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(54) IMPROVED PROCESS FOR THE SYNTHESIS OF UREA /

(71) We, MONTEDISON SPA, an Italian body corporate, of 31 Foro Buonaparte, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention relates to a process for the synthesis of urea from ammonia and carbon dioxide, with the intermediate formation of ammonium carbamate, according to the equation:

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O$$

and in particular to a process in which the by-product of the synthesis are recycled. The invention also relates to apparatus for use in the process.

The first reaction of the above reactions being exothermic, while the second is slightly endothermic. The conversion of carbamate to urea is not quantitative and residual carbamate is usually decomposed into the starting compounds, NH_3 and CO_2, and the prior art discloses different methods by which the NH_3+CO_2 may be recycled.

According to United States Patent Specification No. 3,356,723, a small excess of NH_3 is used in the synthesis (molar ratio NH_3:CO_2 in the reactors is from 2.5:1 to 3:1), the decomposition of the carbamate and the displacement of the excess NH_3 from the liquid product to the gaseous phase are carried out by treating the product, at the synthesis pressure and in a thin-layer heat exchanger (falling film stripper), by heating and using a CO_2 stream as stripping agent. The patent discloses the immediate recycle to the synthesis stage of the gaseous phase and defines the process as "isobar total recycle process in view of the equal pressure in the synthesis and stripping zones. Although such a process is a step forward over prior processes it has various disadvantages. The quantity of stripping gas is limited to the stoichiometric CO_2 requirement and the amount of substance that can be displaced from the liquid phase to the gaseous phase is therefore limited, unless a vigorous heating is carried out which entails excessive consumption of high pressure steam. The excess NH_3 in the synthesis zone must be kept therefore under a certain level and cannot exert all the known beneficial influence on the course of the synthesis, the yields are not very high (55 to 60%) and consequently the quantities of residual carbamate in the solution leaving the reactor reach significant levels.

Other processes, utilizing NH_3 stripping are disclosed in United States Patent Specification No. 3,049,563 and Italian Patent Specification No. 684,929. These processes can work according to higher molar ratios of NH_3:CO_2 (3.5 to 3.8:1) and allow greater conversion yields (62 to 64%). The advantage of the greater yield however is annulled by the large amount of NH_3 present in the urea solution leaving the stripper (22 to 25% NH_3 and 5 to 6% CO_2 by weight), which requires a very large NH_3 recovery section at low pressures, usually 18 to 20 atm. Consequently, these stripping processes, although offering appreciable advantages, due to the decomposition of great part of the residual carbamate at synthesis pressure, are bound to the choice of the stripping agent and to the relatively low conversion yield in the reactor.

The present invention has been made with the above points in mind.

Therefore according to the invention there is provided a process for the synthesis of urea according to the reaction scheme:

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O$$

in which ammonia and carbon dioxide are reacted with a NH_3:CO_2 ratio in the range from 2.5:1 to 10:1 to form a liquid synthesis product, the liquid synthesis product being subjected to a first treatment stage in which it is heated whereby substantially all of the car-

bamate present is decomposed and the decomposition gases together with a portion of the excess ammonia are recycled to the synthesis stage and thereafter the liquid synthesis product is subjected to a second treatment stage in which it is contacted with carbon dioxide and heated to remove the remaining excess ammonia, the resulting solution of urea is collected and the gas phase from the second treatment is condensed (and residual gases purged) before being recycled in the liquid phase to the synthesis stage, the synthesis reaction and the first and second treatments being conducted at substantially the same pressure.

The synthesis temperature generally ranges from 170 to 205°C, preferably from 180 to 200°C. The higher temperatures result in easier successive stripping of the gases using the CO_2 stream and in less heat required for the stripping. The synthesis pressure is generally from 100 to 250 kg/cm², preferably from 180 to 225 kg/cm², the higher pressures being preferred in the presence of the higher temperatures. According to a particular embodiment, the ammonia feed to the reactors is preheated and the CO_2 stream, fed to the second treatment stage, is between 10 and 100% of the synthesis requirement. Preferably the range should be from 50 to 90%, the remaining part being fed directly to the synthesis or to the first stripping.

