Improved Urea Process Is Developed

A new technique, already incorporated into two commercial installations, has reduced steam and water requirements, lowered investment and operating costs, and provided reliable plant operation.

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An improvement in urea processing that increases reactor conversion to from 65% to 72% will provide for a substantial reduction in investment cost for a complete recycle plant. In addition, a new method for heat recovery is included which lowers requirements for steam and for cooling water.

Covered by a number of patents and patent applications both here and abroad, Table 1, the new technology is called the Heat Recycle Urea process. Its development came about as a result of observations in urea manufacturing over the past eight years of consulting engineering practice. Peculiarities were noticed in medium and large urea plants in operation or in upset conditions. These led to new ideas and new concepts in the process design and to their practical application in commercial plants.

Right from the beginning it became apparent that in the liquid carbamate recycle type urea process the key factor is the overall conversion of CO_2-to-urea per pass in the reactor: the higher the conversion rate of CO_2-carbamate to urea, the smaller the amount of unconverted carbamate in the reactor effluent and consequently the smaller the size of the decomposition, absorption and recirculation equipment. Thus, the importance of attaining a high conversion per pass in the reactor is quite obvious.

In 1948, Frejacques determined values for the equilibrium constant of the NH_3—H_2O—CO_2 and urea system with respect to temperature, on the basic assumption that the urea formed in the reactor is in direct equilibrium with the ammonium carbamate formed in the reactor from NH_3 and CO_2. For many years these values were used to determine the maximum conversion one could attain in a reactor, according to Frejacques' basic equilibrium constant formula:

$$K = \frac{x(b + x)(1 + a + b - x)}{(1 - x)(a - 2x)^2} \qquad (1)$$

where: K = equilibrium constant,
a = NH_3-to-CO_2 molar ratio in reactor feed.
b = H_2O-to-CO_2 molar ratio in reactor feed.
x = CO_2 as formed urea to total CO_2 in reactor feed, molar ratio

At 370°F, Frejacques' value for K is about 1.4. From the observation of the performance of urea reactors in commercial plants operating under some upset conditions quite different from the original design conditions, it became apparent that at a given temperature a much higher conversion per pass could be attained than predicted by equation 1.

These findings were reported in an earlier article (1) and a graph was presented, (see Figure 1) which is the exact graphical representation of the above cumbersome equation 1. Handy scales No. 1 and No. 3 are given on the graph for quick determination of the actual K value determined in relation to temperature.

For example, by substituting into equation 1 a set of actual values for a, b, and x obtained in a commercial

Table 1. U.S. patent coverage on the Heat Recycle Urea process.

Patent Title	U.S. Patent No.
Heat Recycle Urea process	3,579,636
Air Injection in Liquid Ammonia	3,574,738
CO_2 Injection in Absorbers & Decomposers	3,759,992

PatentApplication Title	U.S. Patent Application No.
Concentration Analyzer	88,272
Isothermal Reactor	190,519
Decomposer Improved Design	237,644
Ammonia Recovery Stripper	Not Yet Issued
Prilling Tower	Not Yet Issued
Pulsation Dampener for Carbamate Pump	Not Yet Issued
Urea Process with Low-Pressure CO_2 Feed	Not Yet Issued
Liquid Distributor for Decomposers	Not Yet Issued

Licensor: Ivo Mavrovic, New York City.
Exclusive licensee: Technip, Rueil-Malmaison, France
Technip, Inc., New York City.

plant, respectively 4.0, 0.70 and 0.72, the back calculated K is equal to 2.9, instead of Frejacques' value of 1.4.

It is obvious from the above data that at a high K value a high conversion can be attained in the reactor with less excess ammonia and more water. To achieve this result, however, the reactor must be properly designed with respect to all the parameters involved. With this new knowledge it became possible to design a urea plant on a much more economical basis.

Isothermal reactor

It was observed that in a standard plug flow reactor, where the feed streams entered at the bottom and the

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FIND EQUILIBRIUM UREA YIELD . . .

SCALE NO.4
% CONVERSION
X × 100

SCALE NO.5
$\frac{NH_3}{CO_2}$ FEED MOL RATIO
a

$$K = \frac{X(b+x)(1+a+b-x)}{(1-x)(a-2x)^2}$$

K = EQUILIBRIUM CONSTANT

X = CONVERSION, $\frac{UREA\ CO_2}{TOTAL\ CO_2}$

a = $\frac{NH_3}{CO_2}$ FEED MOL RATIO

b = $\frac{H_2O}{CO_2}$ FEED MOL RATIO

REFERENCE CURVES

SCALE NO.1
TEMPERATURE °F
t

SCALE NO.3
EQUILIBRIUM CONSTANT
K

SCALE NO.2
$\frac{H_2O}{CO_2}$ FEED MOL RATIO
b

REFERENCE POINT
P

SCALE FOR (a) WHEN (b) = 0

RESULT

EXAMPLE:

FOR: t = 365°F
a = 3.6
b = 0.5
K = 2.06
X = 67%

STEP NO.1. SELECT OPERATING TEMPERATURE (t) ON SCALE NO.1

STEP NO.2. DRAW A STRAIGHT LINE FROM (t) THROUGH THE FIXED REFERENCE POINT (P) TO INTERSECT SCALE NO.3. READ THE VALUE FOR K AT INTERSECTION.

