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"INTEGRATED PROCESS FOR THE PRODUCTION OF UREA"

We, SNAM PROGETTI S.p.A., an Italian Company, of Corso Venezia, 16, Milan, Italy,

do hereby declare the invention, for which we (~~I~~) pray that a patent may be granted to us (~~me~~), and the method by which it is to be performed, to be particularly described in and by the following statement:-

OUR REF. MRJones/IPS
HL.91735

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This invention relates to a process for the production of urea, and, more particularly, relates to a process for the production of urea which is integrated with the production of ammonia.

The production of urea on an industrial scale usually involves use of two plants, each operating independently of the other. The plants involved are a plant for the production of liquid ammonia in which carbon dioxide is produced as a by-product and a plant for the production of urea involving reaction of the two products of the first plant. When the final product is mainly urea, ammonia can be considered to be an intermediate and for this reason it has already been attempted to integrate the two plants.

It has been considered generally that an ideal scheme of integration would be one wherein a direct reaction between ammonia and carbon dioxide would occur with formation of ammonium carbamate which is subsequently converted into urea, integration being carried out in such a way that it is possible to avoid two steps characteristic of operations with an ammonia line. One step involves the decarbonation of gas being supplied to the ammonia synthesis, using solvents, and regeneration of carbon dioxide from the solvents followed by the compression thereof to the urea synthesis pressure. The other step to be avoided is that of separation, by liquefaction, of ammonia from the mixture of unreacted gases obtained. These two steps are expensive to operate.

Advantages of such a scheme would be the following:

(a) saving of thermal energy required by a conventional decarbonation plant;

required for the separation of the ammonia from unreacted gases;

(c) saving on the plant cost by elimination of the ammonia separation stage;

(d) saving of the mechanical energy required for the CO_2 compression; and

(e) saving on the plant cost for the CO_2 compression.

The subjection of the ammonia production to the production of urea can apparently be considered to be a negative aspect of the integrated process. The word "apparently" is used here, because the integrated scheme will be feasible only in those cases wherein all or a major part of the ammonia produced is converted into urea. Should an integrated process be practicable, then ammonia must be considered as an intermediate product.

In one integrated process for the production of urea known at least in Italy, the raw synthesis gases for use in the ammonia synthesis are compressed and passed to a column, the upper part of which is employed for absorption of CO_2 from the raw synthesis gas by means of ammonia solution leading to formation of carbamate, and the lower part of which is used for the conversion of the carbamate produced into urea. The CO_2 is absorbed by anhydrous ammonia to which an aqueous solution of the decomposition products of the unconverted (to urea) ammonium carbamate is added. Such a decomposition can be carried out at low pressure.

the formation of the carbamate and the presence of inert components (H_2+N_2) (hereinafter referred to as inerts) of raw synthesis gas reduces the partial pressure of the NH_3 and of the CO_2 and makes it necessary to operate at high pressures (about 250 kg/cm^2) to achieve sufficient partial pressure of carbon dioxide to maintain the reactance in the liquid phase. No means for utilising such heat as it develops is described in connection with such a scheme and thermal balance is obtained by the introduction of cold absorbing solutions. The conversion of the carbamate into urea is effected in the lower part of the same apparatus.

The raw synthesis gases from which the CO_2 has been absorbed after other treatments, are forwarded to plant for the synthesis of ammonia at high pressure, namely from 100 to 500 kg/cm^2. In view of the fact that the ammonia produced and employed to obtain the aqueous absorbing solution is initially anhydrous, it can be deduced that its separation from the effluents of the urea synthesis requires, for example, cooling with water followed by vaporisation. This can also be deduced because of the high partial pressure of ammonia required.

In another integrated process, only part of the CO_2 is supplied in the form of raw synthesis gases, some of the CO_2 therein contained being obtained pure by conventionally treating raw synthesis gas. This procedure has been adopted because the ammonium carbamate formation and its conversion into urea is carried out in this process in two different apparatuses, and in order to maintain the

temperature of apparatus in which urea forms within an acceptable range; ammonia and carbon dioxide of relatively pure form are used, the reaction therebetween in the quantities permitted by use of the greater amount of pure CO_2 permitted by the separation, supplying the necessary heat.

The absorption of the carbon dioxide from the raw synthesis gases to produce ammonium carbamate is effected at a lower pressure than the pressure employed for the urea synthesis; aqueous solutions containing the products of decomposition of ammonium carbamate not converted into urea, together with occasional additions of ammonia are also used in this process for the production of urea. The carbamate decomposition products used are scrubbed, partly in a first column to which raw synthesis gases for supply of CO_2 are fed, and partly in a second column to which a diluted ammonia solution is sent as absorbing agent. The solution from this second column is circulated as absorbing medium to the aforesaid first column.