The process of the invention can have various embodiments. For example, the synthesis of urea can be carried out in two zones, the first zone being positioned above the second zone, the recycled components from the first and second treatment stages being fed into the first zone in which the dehydration of a major portion of the carbamate to urea is performed, and further dehydration of the carbamate to urea is carried out until substantially reaching the equilibrium level is performed in the second zone, operating at a molar ratio of $NH_3:CO_2$ equal to or higher than that in the first zone. Furthermore the decomposition of the carbamate in the first treatment stage can be improved, under certain operating conditions, by the injection of a certain amount of stripping ammonia.

The molar ratio of $NH_3:CO_2$ during the synthesis is generally from 2.5 to 10:1, preferably from 4 to 7:1. When the synthesis is performed in two zones, the ratio should be preferably from 4 to 7:1 in the first and uppermost zone and from 5 to 8:1 in the second zone; in such a case, the residence time of the synthesis mixture in the second zone is from 3 to 15 minutes, preferably from 5 to 8 minutes.

The process according to the invention yields a urea solution substantially free from residual NH_3 and CO_2, which up to now had only been possible at the expense of excessive heat consumption, when the $NH_3:CO_2$ ratio in the reaction zone was low as described above. Even if the heat was recovered using a condenser, in such a process the heat recovery occurred at low temperatures thus involving an enthropy rise. In the prior processes using high $NH_3:CO_2$ ratios the yields were better, but the residual NH_3 amount in the urea solution was excessive, which led to an undesired increase in both number and volume of the recovery apparatus.

The present invention has achieved a balance of two contrasting requirements: on one side the necessity of obtaining solutions practically free from residual reagents and on the other side the need of employing high $NH_3:CO_2$ ratios in order to obtain higher yields and a lower heat consumption. A further advantage of the invention is that the not infrequent thermal disturbances, of temporary and oscillating nature, described in Dutch patent publication 68/8472, may be easily controlled by suitable adjustment, of the recycled streams coming from the first and second stripping stages and it is possible to achieve an optimum thermal profile vane that stabilizes the temporary phenomena.

When the synthesis is carried out in two zones, the pre-heated ammonia fed to the (lower) second zone of the synthesis, increases the $NH_3:CO_2$ ratio, in the second reaction zone, above the level of the ratio in the (upper) first zone. Increasing the $NH_3:CO_2$ ratio, raises the level of the carbamate dehydration because of the dehydrating effect of ammonia, which combines with the reaction water and forms a weakly dissociated ammonium hydroxide (NH_4OH) thus promoting the completion of the synthesis. In general, the increase of the $NH_3:CO_2$ ratio involves some disadvantages, e.g. the necessity to operate at higher pressures and at reduced temperatures which in turn causes an increase in the NH_3 excess and therefore a greater consumption of heat is required for the displacement and recycling of the excess NH_3. To overcome these drawbacks, the optimal value of the $NH_3:CO_2$ molar ratio should not exceed 5:1 although it has been found that it is possible to increase this ratio up to 7:1 or more, provided the increase is the second of the two synthesis zones. The partial pressure of ammonia above the liquid phase, in the (lower) second zone, may be greater, with respect to the upper zone, by an amount corresponding to about the partial pressure of the inert gases, plus the pressure corresponding to the overlying liquid column. It is this fact that allows an increase in the $NH_3:CO_2$ molar ratio up to 7:1 or more and thus the conversion yield of the carbamate, a yield that can reach very high values, e g. 80% and even more. The excess of ammonia solubilized in the liquid phase must be recovered in the first of the two stripping stages and is then fed to the uppermost synthesis zone. An intermediate value of the $NH_3:CO_2$ molar ratio, of from 5:1 to 8:1 can be obtained

by feeding part of the preheated ammonia to the first zone and part to the second zone.

The invention will now be described with reference to the accompanying drawings in which:—

Figure 1 represents a layout of the process according to the invention.

Figure 2 illustrates a modification consisting of the splitting of the reactor into two zones.

Figure 3 illustrates a modification comprising the addition of an ammonia injection into the first stripping stage, and

Figure 4 is a modification of the layout of Figure 2, with the addition of an ammonia injection to the first stripping stage.

Referring to Figure 1, urea is synthetized in a vertical cylindrical reactor, equipped with sieve trays in order to maintain a homogeneous axial flow, thus avoiding a back-mixing of the reaction liquid.