STEP NO.3. SELECT VALUE FOR (a) ON SCALE NO.5 AND VALUE FOR (b) ON SCALE NO.2. CONNECT (a) AND (b) AND MARK THE POINT OF INTERSECTION OF THIS LINE WITH THE APPROPRIATE REFERENCE CURVE CORRESPONDING TO THE SAME VALUE OF (b)

STEP NO.4. DRAW A STRAIGHT LINE FROM (K) AS DETERMINED IN STEP NO.2 THROUGH THE REFERENCE POINT AS DETERMINED IN STEP NO.3 AND INTERSECT SCALE NO.4. READ THE VALUE FOR CONVERSION (X) AT THE INTERSECTION.

FOR A SPECIAL CASE WHEN (b) = 0, (a) MAY BE READ DIRECTLY ALONG THE REFERENCE CURVE FOR b = 0, THUS ELIMINATING STEP NO.3.
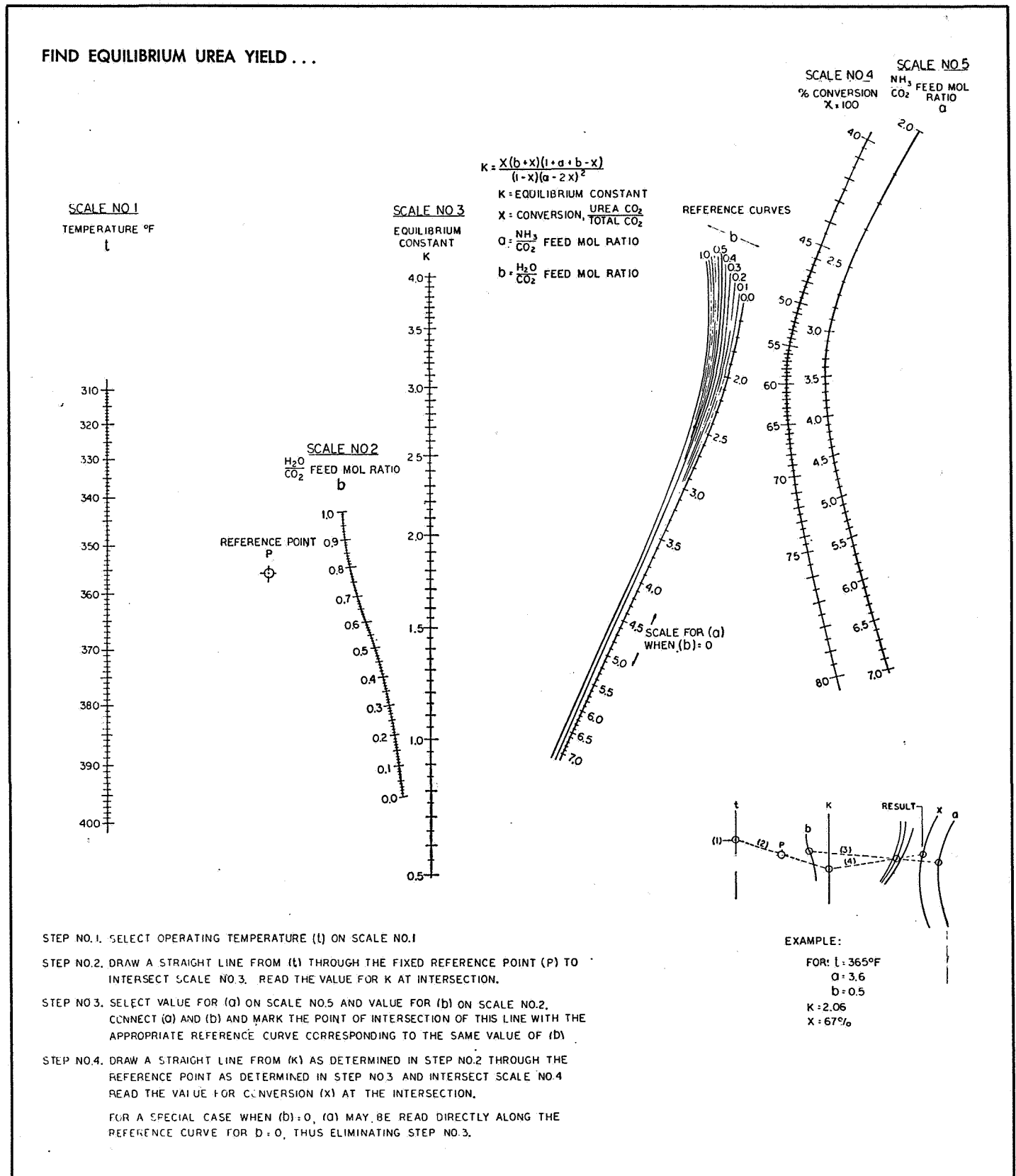
Figure 1. If reactor temperature is known, this nomograph will provide equilibrium conversion for recycled ammonia and carbon dioxide to urea.

reactor effluent was discharged from the top, the temperature of the reactor mixture was invariably higher at the bottom than at the top. This is quite understandable, based on the fact that the reaction of NH_3 and CO_2 to ammonium carbamate in the bottom section is strongly exothermic and almost instantaneous, and the subsequent formation of urea from ammonium carbamate is somewhat endothermic. As a result, the exothermic heat was being stored as sensible heat in the synthesis mixture, and it was later slowly released to supply endothermic heat required for the dehydration of carbamate to urea throughout the reactor.

