The Urea Synthesis Reactor,

its theoretical model and its industrial applications

Introduction Part

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Content

1. **Introduction**

The first generation of the conventional total recycle urea process, also called the conventional process, was created in the late 1950's and prevailing in the 1960's, and was the main urea production technology of earlier Chinese industrialization. In China, Sichuan Lutianhua Company Ltd. introduced the conventional process urea technology from Stamicarbon, the Netherlands in the 1960's.

In order to assure food security, in China the conventional urea plants of small and medium-scale size were twice constructed respectively during the 1960's ~ 1970's and 1980's ~ 1990's, both according foreign technologies. Due to the combined efforts of the technicians in China's urea industry over 20 to 30 years, the plants have been technically modified and further developed. With the increasing refined technology, these plants have become modern versions of the conventional process with Chinese characteristics, being nowadays an important group of urea plants in China.

2. Old reactor model

However, while the stripping urea process was introduced in China, the synthesis theory of early conventional urea processes was assumed to be also valid and this is still the case till now. It is thought that in the conventional reactor, which is fed at the bottom, the urea synthesis reaction takes place in a complete liquid phase. See Figure 1.
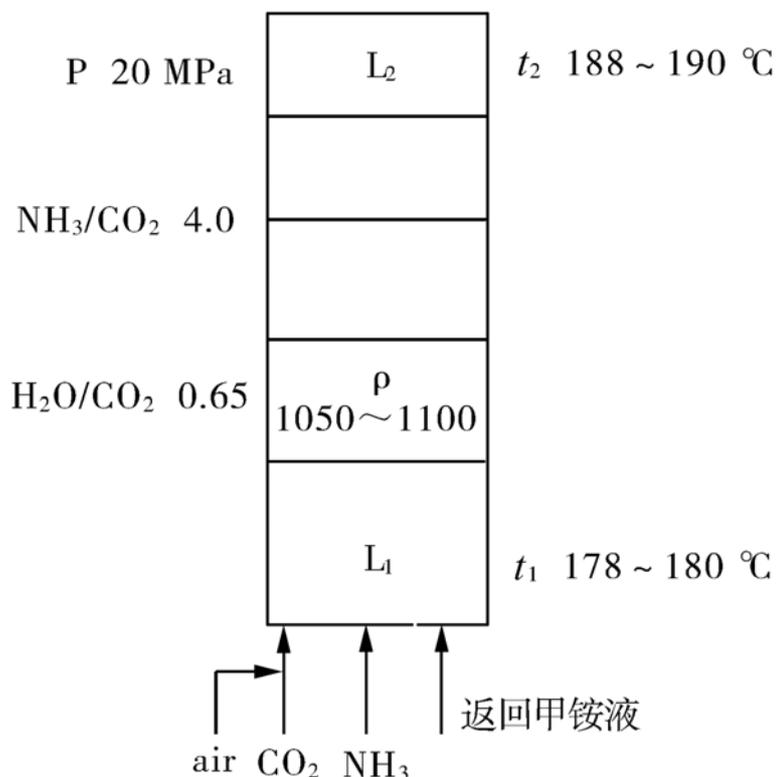

Figure 1: An ideal scheme of the conventional urea synthesis reactor

（返回甲铵液：recycle carbamate solution）

The theoretical basic assumption was that the reaction between ammonia and carbon dioxide generating carbamate is a chemical reaction with a very high reaction rate and with an equilibrium extending approximately to 100%. So the CO_2 and NH_3 feed to the reactor bottom react nearly 100%, generating a carbamate solution; then the carbamate in liquid state flows from bottom to top and slowly reacts to produce urea until it is discharged from the top of the reactor.

