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Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

OVERVIEW OF THE DEVELOPMENT OF CHINA'S NITROGENOUS FERTILIZER INDUSTRY. SOME BASIC EXPERIENCES

Wang Wenshan
China NNFF Association, China.

The build-up of China's nitrogenous fertilizer industry had started around 1920s to 1930s. On the eve of the founding of new China in 1949, only five nitrogenous fertilizer plants existed, including the nitrogenous fertilizer plants of Yongli Chemical Industry Corporation, Tianli Nitrogenous Products plants and so-called "Manchuria Chemical Industry Co., Ltd" set up by the Japanese invaders during its occupation of Northeast China, as well as, two cokeries with ammonium sulfate as by-product in Anshan and Fushun. Some could not put into operation due to the damage suffered, some were brought into complete standstill owing to insufficient feedstock supply. All these showed that the foundation for developing nitrogenous fertilizer industry in China was very poor before liberation in 1949. The actual output of nitrogenous fertilizer only amounted to only 6 000 tons N.

After the founding of new China, the Central government attached great importance to the development of nitrogenous fertilizer industry and rehabilitated and expanded the old plants, and also built new plants in large numbers. At present, an overall scheme combining large-sized, medium-sized and small-sized nitrogenous fertilizer industry spreading over China has been formed. By the year of 2002, the actual output of ammonia in our country has reached 36.75 million tons or 27.426 million tons N. Both the output of ammonia and nitrogenous fertilizer have occupied first place in the world.

I. DEVELOPMENT OF NITROGENOUS FERTILIZER INDUSTRY AFTER THE FOUNDING OF NEW CHINA

1.1 Rehabilitate old plants and build new ones

After liberation, the puppet "Manchuria Chemical Industry Co., Ltd" was reorganized and renamed Dalian Chemical Plant and was one of the major industrial enterprises to be rehabilitated at that time. Within a period of only one and half year, it had restored to full scale production of ammonia, sulfuric acid and ammonium sulfate, etc., by mobilizing a large number of technical personnel and overcoming various difficulties. The renovation and scale-up were closely followed, during which high pressure nitrogen compressor with 2400 horse power was designed and fabricated successfully, therefore

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E-mail: zgdfgyxh@263.net
Address: China Nitrogen Fertilizer Industry Association, N°1 Liupukang, Xichengqu, Beijing 100011, China

creating a precedent for the fabrication of high pressure chemical machinery by ourselves.

The nitrogenous fertilizer plant of Yongli Chemical Industry Corporation had also promptly restored its production and expanded into the nitrogenous fertilizer plant of the newly-built Nanjing Chemical Industry Corporation. In 1951, this plant succeeded in the trial manufacture of catalyst used in our ammonia plant. In 1954, both fixed bed gas generator and high pressure recycling compressor were trial-fabricated successfully. And in 1956, the 32Mpa ammonia synthesis tower with multi-layer wrapping was also manufactured by ourselves. During the same period, the experiment to substitute coke by lump anthracite for the preparation of ammonia feed gas achieved success. Therefore, it created conditions for the utilization of richer resources of anthracite coal in our country and expansion of the resources for the ammonia feedstock and, above all, the speedy development of China's nitrogenous fertilizer industry. The success of the R&D of the above mentioned technologies laid the technical foundation for the development of nitrogenous fertilizer industry by relying on our own efforts locally.

In 1956, in-depth research on the Nitrogenous Fertilizer Plant of Nanjing Chemical Industry Corporation by our designers was conducted. As the result, the Sichuan Chemical plant was completed with an annual capacity of 75 kt ammonia which was designed by ourselves, with improved process and shorter flow. Its establishment and putting into operation marked a new era of our nitrogenous fertilizer industry of self-design and self-construction. In 1958, in accordance with the experience on both the design and construction of Sichuan Chemical Plant, the typical design for the ammonia unit (50Kta) was tested out and based on it, a number of nitrogenous fertilizer plants were successively completed.

After that, the process of natural gas pressurized steam reforming to prepare ammonia feed gas was imported from U.K. and an ammonia unit (100Kta) was built in 1966 in Luzhou, Sichuan Province. At the same time a urea unit with total water circulation process imported from Holland was also completed in the same plant.

In 1970 another ammonia plant (50Kta) was completed, combining the heavy oil pressurized partial oxidation unit imported from Italy and associate domestic facilities. Currently, in China, nitrogenous fertilizer can be produced with natural gas, heavy oil and coal (coke), etc., as feedstocks. Naturally, in the course of the construction of fertilizer plants, large number of technical personnel were trained and developed.