As a consequence, carbamate formation in the bottom hot section of the reactor was hindered, and it was shifted to higher zones of the reactor. At the same time, the rate of formation of urea was reduced in the upper reactor section due to the gradual adiabatic cooling of the synthesis mixture.

It was discovered that by operating the reactor bottom section relatively colder, and by supplying heat to the upper section of the reactor, the conversion increased considerably. One method of attaining this, which eliminates the need of internal heating steam coils, is to install an open-ended coil in the reactor and to introduce the CO_2 and carbamate streams at the top of the reactor through the coil. As this combined stream flows downwards through the coil, part of the heat of reaction of NH_3 and CO_2 to carbamate is released, thereby heating the urea synthesis mixture.

The ideal condition of an isothermal reactor, countercurrently heated, is approached, resulting in a relative boost in conversion.

The direct benefit of an increase in conversion can be illustrated by the following example. The heat load due to carbamate decomposition and absorption within the decomposition, absorption and recirculation sections of a liquid carbamate total recycle, 700 ton/day urea plant, operating at about 65% conversion per pass in the reactor, is exactly the same as the corresponding heat load in a 1,000 ton/day total recycle urea plant with liquid carbamate recycle operating at about 72% conversion.

Because the relative size of the equipment is approximately proportional to the amount of carbamate handled, it is possible in practice to increase the capacity of a 700 ton/day urea plant, operating at 65% conversion, to a 1,000 ton/day urea plant by simply boosting the reactor conversion from 65% to 72%. Of course, additional CO_2 and NH_3 reactor feed capacity would be required in this case.

In most urea plants, the reactor is lined with stainless steel, the most economical material for this use. However, the surface of the stainless steel liner in contact with the process mixture must remain passivated with oxygen to minimize corrosion. For this purpose, air was usually added to the CO_2 before compression to reactor pressure so as to maintain a concentration of O_2 in the reactor at about 2,500 parts/million based on fresh CO_2 feed.

By observing the operation of several such urea plants, it was found that the air supplied to the urea synthesis reactor via the CO_2 gas was not readily dissolved in the urea synthesis mixture, and it had the tendency of escaping toward the upper section of the reactor together with CO_2 gas. As a consequence, the bottom part of the reactor liner was not adequately passivated, and corrosion of the liner often resulted. To be effective, an undesirably high amount of air was used, which it was noted became quite detrimental to the conversion rate of CO_2 to urea. This was due to improper mixing of CO_2 with NH_3 to form carbamate and to the relatively high carbamate vapor pressure in the reactor.

This problem was solved by adding air to the liquid ammonia stream before it entered the reactor. Taking advantage of the fact that air is moderately soluble in liquid ammonia, it is possible to attain much higher O_2 concentrations in the liquid phase with much less air, and therefore prevent corrosion of the bottom part of the reactor liner. At the same time, it was noted that with relatively less air in the reactor the conversion was boosted considerably.

Electrical power consumption is reduced

The fresh CO_2 makeup is usually compressed to reactor pressure and introduced into the urea reactor for conversion to urea. The compression of CO_2 to reactor pressure requires a great deal of power. Almost 70% of the total power consumption within a urea synthesis process is used by the CO_2 gas compressor.

A new system, recently tested in a commercial urea plant, makes it possible to feed almost 40% of the total fresh CO_2 feed directly into the low-pressure stages of the decomposition and absorption stages of the synthesis section and to recycle it as carbamate solution into the reactor, whereas only the remaining 60% of the fresh CO_2 feed is compressed to reactor pressure and directly introduced into the reactor.

The saving in compression power is quite substantial, because only a minor fraction of the electrical power required to compress a given quantity of CO_2 gas to reaction pressure is used in pumping CO_2 in an ammonium carbamate solution.

The idea of feeding part of the fresh CO_2 feed to the low-pressure section of the absorption system does not represent a novelty per se, because it has been tried before. This technique had the drawback of being difficult to control the concentration of the carbamate solution formed by reaction of CO_2 with ammonia. Frequent freeze-ups of the carbamate recycle solution in the associated equipment were the main cause of plant shutdowns and of consequent poor plant efficiency, because time-consuming analytical methods were normally used to determine the carbamate solution concentration.

Following the development and debugging of a continuous carbamate solution concentration analyzer, which will be described later, the low-pressure CO_2 injection technique was very successfully used in a commercial scale urea plant, and a considerable saving in utility consumption was attained.

Improved decomposition with lower biuret

In urea synthesis processes operating above 3.5- to 1.0 NH_3-to-CO_2 molar ratio it was noted that another usual cause of relatively low reactor conversion was the fact that an excess of water was unavoidably recycled to the synthesis reactor along with the unconverted ammonia and CO_2. This was because in the first decomposition step, too high a proportion of the water from the reactor effluent was carried along with the recovered gases, NH_3 and CO_2, which are usually condensed in a body of an ammoniacal aqueous solution of ammonium carbamate and recycled to the synthesis reactor.

