the reactor bottom and conversion of the carbamate into urea takes place. The reactor is sized to allow enough residence time for the reaction to approach equilibrium. The heat required for the urea reaction and for heating the solution is supplied by additional condensation of $NH_3$ and $CO_2$. The reactor which is lined with 316 L stainless steel, contains sieve trays to provide good contact between the gas and liquid phases and to prevent back-mixing. The stripper tubes are 25-22-2 stainless steel. Some strippers are still in service after almost 30 years of operation.

The noncondensable gases introduced in the $CO_2$ (ie, passivation air) and part of the unreacted $NH_3$ and $CO_2$ goes to the high pressure scrubber, which consists of a shell-and-tube exchanger in the bottom portion and a packed bed in the upper part. In the lower part, most of the $NH_3$ and $CO_2$ is condensed, the heat of condensation is dissipated in tempered cooling water. In the upper part, the gases leaving the bottom section

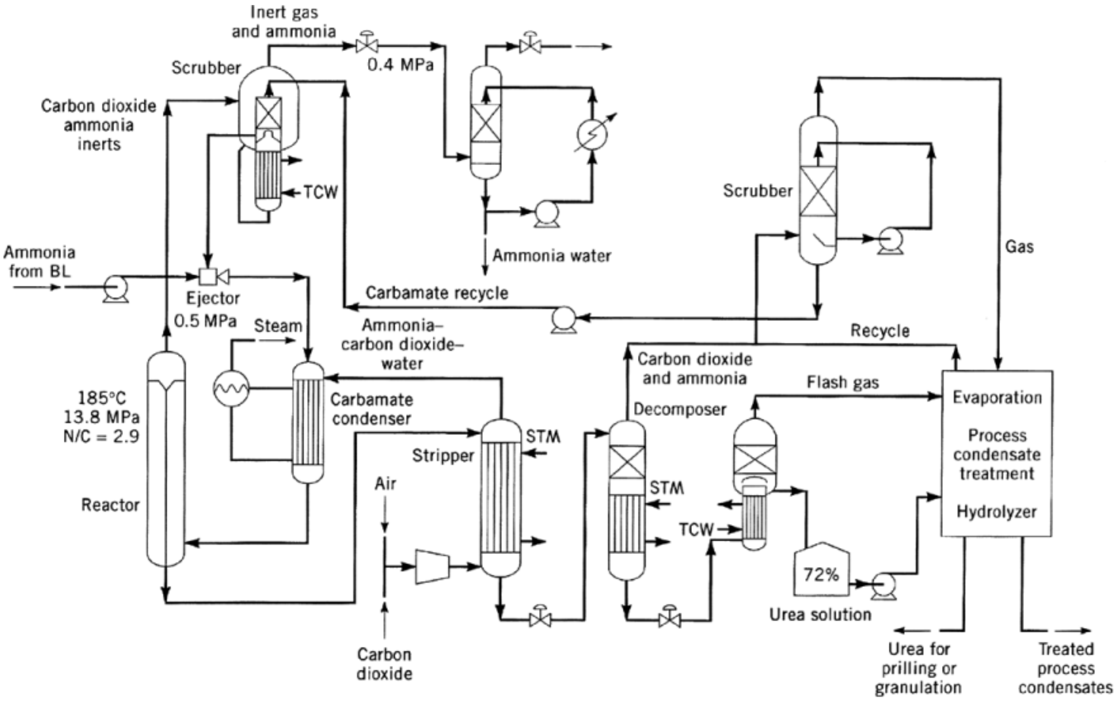


**Fig. 3.** Stamicarbon $CO_2$ stripping process. TCW = tempered cooling water.

are countercurrently contacted with carbamate solution returned from recirculation. The scrubber off-gas, containing nitrogen, oxygen, and very small amounts of $NH_3$ and $CO_2$ are vented to the atmosphere after passing through an absorber.

The carbamate solution from the scrubber flows to a high pressure ejector. The $NH_3$ feed pressure induces enough head to convey the carbamate solution from the scrubber to the carbamate condenser.

As mentioned before, because of design and operating conditions (ie, $NH_3/CO_2$ ratio, pressure, temperature, reactor volume), only one recirculation stage is required (0.4 MPa) (4 bar). On expansion, a large portion of the carbamate left in the urea solution from the stripper decomposes. The remaining solution passes through a rectifying column, heater, and separator. The gases formed go to a carbamate condenser and are pumped via the high pressure carbamate pump (either reciprocating or centrifugal) to the high pressure scrubber.

The urea solution is then evaporated to 99.8% for prilling (2 stages) or plus 95% for granulation (1 stage).

The Stamicarbon wastewater system consisting of two desorbers, hydrolyzer, hydrolyzer heater, reflux condenser, desorber heat exchanger, and a wastewater cooler is very efficient. Also, in many plants, as the water contains less than 1 ppm of $NH_3$ and of urea, it can be used as cooling water make-up, or boiler-feed water.

In 1994 Stamicarbon introduced a pool condenser in the synthesis section (see Figs. 4 and 5). This allowed a 34% decrease in reactor volume and a 45% decrease in carbamate heat-exchange area, thus reducing costs considerably for equipment, structural steel, and construction.