The liquid synthesis product from the reactor flows through pipe (4) due to gravity, into a vertical tube bundle heat exchanger, with inlet at the bottom, heated by steam (10), where the residual carbamate is almost completely decomposed; the decomposition gases and a portion of the excess NH_3 flowing back to the reactor through pipe (3). The solution (6) flowing out from gas-liquid separatory tank (17), connected to the top of the exchanger, passes to a second exchanger, a falling film stripper heated with steam (11); in which 75% of the required CO_2 which has been preheated, is injected and removes almost all the residual NH_3. The solution flowing from the bottom passes, through pipe (7), to be collected or subjected to further conventional process steps.

The gaseous stream (9) leaving the top of the second stripper flows into a condenser together with the purge gases (13) coming from the reactor top and with a solution (8) coming from successive process steps. The heat of condensation is utilized for the production of steam (12). Residual gases are purged from the condenser through pipe (14), while the solution to be recycled to the reactor passes under gravity from the condenser to the reactor via pipe (5).

Preheated NH_3 feed is conveyed to the reactor through pipe (1). The remaining 25% of the required CO_2 is directly fed without preheating to the reactor through pipe (15), branched off from header (16).

The first stripper may alternatively be of the falling film type, as indicated in Figures 3 and 4. Figures 2, 3 and 4 are labelled with like reference numbers to Figure 1 and are fully described in Examples 3, 8 and 10.

Therefore as well as a process for the synthesis of urea the invention also provides apparatus for use in the process comprising

(a) a cylindrical and vertical reactor having an inlet for a feed stream of NH_3 and optionally an inlet for a feed stream of CO_2, an inlet for recycled liquid components, an inlet for recycled gaseous components, a purging nozzle at the reactor top for removal of unwanted gas, an overflow downcomer extending from the head of the reactor to the bottom of the reactor for passage of liquid synthesis product and an outlet for liquid synthesis product in communication with

(b) a first stripper, comprising a vertical tube bundle exchanger with inlet at the bottom in communication with the downcomer for passage of liquid synthesis product and connected to a separation tank, where the separation of a gas phase from the liquid phase occurs, the separation tank having an outlet for gas in communication with the inlet for recycled gaseous components in the reactor and an outlet for liquid in communication with:

(c) a second stripper comprising a heat exchanger, a nozzle near the bottom of the stripper for the inlet of CO_2 as a stripping agent, an outlet for liquid and an outlet for gaseous components in communication with:

(d) a condenser, the condenser having an outlet for liquid in communication with the inlet for recycled liquid components in the reactor.

When the synthesis is performed in two zones the reactor is divided into two zones, a first zone being positioned above a second zone, the two zones having inlets for a feed stream of NH_3 whereby NH_3 may be fed in either zone or both zones simultaneously, an inlet for a CO_2 stream, an inlet for recycled gaseous components and an inlet for recycled liquid components being positioned near the bottom of the first zone, the overflow downcomer extending from the head of the first zone to the bottom of the second zone and the outlet for liquid synthesis product being positioned near the top of the second zone.

Various further modifications may also be made to the apparatus. For example thin-layer heat exchangers may be used for both the condenser as well as for the first stripper, vertical tube bundle heat exchanger (with inlet from the bottom) may be used in the second stripper. Furthermore, the two sections of the reactor may consist of two separate reactors, provided the first zone is positioned above the other. The use of a reactor with two overlying sections, according to the invention, avoids the bulky and cumbersome scaffoldings usually required for the superelevation of the reactors with respect to the supplementary equipment for the treatment of the effluent coming from the synthesis.

When an ammonia injection is used in the first stripper, the inlet is positioned in the lower portion of the stripper as shown in Figures 3 and 4.

The invention will now be illustrated by the following Examples.

Example 1.

The following data refer to a plant as illustrated in Figure 1 having an output capacity of urea of 350 t/d. Urea is synthetized at 200 kg/cm² at 190°C in a vertical cylindrical reactor, equipped with sieve trays suited to maintain homogeneous axial flow, thus avoiding a back-mixing of the reaction liquid; the NH_3:CO_2 molar ratio in the reactor is about 5:1 and the molar ratio of H_2O:C_2O is about 0.5:1. An overall yield of 75% was obtained.