The viewpoint, which considers that in the conventional urea reactor the synthesis reaction takes place in a complete liquid phase, has always existed and even dominated in the Chinese urea industry. It was also common believe that the urea reactor is full of molten liquid, for example, the densities of liquid L_1, L_2 are between 1050 and 1100 kg/m^3. So, it was assumed that the retention time of the material in the reactor is 40 min ~ 1 h. These viewpoints have been prevailing in Chinese urea industry and can be easily found in urea monographs, with no exception to the "Chemistry Fertilizer industry series·urea（《化肥工学丛书·尿素》)":"which I have also edited partly[1].
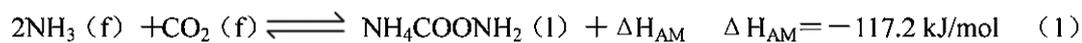
In the conventional views, it is thought that the discharge pipe must be inserted into the reactor by 500~600 mm, in order to allow a gas phase buffer space in the reactor top. This to avoid the risk of blowing out due to the overpressure of the material in complete liquid phase and to ensure safely operation of the reactor[2]. Even some urea technicians have a view that the CO_2, NH_3 feed and inert gas brought in by the anti-corrosion air are soluble in the urea solution and are largely dissolved in urea reactor.

In fact, this assumption of complete liquid phase synthesis reaction lacks any theoretical support. Besides, the speculated temperature profile in the reactor is not consistent with that of the actual condition (the temperature of lower part is low, and the temperature of upper part is high).

3. Thermodynamics

The thermodynamic situation in the urea reactor is as following:

The reaction between ammonia and carbon dioxide generating carbamate takes place in the reactor bottom:

$$2NH_3 \text{ (f) } + CO_2 \text{ (f) } \rightleftharpoons NH_4COONH_2 \text{ (l) } + \Delta H_{AM} \quad \Delta H_{AM} = -117.2 \text{ kJ/mol} \quad (1)$$

At a high temperature and high pressure, the reaction is intensely exothermic, almost instantly converting all the reactants into carbamate. If the heat released ΔH_{AM} is wholly absorbed by the material in liquid phase, the temperature of the process will quickly increase to 206 ~ 210 ^oC.
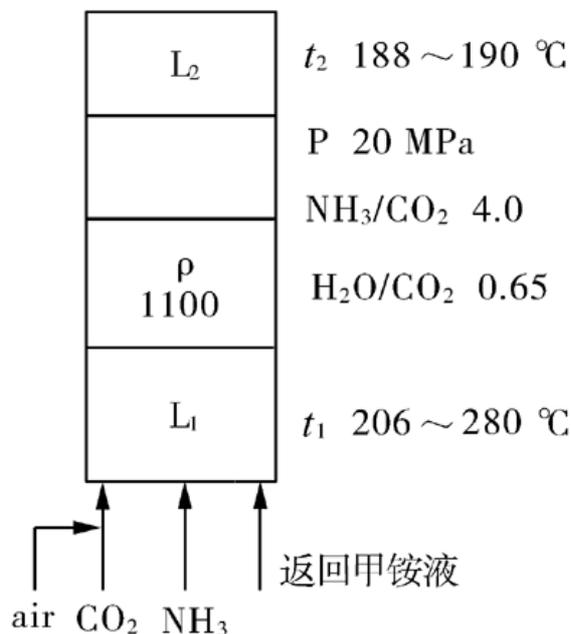
See Figure 2, L_1.

Figure 2: A scheme of the complete liquid phase model in theory

(返回甲铵液 : recycle carbamate solution)

Translator note:
There is a discrepancy between text and figure: text shows 206 -210 °C, figure shows 206-280 °C. The translator believes 210 °C is the right figure.

Then, the urea synthesis reaction takes place in the liquid material moving up.

$$NH_4COONH_2 \, (l) \rightleftharpoons NH_2CONH_2 \, (l) + H_2O \, (l) + \Delta H_U \qquad \Delta H_U = 21.77 \text{ kJ/mol} \qquad (2)$$
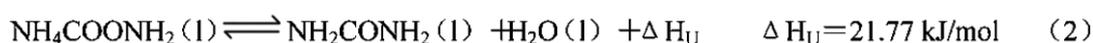
Reaction (2) is a reversible, slightly endothermic reaction in the liquid phase with a slow reaction rate.

