

Process Simulation of High Pressure Urea Production from Carbon Dioxide and Ammonia

1Mohd Rumman Ali, 2Dr. Anjana P. Anantharaman

1,2Department of Chemical Engineering

1,2SRM Institute of Science and Technology

Abstract - The demand for fertilizers has increased globally and as a result, Ammonia/Urea production has paced up. The purpose of this work is to design a process simulation, based on the conceptual understanding of the high-pressure Urea synthesis which provides an improved yield & optimized simulation solution for high-pressure urea synthesis. This steady-state simulation is simulated using SRK thermodynamic model in order to describe the non-ideality of Ammonia-Carbon Dioxide-Urea system under high temperature and high-pressure conditions. Based on the assumption of 60% conversion of Carbon Dioxide and varied conversion of ammonium carbamate between 60 to 90%, Urea 60(± 5) % by weight was obtained by the simulated process. It was found that the yield of Urea increases with higher fractional conversion of CO₂ and Ammonium Carbamate. Also, with increase in the number of separation stages yield of Urea increased. The study addressed here hence provides an improved base-case process which is thermodynamically feasible and can be further optimized and modified.

Key Words: Urea, Simulation, Carbon Dioxide, Ammonia, Ammonium Carbamate, Recycle.

1. INTRODUCTION

Growing population has resulted in increased demand for food globally. In order to cope up with this demand domestic cultivation of crops has increased rapidly and use of nitrogen based fertilizer has become the basic necessity of the farmers. Indian farmers heavily rely on urea and ammonia fertilizers over potash fertilizers due to the subsidy provided on urea making it cheaper. As a result the demand of urea is quite high in India. India imports 6 tonnes/year of urea, making it the second largest consumer of urea in the world. India has around 30 urea manufacturing units comprising of production from public, private and cooperative sectors. National Fertilizers Ltd., Indian Farmers and Fertilizers Cooperative Ltd., Rashtriya Chemicals and Fertilizers Ltd., Tata Chemicals Ltd., Zuari Agro Chemicals Ltd., are few of the major fertilizer producers in India. A lot of research and development is going in the commercial synthesis process of urea to meet the demand of fertilizers in the country. Department of Fertilizers is laying focus and sponsoring the research and development in this field. Aspects of improvement include increasing the yield while

reducing the energy consumption at hand, and reducing the overall specific energy consumption.

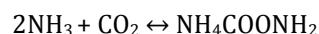
Presently there are few major processes that are being practiced for the commercial synthesis of urea. Once Through Process is the simplest process where CO₂ and NH₃ are fed to the autoclave and underflow from it is concentrated to urea prills whereas the off-gases containing CO₂ and NH₃ are treated with acids in another plant to yield nitrogen based fertilizers. It is known for its low initial cost and high conversion efficiency but requires investment for another plant to utilize ammonia, affecting the capital cost. Thus the cost of the product is relatively high. The drawback is that a significant amount of CO₂ is lost while the Mono-Ethanol Amine gets degraded.

Another process is Partial Recycle Process where CO₂ from the off-gas stream is absorbed in Mono-Ethanol Amine, regenerated and vented. Whereas NH₃ is condensed. The purpose of the work addressed here is to prepare a base-case process which improves the yield while minimizing energy consumption.

Total Recycle and Stripping Process are amongst the sustainable processes that have proven good yield and are preferably used in the large scale commercial synthesis of Urea. Using a driving force apart from the usual addition of heat and reduction of pressure has proven to be beneficial. Decomposition of Ammonium Carbamate can done in two ways at a synthesis pressure in a decomposer, usually referred to as a stripper, by using CO₂ (STAMICARBON) and/or NH₃ vapors (SNAMPROGETTI).

1.1 Urea Synthesis

Urea synthesis is of historical importance, being the first inorganic compound to be synthesized from inorganic compounds in the laboratory. Commercial production of urea was started in Germany by I.C Farben in 1920 based on ammonium Carbamate process. Various commercial urea manufacturing processes today use this base case process i.e. (i) reaction between liquid ammonia and carbon dioxide gas to form ammonium carbamate:



And (ii) subsequent dehydration of ammonium carbamate to yield Urea.



Reaction (i) is strongly exothermic and therefore, heat is liberated as it occurs. This heat of formation is used in the endothermic dehydration of ammonium carbamate [6]. It is known to have a high reaction rate at room temperature. Since the reactor is operated under high-temperature conditions therefore high pressure is required to reach equilibrium. [6] Whereas reaction (ii) is an endothermic reaction and reaches a meaningful rate at high temperature ($170\text{-}200^\circ\text{C}$) and high pressure (13-25 MPa).

