

The Urea Synthesis Reactor, its dynamic model and its industrial applications.

Part 2: Phase Diagram aspects

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Introduction

It has been realized that the core of urea synthesis reaction is dehydrating carbamate in liquid state into urea. This reaction is the main one in urea synthesis and is called urea formation reaction for short hereafter. The goal is to push the reaction to proceed in an ideal direction. However, in industrial production scale, there are lots of difficulties and interferences which hinder the reaction to proceed in the expected direction. The main cause hindering the main reaction from becoming an ideal one is that there are two synthesis reactions interfering each other and these are combined with very complex chemical processes. This will be discussed below.

The first problem is the complex reaction.

In terms of reaction process, the urea synthesis is a complex reaction, which consists of carbamate formation reaction and urea formation reaction in series.



It is known that Reaction (1) is a chemical absorption process of gas under high temperature and high pressure. Under the lab conditions, the reaction is completed instantly with a conversion rate close to 100%.

If the cross-link effect with other factors is not considered, and even under the temperature and pressure conditions of industrial synthesis conditions, Reaction (1) is closely related to Reaction (2), the conversion rate of the carbamate formation reaction is still close to 100% when one applies a proper mixing.

Under the actual conditions in industrial production, however, the complex reactions is interfering with many aspects, especially the combined restriction from heat effects and phase equilibrium, which makes Reaction (1) difficult to proceed, leading to a yield rate of carbamate less than 100%.

The second problem is the complex heat effects.

In terms of the heat effects, Reaction (1) is a strongly exothermic reaction, and Reaction (2) is a slightly endothermic reaction. The complexity of the synthesis reaction leads to the complexity of heat effects.

In an industrial urea reactor, when one considers both reaction and its heat effects, according to thermodynamic analysis, the reactor temperature profile shows an inversion: the temperature of the lower part is high and that of the upper part is low. The thermo-mechanical analysis result is as following: in adiabatic conditions, CO₂ entering the reactor bottom is completely converted into carbamate, instantly releasing heat, which can only be used to heat up the liquid carbamate, and Reaction (2) doesn't start to proceed due to the reaction speed difference; with the lapse of time and the materials moving up, the endothermic reaction of Reaction (2) gradually proceeds, and the temperature in the reactor decreases then. So the combination of the complex reaction and complex heat effects causes the temperature inversion.

However, the reactor temperature inversion deduced from the thermo-mechanical analysis doesn't exist in an actual reactor. According to observations, the urea reactor temperature profile always shows normal, i.e. the temperature of the lower part is the lowest one and that of the upper part is the highest one. The actual temperature profile observed is certainly correct. But what causes the result from the thermo-mechanical analysis is different from that from the actual conditions ?

This shows that the combination of the complex reaction and complex heat effects is unreal and insufficient. In the industrial urea reactor there must be other cross-linking factors, like phase equilibrium. But before 1970's, difference between the result from the thermo-mechanical analysis and that from the actual condition couldn't be correctly explained due to the lack of phase equilibrium theories and phase diagrams under the urea synthesis conditions.

Thirdly, complicated phase equilibrium and phase diagram.

Under urea synthesis conditions, for the systems from Reaction (1) and Reaction (2), there is a unusual supercritical azeotropic phase diagram. Phase equilibrium theory is the basis for the analysis of the changes of material streams during the urea synthesis. These meta-stable and stable phase diagrams in strange shapes were developed and published by Kaasenbrood ^[1], Lemkowitz ^[2] et al. in 1970's and important for understanding industrial urea synthesis, explaining previously unknown phenomena and developing new technology for urea reactors and new urea processes.

For an industrial urea reactor, one should consider how phase equilibrium affects the system. It is not sufficient to consider only one complex, i.e. reaction complex, or two complexes, i.e. reaction complex and heat effect complex. There are three complexes in a urea reactor, i.e. reaction complex, heat effect complex and phase equilibrium complex, which all interact.

Causing that:

- 1) CO₂ in supercritical state (liquidized gas) entering the urea reactor can't be totally converted into liquid carbamate;
- 2) the temperature profile in the urea reactor shows normal profile; and
- 3) the gas stream and liquid streams are formed and make the synthesis reaction proceed under the gas-liquid phase from the bottom to the top in the urea reactor.

The interaction of the three complexes makes the expected reaction process deviate from an ideal one, causing the main reaction time to be shorter and the reaction driving force less, which are reasons for a decreased CO₂ conversion rate.

Part 1 of this paper is presented in the UreaKnowHow.com Process Paper August 2009 and covers the reaction and heat effect aspects. This paper is Part 2 and covers the phase equilibrium aspects.

5. Phase equilibrium aspects

5.1 The phase diagram of synthesis and its features ^[10]

(1) The phase diagram of urea synthesis material system is a supercritical azeotropic one ^[1].

The conditions in the urea synthesis are high temperatures ($t > 160$ °C) and high pressures ($P > 13$ MPa), which are above the supercritical points of pure NH_3 and CO_2 . Therefore, the phase diagram of the urea synthesis is a supercritical azeotropic phase diagram with a saddle shape. See Figure 9.

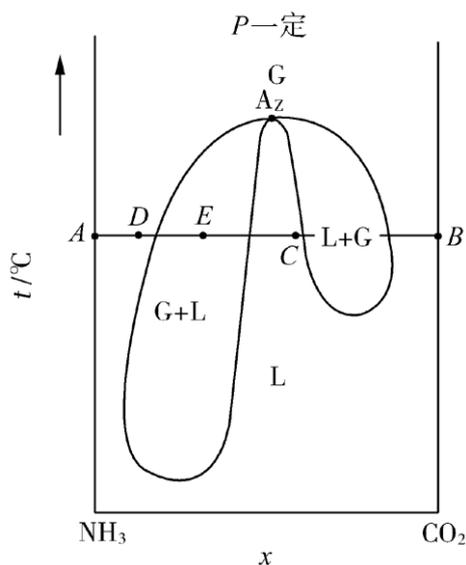


Figure 9: The t-x graph of NH_3 - CO_2 system (schematic)

(P一定 : P is fixed)

t: temperature

x: component

Although the reactants NH_3 and CO_2 are in supercritical state, the mixtures formed show property features of gas and liquid, and the system includes gas and liquid.

(2) Features of the phase diagram

- Impact of pressure

When the pressure increases, the boiling point of the liquid material and the azeotropic point of the system increase, and the area of the liquid phase in the diagram also increases (the saddle moves upwards)

- Influence of water and urea

Water or urea (or the mixture of both) are having relatively high boiling points. When more of these components are present, the boiling point of solution will rise and the area of liquid phase in the diagram also increases (the saddle moves upwards).