According this theory while the synthesis solution is moving upward, the sensible heat of the solution is used as the heat needed for dehydrating carbamate into urea, thus the reactor temperature decreases. The process carries on all through up to the reactor top. When chemical equilibrium is reached, the temperature will drop to 188 ~190 °C. See Fig. 2, L_2.

The calculation example in Figure 2 here above has the purpose to illustrate that the consequence of forming a complete liquid urea synthesis phase is that the reactor temperature profile shows an inversion, i.e. the temperature of the lower part is high and that of the upper part is low. This condition is a prerequisite for having a complete liquid phase in the reactor.

The actual condition in the conventional reactor shown in Figure 1 is contrary to the above mentioned temperature inversion as the temperature of upper part is actually higher than that of the lower part.

Why doesn't the temperature of the reactor decrease but increase ?

According to the thermodynamic analysis, there must be some condensable gas in the reactor, and the condensation or reaction of the gas will be a source for providing heat. It is because of this fact that the material in the urea reactor is of both gaseous and liquid phase, but not a complete liquid phase. The condensable gases are CO_2 and NH_3.

Then, where do these gases come from ?

It is said that the reactants fully convert into carbamate ?

Why are there these un-reacted gases ?

4．**Phase Equilibria**

Because the urea synthesis reaction in the urea reactor is a complicated process conditioned by chemical equilibrium, enthalpy balance and phase equilibrium. It is not sufficient to simply consider the chemical equilibrium and enthalpy balance of reactions (1) and (2), because the phase equilibrium is the main cause preventing carbamate in the bottom from being in a complete liquid state.

The explanation is as follows (see Figure 3)
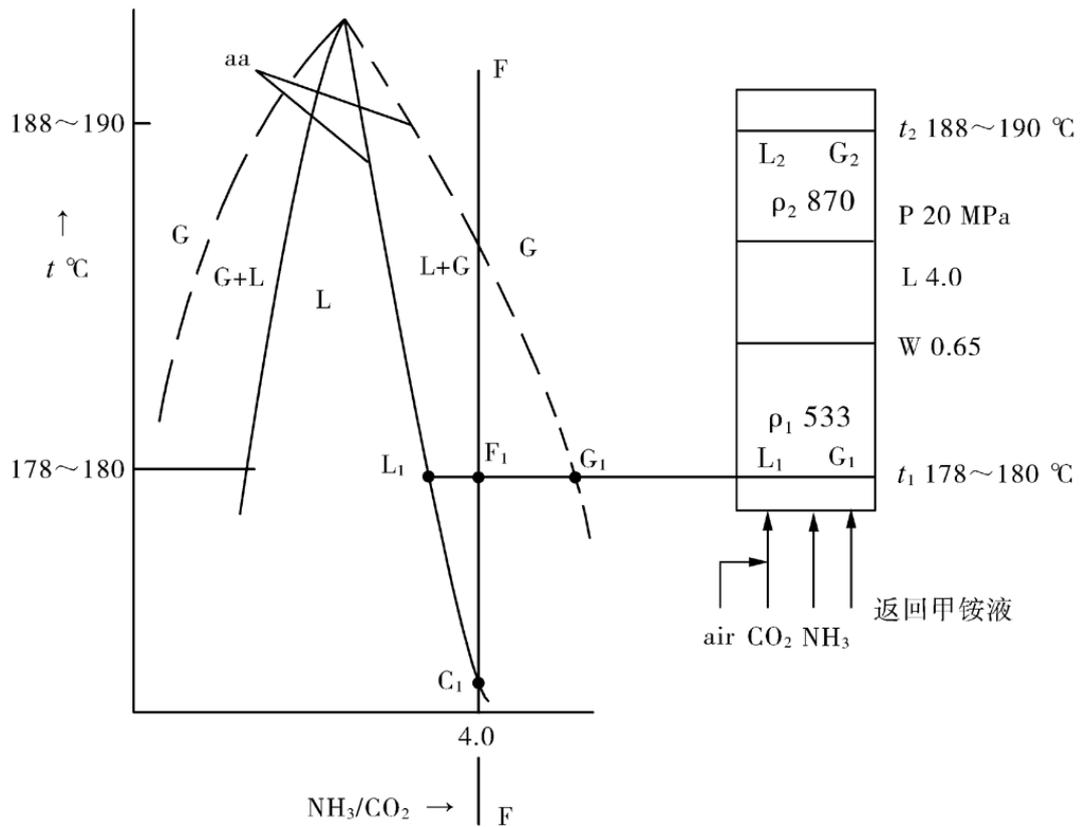
（a）$t - NH_3/CO_2$图　　　　　　　　（b）合成塔工况图

