Application of Computer Process Simulation in Chemical Synthesis of Urea

Xiaohui Wang, Shengpu Li*

Pingdingshan University, College of Computer Science and Technology, Pingdingshan Henan, China
lsp1519@163.com

The computer process simulation technology can simulate the chemical process of urea, effectively reflect the technological parameters of the chemical production process, and provide practical guidance for chemical production of urea. This paper conducts computer process simulation of the high-pressure urea synthesis tower, the center piece of the chemical synthesis of urea. The chemical parameters in the production process of the synthesis tower are simulated and analyzed with the aid of the equilibrium stage model and computer technology. The calculation results are consistent with the design values of the synthesis tower, indicating that the equilibrium stage model satisfies the technological design requirements. Suffice it to say that the research provides meaningful guidance for the chemical production of urea.

1. Introduction

Urea is not only the most-produced and most-used chemical fertilizer in the world, but also a multi-purpose industrial raw material (Naz and Sulaiman, 2016; Puspita et al., 2017). Since the 1930s and 1940s, urea production has been a hot subject amongst theorists and industrial practitioners. Over the years, it has developed into an important research field in the chemical industry (Edris et al., 2016). Facing increasingly severe energy crisis and deteriorating environment, researchers are digging deeper into the industrial process, hoping to reduce energy consumption and realize cleaner production. In chemical production, process simulation is the most fundamental computer technology and an essential tool for computer-aided design, condition analysis, and optimization operations (Yao et al., 2016).

High-pressure urea synthesis tower is the key to the synthesis of urea. The synthetic ratio and quality of urea hinge on the parameters of the tower (e.g. temperature, pressure). Figure 1 illustrates the urea synthesis process in the tower.
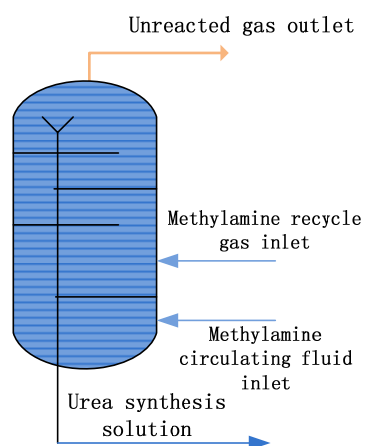

Figure 1: Sketch map of high-pressure urea synthesis tower

The high-pressure urea synthesis tower is separated into several reaction chambers by a number of tower trays that prevent materials from back-mixing. For the equilibrium stage model selected in this paper, it is assumed that each reaction chamber is a continuous mixing reactor containing well-blended gas-liquid mixture (Sahu et al., 2009), that is, an ideal mixing model, that gas-liquid equilibrium is achieved at the outlet of each tray, and that the reaction process fulfils the adiabatic requirements (Victor-Ortega et al., 2016; Gimenes et al., 2016; Freitas and Guirardello, 2016; Villarroel et al., 2016; De Andrade et al., 2016; Lee and Zaini, 2017).

Based on the basic principle of chemical reaction equilibrium and chemical reaction kinetics, and on the assumptions of the equilibrium stage model, this paper conducts the computer process simulation of the urea synthesis procedure in the high-pressure urea synthesis tower. The experimental results effectively reflect the parameter variation in the synthesis process, and provide practical guidance for application of chemical technologies.

2. Calculation and analysis of computer process simulation of urea synthesis tower

2.1 Introduction to chemical equations

The main constituents of urea include NH_3, CO_2 and H_2O. The three substances are turned into a gas-liquid equilibrium mixture of NH_3-CO_2-H_2O-urea in the synthesis tower. When the temperature falls in the range of 160~190°C and the pressure remains between 10 and 20Mpa, the chemical reaction in the synthesis tower can be divided into the following two steps (Boggs et al., 2009):

$$CO_2(I) + 2NH_3(I) \rightarrow H_2NCOONH_4 - 100.4kj \tag{1}$$

$$H_2NCOONH_4(I) \rightarrow H_2NCOONH_2(I) + H_2O(I) + 27.6KJ \tag{2}$$

The two equations are combined into Equation (3):

$$CO_2(I) + 2NH_3(I) \rightarrow H_2NCOONH_2(urea) \tag{3}$$

Equation (1) describes the rapid carbothermic reaction of the intermediate product: ammonium carbamate; Equation (2) illustrates the slow endothermic process of urea production through the hydrolysis of ammonium carbamate. The two reactions automatically reach a thermal equilibrium in the synthesis tower (Rafiee, 2015).