In late 1997, DSM (Stamicarbons parent company) will start up a new plant utilizing, the next step, a pool reactor (see Figs. 6 and 7). In 1999 this process should be offered for licensing.

In order to be 100% safe from a hydrogen explosion (sources: passivation air, $CO_2$), a hydrogen removal system is installed before the $CO_2$ passivation air enters the stripper.

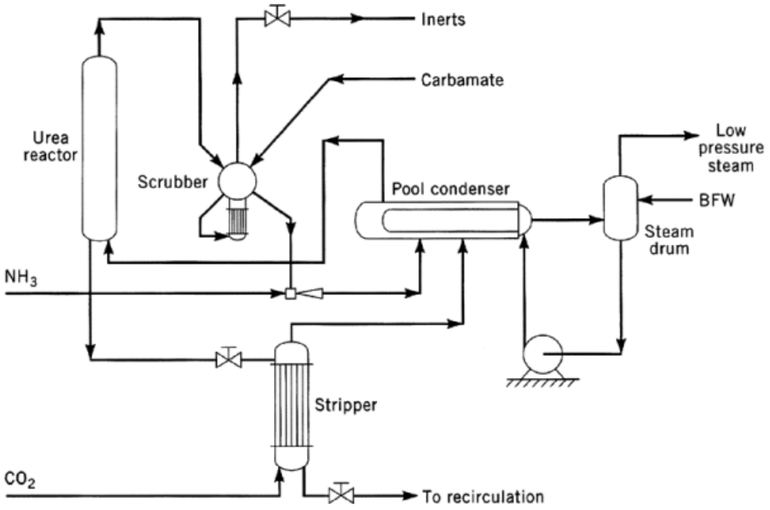


**Fig. 4.** Pool condenser type synthesis section for Stamicarbon $CO_2$ stripping process.

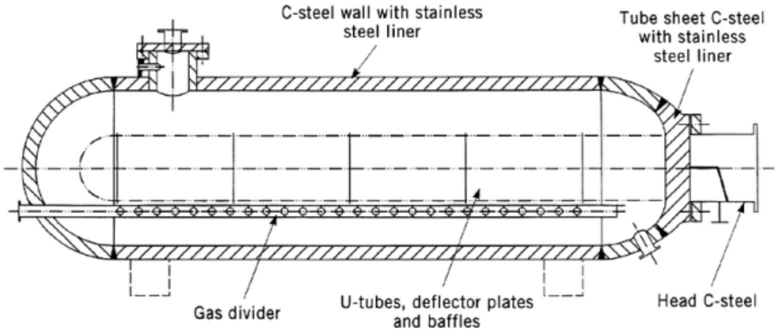


**Fig. 5.** Pool condenser vessel for Stamicarbon $CO_2$ stripping process.

### 3.3. Toyo Engineering-ACES Process

The synthesis section of the ACES process (Fig. 8) consists of a reactor, a stripper, two carbamate condensers, a scrubber and operates at 17.5 MPa (175 bars). The reactor is operated at 190°C with a $NH_3/CO_2$ ratio of 4.0 (mol/mol). Liquid $NH_3$ is fed directly into the reactor by a centrifugal ammonia pump. Gaseous $CO_2$ is sent from the centrifugal $CO_2$ compressor to the bottom section of the falling-film type stripper.

The stream from the reactor consisting of a mixture of urea, unconverted ammonium carbamate, excess water, and $NH_3$, is fed into the top of the stripper. The ACES stripper utilizes a ferrite–austenite stainless steel, as do the carbamate condensers. The reactor and scrubber are constructed with 316 L urea-grade stainless steel.

The stripper has two functions: The upper part contains trays and separates excess $NH_3$ in the feed (which ensures effective $CO_2$ stripping in the falling film type lower section). The solution then passes through the falling-film section where the ammonium carbamate is decomposed and separated by $CO_2$ stripping and steam heating. This overhead gas mixture is fed to the parallel carbamate condensers where the gaseous mixture is condensed and absorbed into the solutions from the scrubber and the 1.8 MPa (18 bar) absorber. One carbamate condenser is used to generate low pressure steam 0.45–0.5 MPa (4.5–5 bar) and the other to heat the urea