Figure 3: A chemical process scheme of the urea synthesis reactor

（甲铵液：recycle carbamate solution)
(a) Temperature-NH_3/CO_2 graph
(b) Condition scheme of the reactor

The process condition of the conventional reactor is:

NH_3/CO_2（I）=4.0 (mole ratio)
H_2O/CO_2＝0.65 (mole ratio)
Pressure P= 20 MPa
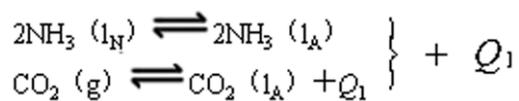
In meta stable supercritical azeotropic phase diagraphs[4], the lines aa are the basic diagram indicating the chemical process of the feed material, so here aa is the NH_3-CO_2 (at a H_2O/CO_2 = 0.65) binary phase diagram in meta stable state at a P=20 MPa.

When the material with NH_3/CO_2 ratio of 4.0 is put in the synthesis reactor, it can be shown by the FF line in Figure 3a.

The material coming into the synthesis reactor includes three streams: supercritical CO_2, subcritical liquid ammonia and the recycle carbamate solution. The mixing process taking place in the reactor bottom, consists of the following parts:

i. Part of supercritical $CO_2(g)$ and subcritical liquid ammonia (l_N) diffuse through the gas membrane layer and liquid membrane layer between the gas phase and liquid phase into the main liquid phase part (the main liquid phase part means the recycle carbamate solution l_A) by mass transfer and merge into the main stream, releasing Heat Q_1.

$$\left.\begin{array}{l} 2NH_3 \ (1_N) \rightleftharpoons 2NH_3 \ (1_A) \\ CO_2 \ (g) \rightleftharpoons CO_2 \ (1_A) +Q_1 \end{array}\right\} + Q_1$$

ii. Liquid ammonia and carbon dioxide of the main liquid phase react and produce carbamate, releasing Heat Q_2.

$$2NH_3 \ (1_A) +CO_2(1_A) \rightleftharpoons NH_4COONH_2 \ (1_A) +Q_2$$
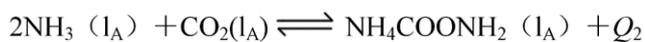
iii. The sum of both heats, Q_1+Q_2, leads to a rapid increase of the temperature of the mixture, thus also an increase of the system pressure Psystem.

In Figure 3, below point C_1, Psystem < Ptotal which is 20 MPa; at C_1, the mixture is at bubble point. If the heat giving off by the carbamate formation is in excess (plus assuming an adiabatic state with no heat removal to the outside), overheating will occur, and the excess heat has to be balanced by decomposition of liquid carbamate and further gasification of ammonia and carbon dioxide.

$$NH_4COONH_2 \ (1_A) \rightleftharpoons 2NH_3 \ (g) +CO_2 \ (g) -Q_3$$

At equilibrium, $\Delta Q=0$, Psystem = Ptotal =20 MPa, and the temperatures of liquid phase and gas phase are 178~180 °C. F_1 indicates the state of the material in the bottom part of the reactor. In the industry data reported by Mavrovic, CO_2 in G_1 accounts for 20%~25% of the gas material[5].

However, analyzing the enthalpy balance, it is necessary that overheating occurs, caused by the feeds from the urea reactor bottom, and taking into account the heat balance in the reactor. The heat discharged from gas condensation (reaction), is exactly what is needed for later dehydrating carbamate into urea and raising the temperature of the synthesis material solution from 178 ~ 180 °C to 188 ~ 190 °C.

