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ALCOHOL-ALKYLATION PROCESS - A PURIFICATION PROCESS FOR FEED GAS IN AMMONIA PRODUCTION

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1. INTRODUCTION

Nitrogen industry is a traditional industry that cannot be replaced by others. According to statistics, China's ammonia production accounts for 20 % of world's total, ranking first. Ammonia production is a complicated chemical processes, with three basic steps: feed gas preparation, feed gas purification and ammonia synthesis. China is rich in coal reserves. Therefore, its primary raw material for ammonia production is naturally coal. However, a coal-based ammonia production generally requires high energy consumption with, heavy pollution, etc. Such problem is more obvious specifically in the purification step. Therefore, China Hunan An Chun Hi-Tech Ltd. Co. was the first to put forward the "Double M Process" that uses methanol synthesis and methanation to purify the feed gases of ammonia production in 1990. It also applied for a national patent, relating to methanol synthesis as a purification step of ammonia production. This process made a successful debut in an industry application. when in January of 1994, the process successfully passed the expert appraisal sponsored by the former Ministry of Chemical Industry of China. The appraisal indicated that the process brought new ideas and stable operation for a breakthrough technology in ammonia production. In 1996, the process was extended to produce alcohol-ether compound as a by-product. This means that some 30% of alcohol-ether compound (dry basis) can be produced directly by using a new alcohol-ether catalyst during methanol synthesis. The process was put into operation, and its product can be used as domestic or automobile fuels.

In October 1999, the process passed the appraisal sponsored by the Hunan Provincial Bureau of Science and Technology. In 2000, the process was awarded the first class prize of Science and Technology Upgrade of Hunan Province. In 2000, the alkylation catalyst was successfully developed. The process uses alkylation catalyst to replace methanation, which upgrades double M process to alcohol – alkylation process, and solved the problems of heat imbalance of methanation, high amount of purge gas in sequent section, and high feed gas consumption. In 2002, the experts of China Nitrogen Industry Association appraised the process. It was listed as the one of ten technologies with good energy saving and economic benefits, which will be extended to the nitrogen industry. At present, about 20 nitrogen fertilizer producers with a total ammonia capacity of 3 million tons adopted this process, and gained good performance. In 2003, the process was awarded the second class prize for national science and technology progress.

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2. PROCESS DESCRIPTION

The principle of alcohol - methane-olefin process is to use alcohol-ether reaction and methane-olefin reaction to remove CO and CO_2 to below 10 ppm. The chemical reactions are as follows.

Alcohol-ether reaction :

$CO + 2H_2 = CH_3OH$

$CO_2 + 3H_2 = CH_3OH + H_2O$

$2CO + 4H_2 = (CH_3)_2O + H_2O$

$2CH_3OH = (CH_3)_2O + H_2O$

Alkylation Reaction :