The raw synthesis gases from which the CO_2 has been removed are used in the ammonia synthesis, after being subjected to the usual pre-treatments.

According to a first aspect of the present invention there is provided a process for the production of urea, comprising a first step wherein carbon dioxide is reacted in a first reactor or carbamate with concentrated aqueous ammonia to form an aqueous solution of ammonium carbamate, and a second step wherein the ammonium carbamate so formed is dehydrated in a second reactor or urea to form urea, in which process unreacted carbamate present in the liquid phase

urea-containing solution from the second reactor is decomposed and the decomposition products so formed are recycled in the gaseous phase to said second reactor to supply the heat required to maintain the contents thereof at the dehydration temperature of the carbamate, and recovering urea from said solution.

This process has the particular advantage that it can be readily adapted for use in an integrated process of the above-described type, and, according to a second aspect of this invention, there is provided an integrated process for the production of urea, comprising the steps of carrying out, in an absorber, absorption in water or in a dilute solution of ammonia, the ammonia present in the gaseous effluent from an ammonia synthesis reactor to obtain a concentrated ammonia solution; in a carbamate reactor, passing raw carbon dioxide-containing synthesis gas for the synthesis of ammonia through said concentrated ammonia solution to absorb the carbon dioxide present in the raw synthesis gas, to produce a concentrated solution of ammonium carbamate; feeding said concentrated ammonium carbamate solution to a urea reactor; dehydrating the ammonium carbamate in the urea reactor to form urea, decomposing, in a decomposer, ammonium carbamate which rema undehydrated after passage through the urea reactor, and supplying the dehydration products thereof to the urea reactor and using the heat of decomposition of the ammonium carbamate as a heat source for the urea reactor; recovering the urea-containing solution from which undehydrated ammonium carbamate has been decomposed into its gaseous components and separated therefrom; and subjecting to methanation the gaseous product of said contacting of the concentrated ammonia

entrained in said gaseous product and subjecting the gaseous product to dehydration and compression before supplying it to the ammonia synthesis reactor.

The process of the present invention has the following characteristic features:

(a) allows use of types of apparatus which allow good contacting of reactants and good heat exchange;

(b) the effective dehydration of gases from the carbamate reactor so that they can be re-used in ammonia synthesis; this dehydration step is in accordance with the invention described and claimed in our copending Britis Patent Application No. 53978/70.

(c) the separation of the ammonia produced in the ammonia synthesis reactor from the other gaseous effluents therefrom by use of water absorption, the ammonia solution obtained being used for the reaction with CO_2 to produce ammonium carbamate;

(d) the direct supply of the ammonium carbamate solution obtained to the urea reactor; and

(e) the carrying out of an isobaric cycle involvi conversion of the carbamate into urea and decomposition o unconverted carbamate.

The process of the present invention permits a substantial reduction of the investment costs, since the amount of plant required is reduced with respect to the amount of plant used in prior art integrated processes. This results in lower operating costs as it reduces remarkably the consumption of mechanical energy and the consumption of thermal energy per ton of urea produced.

In the integrated process for the production of urea according to the present invention, raw gases for ammonia synthesis, generally in the form of a steam reformed mixture of water gas and producer gas, but obtainable by any other way, and wherein the carbon monoxide has been almost completely converted to carbon dioxide, is compressed to a pressure slightly higher than that intended to be used in the urea synthesis. After the compression step, the gaseous stream containing all the carbon dioxide necessary for the production of urea is supplied to the bottom of a vertical tube exchanger (hereinafter termed first exchanger) in which it flows through the tubes in countercurrent with a film of ammonia solution, to produce ammonium carbamate. The heat of reaction involved is removed by passing a cooling fluid through a jacket surrounding the first exchanger. This cooling fluid can be water for feeding boilers. The design of the carbamate reactor is not critical, and many types of commercially available apparatus can be used.

The carbamate solution which has been formed flows out of the bottom of the carbamate reactor, in which the temperature is generally within the range of from 100 to 250°C. and the pressure is in the range of from 100 to 250 kg/cm^2, in the form of a very concentrated solution which is supplied directly to a urea reactor for conversion into urea. The conversion into urea will be described hereinafter. In addition to being supplied to the top of the carbamate reactor, the ammonia solution can be supplied, in part, to the bottom. A gaseous stream of gas saturated with ammonia and substantially free of CO

passes out from the top of the first exchanger to a cooler wherein a part of the ammonia condenses, and is returned to the first exchanger, preferably to the bottom thereof.

