



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

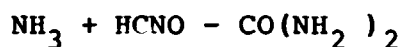
19837

CHAPTER IX UREA

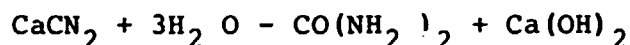
IX Urea

Introduction

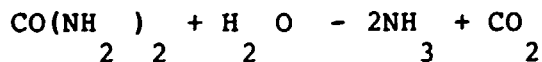
Urea was first identified in 1773 when it was isolated by crystallization from urine. It was first prepared synthetically in 1828 by Wohler from ammonia and cyanuric acid (1):



This preparation was a milestone in science since urea became the first organic compound prepared by synthesis from inorganic materials. Previously it was believed that organic compounds could be produced only by living organisms. The present method of synthesizing urea from ammonia and carbon dioxide has been known in principle since 1868, but commercial production by this method started in 1922 in Germany, in 1932 in the United States, and in 1935 in England. However, there was some commercial production in Canada (by DuPont) starting in 1920 using calcium cyanamide according to the reaction:



Use of urea as a fertilizer developed rather slowly at first, partly because early processes were cumbersome and expensive and partly because of some doubt about its agronomic suitability. Urea has been considered a slow-release fertilizer in Europe since it must undergo two transformations in the soil before it becomes available to most crops (1). The first transformation is hydrolysis:



The second transformation is nitrification in which ammonia is oxidized in the soil by microbiological means first to nitrite and then to nitrate. These reactions proceed rapidly in warm, moist soil, but they are quite slow in cool soils which are characteristic of temperate climates (northern Europe) in the spring season.

Under some circumstances urea can be phytotoxic, and many cases of severe damage to crops have occurred, especially when the urea was placed close to the seeds. These cases were mainly associated with "combine drilling," which is a common practice in some European

countries. The practice consists of drilling fertilizer with small grain seed. The phytotoxicity may be caused by locally high concentrations of ammonia during the hydrolysis stage, or it may be caused by accumulation of nitrite during the nitrification stage. A possible third cause is the presence of excessive amounts of biuret as an impurity in urea.

Aside from toxicity, poor agronomic results may be caused by loss of ammonia to the atmosphere when urea is applied on the surface of the soil or as a topdressing to growing crops. This loss is caused by the formation of ammonia by hydrolysis under such conditions that part of it escapes to the atmosphere rather than being adsorbed by the soil. A major use for straight nitrogen fertilizer in the United Kingdom and many European countries is for topdressing cereals and grass. Studies in England and the Netherlands have shown that on the average urea is only 80%-85% as effective as ammonium nitrate for this use.

For the reasons mentioned above, urea has been unpopular in most European countries, and it still finds little use in northern Europe as a straight nitrogen fertilizer. However, recent studies have shown that urea is as effective as ammonium nitrate when incorporated in the soil at or before planting time.

In the United States the general conclusion of agronomists is that urea is as good as any other nitrogen fertilizer if properly used. However, it is not recommended for some uses, such as surface application on grasslands in humid climates or in placements in contact with or near seeds.

The convenient handling characteristics of urea is a major reason accounting for its rapid development as a nitrogen fertilizer compared with ammonium nitrate or ammonium sulfate. Urea containing 46% N is more concentrated than other straight nitrogen fertilizers. Thus tonnes for tonnes, urea is more economical to transport and handle. This advantage is more apparent in developing countries which generally lack the infrastructural facilities of roads, railways and power supplies.

Urea is generally satisfactory for rice and preferable to nitrates for flooded rice since nitrates are reduced to N_2O or N_2 in the anaerobic zone of the rice paddy and hence lost to the atmosphere. Also the rice plant, unlike most other crops, can utilize the ammonium form of nitrogen efficiently. In tropical, subtropical, and warm temperate zones, the hydrolysis and nitrification (in aerobic soil conditions) are rapidly completed; thus, there is no delayed-release effect. For these reasons and because of its high

concentration and favorable production cost, it has become the most popular nitrogenous fertilizer in Asia and in many countries of other continents. An excellent discussion of the agronomic effects of urea has been presented by Tomlinson who concludes that urea can be used efficiently, but its use requires a higher degree of understanding than is the case with simple inorganic salts (2).

On a world wide basis urea is now the most popular solid nitrogen fertilizer and its use is growing rapidly. In 1987 total world production of urea was 39627 thousand metric tonnes N which had grown to 42260 thousand metric tonnes N by 1991. Urea capacity is expected to rise to 50,901,000 M.T. Nitrogen by 1996 and to 57,520,000 M.T. Nitrogen beyond 1996. Urea is very popular in Asian countries. In 1987 share of Asian countries in total world urea production was 49.7% which had grown to 53.9% by 1991 and is forecasted to reach above 59% after 1996(21).

Urea is also used as a cattle feed supplement where it may replace a part of the protein requirements. It also has numerous industrial uses, notably for production of plastics.

Properties of Urea

Some properties of urea that are of interest for fertilizer use are:

Properties of Pure Urea

Molecular weight	60.06
Nitrogen content, %	46.6
Color	white
Specific gravity	1.335
Melting point, °C	132.7
Solubility in water, parts per 100 parts of water by weight at	
0°C	66.7
20°C	108.0
40°C	167.0
60°C	251.0
80°C	400.0
100°C	733.0
Critical relative humidity at	
20°C	81%
30°C	73%
Specific heat at 20°C	0.320
Heat of solution in water (endothermic), cal/g	- 57.8

The relatively low specific gravity, compared with that of other fertilizer materials, must be taken into account

in calculating storage space requirements. For instance, storage space requirements per unit of nitrogen are about the same for urea as for ammonium nitrate since the higher analysis of urea is offset by its lower specific gravity. Urea is less hygroscopic than ammonium nitrate but more hygroscopic than ammonium sulfate; it requires protection from humid atmosphere in some climates.

Urea forms addition compounds (adducts) with many compounds; some of those frequently found in fertilizers are calcium sulfate, monocalcium phosphate, and ammonium chloride. In some cases formation of these adducts may lead to severe caking. Urea also reacts with phosphoric acid and nitric acid forming the crystalline compounds, urea phosphate and urea nitrate, respectively. Utilization of these salts as fertilizers for fertilizer intermediates has been proposed, and experimental development is in progress in several countries. However, no commercial use is known at present.

Biuret Formation -- Biuret ($\text{NH}_2 - \text{CO} - \text{NH} - \text{CO} - \text{NH}_2$)

is formed during urea synthesis and in the processing of solutions containing urea following the synthesis. Its formation during synthesis is suppressed by excess ammonia. It forms rapidly in urea melts at the usual temperature (about 140°C) used in prilling or granulating urea and at slower rates at lower temperatures in hot solutions. In most processes, biuret formation is limited by minimizing the retention time of the hot solution or melt during the evaporation and prilling or granulation steps.

Urea of very low biuret content (less than 0.25%) can be obtained by vacuum crystallization of urea solution. Less biuret is formed at the lower temperature used in vacuum crystallization, and biuret does not crystallize with the urea. Biuret that accumulates in the mother liquor is disposed of by drawing off a sidestream of the liquor which is returned to the urea synthesis unit where it is reconverted to urea.

Crystalline urea can be dissolved and used for foliar application or melted and prilled or granulated. Some biuret is formed during melting, but prills containing 0.3% or less of biuret can be produced. In the usual evaporation-prilling method, the product commonly contains about 1% biuret. Plant constructors usually will guarantee less than 1% biuret, but with variations in plant operation a range of 0.8% to 2.0% is common.

For most urea fertilizer uses, biuret content up to 2% is of no consequence; it decomposes in the soil and its nitrogen content becomes available to plants (4). However, if urea is placed in contact with the seed or near it, crop damage due to biuret may result. This type of

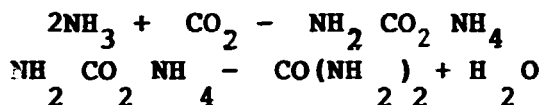
placement can cause damage even with pure urea (or other concentrated fertilizers), but the high-biuret urea (more than 1%) is more toxic than low-biuret urea.

Biuret is toxic to citrus plants and some other crops when applied as a foliar spray. For foliar application on citrus crops, urea containing less than 0.25% biuret is preferred. For other crops sensitivity to biuret in foliar sprays varies widely; solutions made from urea containing 1.5% biuret were considered acceptable for foliar application to maize or soybeans (5).

Biuret is preferred to urea for use in cattle feed as a protein substitute. Processes are under study for recovering biuret from urea production as a profitable by product.

Production Processes

All commercial production of urea is from carbon dioxide and ammonia. The carbon dioxide is obtained as a by product from ammonia production. The reaction proceeds in two steps: (1) formation of ammonium carbamate and (2) dehydration of ammonium carbamate.



The first reaction is highly exothermic (37.7 kcal/g-mole) while the second reaction is moderately endothermic (-7.7 kcal/g-mole). The first reaction is slow at atmospheric pressure, but at the elevated pressures used in practice it is practically instantaneous (1). The second reaction does not go to completion; it approaches equilibrium at a rate which depends on temperature and pressure. A summary of the effects of the main variables follows.

Operating Variables

Temperature -- Conversion of ammonium carbamate to urea in the absence of excess ammonia increases with temperature to a maximum of about 50% at 170°-190°C when the pressure is sufficiently high to keep the reactants in the liquid state. The rate of reaction increases with temperature; it is slow at 150°C and below (with stoichiometric NH₃ : CO₂ ratio) and quite rapid at 210°C. A satisfactory approach to equilibrium can be obtained in the temperature range of 180°-200°C in 0.3-1.0 hours or at lower temperatures with excess ammonia. Corrosion difficulties increase with temperature, and a range of 180°-210°C is generally accepted as optimum for most processes.

Pressure --At constant temperature, conversion increases with pressure up to the critical point which is the point at which the vapor phase is substantially eliminated and the reactants are in the liquid state. Further increase in pressure is not beneficial. The critical temperature is a complex function of the temperature and composition of the reactor contents. For example, at 150°C a pressure of about 100 atm might be near optimum for a stoichiometric $\text{NH}_3 : \text{CO}_2$ ratio, but at this temperature the rate of reaction is unacceptably slow. At the preferred temperature of 180°-210°C, pressures of 140-250 atm are commonly used.

Mole Ratio of $\text{NH}_3:\text{CO}_2$ -- Excess NH_3 above the stoichiometric mole ratio of 2 favors the rate of the reaction. The percentage of CO_2 converted to urea is increased but, of course, the percentage of NH_3 converted to urea is decreased. Since recycling of excess NH_3 is relatively simple (as compared with CO_2 which remains as carbamate), most processes use 50% or more excess ammonia (a mole ratio of 3:1 or more).

Other Factors --- The presence of water decreases conversion; therefore, most processes are designed to minimize the amount of water recycled to the reactor. The presence of small amounts of oxygen (air) decreases corrosion; many processes use this method of minimizing corrosion.

Optimum Conditions --- It is generally not economical to maximize the percentage conversion in the reactor since this would require an excessive retention time. The aim therefore is to attain maximum quantity of urea production per unit of time with due regard to the cost of recycling unreacted CO_2 and NH_3 as well as the cost of increased reactor size and corrosion difficulties which increase with temperature. Typical operating conditions are: temperature, 180°-210°C; pressure, 140-250 atm; NH_3 CO_2 mole ratio, 3:1 - 4:1; and retention time, 20-30 minutes.

Once Through and Partial-Recycle Processes

Most new plants now use total-recycle processes. However, once-through or partial-recycle processes have been popular in some countries and in some cases may still be preferred.

The once-through method is the simplest and least expensive (in both capital investment and operating costs) of the three basic types of processes. A typical unit flowsheet (synthesis section only) is given in figure 1. Liquid ammonia and gaseous carbon dioxide are pumped into the urea reactor

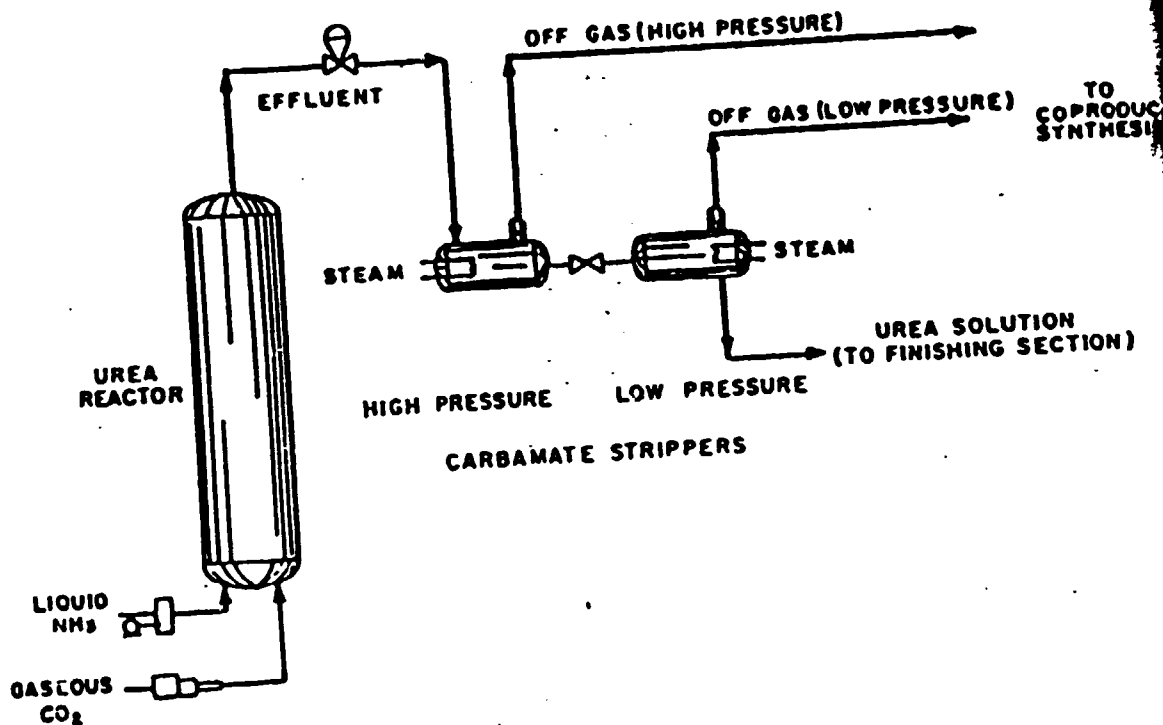


Figure 1. Typical Once-Through Urea Process.

at about 200 atm. The reactor temperature is maintained at about 185°C by regulating the amount of excess ammonia; about 100% excess NH_3 is required, and about 35% of the total NH_3 is converted to urea (75% of CO_2 is converted). The reactor effluent solution contains about 80% urea after carbamate stripping. The unconverted NH_3 and CO_2 are driven off at moderate pressures by steam heating the effluent solution in the carbamate strippers.