The liquid product flows over through pipe (4) due to gravity, into a vertical tube bundle heat exchanger through the inlet at the bottom, the heat exchanger being heated by steam (10) up to 210°C, where the residual carbamate is almost completely decomposed. The decomposition gases and a portion of excess NH_3 are recycled back to the reactor through pipe (3).

The solution (6) flowing out from gas-liquid separation tank (17), connected to the top of the exchanger, passes to a second exchanger, a falling film stripper, heated with steam (11). In this second exchanger, 75% of the required CO_2, preheated to 200°C, removes almost all the residual NH_3 and the solution flowing out from the bottom passes, through pipe (7), to further conventional process steps. In the second stripper the temperature at the top is about 210°C and the pressure about 200 kg/cm². The gaseous stream (9) leaving the top of the second stripper flows into a condenser together with the purge gases (13) coming from reactor top and with a solution (8) coming from successive process steps, the condensation heat allowing the production of steam (12).

Residual gases containing inert substances e.g. nitrogen are purged from the condenser through pipe (14), while the solution from the condenser at 170°C is recycled to the reactor by gravity through pipe (5).

The preheated NH_3 feed is conveyed to the reactor through pipe (1). The remaining 25% of the required CO_2 is directly fed without preheating to the reactor through pipe (15), branched off from header (16).

The reactor is fed with:

7,878 kg of ammonia preheated to 140°C, through pipe (1), 22,093 kg of carbamate solution at 170°C, through pipe (5), having the following composition:

NH_3	46.31% by weight
CO_2	43.28% by weight
H_2O	10.41% by weight

11,607 kg of vapours at 200°C, through pipe (3) having the following composition:

NH_3	78.69% by weight
CO_2	16.24% by weight
H_2O	4.64% by weight
inerts	0.43% by weight

2,570 kg of CO_2 at 100°C, through pipe (15). 43,609 kg of urea solution at 190°C, having the composition given hereinbelow, leave the reactor through pipe (4) to the first stripper:

NH_3	42.98% by weight
CO_2	8.00% by weight
H_2O	16.29% by weight
urea	32.69% by weight
inerts	0.04% by weight

32,035 kg of urea solution at 210°C, having the composition specified below, flow out from the first stripper through pipe (6) to the second stripper:

NH_3	30.00% by weight
CO_2	5.00% by weight
H_2O	20.50% by weight
urea	44.50% by weight

7,888 kg of CO_2 enter the second stripper through pipe (2). 23,042 kg of urea solution having the composition indicated below flow out at 210°C therefrom:

NH_3	5.97% by weight
CO_2	4.97% by weight
H_2O	27.20% by weight
urea	61.86% by weight

and 16,879 kg of vapours at 210°C having the following composition leave through pipe (9):

NH_3	48.79% by weight
CO_2	49.10% by weight
H_2O	1.78% by weight
inerts	0.33% by weight

The heat requirement of the strippers are met by passing through pipe (10) 5,700 kg and, through pipe (11), 2,800 kg of saturated steam at 20 kg/cm² abs. 11,800 kg of steam at 6 kg/cm² abs. are generated in the carbamate condenser.

Example 2.

Example 1 was repeated utilizing, as first stripper, a vertical tube-bundle, falling film exchanger. Results analogous with those of Example 1 were obtained.

Example 3.

The data that follow refer to a plant as illustrated in Figure 2 having an output capacity of 240 t/day of urea.

Urea was synthetized at 200 kg/cm² and 190°C, in a vertical cylindrical reactor subdivided into two overlying sections fitted with sieve trays to maintain a steadily homogeneous axial flow, avoiding the back-mixing of the reaction liquid. The molar ratio NH_3:CO_2 in the uppermost section of the reactor was about 5:1 while the molar ratio H_2O:CO_2 was maintained at about 0.5:1. The yield was 78%.

The intermediate liquid synthesis product flowed by gravity into the underlying reactor section through pipe (18), and from this section it was passed through pipe (4), into a heat exchanger through a bottom inlet. The heat exchanger was heated by steam (10) up to 210°C, whereby the residual carbamate was almost totally decomposed, the decomposition gases and part of the excess NH_3 being passed back into the reactor through pipe (3). Solution (6), which flowed out of the bottom of separator (17), was passed into a second (thin-layer) heat exchanger, heated by steam (11). In this second exchanger 80% of the required CO_2, preheated to 200°C, removed almost the whole residual NH_3, while the solution coming from the bottom through pipe (7) was passed to further conventional steps of the process. At the top of the second heat exchanger there was a temperature of about 210°C and a pressure of about 200 kg/cm².

