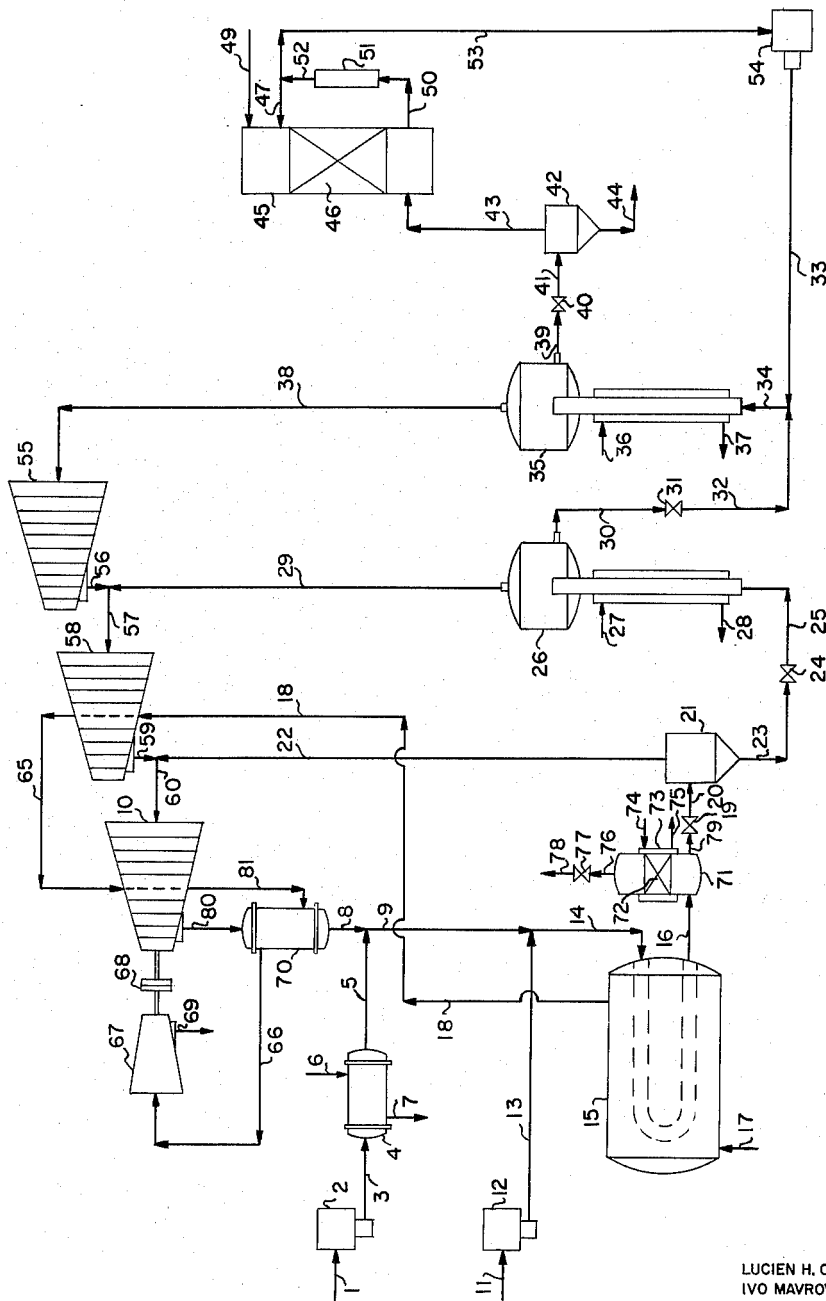


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UREA SYNTHESIS PROCESS

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3,232,985

UREA SYNTHESIS PROCESS

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This invention relates to the synthesis of urea from ammonia and carbon dioxide. An improved and more efficient method for total recycle of unconverted reactants has been developed, which accomplishes direct recycle of the unconverted reactants as a hot gas stream by compression in a multi-stage sequence at an elevated temperature and while in heat exchange with steam.