- The highest temperature limit

When the system pressure increases, the contents of water and urea increase, the NH_3/CO_2 ratio with the highest boiling point (azeotrope) also increases somewhat. Under typical urea synthesis conditions, the molar ratio of NH_3/CO_2 with the highest boiling temperature is between 2.5 - 3.0. In this range, for the gas component, the condensation temperature is highest, and for the liquid component, the boiling point is highest.

(3) Metastable phase diagram and stable phase diagram ^[10]

The urea synthesis reaction consists of two reactions in series, so the phase diagram also includes the metastable one and a stable one. The carbamate generation reaction corresponds to the metastable phase diagram, and the reaction of converting carbamate into urea, i.e. urea generation reaction, corresponds to the stable phase diagram.

The stable phase diagram develops from the metastable phase diagram. In Reaction (2), one carbamate molecule of high boiling point reacts to produce two components of high boiling point, urea and water. So, this means an increase of the concentration of components of high boiling point in the metastable system, and it can be concluded from the above that the boiling point of the stable phase diagram becomes higher. So the gas phase line will move up further and the area of liquid phase will become larger.

5.2 The state points of the synthesis system

In Figure 9, Point A is the system point of pure NH_3 , and Point B is the system point of pure CO_2 .

Because of the synthesis temperature $> 160\text{ }^\circ\text{C}$, and pressure $> 13\text{ MPa}$, both of which are above the critical points of pure NH_3 ($P_c\ 11.3\text{ MPa}$, $t_c\ 132.4\text{ }^\circ\text{C}$) and pure CO_2 ($P_c\ 7.4\text{ MPa}$, $t_c\ 31.0\text{ }^\circ\text{C}$), the system is in supercritical state with two kinds of simple substances.

With the same temperature and pressure, and different NH_3/CO_2 ratios, the state point of the mixture presents different conditions:

Point C is in the liquid phase area in the phase diagram, so Point C has the properties of a pure liquid; Point D is in the gas phase area. so the mixture with composition D is a gas mixture; E is in the gas-liquid mixture area, E is a mixture consisting of gas V_1 and liquid L_1 .

5.3 Heating and cooling

The phase changing rule in the supercritical binary system $\text{NH}_3\text{-CO}_2$ is the same as that of a normal volatile system. With the fixed synthesis pressure, the phase state will change with heating or cooling. This can be explained in the partly magnified figure of Figure 9, see Figure 10.

(1) Heating solution (Point C in Figure 9, Figure 10)

When a mixture of composition C, which is in the liquid phase area is heated, the temperature of the system will rise. The boiling point is at t_1 , and the system point C_1 is on the boiling line of liquid phase. When one would add heat further, the state point will enter the gas - liquid mixture area. When the temperature reaches t_2 , the system point separates into gas phase V_2 and liquid phase L_2 .

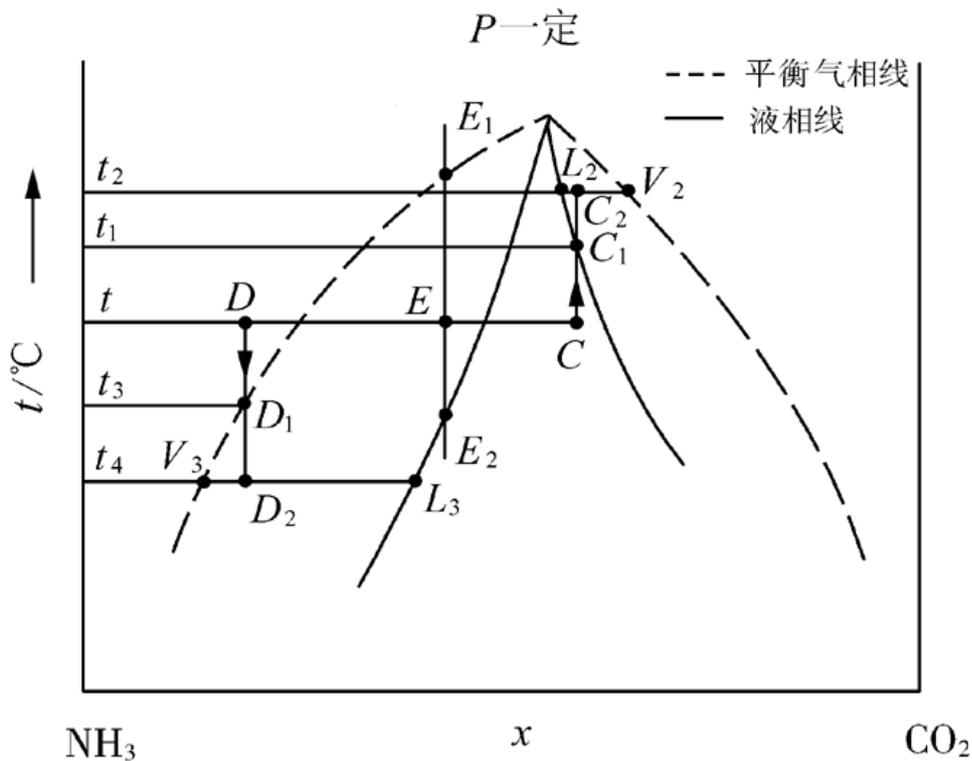


Figure 10: A magnified part of figure 9 of $\text{NH}_3\text{-CO}_2$ system (schematic).

(2) Cooling gas (Point D in Figure 9, Figure 10)

Likewise, when the system with composition D, which is in the gas phase, is cooled, at time t_3 , it reaches the condensation point, i.e. dew point. When one would cool further, the system point will enter the gas - liquid mixture area, and the gas - liquid two phase will appear. When the temperature reaches t_4 , D_2 becomes a mixture of liquid with composition L_3 and a gas with composition V_3 .

(3) As for the gas-liquid mixture (Point E in Figure 9, Figure 10)

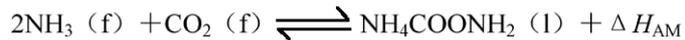
It can be known from the phase diagram that for the gas-liquid mixture, it will become a purely gaseous mixture E_1 when heated, and will be a liquid mixture E_2 when cooled.

6 Interaction of Phase Equilibrium and Heat Effects

6.1 Assumed Chemical Course Regardless of Phase Equilibrium

6.1.1 Thermodynamic Analysis for the Bottom of the Reactor

Reaction (1) of urea synthesis, i.e. carbamate formation reaction, is a rapid reaction; while Reaction (2) proceeds slower. So in the bottom of the urea reactors only carbamate formation reaction should be considered.



The reaction is a strongly exothermic reaction, for every 1 mol carbamate formed, 117.2 kJ of heat is generated.

If the urea reactor is in an adiabatic condition, then the generated heat will totally be used to heat the melts formed in the bottom. If the restriction of phase equilibrium is not considered, the temperature of the melts will rise indefinitely till the heat generated is used up.

