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RELIABILITY OF OPERATING AN ATMOSPHERIC AMMONIA PLANT AND ITS IMPROVEMENTS

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RESUME

En Chine, plus de 900 unités utilisant le procédé de gazéification atmosphérique du charbon (procédé ACG) produisent 67 % du total des engrais azotés chimiques en Chine actuellement. Ce procédé est une technologie ancienne qui date des années 1930. Dans ce procédé, l'anthracite dont la granulométrie varie de 25 à 75 mm sert de matière première. Les principaux stades du procédé sont : d'abord le charbon est gazéifié à la pression atmosphérique avec de l'air le débit se situant dans un intervalle déterminé, ensuite le gaz de synthèse produit est dépoussiéré, désulfuré et comprimé à 17-18 Mpa(g) ; le gaz du compresseur est introduit dans les stades de séparation de CO et CO_2 pour séparer les gaz acides ; après ce stade, les traces de CO et H_2S sont éliminées par lavage avec une solution cuprique ou méthanisation pour produire le gaz de synthèse qualifié contenant H_2 et N_2 qui est comprimé jusqu'à 15 Mpa ou 32 Mpa pour le stade de synthèse produisant l'ammoniac.

Mais une technologie ancienne ne veut pas dire une technologie rétrograde. Durant plusieurs décennies, ce procédé a été amélioré et modernisé en Chine, quelques technologies nouvelles ont été appliquées, comme un système automatique d'alimentation en charbon, un système automatique de réglage de la vapeur, un système automatique de contrôle, etc. Dans cette communication, certaines améliorations sont présentées et certains inconvénients du procédé comme une capacité de production relativement réduite et les effets sur l'environnement sont analysés. Un procédé plus fiable et économe en énergie basé sur ACG est proposé. Comparé à d'autres procédé de production d'ammoniac, il est concurrentiel, en particulier pour les pays en développement grâce aux faibles investissements et une assez grande fiabilité.

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1. INTRODUCTION

China has the largest population in the world. As an agricultural service sector, the fertilizer industry developed rapidly after the foundation of People's Republic of China. Presently, China is the largest ammonia producer country in the world. In 1995, there were more than 900 ammonia producers in China with an output of 18.60 million tons. Even so, China imported large amount of nitrogenous fertilizer each year, for example, 6.96 million tons of urea in 1995.

In 1950's, all ammonia plants used coal or coke as feedstock. With the exploitation of oil and gas resources, some plants using oil or gas as feedstock were built in China. However, the coal-based ammonia plants also take predominance. The structure of ammonia feedstock in 1995 is shown as follows:

coal or coke	natural gas or naphtha	heavy oil	others
63.97%	20.38%	15.31%	0.34%

With the industrialization of the Chinese economy, crop land is shrinking and population is growing. Fertilizer, as an important measure to increase grain output, will be continuously developed in the Ninth-Five-Year Plan period (1996~2000) and future. It is estimated that the ammonia production will reach about 31 million tons/year by the year 2000.

China is relatively deficient in oil and natural gas resources; the high price of oil also limits the development of oil-based ammonia plants. Except for the construction of a few gas-based ammonia plants in some gas rich regions, the increment of ammonia will be mostly from the coal-based ammonia plants.

The atmospheric coal gasification (ACG) ammonia process is an old technology which dates back to 1930's. It is widely adopted by numerous coal based ammonia plants in China, and will play an important role in the development of fertilizer industry. This paper presents the status of the ACG ammonia process and its improvements in China, analyses its advantages and drawbacks; and in addition, based on the improvements, proposes a energy saving and more reliable ACG ammonia process.