Numerous procedures have been developed or proposed for the recycle of unconverted reactants in urea synthesis. Thus, it has been proposed to recycle these reactants to the urea synthesis autoclave as an aqueous ammonium-ammonium carbamate solution or slurry. Another commercial process is based on the use of a hydrocarbon oil as the slurring agent for ammonium carbamate. Finally, it has been broadly proposed in the past to recycle the reactants as a hot gas stream, which is compressed at elevated temperature. In such a procedure, it is necessary to maintain the gas stream above the temperature level at which solid ammonium carbamate is condensed, in order to prevent excessive wear on the compressor due to solids abrasion. This process is described in U.S. Patent No. 1,429,483. In addition, a discussion of a commercial application of the process in Germany is given in P. B. Report No. 47,773, entitled "Urea Manufacture at I. G. Farbenindustrie." The process of the present invention is an improved procedure using the broad concept of hot gas recycle as disclosed in these prior art references, and also provides improvements over compending application Serial No. 220,339 filed August 29, 1962, now U.S. Patent No. 3,200,148.

In the present invention, substantial improvement in process efficiency is achieved, in terms of reduced power, steam and cooling water requirements. The recycling mixed gas stream is compressed by means of an axial or centrifugal compressor or series of compressors. The gas stream is preferably cooled during compression by heat exchange with process steam, which has been previously generated by heat exchange between liquid water and the main process stream during urea synthesis. The resulting superheated steam derived from heat exchange during gas compression is expanded through a power recovery turbine which drives the gas compressor or compressors. The final recycle gas stream is discharged from the gas compressor at urea synthesis pressure and elevated temperature and is cooled to a lower temperature level while superheating steam in a steam superheater. Compressed feed streams of liquid ammonia and gaseous carbon dioxide are added, and the mixed process stream is cooled by heat exchange with liquid water, mentioned supra, during which a portion of the mixed process stream reacts to form urea under the process conditions of elevated pressure and temperature. The resulting process stream is then passed to a lower pressure level, and a mixed off-gas stream containing ammonia, carbon dioxide and water vapor is separated from the product aqueous urea solution. The mixed off-gas stream is then recycled to the compressor. When mixed off-gas is produced in a plurality of stages at descending pressure levels, then the off-gas streams are compressed in a corresponding plurality of gas compressors. These may operate either in series or in parallel, however, the compressors are preferably staged in series, with the input to a compressor

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stage consisting of the discharge from the next lower stage combined with the off-gas portion generated at that stage of pressure level. Thus, one novel aspect of the process of the present invention involves the provision of a plurality of stages of carbamate decomposition and off-gas generation at different pressure levels, together with a plurality of compressors having inlet pressures equal to these pressure levels and outlet pressures corresponding to the next higher pressure level. The off-gas is thus compressed in a cumulative manner in succeeding compressors, until final discharge at urea synthesis pressure.

This process has several noteworthy advantages. Substantially all of the overall exothermic heat of reaction in urea synthesis, including the heat of ammonium carbamate condensation and the excess heat developed during off-gas compression, is recovered as usable superheated process steam. This process steam is expanded through a power recovery turbine linked to gas compression, so that a major portion of the power required for recycle gas compression is generated from within the process itself. Sufficient steam is generated to eliminate outside steam or other external utility requirements.

In addition, cooling the compressed gas stream in the steam superheater serves to prevent possible ammonia decomposition due to high temperature. The conventional ammonium carbamate absorption and recycle equipment of the prior art, such as high pressure absorption equipment and the carbamate solution recycle pump, have now been eliminated. The extremely large urea synthesis autoclave or reactor of the prior art has also been eliminated, since at high temperature the urea synthesis reaction proceeds rapidly and sufficient retention time is provided in the heat exchanger. Finally, the prior art with respect to ammonium carbamate recycle involved heating of the process stream to generate off-gas, which was subsequently condensed to ammonium carbamate using cooling water. The heat of condensation was thereby wasted and in addition cooling water was required. In the present invention, the off-gas is not condensed but instead the gas stream is directly recycled via compression with external cooling via heat exchange with process steam. The heat of condensation is also recovered at a high temperature level via steam generation from condensate water. Cooling water previously needed for carbamate condensation is no longer required. The generated steam is subsequently superheated via cooling of compressor gas and is expanded through the power recovery steam turbine. External steam requirements are eliminated.

It is an object of the present invention to synthesize urea in an improved complete recycle process.

Another object is to produce urea in a process in which reaction heat and heat generated through gas compression are recovered as usable high pressure steam.

A further object is to synthesize urea in a complete recycle process which achieves substantially complete recovery of heat of reaction and gas compression heating values at usable temperature levels.