The cooled gas from the carbamate reactor is then passed to a methanation plant after being suitably pre-heated in suitable heat exchangers. CO present in the gas is converted to CH_4 and the CH_4-containing gas so formed is advantageously used to pre-heat the cooled gas in one of said heat exchangers, and is then passed to a second vertical tubes exchanger (hereinafter termed second exchanger) which can be of similar design to the first exchanger, wherein it passes in counterflow with water or dilute aqueous ammonia solution, which absorbs the ammonia contained in the gases. The second exchanger is also cooled by a cooling fluid which flows in a jacket theresurrounding, in such a way as to maintain in the exchanger a temperature from 10 to 60°C; the pressure in this exchanger generally ranges from 100 to 25[illegible] kg/cm^2. Ammonia-containing gases from an ammonia synthesis reactor are also supplied to this second exchanger and also travel in counterflow to the water or dilute ammonia solution, which absorbs practically all the ammonia present in the gases.

A very concentrated ammonia solution (for example 75 to 85% by weight) is sent out absorbing medium from the second exchanger to the first exchanger wherein it absorbs the CO_2 present in the raw synthesis gas.

The gaseous mixture which issues from the top of the second exchanger now contains a high proportion of inerts and to avoid accumulation of the inerts, part of

this gas stream is vented off. The remainder of this gaseous stream, which is saturated with water, is sent to a dehydration unit in which is effected a "quench" with ammonia as described in the specification of our copendin British Patent Application No. 53978/70.

In such a unit, the gases are dehydrated by injecting therein liquid ammonia, dehydration taking place in a part of the unit which allows a large exchange surfac to exist between the gases and ammonia. Thorough mixing o ammonia and the gases is achieved, in order that the ammonia should partially evaporate. The cooling caused by the adiabatic evaporation of part of the ammonia and the solvent effect of the ammonia itself, made easy by the large area of exchange between the gases and ammoni results in the removal of the last traces of water from the gases. This removal can be preceded by a step in which the gases are cooled in a heat exchanger in which dehydrated gas flows in countercurrent to the gas still to be treated, and results in condensation of part of the moisture content of the gases.

Immediately downstream of the unit in which the liquid ammonia is ejected, for example a Venturi pipe, is provided a gas-liquid separator wherein the cooled gase can be separated from concentrated ammonia solution and the cooled gases passed to the aforementioned heat exchang to undergo heat exchange with gases to be dehydrated and the concentrated ammonia solution can be added to the ures solution which issues from the urea reactor as will be explained hereinafter. This concentrated ammonia solutio is preferably mixed with the weak ammonia solution which

is formed in the heat exchanger wherein the water-containi gases from the second exchanger are initially subjected to cooling.

The dehydrated gases are then compressed to the ammonia synthesis pressure, generally from 100 to 250 kg/c and then sent to the ammonia synthesis reactor in which ammonia synthesis is effected in conventional manner. The ammonia produced is then cooled and supplied to the aforementioned second exchanger in which it is dissolved in water or dilute aqueous ammonia flowing in countercurre therewith.

The freshly produced ammonium carbamate solution from the first exchanger, optionally together with ammonia, is supplied to the bottom of the urea reactor where the products of decomposition of unreacted carbamate are injected. Condensation of these decomposition product furnishes the heat necessary for maintaining the thermal balance of the urea reactor. The temperature in the urea reactor, which may be adjusted by varying the amount of decomposition products introduced thereinto, may vary from 150 to 250°C. and the pressure therein may vary from 100 to 250 atmospheres. The urea, ammonium carbamate and urea solution which issue from the top of the urea reactor flow, for example under gravity to a carbamate decomposer wherein they are heated by suitable heating means, for example a heating fluid in a surrounding jacket. In the decomposer, gaseous NH_3 can flow in countercurrent and plays the role of stripping agent. Under these conditions some of the ammonium carbamate and most of the dissolved ammonia are stripped and sent back to the reactor.

the urea solution obtained in this way is then subjected to aftertreatments which are standard in the art. Inerts are vented from the urea reactor.