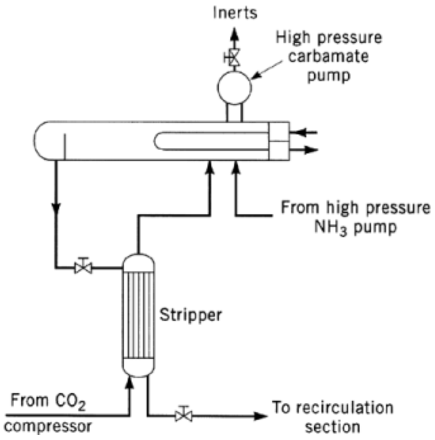


**Fig. 6.** Pool reactor synthesis section for Stamicarbon $CO_2$ stripping process.

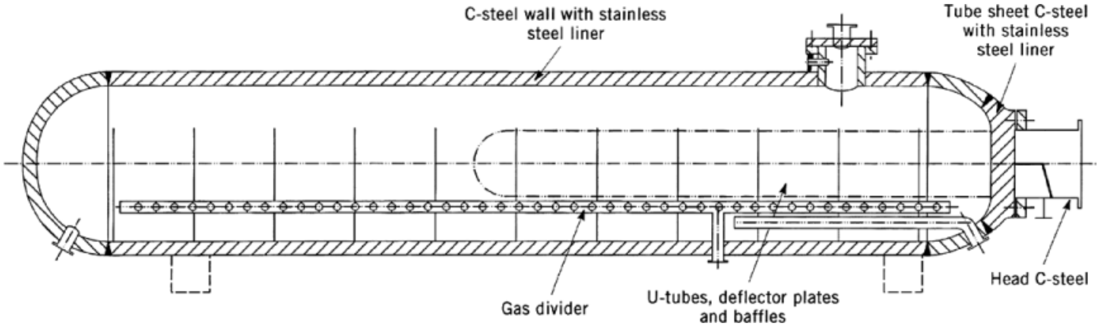


**Fig. 7.** Pool reactor vessel for Stamicarbon $CO_2$ stripping process.

solution from the stripper bottoms. The gas–liquid stream from the condenser is recycled back to the reactor by gravity flow. The inert stream from the top of the reactor is purged to the scrubber for recovery of the $NH_3$ and $CO_2$.

The urea solution leaving the stripper bottom contains about 12 wt% of $NH_3$ and is further purified in the 1.8 MPa (18 bar) and 0.2 MPa (2 bar) recovery sections of the plant. The resultant $NH_3$ and $CO_2$ separated in the decomposers is absorbed and returned to the synthesis section by the high pressure centrifugal carbamate pump.

The urea solution stream is then fed to the vacuum concentrator unit which operates at 17.3 kPa (130 mm Hg abs) and produces 88.7 wt % urea. It then goes to either two-stage evaporators if prills are made, or a single-stage unit for granule production.

As in all the processes, the process condensate and all other sources of waste urea–$NH_3$–water contamination go to a waste recovery unit which includes a urea hydrolyzer. The final water discharge is then below 3–5 ppm of $NH_3$ and urea.

### 3.4. Other Processes

Flow sheets for typical partial-recycle process and typical once-through urea process are given in Figures 9 and 10, respectively.

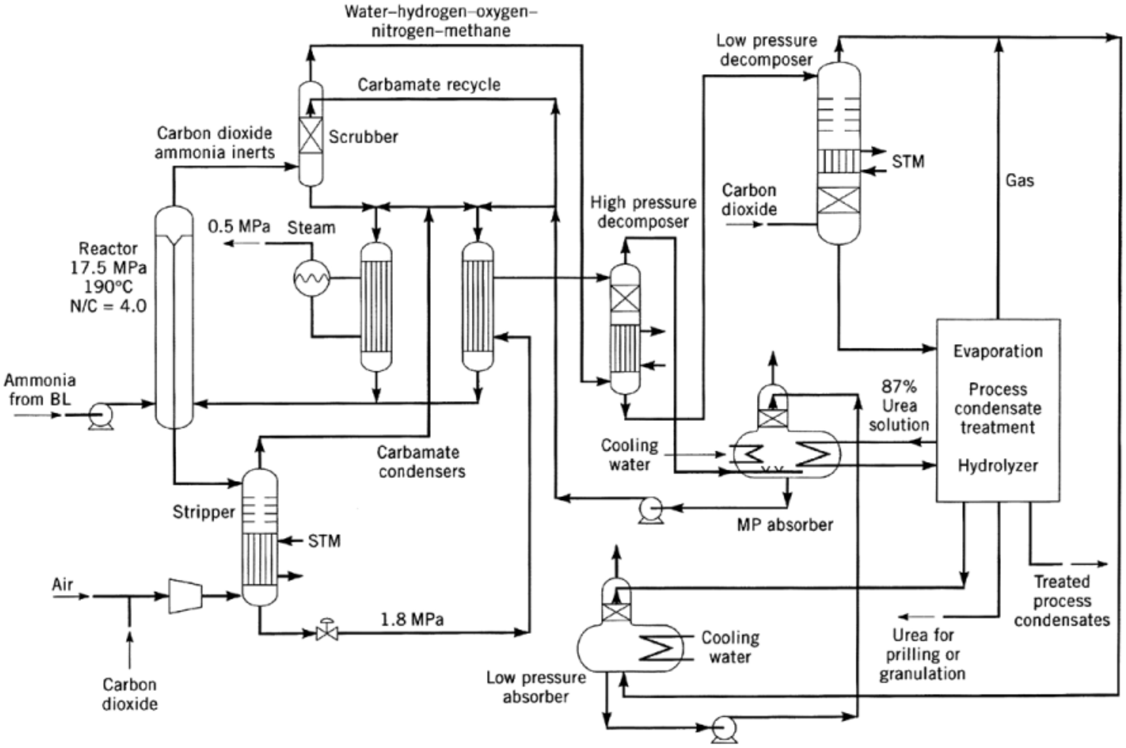


**Fig. 8.** TEC ACES process. MP = medium pressure; BL = battery limits.

## 4. Finishing Processes

Urea processes provide an aqueous solution containing 70–87% urea. This solution can be used directly for nitrogen-fertilizer suspensions or solutions such as urea–ammonium nitrate solution, which has grown in popularity recently (18). Urea solution can be concentrated by evaporation or crystallization for the preparation of granular compound fertilizers and other products. Concentrated urea is solidified in essentially pure form as prills, granules, flakes, or crystals. Solid urea can be shipped, stored, distributed, and used more economically than in solution. Furthermore, in the solid form, urea is more stable and biuret formation less likely.