It can be seen from the above thermodynamic analysis that overheating in the reactor bottom explains the reason for the temperature profile in the urea reactor under actual conditions. Therefore it is concluded that the chemical process in the conventional reactor is taking place with streams in gas and liquid phases, and the urea reactor model (as shown in Figure 1) of a complete liquid phase is wrong.

5. Flow pattern

In industrial production, there is 20%～25% CO_2 feed as gas in the above mentioned reactor bottom. With the phase equilibrium data of the phase diagraphs and the gas and liquid balance models of the NH_3-CO_2-H_2O-NH_2CONH_2 system under high temperature and high pressure conditions, the gas and liquid volume percentages in the whole reactor and their changes over the length of the reactor can be calculated.
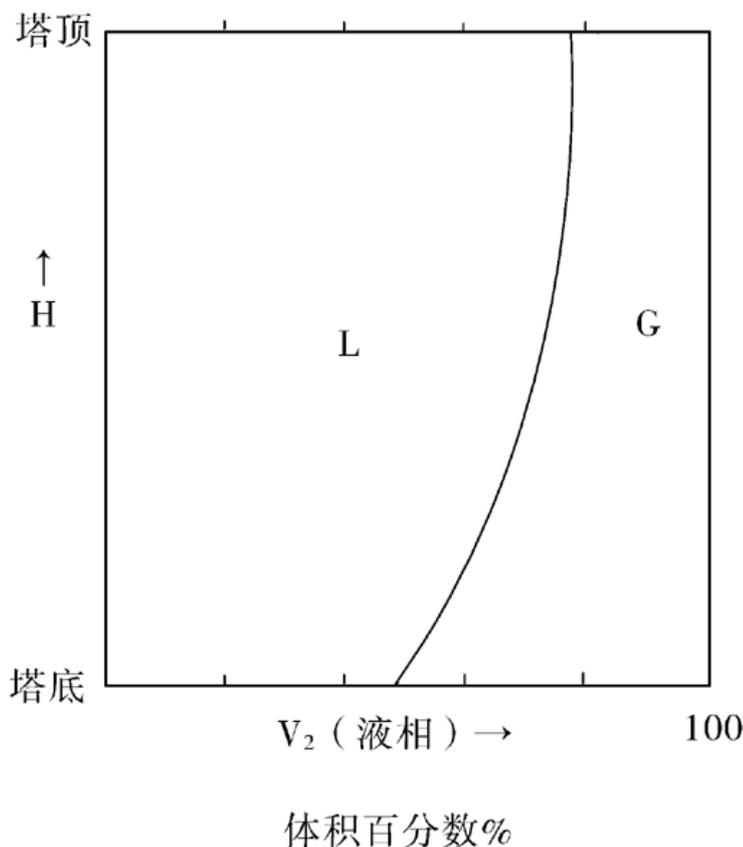

Figure 4: A graph of gas and liquid volumes changes in the urea reactor

(液相：liquid phase 塔顶：the reactor top 塔底：the reactor bottom

体积百分数：volume percentage）

It is obvious that the largest percentage of gas is in the reactor bottom, which is over 50%, then it is descending with the height. This is in accordance with the process requirements, because the gaseous reactants (CO_2 and NH_3) gradually dissolve in the liquid phase with increasing height, releasing the heat required for producing urea and increasing the material temperature. There is minimum gas in the reactor top with a percentage of about 23%. The average percentage of gas in the whole reactor is about 30%.

It is shown by calculations that the density of material in the bottom ρ_1 is 533 kg/m^3, and that in the top is 870 kg/m^3. Please refer to Figure 3.

The abovementioned gas phase is a mixture of two parts. One part is effective gas, including the condensable gases NH_3, CO_2 and H_2O; its volume is significant and changeable. The other part is inert gas, including feed CO_2, NH_3, as well as H_2, O_2, N_2, CH_4 and so on, brought in by anticorrosion air; these are in supercritical state and dissolve only slightly in the synthesis solution. With the calculation model of the NH_3-H_2O-CO_2-H_2-N_2-O_2-CH_4 system gas-liquid balance at high pressure, the solubility's of H_2, N_2, CH_4, and O_2 in the urea synthesis solution can be calculated. See Table 1.