It is pointed out that the system pressures set out above are merely preferred, and it is possible to operate outside the ranges specified, and in particular at higher pressures. An additional processing step which can be carried out on liquid effluent from the two exchangers is one of fractional distillation. This means that the concentrated ammonia solution produced in the second exchanger can be subjected to fractional distillation in known manner before being sent as absorbing solution to the first exchanger. The fractional distillation results in production of liquid ammonia and water or very dilute ammonia solution. The liquid ammonia is then preferably supplied to the bottom of the first exchanger and the water or dilute ammonia solution is supplied to the top of the first exchanger and allowed to flow inside the tubes as a film in countercurrent with raw synthesis gas.

Although the process of the present invention is preferably carried out in the form of an integrated process involving ammonia and urea syntheses, in its broadest aspect, the process can be carried out independent of ammonia synthesis. In this case, instead of using synthesis gas for ammonia synthesis, any CO_2 rich gas can be employed. Likewise, it is possible to employ any ammonia solution as absorbing agent for the carbon dioxide in the formation of the carbamate, which carbamate can then be supplied directly to the urea reactor for de-

hydration and the undehydrated carbamate can be decomposed according to the present invention and the decomposition products supplied to the urea reactor to maintain the temperature therein.

However, as will be clear from the foregoing, the process of the present invention is particularly suitable for use in an integrated urea and ammonia synthesis plant. It is not necessary to work in the ammonia synthesis reactor at pressures as high as those stated previously and, in some cases it is possible to work at substantially lower pressures. In the case of ammonia synthesis at low pressure, the separation of the ammonia from the other components of the gaseous effluent from the ammonia reactor can be carried out by condensing the ammonia in heat exchangers cooled by evaporating ammonia. However, the effective dehydration system for recycling the methanated product of the first exchanger is a much cheaper and more effective way of achieving separation of ammonia from the other gaseous components of the effluent from the ammonia synthesis reactor. This is because it is possible to carry out separation at a single surface at which very good heat and matter exchange can be achieved. This means that water introduced into the cycle can be employed in two ways. Firstly the water can be used to absorb ammonia, and the water produced acts as solvent for the concentrated solution of ammonium carbamate supplied to the urea reactor.

A further important feature of the preferred integrated process according to the present invention, is

namely the ammonia synthesis reactor, the first and second exchangers, the urea reactor and the decomposer for the undehydrated ammonium carbamate, to operate at substantially the same pressure. Such pressure will generally lie in the range of from 100 to 250 atmospheres which range is particularly suitable in not involving excessive pressure. However, it is also possible to work at different pressures in the different stages. In such a case the overall pressure range will be from 30 to 300 atmospheres. A particular advantage of the mode of operation of the urea reactor in the process according to the present invention is that the injection of gaseous products from the carbamate decomposer directly into the bottom of the urea reactor, not only resolves the thermal problems of such a reactor, but allows one to dispense with use of a relatively expensive condenser which is always a problem in urea plant owing to the problem of corrosion which is encountered with such apparatus.

As indicated hereinabove, the absorption of NH_3 from the ammonia containing gases produced and the removal of CO_2 from the raw synthesis gases for synthesis of ammonia to produce carbamate can take place in any kind of suitable apparatus. However, a preferred apparatus is a film exchanger, that is an apparatus which allows effective heat and matter exchange on a single surface. Although more important for the CO_2 absorption to form carbamate, this advantage is also of importance in connection with the ammonia absorption.

The heat of formation of the ammonium carbamate

is mostly recovered by using it to pre-heat water which surrounds the pipes through which the ammonium carbamate solution produced passes in order to maintain such ammonium carbamate solution at a temperature higher than that at which crystallisation of the ammonium carbamate will occur.

A valuable feature of the method employed for drying the gases from the second exchanger is that the liquid ammonia injected thereinto can come from the same source as ammonia to be supplied to the urea reactor. In this way it is possible to save on the amount of energy required for the ammonia separation and to eliminate the need for a separate injection pump.

The cycle in which urea is produced has been designed as in such a manner to avoid the disadvantageous features of lack of available heat of formation of the ammonium carbamate in the urea reactor and the injection of a larger amount of water into the cycle. In fact, owing to the lack of available heat of formation of the carbamate, the temperature in the reactor has to be maintained by an external heat source. According to the present invention, such heat is produced by using the thermal content of the gases obtained by decomposition of the ammonium carbamate in the carbamate decomposer, which gases are directly injected into the urea reactor. Thus it is possible to eliminate a pre-heating stage for the reagents and a carbamate condensation stage by simplifying to a considerable extent the circulation system connected with urea synthesis which is restricted to the urea reactor and the carbamate decomposer. The temperature in the urea reactor may be varied, if desired,

by varying the amount of carbamate decomposition gases recycled to the reactor. Moreover, the supply at a single point of water necessary for producing the ammonia solution and subsequently the ammonium carbamate solution requires the NH_3/CO_2 ratio and the temperatures to be equal if a reduction in reactor yield is to be avoided. However, this poses no problem when, according to the present invention, the relatively large amount of water present in the urea reactor is used to increase the ammonia excess, without substantially increasing the system pressure.