### 4.1. Prilling

The manufacture of prills is rapidly decreasing owing to both environmental problems and product quality as compared to granules.

In a prilling plant the urea solution from the recovery section is evaporated in two stages to +99.8% strength. It is then pumped to the top of a 50-60m cylindrical concrete tower where it is fed into a spinning bucket containing many (+2000) small holes. The emerging small liquid droplets solidify as they fall and are cooled by a forced or induced draft air flow. The very fine dust that is formed and exits at the top of the tower with the air flow is an environmental problem. Many recovery systems have been tried (ie, water baths, dust collection, etc), but none have been very successful. The quality problem is that prill size must necessarily be small in order to obtain proper solidification and cooling in the fall height that is practical (50–60). Generally, both the crushing and impact strength of the prill is much less than for a granule. This causes many problems in

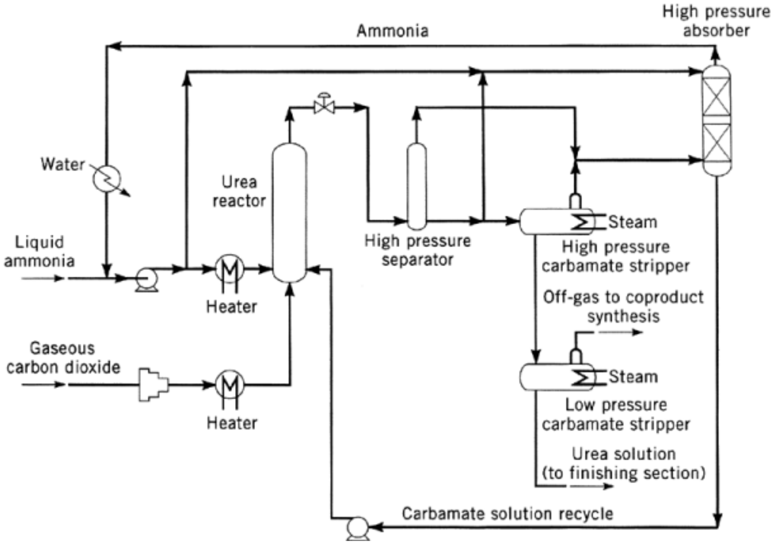


**Fig. 9.** Typical partial-recycle process.

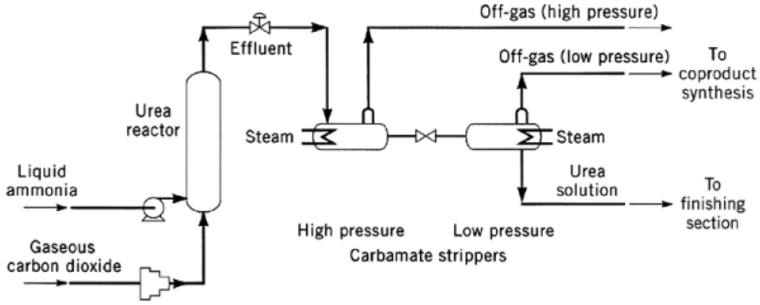


**Fig. 10.** Typical once-through urea process.

handling both at the plant and in shipping. Stamicarbon has introduced a "seeding" system that has improved prill strength. Also, formaldehyde can be added as it not only improves the crushing strength, but is suppresses the caking tendency in storage. If it were not for environmental considerations, prilling would still be a cheaper option than granulation in a small-scale marketing area (ie, not on a global scale).

### 4.2. Granulation

Almost all new plants produce granules and the Hydro-Agri process is used in the majority of plants (Fig. 11). This process was developed by NSM of Holland many years ago. They have no plant size limitation and will design a single-train unit for production over 3000 MTD. The C&I Girdler drum system has been very successful, but cannot compete in today's market because of restrictions in the train size. Toyo has successfully developed a spout-fluid technology (Figs. 12, 13, 14.) Three plants are in operation and others are in either the design or construction stage. Stamicarbon also will license a fluid-bed large-scale single-train plant that is somewhat similar to the Hydro-Agri design (Fig. 15).