2.2 Calculation and analysis of urea synthesis tower based on equilibrium stage model

2.2.1 Establishment of mathematical models for the urea synthesis tower

Considering the material balance, energy balance, phase equilibrium equation, chemical kinetics equation and normalization equation on each tray, the author establishes the following equilibrium stage models (MESHR equations) for each tray in the tower (Kuwabata et al., 1998).

The mathematical models are established as follows (MESHR equations). For the components on the j-th stage of the tower:

$$V_j \cdot y_{i,j} + L_j \cdot x_{i,j} = V_{j-1} \cdot y_{i,j-1} + L_{j-1} \cdot x_{i,j-1} + V_k \cdot u_j \tag{4}$$

$$y_{i,j} = k_{i,j} \cdot x_{i,j}, \sum_{i=1}^{4} x_{i,j} = 1 \tag{5}$$

$$\Delta p = \Delta p_c + \Delta p_l + \Delta p_\sigma \tag{6}$$

Urea generation equation (kinetic equation) (Popoola et al., 2016):

$$u_j = R \cdot \Delta V_j, V_j \cdot H_j^V + L_j \cdot H_j^L = V_{j-1} \cdot H_{j-1}^V + L_{j-1} \cdot H_{j-1}^L + Q_{jL} \tag{7}$$

In the above equations: $x_{i,j-1}$, $y_{i,j-1}$, $x_{i,j}$ and $y_{i,j}$ stand for the mole fraction of the liquid-gas two-phase component i on the j-th tray at the inlet and outlet of the 8-layer synthesis tower, respectively (Hazmi et al., 2016); $k_{i,j}$ refers to the phase equilibrium constant of component i on the j-th tray; V_{j-1}, L_{j-1}, V_j and L_j represent the gas-liquid two phase flow on the j-th tray, kmol/h; H_{j-1}^V, H_{j-1}^L, H_j^V and H_j^L denote the gas-liquid two-phase molar enthalpy on the j-th tray at the inlet and outlet, kj/kmol; u_j means the urea production on the j-th tray, kmol/h; ΔV_j is the equivalent volume of reactants on the j-th tray; Q_{jL} represents heat loss; i=1, 2, 3 and 4 refer to H_2O, NH_3, CO_2 and urea, respectively (Watts et al., 1995).

2.2.2 Solution of mathematical models for the urea synthesis tower

The established models are calculated in the computer. The model for each tray is solved in the following steps:

(1) The equipment parameters and the structural parameters of the tray are taken as given values; the temperature, composition, pressure, flow, etc. of the gas-liquid two-phase components at the inlet are regarded as the known inlet parameters.

(2) Assuming that the outlet temperature is T_j the j-th tray at the outlet and that the liquid-phase component on the tray at the outlet is $x_{i,j}$, calculate the gas phase composition for thermodynamic gas-liquid equilibrium; then, obtain the urea production on the tray by the kinetic equation (Nicoletti et al., 2016).

(3) Solve the gas-liquid flow by overall energy balance (Pang et al., 1997).

(4) Calculate the single-tray pressure drop, and get the outlet pressure of the tray p_j;

(5) Treat the outlet parameters of the j-th tray as the inlet parameters of the next plate, and repeat steps (1) - (4) in the subsequent simulation. The material composition of the last tray is the outlet material composition of the entire synthesis tower (Hamidipour et al., 2005).

The above steps are simulated on the computer to obtain the distribution of flow, composition and temperature across the tower. The procedure is an important part of computer simulation of urea chemical production (Zhang et al., 2005).

2.3 Calculation results and analysis of process simulation

2.3.1 Calculation results

Table 1 lists the results of the calculation results of the equilibrium stage model, namely gas-liquid components, temperature, pressure. Table 2 compares the calculation results of the model and the design values.

Table 1: Simulation results of urea synthesis tower

Tray	Temperature(t/°C)	P/Mpa	x(Mole fraction)			y(Mole fraction)	
			NH$_3$	CO$_2$	urea	NH$_3$	CO$_2$
Inlet	167	14.10	0.6568	0.2309	0.0002	0.6963	0.2321
1	169	14.07	0.6272	0.2076	0.0238	0.6923	0.2541
2	170.63	14.04	0.6000	0.1882	0.0451	0.674	0.2641
3	172.54	14.02	0.5736	0.1713	0.0653	0.6614	0.2666
4	174.67	13.99	0.5482	0.1558	0.0847	0.6506	0.2673
5	176.75	13.97	0.5248	0.1417	0.1028	0.6422	0.265
6	178.81	13.94	0.5028	0.1285	0.1201	0.6357	0.2601
7	180.76	13.91	0.4831	0.1165	0.136	0.6313	0.2526
8	182.66	13.89	0.4645	0.1051	0.1512	0.628	0.2429