In a cycle, which is preferably isobaric like the preferred process of the present invention, it is in fact possible to achieve large circulations of ammonia in a closed circuit between decomposer and urea reactor, whilst applying a relatively small amount of heat, the conditions in the ammonia solution being very close to the critical conditions. Such conditions allow one to realise in the urea reactor a high NH_3/CO_2 ratio, general in the range of from 2:1 to 12:1, preferably from 4:1 to 8:1, and consequently high yields, thus allowing one to reduce the supply of heat to the reactor. It is evident from the aforesaid that the integrated process according to the present invention allows the achievement of a large number of advantages not present with non-integrat processes. These advantages allow the achievement of a considerable reduction in the cost of production of ur

For a better understanding of the invention, and t show how the same can be carried into effect, reference will now be made, by way of example only, to the accompa

process system using as raw material the raw synthesis gas for ammonia synthesis.

Referring now to the accompanying drawing a raw synthesis gas, containing all the carbon dioxide necessa for the urea production, is compressed to a pressure slightly above that employed in the urea synthesis, and then injected through a pipe 1 to the bottom of an exchanger 2 which is a film exchanger wherein the raw synthesis gas flowing inside tubes comes into contact with a film of ammonia solution thereby forming ammonium carbamate; the reaction heat is removed in this case by circulating water outside the tubes, which water enters through a pipe 32 and leaves through a pipe 33. A very concentrated carbamate solution is produced which leaves the exchanger 2 through a pipe 23 and is led to a reactor 35.

By coming into contact with the ammonia solution, the raw synthesis gas tends to become saturated with ammonia, and the decarbonated gas in the upper region of the exchanger 2, which gas contains traces of CO_2 and saturated ammonia, is sent, through a pipe 3 to a refrigerator 4, wherein part of the ammonia condenses. The condensed ammonia is sent back through a pipe 27 to the exchanger 2. The uncondensed cooled gas is sent fro the refrigerator 4 to a methanation reactor 8 to elimina the CO and the CO_2 present therein, which are poisons for the ammonia synthesis catalyst, by transforming them into methane. The gas is first passed through a pipe 5 to a preheater 6, wherein it is heated by methanated gas

already formed, and, after a further preheating in a heat exchanger 7, it enters the methanation reactor 8.

The methanated gas, after having some of its heat recovered in the preheater 6, is cooled in a cooler 9 and in a pipe 10 is sent, together with ammonia-containing gas coming in a pipe 21 from an ammonia synthesis reactor 20 via a cooler 22 and pipe 11, to a film absorber 12, wherein the ammonia present in the gas is absorbed by a water or dilute ammonia solution film moving downwardly inside tubes and injected into the absorber 12 through a pipe 28. The reaction heat is removed with cooling water flowing around the tubes, which enters through a pipe 30 and leaves through a pipe 31. The liquid which passes to the bottom of the absorber 12 is passed out through a pipe 26 to the exchanger 2. The gas in the film absorber which has a low ammonia content is sent through a pipe 13 to a cold recovery apparatus 14, wherein condensation of a dilute ammonia solution takes place. This solution is sent, through a pipe 49 and a pipe 50 into a duct 47. The remainder in the apparatus 14 is additionally cooled and dried in a Venturi 15 by means of liquid ammonia injected through a pipe 24. All the water present is removed by the ammonia and discharged, in the form of a concentrated ammonia solution, from a separator 16 through a pipe 25. This concentrated ammonia solution is sent in the pipe 47 to the pipe 50. The dried gas, after the cold recovery in the apparatus 14, is sent through a pipe 17 to a circulating compressor 18 and then through a pipe 19 to the synthesis reactor 20.

Vent gases are removed from the top of the absorber 12 through a pipe 29.

the exchanger 2 is mixed with a recycled carbonate soluti
and
introduced through a pipe 48,/the resulting mixture is sent through a pipe 34 to the bottom of the reactor 35.