An additional object is to recycle the off-gas from a urea synthesis process in an improved and more efficient manner.

Still another object is to provide a complete recycle urea process in which outside utility requirements for steam, electricity and cooling water are substantially reduced or eliminated.

These and other objects and advantages of the present invention will become evident from the description which follows. Referring to the figure, ammonia feed stream 1 is compressed by pump 2 to urea synthesis pressure, usually in the range of 2000 p.s.i.g. to 6000 p.s.i.g. Since ammonia at its highest enthalpy state is generally pref-

erable, the ammonia feed stream 3 may be heated in vaporizer-preheater 4 to provide heated gaseous ammonia stream 5 at urea synthesis pressure. Heating the ammonia serves to increase the heat liberated in the autoclave. Thus, the amount of steam generated by heat exchange is thereby increased. Unit 4 will usually be steam heated, with steam entry via 6 and removal of condensate and uncondensed steam via 7.

Ammonia stream 5 is added to recycle gas stream 8 to form a mixed process stream 9. Stream 8 is derived from steam superheater 70 at an elevated temperature, and the addition of stream 5 serves to immediately quench stream 8 to a lower temperature level, thereby preventing the decomposition of ammonia in stream 8.

Gaseous carbon dioxide feed stream 11 is compressed in compressor 12 to urea synthesis pressure, and the resulting compressed gas 13 is added to stream 9 to form a mixed urea synthesis process stream 14. Stream 14 is thus formed at an elevated pressure in the range of 2000 p.s.i.g. to 6000 p.s.i.g. and a temperature preferably in the range of 350° F. to 500° F. Stream 14 is now passed into heat exchange-reactor unit 15, in which urea synthesis takes place. Unit 15 may be of any suitable design. Thus unit 15 may consist of a tubular heat exchange or boiler, or unit 15 may simply consist of a vessel as shown, provided with an internal coil through which process stream 14 is passed. It will be understood that in practice stream 14 may be formed inside the coil by separate additions of streams 9 and 13, so as to prevent premature urea formation. Stream 14 is cooled in unit 15, to a temperature preferably in the range of 300° F. to 400° F., and leaves as stream 16. Thus, stream 16 contains urea, ammonium carbamate, excess ammonia and water. Liquid condensate water is passed into unit 15 via 17 for heat exchange with the process stream, and leaves via 18 as high temperature steam. Thus, the prior art requirement of cooling water for the cooling of stream 14 is obviated.

Stream 16 is now processed so as to recover product aqueous urea solution. As a preliminary to the separation of ammonium carbamate as an off-gas, inerts are removed from stream 16 in a separator unit of novel design and operation. Stream 16 is passed directly from autoclave unit 15 to inerts separator unit 71, which is a high pressure vessel in which a pressure level is maintained equal to or greater than the autogenous pressure of the liquid stream 16. Thus, a gaseous stream of inerts plus ammonia, carbon dioxide and water vapor rises from the liquid phase in unit 71. The rising gaseous stream is cooled in packed section 72, provided with cooling jacket 73. Cooling water is admitted via 74 and discharged via 75. The rising ammonia, carbon dioxide and water vapor components are condensed and refluxed in section 72. A residual gaseous phase principally comprising inerts is thus formed in the upper section of unit 71, removed via 76, and passed via control valve 77 to discharge via 78. Valve 77 serves to regulate the liquid level in unit 71.

The liquid phase is now removed from unit 71 via 79, and is substantially free of inerts. Stream 79 is now processed to separate an off-gas containing unconverted ammonia and carbon dioxide from the product aqueous urea solution. Thus, in a preferred embodiment of the present invention, stream 79 is passed through pressure reducing valve 19, leaving as stream 20 at a pressure typically in the range of 1200 p.s.i.g. to 1700 p.s.i.g. Stream 20 is passed to cyclonic flash separator 21, which is any suitable vessel for separating evolved off-gas from the residual liquid solution. The off-gas, which is evolved due to pressure reduction is removed from vessel 21 via 22. The residual liquid solution leaves vessel 21 via 23, and is passed through pressure reducing valve 24, leaving as stream 25 at a pressure typically in the range of 600 p.s.i.g. to 850 p.s.i.g.

