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Research Article

Simulation and Parametric Study of Urea Decomposition Section

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Abstract: In this study, the simulation model for the decomposition section of the urea plant was developed by using Aspen Plus. The decomposition reaction in the physical equipments such as heat exchanger, separator and stripper was handled with the use of the combination of the equilibrium reactors and built-in physical equipments in Aspen Plus. The thermodynamic model SR-Polar was used for the estimation of phase and chemical equilibria, density and other thermodynamic properties of the system. The results of the simulation were compared with the existing plant data and a good agreement was observed. Effects of the important parameters such as temperature, pressure and CO_2 stripping stream flow rate on the liquid distributor and 1st separator were also discussed in the decomposition section of urea plant.

Keywords: ammonium carbamate, simulation, Aspen Plus, urea

1. INTRODUCTION

Urea is one of the most important fertilizers, which is produced by the reaction of NH_3 and CO_2 at high pressure and temperature [1, 2]. The energy demands and environmental challenges for urea process are very high. The need of optimization and energy conservation has increased the interest in simulation of urea plant [3]. There are three different production processes of urea; once through process, partial recycle process and total recycle process. The most widely used process is total recycle process among these processes because this process is most flexible and energy efficient [4]. This process requires the separation of NH_3, H_2O and CO_2 from the product stream. These gases are recycled back in the form of ammonium carbamate to the synthesis reactor to increase overall conversion of the reactor. The removal of NH_3 and CO_2 from the solution could be either carried out by stripping or by decomposition process. The efficient decomposition and removal of ammonia carbamate from urea rich solution in the evaporation section leads to large energy savings. Hence the quality of the product can be increased economically [5]. Several studies have been done to investigate thermodynamic modeling and simulation of urea process [1-4, 6-8]. Most of the research studies have been carried out concerning the most suitable fluid package for urea synthesis section, modeling of synthesis section and the properties estimation of ammonium carbamate (the intermediate product in urea synthesis) [1-4, 8, 9] It has been observed from the literature that there is a knowledge gap for the study of urea decomposition, concentration and recovery section. A very little work has been done published for the simulation of these sections.

Bernardis et al [8] used the extended UNIQUAC equation for simulation of the high-pressure urea synthesis loop. Irazoqui and Isla et al [1, 2] treated isothermal urea reactor as an internal coil and

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main reactor and used the extended UNIQUAC equation to calculate the VLE of NH_3–CO_2–H_2O–urea system. Hamidipour et al [3] performed the modeling of synthesis section of an industrial urea plant and also carried out dynamic study of some of the parameters (e.g. pressure and liquid level in the synthesis reactor) using tuned Willson equation. Xiangping et al [4] used the extended UNIQUAC method to describe the non-linearity of urea system under high pressure and the vapor fugacity coefficient were determined using Perturbed-hard-sphere (PHS) equation of state. Brouwer [10, 11] provided the thermodynamics and phase equilibrium for the urea processes. Goharrokhi et al [12] carried out the urea synthesis reactor modeling based on the electrolytic system and studied the effects of N/C ratio and the temperature changes. Zendehboudi et al [13] proposed an efficient artificial neural network (ANN) technique for the simulation and optimization of the urea plant. The developed technique deals with complex vapour–liquid equilibria for the NH_3–CO_2–H_2O–$(NH_2)_2CO$ system and considers the CO_2 conversion in terms of temperature and the molar ratios of NH_3/CO_2 and H_2O/CO_2 in the liquid phase for urea reactors. Saima [7] performed the simulation of urea reactor in the Aspen Plus considering a plug flow reactor as a series of CSTRs and used the SR Polar method for estimation of thermodynamic properties for capacity enhancement.

In the present research study, the urea decomposition section of an industrial plant is simulated by using Aspen plus. The model development of the decomposition section is carried out using equilibrium reactors to ensure continuous decomposition in the decomposition section. The interaction parameters and binary coefficients are provided to apply SR polar thermodynamic model. This model provides a good approximation for (Vapor Liquid equilibrium) VLE of NH_3–CO_2–H_2O–urea system. The present research work provides simulation approach for decomposition section and simulation results are validated to real plant. Further this model is studied for sensitivity analysis.

2. PROCESS DESCRIPTION

The production of urea commercially occurs at high temperature (170 -200 ^{o}C) and high pressures (13 to 25 MPa) by reaction of NH_3 and CO_2. Fig. 1 shows the process flow diagram of urea plant. Ammonia and carbon dioxide from ammonia unit and ammonium carbamate from recovery section are fed to urea reactor. In the reactor two consecutive reactions such as the formation of ammonium carbamate and dehydration of ammonium carbamate take place to produce urea and water. The formation of ammonium carbamate is an exothermic reaction and this heat of reaction is used to drive the endothermic dehydration of carbamate.

$$2NH_3 + CO_2 \rightleftarrows NH_4COONH_2$$

In recycle process, the synthesis mixture from the reactor is sent to decomposition section where

$$NH_4COONH_2 \rightleftarrows NH_2CONH_2 + H_2O$$

carbamate decomposes to NH_3 and CO_2. The NH_3 and CO_2 are separated by flashing and the stripped off gases are absorbed in absorber in the recovery section with a small amount of water to form ammonium carbamate and this is recycled back in to synthesis reactor. Heat generated in the absorption process is utilized by the decomposers. While urea rich solution leaving decomposer is sent to the filtration unit prior to further concentration and then prilling of urea takes place in the prilling tower. Ultimately the urea is sent either for marketing or for storage.