In some urea processes, this problem is avoided by refluxing the total amount of relatively colder reactor effluent counter-currently to the decomposed gases containing excess moisture, in order to condense some
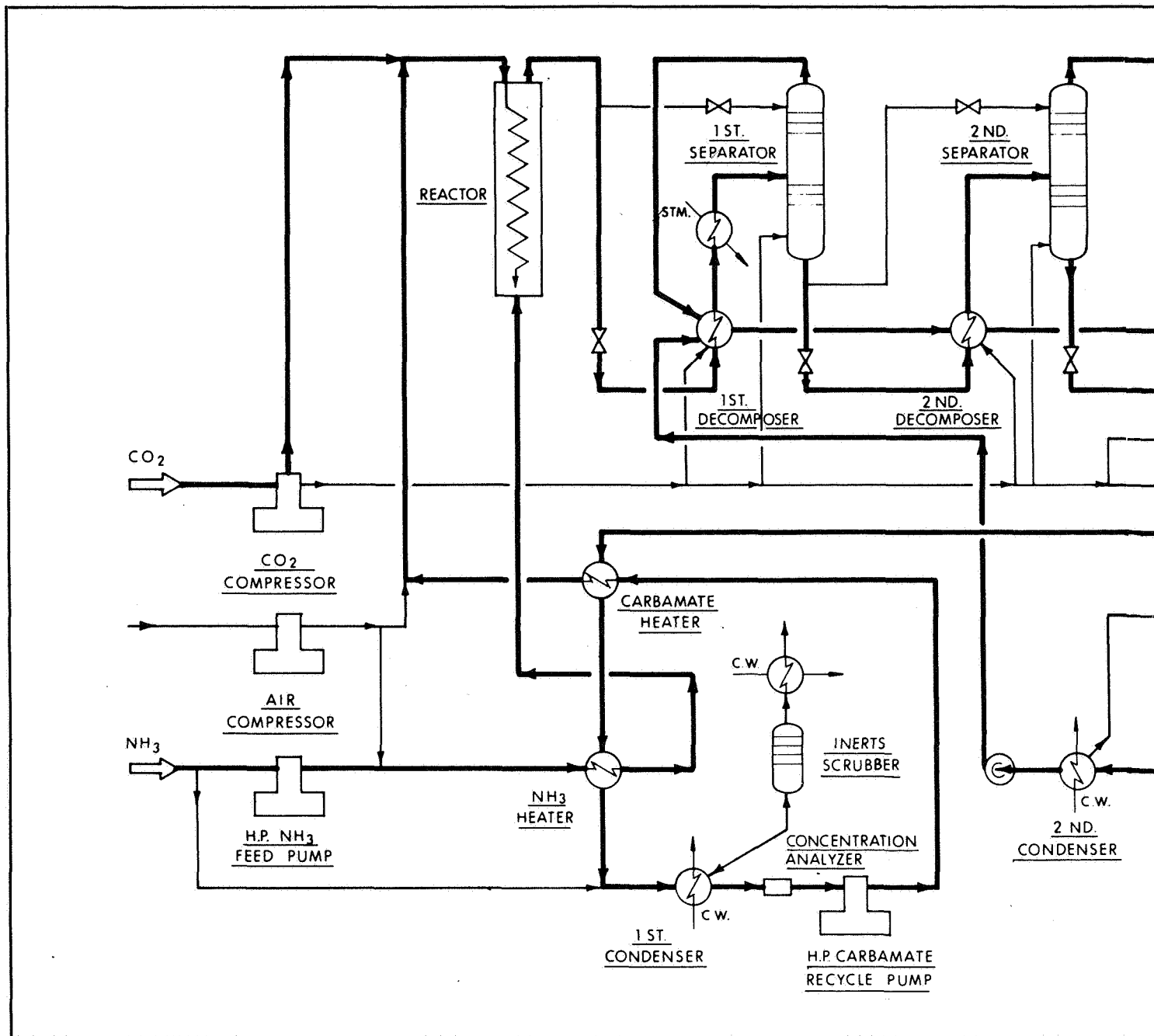
Figure 2. Flow diagram of the Heat Recycle Urea process