1.2 Factors Affecting

The fraction of ammonium Carbamate that dehydrates to urea and water depends on various factors such as:

- With increased NH_3 : CO_2 molar ratio preferably from 2.1 to 6.0 [2] CO_2 conversion to carbamate is increased.
- According to Le Chatelier's principle, higher pressure and lower temperature favor carbamate formation. Ammonium carbamate formation is nearly instantaneous and reaction tends to complete with reaction heat being removed simultaneously. In the case of urea formation, a higher temperature is favorable because the reaction is endothermic. The relation is such that when the temperature increases the conversion increases proportionally.
- Ammonium carbamate dehydration reaction is slow and takes around 20 minutes to attain equilibrium. Considering this urea reactor is so designed that residence time should be more than 20 minutes. Higher residence time favors equilibrium conversion.

Solution pressure of carbamate formation should be greater than its decomposition pressure since (i) is a reversible reaction.

2. SIMULATION ENVIRONMENT

Chemical Processing Industries are facing numerous challenges and there's always a scope of optimization in order to improve the yield and minimize the energy consumption. This demand of optimization and process improvement is closely met by process simulation. Computer aided process simulation software such as Aspen Plus & Hysys, Pro/II, DWSIM, ChemCAD etc. have made it easier for

Chemical Engineers to excel the opportunity of continuous process improvement.

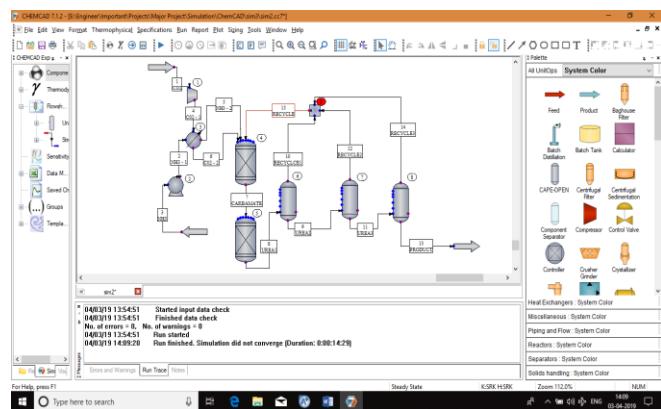


Fig -1: User Interface of Simulation Environment

In the simulation addressed here, considering the high temperature and high pressure operating conditions SRK (Soave-Redlich-Kwong) thermodynamic model was used. SRK single equation of state can accurately define vapor and liquid phases.

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)}$$

$$\text{Where, } b = 0.08664 \frac{RT_c}{P_c}$$

$$a = \frac{0.42748 (RT_c)^2}{P_c} (1 + m (1 - \sqrt{T_r}))^2$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

$$T_r = \frac{T}{T_c}$$

Ammonium Carbamate is added as a user-defined component where the properties are manually provided.

3. PROCESS DESCRIPTION

The process addressed here is a recycle process which involves the use of three flash/separators arranged in series in order to maximize the urea concentration. The process was simulated in ChemCAD using SRK thermodynamic model. As the process involves high temperature and pressure conditions SRK thermodynamic model was preferably chosen. Also, stoichiometric reactors were preferred for the simulation, considering the complexity of the process.

Reaction (i) being an exothermic reaction liberates heat and undergoes at low temperature condition. Whereas reaction (ii) is an endothermic reaction and hence requires heat to attain equilibrium, thus takes place at high temperature. Since both the reactions takes place simultaneously in a single reactor practically i.e. firstly ammonium carbamate is formed and then its dehydration takes place, hence it is preferred to operate the reactor at high temperature and high pressure condition. Here, the base case process is simulated using two stoichiometric reactors where the first reaction takes place feed inlet condition in reactor R-1 and second reaction takes place at elevated temperature in reactor R-2.