The main emphasis of this research is to model the decomposition section of urea plant. Therefore decomposition section of urea plant is discussed in detail.

2.1 Decomposition Section

The decomposition section consists of

- High Pressure Decomposition
- Low Pressure Decomposition

In high pressure decomposition, decomposition is achieved by reducing the pressure and increasing

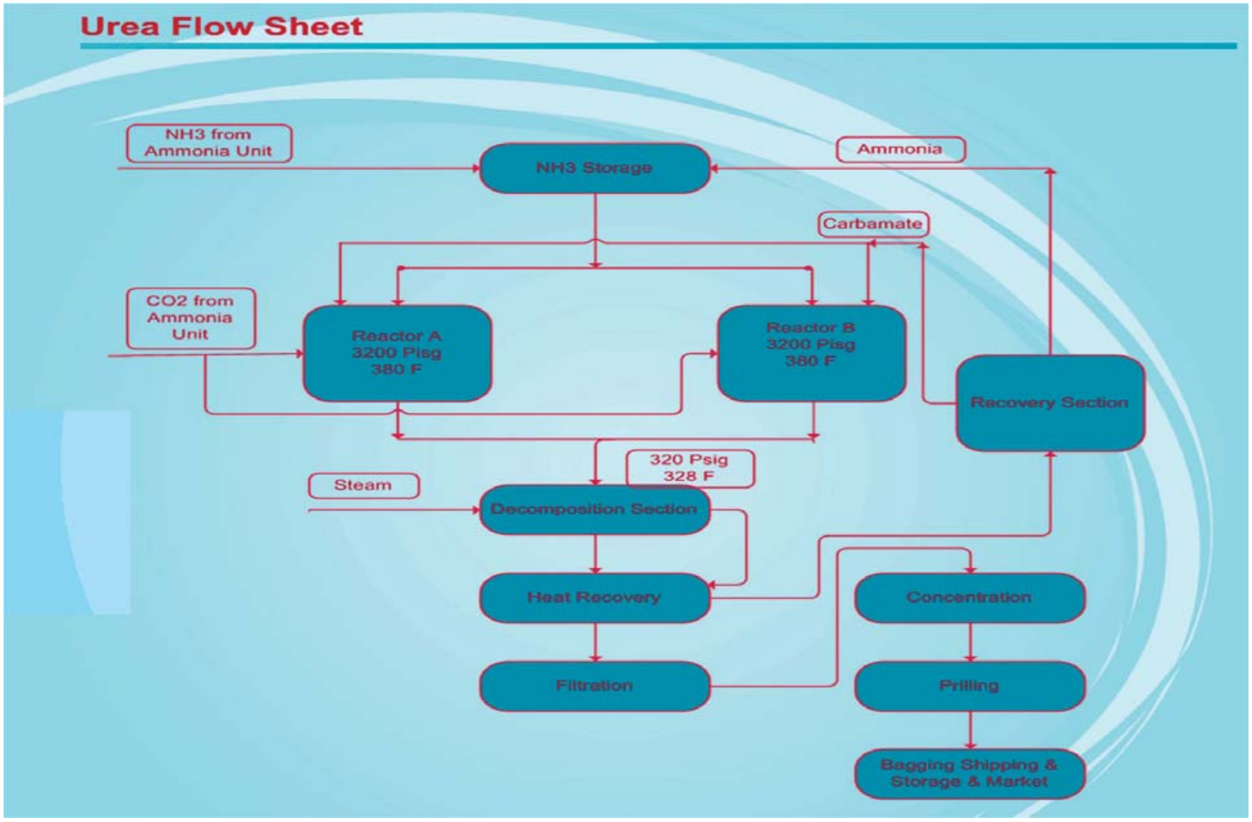

Fig. 1. Process flow diagram for urea plant.