2. PROCESS DESCRIPTION

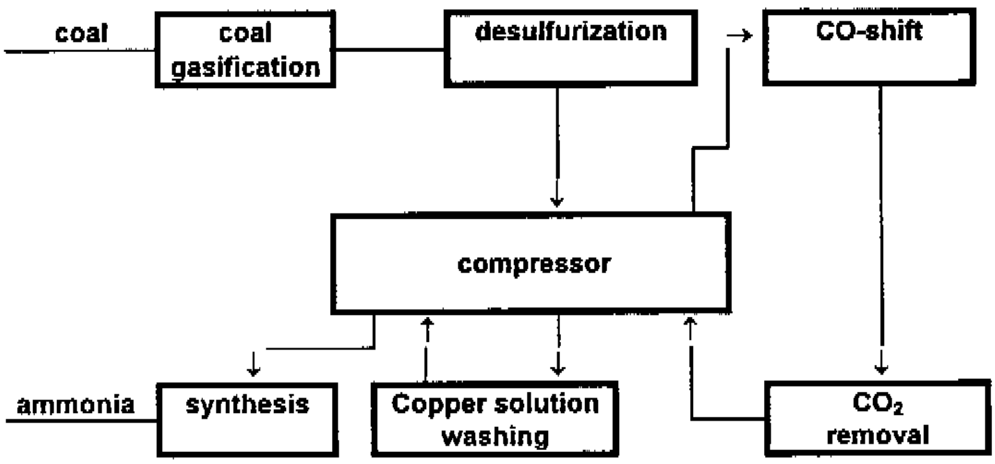
In China, the numerous ammonia plants are divided as three categories:

A. Large-sized ammonia plants, whose capacities are normally more than 300,000 tons per annum; most of these plants used natural gas and naphtha as feedstock. Now there are 30 large-sized ammonia plants including those under construction. Only a few of them use coal as feed-stock.

B. Medium-sized plants, whose capacity are normally between 80,000 to 150,000 tons per annum, most of these plants use coal as feedstock. There are more than 50 medium-sized plants in China.

C. Small-sized plants, whose capacities are between 30,000 to 80,000 tons per annum, most of them use coal as feedstock and produce ammonium bicarbonate as end-product. Because the ammonium bicarbonate is a low-efficient fertilizer, we are changing it to urea to make the product structure more rational. Presently, there about more than 800 small-sized ammonia plants; among them about 150 plants that produce urea.

There are three types of gasification process for coal-based ammonia production in China: the Texaco gasification, Lurgi gasification and the atmospheric coal gasification (ACG) ammonia process. The ACG process is widely adopted by the medium-sized and the small-sized ammonia plants which use anthracite or coke as feed-stock. The gasifier of the process is called UGI gasifier. The main steps of the process are as follows:



2.1 Gasification

Although the UGI gasifier is an old process; it plays an very important role in the Chinese fertilizer industry currently and is adopted by almost all coal-based ammonia plants. This gasifier requires lump coal of 25~75 mm with good thermal stability such as anthracite or coke to guarantee low hydrocarbon content in the coal gas. It is operated under atmospheric pressure and the material is gasified with air and steam. Because the slag of coal is discharged in solid state, it requires that the melting point of the feedstock must be over 1250°C. There are three types of gasifiers of different diameters:

Types (diameter)	Capacity NM^3/hr	Remarks
D-2400	4000	For small-sized plants
D-2740	5000	
D-3000	7500	For medium-sized plants
D-3300	9000	Revised from D-3000
D-3600	12000	For medium-sized plants

In the UGI gasification process, the coal reacts with air and steam intermittently in a fixed bed. Through the exothermic reaction of coal and air, the heat stored in the fixed bed provide the heat needed in the reaction of coal and steam, which is the key step in gasification. Therefore, the gasification process is divided as two parts: air blow and gas generation. Because the gasfication is a interval process, there are five steps in one gasifying circulation: air blow, upward blow, downward blow, second-upward blow and purge blow.

A. In the air blow step, air is introduced from the bottom of the gasifier, which reacts with coal rapidly, and gives out large amount of heat. The heat stored in the coal bed increases the temperature of the bed to a required level. The waste gas after the reaction, mainly contains CO_2, N_2, will be discharged into air through funnels.

B. In the upward blow step, steam is blown from the bottom and reacts with coal; the gas generated is sent to the gas-holder.