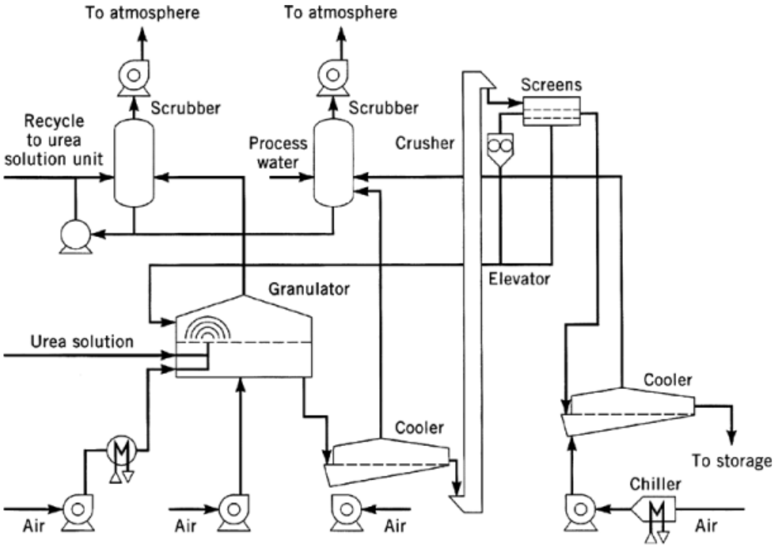


**Fig. 11.** Hydro-Agri urea granulation process.

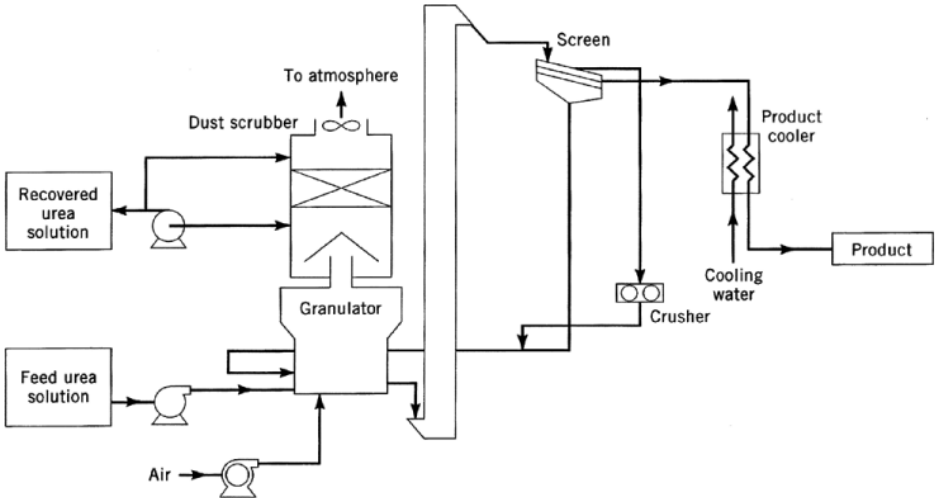


**Fig. 12.** TEC urea granulation process.

## 5. Wastewater Treatment

Under the pressure of progressively more stringent government regulations with regard to permissible levels of residual $NH_3$ and urea content in wastewaters, the fertilizer industry made an effort to improve wastewater treatment (see also Water, sewage).

For each mol of urea produced in a total-recycle urea process, one mol of water is formed. It is usually discharged from the urea concentration and evaporation section of the plant. For example, a 1200 t/d plant discharges a minimum of 360 t/d of wastewater. With a barometric condenser in the vacuum section of the

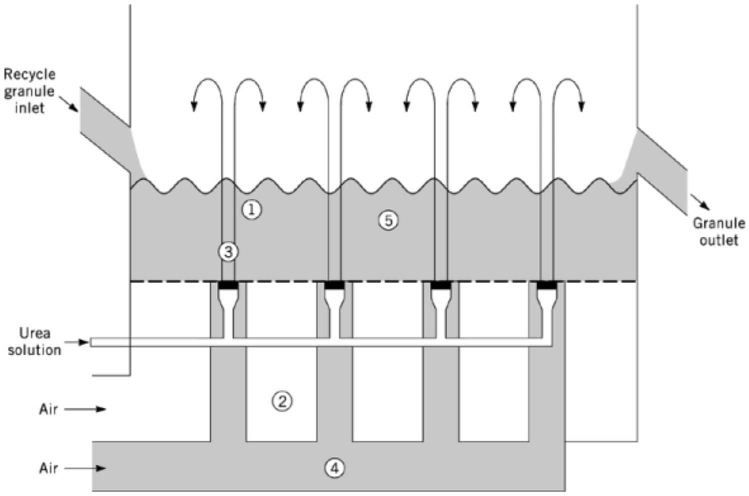


**Fig. 13.** Multistage spout-fluid-bed reactor. 1, spouted bed; 2, perforated plate; 3, spray nozzle; 4, air header; 5, fluidized bed.