moisture out from the gas. This system has the disadvantage of considerable biuret build-up in the reboiler type decomposer which must be used in this case. Thus it affects the product quality and the cost of the additional equipment required to remove part of the biuret from the product before prilling.
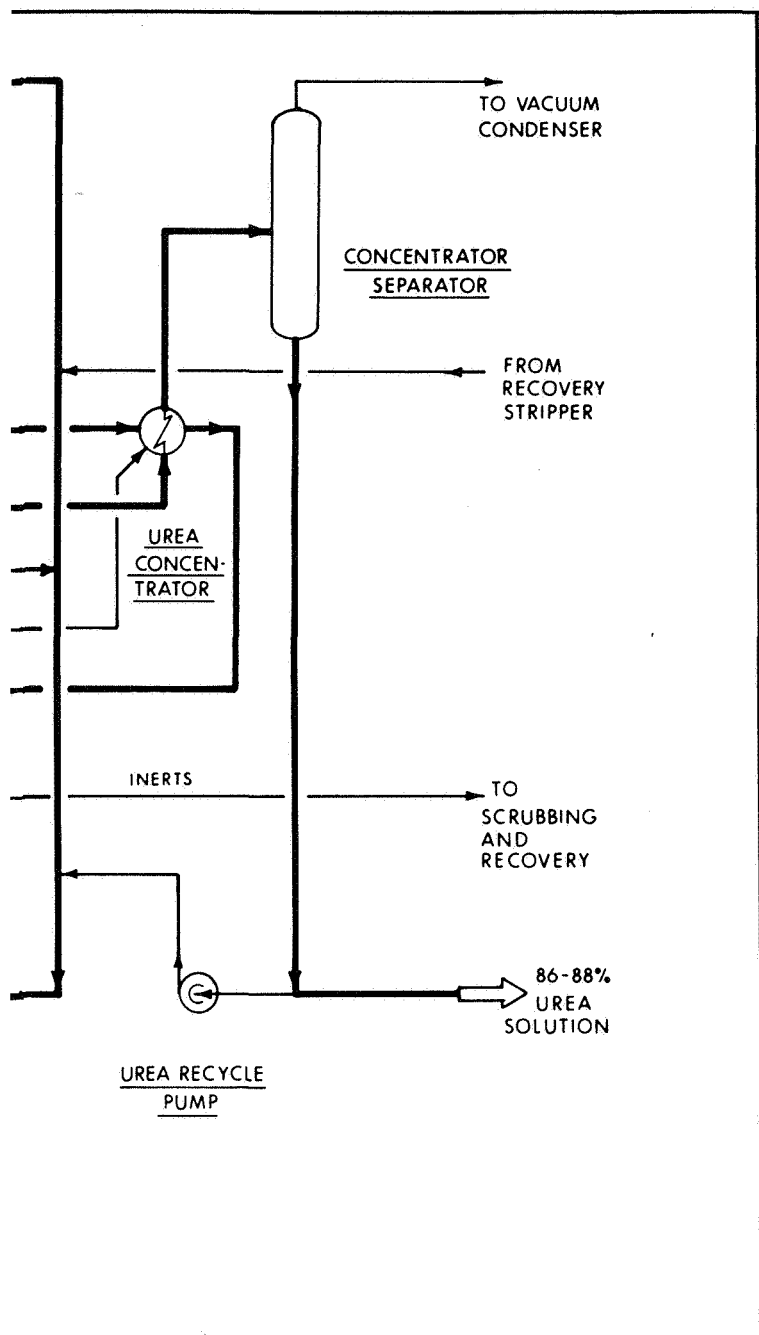
A novel decomposition system that was devised, and which will be described later in this article, substantially lowers this water content in the decomposer off-gas and at the same time yields a urea product with a relatively much lower biuret content. This is accomplished by bypassing a minor portion of the reactor effluent around the forced-feed, high-velocity, vertical decomposer, and by introducing this minor portion into the upper section of the decomposer separator in counter-current contact with the moist decomposer off-gas.

A substantial portion of the water vapor contained in the decomposer off-gas is condensed, and the urea solution product can be used to produce low biuret urea prills by the very inexpensive method of direct evaporation, instead of the relatively expensive crystal-melting method. For instance, it is possible to produce 0.6–0.7 wt. % biuret product by direct evaporation, thus eliminating the need for costly crystallizers, centrifuges, and associated equipment. From experience it appears that a urea prill product containing 0.6–0.7 wt. % biuret is very well suited for the production of synthetic glues. For high-grade technical urea, with 0.25 wt. % urea, the conventional crystal melting route must be used.

Concentration analyzer for carbamate solutions

In reducing the water moisture content in the decomposer off-gas and in feeding fresh CO_2 gas to the absorption and recirculation stages, it became apparent that a reliable method of monitoring and controlling the

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TO VACUUM
CONDENSER

CONCENTRATOR
SEPARATOR

FROM
RECOVERY
STRIPPER

UREA
CONCEN·
TRATOR

INERTS

TO
SCRUBBING
AND
RECOVERY

86-88%
UREA
SOLUTION

UREA RECYCLE
PUMP

water content of the carbamate recycle solution was required to prevent crystallization of the carbamate recycle solution. This problem usually leads to obvious consequent mechanical problems in the high pressure carbamate pumps and associated equipment handling the recycle solution.

Occasional laboratory analyses of the stream are not satisfactory because of the usual six to seven hours time lapse between solution sampling and final analytical results. A very reliable method of obtaining continuous and instantaneous concentration readings and freezing point readings of the carbamate recycle stream was developed, and an apparatus based on a novel principle has been in continuous, trouble-free operation for the past two years in a commercial urea plant. It is now in use in two urea plants, and it has been recently installed in two more.

The concentration analyzer consists of a very simple device of standard construction, with extreme sensitivity and accuracy. It has no mechanical moving parts in contact with the process fluid; and its obstructionless sensing head is mounted directly on the carbamate piping carrying the solution to be analyzed.