Table 2: The comparison of the results of this model with the literature design data

The overhead outlet	Temperature(t/°C)	P/Mpa	x(Mole fraction)			y(Mole fraction)	
			NH$_3$	CO$_2$	urea	NH$_3$	CO$_2$
Calculated value	167	14.10	0.6568	0.2309	0.0002	0.6963	0.2321
Design value	169	14.07	0.6272	0.2076	0.0238	0.6923	0.2541
Relative deviation (%)	170.63	14.04	0.6000	0.1882	0.0451	0.674	0.2641

The overhead outlet	Gas and liquid flow(kmol/hr)		CO$_2$ Conversion rate
	Gas	Liquid	
Calculated value	945.39	8529.68	58.99
Design value	1016.58	8522.58	56.2
Relative deviation (%)	7.09	0.083	4.96

As shown in Table 2, the relative error between the calculation values and the design values is 7.09% for gas-phase components and 0.083% for liquid-phase components; the relative error of CO$_2$ conversion rate stands at 4.96%. All the errors are within the tolerance range for the chemical technologies.

Then, the author analyzes how the temperature of each tray, the flow of each component and the production of urea varies during the urea synthesis process within the tower. The variations are calculated by the equilibrium stage model. Figure 2 shows the temperature trend along the tray level, and Figure 3 presents the urea production trend along the tray level.
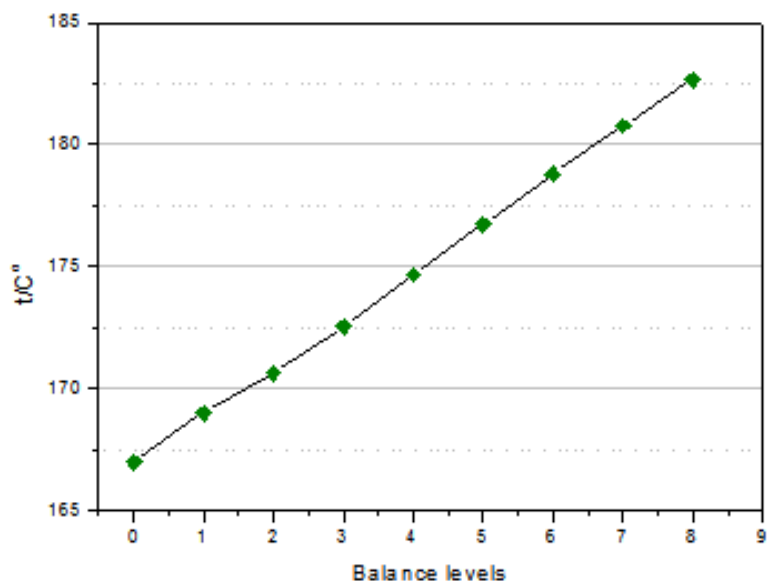
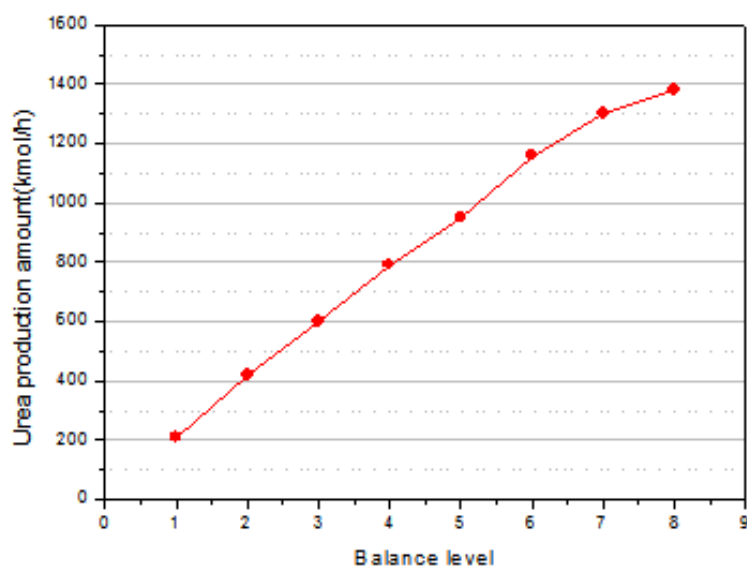*Figure 2: The temperature trend along the tray level*

Figure 3: The Urea production along the tray level

According to Figures 2 and 3, the temperature rises with the increase of the tray level and peaks at 182.66°C; the urea production also increases with the tray level. The results are in good agreement with the actual chemical production results.