To the bottom of the reactor 35 is also sent through a pipe 43 ammonia which is recycled from other plants. This ammonia flow is divided into two streams; one is sent to the dehydrating Venturi 15 through the pipe 24, the other is sent through a pipe 42 to an exchanger 41 where it is vaporized, after which part is sent through a pipe 39 to a carbamate decomposer 38, where it is employed as a stripping means, and part is sent through a pipe 40 to the bottom of the reactor 35.

Inert gases are discharged from the top of the reactor 35 through a pipe 36, and a solution of urea, wat and ammonium carbamate with a large excess of ammonia is passed from the reactor 35 through a pipe 37 to the decomposer 38 where the solution flows downwardly inside tubes and encounters as a countercurrent vaporized ammonia entering the bottom of the decomposer 38 through the pipe 39. A suitable heating medium is passed into a jacket through a pipe 45 and leaves through a pipe 46. In this way, both owing to the stripping effect of the vaporized ammonia and owing to the heat given to the solution coming from the reactor, the decomposition of most of the ammonium carbamate present is effected and it removal in the gaseous phase, as NH_3 and CO_2, together with large amounts of ammonia vapour. The decomposition products of the carbamate are carried by the ammonia stream through a pipe 44 to the bottom of the reactor 35. The aqueous urea solution, containing the equilibrium

is withdrawn through the pipe 47 and sent to any desired subsequent treatment. However, it is not necessary to inject vaporized ammonia as a stripping means into the decomposer 38, in which case the pipe 39 is eliminated.

In order to illustrate the present invention, there is provided the following Example which refers to the reference numerals in the accompanying drawing.

EXAMPLE

The operative data are for a plant having a capacit corresponding to 1000 tons per day of ammonia, 990 tons pe day of which are transformed into ammonium carbamate to be converted into 1700 tons of urea per day, and 10 tons of which are available for other uses.

Into the exchanger 2 were introduced:

- through the pipe 1, raw synthesis gas having the followi characteristics:

flow	151,900	Nm^3/h. (cubic metres (measured under standard conditions) per hour).
pressure	200	kg/cm^2 abs.
temperature	125	°C.
Composition:		
H_2	61.22	% Vol.
CO	0.38	"
CO_2	17.71	"
N_2	19.95	"
CH_4	0.50	"
A	0.24	"

- through the pipe 26, ammonia solution having the following characteristics:

flow	78350 kg/h
Composition	
NH_3	78.8 % by weight
H_2O	21.2 "
Temperature	45 °C.

- through the pipe 27 liquid ammonia having the following characteristics:

flow	8500 kg/h
temperature	40 °C.

From the same exchanger 2 came out:

- through the pipe 23, carbamate and ammonia solution having the following characteristics:

temperature	150 °C.
flow	117050 kg/h
Composition	
NH_2 COO NH_4	80.00 % by weight
NH_3	5.90 "
H_2O	14.10 "

- through the pipe 3, decarbonated gas having the followir characteristics:

flow	154,900 Nm^3/h
temperature	75 °C.
pressure	199.9 kg/cm^2 abs.
H_2	60.02 % by volume
CO	0.38 "
N_2	19.58 "
CH_4	0.49 "
A	0.23 "
NH_3	19.30 "

The heat of reaction, consisting of 14,500,000 kcal/h, was recovered by using it to preheat the boiler feeding water up to 140°C.

Into the exchanger 12 were introduced:

- through the pipe 11, gases coming out from the synthesis reactor and having the following characteristics:

flow	466,000	Nm^3/h
pressure	198	kg/cm^2 abs.
temperature	40	°C.
Composition		
H_2	56.12	% by vol.
N_2	18.71	"
CH_4	8.77	"
A	2.40	"
NH_3	14.00	"

- through the pipe 10, methanated gas having the following characteristics:

flow	141,960	Nm^3/h
pressure	198	atmospheres absolu
temperature	40	°C.
Composition		
H_2	64.26	% vol.
N_2	21.37	"
CH_4	0.94	"
A	0.25	% vol.
NH_3	13.18	"

- through the pipe 28, water having the following characteristics:

flow	16290	kg/h
temperature	40	°C.