6.1.2 Calculation of Enthalpy Equilibrium ^[6] (Figure 11)

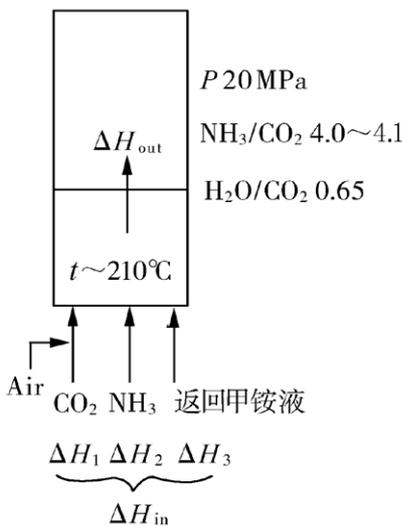


Figure 11: Calculating Chart of Enthalpy of Material Streams in the Bottom of the Urea Reactor

(返回的甲铵液 : recycle carbamate solution)

Pressure: that NH_3 and CO_2 entering the reactor is totally converted into carbamate.

Calculation benchmark: 1 ton urea formed in a medium sized urea reactor of conventional process is set as the benchmark.

Calculation conditions

pressure $P = 20$ MPa, $\text{NH}_3/\text{CO}_2 = 4.0\sim 4.1$ (molar ratio), $\text{H}_2\text{O}/\text{CO}_2 = 0.65$ (molar ratio).

Material stream 1 entering the reactor CO_2 , $t = 125$ °C, 743.27 kg

Material stream 2 entering the reactor NH_3 , $t = 50$ °C, 1333.75 kg

Material stream 3 entering the reactor recycle carbamate solution, $t = 100$ °C, 1275.5 kg

Calculation

The calculation is carried out with the above indicated enthalpy model, and the results are:

$$\Delta H_1 = - 2485 \text{ kcal}$$

$$\Delta H_2 = - 334180 \text{ kcal}$$

$$\Delta H_3 = - 343112 \text{ kcal}$$

$$\Delta H_{in} = \Delta H_1 + \Delta H_2 + \Delta H_3 = - 679777 \text{ kcal}$$

When self heated, $\Delta H_{out} = \Delta H_{in}$

The calculation result is that when $t = 210 \text{ }^\circ\text{C}$, $\Delta H_{out} = -697387 \text{ kcal}$.

$\Delta H_{in} - \Delta H_{out} = +17610 \text{ kcal}$, it is indicated that there is surplus in the heat quality. If it is calculated according to the assumed chemical course, the temperature of material in the bottom of the reactor could be $210 \text{ }^\circ\text{C}$ or even higher.

6.2 Chemical Course with interaction between Phase Equilibrium and Heat Effects

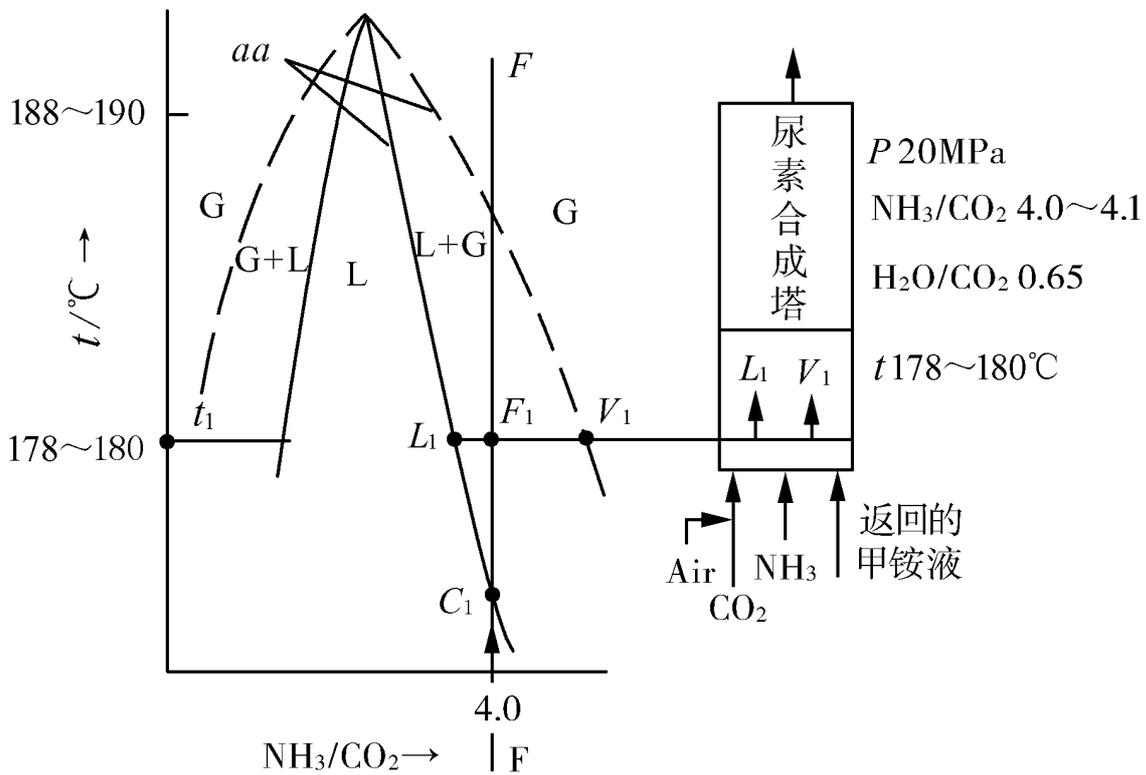
Because of the existence of phase equilibrium in urea synthesis, the described chemical course is only an assumption, and it does not occur in real production.

The chemical course with interaction between carbamate formation reaction, heat effects and phase equilibrium in bottom of the urea reactor under phase equilibrium will be discussed hereafter.

The conventional urea synthesis will be mainly discussed, and the process condition is the same as before: $P = 20 \text{ MPa}$, $\text{H}_3/\text{CO}_2 = 4.0\sim 4.1$ and $\text{H}_2\text{O}/\text{CO}_2 = 0.65$.

6.2.1 Phase Diagram

From the literature [14] it is indicated that a metastable supercritical azeotropic phase diagram of a conventional urea synthesis could be made. As *aa* in Figure 12, *aa* is a binary-like phase diagram in metastable state, with $P = 20 \text{ MPa}$, $\text{NH}_3/\text{CO}_2 = 4.0\sim 4.1$, $\text{H}_2\text{O}/\text{CO}_2 = 0.65$). This phase diagram is a basic one to analyze the chemical course for material streams in the bottom of the urea reactor.