The electrical signal from the sensing head is amplified in a panel-board mounted console and transformed into a proportional pneumatic signal, which activates a standard recorder/controller. The scale on the recording instrument is directly calibrated in terms of temperature units. The reading on the instrument is proportional to the concentration of carbamate in solution. It indicates the salting-out temperature of the carbamate solution analyzed.

The output air signal from the concentration recorder-controller is used to automatically control the water balance in the system by varying the pressure in the second separator and, consequently, by varying the water vapor content in the second decomposer NH_3—CO_2 off-gas. As a result, the operator can maintain an optimum water balance in the synthesis, decomposition and absorption system without fear of carbamate salting-out problems and equipment stoppage.

Heat recovery is major concern

In the development of this urea process, another area of prime concern has been the conservation of heat within the system. In virtually all urea plants, decomposition of the unreacted carbamate contained in the reactor effluent was accomplished by indirect heating with steam, and the resulting NH_3—CO_2—H_2O stream was then condensed in indirect heat exchange with cooling water.

From an overall heat balance calculation on these urea processes, it became obvious that the heat supplied to the system was very uneconomically rejected to the cooling water. Bearing this in mind, with a given overall temperature rise it can be said that the specific cooling water consumption of a urea synthesis process per ton of urea produced is the gauge of its thermic efficiency and heat recovery.

Over the years, field data were collected and analyzed, from which it was possible to develop practical condensing curves for the NH_3—CO_2—H_2O-urea system and to design a novel process in which most of the heat of condensation of carbamate could be used to decompose the unconverted carbamate and to preheat the reactor feed streams for thermic equilibrium. The major part of the heat of condensation of carbamate was recycled back into the system, thus the name "Heat Recycle" Urea process.

By this technique, the cooling water consumption was lowered from the usual 17,000-gal./ton level to a much lower value, of about 13,000 gal./ton. As a result, the steam consumption was also reduced, almost porportionally from the usual figure of 1,800–2,000 lb./ton to about 1,200 lb./ton. Due to the relatively low temperature at which the carbamate decomposer is operated in the Heat Recycle Urea process, 150 lb./sq. in. gauge level steam is used instead of valuable 300–600 lb./sq. in. gauge level steam.

Contrary to prior urea synthesis processes, in the Heat Recycle Process the amount of excess ammonia required for optimum conversion in the reactor is not separated from the carbamate recycle solution, condensed to liquid, and recycled into the reactor. Rather, it is totally condensed and dissolved in the carbamate recycle solution. Thus, the whole system for excess ammonia condensation and recycle has been eliminated at considerable saving in equipment cost.

Stainless steel used in construction

Standard 316 L, and 304 L, stainless steel is used for the equipment of a urea plant designed on the basis of the Heat Recycle Process. The relatively high excess ammonia used appears to be minimizing corrosion problems, whereas actual data gathered so far indicates that the low NH_3-to-CO_2 mole ratio urea synthesis processes have a higher rate of corrosion. The iron content in the untreated urea product solution from the urea synthesis section is usually taken as a relative measure of the corrosion rate throughout the synthesis and decomposition system. The Heat Recycle Process rates well with only 0.4-0.6 parts/million iron content in the urea product solution.

In the synthesis of urea from NH_3 and CO_2, 18 lb. of water are formed in the urea synthesis reactor per 60 lb. of urea produced. Quite often the common problem in all urea processes is the disposal of this amount of process water which is contaminated with residual NH_3 and nitrogen compounds, whether it is released to the atmosphere as water vapor or rejected to the sewer in the liquid phase.

A novel and relatively economical recovery stripper was developed for processing the waste effluent stream from a urea plant. It reduces the content of residual NH_3 in the waste liquid stream to about 20 parts/million. The overhead gas containing NH_3 is totally recovered in the urea synthesis section. All gaseous vents from the urea synthesis section are scrubbed with water, and the weak aqua solution is sent to the recovery stripper for NH_3 recovery. The novel design of the prilling tower incorporates a wet dust abatement system to remove the solids from the exhausted air to acceptable standards to meet Environmental Protection Agency (EPA) requirements.

The improvements described above, and many other refinements not mentioned in this article, have been incorporated into the design of this new process, resulting in a considerable overall reduction in production costs. The main contributing factors are 1) lower investment cost, 2) lower operating cost, 3) reliable plant operation, 4) simplicity of equipment, 5) conventional plant operating conditions, proven in many years of experience, and, 6) very economical waste effluent treatment system.

Process description

Preheated carbamate recycle solution and gaseous CO_2 are introduced into the reactor at its top through the inner reactor coil with open end (see Figure 2). They are mixed with preheated liquid ammonia introduced into the bottom section of the reactor.

About 73% of the total CO_2 present in the reactor is converted to urea. The major portion of the reactor effluent is reduced in pressure and heated in a conventional carbamate decomposer. The lower section of the first decomposer is heated by condensing NH_3—CO_2—H_2O off-gas, and the upper section is heated with steam. The first decomposer gas separated from the urea product solution is reduced in water content by a wash of a minor portion of the reactor effluent, and it is directly used to heat the lower section of the first decomposer. CO_2 is used for stripping the residual excess ammonia from the urea solution in the first decomposer separator.