From the same exchanger 12 there were discharged:

- through the pipe 13, synthesis gas having the following characteristics:

flow	513600	Nm^3/h
pressure	197.8	atmospheres absolu
temperature	45	°C.
Composition		
H_2	67.01	% by volume
N_2	22.34	"
CH_4	7.97	"
A	2.18	"
NH_3	0.50	"
water	200	kg/h

- through the pipe 29, venting gas having the following characteristics:

flow	521000	Nm^3/h
pressure	195	kg/cm^2 absolute
temperature	-17	°C.
Composition		
H_2	66.00	% by weight
N_2	22.00	"
CH_4	7.85	"
A	2.15	"
NH_3	2.00	"
H_2O	3	ppm

The gas in pipe 13, after the recovery of the refrigeration units in apparatus 14, was compressed by the compressor 18 to 207 kg/cm^2 absolute and forwarded to the synthesis reactor 20.

To the urea reactor 35, running at a pressure

of 195 kg/cm^2 and capable of obtaining a 70% conversion, were sent:

- through the pipe 23, the aforecited carbamate and ammoni solution
- through the pipe 48, the recycled carbonate solution having the following characteristics:

flow	39950	kg/h
temperature	100	°C.
Composition		
CO_2	30.9	% by weight
NH_3	39.0	"
H_2O	30.1	"

- through the pipe 40, ammonia having the following characteristics:

flow	34780	kg/h
temperature	140	°C.

- through the pipe 44, vapours coming out from the decomposer 38 having the following characteristics:

flow	117370	kg/h
temperature	190	°C.
Composition		
CO_2	7.9	% by weight
NH_3	85.3	"
H_2O	6.8	"

From the same reactor there is discharged, through the pi 37, the urea solution having the following characteristic

flow	309545	kg/h
temperature	180	°C.
Composition		
CO_2	7.2	% by weight
NH_3	51.3	"

H_2O	18.5	% by weight
Urea	23.0	"

From the decomposer 38 there is discharged through the pipe 47, the urea solution, which can be sent to a final treatment, having the following characteristics:

flow	192175	kg/h
temperature	220	°C.
Composition		
CO_2	6.8	% by weight
NH_3	30.5	"
H_2O	25.7	"
Urea	37.0	"

The heat requirement of the decomposer 38 was satisfied by sending through the pipe 45, 55000 kg/h of steam at 40 kg/cm^2.

In the present Example, no vaporized NH_3 was sent to the decomposer 38 through the pipe 39.

1. A process for the production of urea, comprising a first step wherein carbon dioxide is reacted in a first or carbamate reactor with concentrated aqueous ammonia to form an aqueous solution of ammonium carbamate, and a second step wherein the ammonium carbamate so formed is dehydrated in a second or urea reactor to form urea, in which process unreacted carbamate present in the liquid phase urea-containing solution from the second reactor is decomposed and the decomposition products so formed are recycled in the gaseous phase to said second reactor to supply the heat required to maintain the contents thereof at the dehydration temperatu of the carbamate, and recovering urea from said solution.

2. A process as claimed in Claim 1, wherein the carbon dioxide flows in counterflow with the concentrated aqueous ammonia in the first reactor.

3. An integrated process for the production of ure comprising the steps of carrying out, in an absorber, absorption in water or in a dilute solution of ammonia, the ammonia present in the gaseous effluent from an ammoni synthesis reactor to obtain a concentrated ammonia solution, in a carbamate reactor, passing raw carbon dioxi containing synthesis gas for the synthesis of ammonia through said concentrated ammonia solution to absorb the carbon dioxide present in the raw synthesis gas, to produce a concentrated solution of ammonium carbamate, feeding said concentrated ammonium carbamate solution to a urea reactor, dehydrating the ammonium carbamate in the

urea reactor to form urea; decomposing, in a decomposer, ammonium carbamate which remains undehydrated after passag through the urea reactor, and supplying the dehydration products thereof to the urea reactor and using the heat of decomposition of the ammonium carbamate as a heat source for the urea reactor; recovering the urea-containing solution from which undehydrated ammonium carbamate has been decomposed into its gaseous components and separated therefrom, and subjecting to methanation the gaseous product of said contacting of the concentrated ammonia solution with the raw synthesis gas, removing the ammonia entrained in said gaseous product and subjecting the gaseous product to dehydration and compression before supplying it to the ammonia synthesis reactor.

4. A process as claimed in Claim 3, wherein the pressure is the same in the ammonia synthesis reactor, absorber, carbamate reactor, urea reactor and ammonium carbamate decomposer.

5. A process as claimed in Claim 4, wherein said pressure is in the range of from 100 to 250 kg/cm^2.

6. A process as claimed in Claim 3, wherein the operating pressure is not the same in all of the ammonia synthesis reactor, absorber, carbamate reactor, urea reactor and ammonium carbamate decomposer.