Table 1: The solubility of inert gas in the urea synthesis solution

Inert gas	solubility /10^{-6}
H_2	98
N_2	79
CH_4	22
O_2	23

It is seen that the solubility of these inert gases is below 100×10^{-6}. So it can be considered that the inert gases entering the reactor are approximately all in the gas phase.

6. New reactor model

From the above discussion, the model of flow situation for a urea reactor in an industrial plant can be obtained with the following key points:

a. Gas-liquid two phase streams system

The urea synthesis reaction is a complicated chemical process in which chemical equilibrium balance, enthalpy balance and phase equilibria coexist. That is the main reason that material streams are in both gas and liquid phases.

In the conventional reactor, the three feed streams going to the reactor bottom are overheated due to the existing phase equilibria, which is the foundation of forming a gas-liquid mixture flow type reactor. The material stream leaving the reactor is also a gas-liquid mixture due to the existence of gas-liquid balance.

Therefore, the conventional theory of a complete liquid phase in the urea reactor is not correct.

b. *The composition of gas and liquid material streams*

The material in liquid phase is a urea-carbamate molten system. The liquid mixture in the bottom consists of NH_3 in free state, CO_2 in free state, H_2O, NH_4COONH_2, negligible biuret and minimum (< $100 \ 10^{-6}$) dissolved inerts such as H_2, N_2, O_2, CH_4. The liquid mixture in the top consists of NH_3 in free state, CO_2 in free state, H_2O, NH_4COONH_2, negligible biuret, and minimum (< $100 \ 10^{-6}$) dissolved inerts such as H_2, N_2, O_2, CH_4.

The gas phase is a mixture of seven components NH_3, CO_2, H_2O, N_2, H_2, O_2 and CH_4. Therein, NH_3, CO_2, H_2O are condensable and H_2, N_2, O_2, CH_4 are supercritical non-condensable gases.

c. *The volume changes of gas and liquid streams*

The gas and liquid composition and volume percentages can be calculated by applying the gas-liquid balance thermodynamic models of NH_3-CO_2-H_2O-NH_2CONH_2 and NH_3-H_2O-CO_2-H_2-N_2-O_2-CH_4 system at high pressure and high temperature. In the reactor bottom, the gas percentage of over 50% is the highest one, and the liquid percentage of less than 50% is the lowest one.

When the streams go up along the reactor, NH_3 and CO_2, the effective components in the gas mixture, condense and the carbamate produced goes into the liquid phase and delivers heat, which is required for converting carbamate in the solution into urea and increasing the solution temperature. So, the amounts of NH_3 and CO_2 in the gas phase decrease, and the amounts of other parts of the gas mixture, i.e. the inert gases H_2, N_2, O_2, CH_4, are basically constant. Of course, the volume percentage of the inert gases will increase slightly while the percentages of the effective components decrease. In Figure 5, it is shown how in the whole reactor the gas streams change with the height of the reactor. It can be known that the effective gas distribution profile is like a tower with the lower percentage in the upper and the higher percentage in the lower.
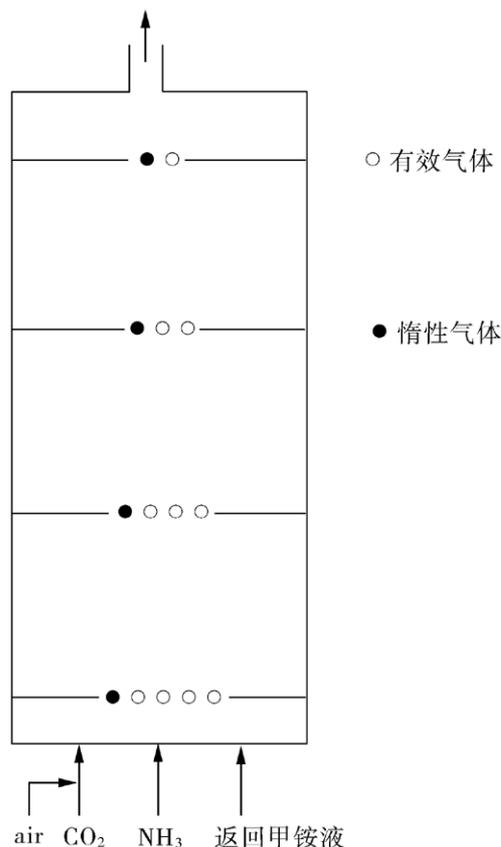
Figure 5: A scheme of the gas phase distribution in a urea reactor