Stream 25 is passed into ammonium carbamate de-

composer unit 26, where decomposition of a portion of the ammonium carbamate in the stream is attained by suitable heating. Unit 26 may be of any suitable configuration, with one typical arrangement being shown in the figure. Stream 25 is heated while passing upward through the lower steam-jacketed section of the unit, by steam passing into the jacket via 27 with condensate removal via 28. A portion of the ammonium carbamate present is decomposed to ammonia and carbon dioxide, and further off-gas is separated from residual liquid solution in the upper section of unit 26. The off-gas is removed via 29, while the residual liquid stream with lowered ammonium carbamate content is withdrawn via 30, and is passed through pressure reducing valve 31, leaving as stream 32 at a pressure typically in the range of 275 p.s.i.g. to 500 p.s.i.g.

Stream 32 is combined with aqueous recycle stream 33, which is derived in a manner to be described infra. The combined stream 34 is passed into ammonium carbamate decomposer unit 35, where decomposition of a further portion of the ammonium carbamate in the stream is attained by suitable heating. Unit 35 is similar to unit 26 described supra. Thus, stream 34 rises through the lower steam jacketed section of unit 35, which is heated by steam admitted via 36 with condensate removal via 37. The decomposition of most of the remaining ammonium carbamate present in the liquid stream is thus achieved.

The mixed off-gas generated in unit 35 is removed via 38, and the residual liquid stream with minor ammonium carbamate content is withdrawn via 39, and is passed through pressure reducing valve 40, leaving as stream 41 at a pressure typically in the range of 5 p.s.i.g. to 50 p.s.i.g. Stream 41 is now passed to cyclonic separator 42, which is a unit similar to vessel 21 described supra. Due to the lower pressure level and elevated temperature of the process stream in unit 42, the balance of contained ammonium carbamate is decomposed and evolved via 43 as a mixed off-gas. The residual liquid stream consisting of product aqueous urea solution is withdrawn via 44 and passed to product utilization.

Final off-gas stream 43 is now passed to absorber 45, which is provided with a packed section 46 or other gas-liquid contact means. A circulating stream 47 consisting of aqueous absorbent solution is passed into unit 45 above packed section 46, and passes downward countercurrent to the rising gas stream. Ammonia and carbon dioxide from stream 43 are absorbed into the liquid solution. A small stream 49 consisting of makeup water is admitted into the top of unit 45. Stream 49 may be omitted in some cases, depending on the relative proportion of water in stream 43. The scrubbing solution is removed via 50 from the bottom of unit 45, suitably cooled in cooler 51, removed via 52, and partially recycled via 47 to unit 45. The balance of stream 52 is passed via 53 to pump 54, and is compressed to a pressure in the range of 275 p.s.i.g. to 500 p.s.i.g. for recycle via 33. The ammonia and carbon dioxide content of stream 33 is thus recycled to urea synthesis via 38. It will be understood that stream 43 may alternatively be recycled to urea synthesis by gas recompression, as is the case with streams 22, 29 and 38 to be described infra. This alternative is less desirable because of high compression cost for recompression from the low pressure level of stream 43.

Referring now to decomposer unit 35, mixed off-gas stream 38 is passed to unit 55, which is an axial or centrifugal compressor of conventional design. Here the off-gas is compressed to an elevated pressure level equal to that of the off-gas generated in the next higher stage of carbamate decomposition. The resulting compressed off-gas stream 56 is thus combined with off-gas stream 29 produced from unit 26. The combined off-gas stream 57, at a pressure level in the range of 600 p.s.i.g. to 850 p.s.i.g., is now passed into compressor unit 58, which is similar to

unit 55 described supra. The resulting compressed off-gas stream 59 is discharged at a pressure level in the range of 1200 p.s.i.g. to 1700 p.s.i.g., and is combined with off-gas stream 22 derived from unit 21. The final combined off-gas stream 60 is now passed into the final compressor unit 10, which is similar to unit 55 described supra. In unit 10 the total combined off-gas stream is compressed to final urea synthesis pressure in the range of 2000 p.s.i.g. to 6000 p.s.i.g. The final compressed off-gas is discharged via 80, cooled in steam superheater 70, and is recycled to urea synthesis via 8 in a manner described supra.

The general sequence of off-gas compression in pressure increments, followed by cumulative addition of further off-gas derived at a next higher pressure level from the main process stream, forms an important aspect of the present invention. Thus, it has been found that gas re-compression in this manner provides important advantages in terms of power savings and also because control of gas temperature during compression is simplified.