The gaseous stream leaving the head of the second exchanger was passed into a condenser together with the gases (13) coming from the head of the reactor together with a solution (8) coming from the successive steps of the process. The heat of condensation was utilized for the production of steam (12). The purge of the residual gases from the condenser was passed through pipe (14), and the solution to be recycled to the reactor left the condenser by gravity at 170°C through the pipe (5).

The required NH_3 was preheated and fed to the reactor through pipe (1) from header (20); the remaining 20% of the required CO_2 being directly fed, without preheating, to the reactor through pipe (15) which branches from header (16).

The reactor was fed with:

5670 kg of preheated ammonia at 140°C, through pipe (1); 15330 kg of carbamate solution at 170°C, through pipe (5), having the following composition:

NH_3	44.1% by weight
CO_2	45.3% by weight
H_2O	10.6% by weight

7110 kg of vapours at 200°C, through pipe (3), having the following composition:

NH_3	80.5% by weight
CO_2	13.3% by weight
H_2O	6.2% by weight, and

1500 kg of CO_2 at 100°C, through pipe (15). From the reactor, through pipe (4), a flow of 29610 kg of urea solution at 190°C, having the following composition was passed to the first stripper:

NH_3	42.4% by weight
CO_2	6.9% by weight
H_2O	17.1% by weight
urea	33.8% by weight

22500 kg of urea solution at 210°C having the following composition below were passed from the first stripper to the second stripper through pipe (6):

NH_3	30% by weight
CO_2	5% by weight
H_2O	20.5% by weight
urea	44.5% by weight

5830 kg of CO_2 were introduced into the second stripper through pipe (2). 16080 kg of urea solution at 200°C having the composition below were withdrawn from the second stripper via pipe (7):

NH_3	6.0% by weight
CO_2	5.0% by weight
H_2O	26.8% by weight
urea	62.2% by weight

together with 12,250 kg of vapours at 200°C having the composition below via pipe (9):

NH_3	47.2% by weight
CO_2	50.1% by weight
H_2O	2.7% by weight

The heat requirement of the strippers were met by passing 3400 kg of saturated steam at 20 kg/cm² (absolute) through pipe (10), and 1900 kg of the steam through pipe (11).
In the carbamate condenser 9000 kg of steam are produced, at 6 kg/cm² (absolutes).

Example 4.

Example 3 was repeated using as first stripper a thin-layer heat exchanger similar to that used for the second stripping stage. Analogous results as in Example 3 were obtained.

Example 5.

Example 3 was repeated, feeding the whole preheated NH_3 (at 170°C) to the base of the lower section of the reactor, through pipe (19). It was thus possible to attain a molar ratio NH_3:CO_2 in the lower section of 7:1, thereby obtaining an 80% conversion yield.

Example 6.

Example 5 was repeated using as first stripper a vertical tube bundle heat exchanger of the falling film type, having an inlet for the liquid synthesis product from the reactor fitted in the head of the heat exchanger and an outlet for the treated liquid, connected to pipe (6), in the lower portion of the heat exchanger. Results analogous to those of Example 5 were obtained.

Example 7.

Example 4 was repeated, passing 45% of the preheated ammonia feed (at 170°C) to the base of the lower reaction section, while the remaining part was conveyed (at 140°C) to

the base of the uppermost section. Results were obtained which were intermediate those of Example 4 and Example 6.

Example 8.