(有效气体：effective gas 惰性气体：inert gas 返回甲铵液：recycle carbamate solution)

The discussion subject of the above mentioned model is based on the conventional urea synthesis process.

However, A comprehensive view of other urea synthesis processes in China is made, and the synthesis process of a gas-liquid phase in the reactor is proven to be universal. For the reactor fed at the bottom, such as the ones with Stamicarbon CO_2 stripping, SNAM NH_3 stripping and TEC/MTC ACES, the synthesis conditions are similar to the above urea synthesis model. This means that the chemical process of a urea synthesis reaction is mainly featured with a gas-liquid binary phase. Furthermore, the main cause for the formation of a gas-liquid binary phase is that the effective feed gases NH_3 and CO_2 are conditioned by the phase equilibrium with the supercritical azeotrope NH_3-CO_2; the inert gases in the system aggravate the phenomena of the two-phase material streams.

Without taking into account the existence of inert gas, only the counter flow isothermal synthesis reactor fed from the top of UTI Company in U.S. (now Monsanto Company) is an exception, which is equipped with a coiled pipe for heat exchange in the reactor. The heat exchange between the inside and outside of the coiled pipe makes that the streams in the reactor are not in two phases, but actually in a complete liquid phase, thus also increasing the reaction time for dehydrating liquid carbamate into urea. Although, in fact there is not truly a complete liquid phase in the UTI urea reactor due to the inerts inside. Compared with reactors of other type, the time for carbamate in liquid state converting into urea in the UTI urea reactor is indeed the longest one, so that the conversion rate is the highest one in industrial synthesis at present, reaching 75%[4]. Also it is known that the

core technology of the UTI urea reactor is not the "isothermal condition" alleged externally, but the "complete liquid phase".

7. Industrial applications

At present, China has entered a new stage when continuing development is only based on independent innovation. For urea industry, it's no doubt that the base point of independent innovation lies in how to use the advanced and applicable technology to modify and improve the state of the art of urea plants. But, the core of the foreign advanced technology can't be bought with money. The characteristic of a time of knowledge based economy is that the new knowledge and new technology fuse as a whole, becoming a component of a patented technology and belonging to an assembly of intellectual property.

The advance for technology with time is attained on the base of the advance for knowledge with time. In 1960s~1970s, after grasping that the urea synthesis is a complicated chemical process conditioned by chemical equilibrium, enthalpy balance and phase equilibria together, Mr. Mavrovic with UTI analyzed the disadvantage of overheating in the conventional reactor due to feeding from the bottom, and through over ten years' modifying with great concentration, finally succeeded in developing the existing UTI technology of feeding from the top, the new counter flow isothermal synthesis technology.

The above example has fully shown how important it is in leading the technology innovation to perfection and update urea synthesis knowledge, which is especially significant for Chinese urea industry which is tied by accustomed thoughts in long term. How the core technology of the counter flow isothermal synthesis reactor of UTI is understood? The answer is no other than collecting the information and data bit by bit depending on our own technology force, further analyze them in technology level and draw the advanced skills and theories to renovate knowledge independently and pave a path for the technology renovation. For the UTI urea reactor, if there is no substantially theoretic analysis of it or the update of the knowledge for the dynamic urea synthesis model in industry production, there will be no understanding of the true core technology through analysis but still a misunderstanding of "isothermal condition" for the core technology. Suppose that we stick to the wrong theory of last century that the conventional urea reactor is operated in a complete liquid phase, how could we realize the advantage of the UTI urea reactor operated in a complete liquid phase? Only when we discard the wrong theory and take the theory that the conventional urea reactor is operated in gas-liquid binary phases, than we can exactly understand the technology advantage of the UTI urea reactor and its essence.