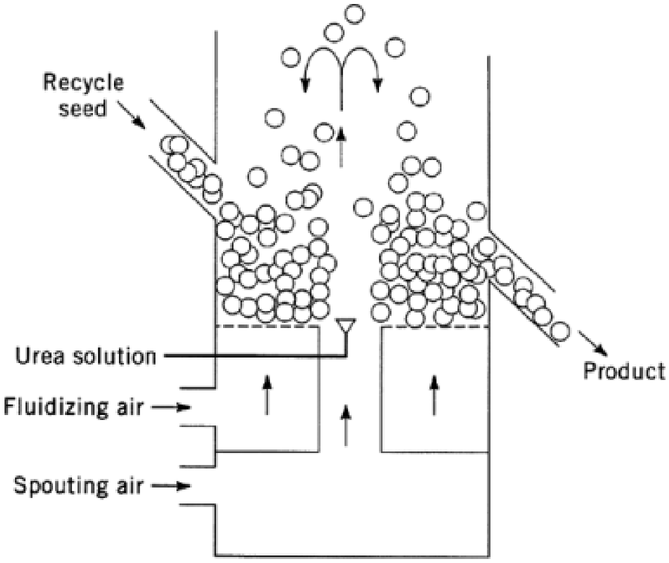


**Fig. 14.** Single spout-fluid-bed granulator.

evaporation unit, the amount of wastewater is even higher. Small amounts of urea are usually found in wastewaters because of entrainment carry-over.

The problem in reducing the $NH_3$ and urea content in the wastewaters to below 100 ppm is because it is difficult to remove one in the presence of the other. The wastewater can be treated with caustic soda to volatilize $NH_3$. However, in a more efficient method, the urea is hydrolyzed to ammonium carbamate, which is decomposed to $NH_3$ and $CO_2$; the gases are then stripped from the wastewater.

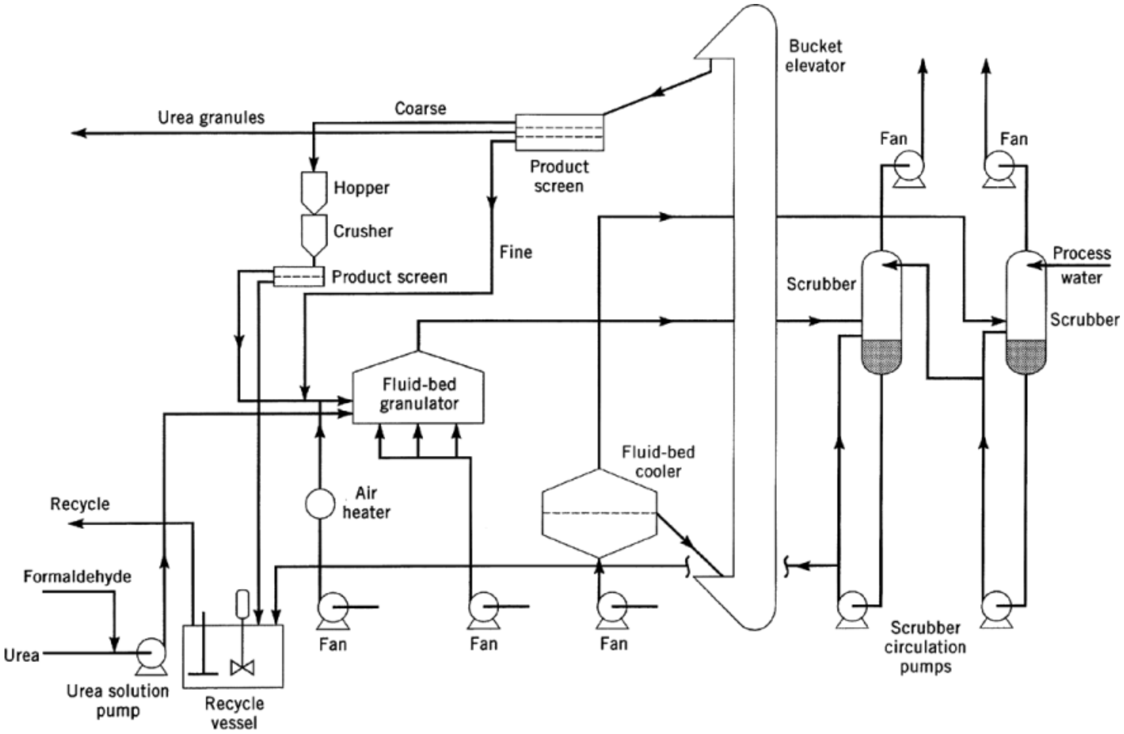


**Fig. 15.** Stamicarbon urea granulation.

All process licensors also feature wastewater treatment systems. Stamicarbon guarantees the lowest $NH_3$–urea content and has plants in operation confirming the low $NH_3$–urea (1 ppm $NH_3$–1 ppm urea). This water is very satisfactory to use as boiler feed water. See Figures 16 and 17 for this system.

## 6. Economic Aspects

The U.S. urea production from 1976 to 1980 (18, 19) is given in Table 8. During this period, urea became the most important solid nitrogen fertilizer. Urea solution production almost doubled from 1977 to 1978, proving its importance as a liquid fertilizer.