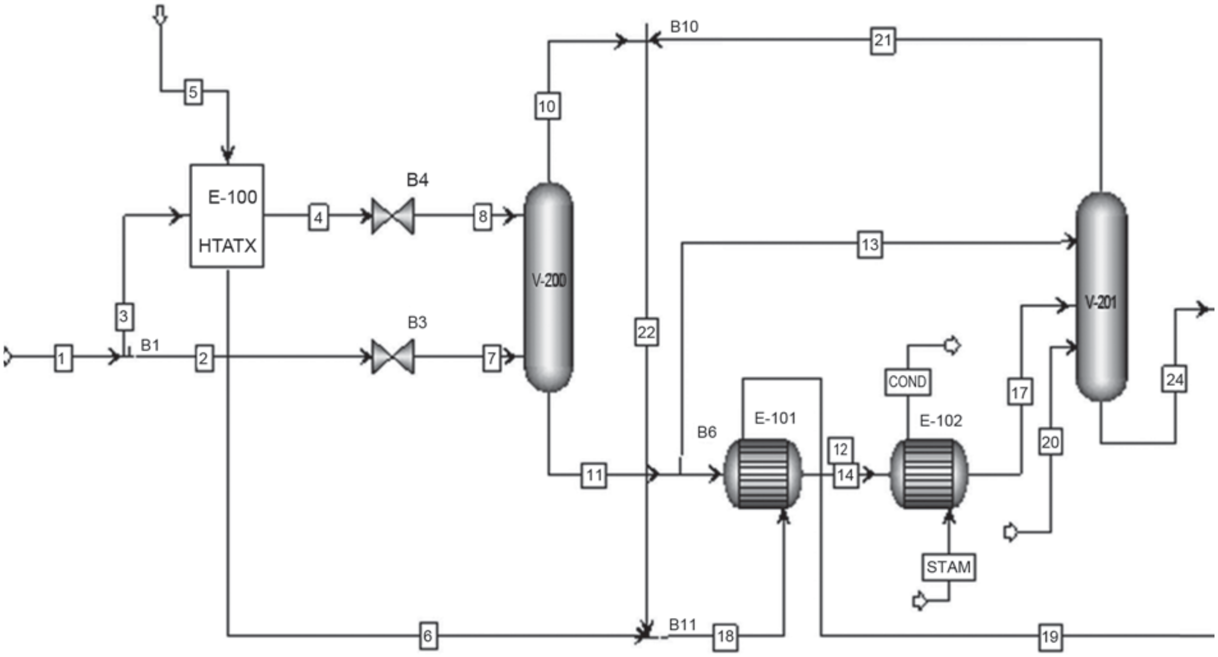

Fig. 2. High pressure decomposition section of urea plant.

the temperature in following equipment as shown in the (Fig. 2).

- Reflux Cooler (E-100)
- Liquid Distributor (V-200)
- 1st Pre Decomposer (E-101)
- 1st Decomposer (E-102)
- 1st Separator (V-201)

Stream (1) from outlet of the reactor is splitted into two streams; stream (2) and (3). Stream (3) is sent to the reflux cooler (E-100) for cooling by a heat recycle stream(5). After that its pressure is reduced to 300 psi by a mini let down valve (B4) and then it is introduced to the top of liquid distributor (V-200). Stream (2) is sent to the bottom of the liquid distributor (V-200) by reducing pressure to 300 psi through main let down valve (B3). This causes the considerable cooling and flashing of NH_3, CO_2 and H_2O. Stream (3) coming from the top of liquid distributor reduces H_2O and CO_2 contents in the off gas stream (10) from V-200. The stream (11) from liquid distributor is divided into two streams (12) and (13). Stream (12) is sent to the 1st pre-decomposer (E-101) where it is heated by a heat recycle stream (18).Which is further heated by a 185 psig steam in the 1st decomposer (E-102) and then urea rich solution stream (17) is introduced to the bottom of V-201. Stream (13) is used as a reflux to 1st separator (V-201). The CO_2 stream (20) is introduced from the bottom of 1st separator for stripping and decomposition of ammonium carbamate. CO_2 rich stream (21) from the top of V-201 is mixed with ammonia rich stream (10) from V-200 and is mixed with heat recycle stream (6) to recover its heat completely in E-101.

The low pressure decomposition includes the following components (Fig.3):

- Second Flash Separator (V-202)
- Second Decomposer (E-103)
- Second Separator (V-203)

The product stream (24) leaving the bottom of 1st separator is sent to the flash separator (V-202) and decomposition is achieved by flashing. The gaseous phase is separated from liquid and concentration is further increased. The residual carbamate solution (26) from V-202 is sent to the second decomposer (E-103) where it is heated from the low pressure heat recycle stream (19) coming from the shell side of E-10. It is then sent to the second separator (V-203). The low pressure CO_2 stream (29) leaving the top of the second separator (V-203) is mixed with low pressure gaseous stream (25) from V-202 and then sent to the recovery cycle. Urea rich solution (30) is sent to evaporators where excess water is removed and the concentrated urea solution is then sent to prilling tower and urea granular product is stored in the storage vicinity.

3. SIMULATION MODEL DEVELOPMENT

The simulation of decomposition section of urea is a challenging research area because of the unavailability of thermodynamic properties of urea, ammonium carbamate and biuret and solid handling in commercial simulators such as Aspen Plus & HYSYS etc. [14, 15].It requires a critical approach in simulating urea production process in Aspen Plus. The solid handling and VLE properties of urea and ammonium carbamate are estimated in Aspen Plus using a FORTRAN code, linker file urea.dll and urea.opt based on a pilot plant data provided by Aspen Tech [15]. The binary coefficients are added for urea and ammonium carbamate for the estimation of other thermodynamic properties like phase & chemical equilibria. The formation of biuret is normally controlled by process conditions, so plant is operated at the conditions where biuret formation is negligible. The unavailability to account for reactions in the physical separation units and heat exchangers is handled by using Redrac model for strippers [16]; and equilibrium reactors before separators and heat exchangers. The analysis of ammonium carbamate in plant is available in the form of CO_2 and NH_3 only, so the carbamate is estimated from the literature based on assumption that the free CO_2 is present to a minimum extent in liquid phase.

3.1 Assumptions

The simulation of urea decomposition section is based on the assumptions:

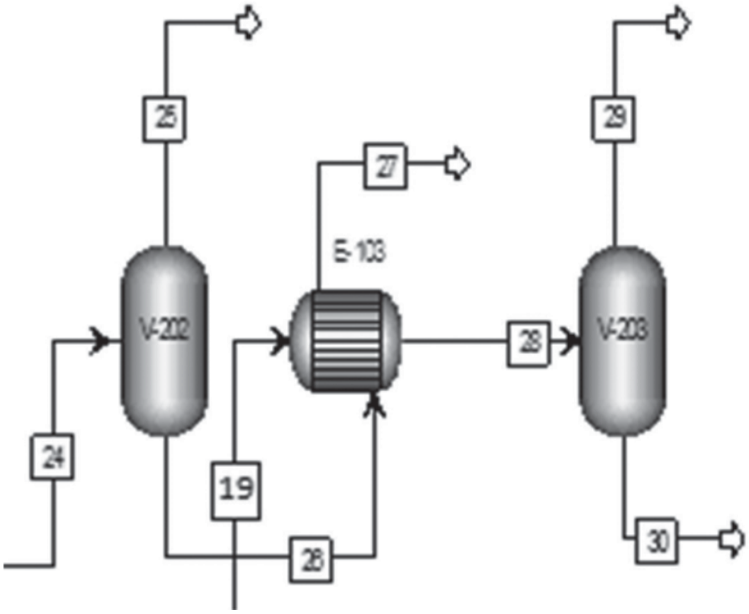

Fig. 3. Low pressure decomposition section of urea plant.