While this process is the simplest of the urea processes, it is the least flexible and cannot be operated unless some provision is made to utilize the large amount of off-gas ammonia. It is thus tied to the coproduction of some other material, e.g., ammonium sulfate, ammonium nitrate, nitric acid, or ammonium phosphate, for which the ammonia can be used. One case in which the system can be used is the production of urea-ammonium nitrate solution; the unconverted NH_3 is used to make ammonium nitrate solution which is then mixed with the urea solution. Even in this case, most new plants use a total-recycle process.

In the partial-recycle process, part of the off-gas ammonia and carbon dioxide from the carbamate strippers is recycled to the urea reactor. Recycling is accomplished by absorbing the stripper gases in a recycle stream of partially stripped urea effluent, in process-steam condensate, or in mother liquor from a crystallization finishing process. In this manner, the amount of NH_3 in off gas is reduced. Any proportion of the unreacted ammonia can be recycled; typically, the amount of ammonia that must be used in some other process is reduced to about 15% of that from a comparable once-through unit.

The Mitsui Toatsu partial-recycle process flowsheet is typical of the first method and is shown in figure 2. Liquid NH_3 and gaseous CO_2 are pumped to the urea reactor at 200 atm. The temperature of the reactor is maintained at about 185°C by proper balance of excess NH_3 and carbamate solution recycle feed. About 100%-110% excess NH_3 is used; about 70% of the NH_3 and 87% of the CO_2 are converted to urea. The remaining 30% of the NH_3 must be used in some other process. The reactor effluent contains about 80% urea.

Unreacted NH_3 and CO_2 are separated from the urea solution in the high-pressure separator and in two to three steam-heated carbamate strippers at successively lower pressures. The offgas from the separator and the first-stage stripper is absorbed in the high-pressure absorber by a side stream of partially stripped reactor effluent from the high-pressure separator. Heat evolved in the absorber reaction is removed (to increase absorption capacity) by the addition and expansion of part of the liquid ammonia feed at this point. Pure gaseous ammonia from the top of the absorber is also recycled to the urea reactor after being condensed.

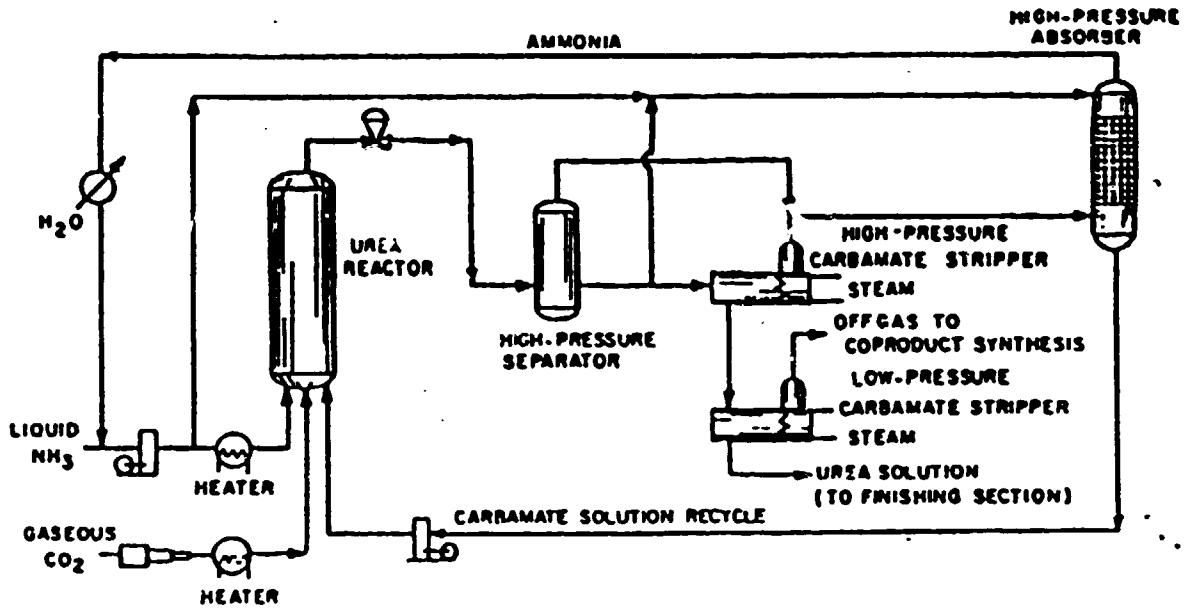


Figure 2. Typical Partial-Recycle Process.

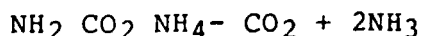
Since the amount of ammonium carbamate which can be absorbed in the absorber solution described above is limited by its solubility in the system H_2O - urea - NH_3 , part of the ammonia and carbon dioxide cannot be recycled and must be used in the production of a coproduct nitrogen material. As in the once-through process, the operation of the urea plant still must coincide with that of the coproduct plant.

Other partial-recycle processes differ in detail but accomplish similar results. There is little interest in such processes at present. While the investment cost is somewhat lower than that for total recycle, this advantage apparently does not compensate for the inflexibility arising from the necessity of operating a coproduct plant with mutual interdependency problems.

Total-Recycle Processes

In total-recycle processes, all the unconverted ammonia-carbon dioxide mixture is recycled to the urea reactor (conversion is about 99%), and no nitrogen coproduct is necessary. This is the most flexible of the urea processes because it depends only upon the CO_2 and NH_3 supply from its supporting ammonia plant for operation. However, it is also the most expensive in investment and operating costs. Therefore, if the production of other materials requiring ammonia is planned, an integrated once-through or partial-recycle unit would have lower investment and perhaps lower operating costs. The disadvantages are decreased reliability arising from mutual dependence of two plants, inflexibility in proportions of coproducts, and difficulties in synchronizing the operation of two plants. Because of these difficulties, most manufacturers prefer a total recycle process, even when second nitrogen product is desired.

The urea reactor effluent contains urea and water resulting from the synthesis reaction; it also contains unconverted carbamate and excess ammonia. These ingredients must be separated to give a urea solution reasonably free from the other materials and to recycle the CO_2 and NH_3 to the synthesis reactor. In order to separate carbamate from urea, it must be decomposed according to the equation:



This reaction is the reverse of the first step of the synthesis process and is strongly endothermic (37.7 kcal/g-mole). The decomposition is accomplished by various combinations of supplying heat, lowering pressure, and "stripping" which lowers the partial pressure of one or more ingredients. The NH_3 and CO_2 are removed from the urea solution as gases accompanied by some of the water in vapor form. Naturally the CO_2 and NH_3 will recombine (releasing heat) when the temperature is decreased or the pressure increased. Hence, condensing by cooling and/or compressing a gaseous mixture of CO_2 , NH_3 , and H_2O produces a carbamate solution.

Total-recycle processes can be classified in five groups according to the recycle principle: (1) hot-gas mixture recycle, (2) separated-gas recycle, (3) slurry-recycle, (4) carbamate-solution recycle, and (5) stripping. The first four groups use carbamate decomposition steps basically similar to those of the once-through and partial-recycle processes; whereas, the last one differs even in this respect.

Hot-gas recycle of mixed CO_2 , NH_3 , and H_2O has been used in Germany between the two World Wars by I.G. Farbenindustrie at Oppau. The hot gas was compressed in five stages by reciprocating compressors with interstage cooling to an end temperature of $260^\circ\text{--}270^\circ\text{C}$ and a pressure of 120-130 atm. It was then cooled to 160°C to condense the gases (with carbamate formation), and the heat was recovered as steam. The process was not very successful; when the plant was destroyed during the last war, it was not rebuilt. The idea was revived by Chemical Construction Company with the proposal that the compression be done with large centrifugal compressors that became available in the 1960s using new materials of construction that can operate at high temperature ($400^\circ\text{--}540^\circ\text{C}$) without interstage cooling. The proposed process seems technically sound, but centrifugal compressors of this sort are feasible only in such large sizes that the minimum scale would involve a urea plant of about 1,200 - tpd capacity. No organization has been willing to risk using the untried process on such a large scale.

The separate-gas recycle method was developed to overcome the difficulties of the mixed hot gas recycle process. The CO_2 and NH_3 can be compressed separately without difficulties caused by carbamate formation. Processes of this type were developed by Inventa (Switzerland) and CPI-Allied (United States). The principle of the processes is that CO_2 in the gas mixture from the decomposers is absorbed selectively in a solvent such as monoethanolamine (MEA). The NH_3 remaining after CO_2 removal is compressed and recycled to the synthesis reactor. The CO_2 is desorbed from the MEA solvent by heating, and it is recycled separately (6).

The process has the advantage that conversion is not reduced by recycling water to the reactor and that the problem of recycling corrosive solution to the reactor is avoided. Offsetting this is the difficulty in recovering heat and cost of MEA makeup. The number of plants using the method is relatively small, and it is not known to be in use in any of the large plants (1,000 tpd and up) built in recent years.

The principle of the slurry-recycle process is that the $\text{CO}_2\text{--NH}_3\text{--H}_2\text{O}$ gas mixture goes to a reactor where a light paraffin oil is added. Carbamate is formed in the reactor as a suspension in oil. This suspension containing 35%-40% solids is pumped into the urea synthesis unit together with fresh

CO₂ and NH₃. The mixture then goes through the carbamate decomposers, and the oil is separated from the urea solution by decantation for reuse. The process was developed by Pechiney (France) and has been used by that organization.

In carbamate-solution-recycle process advantage is taken of ammonium carbamate solubility in water to recycle with water the reagents not transformed into urea. These solution-recycle processes are generally referred to as "Conventional" processes. These processes gained popularity in 1960's and 1970's. General proprietary processes were developed by Stamicarbon, Mitsui Toatsu, Montedison, Snamprogetti etc. These processes differ mainly in engineering details, methods of heat recovery and means of energy conservation. In general, all solution-recycle processes involve absorbing CO₂ and NH₃ in water and recycling it to the synthesis step as an aqueous carbamate solution. The amount of water must be kept to a minimum, however, because addition of water lowers the percentage of conversion to urea. Also the evaporation of additional water has a negative impact on the economy of the process.

Originally there was considerable variation in the design features of the various solution-recycle processes, these differences gradually disappeared and most of the "Conventional" processes became much the same.

All use similar reactor conditions (temperature about 185°C and pressure about 200 atm), maintain an NH₃ : CO₂ mole ratio of about 4:1 in the synthesis loop, and get about the same conversion (65%-67%) of CO₂ to urea for each pass through the synthesis reactor. Overall conversion of NH₃ to urea is 99% or more. All reduce the reactor effluent pressure to an intermediate level and then pass the solution through two or three stages of decomposition (by heating) at successively lower pressure levels. In each stage, the evolved gas mixture is condensed (or absorbed in weak solution condensed in a later stage), and the resulting solutions are worked back through the system to the reactor. The excess ammonia (from the excess used in the initial reactor feed) passes through the absorbers, is condensed, and is fed back to the reactor.

Although these major steps are common to the various conventional methods, there is considerable difference in the carbamate solution-recycle systems in pressure and temperature levels of the decomposition steps, equipment arrangement, and process flow. The general design objectives are to:

1. Maximize heat recovery.
2. Minimize amount of carbamate solution recycled (smaller pumps and less power) and amount of water returned to the reactor (better conversion).
3. Minimize power requirement.
4. Maximize ammonia recovery (lower operating cost and less pollution).

Since another major objective, of course, is to minimize investment, the problem becomes the usual one of finding the best balance between utility consumption and maintenance on the one hand and investment on the other.

Several parameters are involved in design of the carbamate-solution-recycle system, and they are so interrelated and interdependent that it is difficult to analyze them separately. Changing one parameter in the direction of improvement almost always changes one or more of the others in an adverse direction, and the extent of the adverse effect can only be determined by somewhat complicated calculations. Hence, it is difficult to evaluate quantitatively the various schemes that have been developed.

One important consideration is the number of decomposition stages. Reducing the number lowers plant investment but increases the amount of water returned to the reactor, makes heat recovery less attractive (decomposer pressures generally lower), and results in higher ammonia loss in gaseous or liquid effluents.

Three decomposition stages are generally considered as optimum number. The third stage generally involves both decomposition of carbamate and evaporation of water, with vacuum applied to remove the ammonia down to a very low level as a means of minimizing atmospheric pollution. The flashed gas is passed through a water-cooled condenser, the condensate stripped of ammonia, and the stripped condensate preferably discarded rather than returned to the reactor. Such a procedure gives only traces of ammonia in the gaseous and aqueous effluents.

The point of heat recovery also varies. The main source of heat in the system is carbamate formation in the reactor. In some past designs, recovery or removal of heat directly from the reactor was practiced by water coils in the reactor or a cooling jacket outside. In later designs recycled ammonia and carbamate solution took up the reaction heat and carried it out of the reaction zone.

In the decomposition section, heat must be added in order to get an adequate rate of carbamate decomposition. Much of this is heat released when the evolved gases are recondensed, and it is at this point that heat is usually recovered. The recovery is limited to the first decomposition stage, however, because the gases are at so low a pressure in the later stages that condensation temperature is too low for economical recovery of the heat.

Thus, the usual source for heat recovery is hot condensed liquor from the first-stage absorber. Practice varies as to the stream used to absorb this heat. In some cases, water is heated and steam is produced; in other published flowsheets a process stream is involved.

Gas release procedure can have an important effect on the amount of water recycled to the reactor. The simplest arrangement-merely releasing pressure, flowing the solution into a vessel, heating it, and allowing the evolved gases to escape-is relatively inefficient because it gives maximum evaporation of water. Two systems have evolved, both of which minimize water evaporation. The first involves a sequence, in each stage, of (1) pressure reduction, (2) gas release, (3) heating, and (4) further gas release. The advantage is that gas which can be evolved by release of pressure alone comes off at lower temperature than than heated decomposer. The partial-pressure relationships involved are such that this procedure gives less evaporation of water.