In 1980, urea consumption in other areas had declined, but not enough to detract from the overall bright future for the material, which had a total U.S. production of $7.103 \times 10^6$ metric tons in 1980 in plants with a nameplate capacity of 7.1 t. Estimated urea production in the United States for 1981 is lower than the 1980 production by ca 3%, because of a decline in exports from 1.8 t in 1980 to ca 1.45 t in 1981 (20). Nameplate capacity of urea plants in the United States and Canada is projected to be ca $9.075 \times 10^6$ t/yr by 1984 (21). World capacity should be ca $95.150 \times 10^6$ t/yr (21). World capacity increased from $27.200 \times 10^6$ t/yr in 1970 to ca $77.300 \times 10^6$ t/yr in 1980 (22).

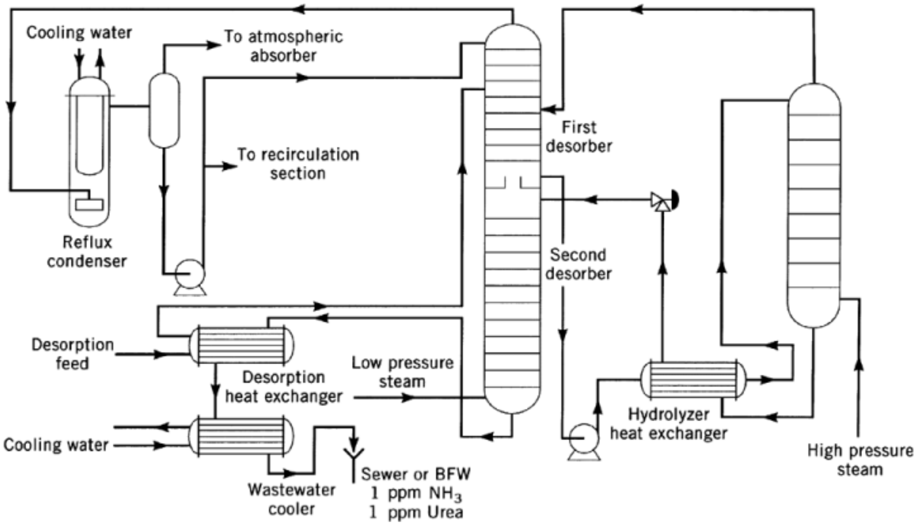


**Fig. 16.** Simplified flow sheet of wastewater treatment.

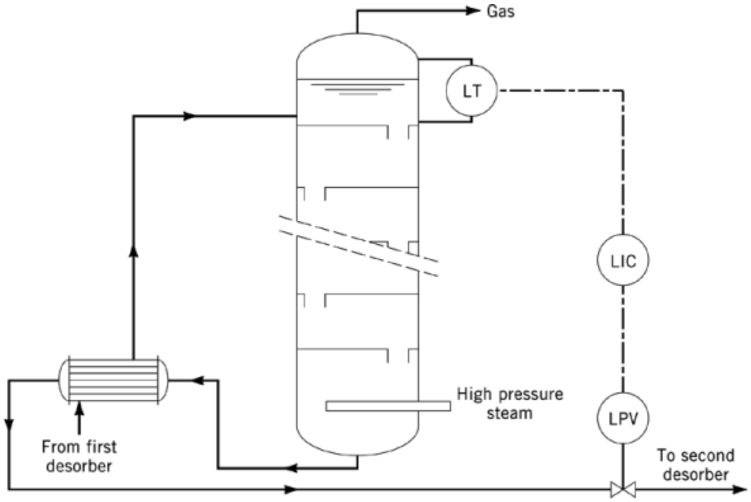


**Fig. 17.** Countercurrent hydrolyzer.

## 7. Uses

Solid urea containing 0.8–2.0 wt% biuret is primarily used for direct application to the soil as a nitrogen-release fertilizer. Weak aqueous solutions of low biuret urea (0.3 wt% biuret max) are used as plant food applied to foliage spray.

Mixed with additives, urea is used in solid fertilizers of various formulations, eg, urea–ammonium phosphate (UAP), urea–ammonium sulfate (UAS), and urea–phosphate (urea + phosphoric acid). Concentrated solutions of urea and ammonium nitrate (UAN) solutions (80–85 wt%) have a high nitrogen content but low crystallization point, suitable for easy transportation, pipeline distribution, and direct spray application.

**Table 8. U.S. Urea Production, $10^6$ t**[a]

| Year | Fertilizer |  | Other | Total |
|---|---|---|---|---|
|  | Solid | Solution |  |  |
| 1970 | 1.090 | 1.278 | 0.580 | 2.948 |
| 1974 | 1.302 | 1.221 | 0.916 | 3.439 |
| 1976[b] | 2.207 | 1.094 | 0.779 | 4.080 |
| 1977 | 2.435 | 1.337 | 0.829 | 4.601 |
| 1978 | 2.868 | 2.376 | 0.446 | 5.690 |
| 1979 | 3.888 | 1.964 | 0.498 | 6.350 |
| 1980[b] | 3.921 | 2.583 | 0.599 | 7.103 |
| 1996[c] | 5.707 | 1.982 | — | 7.689 |

[a] Refs. (18, 19).
[b] Annual growth rate $>11.5\%$
[c] U.S. capacity.