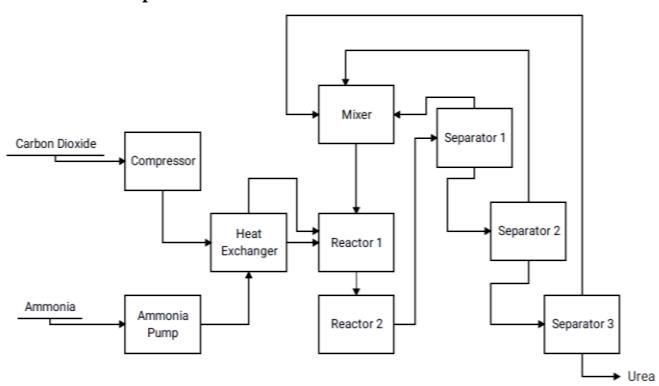


Fig -2: Block Flow Diagram of Simulated Process

Carbon dioxide gas at 1.5 bar and 40°C is compressed adiabatically to attain a pressure of 160bar. This raises the temperature of the gas significantly. Liquid ammonia, on the other hand, is pressurized from 24bar to 240bar using a high-pressure pump. Using a heat exchanger, heat is transferred from hot CO₂ to cold NH₃. Both the streams are then fed to the stoichiometric reactor R-1. Since the carbamate formation favors elevated pressure and low temperature, therefore, the reaction takes place at the feed input condition. The product stream from R-1 consists of a significant amount of ammonium carbamate along with unconverted CO₂ and NH₃, and small traces of oxygen.

This stream is then fed to the stoichiometric reactor R-2 where dehydration of ammonium carbamate takes place in order to yield Urea. The reactor operates isothermally at 188°C.

Product stream from R-2 consists of urea, water, unconverted CO₂ and NH₃, and traces of oxygen. This stream is fed to the separator vessel S-1 where the temperature and pressure of the stream is lowered to 130°C and 105bar. This being the pre-treatment step prepares the stream for flashing. Off-gas stream contains traces of unconverted CO₂ and NH₃ is fed to the mixer M-1. The pre-treated stream then

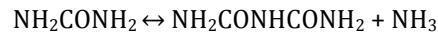
flows to the flash/sePARATOR S-2 which is operated at elevated temperature and low pressure in order to maximize urea concentration. Underflow stream, containing concentrated urea, unconverted CO₂ and NH₃, and water, is again flashed in the third separator S-3 and overflow vapor stream is fed to the mixer M-1. Similarly, underflow stream from S-2 is again flashed in separator S-3. Vapor stream from S-3 is fed to mixer M-1.

All the three overflow streams are mixed in the mixer and recycled back to the reactor R-1. The final product from S-3 consists of 60(±5)% Urea.

4. ASSUMPTIONS:

The presented process simulation is based on several assumptions:

- 1) The process is a steady state simulation process.
- 2) The molar ratio of NH₃: CO₂ is maintained at 2.6. Hence, 2600kmol/hr of NH₃ is taken as feed.
- 3) Pure CO₂ gas is considered i.e. the simulation is carried out in the absence of air.
- 4) When Urea is heated in the absence of free ammonia a side-product/unavoidable compound known as Biuret is formed in traces. It should not be more than 1.5% by weight. Hence, the above simulation is considered to be biuret free i.e. no formation.



- 5) Formation of any other by-product is neglected.
- 6) Fractional conversion of CO₂ is assumed to be 60% in reactor R-1 whereas that of conversion of ammonium carbamate is varied from 60% to 90%.

5. SIMULATION AND RESULTS:

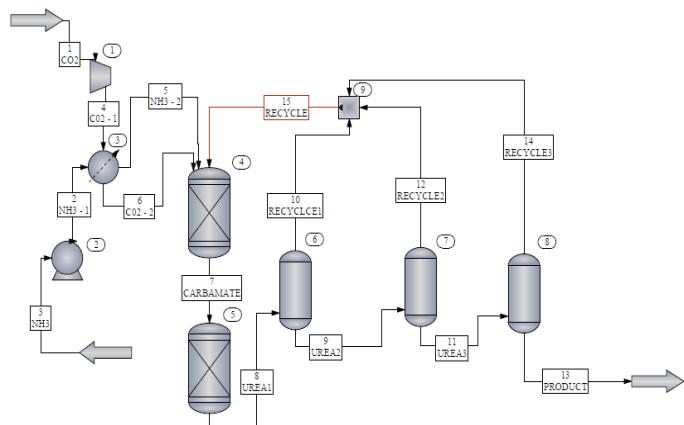


Fig -3: Process Flowsheet of Simulated Process

The simulation is divided into four parts:

4.1 Feed Preparation:

As described above CO_2 and NH_3 are firstly pressurized from their normal conditions. Using a heat exchanger HX-1 their temperatures are elevated with respect to the reaction (i). Following are the composition and properties:

Table -1: Input Feed to Reactor R-1

Component	Molar Flow (kmol/hr)	T_i (°C)	To (°C)	P_i (bar)	P_o (bar)
NH_3	2600	8	113.95	24	240
CO_2	1000	40	130	1.5	160