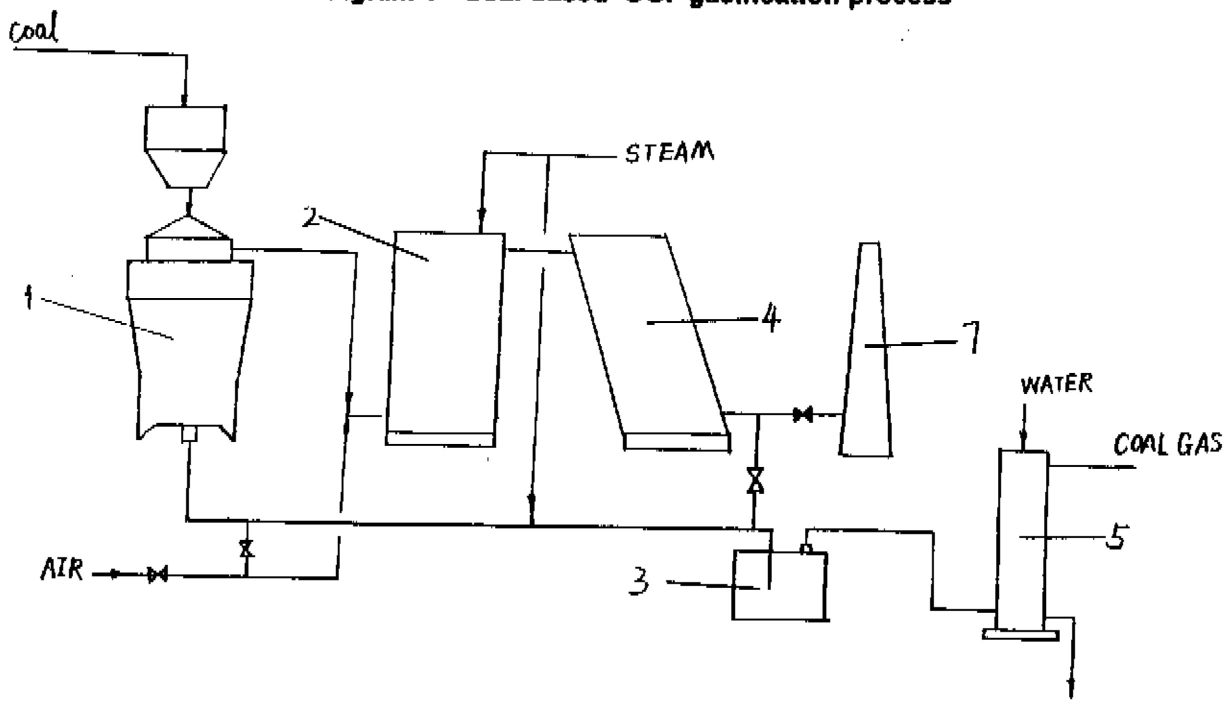
C. To maintain the good thermal state in the coal bed, the steam is then blown from the top, so it is called downward blow; the gas produced in this step is also sent to the gas-holder.

D. In the second-upward blow step, the purpose is to use steam to blow all the coal gas in the bottom chamber of the furnace to prevent explosion when blows air again.

E. In the purge blow step, the air is blown from the bottom again to recover the coal gas in the top chamber and pipe. It is also the forerunner of the air blow of the next circulation.

Based on the UGI gasifier, there are several types of gas producing processes, the following is a typical process diagram used in medium-sized plants.

Diagram 1 - Coal-based UGI gasification process



1 gasifier 2 combustion chamber 3 water seal tank 4 waste heat boiler
5 scrubber 6 coal storage chamber 7 funnel

The purpose of combustion chamber is to recover the heat in the gas after the air blow. When the air blow gas arrives here, some air is added into it to react with the CO in the gas, the heat produced will increase the temperature of the bricks in the chamber; the exhaust gas is discharged through funnel.

To produce stoichiometric $(CO+H_2)/N_2$ ratio for ammonia synthesis, sufficient nitrogen must be added in the gasifying process. This requirement is achieved through adding some air in the steam in the upward blow step; the air is called nitrogen-adding air. The air is also benefit to stabilize the temperature and increase the production of the gasifier.