Urea is also used as feed supplement for ruminants, where it assists in the utilization of protein. Urea is one of the raw materials for urea–formaldehyde resins. Urea (with ammonia) pyrolyzes at high temperature and pressure to form melamine plastics (see also Cyanamides). Urea is used in the preparation of lysine, an amino acid widely used in poultry feed (see Amino acids; Feeds and feed additives, pet foods). It also is used in some pesticides.

Partially polymerized resins of urea are used by the textile industryto impart permanent-press properties to fabrics (see also Textiles, finishing).

The consumption of urea for urea–formaldehyde resins has decreased in recent years because of the new findings about the toxicity of formaldehyde slowly released by the resin.

Reagent-grade urea is used in some pharmaceutical preparations. In these applications, urea must meet the purity specifications issued by the ACS.

## 8. Clathrates

Urea has the remarkable property of forming crystalline complexes or adducts with straight-chain organic compounds. These crystalline complexes consist of a hollow channel, formed by the crystallized urea molecules, in which the hydrocarbon is completely occluded. Such compounds are known as clathrates. The type of hydrocarbon occluded, on the basis of its chain length, is determined by the temperature at which the clathrate is formed. This property of urea clathrates is widely used in the petroleum-refining industry for the production of jet aviation fuels (see Aviation and other gas-turbine fuels) and for dewaxing of lubricant oils (see also Petroleum, refinery processes). The clathrates are broken down by simply dissolving urea in water or in alcohol.

## BIBLIOGRAPHY

"Urea" in *ECT* 1st ed., Vol. 14, pp. 458–466, by F. A. Wolff and D. J. O'Flynn, E. I. du Pont de Nemours & Co., Inc.; "Urea" in *ECT* 2nd ed., Vol. 21, pp. 37–56, by I. Mavrovic, Consulting Engineer; "Urea" in *ECT* 3rd ed., Vol. 23, pp. 548–575, by Ivo Mavrovic, Consultant and A. Ray Shirley, Jr., Applied Chemical Technology.

## Cited Publications

1. E. Blasiak, *Technology of Nitrogen Compounds*, Vol. **2**, State Technical Publisher, Warsaw, 1956, 596–642.
2. E. Janecke, *Z. Elektrochem.* **36**, 645 (1930).
3. A. Seidell, *Solubility of Inorganic Compounds*, 2nd ed., D. Van Nostrand Co., New York.
4. D. F. Du Toit, *Proc. Koninkl. Akad. Wetenschap, Amsterdam* **16**, 555 (1913).
5. R. Escales and H. Kopke, *Chem. Zig.* **33**, 595 (1911).
6. U.S. Pat. 3,232,984 (Feb. 1, 1966), J. A. Finneran (to Pullman, Inc.).
7. U. S. Pat. 3,255,246 (June 7, 1966), (to E. I. du Pont de Nemours & Co., Inc.).
8. Knop and Hufner in A. E. Werner, ed., *Chemistry of Urea*, Longmans, Green and Co., London, 1923, p. 161.
9. C. Matignon and M. Fréjacques, *Bull. Soc. Chim. France* **29**, 21 (1921); **31**, 394 (1922).
10. T. R. Briggs and V. Migrdichian, *J. Phys. Chem.* **28**, 1121 (1924).
11. E. Briner, *J. Chim. Phys.* **4**, 267 (1906).
12. N. F. I. Isambert, *Compt. Rend.* **92**, 919 (1881).
13. F. Fichter and B. Becker, *Ber.* **44**, 3470 (1911).
14. C. Matignon and M. Fréjacques, *Bull. Soc. Chim.* **31**, 394 (1922).
15. K. K. Clark, V. L. Gaddy, and C. E. Rist, *Ind. Eng. Chem.* **25**, 1092 (1933).
16. *Eur. Chem. News* (Jan. 17, 1969).
17. S. Kawasumi, *Bull. Chem. Soc. Jpn.* **24**, 148; **25**, 227; **26**, 218; **27**.
18. J. D. Bridges, *TVA Bulletin Y-150*, 1980.
19. *Inorganic Chemicals Series M28A*, Bureau of the Census, U.S. Department of Commerce, Washington, D.C., annual reports, 1978–1980.
20. *Chem. Eng. News* **60**, 22 (1982).
21. A. R. Shirley, Jr., L. M. Nunnelly, and F. T. Carney Jr., *paper presented at 182nd National Meeting of American Chemical Society, TVA Circular Z-125*, 1981.
22. *World Fertilizer Market Information Services*, TVA, National Fertilizer Development Center, Muscle Shoals, Ala.

## General References

23. J. Meesen, “Urea” in *Ullmann’s Encyclopedia of Industrial Chemistry*, 5th ed., vol. **A27**, VCH Publishers, 1996, Chapts., 1–7.
24. Jonckers, V. Mennen, J. Meesen, and W. Lemmen, *Stamicarbon New Process Urea 2000* and *Stamicarbon, Wastewater Process*, Stamicarbon AB Geleen, The Netherlands, Feb. 1997.

IVO MAVROVIC
Consultant
A. RAY SHIRLEY JR.
Applied Chemical Technology
G. R. “BUCK” COLEMAN
Consultant

## Related Articles

Amino resins and plastics; Water, sewage