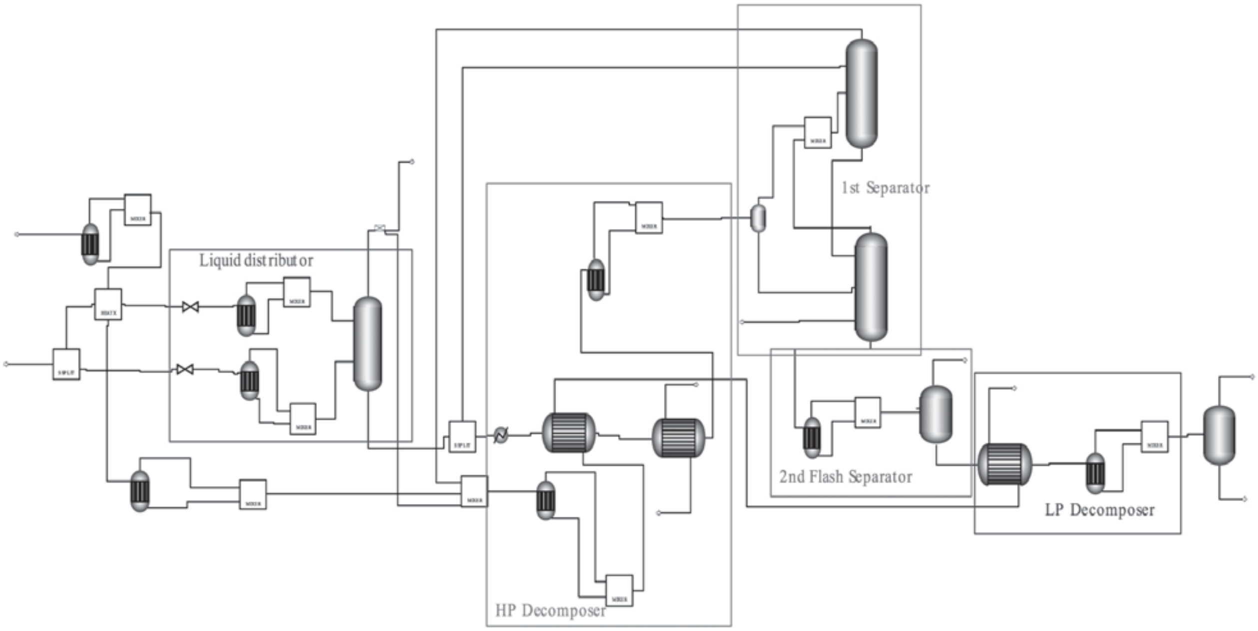

Fig. 4. Aspen Plus Flow sheet of decomposition section of urea plant.

i. The process is at steady state;
ii. Formation of biuret and other by-products has been neglected;
iii. Free CO_2 is present to a minimum extent in the liquid phase and present only in the form of ammonium carbamate;
iv. No carbamate and urea is present in gas phase; and
v. All Inert gases are considered only in the form of air.

In P & ID there are two reactors and two reflux coolers, and in the aspen plus the single reflux cooler is modeled.

3.2 Thermodynamic Property Package

The model for thermodynamic properties is based upon SR-POLAR. The model uses an equation of state and is suitable for the non-ideal mixtures as well as for even high temperature and pressure. Further, the model contains extensions that enable an accurate description of the phase and chemical equilibria, the density and other thermodynamic properties (e.g., enthalpy).

The UNIQUAC thermodynamic package is used in previous studies [1, 2, 8], but in the present study it is not used because it assumes that under high temperature (160 to 200°C) and relatively low water concentration, the extent of ionization will be small. Also, modern equations of state such as SR-POLAR model are well suited to the description of thermodynamic properties of non-ideal systems.

The SR-POLAR property method is based on an equation-of-state model by Schwarzentruber and Renon, which is an extension of the Redlich-Kwong-Soave equation of state. SR-POLAR method can be applied to both non-polar and highly polar components. It is also applicable to highly non ideal mixtures and mixture of light gases with polar and non-polar compounds. Reasonable results at any condition can be achieved, provided UNIFAC interaction parameters are available. But results are least accurate close to the critical point. The simulation case is beyond the critical range thus this model can be used with UNIFAC interaction parameters. The system of ammonium carbamate is highly polar solution and there are some light gases along with the mixture. So the SR-POLAR is used for the estimation of phase equilibrium for that purpose the temperature dependent binary parameters are used to accurately represent phase equilibria.

3.3 Simulation Model

The reactor effluent composition (Table 1) is estimated from the assumption mentioned in section 3.1. The different equipments at the real plant are modeled using built in aspen plus model described in Table 2, simulation flow diagram is shown in Fig. 4 and the stream input specifications are given in Table 3. The simulation approach for the individual units is described below.

Table 1. Reactor effluent composition in terms of carbamate.