$CO + 3H_2 = CH_4 + H_2O$

$CO_2 + 4H_2 = CH_4 + 2H_2O$

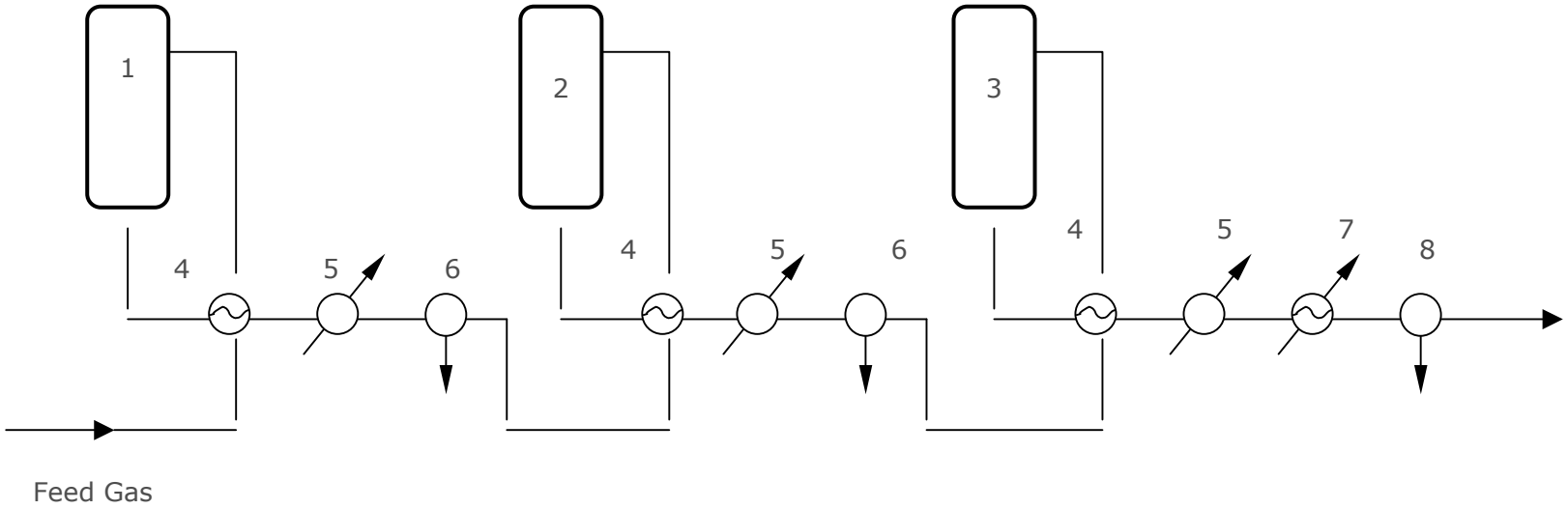
$(2n+1)H_2 + nCO = C_nH_{(2n+2)} + nH_2O$

$2nH_2 + nCO = C_nH_{2n} + nH_2O$

$2nH_2 + nCO = C_nH_{(2n+2)}O + (n-1)H_2O$

$(3n+1)H_2 + nCO_2 = C_nH_{(2n+2)} + 2nH_2O$

The flow sheet of Alcohol-Alkylation is as follows.



1、Alcohol tower 2、Alcohol tower 3、Alkylation tower 4、Gas-Gas heat exchanger 5、Water Cooler 6、Gas-Liquid Separator 7、Ammonia Chiller 8、Gas-Liquid Separator

Flow Sheet of Alcohol – Alkylation Process

Description of alcohol–alkylation process

The fine sulfur-removed feed gas contains 2～7% CO、0.2～0.5% CO_2， firstly passes the No.4 gas-gas heat exchanger. After being preheated, the gas enters No.1 alcohol-ether tower where alcohol-ether reaction takes place. The reacted hot gas then re-enters No.4 gas-gas heater exchanger and is cooled by the feed gas, and passes through No.6 separator and separates alcohol-ether compound.

The gas containing 1～2% CO and 0.1～0.2% CO_2 passes No.4 preheater of alcohol system, and enters No.2 alcohol-ether tower. The reacted gas containing CO+CO_2 0.2～0.3% passes No.4 gas-gas heat exchanger, No.5 water cooler, No.6 gas-gas separator, that separates alcohol-ether compounds. The gas enters alkylation system again, and passes No.4 gas-gas heat exchanger, and enters No.3 methane-olefin tower in which methane-olefin reaction takes place. The reacted gas containing less than 10 ppm CO+CO_2 passes No.4 gas-gas heat exchanger, No.5 water cooler and No.7 ammonia chiller to reach about 5℃. Alcohol, methane, hydrocarbon generated in the reaction are condensed. After separation at No.8 separator, the gas enters ammonia synthesis system. In the process, alcohol-ether system includes two reactors, No.1 reactor is mainly used to producing alcohol-ether compound; No.2 tower is mainly used for purification. No.1 and No.2 can be arranged in parallel or in series. No.2 can also be used to producing alcohol-ether when No.1 is aged, while No.1 can be used for purification. Alternatively, No.1 and No.2 can be arranged in parallel when the ration of alcohol and ammonia is high.

Alcohol–alkylation process can operate over wide pressures. The operation pressure could range from 5.0 MPa, 8.0 MPa, or 12.0 MPa based on the configuration of a feed gas compressor. If a retired pressure vessel is used, alcohol-ether reaction can select above pressure level, while the alkylation reaction can select a pressure that equal to the pressure of ammonia synthesis (30 MPa). If the pressure of ammonia synthesis is 10-15 MPa, alcohol –alkylation reaction can select same pressure as the ammonia synthesis.

