

Study on the Synthetic Ammonia with Methanol Purge Gas of Huangling

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Abstract—Methanol purge gas produced in the side reaction in the methanol production were the inert gas including H_2 , CO , H_2O , CH_4 and others, which was used to produce synthetic ammonia as an important part in circular economy industrial chain of Huangling coal chemical industry. In this paper, the process and the optimal processing conditions to produce synthetic ammonia with N_2 in the air separation and H_2 in methanol purge gas as raw material were discussed. It was shown that the research results had a significant enhancing effect on the realization of energy conservation and emission reduction, environment protection, the green development patterns to change waste into valuable, and the sustainable development of coal chemical industry for Huangling Coal Chemical Industry Group.

Keywords—methanol purge gas; pressure-swing adsorption; synthetic ammonia; raw gas compression

I. SIGNIFICANCE OF PRODUCING SYNTHETIC AMMONIA WITH HUANGLING METHANOL PURGE GAS

The production equipment for annual output of 2 million tons of coke and 300,000 tons of coke gas methanol has been established by Huangling Coal Chemical Industry Group. Methanol production plant generated a large amount of methanol purge gas ($36412 \sim 40053 \text{ Nm}^3/\text{h}$, average $38232 \text{ Nm}^3/\text{h}$) which had a high concentration of hydrogen (77.05%). It would not only cause serious environmental pollution, but also bring a great waste of resources if methanol purge gas could not be used properly. Methanol purge gas which was generated by the equipment was sufficient to produce synthetic ammonia with an annual output of 100,000 tons. It was consistent with the China's industry policy and was the best way to maximize the benefits of that kind of resources that H_2 in methanol purge gas and N_2 in air separation plant were used to produce synthetic ammonia[1]. The way to use methanol purge gas had a low investment cost, low energy consumption, significant economic and social with great significance benefits to the sustainable development of enterprises.

II. SYNTHETIC AMMONIA PREPARATION TECHNOLOGIES WITH HUANGLING METHANOL PURGE GAS

A. Components Composition of Methanol Purge Gas

Huangling methanol purge gas contained kinds of gas components such as H_2 , N_2 , CH_4 , CO , CO_2 , H_2O , H_3OH , and others. The order of content of main gases in methanol purge gas from the larger one to the small one were H_2 , N_2 , CO , CO_2 , CH_4 , H_2O and CH_3OH , with 77.05%, 9.56%, 6.85%, 3.65%, 2.70%, 0.12% and 0.07% respectively, from which it was

shown that the content of CO_2 and CH_4 were similar, and that of H_2O and CH_3OH were little.

B. Synthetic Ammonia Process with Methanol Purge Gas

First, the methanol purge gas flowed through a pressure swing adsorption apparatus to obtain hydrogen with more than 99.9% purity. Then high purity hydrogen and nitrogen in air separation plants were compressed and introduced into the mixer to blend well. Secondly, the mixed gas after mixing get into the ammonia plant by being pressurized, and refrigeration cooling energy for the ammonia plant was provided by ammonia refrigeration system. Finally, the ammonia products were put into liquid ammonia storage tank. The purge gas in liquid ammonia tank was recycled to produce ammonia, which was sent to thermoelectric plant as raw materials to desulfurize and reduce nitrogen.

1) Feed gas compressor

Piston compressor was driven by steam turbine. The nitrogen, produced in ASU and then increased pressure by screw compressor, was impressed and introduced into methanation units, and mixed gas after methanation and then pressurized was feed into synthesis devices.

2) Ammonia synthesis unit

The mixed hydrogen and nitrogen through heat exchanger was introduced into the synthesis tower, and then was produced into synthesis ammonia with catalyst at a certain temperature and pressure conditions. After air cooling and ammonia cooling, ammonia in the mixed gas was condensed into liquid ammonia and separated, and sent to ammonia storage.

3) Recycle gas compressor

Hydrogen and nitrogen after ammonia separation in synthesis system returned to the system to continue react by the cycle gas centrifugal compressor, the task of which was to provide circulated process gas for the ammonia production systems, and to increase the rate of ammonia synthesis.

4) Ammonia compressor

The ammonia gas cooled by liquid ammonia flowed through synthesizer, and then was compressed by the screw compressors into cooling liquid ammonia, which was sent into synthesizer to cool gas circularly.

5) Storage and filling of liquid ammonia

Commodity liquid ammonia was stored by two 2000 cubic meters of liquid ammonia tanks and liquid ammonia was sold by two automated filling systems.