The general method of gas temperature control during recompression combined with power recovery forms another significant aspect of the present invention. Thus, the saturated steam 18 generated by heat exchange with the process stream in synthesis unit 15 is employed to provide both temperature control and power recovery. Steam produced via 18 is passed through unit 58, in heat exchange with the mixed gas stream during compression. The steam is superheated, and serves to lower the temperature of the off-gas during compression. The steam now leaves unit 58 via 65, and is further superheated by heat exchange with the off-gas stream in compressor 10. The resulting superheated steam is removed from unit 10 via 81, and is further superheated by heat exchange with hot process gas stream 80 in superheater unit 70.

In some cases it will be necessary to increase the temperature driving force for case cooling of process gas in unit 10. In such circumstances, condensate may be directly injected into stream 65 to reduce superheat. Alternatively, stream 65 may be desuperheated by heat exchange with condensate.

A portion of stream 81 may be diverted for various process heating usages, not shown, such as carbamate decomposition via 27 and 36, or for steam tracing. In any case, a major portion of stream 81 is superheated in unit 70, removed via 66, and utilized as an energy source in power recovery. Thus, stream 66 is expanded through power recovery steam turbine 67, which is linked by shaft coupling 68 with compressor 10. Thus unit 67 serves to provide the required power for operation of unit 10. In addition, some smaller power users could be driven by unit 67, not shown.

The expanded steam is removed from turbine 67 via 69. The steam 69 may be used via 6 to preheat the ammonia feed stream, prior to condensation with cooling water. The resulting condensate water streams 7, 28 and 37, together with condensate derived by condensation of the balance of stream 69, are recycled to the steam circuit as condensate water via 17 and 49.

It is evident that substantial differences and contrasts exist between the process of the present invention and prior art which employed multistage reciprocating compressors in series to compress the off-gas stream. Thus, in a typical compression sequence of the prior art, the gas stream is alternatively heated to prevent condensation of carbamate and externally cooled, using cooling water to provide a maximum discharge temperature of 350° F. In contrast, in the present invention using a centrifugal or axial rotary compressor, the gas stream is compressed at elevated temperatures up to 1000° F. and the compression may be substantially adiabatic. Thus, in essence the gas stream is internally heated due to compression, and cooling is require only to protect the compressor. In this respect, cooling takes place through heat exchange with steam, and thus the heat is not wasted via cooling water

as in the prior art, but instead is recovered as useful high temperature steam.

In addition, it should be noted that prior art compression required external heating of the compressor while in the present case heating of the compressor takes place through the substantially adiabatic compression of the off-gas. Finally, in the prior art the fully compressed off-gas is not recycled to urea synthesis at elevated temperature while in the present process the gas stream is at a very high temperature after compression and thus additional steam generation is obtained during urea synthesis.

It will be evident to those skilled in the art that various alternatives may be practiced within the scope of the present invention. Thus, the off-gas compression sequence described supra is a preferred embodiment of the present invention and forms the most advantageous mode of practice of the process. However, other compression sequences could also be adapted. Thus for example, streams 38, 29 and 22 could be separately compressed up to the final urea synthesis pressure of stream 8, and then combined to form stream 8. This alternative is less advantageous, since the individual compressors must operate over a much greater pressure range and thus are less efficient. In addition, the cooling of individual compressors, particularly those compressing low pressure off-gas, could not be satisfactorily accomplished using steam because of the large pressure changes involved.

It will be noted that the use of steam as the cooling medium for the compressors followed by expansion of the steam through a power recovery turbine forms another preferred embodiment of the present invention. Thus, it is also possible to operate the process with other cooling mediums or without any cooling. In the latter case, the off-gas compression would be essentially adiabatic.

In another alternative, unit 21 and its function may be omitted if desired or replaced by an ammonium carbamate decomposer unit similar to 26. The omission of unit 21 is relatively less desirable, because the extra gas evolution in the steam-jacketed section of unit 26 reduces the heat transfer coefficient thus making unit 26 less efficient. In addition, this variation is also less desirable because proportionately more water vapor will be present in the recycling off-gas stream.