The typical coal gas composition is shown as follows, when using anthracite as feed-stock.(%v)

H_2	CO	CO_2	N_2	CH_4	Ar	H_2S	O_2
38.55	30.33	7.03	22.93	0.54	0.27	2.0 g/Nm^3	0.35

2.2 De-sulfurization

The purpose of de-sulfurization is to remove the hydrogen sulfide and organic sulfide in the coal gas. The sulfide content must be removed because it is toxic to the catalysts and will cause corrosion to the pipes and equipment. It is also operated under atmospheric pressure. Several kinds of sulfide absorbing solvent have been used in China, such as catalytic ammonia solution, anthraquinone disuphonic acid (ADA), EDTA, tannic solution, etc. Now the tannic solution are replacing others gradually and takes most part in the de-sulphurization solutions. This solution is developed by a Chinese Institute in 1978. It has the following salient features compared with other solutions:

A. Higher efficiency in sulfide removal than other solutions;

B. It is much cheaper than others; the present price of tannic solution is about 1/5 of ADA;

C. No sulfur plug occurs in the column;

D. It is an non-toxic solution and does no harm to human beings;

E. It is more stable and easy to operate.

Normally, the hydrogen sulfide content in the coal gas can be reduced from 2.0 g/Nm^3 to 20 mg/Nm^3 through de-sulfurization.

The sulfur content will be recovered as element sulfur through oxidation, re-generation, and filtration.

2.3 Compression

The coal gas from de-sulfurization will be compressed by the I, II and III stages of the compressors normally to 17.0 barg in medium-sized plants or 7.0 barg in small-sized plants. Almost all coal-based ammonia plants use reciprocating compressors. These compressors are all driven by electric motors. Although their capacity are comparatively small and are more difficult to maintain, its low price attracts most plants to choose them. There are several types of reciprocating compressor in China, main capacities of them are 9900, 11000 and 14000 NM^3/hr respectively.

The gas from de-carbonization unit is called synthesis gas, which will be compressed in IV and V stage of the reciprocating compressors, to 15.0 barg.

The VI stage of the compressor is to pressurize the gas to the synthetic pressure–320 barg.

2.4 CO-shift

The purpose of CO-shift is to convert the CO to CO_2 and H_2; at the same time, to change trace organic sulfide contents to inorganic ones, which could be absorbed by solutions in following steps. Actually, there are two types of CO-shift ways in China: high temperature shift and high/low temperature shift. Most plants only have single high temperature shift, in which the residual CO after shift is about 3%. Some plants adopt high/low temperature shift i.e. the coal gas is first shifted under high temperature and then introduced to the low temperature column directly. Through these two steps, the residual CO will be about 0.1~0.3%.

2.5 De-carbonization

In this step, the acid gas, mainly containing CO_2, will be removed through solution absorption. There are many CO_2 removal technologies existing in China, for example, water absorption, hot carbonate, propenyl carbonate, etc. Generally speaking, most CO_2 removal technologies in existing plants in China are backward and high energy consuming, and has low capability in absorbing H_2S. Some technologies, like water absorption, have been abandoned in other countries. It is urgent to revamp these old technologies.

2.6 Refining

The minor quantities of CO, CO_2 and H_2S is toxic to the synthetic catalyst and have to be removed from the syn-gas. It is called refining step. Presently, there are two technologies for the removal of the trace impurities in China , i.e. methanation and copper solution scrub. In some existing plants, because the low efficiency of CO shift, the residual CO content is relatively high. So, it is compulsory to use copper solution to absorb the high CO in the syn-gas, due to the high absorbing capability of the solution. But the copper solution is toxic and cause pollution to the environment. With the reversion of single high temperature shift to high/low temperature, the CO content in syn-gas decreased substantially; so that the methanation process is replacing the copper solution process gradually.

2.7 Synthesis

After the refining step, the qualified syn-gas containing N2 and H2 will be compressed to 32.0 Mpa in the VI stage of the compressor. The synthesis loop and ammonia converter in most medium and small plants are designed by Chinese institutes. Most existing plants use the cool pipe type convectors; they have higher pressure drop and low synthesis efficiency compared with radial flow converters today. The ammonia difference between the inlet and outlet of the converter is about 8~10%. There are also several converters imported from designers abroad.