Components	% (Wt)	lb/hr
Urea	31.06	145305.07
CO_2	0.10	471.10
NH_3	31.07	145382.03
H_2O	20.09	93985.15
Carbamate	17.67	82677.23
Total	100.00	467820.57

Table 2. Real plant units and model developed in Aspen Plus.

Real Plant Units	Aspen Plus Model
Liquid Distributor V-200	**Liquid Distributor Model** o Equilibrium Reactor(B1,B2) o Mixers(B3,B5) o RedFrac Model (Liquid Dist)
1st Pre Decomposer E-101	**1st Pre Decomposer Model** o Heater o Shell and Tube Heat Exchanger
1st Decomposer E-102	**1st Decomposer Model** o 1st Dec o Equilibrium Reactor(B11) o Mixer(B12)
1st Separator V-201	**1st Separator Model** o Rectifying Section(1ST-SEPT) o Flash separator(B24) o Mixer(B14) o Stripping Section(1ST-SEP)
2nd Flash Separator V-202	**2nd Flash Separator Model** o Equilibrium Reactor(B16) o Flash separator(2ND-SEP) o Mixer(B17)
2nd Decomposer E-103	**2nd Decomposer Model** o Shell and Tube Heat Exchanger (2ND-DEC) o Equilibrium Reactor(B13) o Mixer(B10)
2nd Separator V-203	**2nd Separator Model** o Flash separator(2ND-SEP)

The reactor effluent is introduced to S Split to split the stream to be used as a reflux in liquid distributor and main feed for the liquid distributor. It divides the stream only on the basis of flow rate. The composition, temperature and pressure remain constant. The reflux to liquid distributor is passed to the double pipe heat exchanger which is modeled as a Heatx model. Only one heat exchanger is used instead of two to give the total surface area for the simulation.

RedFrac model is used for the simulation of liquid distributor. The purpose of liquid distributor is to separate the free NH_3 from the urea solution. The decomposition in liquid distributor due to reduction in pressure is accommodated by the introduction of

Table 3 Stream input data.

Stream Name &Number	**Reactor Effluent (1)**	**Heat Recycle (5)**	**Steam**	**CO2 stream (20)**
Temperature (°F)	382	162.5	395	246
Pressure (psig)	3199	292.5	185	296
Total Flow (lb/hr)	467820.57	48847.35	52356	20709
Composition	Wt%	Wt%	Wt%	Wt%
Urea	0.311	0.132	-	-
CO_2	0.001	0.213	-	0.999
NH_3	0.311	0.341	-	-
H_2O	0.200	0.314	1.000	-
Carbamate	0.177	-	-	-
Air	-	-	-	0.001
Total	1.000	1.000	1.000	1.000

equilibrium reaction. The ammonium carbamate decomposes to form NH_3 and CO_2 by reduction in pressure and increase of temperature.

$$2NH_3 + CO_2 \rightleftarrows NH_4COONH_2$$

This reaction is highly endothermic and reaches to chemical equilibrium very quickly. So the decomposition reaction is included in the simulation as React1 to account for the reaction in the RedFrac Models. The reaction is added as the equilibrium reaction and model estimates the K_{eq} from the Gibbs free energy.

Four equilibrium stages are used in the Redfrac model to separate the free ammonia from the urea solution. The decomposition occurring because of let-down valves is accommodated by the use of the equilibrium reactors after let-down valves. The pre-decomposer is designed as a combination of a heater and a shell and tube heat exchanger. The heater accounts for transferring of exothermic heat of reaction of the ammonium carbamate formation in the heat recycle stream and then the remaining sensible heat transfer is carried out in shell and tube heat exchanger.

1st Decomposer is a shell and tube heat exchanger and the decomposition reaction of ammonium carbamate also takes place in tube side. In Aspen Plus, reaction cannot be accommodated to the heat exchangers so an equilibrium reactor is used to account for the decomposition in 1st decomposer.

The first separator is modeled as a combination of two RedFrac models and a flash separator between them. As actual separator has three trays at the top and three trays at the bottom and a larger space for the flashing at the center. Top section acts as a distillation column with a reflux stream from the top. The bottom section acts like a stripping section where medium pressure (MP) CO_2 stream is used as a stripping agent. The purpose of separator is to remove most of the CO_2 and NH_3 by introduction of MP CO_2 as stripping medium.

So the unit is designed as a combination of three units (Fig. 4):

- Rectifying section
- Flash separator
- Stripping column

Flash Separator is a simple vessel and operating temperature and pressure are 228 °F and 43.5 psig respectively. The decomposition in the flash separator is considered by employing an equilibrium reactor before it. The 2nd decomposer is a shell and tube heat exchanger with an equilibrium reactor. Second separator is also designed as a flash separator to separate the decomposed ammonium carbamate in the 2nd decomposer. The temperature and pressure of 2nd flash separator are 230 °F and 28.45 psig, respectively.