The following data refer to a plant according to Figure 3 having an output capacity of 350 t/d of urea. Urea was synthetized at 200 kg/cm² and at 190°C in a vertical cylindrical reactor, supplied with sieve trays which maintain a homogeneous axial flow, thus avoiding a back mixing of the reaction liquid. The NH_3:CO_2 molar ratio in the reactor was about 5:1 and the H_2O:CO_2 molar ratio was about 0.5:1. The intermediate liquid synthesis product flowed by gravity, through pipe (4) into a vertical tube bundle heat exchanger, heated by steam (10) up to 210°C, whereby the residual carbamate was almost completely decomposed, with the aid of a stream of ammonia (21) preheated at 200°C, equal to 50% of stoichiometric need. The decomposition gases and a portion of the NH_3 excess were recycled back to the reactor through pipe (3). The solution (6) was passed to a second exchanger, a falling film stripper, heated with steam (11). 75% of the CO_2 required for synthesis, and preheated to 200°C, was passed into the second exchanger whereby almost all the residual NH_3 was removed and the solution flowing out from the bottom passed through pipe (7), to further conventional process steps. In the second stripper the temperature at the top was about 210°C and the pressure about 200 kg/cm². The gaseous stream (9) leaving the top of the second stripper was passed into a condenser together with the gases (13) coming from the reactor top and with a solution (8) coming from successive process steps. The heat of condensation was utilized in the production of steam (12). Residual gases were purged from the condenser through pipe (14), while the solution was recycled to the reactor from the condenser at 170°C through pipe (5) under gravity. The remaining 50% portion of the NH_3 feed, preheated at 140°C was conveyed to the reactor through pipe (1), and the remaining 25% of the required CO_2 is directly fed without preheating to the reactor through pipe (15), branched off from header (16).

The reactor was fed with:

3,939 kg of ammonia preheated at 140°C, through pipe (1); 24,778 kg of carbamate solution at 170°C, through pipe (5), having the following composition:

NH_3	51.7% by weight
CO_2	39.0% by weight
H_2O	9.3% by weight

13,008 kg of vapours at 210°C, through pipe (3), having the following composition:

NH_3	81.3% by weight
CO_2	14.5% by weight
H_2O	4.2% by weight and

2,537 kg of CO_2 at 100°C, through pipe (15).

43,593 kg of urea solution at 190°C, having the composition given below, left the reactor through pipe (4) to the first stripper.

NH_3	43.0% by weight
CO_2	8.0% by weight
H_2O	16.3% by weight
urea	32.7% by weight

3,939 kg of ammonia preheated at 200°C was passed to the first stripper and 34,523 kg of urea solution having the composition below was removed from the first stripper and passed to the second stripper via pipe (6):

NH_3	35.0% by weight
CO_2	4.6% by weight
H_2O	19.0% by weight
urea	41.4% by weight

7,847 kg of CO_2 were injected into the second stripper through pipe (2), and 23,043 kg of urea solution having the composition indicated below were removed at 210°C through pipe (7):

NH_3	6.0% by weight
CO_2	5.0% by weight
H_2O	27.1% by weight
urea	61.9% by weight

together with 19,328 kg of vapours at 210°C through pipe (9) having the following composition:

NH_3	55.7% by weight
CO_2	42.7% by weight
H_2O	1.6% by weight

The heat requirement of the strippers was met by passing 6,300 kg of saturated steam at 20 kg/cm² abs. through pipe (10) and 2,600 kg of the steam through pipe (11). 12,000 kg of steam at 6 kg/cm² abs. were generated in the carbamate condenser. The overall conversion yield was comparable to that of Example 1.

Example 9.

Example 8 was repeated by feeding 100% of the required CO_2 to the second stripper. Results analogous with those of Example 8 were obtained.

Example 10.

The following data refer to a plant in accordance with Figure 4 having an output of 240 t/day of urea. Urea was synthetized at 200 kg/cm² and at 190°C, in a vertical cylindrical reactor sub-divided into two overlying sections fitted with sieve trays which maintain a homogeneous axial flow, avoiding the back-mixing of the reaction liquid. The molar ratio NH_3:CO_2 in the upper section of the reactor