(a) t - NH_3/CO_2 图

(b) 合成塔底工况图

Figure 12: Schematic Diagram for the Chemical Course in the Bottom of Urea Synthesis Reactor

(尿素合成塔 : the urea reactor

返回的甲铵液 : recycle carbamate solution

t - NH_3/CO_2 图 : t - NH_3/CO_2 Diagram

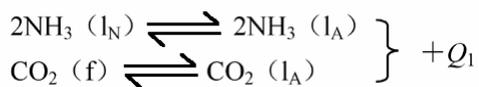
合成塔底工况图 the operation conditions of the bottom

6.2.2 Chemical Course in the Bottom of the Reactor

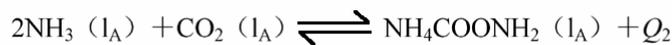
(1) State Points of the Material System

There are three material streams entering the reactor: CO_2 in supercritical state, liquid ammonia in subcritical state and recycle carbamate solution. The mixing courses for these streams in the bottom could be divided into:

- (1) the two streams, CO_2 in supercritical state (f) and liquid ammonia in subcritical state (l_N), pass through the gas film layer and liquid film layer between the main volumes of gas and liquid phases. The diffusion transfer to the main stream of liquid phase occurs by mass transfer (in the example the main volume of the liquid phase is the recycle carbamate solution l_A), and the two streams CO_2 and NH_3 dissolve in the main stream of liquid phase while heat Q_1 is released.



- (2) Liquid ammonia and CO₂ react in the main stream of the liquid phase to form carbamate and generate heat.



- (3) the three streams all dissolve in l_A, and become a material stream with NH₃/CO₂ = 4.0. The state point for the system is on line FF (See Figure 12).

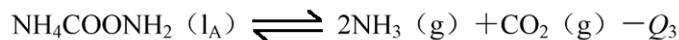
(2) *Reaction Heat Effect*

The reaction heat effect is the sum of dissolving heat Q₁ (the dissolving heat of NH₃ of subcritical state and CO₂ of supercritical state in carbamate solution) and chemical reaction heat Q₂ (the reaction heat of NH₃ and CO₂ in solution state forming carbamate).

(3) *Interaction of Heat Effect and Phase Equilibrium*

As the carbamate formation reaction is a rapid reaction with huge amount of heat released in the bottom instantly. In the adiabatic urea reactor, the newly formed ammonia – carbamate stream in liquid state is equivalent to a heat source. As described above, when the FF material stream is heated under a fixed pressure, the temperature of the solution will rise rapidly, as well as the equilibrium pressure P_e of the material system.

Below C₁, (Figure 12), P_e < P_{external pressure} (20 MPa); at C₁, the material system is in boiling point state, with P_e = P_{external pressure} = 20 MPa; if the heat is still excessive, i.e. Q > 0, overheating will occur, and the remaining heat can only be balanced by the self-decomposition of carbamate and vaporization of NH₃ in the solution, and the temperature of the system will keep on rising.



The self-decomposition is a chemical course caused by a combination of phase equilibrium, enthalpy equilibrium and material equilibrium. The material system originally in liquid state is converted into a mixed material system of gas-liquid phase. When the temperature rises, the materials decomposed are increasing, and the heat consumed is larger. Until the terminal state F₁, ΔQ = 0, re-decomposition ends.

The terminal state point of material in the bottom, F₁, is consisting of liquid phase L₁ and gas phase V₁. The final temperature t, could be calculated with material equilibrium, phase equilibrium and enthalpy equilibrium, which course will be introduced briefly hereafter.

(4) Calculation of the Process

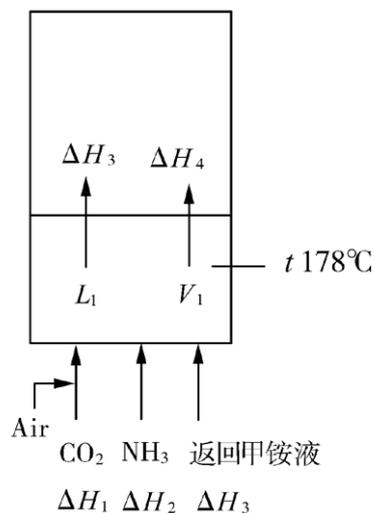


Fig. 13 Calculating Chart for Enthalpy of Carbamate Decomposition
(返回甲铵液 : recycle carbamate solution)

The calculation benchmark, calculation conditions and material streams entering the reactor are the same as before, the material streams in and out are shown in Figure 12.

$$\Delta H_{in} = -679777 \text{ kcal}$$

Pressure $t = 178 \text{ }^\circ\text{C}$, and the data for L_1 and V_1 are available in the phase diagram

Enthalpy for the liquid phase L_1 , $\Delta H_3 = -690660 \text{ kcal}$

Enthalpy for gas phase V_1 , $\Delta H_4 = 5595 \text{ kcal}$.

$$\Delta H_{out} = \Delta H_3 + \Delta H_4 = -685065 \text{ kcal}$$

$$\Delta H_{in} - \Delta H_{out} = +5288 \text{ kcal}$$

There is 0.8% excessive heat, which could be considered as heat waste.

The temperature at terminal state, t_1 is about $178 \text{ }^\circ\text{C}$ from calculation, which is quite consistent with the real conditions.

7 Model Structure of Urea Synthesis

From the above one can conclude that the interaction effect of heat effects and phase equilibrium cause a re-decomposition of the carbamate formed in liquid state and thus a larger gas-liquid two-phase flow is formed in the bottom of the urea reactor. In the gas material stream, apart from the earlier described small amount of inert gas that does not condense, there are CO_2 equivalent to about 20% material which didn't take part in the carbamate formation and enters into the gaseous stream in gas phase state. Of course, there is balancing NH_3 gas. Besides, according to observation, the formation of gas-liquid two-phase flow is all over the entire urea reactor length, and a key parameter of the main reaction for urea synthesis. This is different from the earlier conventional conceptual ideas.

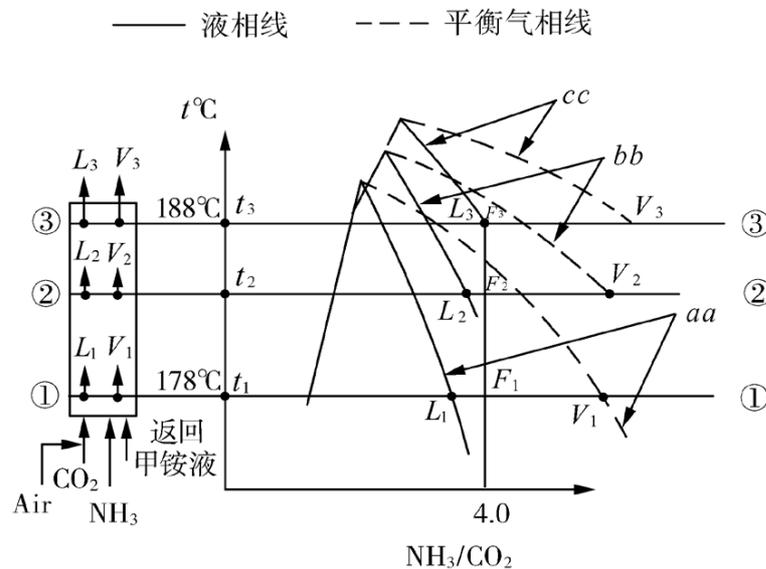
7.1 Thermodynamic Analysis

The main reaction in the urea reactor, i.e. Reaction (2), proceeds under the interaction of phase equilibrium and heat effects, just as in the bottom. During this, the phase equilibrium plays an important role, and the process totally depends on the changes of the phase diagram.