1.2 Develop new process for ammonia production

By the end of 1964, some Chinese specialists put forward a scheme for the production of ammonia based on coal by adopting the process flow of medium temperature conversion, low temperature conversion, methanation (so-called three catalysts) and purification. In the spring of 1965, the technical breakthrough on the above topic was organized by relevant departments. Dalian Research Institute of Chemical Physics, Academy of Sinica, was assigned to be in charge of the experiment for low temperature conversion, recipes and preparation methods of methanation catalysts and desulfurizing agent; Shanghai Chemical Research Institute was responsible for the experiment on one cubic liter original granular size catalyst and desulfurizing agent; Beijing Chemical Experimental Plant was for the process experiment for 200 cubic liter catalyst; Nanjing

Catalyst Plant was for the trial manufacture and production of catalyst. The pilot test for the purification process flow to produce ammonia was taken by the First Design Institute of former Ministry of Chemical Industry (MCI) and Beijing Chemical Experimental Plant; the engineering design by adopting three catalyst purification process flow for the preparation of ammonia was made by the First Design Institute of MCI. By using this new process flow, the third phase of Shijiazhuang Chemical Fertilizer plant was completed and put into operation in October 1966. It took only over two years from one small sampling experiment of catalyst to the completion and operation of the plant. The success of the research on this new process greatly enhanced the confidence of broad masses of technical personnel for developing and building up the nitrogenous fertilizer industry of our country through self-reliance. After that, a number of scientific research achievements were obtained, such as, the following processes for the preparation of ammonia: process of coking dry gas (containing 10% olefin) steam reforming; coke oven gas steam reforming process and refinery gas catalytic partial oxidation process, etc. By the application of these scientific research achievements, a number of nitrogenous fertilizer plants based on oil, gas and coal as feedstocks were completed. Such type of nitrogenous fertilizer plants in China were considered as "medium-sized nitrogenous fertilizer plants". Since the initial construction of such plants in 1956 there are now a total of 55 put into operation.

Alongside with the development of agriculture, chemical fertilizers were in urgent demand. The government decided to speed up the development of chemical fertilizer industry. The then Ministry of Chemical Industry (MCI) raised the assumption of initialing small-sized nitrogenous fertilizer plant and called a technical symposium. The participants of the meeting held that in case of producing ammonium sulfate or ammonium nitrate, etc., corresponding units of sulfuric acid and nitric acid would have to be built. It not only involved more investment and longer construction cycle, but also required large amount of lead or stainless steel. It was absolutely impossible at that time.

According to the test result done by certain scientific research departments in agriculture, ammonium bicarbonate had good fertilizer effects. Therefore, they considered it practical and feasible to produce ammonia bicarbonate.

At that time, our engineers found from experiment that ammonia bicarbonate could be turned out by the direct reaction of ammonia and ammonia feed gas containing more CO_2. In so doing in the course of purifying ammonia feed gas, product of ammonia bicarbonate could also be obtained. After that, research and experiment were conducted by our engineers headed by the well-known chemist Hou Debang and a brand new process to produce ammonia through ammonium bicarbonate was completely advanced. The nitrogenous fertilizer plants built by adopting this process were called "small-sized nitrogenous fertilizer plants" with an annual capacity of 2 000 tons of ammonia and 8 000 tons of ammonia bicarbonate. Due to the speedy development of this type of plants, up to now, the total production capacity of small-sized nitrogenous fertilizer plants account for over half of the output of ammonia in our country.

At present, the so called "small-sized nitrogenous fertilizer plants" has become associated with history as many plants of such type have gone through renovation and expansion. Their production capacity has been gradually expanding. Some of them even

reached an annual capacity of 200,000 tons of ammonia and in addition their products were also not limited to ammonium bicarbonate. Some have already changed to produce urea.

Up to now, the nitrogenous fertilizer products of our country through ammonia processing are urea, ammonium bicarbonate, ammonium nitrate and ammonium chloride, and small quantities of ammonium sulfate.

1.3. Importation and development of large-sized nitrogenous fertilizer units

With increasing demand for chemical fertilizer for agricultural production and the development of petroleum and natural gas in our country, beginning from 1973, we imported successively many units of complete ammonia plants with daily capacity of 1000 tons and complete urea plants with daily capacity of 1740 tons. Up to the present, there are in total 32 units of complete ammonia plants in operation. In term of feedstock, 16 units are based on natural gas, 5 units on naphtha, 9 units on residue oil and 2 units on coal. In term of patent technologies, 10 units are by the traditional Kellogg-TEC process based on natural gas and naphtha; 2 units by Kellogg-TEC process; 3 units by Topsoe Process; 2 units by AMV process; 4 units by Brown process; 6 units by Texaco process based on residue oil; 3 units by Shell process; one unit by Lurgi powder coal pressurized gasification process, and one unit by Texaco coal slurry pressurized gasification process based on coal. We can say the large-sized ammonia units of our country have a collection of major ammonia process technologies in the contemporary world.