3. IMPROVEMENTS OF THE ACG AMMONIA PROCESS IN CHINA

Although the ACG ammonia is an old process, it has been successfully promoted in China and was considered a typical ammonia process fit for the national circumstances in China. Through many years operation, we have accumulated large amount of experience of the process and improved this process greatly. In a lot of aspects, new technologies have been applied to the process and had achieved good results. The main improvements of the process are described as follows:

3.1 Feed coal after sieving and washing

The powder in the material coal affects the gasifying efficiency and increase the dust content in the outlet gas; and uniform diameter of the coal will improve the gasification process. Therefore, some plants sieve the material coal to 3 specifications by the diameter and wash the coal to remove the powder in it.

Through this approach, the powder content in the coal is decreased from 4~5% to 0.8~1.5%, and quite amount of powder coal is recovered.

3.2 Adoption of new-type grate

Grate is the key component of the fixed-bed gasifier, which bears the well-distribution of the gas flow and stead removal of the slag, in order to guarantee the even reaction of the gas and coal. In addition, it must have strong capability in crushing slag. A new type of grate called well-distributing grate was developed by a Chinese institution combining with a medium-sized plant in recent years. It has been proved that adoption of the new grate increases the capacity of gasifier by more than 10%, saves 150 kg steam for per ton ammonia, decrease the residual carbon in slag by 6%, meanwhile, the capability of slag crushing and discharging is improved and the gas flow is better distributed.

3.3 Steam automatic adjustment system for the gasifier

With the proceeding of gasification, the temperature in the bed will decrease continuously (about 105°C difference between the beginning and end period), accordingly, the gasifying rate must decrease with it; that means, the quantity of steam added to the gasifier should decreasing with the temperature.

In some plants, the steam automatic adjustment system was adopted to control the steam flow in the gasifying step. The flow of steam is controlled through a computer which automatically adjust the flow according to the temperature in the bed. This improvement can increase the decomposition ratio of steam and save large quantities of steam.

3.4 Using super-heated steam in gasification

Previously, the steam for gasification is from the waste heat boiler of the gasification unit. Because the steam is saturated, condensation may occur in the gasifier and cause corrosion in the equipment. Now, most plant have used super-heated steam instead of saturated one. It proves that it can increase the decomposition ratio of steam and saves about 38 kg coal for per ton ammonia as well as prolonging the life span of the equipment.

3.5 Increasing the steam pressure of waste heat boilers

Due to the high dust content in the coal gas, the steam pressure of the gasifier is very low (13 barg or 7 barg), the steam can only be used in gasification. Now with the progress of de-dusting technique–the electric de-duster, and the improvement of boiler manufacturing technology, especially in the hot pipe boilers, the pressure of the steam can be increased to 25 barg or higher. The higher pressure steam can be used in CO-shift or other units. Therefore, large amount of steam is saved.

3.6 Adoption of automatic coal feeding system

Previously the coal was added manually to the gasifier, which is a labor intensive job. The poor working conditions discouraged workers from doing it in ammonia plants. Now, most plants have used the automatic coal feeding system which is controlled by the computer; it improved the working conditions greatly and stabilized the gasification process and prolong the effective gasifying period.

3.7 Using computer control to optimize the operation

In some plants, the computer control system has been applied to the gasification process to replace the outdated water control machines. While some plant have used PLC or DCS. Generally speaking, the automatic control system has been stabilized the gasification process, reduced energy consumption and improved working conditions.

3.8 Waste water circulation of the gasification unit

Previously, the waste water form the scrubber which contains large quantity of SSP, COD, BOD is discharged directly to the drainage system; and have very serious pollution to the environment. Now, this waste water was re-utilized through water circulation system. The drainage water form the circulation is treated through physical and biological means to obtain clean water, which will re-enter the circulation system. The discharge water from the gasification unit is nearly zero.

3.9 Heat recovery from the exhaust gas of air blow

Previously, in small-sized plants, the exhaust gas from the funnel, which contains about 5~8% CO_2+H_2, is discharged into atmosphere directly ; thus, polluting the air and wasting large amount of useful gas. Now, due to the environmental requirements, most plants have built the heat recovery system to recover the potential heat in the exhaust gas. In the system the gas is reacted with air to produce heat, with is used to generate low pressure steam in the waste heat boilers.