In the second system a rectifying column is used as the decomposer; relatively cold incoming solution flows downward in countercurrent flow to the hotter gas evolved in a heated section (or reboiler) at the bottom. Thus, the composition of gas leaving the column approaches equilibrium with the incoming solution, which has a relatively low partial pressure of water because of the reduced temperature.

Both systems are used, but there seems to be a trend toward the rectifying column type. Heaters on the main flow line are preferred by some, however, because of the rapid heat transfer at the high flow rate.

Because of the large number of processes offered and frequent changes in flowsheets, it is not feasible to show flow diagrams for all processes. Figure 3 shows a flow diagram for the Mitsui Toatus total-recycle process(Process C). No implication is intended that this process is necessarily superior to others.

In the late 1960s, the only really revolutionary development in urea manufacturing processes occurred, with the advent of stripping technology. In essence, stripping technology is based on the principle that carbamate can be decomposed without lowering the total pressure of the system, so long as the partial pressure of one of its decomposition products-ammonia or carbon dioxide-is lowered. This can be done by sweeping the carbamate decomposer with a large volume of another gas, but in practice the gas used is either ammonia or carbon dioxide.

In stripping processes, the bulk of carbamate decomposition can thus take place at the same pressure as the synthesis reaction and, moreover, heat of reaction can be recovered at higher temperature in the carbamate condenser circuit. However, the synthesis reaction is run at lower pressure because stripping efficiency drops off at higher pressure. The real appeal of stripping technology, however, was its relative simplicity in comparison with the conventional total recycle approach.

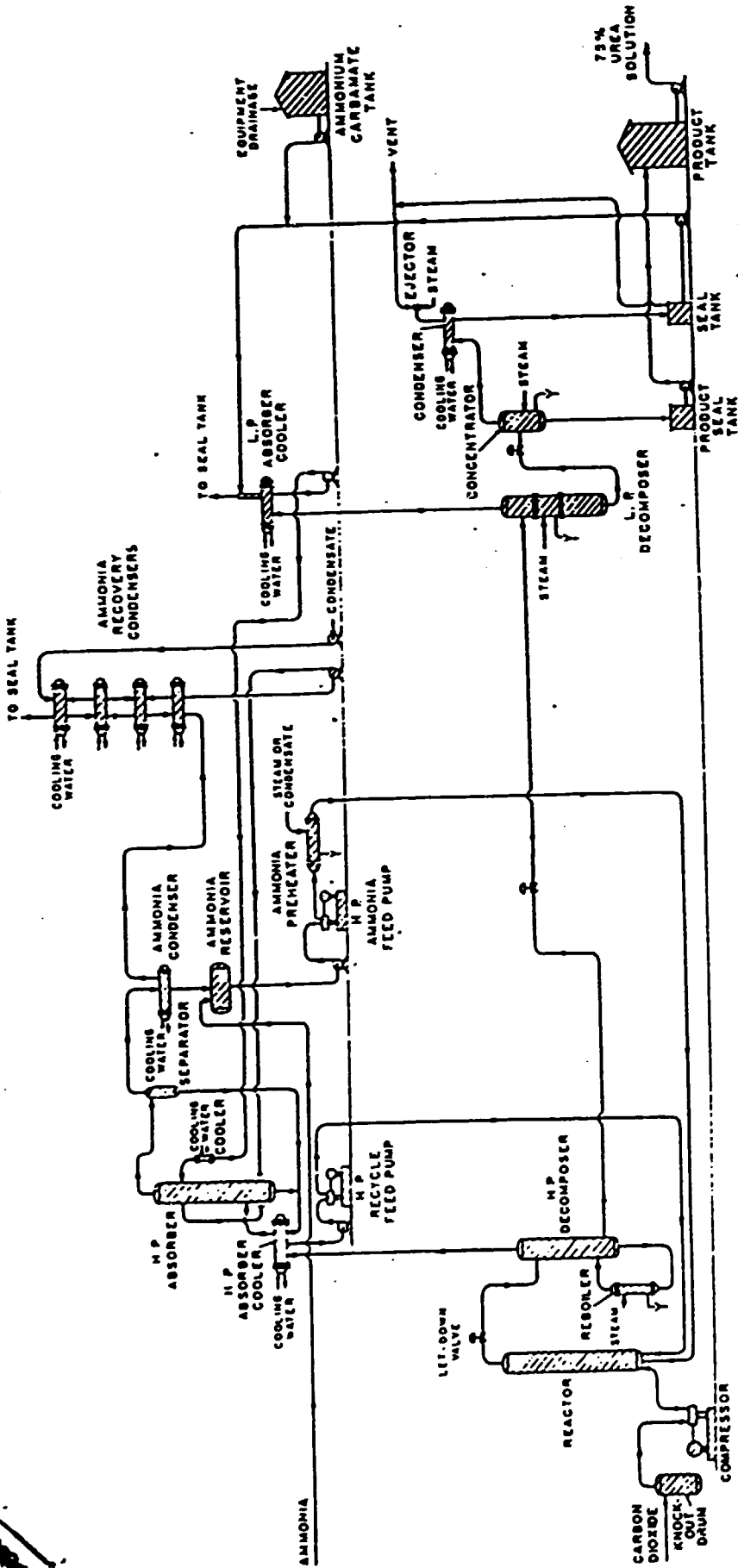


Figure 3 Typical Total-Recycle Urea Process (TVA Plant).

The Dutch State Mines developed a stripping process using CO₂ as the stripping agent, starting with a 20-tpd pilot plant in 1964. The process is available through Stamicarbon and numerous licensees and is widely used. It is generally known as the Stamicarbon stripping process.

Kaasenbrood and Chermin have described the process in a paper which also explains the complicated thermodynamics and phase equilibria that are involved (7). The stripping operation is best explained with the help of figure 4, which shows the four units comprising the synthesis section. The urea reactor is operated at a pressure of about 140 atm and a temperature of 180°-195°C with an NH₃ : CO₂ mole ratio of about 2.8 (40% excess NH₃). The solution from the reactor flows by gravity to the stripper. As in all urea synthesis processes, the solution contains urea, carbamate, excess ammonia, and water. The stripper resembles a falling-film evaporator; it contains parallel tubes externally heated by steam. The steam supplies the heat which is absorbed by decomposition of carbamate; the solution temperature is maintained in the range of 180°-190°C. The solution flows as a film down the interior walls of the tubes. All of the CO₂ required in the process enters the bottom of the stripper and flows upward through the tubes countercurrent to the solution. A small amount of air is added to the CO₂ to inhibit corrosion. The amount of air should be sufficient to give a concentration of at least 5 ppm of oxygen in the synthesis loop. The gas stream plus NH₃ and CO₂ that has been stripped from the solution, flows to the condenser. The stripped solution, which contains urea and water plus a relatively small amount of carbamate, flows to another section of the plant (described later) for further treatment. The gas stream from the stripper enters the top of the condenser together with the NH₃ input for the system. The condenser also receives a stream of recycled carbamate solution and a relatively small sidestream of solution directly from the reactor which provides enough solvent to prevent deposition of solid carbamate. The mixture flows downwardly through the condenser which contains a series of sieve plates to prevent back mixing. The reactor is cooled by water (generating steam at 4-5 atm) which removes the heat released by carbamate formation and condensation.

Condensation is only partially completed in the condenser; the mixture flows to the bottom of the reactor and upwardly through the reactor where carbamate formation is completed and conversion of carbamate to urea takes place. The reactor solution then goes to the stripper; the cycle is completed.

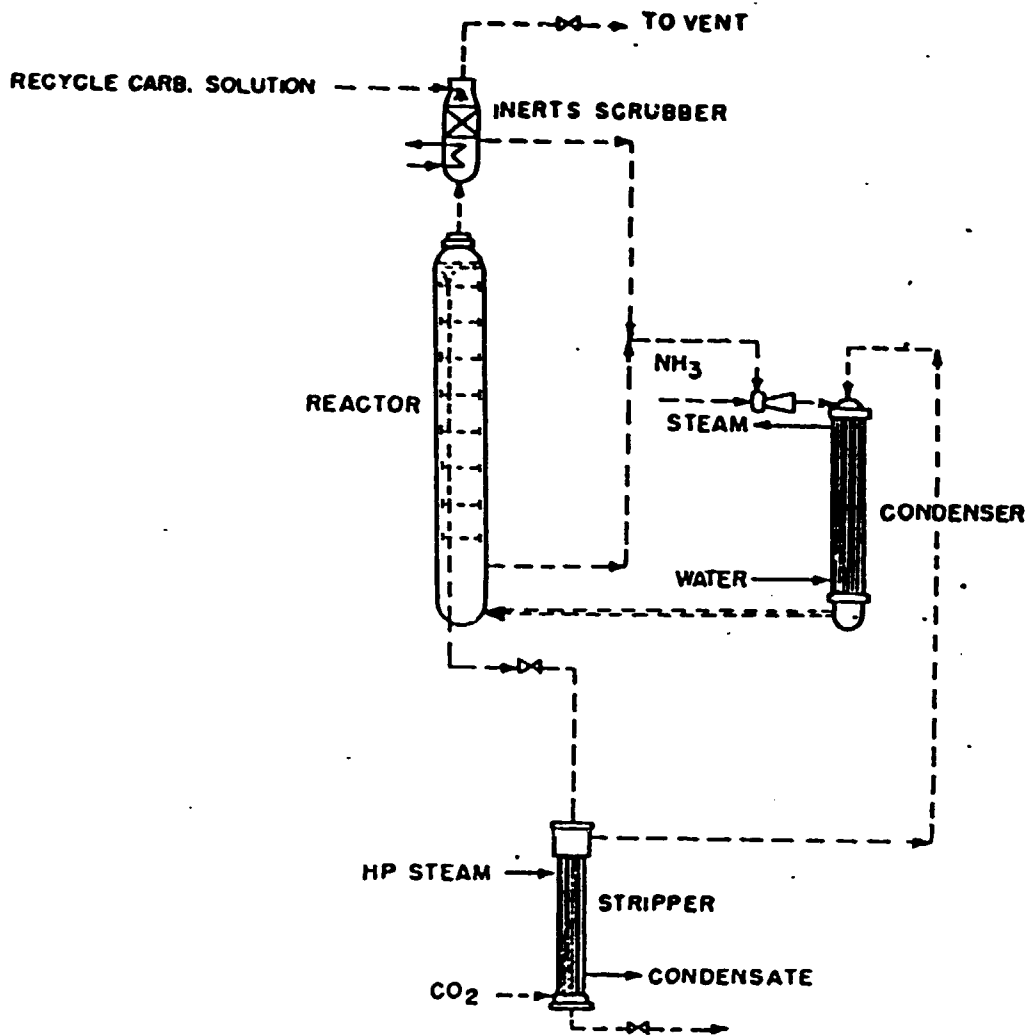


Figure 4. Synthesis Section of Stamicarbon CO₂ Stripping Process.

Small amounts of gases accumulate in the top of the urea reactor. The gases consist of air that was added for corrosion control plus H_2 and N_2 dissolved in liquid ammonia and minor impurities in the CO_2 . The gases are vented through a high-pressure scrubber where they are washed with carbamate solution to recover most of the NH_3 and CO_2 and then vented to a low-pressure washing column (not shown in figure 4).

The basic flow diagram of the entire process is shown in figure 5. The urea solution leaves the synthesis section through an expansion valve at $160^\circ C$; it is first treated at an intermediate pressure (about 2.5 atm) in a rectification column and a heater and a separator to remove most of the remaining carbamate as CO_2 and NH_3 . The solution pressure is then reduced to atmospheric pressure for final purification. The NH_3 and CO_2 recovered in these steps are condensed to form a carbamate solution which is recycled to the synthesis section.

Most of the equipment is made of low-carbon stainless steel of the 316 or 317 type containing 17%, 12%, and 2% or 17%, 13%, and 4%, Cr, Ni, and Mo, respectively. However, corrosion conditions are particularly severe in the stripper, and a 25-22-2 alloy is preferred for this equipment. For some processes, titanium-lined stainless steel vessel is used for the synthesis step.

The advantages of the stripping process are lower net energy consumption (steam and electricity), somewhat lower investment cost, and reduced maintenance requirements. Energy saving results from doing most of the recycling at synthesis pressure thereby avoiding recompression of reactants. The pumps for recycling hot, concentrated carbamate solution are a major source of maintenance in "conventional" processes, but they are not required in the stripping process.