The above-mentioned chemical equations in the synthesis tower are, in essence, the gas-liquid phase conversion of NH_3, CO_2 and H_2O under different pressure and temperature conditions. The variation in the flow of each liquid-phase component along the tray level is shown in Figure 4.

As shown in the figure, as the material enters the synthesis tower from the bottom tray, the liquid-phase molar flows of NH_3 and CO_2 decrease gradually, but flow of urea rises along the tray level. The result also echoes the actual situation in chemical production. Influenced by opening rate, tray, etc., the CO_2 conversion rate is a key determinant of urea production. Through computer flow simulation, the rate is calculated as 58.99%, while the design conversion rate is 56.2%. The relative error is merely 4.96%, signifying high accuracy. The CO_2 conversion rate is mainly reflected by the distribution of calculated pressure in the equilibrium stage model. This means the model offers some instructions on the design of structure parameters of the trays in the tower.
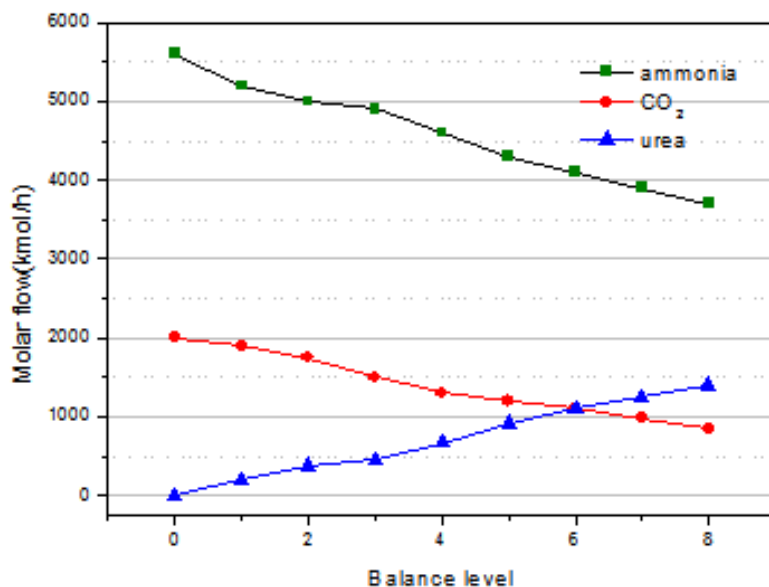
Figure 4: Liquid-phase composition flow along the tray level

3. Conclusion

In order to realize the process simulation of the technologies in urea synthesis tower, this paper calculates the variation in temperature and each component in the tower based on the theory of equilibrium stage model and with the aid of computer flow simulation. The conclusions are drawn as below:

(1) The calculated temperature increases with tray level, and the pressure goes in the opposite direction. The trend is consistent with the results of the actual chemical process.

(2) The simulation results are proved accurate by the minimal relative errors between the calculated parameters and the design parameters of the actual chemical process.

(3) The application of computer process simulation technology in urea production demonstrates the guiding effect of theoretical simulation on the actual production.

References

Boggs B.K., King R.L., Botte G.G., 2009, Urea electrolysis: direct hydrogen production from urine. Chemical Communications, 32, 4859. DOI: 10.1039/b905974a.

De Andrade J.R., Da Silva M.G.C., Gimenes M. L., Vieira M. G. A., 2016, Equilibrium and thermodynamic studies on adsorption of trivalent chromium by sericin-alginate particles prepared from bombyx mori cocoons, Chemical Engineering Transactions, 52, 169-174, DOI: 10.3303/CET1652029

Edrisi A., Mansoori Z., Dabir B., 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, 42-51. DOI: 10.1016/j.ijggc.2015.10.020.

Freitas A.C.D., Guirardello R., 2016, Predictive thermodynamic modelling of liquid-liquid-vapor-fluid (llvf) equilibrium in synthetic hydrocarbon synthesis from syngas, Chemical Engineering Transactions, 50, 313-318, DOI: 10.3303/CET1650053

Gimenes M.L., Silva V., Hamerski F., Ribani M., Scheer A., 2016, Biosorption of copper(ii) onto sericin powder derived from cocoons of the silkworm bombyx mori: kinetics, equilibrium and thermodynamics studies, Chemical Engineering Transactions, 49, 205-210, DOI: 10.3303/CET1649035

Hamidipour M., Mostoufi N., Sotudeh-Gharebagh R., 2005, Modeling the synthesis section of an industrial urea plant. Chemical Engineering Journal, 106(3), 249-260. DOI: 10.1016/j.cej.2004.12.020.