4.2 Reaction:

The second phase is the reaction between CO_2 and NH_3 to yield ammonium carbamate and then dehydration of ammonium carbamate to Urea. The first reaction being exothermic is carried out at feed inlet temperature and pressure in a stoichiometric reactor R-1. Key component being CO_2 is assumed to undergo 60% fractional conversion inside this reactor. Following is the output from R-1 based on varying fractional conversion of ammonium carbamate from 60% to 90% inside R-2:

Table -2: Product Stream from Reactor R-1 (Weight%)

Component	60%	70%	80%	90%
NH_3	34.68	35.61	36.62	36.71
CO_2	10.24	11.02	11.90	12.92
Carbamate	39.28	38.12	37.54	37.32
Urea	09.29	08.51	08.28	07.80
Water	04.97	04.53	04.50	04.29
Oxygen	01.54	02.21	01.16	0.96

The stream then enters stoichiometric reactor R-2. Using Le Chatelier's principle for an endothermic reaction, the dehydration reaction takes place at an elevated equilibrium temperature of 188°C. In the simulation the fractional conversion of ammonium carbamate is varied from 60% to 90%. Based on this following results are obtained:

Table -3: Product Stream from Reactor R-2 (Weight%)

Component	60%	70%	80%	90%
NH_3	34.87	35.62	36.62	36.72
CO_2	10.24	11.02	11.90	12.92
Carbamate	15.71	11.43	07.51	03.73
Urea	27.42	29.04	31.38	33.63
Water	10.41	10.68	11.43	12.04
Oxygen	01.35	02.21	01.16	0.96

4.3 Separation:

The third phase of the addressed process is separation which concentrates the urea stream. Separator S-1 is used to lower down the stream temperature and pressure to 130°C and 105 bar from 188°C and 160 bar. S-1 is used to pre-treat the stream and prepare it for flash/separator S-2. S-2 operates at 150°C and 85 bar. The following result is obtained:

Table -4: Underflow Stream from Separator S-2 (Weight%)

Component	60%	70%	80%	90%
NH_3	28.89	27.44	27.94	27.20
CO_2	06.38	05.69	05.90	05.86
Carbamate	16.28	11.53	07.25	03.40
Urea	34.93	40.36	43.37	47.13
Water	12.98	14.34	15.23	16.20
Oxygen	00.54	00.64	00.29	00.21

This stream is again flashed at 170°C and 65 bar in separator S-3. The resultant stream contains 60(± 5) % concentrated Urea. This can be further concentrated in low pressure (LP) and vacuum sections:

Table -5: Product Stream from Separator S-3 (Weight%)

Component	60%	70%	80%	90%
NH_3	12.61	12.52	12.61	12.60
CO_2	01.38	01.26	01.25	01.25
Carbamate	11.61	07.75	04.46	02.01
Urea	57.20	60.34	62.82	64.71
Water	17.15	18.08	18.84	19.41
Oxygen	00.05	00.05	00.02	00.02

4.4 Recycle:

The final phase is recycling. Overflow stream i.e. vapor stream from separators S-1, S-2, and S-3 are sent to the mixer M-1. M-1 raises the pressure of this stream with respect to that of the reactor. The stream consists of unconverted ammonia, carbon dioxide, ammonium carbamate, a small amount of urea and water, and traces of oxygen.

The reason why pressure is raised is that the reactor is operated at 160 bar and when the recycle streams are directly fed to the reactor it creates an error that the unit operation pressure is lower than the input pressure.

The stream 15-RECYCLE at 165 bar and 210°C is fed to the reactor R-1. Following is the vapor phase composition of the recycle stream:

Table -6: Recycle Stream to Reactor R-1 (Weight%)

Component	60%	70%	80%	90%
NH ₃	45.19	47.52	50.59	52.76
CO ₂	14.35	16.05	18.11	20.68
Carbamate	17.63	13.33	09.28	04.87
Urea	13.61	12.91	13.10	12.97
Water	07.28	06.97	07.12	07.15
Oxygen	01.94	03.31	01.80	01.57

5. EFFECT OF STAGE(S) ON SEPARATION:

The effect of separation stages on the yield of Urea is discussed here. Figure-4 represents a plot between weight % of Urea in the product stream in each stage and Ammonium Carbamate % conversion.

When the process addressed here is simulated using only one separator then the stream composition clearly tells us that the yield of Urea is very low.