Shortly after stamcarb's introduction of the CO_2 stripping process, Snamprogetti launched its ammonia stripping technology. In this process stripping gas is ammonia and carbon dioxide is introduced directly into the synthesis reactor. The route is also distinguished by the use of two-stage carbamate decomposition, the first operating at 17 kg/cm^2g and the second at 3.5 kg/cm^2g . The synthesis conditions are maintained at $185-190^\circ C$ and 155-166 Atm. Ammonia coming from M.P. section is raised to 210 kg/cm^2g and is used as driving fluid in carbamate ejector where the recycled carbamate is compressed up to synthesis pressure. The reaction products leaving the reactor flow to the steam heated falling film stripper which operates at 150 kg/cm^2g . The carbon dioxide in the solution is reduced by stripping action of ammonia which in fact boils out of the solution. Overhead gases from the high pressure stripper and the recovered solution from the medium pressure absorber all flow to high pressure carbamate condenser. Condensing the gases

- 1. REACTOR
- 2. STRIPPER
- 3. CONDENSER
- 4. EXPANSION VALVE
- 5. RECTIFYING COLUMN
- 6. SEPARATOR
- 7. CARBAMATE PUMP
- 8. CONDENSER
- 9. DESORBER, HYDROLYZING SYSTEM
- 10. UREA MELT PUMP

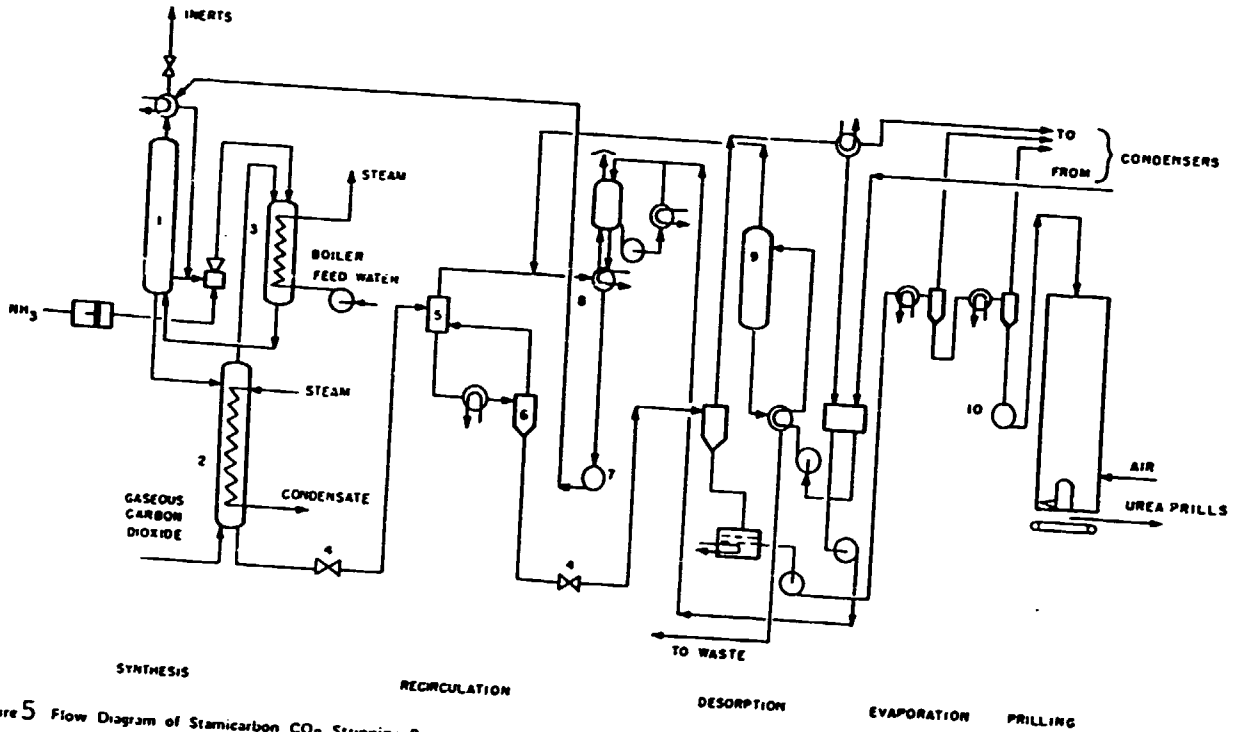


Figure 5 Flow Diagram of Stamicarbon CO₂ Stripping Process.

at high pressure and temperature permits the production of steam at 5.0 and 3.5 kg/cm²g. The solution leaving the bottom of the stripper is decomposed in two stages at 17 kg/cm²g and 3.5 as shown in figure 6. Energy requirement per metric ton of prilled urea produced through ammonia stripping route are, electric power 20.5 KWH, saturated steam (23 Ata) 650Kg, circulating cooling water 60M³ while recovery of low pressure steam at 4.5 Ata is 150 Kg (22).

New generation processes

At one time it appeared that by virtue of their simplicity and effectiveness, stripping processes might eventually eclipse the outmoded total recycle concept entirely. They certainly have been tremendously successful but protagonists of the conventional total recycle technology, most notably Montedison, Toyo Engineering Corporation and Urea Technology Inc. (UTI) have continued to develop process improvements right up to the present. Most new -generation urea processes combine the best features of both conventional and stripping processes. One example of this is the ACES (Advanced Process for Cost and Energy, process offered by Toyo Engineering (23).

In the ACES process (Fig.7) the reactor operates at relatively high pressure, 170 bar and 190°C, and at the high NH₃ : CO₂ ratio of 4:1. In this way, conversion per pass of 68% is obtained in a short residence time, because of a specially designed reactor with baffleplates to prevent back-mixing of the synthesis solution.

The two-tier stripper is flushed with carbon dioxide feed gas at the synthesis pressure. In the upper part, vapours from the lower section strip out part of the ammonia excess, reducing the NH₃ : CO₂ ratio to about 3:1, while in the lower part, falling-film evaporation decomposes the carbamate and flashes off the remaining excess of ammonia. High-pressure and low-pressure decomposers remove further carbamate from the urea solution before it undergoes final evaporation and conversion to a solid form.

In Montedison's² IDR (Isobaric Double Recycle) process, there are two strippers, one fed with ammonia as the stripping gas and the other with carbon dioxide. The synthesis reactor operates at 185-190°C and 180-200 bar with an NH₃ : CO₂ ratio of 4, giving a per-pass conversion of around 70%.

The strippers are heated with 25-bar steam raised from the heat of reaction. In the first stripper, the sweep gas is ammonia, ensuring that virtually all the carbon dioxide in the decomposition vapours are removed. Remaining ammonia is removed in the second stripper, which is swept with carbon dioxide. The two gas streams from the strippers are recycled separately to the reactor isobarically, requiring no energy in the form of applied pressure.

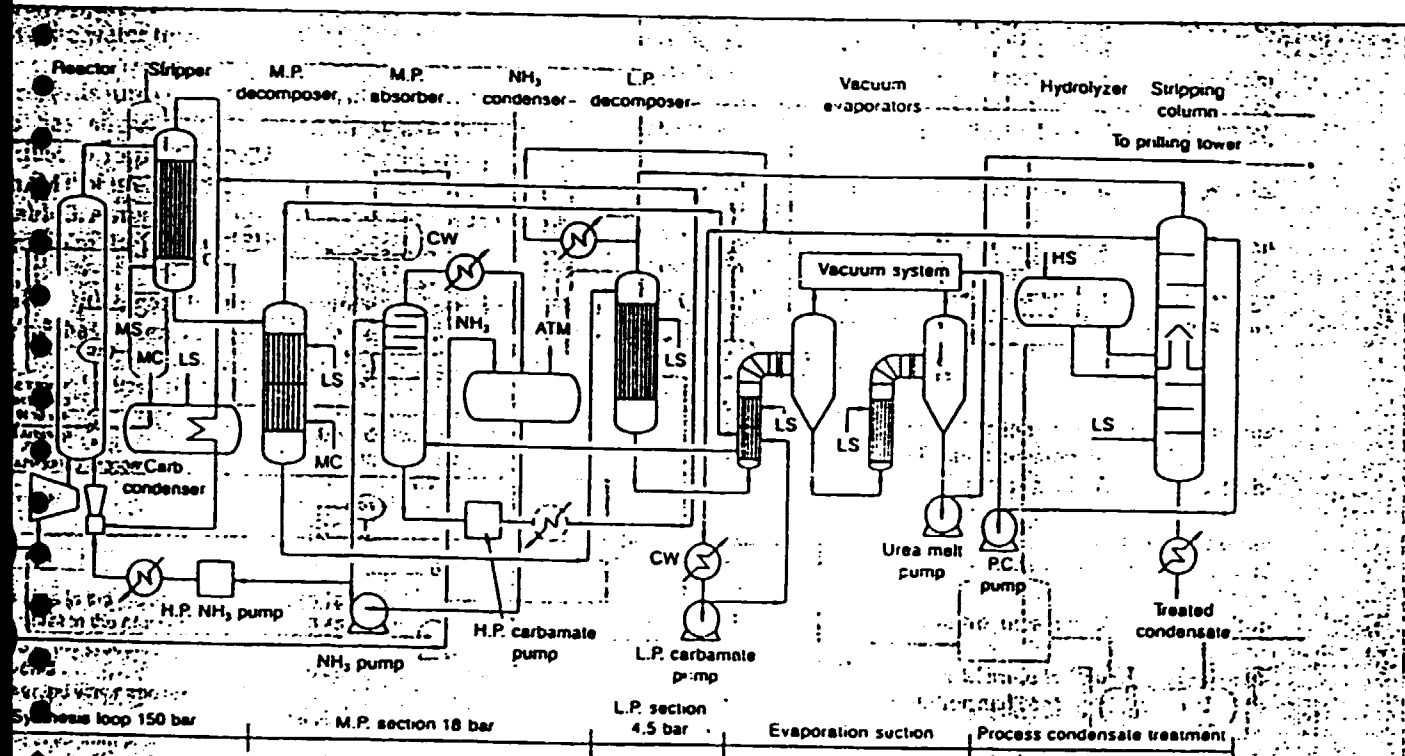


Figure 6 - Snamprogetti urea process flow sheet

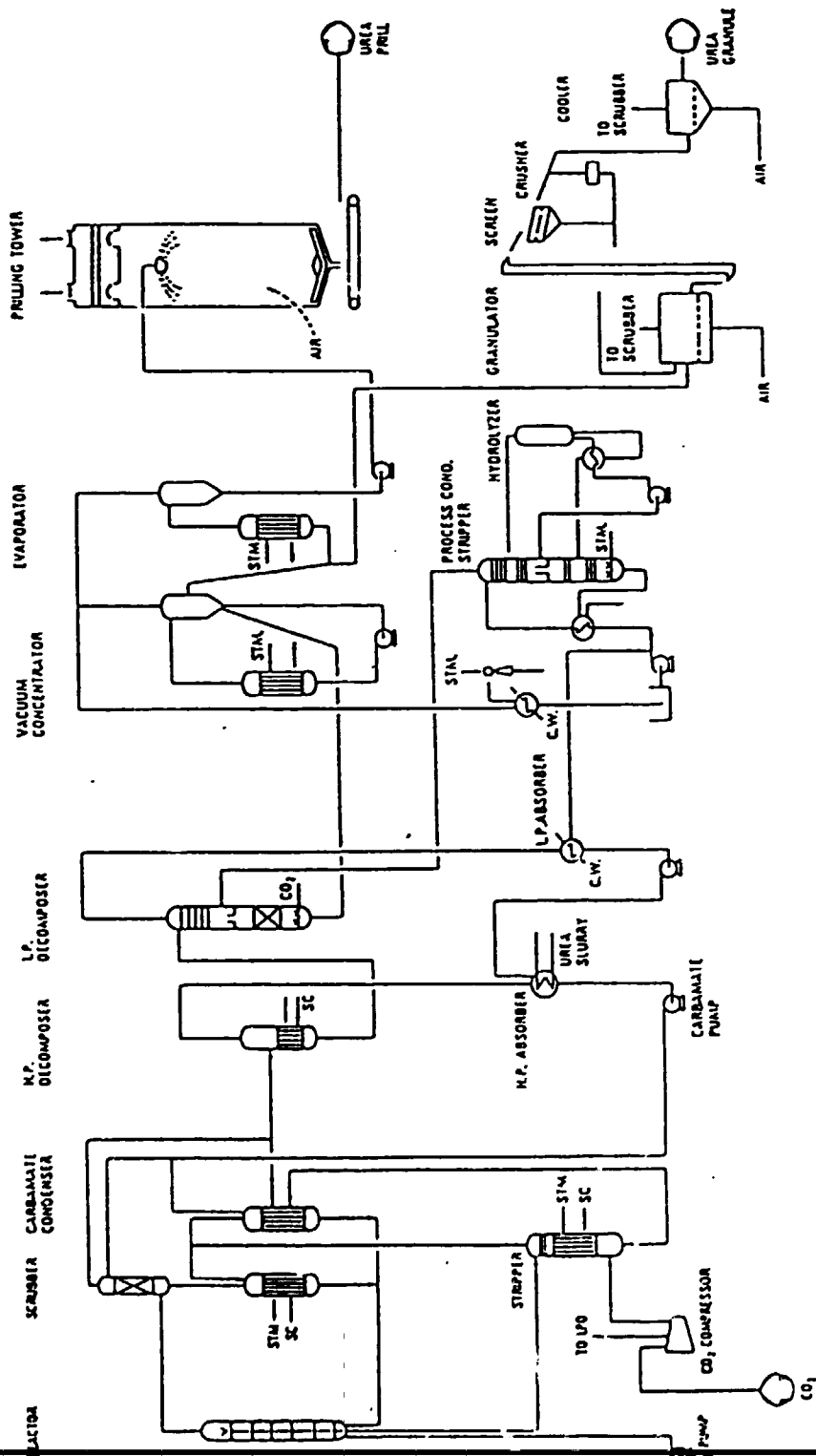


Figure 7: ACES Process

Of all modern processes, the HRU (heat recycle urea) process developed by Urea Technologies has the highest per-pass conversion, at 76%. This is achieved by paying close attention to the internals of the synthesis reactor itself. A specially-designed isothermal reactor, equipped with a spiral reactor coil, is the heart of the process (Fig.8). This operates at 195°C and 207 bar and at an $\text{NH}_3 : \text{CO}_2$ ratio of 4.2:1. Ammonium carbamate is formed in the bottom of the coil and flows up and around it, driving the endothermic dehydration of carbamate, which takes place on the outside of the coil. Unlike conventional bottom-fed reactors, the UTI design is isothermal practically throughout its height.

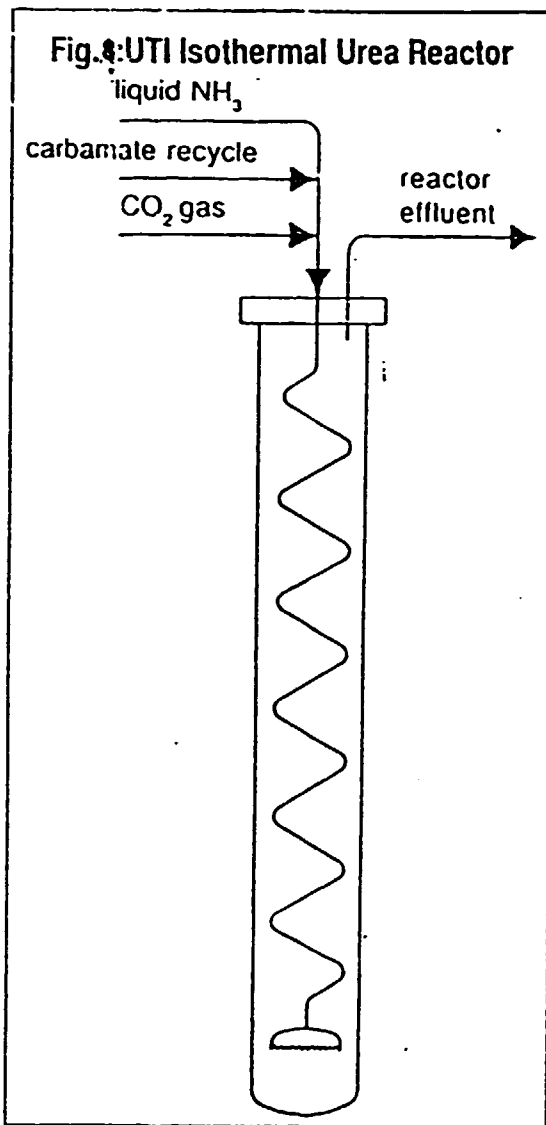
Decomposition and separation takes place in two stages-at 21 bar and 1.5 bar. The process concentrates on maximizing heat recovery, rather than attempting to save energy by operating isobarically(24).