The residual carbamate in the urea product solution is further decomposed in the second decomposer at reduced pressure in indirect heat exchange with the stream of condensing NH_3—CO_2—H_2O off-gas originating from the first decomposer.

Addition of urea and fresh CO_2 to the condensing off-gas ensures proper heat utilization. The NH_3—CO_2—H_2O off-gas from the second decomposer separator is condensed in the second condenser, to which urea recycle is added. The resulting solution is pumped into the first decomposer off-gas to ensure proper condensation of gas and heating of the lower section of the first decomposer.

The mixture of first decomposer NH_3—CO_2—H_2O off-gas and second condenser liquid gives off heat consecutively to the first decomposer, the second decomposer, the urea concentrator, the carbamate heater and the ammonia heater. Fresh CO_2 gas, required to produce urea in the reactor, is added to each of the above heat exchanger shells for proper temperature control and heat utilization. The mixture of off-gas and second condenser liquid is totally condensed in the first condenser and pumped into the reactor.

The continuous concentration analyzer installed at the suction of the high-pressure carbamate recycle pump maintains the recycle solution at a constant concentration by varying the pressure in the second separator, and consequently by varying the rate of water evaporation from the urea solution in the second decomposer. The 75 wt. % urea product solution from the second separator is further concentrated to 86-88 wt. % solution by utilizing the heat given off by the first decomposer off-gas condensing in the concentrator shell side.

The 86-88 wt. % urea solution from the concentrator is further evaporated to pure melt and then processed to solid urea prills in a prilling tower, which is provided with a highly efficient wet dust abatement system for air pollution control.

Condensate from the hot well of the urea evaporator, containing 2-5 wt. % of NH_3, is processed in a novel ammonia recovery stripper and rejected to sewer with only 20-30 parts/million of residual NH_3. The overhead gas containing all the NH_3 recovered from the solution is sent to the second condenser for total utilization.

A plant producing urea in the form of 0.6-0.7 wt. % biuret prills by the evaporative route has the following expected raw material and utility consumption per short ton of prilled urea produced: NH_3, 0.575 ton/ton; CO_2, 0.74 ton/ton; steam at 150 lb./sq. in. gauge, saturated, 1,260 lb./ton; electric power, 110 kw. hr. and cooling water, 86°F, 20°F temperature rise, 13,300 gal./ton. (*Note:* the 110 kw. hr. is reduced to 30 kw. hr./ton when 600 lb./sq. in. gauge steam is used for the CO_2 compressor drive. The exhausted 150 lb./sq. in. gauge steam from the drive is used in the process at no overall steam consumption increase.)

Features of the Heat Recycle Process described in this article have been successfully incorporated in two total-recycle urea plants of an aggregate capacity of 460 ton/day, presently in operation. #

Literature cited

1. Mavrovic, I., *Hydrocarbon Proc.*, **50** (April, 1971).

I. Mavrovic is a consulting engineer specializing in the fertilizer industry, particularly in urea manufacturing. He graduated from Liceo Scientifico of Fiume, Italy and received his B.S. and M.S. in chemical engineering from the University of Zagreb, Yugoslavia. He also also worked as a process engineer.

DISCUSSION

E.R. JOHNSON, Allied Chemical Corp.: It's pretty well established that Frejacques is in considerable error in his equilibrium constants, and we found that he seems to run pretty high on the required volume one would consider you'd need to reach equilibrium. Have you been able to develop any correlation of the volume against time where the conversion would fall off due to insufficient reactor volume? In other words, the retention time required?

MAVROVIC: Yes; the main problem is that there is not only one variable (parameter) affecting the conversion. There are about five or six such variables. Unless you optimize all of these variables, the variation in one variable will not appreciably affect the conversion. It means that, unless you attain the optimum operating point for all the variables involved, the optimization of one single variable will not yield the right effect on the conversion.

JOHNSON: That's why I was thinking it is rather complicated. Have you been able to develop a nomograph similar to the one for the equilibrium constants for the reactor volume under those conditions?

MAVROVIC: No. At the present time we have only empirical formulas, based on actual data taken from operating urea plants. It's extremely difficult I believe to try even to describe in exact formulas or mathematical expressions what is actually happening inside the reactor. I believe, Frejacques equation determines just an overall reaction, it does not determine the single step reactions occurring in the reactor.

JOHNSON: I am glad to see that you observed the same phenomena. We found this same thing. We have one plant we've debottlenecked twice and now we're down to about one third of the reaction volume that you'd predict needed, and we're about to go a little further. I guess we'll develop empirically where it starts to fall off.

MAVROVIC: Absolutely correct.

Q. How do you get passivation of equipment in the recycle area?

MAVROVIC: It is best to treat the critical parts with a 5% dichromate solution containing about 5% nitric acid for about five minutes, for instance by dipping the lens rings into the solution or by simply applying a small amount of solution directly to the flanges or to the part to be passivated.

JOHNSON: Did you say dichromate?