Other methods of off-gas generation and recycle besides those described may be adopted. Thus, it will be apparent that stream 8 may be first combined with stream 13, and then with stream 5. Final off-gas stream 43 may also be recycled in different ways. Absorber 45 and its function may alternatively be carried out by means of the process described in U.S. Patent No. 3,038,285, in which case pump 54 may also be omitted. In another alternative sequence, as mentioned supra, stream 43 may be passed to an off-gas compressor, compressed to the pressure level of stream 38, combined therewith and thus recycled via unit 55.

An example of an industrial application of the process of the present invention will now be described.

Example

A urea synthesis process was designed for operation in accordance with the present invention. Basis of the plant sizing was an output of 100 mols/hour of urea. Thus, in the process description infra, all stream compositions will be given on the basis of mols/hour of component, based on a plant output of 100 mols/hour of urea.

The urea synthesis feed stream consisted of 135 carbon dioxide, 378 ammonia and 21 water, and was passed into the synthesis reactor unit at 3000 p.s.i.g. Urea synthesis took place while the process stream was in heat exchange with condensate water, thus saturated steam was produced at 180 p.s.i.g. (380° F.)

The synthesis melt was discharged at 400° F., and contained 100 urea, 35 carbon dioxide, 178 ammonia and 121

water. Inerts were separated at 3000 p.s.i.g. by vaporization, followed by internal condensation and reflux of carbamate solution. The melt was flashed down to 1500 p.s.i.g. and 350° F., and an off-gas containing 10 carbon dioxide, 50 ammonia and 3 water was removed at this 1500 p.s.i.g. pressure level. The residual liquid phase, consisting of 100 urea, 25 carbon dioxide, 128 ammonia and 118 water, was now passed to the first stage of steam heated ammonium carbamate decomposition at 340° F. and 750 p.s.i.g. An off-gas containing 15 carbon dioxide, 77 ammonia and 8 water was removed at this 750 p.s.i.g. pressure stage. The residual liquid phase consisting of 100 urea, 10 carbon dioxide, 51 ammonia and 110 water was reduced in pressure to 375 p.s.i.g. and combined with an aqueous recycle solution containing 2 carbon dioxide, 10 ammonia and 14 water. The combined stream was passed to the second stage of steam heated ammonium carbamate decomposition at 340° F., and 375 p.s.i.g. An off-gas containing 10 carbon dioxide, 51 ammonia and 10 water was removed at this 375 p.s.i.g. pressure stage. The residual liquid phase consisting of 100 urea, 2 carbon dioxide, 10 ammonia and 114 water was now passed to the final stage of ammonium carbamate decomposition and off-gas removal at 15 p.s.i.g. and 250° F. A product aqueous urea solution containing 100 urea and 100 water was produced at 250° F.

The residual final off-gas produced at 15 p.s.i.g. and 250° F. and containing 2 carbon dioxide, 10 ammonia and 14 water was contacted with an aqueous scrub solution containing these components in the same relative proportion. The recirculating liquid phase was cooled to 100° F. in an external cooler and heated to 125° F. in contact with the condensing off-gas. A portion of the recirculating liquid phase was withdrawn, pressurized from an initial pressure of 15 p.s.i.g. to 375 p.s.i.g. and returned to the process as the aqueous recycle solution described supra.

The 375 p.s.i.g. off-gas was compressed to 750 p.s.i.g. and heated from 340° F. inlet to 527° F. outlet in a first compressor. The compressor operated at 72% efficiency with 141,000 B.t.u./hour work input. The compressed off-gas was combined with the 750 p.s.i.g. stage off-gas to give a combined gas stream at 417° F. and 750 p.s.i.g. containing 25 carbon dioxide, 128 ammonia and 18 water.

This gas stream was compressed to 1500 p.s.i.g. and heated from 417° F. to 610° F. in a second compressor provided with case cooling, which employed the saturated steam produced at 180 p.s.i.g. in the urea synthesis unit as the cooling medium. Thus an increment of superheat was added to the steam. The compressor operated at 72% efficiency with 430,000 B.t.u./hour work input. The compressed off-gas was combined with the 1500 p.s.i.g. stage off-gas, to give a combined gas stream at 540° F. and 1500 p.s.i.g. containing 35 carbon dioxide, 178 ammonia and 21 water.

This gas stream was compressed to urea synthesis pressure of 3000 p.s.i.g. and heated from 540° F. to 750° F. in a third compressor provided with case cooling. The superheated steam produced by heat exchange in the second compressor was desuperheated by the addition of condensate water, and was then employed as the cooling medium in the third compressor. The final steam produced from the third compressor was obtained at 150 p.s.i.g. and 414° F. The third compressor operated at 72% efficiency with 580,000 B.t.u./hour work input.