4. MODEL VALIDATION

The licensors' material balance of the liquid distributor, 1st and 2nd separator is compared with the simulation results. The results in Aspen Plus are given in the form of carbamate, for the sake

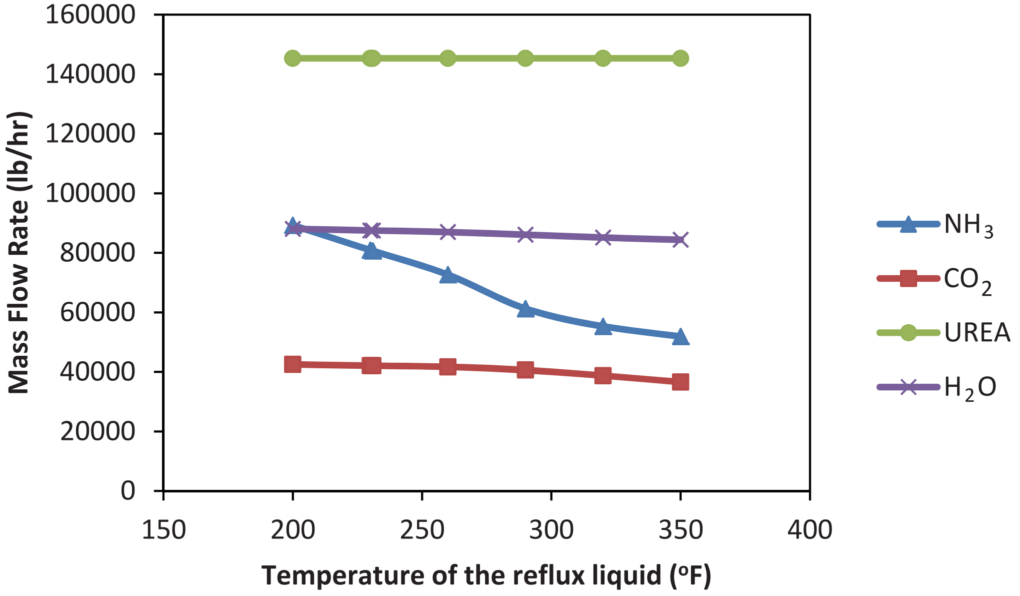

Fig. 5. Effect of temperature on the mass flow rate of the liquid stream of liquid distributor.

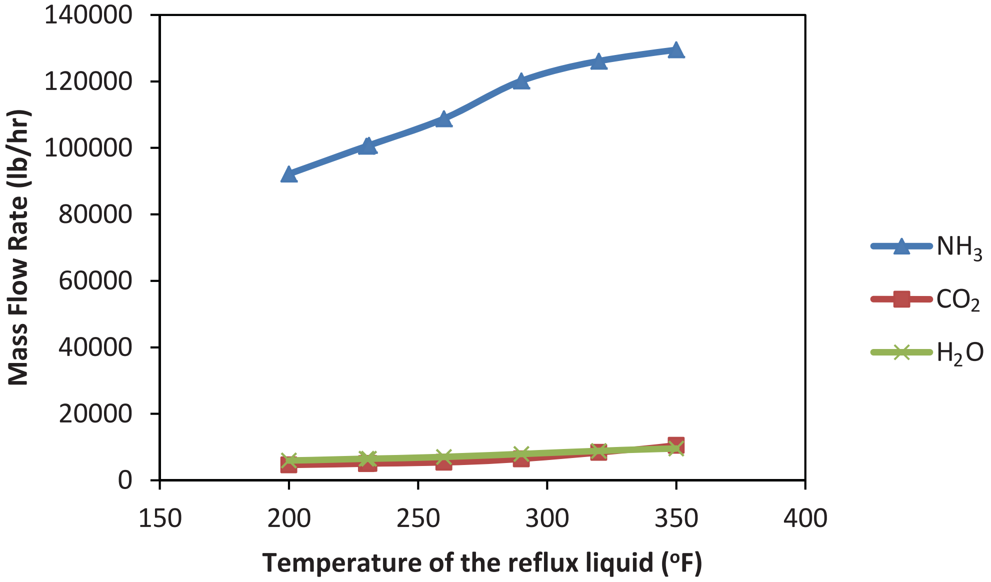

Fig. 6. Effect of temperature on the mass flow rate of the vapour stream of liquid distributor.

of composition; the carbamate is mentioned as ammonia and carbon dioxide. The results of Aspen plus model are shown in Table 4 for validation.

1st separator is a single unit in actual plant but it is simulated as a combination of three units because of large disengagement region between the top and bottom three plates. When the material balance of the real plant is compared with the Aspen plus model the results showed in Table 4 are more close to the plant model as compared to modeling a single separator (for details, see [18]). The material balance is compared for the purpose of data validation across the 2nd separator as well. The comparison of the results with the industrial plant data showed a close agreement with the plant data and the % error is ranging from 0 to 15%. Hence the model can be extended for the purpose of further studies.

Table 4. Model Validation of simulation results.

Stream	Liq. from Liquid Distributor			Gas from Liquid Distributor			Liq. from 1st Separator			Gas from 1st Separator			Liq. from 2nd Separator			Gas from 2nd Separator		
	Mass Fraction		Error	Mass Fraction		Error	Mass Fraction		Error	Mass Fraction		Error	Mass Fraction		Error	Mass Fraction		Error
	Plant Data	Aspen	%	Plant Data	Aspen	%	Plant Data	Aspen	%	Plant Data	Aspen	%	Plant Data	Aspen	%	Plant Data	Aspen	%
Urea	0.412	0.407	1.00	0.000	0.000	0.00	0.571	0.572	0.19	0.000	0.000	0.00	0.661	0.655	0.92	0	0.001	100.00
CO_2	0.116	0.117	0.86	0.053	0.049	7.54	0.064	0.058	10.74	0.380	0.388	1.95	0.023	0.02	13.04	0.225	0.243	8.00
NH_3	0.229	0.233	1.72	0.874	0.883	1.09	0.072	0.072	0.13	0.527	0.527	0.04	0.024	0.023	4.35	0.48	0.418	14.81
H_2O	0.242	0.243	0.41	0.073	0.067	8.81	0.293	0.299	1.97	0.093	0.085	9.18	0.292	0.302	3.31	0.295	0.338	12.78
Air	-	-	-	-	-	-	-	-	-	0.000	0.000	1.84	-	-	-	0.000	0.000	0.00
Total	1.000	1.000		1.000	1.000		1.000	1.000		1.000	1.000		1.000	1.00		1.00	1.00	
Mass Flow (Ton/hr)	176.51	178.24	0.87	57.40	55.67	3.01	127.19	126.95	0.19	59.67	61.41	2.83	09.86	110.31	0.40	8.79	9.01	2.45
Phase	Liq	Liq		Gas	Gas		Liq	Liq		Gas	Gas		Liq	Liq		Gas	Gas	
P (psig)	317.40	317.40	0.00	317.40	317.40	0.00	287.60	287.60	0.00	287.60	287.60	0.00	28.45	28.45	0.00	28.45	28.45	0.00
T (°F)	250.00	250.90	0.36	263.00	263.00	0.00	280.00	279.40	-0.21	274.40	274.39	-0.004	30.00	230.00	0.00	230.00	230.00	0.00