3.10 Utilization of low temperature CO-shift

The former CO-shift process used in medium and small sized plants is only high temperature shift, which has higher steam and energy consumption compared with the high/low temperature CO-shift. Now in some plants, the high/low temperature shift has implemented considerable energy-savings using domestic technology and catalysts. The catalysts used in CO-shift now are all supplied domestically and some some of their properties have exceeded that imported. Presently, a wide temperature CO-shift process using CO containing catalyst is being promoted in the small and medium sized plants, which need only 300~400 kg steam for per ton ammonia.

3.11 New technology in the CO_2 removal unit

For most small sized ammonia plants which produce ammonium bicarbonate (ABC) as end product, the CO_2 removal process is also the ABC producing process, i.e. the ammonia is carbonized by CO_2 in the syn-gas to generate ABC.

For the plants producing urea, there must be a independent CO_2 removal unit. Now most plants using hot alkali process. China has make a lot of progress for the process in many aspects, for example, adding complicated catalyst and amino promotion agent to promote the absorbing effect, using flash equipment to reduce steam consumption. These improvements have been successfully implemented in the existing plants with good effects.

3.12 Methanol Co-production

In China, the ammonia-methanol co-production has existed for more than 20 years. In this process, a methanol unit is connected between the CO_2 removal and methanation unit and is called methanol integration. The co-production has three benefits: first it the decreases the CO content in the syn-gas so as to reduce the duty of the methanation unit; second, the co-production widens the requirement of CO content after CO-shift; third, the methanol by-product increases the economical effect of the plant. Therefore, there are a lot of ammonia-methanol co-production units with methanol capacity of 5,000 to 50,000 tons/year and these plants take most part of the methanol production in China.

3.13 New type ammonia converters

Formerly, the converter in ammonia plants are all axial type with cooling tubes; this converters are all operated under high pressures, for instance 32Mpa. With the development of high-efficient catalyst, the radial type converters are replacing the axial type ones, and the synthetic pressure are decreasing. In China, several new types of ammonia converters have been developed in recent years; some of them proved very successful. For instance, in a medium size plant, after the internal part of an old axial converter was replaced by a new axial-radial one, the pressure drop of the converter decreased, the capacity increased by 30%, and ammonia synthetic efficiency also increased, and 50 kwh electricity was saved for each ton ammonia.

4. ADVANTAGES AND DISADVANTAGES OF THE ACG AMMONIA PROCESS

In the past several decades, the ACG ammonia process have been successfully operated in China and a lot of experience was accumulated. Generally the process has the following advantages:

- High reliability

The ACG ammonia process is very mature in China and has high reliability. Most plants have operated the process for more than 20 years. The equipment of process is nearly all fabricated in China and was easy to maintain. The following is the operating data of a medium size plant in recent years. The plant started up from 1970 and has operated for 25 years. (unit: metric tons)

Year	1990	1991	1992	1993	1994	1995
Capacity	78,000	78,000	78,000	78,000	78,000	150,000*
Production	75,791	82,615	85,551	81,176	102,906	125,888
Operating days	342	345	349	347	355	356
Planning shut down days (for maintenance)	18	14	15	16	7	8

**An expanding plant of capacity of 72,000 ton/year started from April 1995.*

The typical energy consumption for per ton ammonia is as follows:

Items	Consumption/unit energy(KJ)	Energy consumption / GJ
1. coal	1162 kg/30146	35.028
2. electricity	1212.3 kw/11840	14.303
3. fresh water	20.5 ton/7537	0.155
4. soft water	2.658 ton/14235	0.033
5. steam (25 bar)	1194 kg/2809	3.354
6. steam (5 bar)	1050 kg/2738	2.872
7. cooling water	260 ton/5443	1.415
Total		**57.16 GJ**

From the above table, we can see that the plant was operated at more than 106% above the design capacity in recent years. The plant has steadily and continuously operated except only several days out of planning shutdown.

The energy consumption of the plant is relatively high due to the low efficiency of the old equipment.