The final recycle off-gas stream produced at 3000 p.s.i.g. and 750° F. from the third compressor was cooled to 500° F. in a steam superheater, which served to superheat the steam produced from the third compressor to 720° F. The off-gas stream was then passed to urea synthesis as described supra.

Most of the superheated steam produced at 150 p.s.i.g. and 720° F. was expanded through a power recovery turbine which was the power source for operation of the

third compressor. Portions of the resulting exhaust steam were employed in preheating input ammonia from 70° F. to 205° F. The balance of the exhaust steam was condensed using cooling water, and the condensate was recycled to the urea synthesis unit. The balance of the original superheated steam was desuperheated by the addition of condensate, and was then employed as heating steam for carbamate decomposition.

The overall process showed substantial savings in utility charges. Based on 85° F. cooling water, 11,500 gallons/ton urea were consumed, compared to 18,000 gallons/ton urea in a prior complete recycle process. All required process steam was generated internally and was thus supplied from within the process, compared to a prior complete recycle process which required 2400 lbs. of 150 p.s.i.g. process steam per ton of urea. Finally, power recovery in the steam turbine amounted to 642,000 B.t.u./hour, based on 2 p.s.i.a. steam outlet pressure with extraction of tracing at 50 p.s.i.g. Thus the process only consumed 140 kwh. of electric power/ton urea, compared to 185 kwh./ton urea in a prior process. It was clearly evident that the new process as outlined in the example supra showed substantial savings in utility charges, compared to the prior art.

We claim:

1. Urea synthesis process with total recycle of unconverted process components which comprises compressing input streams of ammonia and carbon dioxide to elevated urea synthesis pressure, combining said input streams with a gaseous recycle stream whereby said recycle stream is quenched and a combined urea synthesis stream is formed at elevated pressure, cooling said combined stream in heat exchange with liquid water whereby said water is vaporized to steam and a portion of said combined stream is converted to urea, heating the resulting stream at reduced pressure to decompose ammonium carbamate, removing off-gas comprising unconverted ammonia and carbon dioxide together with water vapor, recovering a final process stream comprising product aqueous urea solution, compressing said off-gas to urea synthesis pressure in compression means while in heat exchange with said steam, whereby said steam is superheated and said off-gas is also heated to elevated temperature, recycling the compressed off-gas stream as said gaseous recycle stream, and expanding said superheated steam through power generating means combined with said compression means whereby power derived from steam expansion is utilized in off-gas compression.

2. Urea synthesis process with total recycle of unconverted process components which comprises compressing input streams of ammonia and carbon dioxide to elevated urea synthesis pressure, combining said input streams with a gaseous recycle stream whereby said recycle stream is quenched and a combined urea synthesis stream is formed at elevated pressure, cooling said combined stream in heat exchange with liquid water whereby said water is vaporized to steam and a portion of said combined stream is converted to urea, decomposing ammonium carbamate in the resulting stream in a plurality of stages at successively lower pressure, removing off-gas streams comprising unconverted ammonia and carbon dioxide together with water vapor from each stage, recovering a final process stream comprising product aqueous urea solution, compressing said off-gas streams to urea synthesis pressure in compression means while in heat exchange with said steam, whereby said steam is superheated, said off-gas streams being combined and heated to elevated temperature, recycling the compressed combined off-gas stream as said gaseous recycle stream, and expanding said superheated steam through power generating means combined with said compression means whereby power derived from steam expansion is utilized in off-gas compression.

3. Process of claim 2, in which the urea synthesis effluent stream derived from said urea synthesis step is flashed down to an intermediate lower pressure in the first stage

and a first stream of off-gas is removed without heating, the residual effluent stream being heated in at least one of the succeeding stages.