The difference is that, Reaction (2) acts a leading role instead of Reaction (1).

It is the urea and water formed in the Reaction (2) that changes the structure of the original phase diagram, causing the condensing temperature of solution for the newly formed phase diagram moving upwards. Thus the base for gas condensation is set, then gas condensation occurs under the new phase diagram condition, carbamate forms once again, heat releases, providing heat for Reaction (2), and the temperature of the solution rises as well. The above is the thermodynamic course of urea synthesis in a two-phase flow.

7.1.2 Chemical Course (Figure 14)



(b) 合成塔工况图

(a) t - NH_3/CO_2 图

Figure 14: Chemical Course Chart for Urea Synthesis

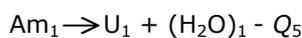
液相线 : liquid phase line
 平衡气相线 : gas line at equilibrium
 返回甲铵液 : recycle carbamate solution
 合成塔底工况图 : the operation conditions of the synthesis reactor
 t -NH₃/CO₂图 : t -NH₃/CO₂ Diagram)

It continues with the chemical course in the bottom of Figure 12.

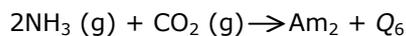
Line (1) - (1) is the mixed state of the three streams at the bottom of the urea reactor, F_1 is the state point of the system, L_1 is the state point of liquid stream; V_1 is the state point of gas stream. The temperature for terminal state, t_1 , is about 178 °C. The gas-liquid two-phase flow constituted of L_1 and V_1 , moves up as a plug flow.

The explanation for the course (1) -> (2)

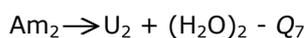
With the lapse of time, $\tau_1 \rightarrow \tau_2$, the carbamate₁ in the liquid phase L_1 , Am_1 , is converted gradually into urea, the reaction of which is:



With the formation of U_1 and $(H_2O)_1$ in the material stream L_1 , the concentration of components with high boiling point in the liquid phase rises, the phase diagram changes from aa to bb , the condensing temperature for the phase diagram rises. In order to establish a new gas-liquid equilibrium, CO₂ and NH₃ in the gas phase V_1 , dissolve in the L_1 liquid phase, which becomes L_2 , liquid carbamate₂ (Am_2 , in fact Am_2 is an integral value) is newly formed and heat is released. The reaction is:



The heat Q_6 is partly consumed by Q_5 in the Am_1 dehydration, meanwhile, the temperature of the material system rises from t_1 to t_2 ; the newly formed liquid carbamate₂ (Am_2) begins to carry out the dehydration and conversion reaction, with urea₂ (U_2) formed.



As the reaction time is less than that of Am_1 , the conversion rate is lower than that of Am_1 . The overall conversion rate x_{CO_2} of this process should be the sum of U_1 formed from Am_1 and U_2 formed from Am_2 .

When the system reached Line (2)-(2), a new gas-liquid equilibrium will be established, with the liquid phase constitution of L_2 and the gas phase constitution of V_2 ; the quantity of the liquid phase L_2 increases, while the quantity of the gas phase V_2 is less than that of V_1 . According phase rules the quantity of L_2 can be calculated by line F_2-V_2 / line L_2-V_2 , likewise the quantity of V_2 can be calculated by line F_2-L_2 / line L_2-V_2 .

The enlargement of the extent for liquid phase in bb phase diagram is the basis for the above changes. In other words, in the process the dissolution of material system in the liquid phase from the gas phase, leading to a series of physical and chemical changes, such as the increase of liquid phase quantity and the liquid/gas ratio, the conversion of carbamate to urea, the rising of temperature of the material system, is base on the new phase diagram bb .

The explanation for the course (2) -> (3)

With the lapse of time, $\tau_2 \rightarrow \tau_3$, in this process, the course of (1) -> (2) is repeated, and the following changes happen: (i) Reaction (2) proceeds; (ii) the new phase diagram cc is established; (iii) Reaction (1) proceeds, the CO_2 and NH_3 in the gas phase dissolves in the liquid phase; and (iv) the total x_{CO_2} of the system increases, and the quantity of the liquid phase increases. In the present process, the terminal state is when almost all of the CO_2 in the gaseous state dissolves in the liquid phase. Section (3)-(3) nearly reaches a chemical equilibrium.

7.2 Determination of the Flow Type of Two-Phase Flow

7.2.1 the Calculation of the Bottom

- (1) Volume of the Material Stream
 $V_l = 44.4 \text{ m}^3/\text{h}$ $V_g = 60.8 \text{ m}^3/\text{h}$
- (2) Holding Rate
 $\varepsilon_g = 0.58$ $\varepsilon_l = 0.42$
- (3) Apparent Velocity
 $W_{sg} = 0.0109 \text{ m/s}$ $W_{sl} = 0.008 \text{ m/s}$
- (4) Actual Velocity
 $W_g = W_l = 0.019 \text{ m/s}$

7.2.2 Calculation of the Top

- (1) Volume of the Material Stream
 $V_g = 14.86 \text{ m}^3/\text{h}$ $V_l = 51.94 \text{ m}^3/\text{h}$
- (2) Holding Rate
 $\varepsilon_g = 0.22$ $\varepsilon_l = 0.78$
- (3) Apparent Velocity
 $W_{sg} = 0.0027 \text{ m/s}$ $W_{sl} = 0.0094 \text{ m/s}$
- (4) Actual Velocity
 $W_g = W_l = 0.012 \text{ m/s}$

7.2.3 Determination of the Flow Type

From the data of apparent velocity for the bottom and the top, the averages are achieved: $W_{sg} = 0.0068 \text{ m/s}$; $W_{sl} = 0.0087 \text{ m/s}$

From Figure 7 (indicated in Part 1 of this Paper, UreaKnowHow.com Process paper August 2009 and repeated here below), the state point of the material system is at Z_1 .