Ammonia Casale's SRR(Split Reaction Recycle) process is specially developed for revamping plants based on urea technology of either Snamprogetti or stamicarbon and includes installation of a secondary high pressure section for extending the urea formation reaction. The secondary high pressure section consists of a feed pump, a reactor, a supplementary decomposer and a separator. The operating condition namely the pressure, temperature and fluid compositions in the secondary section are typical of any conventional non-stripping urea synthesis section. The supplementary decomposer operates under conditions typical of the first treatment step of the two step treatment synthesis loop of the ACES and IDR process.

Integrated Ammonia-Urea Processes-- Many new plants produce ammonia solely for the production of urea. It is possible to integrate certain steps of the two processes which, theoretically at least, should result in a saving in both capital and operating costs. Two coincidences make such integration attractive: (1) Since the ranges of pressure commonly used in ammonia and urea syntheses overlap, the same pressure can be used in both processes, and (2) The amount of CO_2 generated by an ammonia plant using natural gas feedstock is approximately equal to that required to convert the ammonia to urea.

Several organizations have studied integrated ammonia-urea processes experimentally. Mitsui Toatsu has operated a pilot plant in Japan for several years (6), and Snamprogetti (SNAM) has developed and tested the process in a small plant (80 tpd of urea) in Silcily (8).

One point at which the ammonia and urea processes can be integrated is by combining the CO_2 removal step of the ammonia process with the carbamate formation step of the urea process. In the SNAM flowsheet this is done by absorbing the CO_2 from the ammonia synthesis gas in a strong ammonia solution in two falling-film heat exchangers in series, one operated at high temperature(130°C) with heat recovery and the other operated at low temperature (40°C). In the Mitsui



process the CO_2 is removed from the ammonia synthesis gas by scrubbing with recycled carbamate solution with ammonia addition in a packed tower. In both cases the step is carried out at synthesis pressure (200-250 atm), and the resulting strong carbamate solution is transferred directly to the urea synthesis unit while the scrubbed gas goes to the NH_3 synthesis unit. The potential advantages of this integration are obvious. It replaces a major energy-consuming step in the ammonia synthesis gas purification in which the CO_2 is absorbed in a solvent and then desorbed to liberate CO_2 which must then be recompressed for use in a urea plant.

The other principal point of integration is in the extraction of ammonia from the synthesis loop. In a conventional ammonia plant the gas leaving the ammonia converter, containing about 14% NH_3 is cooled by refrigeration to condense liquid NH_3 and thus separate it from the unreacted N_2 and H_2 . In the SNAM integrated process, the NH_3 is absorbed in water in a falling-film absorber producing a solution containing 80% NH_3 and 20% H_2O which goes to the CO_2 absorption step. Liquefaction of ammonia and storage of liquid ammonia are thus avoided. This step also is carried out at high pressure (200 atm or more).

The above descriptions of the integrated ammonia urea processes are very much simplified. A more complete description of the SNAM process is given by Lagana and Zardi (8) and Lagana (9). The authors claim a 15% saving in capital investment and a 17% saving in raw materials and utilities costs for the integrated process as compared with separate NH_3 and urea plants.

However no large scale plants have been built so far, although the principle has proved viable. One reason might be the unwillingness of compressor manufacturers to guarantee their equipment for mixed gas stream containing CO_2 with water and or ammonia. Certain amount of risk is therefore involved in scaling up the process. Snamprogetti sees no basic difficulty in scaling up the process even to 2,000 tpd of urea. On the other hand, the company suggests that small integrated ammonia-urea plants of 150-tpd capacity might, prove more economical than large (1,500 tpd) urea plants. Although 10 small plants would cost about 13% more than one large plant, this disadvantage would be more than offset by a saving in marketing costs and in infrastructure requirements (10). The case for decentralized production in small plants has been put forth by others and does not necessarily depend on an integrated ammonia-urea process. However, there would be an obvious advantage in using some standardized design if numerous small plants were built (11).

There are some disadvantages in integrating two processes because of loss of flexibility. Neither the urea plant nor the ammonia plant can operate independently. Even in an ammonia-urea complex that consists of separate ammonia and urea units, there are some problems of interdependency, an interruption of ammonia plant operation forces a shutdown

of the urea plant for lack of CO₂. The ammonia plant can continue in operation when the urea plant is shut down as long as ammonia storage is available or when there is some other outlet (use or sale). It is an engineering precept that when two processes (or process steps) are mutually interdependent, the reliability of the combination is the product of the reliability of the individual processes. For example, if a urea plant and an ammonia plant each have a reliability of 90%, the reliability of an integrated plant would be $0.90 \times 0.90 = 0.81$ or 81%.

When part of the ammonia is to be used for products other than urea or when the ammonia feedstock has a higher C:H ratio than required for urea production, there will be an excess of CO₂ over that required for urea production. That integrated urea-ammonia processes can be modified to meet these conditions but at the expense of losing part of the advantages claimed.

Urea Finishing Processes

The urea synthesis processes described in the previous section produce an aqueous solution containing about 75% urea. The solution can be used directly to prepare nitrogen fertilizer solutions (see chapter X). It can also be used to prepare granular compound fertilizers (in chapter XIX) although further concentration usually is desirable for this purpose.

Methods for production of solid urea include flaking, prilling, granulation, crystallization, and a combination of crystallization followed by melting and prilling or granulation.

Flaking is done by evaporating the solution to a melt (less than 1% H₂O) and solidifying the melt on a cooled metallic surface such as a Sandvik conveyor. The solidified melt is broken up into flakes. This is a convenient means for producing a material material for shipment when the product is to be used in industrial processes or in solutions. Flaked urea is not used directly for fertilizer. Vacuum crystallization has been described briefly under "Biuret Formation". The crystallization process is similar to that described under "Ammonium Sulfate" (chapter VIII). The crystals are separated from the mother liquor by centrifuging and dried, usually in a rotary fuel-fired dryer. In some countries crystalline urea is bagged and distributed for use as fertilizer, but it is not very satisfactory for this use because of the small size of the crystals which leads to caking. Crystalline urea may also be used for preparing fertilizer solutions for foliar application or for nonfertilizer purposes. For the foliar application a low-biuret content is a specific advantage for crops like citrus fruits that are sensitive to biuret.

Prilling.

Until recently nearly all straight urea was prepared for fertilizer use by prilling, and this is still the most widely used process. The prilling process is similar to that described in chapter VIII under "Ammonium Nitrate." The 75% urea solution is evaporated to a melt and prilled using one of three drop-forming devices: (1) a "shower-head" spray consisting of a number of pipes with holes drilled in them or (2) a rotating perforated bucket usually of conical shape. Alternatively, the urea melt may be formed by melting crystalline urea. (3) Acoustic nozzle plate which is a recent development. This device was developed in U.S.S.R and commercialized by Toyo Engineering Corporation. In this apparatus uniform sized droplets of urea melt are formed by means of acoustic vibration. Acoustic vibration is produced by an internal resonator and transferred to urea melt (24).

The droplets formed by the prilling devices cool and solidify as they fall through an ascending airstream. Urea has a lower melting point than ammonium nitrate or other fertilizer materials that are prilled. Therefore, a longer time is required for solidification for the same size prills, or in a prill tower of given height, the prills may need to be smaller. In practice, urea prills in general are smaller than the usual size of granular fertilizers.

Prilled urea is also weaker than granular urea, both in crushing strength and resistance to abrasion, as shown by the following data from TVA, which also show the effects of particle size and formaldehyde addition (12):

Crushing Strength of Prilled and Granular Urea

Type of Urea	Crushing Strength, Kg			Increase of -16 Mesh in Abrasion Test, %
	(-2.74+2.36 MM)	(-2.36+1.98 MM)	(-1.98+1.65 MM)	

Products Without Formaldehyde Additive

Prilled urea	1.20 ^b	1.0	0.7	20
Granular urea, spray drum		(No data available)		

Granular urea, TVA pan	1.6	1.2	0.9	2
---------------------------	-----	-----	-----	---

Products With Formaldehyde Additive (0.3%-0.4% HCOH)

Prilled urea	1.4 ^b	1.0	0.9	10
Granular urea, spray drum	3.3	2.5	2.1	<1
Granular urea, TVA pan	2.4	2.0	1.6	1

- a. The resistance to abrasion is determined by measuring the increase in minus 16-mesh (0.99 mm) fraction after the material has been rolled for 5 minutes with steel balls.
- b. This fraction is extremely minor (usually less than 5%) in prilled urea; most of the particles are smaller;

In addition to improved strength, granular urea has the advantage of greater flexibility in particle size; any desired size can be made, at least in the range of 1.5 to 15.0 mm. For instance, a size-matching granular DAP or KCl (1.5-3.3 mm or 2.5-4.0 mm) can be produced for bulk blending, or a larger size (6-10 mm) can be produced for aerial forest fertilization or for other special uses, such as deep placement in flooded rice fields. Another advantage of granulation over prilling is the greater ease of control of fume and dust, as mentioned under "Ammonium Nitrate" (chapter VIII).

The advantages of granulation over prilling are sufficiently important that most new urea plants built in the United States and Canada have used granulation, and granulation facilities have been added to some older plants that previously used prilling. Use of urea granulation in some other countries is planned.

The following description of urea granulation process is taken mainly from an IFDC report (13). Three processes have produced granular urea in commercial-sized units. They are (1) the Spherodizer spray-drum granulation process developed by C&I Girdler, (2) the TVA pan-granulation process, and (3) the Norsk Hydro pan-granulation process. In addition, two more processes have proven feasible they are Fison's rotary-drum process and the spouted-bed granulation process which has been studied by several companies in Japan, Italy, France, and Netherlands.

TVA Pan Granulation

TVA pan granulation process and the internal recycle or classifying action in the pan have been described by Young and McCamy (14) and Waggoner, et al. (15). Figure 9 is a sketch of the pan operation. The feed to the process consists of urea melt from an air-swept, rotary-disc, falling-film evaporator. The melt at a concentration of more than 99% and at temperature of 141°C is pumped from the bottom of the evaporator to multiple sprays over the bed of moving solids in the pan granulator. With proper positioning of the hollow-cone spray nozzles which feed the melt and with proper distribution of the recycled undersize on the pan, the melt solidifies in even layers on the undersize in the upper area of the pan. When the particles reach the proper size by layering or "onion-skinning" process, they are discharged by the natural classifying action of the pan before any appreciable amount of oversize is formed. The pan may be rotated in either

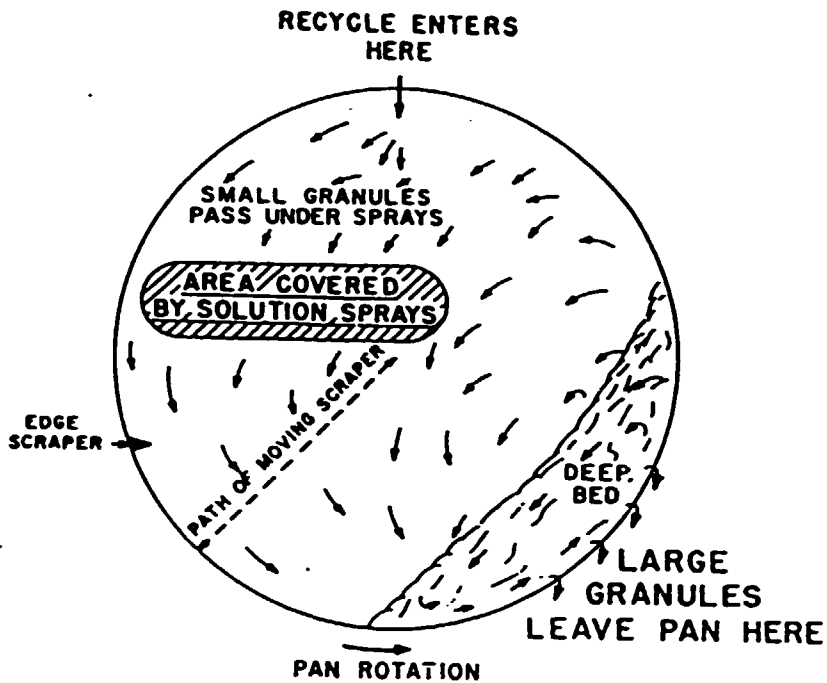


Figure 9 Sketch of Pan Operation.

a clockwise or counterclockwise direction. The particle size and shape are influenced by the rotational speed and slope of the pan. Critical features for best operation of the pan granulator include slope, rotational speeds, location of sprays, and the amount, particle size, and temperature of the recycled material.

TVA has made pilot-plant studies of both "high-temperature" and "low-temperature" methods for granulation of urea in the pan granulator. In high-temperature granulation, the bed temperature was kept at only a few degrees below the crystallization temperature of the feed melt (132°C). This was accomplished by regulating the temperature and quantity of recycle. When the recycle temperature was 49°-57°C, a recycle-to-feed ratio of 1.0-1.5 was required. Best granulation was obtained when the bed temperature was maintained at 107°-121°C. In this type of operation the granules are soft while hot and attain a spherical shape by rolling in the pan. An advantage of high-temperature granulation is that the granules are stronger than those made by the low-temperature method. A disadvantage is that an upset in the recycle system can cause the bed in the granulator to melt and interrupt the operation.

Figure 10 is a basic flowsheet for low-temperature granulation

The bed temperature is maintained at 93°-102°C which is substantially lower than the melting temperature of 132°C. Material from the granulator flows to a rotary cooler where the temperature is reduced to approximately 66°C prior to screening. The cooler discharge is screened to separate oversize, onsize, and undersize. The oversize is crushed and returned to the recycle system or dissolved and returned via the scrubber solution system. Undersize is returned to the granulator as recycle. Product from the screens goes to a cooler where the temperature is lowered to 43°C. A drum is provided for coating the product with oil and clay. However, if coating is not desired the product can be conditioned by adding 0.3%-0.4% formaldehyde to the urea solution before granulation. Use of formaldehyde increases the strength and abrasion resistance of the granules which significantly lowers dust formation. Typical operating data are shown in table 1.