was about 5:1, while the molar ratio H_2O:CO_2 was about 0.5:1. The intermediate liquid synthesis product flowed under gravity into the underlying section through pipe (18) and from there passed, through pipe (4), after a residence time of about 6 minutes, into a vertical, thin-layer tube bundle heat exchanger of the falling film type. The heat exchanger was heated with steam up to 210°C, and the residual carbamate was almost totally decomposed, with the aid of an ammonia stream (21), preheated at 180°C, equivalent to about 50% of the stoichiometric requirement of NH_3. The decomposition gases and part of the excess NH_3 was passed back to the reactor through pipe (3). Solution (6), flowed out through the bottom of the heat exchanger and was passed into a second heat exchanger, of the thin-layer type, heated with steam (11). In the second heat exchanger about 80% of the CO_2 requirement, preheated at 200°C, removed almost the whole residual NH_3 and the solution flowing out of the bottom passed through pipe (7) to further conventional process steps. In the second heat exchanger the temperature at the top was about 210°C and a pressure was about 200 kg/cm². The gaseous stream (9) leaving the top of the second heat exchanger passed to a condenser together with purge gases (13) coming from the head of the reactor and with a solution (8) coming from further steps of the process. The condensation heat was utilized in the production of steam (12). The residual gases are purged through pipe (14) while the solution, was recycled back to the reactor from the condenser at 170°C through pipe (5). The whole remaining part of the NH_3 feed preheated at 140°C was introduced to the reactor through pipe (1). The residual 20% of the required CO_2 was directly fed into the reactor without any preheating through pipe (15), branched from header (16). The reactor was fed with:

3,000 kg of preheated ammonia at 140°C, through pipe (1); 16,210 kg of carbamate solution at 170°C, through pipe (5), having the following composition:

NH_3	47.8% by weight
CO_2	42.1% by weight
H_2O	10.1% by weight

8,900 kg of vapours at 200°C, through pipe (3), of the following composition:

NH_3	83.2% by weight
CO_2	11.9% by weight
H_2O	4.9% by weight

1,500 kg of CO_2, at 100°C, through pipe (15). From the reactor, 29,610 kg of urea solution at 190°C, having the composition below were withdrawn through pipe (4) and introduced into the first stripper:

NH_3	42.2% by weight
CO_2	6.9% by weight
H_2O	17.1% by weight
urea	33.8% by weight

A stream of 2,670 kg of ammonia, preheated at 180°C, entered through pipe (21) into the first stripper and 23,380 kg of urea solution having the composition below were passed from the first stripper to the second stripper via pipe (6):

NH_3	32.1% by weight
CO_2	4.3% by weight
H_2O	20.8% by weight
urea	42.8% by weight

5,830 kg of CO_2 were introduced into the second stripper through pipe (2), and 16,080 kg of urea solution at 200°C having the composition below were removed through pipe (7):

NH_3	6.0% by weight
CO_2	5.0% by weight
H_2O	26.8% by weight
urea	62.2% by weight

and 13,130 kg of vapours at 200°C having the composition below were removed through pipe (9):

NH_3	51.7% by weight
CO_2	45.6% by weight
H_2O	2.3% by weight

The heat requirements of the strippers were met by passing 3,600 kg of saturated steam at 20 kg/cm² (absolute) through pipe (10) and 2,000 kg of the steam through pipe (11) respectively. The condenser produced 9,200 kg of steam at 6 kg/cm² (absolute). The whole conversion yield in the reactor was about 78%.

Example 11.

Example 10 was repeated feeding 100% of the CO_2 into the second stripper. Results virtually the same as in Example 10 were obtained.

Example 12.

Example 10 was repeated by feeding 50% of the NH_3 feed preheated at 170°C to the base of the lower section of the reactor, through pipe (19); to attain a molar ratio NH_3:CO_2 in the lower section equal to 7:1. A yield of about 80% was obtained.

Example 13.

Example 10 was repeated, feeding 25% of the ammonia feed preheated at 170°C to the base of the lower section of the reactor and the same quantity of ammonia preheated at 140°C to the base of the upper section. Results lying between the results of Example 10 and those of Example 12 were obtained.

WHAT WE CLAIM IS:—

1. A process for the synthesis of urea according to the reaction scheme:

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O$$

in which ammonia and carbon dioxide are reacted with a $NH_3:CO_2$ ratio in the range from 2.5:1 to 10:1 to form a liquid synthesis product, the liquid synthesis product being subjected to a first treatment stage in which it is heated whereby substantially all of the carbamate present is decomposed and the decomposition gases together with a portion of the excess ammonia are recycled to the synthesis stage and thereafter the liquid synthesis product is subjected to a second treatment stage in which it is contacted with carbon dioxide and heated to remove the remaining excess ammonia, the resulting solution of urea is collected and the gas phase from the second treatment is condensed (and residual gases purged) before being recycled in the liquid phase to the synthesis stage, the synthesis reaction and the first and second treatments being conducted at substantially the same pressure.