6) Membrane hydrogen extraction unit

Hydrogen gas from the discharge air was purified through the membrane hydrogen device, which was used as feed gas of synthesis ammonia by pressure swing adsorption, production and recovery of ammonia was sent to the thermoelectric plant as a raw material of desulfurization out of stock. Under the effect of certain pressure, when the synthesis discharge air flowed through the polymer membrane, H₂ could quickly penetrate through the membranes, and N₂, CH₄ and other gases would be much slower. In the low-pressure side of the membrane, H₂ concentration increased rapidly, and the majority of N₂, CH₄ were stagnant in the high-pressure side of the membrane, so as to achieve the purpose of separation of hydrogen mentioned.

III. MAIN TECHNOLOGY OF METHANOL PURGE GAS DEFLATION SYNTHETIC AMMONIA

A. Turbine Driven Reciprocating Compressors

1) The selection of compressor

The requirements on feed gas compressor during synthetic ammonia production were as follows: ①The change of gas volume and pressure should be regulatory. It was required to be convenient for compressor installation, inspection and maintenance in the production process to detect and operate easily. ②It was required the project should have low-investment and high-efficiency equipment, small construction coverings and workshop foundation, low-energy consumption and long-periodic operation, strong standardization and interoperability of easy-damaged parts. ③It was required to set security early warning and exceeded facilities to prevention of pressure, temperature to ensure tightness (static seals, dynamic seals) to prevent gas leakage avoiding the explosion during gas combustion. It was needed to set up automatic test and recording equipment for pressure, temperature, vibration, flowing, displacement of the movable member. ④Since the steam turbine driven generator would change heat into electricity, and electrical energy would be transferred into kinetic energy by motor driving compressor, causing losses and waste of energy, reciprocating compressors was driven by steam turbine to reduce energy losses and increase energy efficiency[3].

2) Key techniques

a) Vibration elimination

High-speed coupling, low coupling of coil spring type and flywheel were set up in the transmission chain consisting of a steam turbine, gear unit and the compressor. Load of reciprocating compressor was uneven, while the steam turbine required loads must be uniform. In order to meet the vibration requirements of turbine in the drive train consisting of steam turbine, high-speed coupling, the low coupling of coil spring type and flywheel were set up in gear unit and the compressor. First, the pulse load of the compressor was even eliminated by the flywheel, and then no-elimination impact load, axial movement were isolated out of reducer through special helical spring low speed coupling.

b) High-speed coupling and clutch operation

Setting high-speed gear sleeve with a clutch function coupling was set up between the turbine and gear. If there was an emergency stop, such as the compressor in a failed state, system could be equally stop as quickly as the motor drive, the clutch could disengage the reducer, compressor and turbine after the system would shut down quickly, which the turbine would return the back into the slow cranking state to ensure uniform cooling of its various parts. At the same time, high-speed gear sleeve couplings also had axial thermal displacement compensation function between turbine and decelerator.

c) Compressor features

(1)The energy consumption of steam turbine driven reciprocating compressor would be more 30% than the energy-efficient electrically driven reciprocating compressors, and the cost of ammonia per ton would be lower than the same scale synthetic ammonia manufacturers about \$300.

(2)High-speed coupling, the coil spring type low coupling and flywheel were set up in the transmission chain consisting of turbine, reducer and compressor.

(3)High-speed gear sleeve coupling was set up between the turbine and gear. When the reciprocating compressor open and park frequently, steam could enter into a slow cranking state.

B. Hydrogen Extraction by PSA Technology

1) Process selection of hydrogen extraction from methanol purge gas

There were two main technologies to extract hydrogen from methanol purge gas that PSA technology [4] and membrane separation technology[5]. Because the membrane separation technology were not suitable for this unit process conditions and had high investment costs, PSA technology was adopted to purify the methanol purge gas.

2) PSA technology characteristics

(1)PSA principle: H₂ is the main component of methanol purge gas, with the rest made up of CO, O₂, CO₂, CH₄, N₂ and hydrocarbons of C₂~C₄. The purpose to separate H₂ and other impurities was achieved with adsorbent selective absorption on the various components of the gas.

(2)Saving energy: During the production of hydrogen, the gas for regeneration could be utilized circularly, and analytical gas returned back to the gas system or may be used as methanol raw material gas without waste.

(3)The process high-purity hydrogen could be separated from methanol purge gas with this technology, which was simple, low-investment, and low-cost with high degree of automation.