7. A process as claimed in Claim 6, wherein the operating pressures in said reactors, absorber and decomposer are in the range from 30 to 300kg/cm^2.

8. A process as claimed in any one of Claims 3 to 7, wherein the synthesis gas from which carbon dioxide has been removed in the carbamate reactor, is passed to a condensation unit in which part of the ammonia with which it has become saturated in the carbamate reactor is condensed and recycled to the carbamate reactor.

9. A process as claimed in Claim 8, in which the condensed ammonia is recycled to the bottom of the carbamat reactor.

10. A process as claimed in any one of Claims 3 to 9, wherein the concentrated ammonia solution produced in the absorber is subjected to fractional distillation to yield liquid ammonia for reaction with carbon dioxide in the carbamate reactor, and water or dilute aqueous ammonia.

11. A process as claimed in Claim 10, wherein the liquid ammonia is supplied to the bottom of the carbamate reactor and the water or dilute aqueous ammonia is supplied to the top of the carbamate reactor.

12. A process as claimed in any one of Claims 3 to 11, wherein part of the gaseous effluent from the ammonia synthesis reactor is vented, after passage thereof through the absorber.

13. A process as claimed in any one of Claims 3 to 12, wherein the methanised gaseous product of said contacting undergoes heat exchange with the yet-to-be methanised gaseous product of said contacting.

14. A process as claimed in any one of Claims 3 to 12, wherein the methanised gaseous product of said contacting is also fed to the absorber to remove ammonia entrained therein.

15. A process as claimed in Claim 13, or Claim 13, or 14 when appendant to Claim 13, wherein the gaseous effluent from the ammonia synthesis reactor is mixed with the methanised gaseous product after passage of both throug the reactor and the venting off of part of the former, to produce the moist feed stream to the ammonia synthesis reactor.

16. A process as claimed in Claim 15, wherein the moist feed stream is dehydrated by injecting the same with liquid ammonia and partially adiabatically evaporating off the ammonia content thereof to cause condensation of the moisture.

17. A process as claimed in Claim 16, wherein the injection of ammonia is preceded by a step in which the moist feed stream is cooled by heat exchange with the dehydrated feed stream to effect partial condensation of the moisture to form a dilute aqueous ammonia solution.

18. A process as claimed in Claim 16 or 17, wherei the feed stream is subjected to a gas/liquid separation after condensation of the moisture to separate a concentrated aqueous solution of ammonia from a dried feed stream for the ammonia synthesis reactor.

19. A process as claimed in Claim 18, wherein the concentrated aqueous solution of ammonia is mixed with said urea-containing solution.

20. A process as claimed in Claim 17, 18 or 19, wherein the dilute aqueous ammonia solution resulting from said heat exchange step, is mixed with said urea-containing solution.

21. A process as claimed in any one of the preceding claims, wherein urea is separated from the urea-containing solution which is recycled to the urea reactor.

22. A process as claimed in any one of the preceding claims, wherein ammonia is additionally supplied to the urea reactor to maintain an excess of ammonia therein.

23. A process as claimed in any one of the preceding claims, wherein the temperature in the carbamate reactor is from 100 to 250°C.

24. A process as claimed in any one of the preceding claims, wherein the temperature in the urea reactor is from 150 to 250°C.

25. A process as claimed in any one of the preceding claims, wherein the urea-containing solution from the urea reactor descends in countercurrent with gaseous ammonia in the ammonium carbamate decomposer.

26. A process as claimed in any one of the preceding claims, wherein the quantity of gases obtained by decomposition of undehydrated ammonium carbamate and which is supplied to the urea reactor is variable in order that the dehydration can be regulated.

preceding claims, wherein the temperature of the carbamate solution being formed in the carbamate reactor, is maintained in all regions, at a temperature above that at which the ammonium carbamate crystallizes out, depending on its concentration in said regions.

28. A process as claimed in Claim 27, wherein the temperature of the carbamate solution is so maintained by passage of cooling fluid around the carbamate reactor.

29. A process as claimed in any one of the preceding claims, wherein the passage of the raw carbon dioxide-containing synthesis gas through the concentrated ammonia solution is effected in a vertical tube exchanger in the tubes of which said synthesis gas and a film of said concentrated ammonia solution pass in countercurrent and heat produced is removed by passing a cooling fluid through a jacket surrounding said tubes.

30. A process for the production of urea, substantially as hereinbefore described with reference to the accompanying drawing.

31. A process for the production of urea, substantially as described in the foregoing Example.

32. Urea, whenever produced by the process claimed in any one of the preceding claims.

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