2. A process as claimed in claim 1, in which the synthesis temperature is from 170 to 205°C.

3. A process as claimed in claim 2 in which the synthesis temperature is from 180 to 200°C.

4. A process as claimed in any preceding claim in which the synthesis pressure is from 100 to 250 kg/cm².

5. A process as claimed in claim 4 in which the synthesis pressure is from 180 to 225 Kg/cm².

6. A process as claimed in any preceding claim in which the ammonia feed to the synthesis stage is preheated.

7. A process as claimed in any preceding claim in which the CO_2 stream, fed to the second treatment stage, is from 10 to 100% of the CO_2 synthesis requirement.

8. A process as claimed in claim 7, in which the CO_2 stream, fed to the second treatment stage is from 50 to 90% of the CO_2 synthesis requirement, the remaining part being fed directly to the synthesis stage or to the first treatment stage.

9. A process as claimed in any preceding claim in which ammonia is injected into the liquid synthesis product in the first treatment stage.

10. A process as claimed in any preceding claim in which the molar ratio of $NH_3:CO_2$ during the synthesis is from 4 to 7:1.

11. A process as claimed in any preceding claim in which the synthesis of urea is carried out in two zones, the first zone being positioned above the second zone, the recycled components from the first and second treatment stages being fed into the first zone in which the dehydration of a major portion of the carbamate to urea is performed, and further dehydration of the carbamate to urea is carried out until substantially reaching the equilibrium level is performed in the second zone, operating at a molar ratio of $NH_3:CO_2$ equal to or higher than that in the first zone.

12. A process as claimed in claim 11 in which the molar ratio of $NH_3:CO_2$ is from 4 to 7:1 in the first zone and from 5 to 8:1 in the second zone.

13. A process as claimed in claim 11 or claim 12 in which the excess ammonia stripped in the first treatment stage is fed to the first zone, an intermediate value of the molar ratio of $NH_3:CO_2$ of from 5:1 to 8:1, being obtained in the second zone by feeding a portion of preheated ammonia feed to the first zone and a portion of preheated ammonia feed to the second zone.

14. A process as claimed in claim 13, in which the temperature of the NH_3 feed to the second zone is higher than the temperature of the NH_3 feed to the first zone.

15. A process according to claim 1 which is carried out in apparatus comprising:

(a) a cylindrical and vertical reactor having an inlet for a feed stream of NH_3 and optionally an inlet for a feed stream of CO_2, an inlet for recycled liquid components, an inlet for recycled gaseous components, a purge nozzle at the reactor top for removal of unwanted gas, an overflow downcomer extending from the head of the reactor to the bottom of the reactor for passage of liquid synthesis product and an outlet for liquid synthesis product in communication with

(b) a first stripper, comprising a vertical tube bundle exchanger with an inlet at the bottom in communication with the downcomer for passage of liquid synthesis product and connected to a separation tank, where the separation of a gas phase from the liquid phase occurs, the separation tank having an outlet for gas in communication with the inlet for recycled gaseous components in the reactor and an outlet for liquid in communication with

(c) a second stripper, comprising a heat exchanger, a nozzle near the bottom of the stripper for the inlet of CO_2 as a stripping agent, an outlet for liquid and an outlet for gaseous components in communication with

(d) a condenser, the condenser having an outlet for liquid in communication with the inlet for recycled liquid components in the reactor.

16. A process as claimed in claim 15 in which the reactor is divided into two zones, a first zone being positioned above a second zone, the two zones having inlets for a feed stream of NH_3 whereby NH_3 may be fed in either zone or both zones simultaneously, an inlet for a CO_2 stream, an inlet for recycled gaseous components and an inlet for recycled

liquid components being positioned near the bottom of the first zone, the overflow downcomer extending from the head of the first zone to the bottom of the second zone and the outlet for liquid synthesis product being positioned near the top of the second zone.

17. A process as claimed in claim 15 or claim 16 in which the first stripper includes a thin-layer heat exchanger.

18. A process as claimed in claim 17 in which the first stripper additionally comprises an inlet in the lower portion for injection of ammonia or CO_2.

19. A process for the synthesis of urea substantially as herein described with reference to any of the accompanying drawings.

20. A process for the synthesis of urea substantially as herein described with reference to any one of the Examples.

21. Urea when prepared by a process as claimed in any preceding claim.

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