In 1970s~80s, the stripping technology did replace the conventional total recycle process with its gradual perfection. At the same time, the urea synthesis theory and experiment is gradually improved and grown up in the international urea industry. The practice and data now also have approved the fact of a gas-liquid phase in the urea reactor.

After the stripping technology, with the complicated chemical process conditioned by chemical equilibrium, enthalpy balance and phase equilibria together in the urea reactor, how to improve the urea reactor efficiency and synthesis conversion further is certainly a project intensively researched by large urea companies worldwide.

Based on the fact of two-phase streams, there are two paths to improve urea synthesis conversion. The first one is concentrating on the research of lowering the gas percentage in the system. Because the existence of gas phase substantially shortens the retention time, finally causing a lower synthesis

conversion. Since 1980's, various new reactors, new processes and new procedures developed are mostly according to the above idea. The second one is intensifying the research on gas-liquid contact. Due to the necessity of inerts inside the reactor and the requirement for improving the conversion of the old plants, the research on high efficiency tray accordingly emerges.

The worldwide urea technology trend and new technology development after 1980's are both developed with centering the above technical paths.

There are two ways for lowering the gas percentage in the system:

1. *A single-phase stream method*

The effective gases of NH_3 and CO_2 in the system are completely converted into liquid carbamate. The most successful example is the counter flow isothermal synthesis reactor of UTI, and the other ones include the overlapped reactor of Montedison IDR, the two-reactor-combined reactor and the two-reactor-type reactor with stripping of Casale.

2. *Reducing the inerts into the system*

It is mainly to reduce the amount of oxygen-adding air. Adding anticorrosion air into liquid ammonia of UTI, applying the oxygen reducing methods such as anticorrosion with hydrogen peroxide plus oxygen of Casale company as well as developing anticorrosion material and reducing oxygen operation are becoming the direction of urea technology improvement and development. Comprehensively viewed the urea technology worldwide, in almost all the new urea technologies and the well known classic urea processes, such as ACES of TEC/MTC, IDR of Montedison, counter flow isothermal reactor of UTI, improved C method of Mitsui Toatsu Chemical Inc. etc., the amount of adding oxygen has been reduced to 0.2%~0.35%. Reducing the amount of added oxygen is becoming the new trend in urea technology which is copied by each other worldwide, for it has double functions of improving synthesis conversion and preventing explosion.

Now, China is in the new era of independent innovation in technology. For the conventional industries, it is necessary to draw the advanced theory from foreign countries as the nourishment for knowledge innovation and then service the technology innovation with the improved knowledge. In urea industry being a conventional one, it is particularly necessary to filling new concepts to provide a theoretical base for improving the industry.

The new synthesis model mentioned above is based on combining the three balances (chemical equilibrium, enthalpy balance and phase equilibria) being theoretical knowledge from other countries: For the urea industry in China, it is especially required to emphasize that the supercritical azeotropic phase balance is playing a unique and indispensable role in forming a gas-liquid phases in the system.

It is necessary and important to introduce the new synthesis model into the urea industry in China, first of all, making Chinese urea industry be in line with the international ones, even if it is several decades late.

Introducing the model, except that synthesis in a gas-liquid phase is newly correctly reorganized, but also the related parameters, such as synthesis reaction rate r, material retention time τ, the density of material, etc., are adjusted. Additionally, the new model can reasonably explain the phenomena occurred during short time shut down, which have been well known but bothering for long term. The causes mainly lie in that there is a slight drop in the synthesis system pressure during a short term

shut down, and with the continuous descending of level in the urea reactor, the increase gas phase space largely exceeds the volume of inert gas remaining in the system.

At the same time, the introduction also effects the following aspects and play a positive role thereof: the ideas of urea reactors, operating instructions, chemical process analysis, explosion prevention and safety, as well as how to improve urea conversion and technology modification and innovation.

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Translator notes:

This is the first 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.