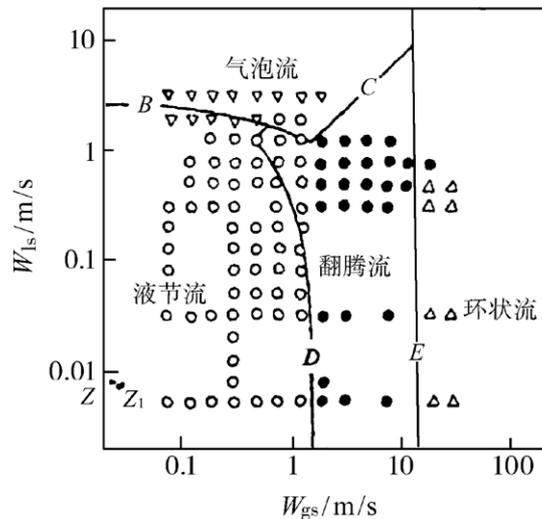


Figure 7 Determination of type of two-phase flow in a vertical pipe

It is known that, because of the coexistence of effective gas and inert gas, the material system is still in the throttling range of liquid, with tiny bubbles in the liquid stream and a few larger ones around the liquid film. And the gas and liquid together flows up in this way.

7.3 Dynamic Model for Industrial Applications

By the discussion of chemical course for industrial urea synthesis and the determination of gas-liquid two-phase flow in the urea reactor, the authenticity of gas-liquid two-phase flow synthesis under flow stage in the industrial urea reactor has been fully verified. Now main points of dynamic model structure is summarized as follow:

(1) Chemical Course of Urea Synthesis

The chemical course of urea synthesis is a complex chemical course proceeding in a two-phase flow. The urea synthesis is complex, both Reaction (1) – carbamate formation reaction and Reaction (2) - dehydration of carbamate converting to urea, are all in a complex chemical course in which chemical equilibrium, enthalpy equilibrium and phase equilibrium coexist. The restriction of phase equilibrium is the main reason to cause two-phase flow reaction process in the urea reactor.

In a conventional urea reactor, because of the interaction between heat effect from the carbamate formation reaction and phase equilibrium in metastable state, the heat is in excess, carbamate re-decomposition occurs in the three material streams from the bottom, which is the basis for the formation of gas-liquid mixing flow in the bottom. In the reactor, since the conversion of carbamate into urea plays the leading role, as shown in the phase diagram for transition state, the re-condensing of NH_3 and CO_2 at gaseous state occurs, which is the basis for the decrease of the gas material stream. And because of the existence of inert gas, there will be gaseous equilibrium state in the material system reaching chemical equilibrium, thus the streams off the reactor will be discharged out of the reactor as a mixture of gas and liquid. Therefore, from the bottom to top and from the lower part to the upper part, there is a two-phase flow material system in which the gas and liquid material streams coexist.

(2) Composition of Gas-Liquid Material Streams

The urea and carbamate melts system are in the liquid phase. The liquid mixture at the bottom is consisting of the following substances: NH_3 (free state), CO_2 (free state), H_2O , $\text{NH}_4\text{COONH}_2$, if urea is

neglected, there are still trace amount (dozens of ppm) of inert gases such as H_2 , N_2 , O_2 , CH_4 in solution state. The liquid mixture at the top is consisting of the following substances: NH_3 (free state), CO_2 (free state), H_2O , NH_4COONH_2 , NH_2CONH_2 , if biuret is neglected, there are still trace amount (dozens of ppm) of inert gases such as H_2 , N_2 , O_2 , CH_4 in solution state.

The gas mixture from the bottom to the top is consisting of a mixed gas of multiple components like NH_3 , CO_2 , H_2O , N_2 , H_2 , O_2 , CH_4 etc, in which NH_3 , CO_2 , H_2O are condensable gases, H_2 , N_2 , O_2 , CH_4 etc. are non-condensable gases at supercritical state.

(3) Volume Changes of the Liquid-Gas Streams (Fig. 15)

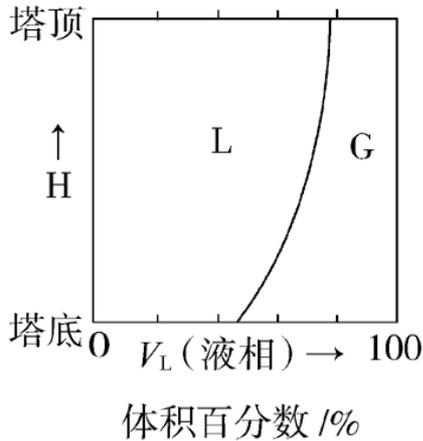


Figure 15: Volume-Change Chart of Gas-Liquid in the Urea Reactor

塔顶 : Top

塔底 : Bottom

液相 : Liquid Phase

体积百分数 : percentage by volume

The volume of gas-liquid streams in the urea reactor could be calculated. In the bottom the volume fraction of gas phase of about 58% is the highest, that of the liquid phase of about 42% is the smallest.

When material streams are moving up along the reactor, the effective components NH_3 and CO_2 in the mixed gas will condense to liquid carbamate and urea while phase equilibrium changes, and reaction heat will be released to provide the heat needed for the conversion of carbamate into urea in the solution and in the temperature increase of the solution. Therefore, in the process of material stream moving up, the NH_3 and CO_2 in the gas phase reduces gradually, and the volume fraction of the gas phase reduces as well. While the other part of insert gas like H_2 , N_2 , O_2 , CH_4 etc. in the mixed gas, the values remains basically the same.

In the top the volume fraction of gas phase of about 22% is the smallest; while that of the liquid phase of about 78% is the largest.

7.4 Retention Time and Conversion Rate

7.4.1 Retention Time

When the effective gas enters the gas phase, in the urea synthesis reactor, the two-phase flow of the material system becomes larger (gas phase is made up of inert gas and effective gas - NH₃ and CO₂).

The calculation equation for retention time:

$$\tau = \frac{V_R}{V_0} = \frac{V_R}{V_G + V_L}$$

In which,

V_G stands for the volume of gas phase, m³/h;

V_L stands for the volume of liquid phase, m³/h.

As the gas-liquid streams changes along the reactor, the calculation equation for the average retention time in the reactor is $\tau_s = (\tau_{\text{bottom}} + \tau_{\text{top}})/2$

When calculated with a conventional urea reactor and the volume fraction gas and liquid in the Figure 15, the results are:

$$\tau_{\text{bottom}} = 23 \text{ min}$$

$$\tau_{\text{top}} = 36.7 \text{ min}$$

$$\tau_s = 30 \text{ min}$$

From the previous calculation, it is known that, when there is only liquid phase the retention time is 48 min; when inert gas like anti-corrosion air enters in to the reactor, the retention time reduces to 45.8 min; in the present instance, the retention time further reduces to 30 min due to the existence of effective gas.