Norsk Hydro Pan Granulation.

The Norsk Hydro High Temperature Pan Granulation Process (HTPG) was originally developed to make non-dusting, coarse (7-11 mm) ammonium nitrate granules for aerial spreading, the process has been developed to produce AN and CAN (2-4 mm), urea (2-4 mm) and urea super granules (USG 1 gm), Calcium nitrate (2-4 mm) and NPK fertilizers (25) Plants with unit capacity up to 1500 MTPD are in operation. The process

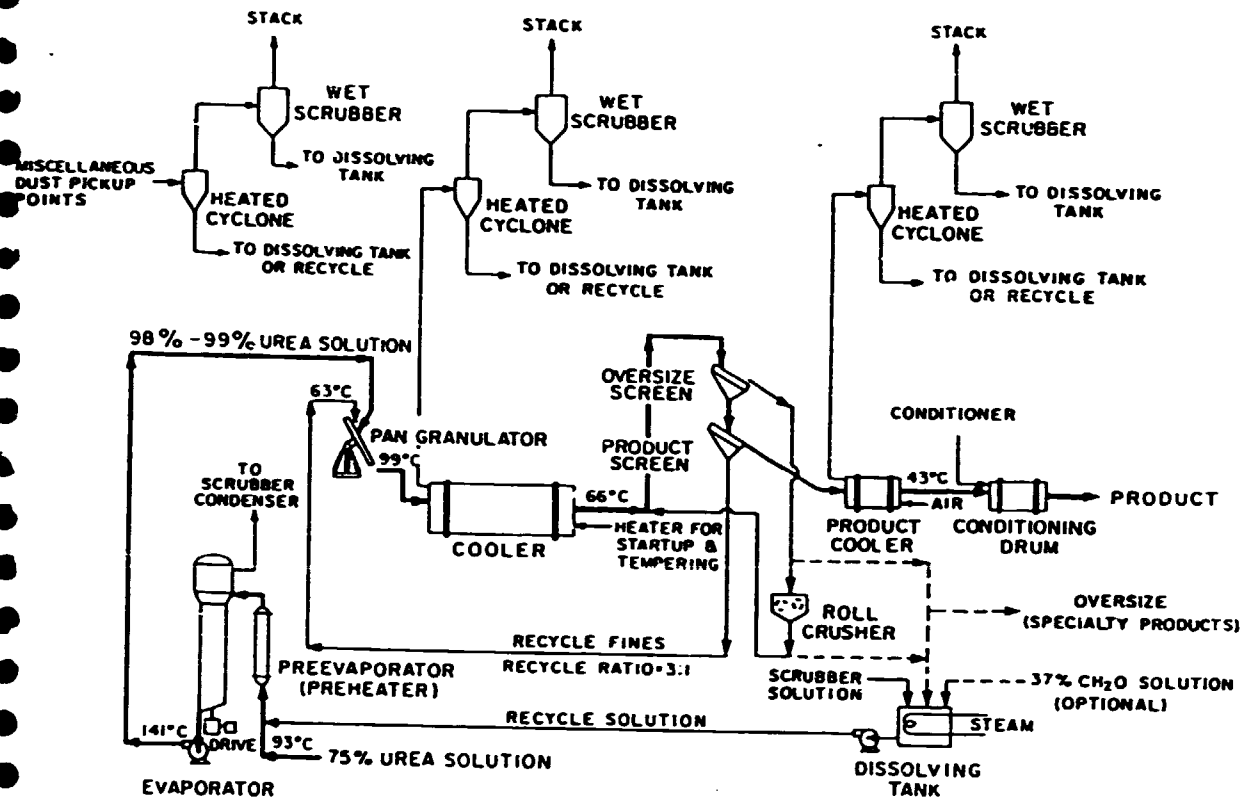


Figure 10 JVA Pan Granulation Process for Urea.

employs a pan granulator of conventional design. However, since the process operates at temperatures very close to the crystallization temperature, close control of the pan parameters is necessary. The primary control is the location of the point at which solid recycle is fed to the pan. Norsk Hydro reports that 80% of the material in the pan discharge is onsize (2-4 mm) and that the recycle ratio(solid-to-melt) is about 1. The particles are three times harder than prills of the same size and exhibit good storage and handling properties.

Figure.11 is a simplified flowsheet of the process. The pan granulator is an inclined, cylindrical vessel with a relatively low rim. The pan has variable inclination and the speed of rotation can be changed.

Recycle material from a recycle bin (and solid filler when required) is fed continuously to the pan granulator at a controlled rate by a recycle feeder. Granules are gradually built up by spraying melt on the moving bed of solid particles. The melt is fed to the pan through spray nozzles which give a fine dispersion of melt on the solids. The melt solidifies on the colder particles and granules are formed by agglomeration and layering mechanisms.

In the pan the granules are classified according to their size. As they increase in size they are gradually displaced towards the surface of the deep bed of particles and in the direction of the periphery of the pan. When the granules have attained adequate size they roll over the granulator rim. By adjusting the pan operating parameters the granule size can be adjusted to meet product requirements.

The operating temperature in the granulator is close to the melting point of the material. This temperature is an important process parameter and it is necessary to keep it within narrow limits. This is achieved by controlling the rate of recycle material fed to the pan. The total quantity of solids which is required as dry feed to the granulator is automatically controlled by the pan temperature. The quantity of recycle material to the recycle bin must balance with this requirement. The variable in this recycle stream to the recycle bin is the onsize product flow which is controlled by a splitter.

Small quantities of haze and dust are vented from the pan and cleaned in a venturi scrubber before being vented to stack.

The granules leaving the pan are soft due to the fact that they still contain a certain fraction of unsolidified melt. In the polishing drum the granules are exposed to mild mechanical forces and their appearance is thereby changed towards a smoother surface,

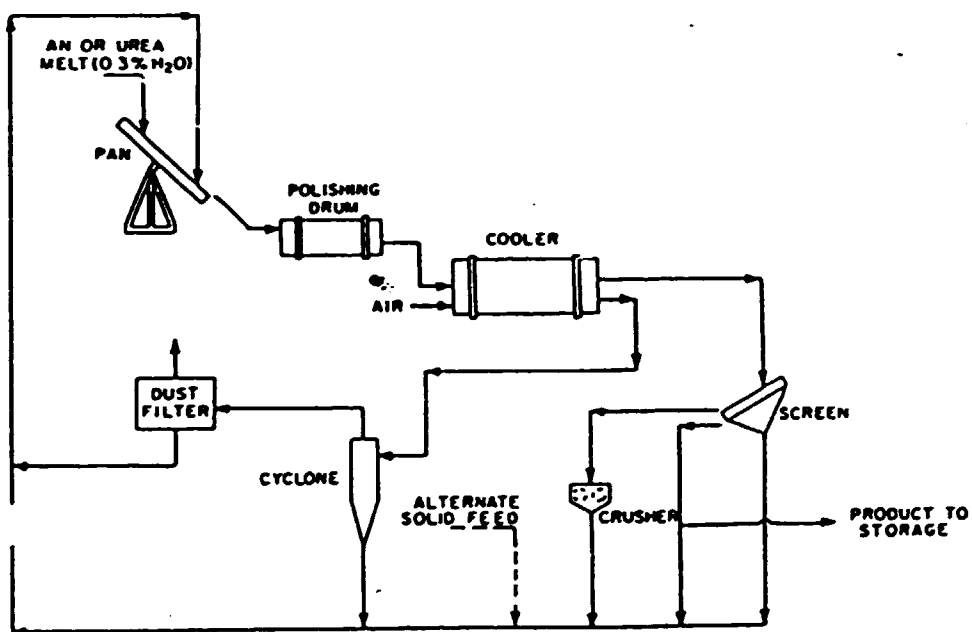


Figure 11. Norsk Hydro Pan Granulation Process for Urea or Ammonium Nitrate.

From the polishing drum to the product cooler the granules flow by gravity. Vent air from the drum is combined with vent air from the granulator. The cooler discharge is screened to separate the oversize, onsize, and undersize fractions. The oversize is crushed and recycled to the pan along with the undersize and dust from the dust-control system.

TABLE 1. TYPICAL OPERATING DATA--UREA PAN GRANULATION

Production rate, tph	7.65
Pan granulator	
Speed, rpm	18 to 19
Slope, degrees	60
Number of sprays	10
Urea, 75% solution from plant	
Temperature, °C	93
Concentrated melt to granulator	
Temperature, °C	141
Concentration, %	98.5-99.5
Granulation	
Recycle temperature, °C	60
Recycle ratio, kg/kg of product	2.5 to 3.0
Granulator temperature, °C	93-102
Cooler temperature, °C	43
Product chemical analysis, %	
Total N ^a	45.5
Biuret	1.1
H ₂ O (Karl Fisher)	0.1 to 0.2
Conditioner, %	
Oil-wax mixture	0.3
Clay	0.7
Screen analysis, % (Tyler screen)	
+6 mesh (+3.3 mm)	0
-6+10 mesh (-3.3 mm +1.7 mm)	85
-10+16 mesh (-1.7 mm +0.99 mm)	15
-16 mesh (-0.99 mm)	0

a. In recent operation, the oil-wax plus clay conditioner has been omitted and about 0.35% formaldehyde added; the total N content of the product is 46%.

C&I Girdler Spherodizer Granulation

The Spherodizer, which is a proprietary drum-granulator process, is designed to avoid agglomeration and promote a layering type of granulation. The adaptation of the Spherodizer to a melt granulation process was developed by

COMINCO (Canada) which holds the original patents with C&I Girdler as the sole licensor for the process. The process is well proven commercially. Complex fertilizers were first produced in a Spherodizer in 1958, and production of granular urea and ammonium nitrate was introduced in 1965 (17).

A simplified flowsheet is given in figure 11. Molten urea is sprayed inside a rotating drum onto a rolling bed of solid particles. As a result of the rolling action, the particles are coated with thin layers of liquid and gradually build up to hard spherical granules. Cooling air is drawn through the drum countercurrent to the flow of granules. Dust removed by the cooling air is collected in an impingement-type wet scrubber and the liquor is recycled to the concentration section of the urea unit. After cooling, the granules flow to a conventional screening section for separation of oversize, onsize, and undersize. The oversize is crushed and returned to recycle along with the undersize. The product size is treated with the conditioner, if desired, and transferred to storage. Typical operating data are shown in table 2 for production of urea by the Spherodizer process at a production rate of 300 tpd and a recycle ratio of 2.

TABLE 2. TYPICAL OPERATING DATA--UREA SPHERODIZER GRANULATION

Melt temperature, °C	138
Melt concentration, %	99.3
Moisture in product, %	0.06
Air inlet temperature, °C	10
Production rate, tpd in 14-foot (4.27 m) diameter drum	300
Recycle ratio (recycle/product)	2
Product temperature, °C	43

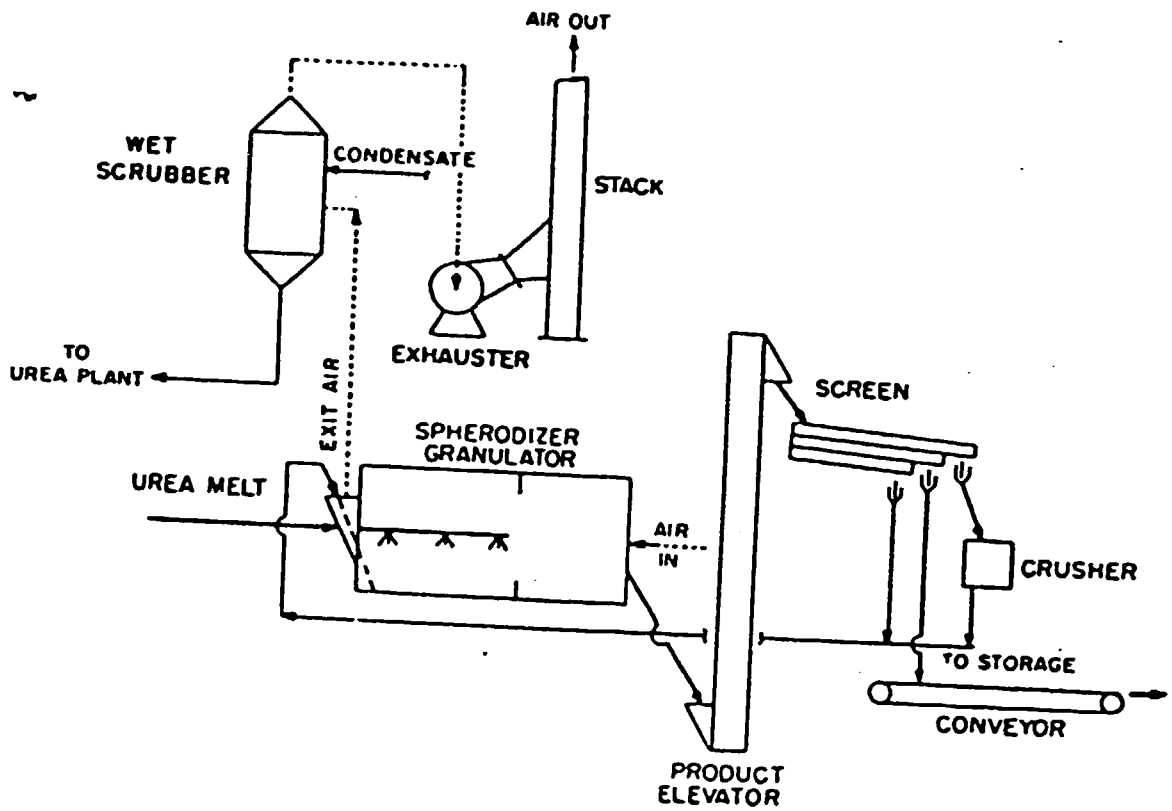


Figure 12. C&I Girdler Urea Spherodizer Process.