Alcohol-alkylation reaction has double functions: producing alcohol-ether compounds and purifying feed gases. The production ratio of alcohol-ether and ammonia can be 1 to 20. If methanol is required to be a final product, then alcohol-ether catalyst can be switched into methanol catalyst, which can then produce 93% raw methanol.

3. MAIN FEATURES

3.1 The features of alcohol-methane olefin new process is to combine alcohol-ether reaction and alcohol-alkylation reaction, which can purify synthesis gas, reduce the consumption of effective hydrogen in the purification step, convert CO、CO_2 into useful methanol or alcohol-ether compound, converting the waste into valuable products, improve product structure and realize heat balance in alcohol-alkylation reaction without heat supply from outside.

3.2 Alcohol-ether system adopts a double system that can be arranged in parallel or series based on the change of alcohol-ammonia ratio and the application period of catalysts, to guarantee C0+$C0_2$ below 10ppm.

3.3 The reactors include alcohol-ether reactor and alcohol-alkylation reactor. The application for an invention patent was approved in 1993. Alcohol–ether reactor adopt a

unique structure, the gas flows in axial-diametral direction and the catalyst unloads automatically, which makes the reaction stable and temperature control convenient, and increases reaction efficiency while reduces reactor resistances, and provide convenience in installation and inspection.

3.4 Catalysts are the heart of reaction engineering. A good reaction system must have good catalysts. In this project, new developed alcohol-ether and alcohol-alkylation catalysts are a double-function catalysts that can promote methanol synthesis and hydrolysis. By adjusting the contents of catalysts, the products with different alcohol-ether contents can be obtained. The highest ether content can reach over 30% (dry basis). In alkylation reaction, $CO+CO_2$ reacts with H_2 : 80% forms olefin and 20% forms methane, which largely reduces the amount of methane, purge gases in sequent sections, and comprehensive energy consumption. Compare with the previous methane catalyst, alkylation catalyst has good heat resistance, and it is easy to obtain the raw material of such catalyst. Two alcohol-alkylation catalysts are Cu-Zn-Al rare earth and Fe-Cu rare earth series. The application temperature of former one is 220～270℃，and the latter one is 210～290℃.

4. CONCLUSIONS

Alcohol-alkylation purification process combining the production of alcohol-ether compound is a new technology in terms of process flow sheet, reactor structure, operation control and catalysts as well as ether content, which has a high purification efficiency ($CO+CO_2$<10ppm), stable operations, short flow steps, small capital cost, good economic benefits, and environment friendly. It is easy to adjust process ratio of alcohol-hydrocarbon, it can also co-produce methanol or alcohol-ether compound. The ration of ammonia and byproducts can be changed based on the market demands. The new catalysts, alcohol-ether and alcohol-alkylation catalysts, have high purification efficiency at low temperature and good heat resistance.

In low temperature shift and methanation process, CO needs to be reduced to below 0.3%, which consumes much steam. Then in methanation, all $CO+CO_2$ is converted into methane, which increases the amount of purge gases in ammonia synthesis and steam consumption. Alcohol-alkylation purification process can match with ambient carbon dioxide removal system, forming a complete purification process. Compare with Rectisol and liquid nitrogen washing, alcohol-methane-olefin process is simple and can save capital cost. Compare with copper washing process that is widely used in China, alcohol-alkylation process has obvious strengths. Alcohol-alkylation process can be used in ammonia plants based on coal, natural gas or oil and hydrogen plants with different capacities.

Counting from the application of double M (Methanol-Methane) process, alcohol-methane-olefin process is a mature process, having 11 years' experiences. In China's ammonia revamping cases, alcohol-alkylation process was selected and adopted as first choice without exception. Shanxi Tianji Jincheng Chemical Limited Company with a total ammonia capacity of 220,000 tons adopted alcohol-methane-olefin process with good performance. We hope to have closer communications with domestic and foreign experts attending the 2004 IFA Technical Conference and introduce this process to international markets.