MAVROVIC: Dichromate, right. You don't have to passivate the equipment of the whole system with solution. It's important that at the very first start up of the urea plant milder conditions and excess of oxygen feed to the reactor are used. Within three or four hours from the start up the same result is attained as by pumping large amounts of pickling solution throughout the whole system. This can become a rather expensive and complicated proposition. By passivating the individual and most critical parts of the equipment the need for passivation of the whole system is eliminated.

JOHNSON: We have used the mixture of nitric and hydrofluoric acids. Your dichromate sound like a much simpler solution. I think we'll try it.

MAVROVIC: We usually find that a five percent nitric acid and five percent dichromate solution is very effective. The dichromate is used to degrease (take the grease away from) the surface of the alloy and to facilitate the oxidation of the alloy surface.

JOHNSON: Right. Lastly, what design do you favor for the bottom of the prilling tower for the removal of the prills and to minimize caking, attrition, etc.?

MAVROVIC: There are many designs, such as horizontal fluidized bed bottom and flat bottom with collecting rake, but we adopted a very simple design which is actually a fluidized cone, it's an air slide cone. There are no other moving parts. Opposite to the standard bottom cone (with solid walls), our cone is fluidized with air, and it acts as a diverter for the (free falling) prills. The prills never hit the cone, they are simply diverted from their path. It takes much less air to simply divert the prills from their path, than to stop them totally (in their free fall, as it is done in the horizontal fluidized bed).

JOHNSON: Yes, it sounds like it should be less subject to caking.

MAVROVIC: Absolutely. Less subject to caking and you have a better chance of operating it for a longer time between cleaning.

ANON: One of the principles of your process is that you have observed that a reactor temperature in the bottom is higher than at the top. There is one thing that bothers me because in all our urea plants, both stripping and conventional, we see the opposite. We have the highest temperature at the top (of the reactor). And we think that the fact is that the composition of the reactor liquid phase follows the so-called top ridge line. You know, the top ridge line is the line of the maximum possible temperatures at a given pressure, and this top ridge line says that if you have the highest possible urea concentration at that point you must have automatically predicted by the equilibrium the highest possible temperature.

One thing you must prevent in a urea reactor is the so-called back-mixing. And you can prevent the back-mixing by installing a certain number of trays in it.

MAVROVIC: I know of the same problem — not only in your urea plants, regarding the problem you mentioned that you have hotter reactor tops and colder bottoms. I know of this problem in other urea processes too — I don't want to mention names — the reactor top was hot and the reactor bottom was cold. We found out by analyzing the system that carbamate was simply not being formed in the bottom, but it was being formed at the top of the reactor.

We proved this point with a very simple test. Urea acts as a very good solvent for ammonia and ammonia forms carbamate (with CO_2) whenever you have urea present in a certain region of the reactor. As soon as we fed a recycle stream of urea into such a reactor where the top was hot and the bottom was cold, we simply shifted the whole temperature profile upside down: the hot spot moved to the bottom of the reactor and the cold spot moved to the top of the reactor. It seems that the carbamate was then forming in the bottom section of the reactor — the correct place — and not at the top of the reactor.

Q. Is it true that you must have the carbamate formation at that point where urea is formed, because the urea formation is endothermic — it needs some heat? So what is easier than to make the carbamate on the spot where urea is formed? This is automatically accomplished in a normal vertical reactor with upward flow.

MAVROVIC: That is true, but in such vertical reactor with up flow, if the exothermic reaction of carbamate formation is to supply the endothermic heat of formation of urea, it happens that carbamate remains in the reactor for 10-12 minutes, instead of 30 minute, for instance. So that this part of carbamate normally is not retained in the reactor long enough to form urea and ends up exiting the reactor with the reactor effluent mixture. This fact compels you to overdesign the reactor volume, to provide a longer retention

time of carbamate in the reactor.

Q. One other question: you said that for technical urea you need product with low biuret content, and well, I think that it is confusing because some people say they use low biuret product for technical grade urea. Some other people say that it doesn't matter what the biuret content is because the first step (in the production of) resins from urea is to heat urea. And if you heat urea, you have automatically biuret, triuret and cyanuric acid and so on, you see.

MAVROVIC: I investigated this problem of low biuret product because I believe that urea manufacturers are committing themself to high expenditures (for the production of low biuret product) for no good reasons. For instance, a urea product containing 0.8-0.9 wt% of biuret is absolutely acceptable for the production of glues used in the plywood industry. On the contrary, for the production of high grade resins, for instance, whenever transparency is required, the biuret content of the urea product (used as raw material) affects the color of the resin. Whenever the biuret content exceeded about 0.25 wt%, the resin manufacturers found out that the resin ages sooner — within six months it becomes yellowish. And this is the only reason why people want low biuret product.

ANON: Well, I do not disagree with this. In our DSM plant in Holland we use 60% of our urea production for melamine, and the urea which is used for the melamine production has about 1.2-1.3 wt% of biuret, and we have an excellent (melamine) product. So we meet the international requirements. (specifications).

MAVROVIC: I did not refer to urea product used for the production of melamine, if I did I made a mistake. I was referring to the process of mixing urea product with another agent to produce a resin, not to the process of forming a resin via the melamine route. The former is definitely affected by the biuret content in the urea product, as mentioned before.