TVA Falling Curtain Granulation Process

This process is shown in figure.13.(25). The key to the falling -curtain granulation process is the rotary drum. The drum has specially designed internals including collecting pans, air circulation fans, urea spray header, and water spray header. As the drum rotates, seed particles, recycled undersize granules, and intermediate-size granules are lifted by flights and discharged onto inclined collecting pans.

The material forms a dense falling curtain of granules as it slides from the collection pans. The urea melt is sprayed through hydraulic atomizing nozzles onto this falling curtain and quickly solidifies. Thus, granules of the desired size are produced by successive layering of urea melt on the undersize granules as they pass through the drum. The product size is controlled by the size of the oversize and product screen cloths installed. The distribution of the product size within the screening range is controlled by the recycle-to-melt ratio. Heat liberated in the drum is removed by: 1) air flowing through the drum; 2) evaporation of fine water mist sprayed into the air stream, and 3) introduction of cool recycle.

Additional cooling of the urea granules leaving the drum is necessary to minimize granule breakage during screening and to prevent blinding of the screen cloth. This cooling is accomplished in a dual-service, fluid-bed cooler following the granulator. The granules are then elevated, screened, and the product transferred to storage after further cooling in the dual-service, fluid-bed cooler.

The seed particles are metered into the drum so that they replace the product taken out of the system on a granule-to-granule basis. Seed particles [predominately 0.8 to 0.5 mm (-20+35 Tyler mesh)] are generated by crushing oversize material and some product granules as needed to produce sufficient seed material. After the oversize material is crushed, it passes through an air classification system to remove dust which is collected in a cyclone, remelted and returned to the drum granulator.

Air leaving the granulator is scrubbed first in a spray chamber followed by an irrigated mist eliminator. The high humidity in the air stream leaving the granulator precludes using a dry collection system. Particulate emissions from the fluid-bed cooler are collected in a low-pressure drop cyclone and returned to the process via the recycle stream. This air stream is further cleaned in a spray chamber and low-pressure drop mist eliminator. Dust collected from miscellaneous transfer points is likewise scrubbed from the exhaust system. Scrubber liquor is concentrated to about 40 wt.% by evaporation in the exhaust system and is fed back to the process evaporator.

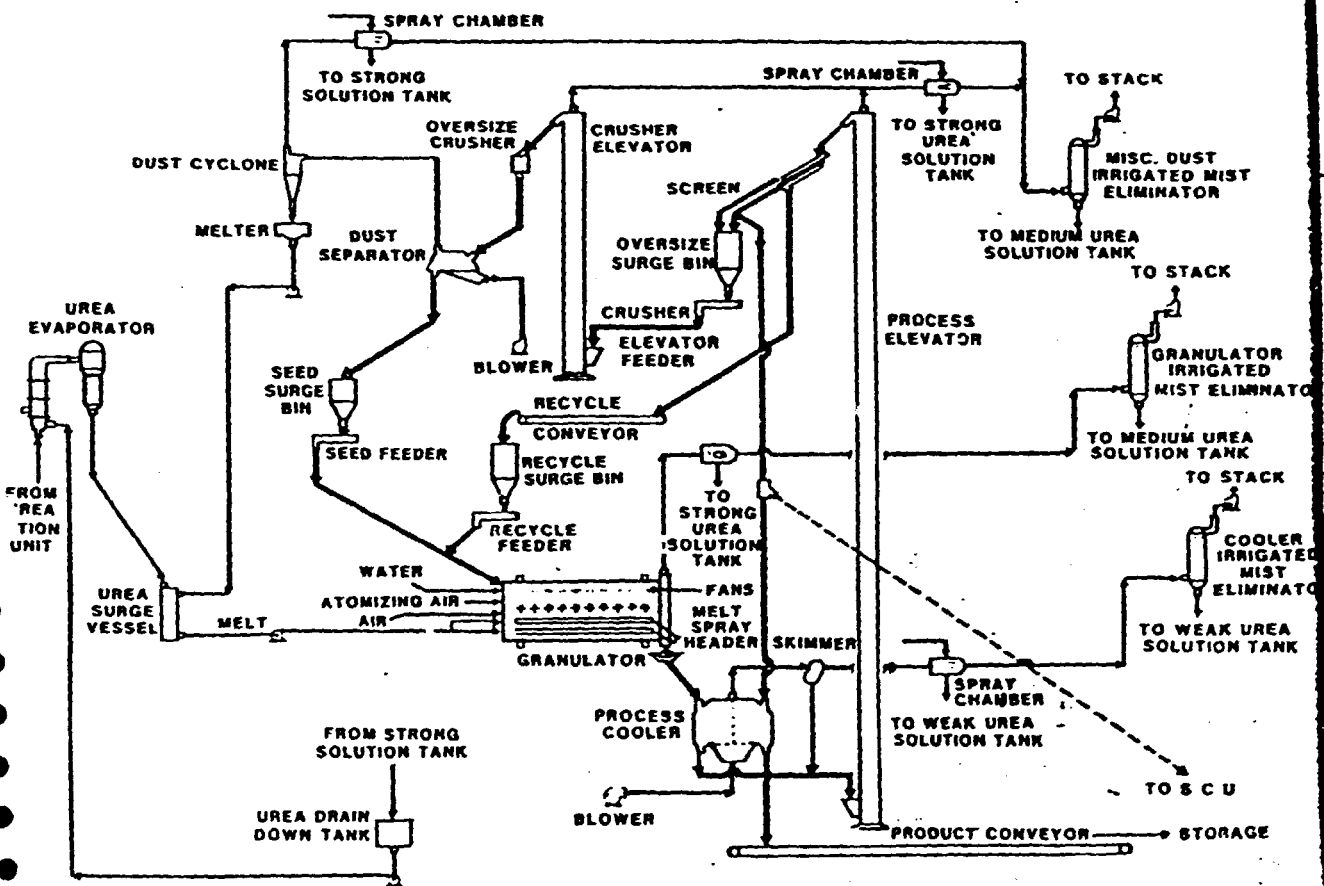


Figure 13 Falling-curtain evaporative cooling demonstration unit.

NSM Fluid Bed Granulation Process

NSM first commercialised this process in July, 1979. A typical flow diagram is given in figure.14(26). The feedstock is 95-96% aqueous urea solution.

Inside the granulator the urea solution is atomized into a bed of fluidized granules, using hot low pressure air supplied by a blower, through non plugging, maintenance free spray nozzles.

Ambient air is used as fluidizing gas, without any dehumidification even if the climate is hot and damp.

The disengaging top section of the granulator, above the fluidized layer, retains efficiently the coarse urea dust.

The fine urea dust entrained with the air extracted from the top of the granulator does not exceed 4% of the plant production and is washed off in a wet type scrubber before discharging the air to the atmosphere.

Process condensate from the urea synthesis plant is used for scrubbing and the recovered urea is recycled to that same plant in the form of a 45% solution.

The granulated product extracted from the granulator is cooled in a standard fluid bed cooler using ambient air as cooling medium. In hot and wet climates, air conditioning may be required on the second half of the cooler.

The cooled product is sent to a screen where oversize and undersize granules are separated. The oversize fraction is first ground to size in a roll crusher and then fed back, together with the undersize fraction, to the granulator to be used as seed material to initiate granulation. On size product is sent to storage. The average diameter of the granules is controlled by the screen mesh size and the crusher adjustment. Basically, crusher adjustment sets the amount of seeds supplied to the granulator per unit time, and so determines on how many nuclei per unit time the total feed solution will be sprayed.

The plant can produce bulk blending grade urea fertilizer (average particle diameter from 2 to 3 mm) but also the larger bead size urea (6-8 mm granules).

Fluidized Drum Granulation

A recent development tested on pilot plant scale by Kaltenback, France is the Fluidized Drum Granulation (FDG) which is a combination of drum granulation and fluidized bed technology (27).

The FDG process is suited to the granulation both of melts (by which is understood molten salts or other materials, containing not more than 4% water) and of slurries (i.e. suspensions of solid salts in a saturated solution, with or without other insoluble materials). But the FDG process can also be used for improving the characteristics of products originally made in other ways. For example, it can be used to increase the size of prills. Or it can be used for "rounding off" the irregular shaped particles of a compacted product, which is formed by compressing dry solids between rollers and then breaking up the resulting sheet.

The heart of the process is a horizontally-aligned cylindrical granulator drum, which rotates about its axis in the conventional fashion. The interior of the drum is fitted with special anti-clogging lifters. But the main feature distinguishing it from conventional drum granulators is an internal fluidized bed Fig.15. This comprises a flat, slightly inclined perforated plate through which fluidizing air is blown (direct from the atmosphere or after conditioning, according to the product being granulated).

The granulator is supplied with seed material, which can be recycled off-size but might also be prills that it is desired to enlarge or a compacted product that it is desired to make smoother and rounder. In the granulator it has to undergo the dual operations of being increased in size and being cooled or dried, as the case may be. This occurs progressively in the following cyclic sequence.

The lifters raise the seed material to the upper part of the drum, whereupon it falls onto the surface of the fluidized bed. This is where the product is cooled or (when the feed material is slurry) dried. The product flows down the inclined base of the bed and falls into the lower part of the drum. As it is sprayed with the feed melt or slurry. The coated granule is then lifted back to the fluidized bed, where the new surface layer solidifies by cooling or evaporation of its moisture content.

The same cycle is then renewed as many times as are necessary to reach the desired grain size.

The number of cycles is determined by the residence time in the drum, which is controlled by adjusting the overflow threshold.

TEC SPOUTED BED GRANULATION.

Two paragraphs missing in this process developed by Toyo Engg. Corporation. The urea solution from the Evaporator at 98.5 wt.% urea concentration is sprayed in the spouted beds in the Granulator, where one spray nozzle is provided for each bed. (Fig.16). Aqueous formaldehyde solution is injected to the feed urea solution to reduce dust formation in the Granulator and to improve anticrushing strength and free flowing property of the product urea granules.

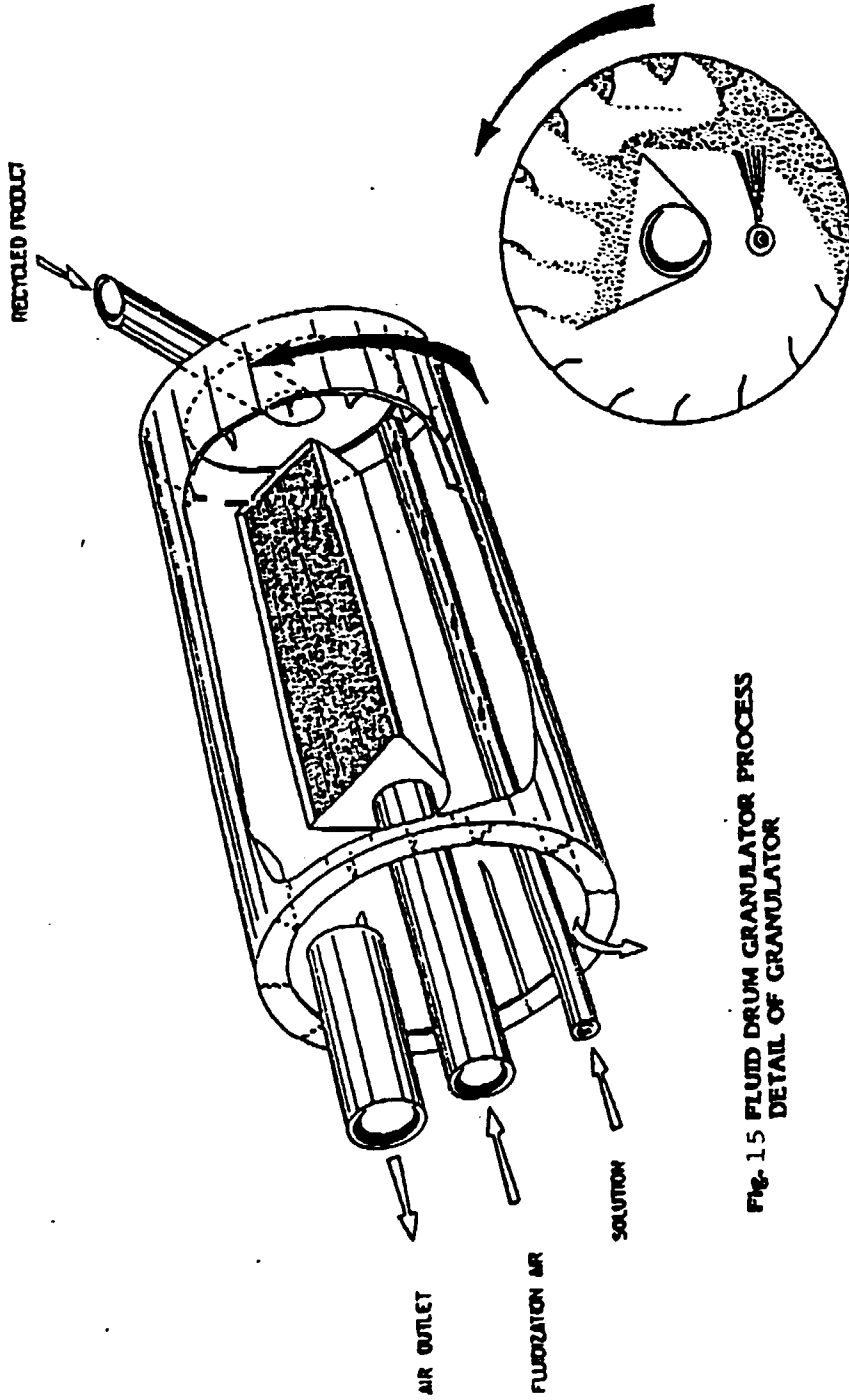
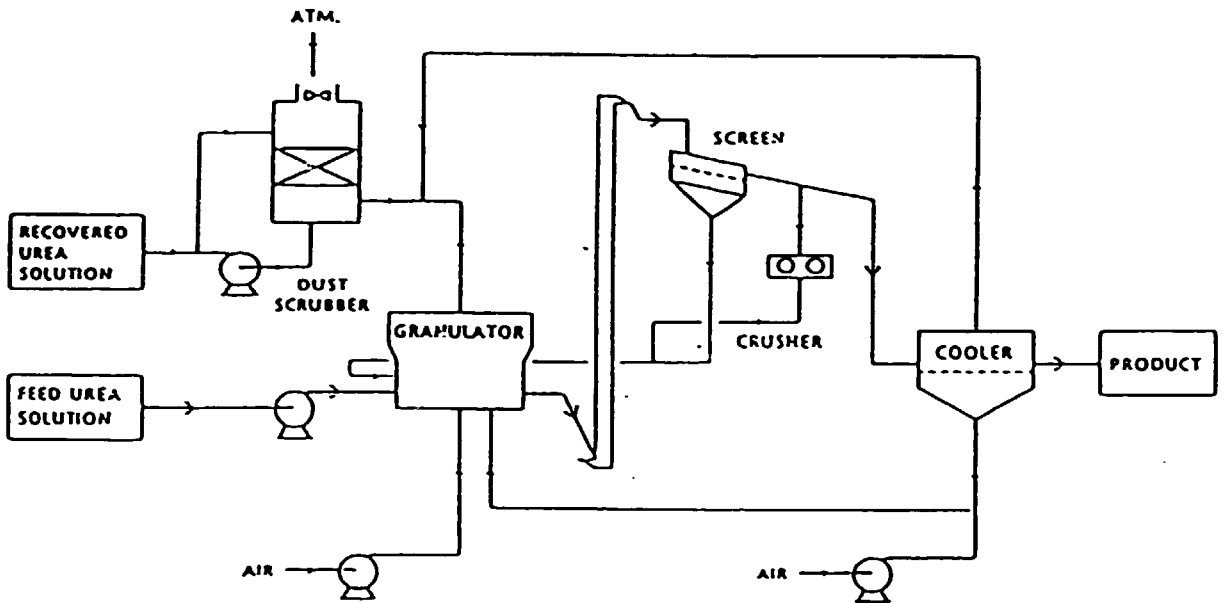
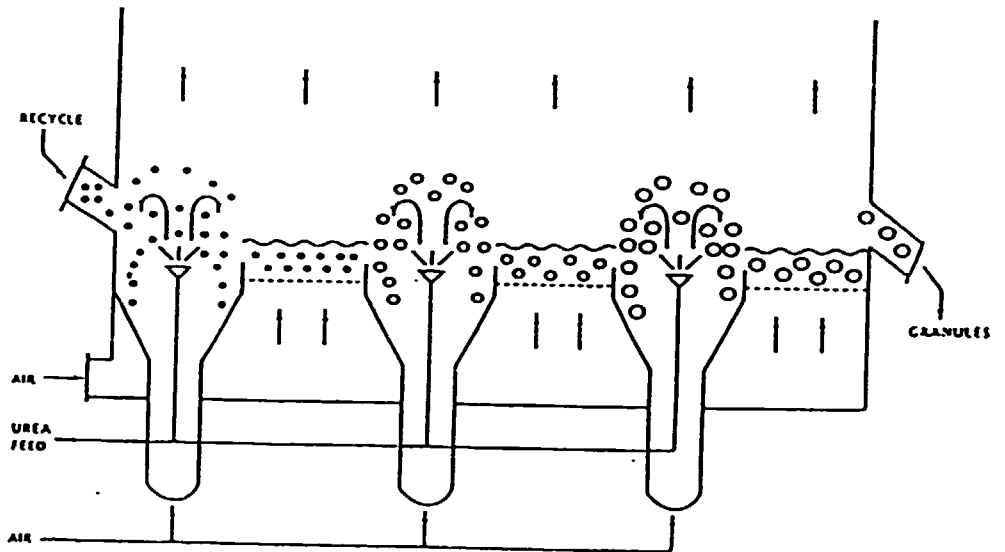