Hazmi A.S.A., Maurad Z.A, Pauzi N.N.P.N., Bakar Z.A, Idris Z., 2016, Rapid evaluation of plate heat exchanger performance and fouling analysis in epoxidation of oleochemical at pilot plant scale, International Journal of Heat and Technology, 34(4), 558-564. DOI: 10.18280/ijht.340402.

Kuwabata S., Yamauchi H., Yoneyama H., 1998, Urea photosynthesis from inorganic carbon and nitrogen compounds using TiO2 as photocatalyst. Langmuir, 14(7), 1899-1904. DOI: 10.1021/la970478p.

618

Lee L.Z., Zaini M.A.A., 2017, Equilibrium and kinetic adsorption studies of reactive orange onto resorcinolformaldehyde carbon gel, Chemical Engineering Transactions, 56, 811-816, DOI: 10.3303/CET1756136

Nicoletti G., Arcuri N., Bruno R., Nicoletti G., 2016, On the generalized concept of entropy for physical, extra-physical and chemical processes, International Journal of Heat and Technology, 34(S1), S21-S28. DOI: 10.18280/ijht.34S103.

Naz M.Y., Sulaiman S.A., 2016, Attributes of natural and synthetic materials pertaining to slow-release urea coating industry. Reviews in Chemical Engineering, 33(3), 293-308. DOI: 10.1515/revce-2015-0065.

Pang G., Wang B., Zhang Z., Wei S., 1997, Application of process simulation in the optimization of urea production operation. Large Scale Nitrogenous Fertilizer Industry. 6(3), 24-26.

Popoola A.O., Baoku I.G., Olajuwon B.I., 2016, Heat and mass transfer on MHD viscoelastic fluid flow in the presence of thermal diffusion and chemical reaction, International Journal of Heat and Technology, 34(1), 15-26. DOI: 10.18280/ijht.340103.

Puspita A., Prawati G., Fatimah I., 2017, Chitosan-modified smectite clay and study on adsorption-desorption of urea, Chemical Engineering Transactions, 56, 1645-1650, DOI: 10.3303/CET1756275

Rafiee S.E., Sadeghiazad M.M., 2015, 3D numerical analysis on the effect of rounding off edge radius on thermal separation inside a vortex tube, International Journal of Heat and Technology, 33(1), 83-90. DOI: 10.18280/ijht.330112.

Sahu J.N., Gangadharan P., Patwardhan A.V., Meikap B.C., 2009, Catalytic hydrolysis of urea with fly ash for generation of ammonia in a batch reactor for flue gas conditioning and nox reduction. Industrial & Engineering Chemistry Research, 48(2), 727-734. DOI: 10.1021/ie801491j.

Villarroel Rojas J., Stinguel L., Wolf-Maciel M.R., Guirardello R., 2016, Modeling and simulating complete extractive distillation process of ethanol-water mixture using equilibrium-stage distillation model and efficiency correlations (barros & wolf) on emso platform, Chemical Engineering Transactions, 50, 331-336, DOI: 10.3303/CET1650056

Victor-Ortega M.D., Ochando Pulido J.M., Martinez-Ferez A., 2016, Equilibrium studies on phenol removal from industrial wastewater through polymeric resins, Chemical Engineering Transactions, 47, 253-258, DOI: 10.3303/CET1647043

Watts P., Smith M.D., Edwards I., Zammit V., Brown V., Grant H., 1995, The influence of medium composition on the maintenance of cytochrome p-450, glutathione content and urea synthesis: a comparison of rat and sheep primary hepatocyte cultures. Journal of Hepatology, 23(5), 605. DOI: 10.1016/0168-8278(95)80069-7.

Yao S.G., Jia X.W., Huang T., Duan L.B., 2015, Numerical simulation of bubble motion in boiling nanofluids based on Lattice Boltzmann method, International Journal of Heat and Technology, 33(1), 71-76. DOI: 10.18280/ijht.330110.

Zhang X., Zhang S., Yao P., Yuan Y., 2005, Modeling and simulation of high-pressure urea synthesis loop. Computers & Chemical Engineering, 29(5), 983-992. DOI: 10.1016/j.compchemeng.2004.10.004.