5. SIMULATION RESULTS

5.1 Analysis of Liquid Distributor

The purpose of the liquid distributor is to separate the free ammonia present in effluent from the reactor so that the decomposition of ammonium carbamate in the next sections is not hindered by free ammonia present in urea solution. The effect of temperature and pressure of liquid distributor is also studied.

5.1.1 Effect of Temperature on the Liquid Distributor

Fig. 5 shows the effects of temperature of the reflux liquid stream (4) on the mass flow rates of NH_3, CO_2, H_2O and urea. The mass flow rate of NH_3 and CO_2 deceases with the increase in temperature of stream (4) while that of H_2O and urea remains constant. There is only a slight decrease in CO_2 as compare to NH_3 as CO_2 in liquid stream condenses with ammonia to form ammonium carbamate. This slight decrease in CO_2flow rate indicates that the decomposition of ammonium carbamate is very small. The decrease in mass flow rate of ammonia is more pronounced than CO_2 in the liquid stream of liquid distributor due to ammonia present in free form and ammonia produced by decomposition of ammonium carbamate.

In Fig. 6 the effect of temperature on the gaseous stream is also shown in the liquid distributor. Free ammonia is released to a maximum extent in the liquid distributor. Increase in the temperature of reflux liquid increases the mass flow rate of NH_3 in gaseous phase appreciably, showing the decomposition of the ammonium carbamate. While the water vapor and CO_2 does not change appreciably as the liquid from the top of liquid distributor suppresses H_2O and CO_2 flow in vapor phase. Urea composition is not shown in Fig.6 as urea remains in the liquid phase.

5.1.2 Effect of Pressure on the Removal of NH_3 from Liquid Distributor

The amount of ammonia decreases with increase in pressure of the liquid distributor (Fig. 7). High pressure section of decomposition acts as the heat source for the decomposition in the low pressure section, so the pressure is maintained in such a way that the removal of NH_3 and CO_2 is sufficient to meet the heat loads of low pressure decomposition section.

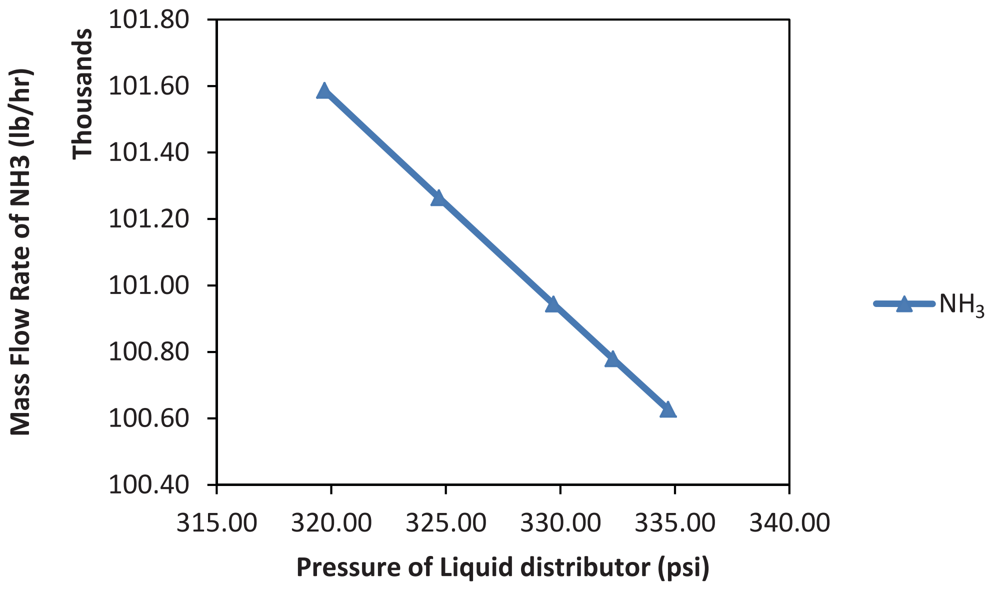

Fig. 7. Effect of pressure on ammonia removal in Liquid Distributor.