- Low investment

Compared with other coal-based ammonia processes, the investment of the ACG process is very low, due to its domestically produced equipment and without the need for a air separation unit. We compare the investment of a 600 tons per day ammonia plant using different technologies and find that the plant using ACG process can save more than 30% cost than that using Lurgi or Texaco process.

Besides the above advantages, the ACG process also has some aspects to be perfected. The main problems of the process are:

- Pollution of the exhaust air blow gas

The exhaust gas from the funnel contains about 1~2% CO and 1-2 g/Nm^3 H_2S is polluted to the atmosphere. With the stringency of environmental regulations, this exhaust gas must be treated before discharging. Now, some measures of recovering potential heat and sulfide in gas are under consideration in China.

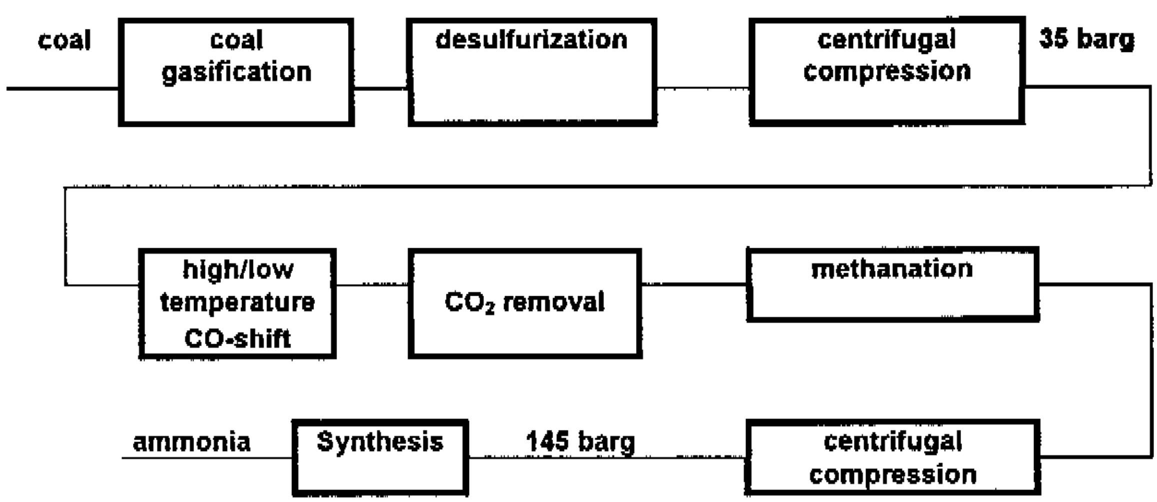
- Small capacity of the process

Because the capacities of the gasifers and reciprocating compressors are quite small compared with the natural gas based ammonia plants, the capacity of the ACG ammonia process is limited. Now the largest capacity of single train in China is only about 140,000 ton/year. In the preparation for new ACG plants, we are considering building large scale plants, for example 300,000 tons/year, using centrifugal compressors instead of reciprocating ones.

5. CONCLUSION

The ACG ammonia process is a typical Chinese ammonia process, which has been improved in many aspects and we cannot consider it as backward. Based on the improvements of the ACG ammonia process in past several decades, we propose a new ammonia process based on anthracite:

Block Diagram 2



The expected energy consumption of the process is:

Items	Consumption/unit energy(KJ)	Energy consumption / GJ
1. feedstock	1185 kg/29309	34.731
2. fuel coal	820 kg/26537	21.760
3. fresh water	18 ton/7537	0.136
4. electricity	448 kwh/11840	5.778
5. steam (25 bar)	- 1520 kg/2801	- 4.258
6. steam (13 bar)	- 2252 kg/2784	- 6.270
7. steam(5 bar)	- 720 kg/2747	- 1.978
Total		**49.899 GJ**

In this process, new energy saving technologies and some advanced equipment are adopted. Based on our study, if the proposed process was combined with the power generation unit and the utilization of steam of different pressure was rational, the energy consumption for per ton ammonia can reach 49~51 GJ, which is competitive to other coal-based ammonia technologies. In addition, the ACG ammonia process is also a low investment process. In general, the ACG ammonia is a technically and economically competitive process which is especially suitable for the developing countries.