Table -7: Single Stage Separation (Weight%)

Component	60%	70%	80%	90%
NH ₃	27.02	27.01	27.01	27.01
CO ₂	19.93	19.94	19.94	19.94
Carbamate	21.22	15.91	10.61	5.30
Urea	24.48	28.57	32.65	36.73
Water	7.35	8.57	9.79	11.02
Oxygen	0	0	0	0

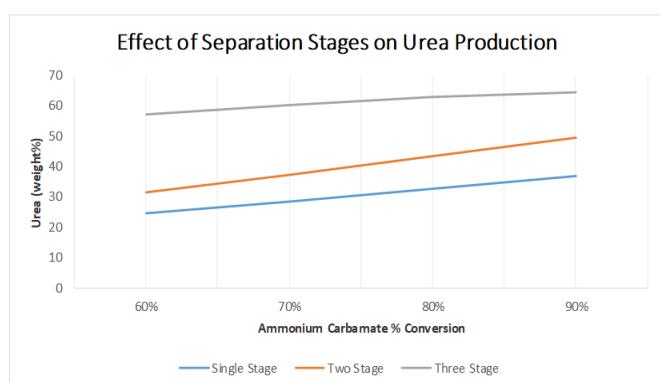
When the same process is simulated using two stages of separation only, then the yield of Urea improves but when compared to the yield obtained in the three stage separation simulation it is still lower.

Table -8: Two Stage Separation (Weight%)

Component	60%	70%	80%	90%
NH ₃	22.57	21.73	20.83	19.93
CO ₂	14.19	13.12	11.94	10.78
Carbamate	22.44	16.68	10.79	05.10
Urea	31.39	37.29	43.42	49.38
Water	09.41	11.18	13.02	14.81
Oxygen	0	0	0	0

Hence we can conclude that the yield of Urea improves with increase in the number of separation stages and

fractional conversion of Ammonium Carbamate and CO₂.

**Chart -1:** Effect of Separation Stages on Urea Production

6. CONCLUSIONS

The process simulation designed here for the urea synthesis can be used for optimization and improving yield. This base case process yields 60(±5) % concentrated urea with an energy consumption of around 500-600x10⁶ kJ/h. Hence, it is suitable for optimization and reducing real plant energy consumption. There is the scope of improvement in the reactor section based on an engineer's choice, therefore, stoichiometric reactors are used for a conceptual understanding.

REFERENCES

- [1] Carlo Rescalli. June 9, 1998. High Yield Process for Urea Synthesis. United States Patent US005763660A.
- [2] J. Jeenay and K. Siemanond. 2018. Ammonia/Urea Production Process Simulation/Optimization with Techno-Economic Analysis. Proceedings of the 28th European Symposium on Computer Aided Process Engineering.
- [3] Xiaohui Wang and Shengpu Li. 2017. Application of computer process simulation in chemical synthesis of urea. Chemical Engineering Transactions, 59, 613-618
- [4] X. Zhang et al. 2005. Modelling and simulation of high-pressure urea synthesis loop. Computers and Chemical Engineering, 29 (2005) 983–992
- [5] A. Edrisi et al., 2016. Urea synthesis using chemical looping process – Techno-economic evaluation of a novel plant configuration for a green production. International Journal of Greenhouse Gas Control 44 (2016) 42–51
- [6] Sana Zahid et al., 2014. Simulation and Parametric Study of Urea Decomposition Section. Pakistan Academy of Sciences 51(4): 277-288(2014).

- [7] Dente, M., S. Pierucci, A. Sogaro, G. Carloni and E. Rigolli. 1988. Simulation program for urea plants. Computers and Chemical Engineering 12: 389
- [8] Ivan A Gargurevich. 2016. Aqueous Urea Decomposition Reactor: Reaction Modeling and Scale Up. J Chem Eng Process Technol 2016, 7:2
- [9] J.N. Sahu et al., 2010. Optimization of ammonia production from urea in continuous process using ASPEN Plus and computational fluid dynamics study of the reactor used for hydrolysis process. Journal of Industrial and Engineering Chemistry 16 (2010) 577-586
- [10] Alexey L. Voskov and Gennady F. Voronin. 2016. Thermodynamic Model of the Urea Synthesis Process. Journal of Chemical & Engineering Data.
- [11] <http://www.icis.com/explore/resources/news/2018/08/14/10250649/india-expected-to-stop-urea-imports-by-2021-on-rising-domestic-production-/>
- [12] <http://www.krishijagran.com/farm-data/indian-fertilizer-sector-at-a-glance/>