FIG. 15 FLUID DRUM GRANULATOR PROCESS
DETAIL OF GRANULATOR



FIGURES 16: TEC SPOUTED BED PROCESS



FIGURES 17: TEC SPOUDED BED DETAIL

Since the air introduced for spouting has the effects of cooling and drying of the granules in the spouted beds, this urea granulation process results low utility consumption and low biuret content in the product.

The coarse granules from the Granulator are classified into the product size and under size by the Screen.

The product size granules are cooled in the fluidized bed type Cooler and delivered to the product storage house.

The under sized granules are recycled back to the Granulator as the seed particles. (23).

Conversion from Prilling to Granulation

Existing plants that are equiped for prilling may be converted to granulation by using the prilled urea as a part of the feed for the granulation unit, replacing part of the recycle. In this case the granulation unit serves to build up the size of the prills to the desired level by layering. This modification has been demonstrated with the Norsk Hydro pan-granulation process and, presumably, could be used with the other granulation process.

Dust and Fume Recovery

A part of the decision to produce granular urea involves not only choice of the process but also choice of the dust recovery method. The TVA process utilizes impingement-type wet scrubbers which were previously installed for another process. The Spherodizer process usually employs wet scrubbing. However, dry collection and a bag filter could be used with either the pan-granulation or the drum granulation process. Bag filters usually require more maintenance than wet scrubbers, but they do achieve a very low level of particulate matter in the effluent stack gas. Simple wet scrubbers, however, are also able to satisfy the most stringent environmental standards for dust emissions. A wet-scrubbing system of the type envisioned for a new plant has been included on the flowsheet for the TVA process, figure 10. A separate system is used for each of the coolers and another for the fugitive dust-control system. Each consists of a heated cyclone, wet scrubber, circulation pump, blower, and liquor tank; gas from the three scrubbers is vented to a common stack. Dust from the cyclones is dissolved in the scrubber liquor is collected and fed back to the concentration section. As a variation, the liquor tank and pump could be common to the three system.

A very important consideration in designing a dust-collection system is flexibility to allow either dissolving the dry collected dust or returning it dry to the granulator. None of the granulation processes operate well if there is a high proportion of dust in the recycle. Therefore, it may be necessary at times to dissolve the dust from the cyclones and bag filters and the crushed oversize and feed it back as a liquor into the concentration section. The concentrator should have this additional capacity designed in at the beginning.

Effect of Finishing Process on Biuret Content

Several investigators have found that biuret is not formed in detectable amounts during the prilling or granulation operation itself, but it is formed during preparation of the melt whether by evaporation of solution or by melting crystalline urea. Also biuret continues to form in the melt so long as it remains in molten form. The practice of recycling recovered urea dust and fume to the evaporation step tends to increase the biuret content. There is probably more recycled material in granulation processes than in prilling. Granular urea produced in U.S. plants averages about 1.5% biuret. In the United States, low-biuret content is not regarded as important, and no special effort is made to control it at a low level. However all European and Japanese processes like Stamicarbon, Snamprogetti TEC guarantee biuret less than 1% in their urea product. Presumably low-biuret granular urea could be produced by exercising more care in minimizing the retention time in the evaporation step and in melt handling and by recycling recovered scrubber solution and fines to the synthesis step or to a crystallization step rather than to the evaporation step.

As mentioned previously, low-biuret product is produced by vacuum crystallization of urea followed by drying the crystals and then remelting them for prilling or granulation. However, the capital cost of a urea plant using the crystallization step is substantially greater than that of a plant using the evaporation method.

Comparative Cost of Granulation and Prilling

The relative cost of prilling and various granulation methods depends on the scale of operation. Production of as much as 1,800 tpd is feasible in a single prilling unit; whereas, the spray-drum (Spherodizer) granulation process has been limited to 300-tpd units because of difficulties in fabricating and transporting larger units. (The standard Spherodizer drum for melt granulation of urea is 3.6 m in diameter.) The upper limit of pan granulators is not precisely known, but 600 tpd is known to be feasible for a 4.3-m diameter pan. The upper capacity limit of other types of granulators is speculative although Nørsk Hydro is claimed to have built a fluid bed granulation plant of 1725 MTD capacity (26).

The cost of a prill tower increases only moderately with capacity ; whereas, with other types of granulators the rate of increase in cost with capacity is generally greater, especially if multiple units are required. The comparison is also complicated by the dust and fume recovery requirements; meeting stringent requirements is more expensive with prilling than with granulation. Thus, for a small (300 tpd) unit, equipment for granulation may be less expensive than for prilling, particularly if good dust control is required. For large units, such as 1,200 tpd, prilling may have a lower capital cost. Hydro Agri claim that its fluid bed granulation process can be built to any capacity presently reached by prilling. The investment is thus similar to prilling, when both systems correspond to identical up-to-date standards of product quality and environmental emission.

Conditioning

Prilled or granulator urea may be marketed without conditioning treatment in some areas, but it is often treated with conditioner to improve its physical strength and increase resistance to caking. The most popular conditioning treatment at present is the addition of formaldehyde to the concentrate solution just before prilling or granulating. The amount added usually is 0.3%-0.4%. The formaldehyde may be added in form of 37% aqueous solution or as a solution containing formaldehyde, 26% urea, and 15% water. The latter solution is called "UF Concentrate-85." Both solutions are available in tank-car lots in the United States and probably in other countries. The formaldehyde conditioning treatment increases the strength of prills and granules and decreases their caking tendency.

Coating of prills and granules also is used as a conditioning treatment although its use is decreasing because the formaldehyde treatment is generally preferred. Coating materials include powdery materials such as kieselguhr, china clay, talc., etc. A combination of about 1% clay with 0.5% oil has been used; the oil promotes adherence of the clay to the urea prills or granules. Some types of powdery coating materials will adhere without oil. Conditioning treatments and conditioner adherence as related to fertilizers in general are discussed in chapter XXII.

A coating of medium-viscosity oil (without clay) has been developed by the Dutch State Mines for prilled urea to retard moisture absorption. It is intended for treatment of urea that will be marketed in warm humid climates. In such climates, the free-flowing properties of prilled urea can deteriorate very rapidly after the bag is opened and before the urea is used. The treatment is reported to be effective in preventing rapid deterioration.

Process Requirements

The economics of urea production will be discussed in chapter XI. The present section deals with process requirements. Utility requirements claimed or guaranteed by engineering and construction firms vary considerably and are influenced by local requirements, the degree of caution used by the estimator, and process variations. There are numerous trade-offs; steam requirements can be reduced at the expense of increased electric power consumption or at the expense of higher capital cost for heat recovery equipment. Nitrogen losses can be reduced at the expense of higher capital cost and higher energy requirements. Pollution control requirements may add substantially. For these reasons, it is difficult to make an accurate comparison of the processes, and no such comparison will be attempted.

The following tabulation shows a range of process requirements (per ton of urea) from several sources and a "selected value" which will be used in comparative estimates in chapter XI. These requirements are for total-recycle processes and do not include integrated urea-ammonia processes since experience with such processes is limited.

References

1. Honti, G.D. 1976. "Urea," IN The Nitrogen Industry, Akademia Kiado, Budapest.
2. Tomlinson, T.E. 1970. "Urea-Agronomic Implication," Proceedings of the Fertilizer Society (London), No.113.
3. Tennessee Valley Authority, 1975. "An Appraisal of the Urea Fertilizer Market in Asia," TVA Bulletin Y-95, Muscle Shoals, Alabama 35660.
4. Tennessee Valley Authority, 1973. "Crop Response to Biuret in Urea," TVA Bulletin Y-57, Muscle Shoals, Alabama 35660.
5. Gray, R.C. 1977. "Foliar Fertilisation with Primary Nutrients During the Reproductive Stage of Plant Growth," Proceedings of the Fertiliser Society (London), No.164.
6. Slack, A.V. 1969. "Urea Technology, A Critical Review," TVA Circular Z-4, Proceedings on Fertilizer Technology, New Delhi, India.
7. Kaasenbrood, P.J.C., and H.A.G. Chermin, 1977. "The Urea Stripping Process, Stripping Technology, Phase Equilibria, and Thermodynamics," Proceedings of the Fertilizer Society (London), No.167.
8. Lagana, V., and U. Zardi. 1977. "An Integrated Process for Ammonia-Urea Manufacture," Proceeding of the Fertilizer Society (London), No.166
9. Lagana, V, 1977. "Snamprogetti's Intergrated Process-New Trend in Urea Production," Chemical Age of India, 28:944-952.
10. Cima, F., P. Casarin, and A. Viglietto. 1977. "Small-Scale Urea Plants at Farmers Site with Snamprogetti Integrated Process," Chemical Age of India, 28;953-965.
11. "Realizing the Potential of the Small Ammonia Plant." 1976. Nitrogen, 100:77-79.
12. Hoffmeister, G., and C.P. Harrison. 1975. "Physical Testing of Fertilizers", Paper presented at the 170th National Meeting of American Chemical Society, Chicago, Illinois.

13. Waggoner, D.R. 1975. "Granular Urea: Advantages and Processes," IFDC Report T-1, International Fertilizer Development Centre, Muscle Shoals, Alabama 35660.
14. Young, R.D., and I.W. McCamy. 1967. "TVA Development Work and Experience with Pan Granulation of Fertilizers," The Canadian Journal of Chemical Engineering, 45:50-56.
15. Waggoner, D.R., and I.W. McCamy, G.C. Hicks, and J.R. Gahan. 1974. "The TVA Pilot-Plant Development work and Demonstration-Plant Proceedings of the 24th Annual Meeting of the Fertilizer Industry Round Table, P.70-79, Washington, D.C.
16. Skauli, O. 1974. "Pan Granulation of Ammonium Nitrate and Urea," Paper presented at the 168th National Meeting of the American Chemical Society, Atlantic City, New Jersey.
17. Reed, R.M., and J.C. Reynolds. 1974. "Progress Report on Spherodizer Granulation of Anhydrous Melts," Proceedings of the 24th Annual Meeting of the Fertilizer Industry Round Table, Washington, D.C.
18. "The Fisons Granular Urea Process." 1975. Nitrogen, 98:37-39.
19. Berquin, Y.F. 1977. "Prospects for Full-Scale Development of the Spouting Beds in Fertilizer Granulation," IN Granular Fertilizers and Their Production, p.296-301, British Sulphur Corporation, London.
20. Ruskan, R.P. 1976. "Prilling vs. Granulation for Nitrogen Fertilizers," Chemical Engineering, 83(12):114-118.
21. IFA survey report.
22. Snamprogetti Broucher
23. TEC Urea Process, Technical Department, Toyo Engg. Corporation March 1992.
24. Urea Production Technology-A status Reports Fertilizer International No,296, April,1991.
25. "Energy-Efficient Route to Granular Urea", Ronald W.Kirkland, TVA.
26. "NSM'S Fluid Bed Granulation Process" Brocher of NSM. Netherland.
27. "The fluid bed granulation process", E.Vogel, Kaltenbach-Thuring SA, Frnace.