7.4.2 Conversion Rate of Urea

For a urea reactor with gas-liquid two-phase flow, the total conversion rate of carbamate to urea couldn't be calculated with conventional method in one step. Instead, it should be calculated with sectional calculation method. The total conversion rate of urea depends on the liquid carbamate amount formed in every time quantum, as well as the respective retention time in the reactor of the liquid carbamate formed in different time quantum.

The total conversion rate of the urea:

$$x_{\text{CO}_2} = \sum_{i=1}^n Z_i x_i$$

In which,

Z_i stands for liquid carbamate fraction formed in different time quantum,

Am_i/CO₂ integral molar quantity,

∑Z_i=1.0;

x_i stands for the fraction of carbamate converted to urea in different time quantum.

The conversion rate of the two-phase flow urea reactor could only be achieved when the liquid carbamate formed in the bottom takes the average conversion time all over the reactor, i.e. τ_s; after

that, the retention time of carbamate formed by condensation in the up moving stream descends as well.

Take the conventional process as an example, for the carbamate formed in the bottom (the sum of carbamate in the recycle carbamate solution and carbamate formed in the charged gas with CO₂ conversion rate of about 80% included), i.e. carbamate in liquid state of $Z_1=85\%$, the conversion rate of urea, x_1 , could be calculated with a retention time of 30 min; after that, the carbamate formed in sectional condensations, Z_2, Z_3, \dots , is converted in period less than 30 min.

Because of the restriction of retention time, it is obvious that only the equilibrium degree of carbamate formed in the lower and middle part of the reactor could reach 90%~98%; carbamate formed in the upper part would be discharged out of the reactor without being converted to urea due to insufficient retention time.

For the calculation method for the conversion rate of urea, the previous equation (2) or (5) could be referred (please refer to Part 1 of this Paper, UreaKnowHow.com Process paper August 2009).

8 Back Mixing and Channeling

8.1 Back Mixing

Just as its name implies, the back mixing in chemical course is axial mixing. For example, the upper material (mainly liquid material) flows to lower part naturally, and is mixed with the lower material mutually, inducing uniform mixing of the material all over the reactor, and this is called back mixing. Here "naturally" means that the flow moving up and down formed without artificial stirring. It is caused by the changes in parameters of the material system such as density and temperature during the chemical reaction process. For instance, when the density of the upper material is higher than that of the lower one, or the temperature of the upper stream is higher than that of the lower one, the back mixing from top to bottom would naturally and necessarily happen.

As described previously, in the chemical course of urea synthesis, the urea concentration of the material moving up in a plug flow increases gradually for the proceeding of Reaction (2). In the course of moving up, the temperature of the material increases due to the condensation of CO_2 and NH_3 in the gas phase, and this sets the stage for back mixing.

In summary, for urea synthesis, back mixing is caused when the density and temperature of upper urea material with a high concentration are higher than those of the lower material, as shown in Figure 16.

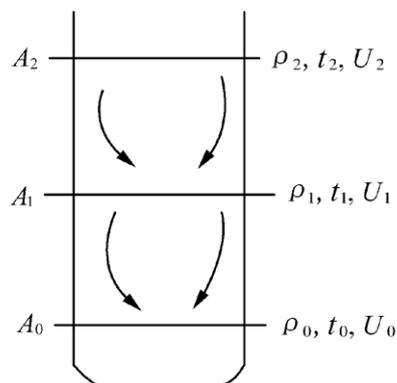


Figure 16: Schematic Diagram for the Back Mixing in the Urea Reactor

Imagine that the urea reactor is a hollow reactor, as $\rho_2 > \rho_1 > \rho_0$, $t_2 > t_1 > t_0$ and $u_2 > u_1 > u_0$, from Section A_2 to Section A_1 , to Section A_0 , a violent back mixing would happen. It could not be avoided even if there is an excellent mixer in the bottom.

The harmful back mixing would reduce the driving force for urea synthesis, thus decrease the conversion rate of CO_2 in the urea reactor.

For reactors in early stage of urea industrialization, usually empty reactor structures, there was serious back mixing, causing a significant lower conversion rate of urea.

8.2 Channeling

Channeling is a natural convection occurring in the gas-liquid two-phase flow. It is a natural convection with gas up and liquid down due to the density difference between gas and liquid. As described previously, gas-liquid two-phase flow in the urea reactor is a liquid throttling, in which tiny bubbles are mixed with the solution mutually in the forms of bubbling; and that's advantageous for the mass and heat transfer between gas and liquid and the carbamate formation reaction. Some of the large bubble in the liquid throttling will proceed through the liquid in the form of bullets; and if those large bubbles could not be broken up, the reactants, NH_3 and CO_2 in them would seldom take

part in any reaction, and be discharged out of the reactor directly. This would finally bring about the low conversion rate of urea.

8.3 Improvements

Technically, in order to alleviate the back mixing in the liquid phase, multiple simple baffles should be placed radial along the length of the reactor in order to guide the liquid phase so that it will move up like a snake thus reducing the back mixing in the liquid phase. As the horizontal baffle can prevent the liquid phase from flowing down and accelerate the rate of the liquid stream. In this way it strengthens the mixing degree and mass and heat transfer of the material system, therefore it is beneficial for the conversion of the urea synthesis.

As the flow mode of two-phase flow in the urea reactor is liquid throttling, effective measures should be taken to break the large bubbles into tiny bubbles, in order to avoid channeling that large bubbles carrying large amount of effective gas such as NH_3 and CO_2 take short cut. Then the above horizontal simple baffles would not be enough. The baffles should be replaced by porous sieve plate, or trays should be set on the baffles. Meanwhile, the rate of gas and liquid streams should be increased to promote the process of carbamate formation.

Based on the above analysis, from 80's and 90's of the past century, trays (column plates) have already been installed in the urea reactors outside the People's Republic of China, to alleviate back mixing and channeling and increase the conversion rate of urea. It has three functions: (1) to avoid the back mixing in the liquid phase; (2) to enhance the mixing and contact between gas and liquid and to strengthen the mass and heat transfer between the two reactions of urea synthesis; (3) to avoid the channeling of the gas.

9 Conclusions

9.1 General

Multi-disciplinary theory analysis with chemical engineering-related subjects: chemical engineering thermodynamics, chemical reaction kinetics, supercritical azeotropic phase equilibrium under high pressure, mass transfer engineering, hydrodynamics etc. is applied in this paper, to analyze the chemical course of urea synthesis in the complex industrial production, and the following conclusion is achieved: the urea synthesis is a complex chemical course consisting of chemical equilibrium, enthalpy equilibrium and supercritical azeotropic phase equilibrium. Based on this it has been concluded that the dynamic model of urea synthesis in the industry is a chemical reaction model of gas-liquid two-phase flow (liquid throttling type).

In the present paper, thermodynamic calculations are carried out for the gas and liquid streams on the important state points of bottom and top in the conventional reactor with calculation equations for gas-liquid equilibrium thermodynamics and enthalpy. The calculated values are quite consistent with the actual data from industry. This demonstrates the correctness of chemical course and rationality of dynamic model in the urea synthesis described herein.