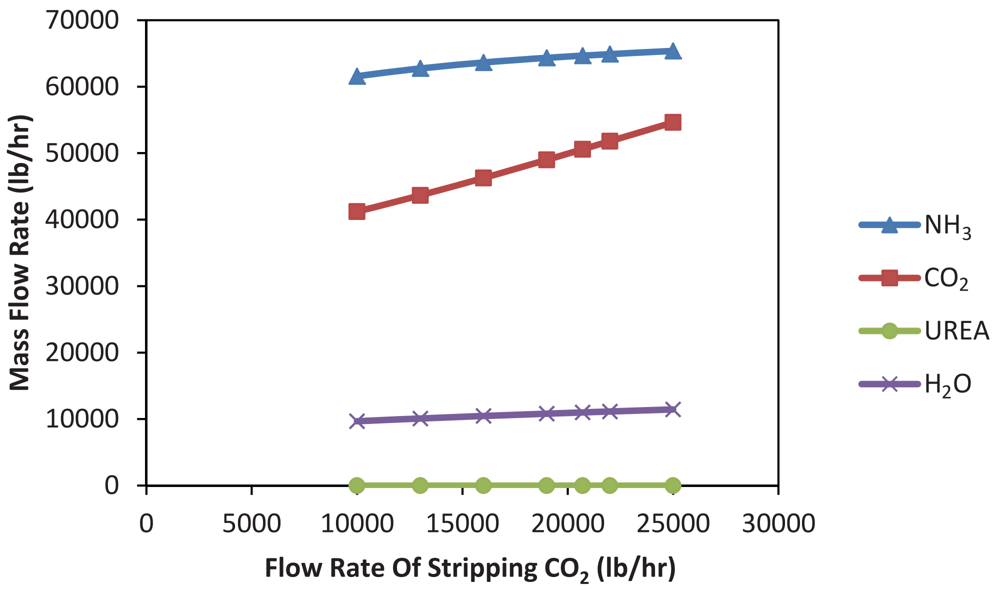

Fig. 8. Effect of CO_2 stripping gas flow in the vapor stream of 1st separator.

5.2 Analysis of 1st Separator

1st separator is one of the critical equipment of decomposition section. The purpose of separator is to remove NH_3 and CO_2 from liquid stream leaving from 1st decomposer. The relatively colder stream is delivered as a reflux solution to the top of the tray. The purpose of reflux stream is to decrease water vapor contents in the gaseous phase. High temperature leads to hydrolysis of urea and that is why sensitivity analysis is considered in the temperature range of 270 -275 ^{o}C.

5.2.1 *Effect of CO_2 Stripping Gas on the Stripper*

A stream of CO_2 is introduced through the 1st separator bottom tray for stripping of some of the residual ammonia from urea product solution. Fig.8 shows increase in CO_2 stripping gas flow rate increases the mass flow rate of NH_3 and

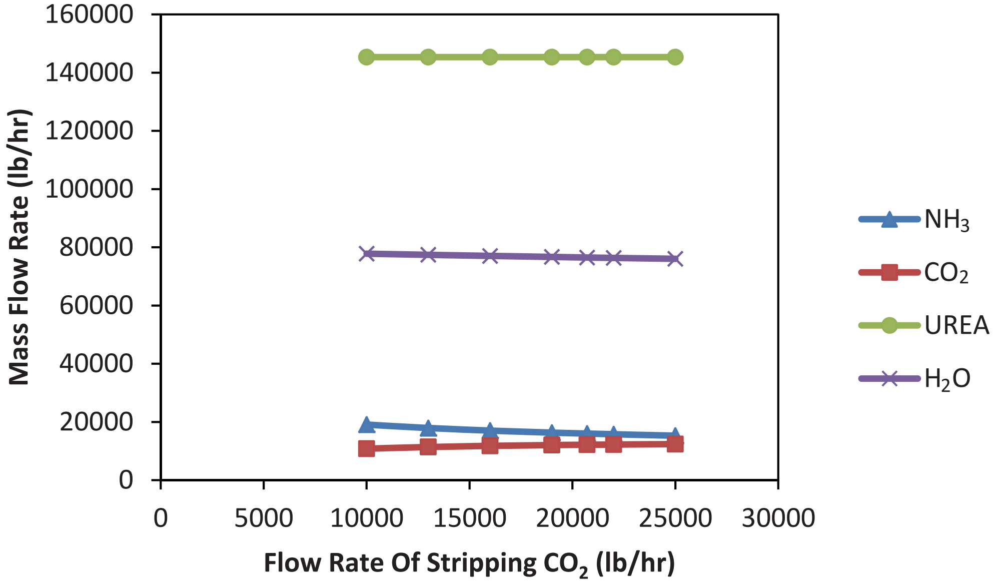

Fig. 9. Effect of CO2 stripping gas flow in the liquid stream of 1st separator.

CO_2 in vapor stream. The sharp increase in CO_2 shows the flow of the stripping gas as well as the decomposition of ammonium carbamate. While there is a slight increase in mass flow rate of H_2O that shows the evaporation of water in vapor phase and urea remains constant as it does not strip off.

Fig.9 presents the effect of CO_2 stripping gas flow on liquid stream of 1^{st} separator. The quantity of ammonia and water is decreased with the increase in mass flow rate of stripping CO_2.While the mass flow rate of CO_2 is increased with the increase in mass flow rate of stripping CO_2. It has been observed that there is a little formation of ammonium carbamate along with the decomposition of ammonium carbamate. The amount of urea remains constant in the liquid phase.

6. CONCLUSIONS

Simulation model developed for the decomposition section of urea plant can be used for optimization purposes. It can also be used to investigate the effects of operating conditions on the decomposition of carbamate. Hence the model is suitable for conservation of energy and optimized plant performance. The model is fine tuned to the operating plant and the error (%) is small which makes it acceptable for further studies.

7. ACKNOWLEDGEMENTS

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