4. Urea synthesis process with total recycle of unconverted process components which comprises compressing input streams of ammonia and carbon dioxide to elevated urea synthesis pressure, combining said input streams with a gaseous recycle stream whereby said recycle stream is quenched and a combined urea synthesis stream is formed at elevated pressure, cooling said combined stream in heat exchange with liquid water whereby said water is vaporized to steam and a portion of said combined stream is converted to urea, reducing the pressure of the resulting stream to an intermediate level, removing a first off-gas comprising ammonia, carbon dioxide and water vapor, further reducing the pressure of the residual stream, heating said residual stream, removing a second off-gas comprising ammonia, carbon dioxide and water vapor, further reducing the pressure of the residual stream, heating said residual stream, removing a third off-gas comprising ammonia, carbon dioxide and water vapor, recovering a final process stream comprising product aqueous urea solution, compressing said third off-gas and adding the compressed gas stream to said second off-gas, compressing said first and second off-gas streams to urea synthesis pressure in compression means while in heat exchange with said steam, whereby said steam is superheated, said off-gas streams being combined and heated to elevated temperature, recycling the compressed combined off-gas stream as said gaseous recycle stream, and expanding said superheated steam through power generating means combined with said compression means whereby power derived from steam expansion is utilized in off-gas compression.

5. Process of claim 4, in which said off-gas streams are compressed in a plurality of stages, said third off-gas stream being compressed to the pressure level of said second off-gas stream and combined therewith, the combined off-gas stream being compressed to the pressure level of said first off-gas stream and combined therewith, and the total combined off-gas stream being compressed to urea synthesis pressure and recycled as said gaseous recycle stream.

6. Process of claim 5, in which said steam is successively passed in heat exchange with off-gas and is superheated during successive compressions of the combined stream of third and second off-gas, and compression of the final combined stream comprising total off-gas, and thereafter the steam is further superheated by heat exchange with the total off-gas stream after compression.

7. Process of claim 6, in which said steam is at least partially desuperheated by the addition of liquid water, after heat exchange with the combined stream of third and second off-gas.

8. Urea synthesis process with total recycle of unconverted process components which comprises compression input streams of ammonia and carbon dioxide to urea synthesis pressure in the range of 2000 p.s.i.g. to 6000 p.s.i.g., combining said input streams with a gaseous recycle stream whereby said recycle stream is quenched and

a combined urea synthesis stream is formed at a temperature in the range of 350° F. to 600° F., cooling said combined stream in heat exchange with liquid water to a temperature in the range of 300° F. to 400° F., whereby said water is vaporized to steam and a portion of said combined stream is converted to urea, reducing the pressure of the resulting stream to the range of 1200 p.s.i.g. to 1700 p.s.i.g., removing a first off-gas comprising unconverted ammonia and carbon dioxide together with water vapor, reducing the pressure of the residual stream to the range of 600 p.s.i.g. to 850 p.s.i.g., heating the residual stream to further decompose ammonium carbamate, removing a second off-gas comprising ammonia, carbon dioxide and water vapor, reducing the pressure of the residual stream to the range of 275 p.s.i.g. to 500 p.s.i.g., heating the residual stream and removing a third off-gas comprising ammonia, carbon dioxide and water vapor, reducing the pressure of the residual stream to the range of 5 p.s.i.g. to 50 p.s.i.g., removing a fourth off-gas comprising ammonia, carbon dioxide and water vapor, absorbing said fourth off-gas in aqueous absorbent solution, combining the resulting solution with said residual stream at a pressure in the range of 275 p.s.i.g. to 500 p.s.i.g., compressing said third off-gas to the pressure level of said second off-gas and combining said gas streams, compressing the combined gas stream to the pressure level of said first off-gas and combining said gas streams, compressing the total combined gas stream to urea synthesis pressure to form said gaseous recycle stream, cooling said combined gas streams during compression by heat exchange with said steam generated by heat exchange during urea synthesis, whereby said steam is superheated, and expanding said superheated steam through power generating means combined with means for said compression of off-gas whereby power derived from steam expansion is utilized in off-gas compression.

9. Process of claim 8, in which said steam is initially passed in heat exchange with the combined third and second off-gas during the compression of the combined gas stream, and the resulting superheated steam is further heated by passing in heat exchange with the total combined off-gas streams during the compression of the total combined gas stream to urea synthesis pressure.

References Cited by the Examiner

UNITED STATES PATENTS

1,429,483	9/1922	Bosch et al.	260—555
3,155,722	11/1964	Mavrovic	260—555

FOREIGN PATENTS

58,503	3/1950	France.
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OTHER REFERENCES

Dewling et al.: Fiat Final Report No. 889, Sept. 3, 1946, pages 1-6 and 13.

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