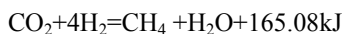
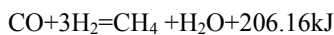
C. Methanation Technology

Selection of Methanation process was that a small amount of CO, CO₂ ($\leq 0.2\%$) in the H₂ after hydrogen extracting with PSA and O₂ ($\leq 0.1\%$) among N₂ in air separation plant, which was harmful to the ammonia synthesis catalyst, must be removed. There were many methods to deal with the difficulty,

such as copper acetate liquid ammonia cleaning method (chemical method), the depth of the low variant methanation (chemical method), low temperature liquid nitrogen washing method (physical method), double-A (methanol, methanation) methanation process (chemical method) and alcohol alkylation method.

The more advanced low pressure (3.1MPa) methanation process[6] was adopted to remove harmful ingredients in the feed gas, making it less than 10ppm, which had a wide range of applications in small domestic fertilizer plant in recent years.

The technology principle:



The methanation reaction was a strong oxidation reaction, and there was water produced by the reaction between H_2 and O_2 on the condition of the presence of O_2 .

The technology characteristics were that it had simple equipment, easy operation, low pressure, stable system, convenient start-up and shut-down, high-degree of automation, low investment and operating cost, and other advantages.

D. The Recovery and Utilization Technology of Synthetic Ammonia Purge Gas

There were two parts of purge gas in the production of synthetic ammonia that could be recycled. 1, there was purge gas in synthetic equipment about $1300 \text{ Nm}^3/\text{h}$, including 62.6% H_2 , 5.2% NH_3 which could be recycled. 2, there was purge gas about $1988 \text{ Nm}^3/\text{h}$ in two liquid ammonia tank of 2000 m^3 , including 48.4% NH_3 which was the effective components to be recycled. Combined with the company's actual conditions, there were two methods. The first was that H_2 was extracted from purge gas in synthetic tower by membrane separation technology. The NH_3 was washed by packed tower with the content of NH_3 , CO and CO_2 within 10ppm and the pressure controlled within 3.1MPa. The processed gas after PSA was used as the feed gas. The second was that NH_3 of purge gas in liquid ammonia tank was washed by double tower circulation method to produce 10% ammonium hydroxide which was used to desulfurize and remove nitrogen. And the residual gas was sent to analytical gas manifold after PSA.

There were two social and economic benefits. The first was that H_2 and NH_3 in purge gas could be recycled at the extreme, and the emission of purge gas was reduced to the environment to minimize the environment pollution. The second was that the quantity of 10% ammonium hydroxide recycled could be up to 17088t/a with increasing benefits 1.7 million RMB a year (10% ammonia hydroxide calculated at 100 RMB/t), amounting to 5.47 million RMB.

IV. MAIN TECHNICAL INNOVATIONS

A. Energy Conservation

- Reciprocating compressor driven by steam turbine could save energy more than 30% than that of driven by electricity. The cost of per ton of ammonia was less than

similar scale ammonia using electrically driven reciprocating machine manufacturers about 300 RMB.

- Feed gas was the 3.2MPa methanol purge gas, which was directly access to the PSA, without gas compression process saving energy.

- The pressure in the equipment was 16MPa to save a lot of energy.

- The system with methanol purge gas deflation to synthesize ammonia had low energy consumption. A series of innovative technologies and energy-saving measures were used in the project, and there was about 13.99Gt/t of comprehensive energy consumption lower than the existing ammonia synthesis equipment with coal and coke as the raw material. There was energy consumption about $13.99 \text{ GJ/t} \times 10^5 \text{ t/a}$, equivalent to standard coal of about 47,700 t/a.

B. Cyclic Utilization

- The hydrogen and nitrogen extraction equipment were used for ammonia synthesis purge gas and gas in storage tank to make H_2 return back to PSA for cyclic utilization, which could increase the production of ammonia synthesis, and the residual gas was used to produce methanol to realize the zero discharge of ammonia synthesis purge gas. NH_3 was recycled to produce ammonium hydroxide which was used as the raw material to desulfurize and remove nitrogen in thermal power plant. It was a new bright technology spot to the project of purge gas cyclic utilization.

- The cyclic utilization of pressure swing absorbed and desorbed gas. After the hydrogen extraction of methanol under PSA, it was needed to make the absorbent recycled. The amount of desorbed gas was $12275 \text{ Nm}^3/\text{h}$, whose calorific value was equivalent to that of methanol purge gas, which could be used as the raw material of coke oven gas or methanol. The raw material gas of methanol could be swapped out to use the desorbed gas circularly without any synthetic ammonia emission.

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