The present research provides novel knowledge and new thoughts for the most complex process of the urea synthesis in Chinese urea technology; meanwhile, it would also provide beneficial assists and inspirations for the sustainable development and independent innovation in technology of the Chinese urea industry.

9.2 the Complexity of Reaction Process in Industrial Urea Synthesis

In industrial production, the main reaction [Reaction (2)] of urea synthesis would usually be interfered by three by-physicochemical-processes, and the reaction would deviate from the expected plug flow course, so that the reaction would be quite difficult and non-ideal. The three courses are: the mixing course, the reaction process of gas-liquid two-phase flow, and the back mixing and channeling.

(1) the Mixing Course

In this paper, double-film theory and chemical absorption mechanism of the mixing course for the material streams entering the reactor is reviewed. And the research points out that, the formation rate of carbamate is controlled by the rate of CO₂ in supercritical state dissolving in liquid. The unreasonable non-availability of a mixer in the conventional urea reactor is one of the main reasons for the incomplete carbamate formation reaction after mixing.

(2) Synthesis in the Gas-Liquid Two-Phase Flow

In the text, the process of urea synthesis reaction in series all over the length of the reactor is reviewed in combination of subjects such as chemical engineering thermodynamics, chemical reaction kinetics and supercritical azeotropic phase diagrams. And the conclusion is made that, the latter reaction [Reaction (2)] in the gas-liquid two-phase flow proceeds all the time due to the incomprehensive completion of carbamate formation as a gas-liquid reaction from the bottom to the top.

The anti-corrosion air and other inert gases entering the reactor is one of the factors that keep the urea synthesis in the gas-liquid two-phase flow state; while the complex interaction of the three: reaction complex, the heat effects complex and the complex supercritical azeotropic phase equilibrium of the urea synthesis, is the main reason for urea synthesis proceeding in the gas-liquid two-phase flow state. And the interaction of the three is another main reason for the incapability of converting

into liquid carbamate by carbamate formation at one time. It must be pointed out that, however, the incompleteness for the formation of liquid carbamate caused by this interaction is different from the incompleteness of liquid carbamate formation in the in point (1) described mixing course. It has been demonstrated by the practical data that, even in the existence of an excellent mixer in the bottom or the complete conversion into liquid carbamate after mixing, the formed liquid carbamate would once again decompose to CO_2 and NH_3 in gaseous state due to the restriction of phase equilibrium and cross linking of the material; the gas-liquid two-phase flow will be inevitable.

After that, the chemical course of the gas-liquid two-phase flow proceeding in the reactor could be described as follow: Reaction (2) takes the main role of urea synthesis. With the changes of the interaction and the variations of the supercritical azeotropic phase diagram, the course of the gas absorption and condensation is promoted and gas NH_3 and CO_2 formed by decomposition in the bottom turns into liquid carbamate again. The complex chemical course proceeds repeatedly until in the top.

(3) Back mixing and Channeling

Back mixing and channeling are physical phenomenon during the chemical course. In the paper, it is further discussed that with the proceeding of urea synthesis in the reactor and the increasing of urea concentration, the temperature of the material system rises. If the reactor is an empty reactor, violent back mixing and channeling would occur. An excellent mixer installed in the bottom could not stop back mixing and channeling from happening. As it is impossible to install multiple mixers, it is reasonable to install multiple layers of efficient trays (column plates) to alleviate back mixing and channeling. Therefore, it is natural that empty urea reactors in early stage of industrialization have been transformed into a design with multiple efficient trays (column plates) gradually.

9.3 Universality of Two-Phase Flow Urea Reactors

Although the urea synthesis with gas-liquid two-phase flow would reduce the retention time of the material system, and lower the conversion rate of urea, it still gains international universality due to the advantages like easy control of the heat equilibrium in the reactor.

From the comprehensive view of the international urea processes, for urea reactors charged in the bottom, such as Stamicarbon CO_2 stripping process, SNAM NH_3 stripping process and TEC/MTC ACES process, the chemical course of urea synthesis in the urea reactors are all mainly characterized by gas-liquid two-phase flow. The reaction processes in those urea reactors are similar with the above conventional urea reactors.

When the existence of inert gas is ignored, the only exception is the countercurrent isothermal reactor with top charging from UTI, USA (now MECS). The reactor with coil pipes for heat exchange enables the material streams inside it being in the totally liquid phase in its true sense, instead of two-phase flow state, and in this way, the reaction time of liquid carbamate converting to urea by dehydration is prolonged. Although in actual operation of UTI urea reactor, the totally liquid phase in its true sense could be weakened by the presence of inert air. While compared with the urea reactors of other type, the conversion time of liquid carbamate in the UTI urea reactor is indeed the longest. Consequently, it achieves the highest CO_2 conversion rate of 75% in the current industrial applications^[11,12,13]. And it can be concluded that the core technology of the UTI reactor is "the totally liquid phase" instead of "the isothermal conditions" it pronounced.

Symbol Descriptions

U - urea;
 P - pressure ;
 T - temperature;
 ρ - density ;
 W - flow rate, m/s;
 x - conversion rate for CO_2 ;
 x_e - conversion rate for CO_2 in equilibrium;
 b - $\text{H}_2\text{O}/\text{CO}_2$ (molar ratio);
 k_1 - constant for reaction rate;
 A - section area of reactor, or parameter for the expression of conversion rate in the reaction;
 B - parameter for the expression of conversion rate in the reaction;
 τ_i - retention time of material stream at levels of the urea reactor material;
 n - levels for urea reactors;
 f - supercritical state;
 L or l - liquid state;
 G or g - gaseous state;
 V - gas phase;
 W_l - actual velocity of the liquid phase, m/s;
 W_g - actual velocity of the gas phase, m/s;
 Q - heat;
 A_m - carbamate;
 N_A - the rate of absorption;
 k_G - absorption coefficient of the gas film;
 k_L - absorption coefficient of the liquid film;
 ΔP - driving force in gas phase denoted by pressure;
 ΔC - driving force in liquid phase denoted by concentration;
 ΔH - enthalpy value of material stream;
 ΔH_{in} - sum of enthalpy for the material stream entering the reactor;
 ΔH_{out} - sum of enthalpy for the material stream off the reactor;
 V_l - volume rate of liquid material, m^3/h ;
 V_g - volume rate of gas material, m^3/h ;
 Z_i - the ratio gross liquid carbamate (mole) and gross CO_2 (mole)

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Translator notes:

This is a Technical Paper originating from our Chinese partner: www.Ureanet.cn. The paper was original in Chinese language and it is translated and interpreted into English with care and as much as reasonable possible accuracy, all to the best of our abilities.