As for the urea process technologies, there are 16 units by Stamicarbon CO_2 stripping process; 2 units by the Modified C process of Mitsui Toatsu Chemical, Inc.-Toyo Engineering; 10 units by Stamicarbon stripping process and one unit by ACES process, etc. As for large–sized urea units we also have the availability of major urea process technologies from the world over. In addition, we also have a nitro-phosphate unit.

The total capacity of imported large-sized ammonia plants by our country is close to 10 million tons annually, accounting for approximately 1/4 of the total capacity of ammonia of the whole country. Therefore, we can say the nitrogenous fertilizer industry of China has grown mainly by self-reliance.

2. TECHNICAL DEVELOPMENT OF NITROGENOUS FERTILIZER INDUSTRY

In China, the market for nitrogenous fertilizer production technologies, apart from above-mentioned and imported technologies, has also stimulated the development of a series of technologies that promote the development of nitrogenous fertilizer production and upgrade the technical capability.

2.1 In the field of the preparation of ammonia feed gas

The following technologies were developed including coal (coke) fixed bed rich oxygen continuous gasification; powder coal gasification; natural gas or refinery gas catalytic partial oxidation; natural gas heat exchange type reforming, etc.

2.2 In the field of CO reforming

We developed total low temperature conversion process based on coal(coke) as feedstock; medium temperature-low temperature conversion process; medium temperature-low temperature-low temperature conversion process as well as corresponding catalysts with broad temperature range and sulfur resistance.

2.3. In the gas purification

a. Desulfurization technologies

- By wet process

Aqua ammonia desulfurization

Modified ADA and NHD

- By dry process:

Refined desulfurizing agent shall include refined desulfurizing agents of different models that are able to remove not only H_2S, but also organic sulfur at the same time. The precision can reach 0.1 ppm and below.

b. CO_2 removal technologies

Physical absorption process: PC process NHD process, low temperature methanol washing process and pressure swing absorption process, etc.

Chemical absorption process:

Hot potassium alkali with diethanolamine, hot potassium alkali with amino-acetic acid, hot potassium alkali with sterically hindered amine and compound catalytic hot potassium alkali process, etc. Their process flow shall consists of a two-stage absorption, two–stage regeneration, steam injection regeneration, etc., as well as low temperature heat source pressure swing regeneration process based on coal (coke) as feedstock.

c. Gas purification: i.e. the removal of traces of CO

Apart from the conventional method to remove trace of CO by cupric acetate-ammonia solution scrubbing, we also developed the dual process for the production of ammonia and by-product methanol; methanolizing-methanation process; methanolizing – alkylation process.

2.4. Ammonia Synthesis Technologies

There are varieties of the structures of the ammonia synthesis tower developed by ourselves, the typical one is the axial-radial intermediate heat exchange type of ammonia synthesis tower and axial-radial ammonia synthesis tower with automatic catalyst unloading, etc. As for the ammonia synthesis catalysts, we not only have traditional ammonia synthesis catalyst based on Fe_3O_4, but also developed by ourselves those ammonia synthesis catalysts based on FeO, or with cobalt content and in ball-shaped catalyst, etc.

In a nutshell, the relevant ammonia technologies developed by China are rich and varied.

3. OUR BASIC EXPERIENCE

Through the exploration and practice in the past several decades, we have come to the following conclusion that for the developing countries, like China, the R&D of nitrogenous fertilizer industry should be based on self-reliance through the technology development. The importation of technology shall have a role. It is imperative to develop the technology with full consideration of the actual national situation and characteristics. In such a way, better result can be achieved with less investment. That is our basic experience.

4. EXISTING PROBLEMS FOR THE NITROGENOUS FERTILIZER INDUSTRY OF CHINA AND OUR FUTURE ORIENTATION

The existing problems for the nitrogenous fertilizer industry of China are as follows:

1. Feedstock structure is not rational. The existing large-sized ammonia plants based on naphtha and residue oil make up 44% of the total. These units are now under pressure of losses owing to the high oil price.

2. For the plants with lump anthracite as feedstock, the economic benefit of the enterprises is seriously affected by the high cost of freight, especially if they are located far from the anthracite base.

3. The small-sized nitrogenous fertilizer plant is in large numbers and their capacity is even smaller, thus affecting their viability.

Our future orientation

1. For the large-sized ammonia plant based on oil, the feedstock shall have to be changed from oil to natural gas or powder coal.

2. The nitrogenous fertilizer enterprises far from anthracite base have to adopt relevant technologies, and change their feedstock from anthracite to powder coal or high sulfur coal found nearby.

3. The number of small-sized nitrogenous fertilizer plants has to be reduced, output has to be increased so as to form big capacity. Certain small plants can produce compound or mixed fertilizers and should serve as bases for agricultural and chemical service centres.