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# *Comparison of Several Methods for Industrial Methanol Production*

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***Abstract:*** Methanol is a long-term chemical product. Methanol is used as raw material or solvent in the production of pesticide, medicine, dye, perfume, coating and three synthetic materials. In addition to synthetic ammonia, methanol is the only large-scale chemical synthesized by coal gasification and natural gas reforming. It is the basic product and organic chemical raw material of one carbon chemical industry. Methanol is also a liquid clean fuel converted from solid coal or natural gas, which is convenient for storage and transportation, and is an important energy carrier. This characteristic can be used not only to produce high value-added chemical products, but also to be used as alternative fuel for vehicles. Methanol has become an important product of the development of coal chemical industry and natural gas chemical industry in recent years. At the same time, the development of methanol chemistry and methanol chemical industry has become an important field of chemical industry and energy industry.

## 1. Introduction

With the continuous expansion of methanol application field and sharp increase of consumption, methanol synthesis industry has obtained unprecedented development. According to statistics, there are about 110 sets of methanol production units abroad, with an average annual production capacity of more than 500000 tons and a total annual production capacity of 64 million tons, including 32 units with a production capacity of more than 800000 tons. Methanol production units are developing to large scale, and more large-scale methanol plants will be put into operation in the next few years.

How to make methanol more reasonable? Let's analyze and compare several production methods of methanol.

## 2. Summary of Methanol

Methanol is a transparent, colorless, flammable and toxic liquid with a slight alcohol smell. The melting point is - 97.8 ℃, the boiling point is 64.8 ℃, the flash point is 12.22 ℃, the spontaneous combustion point is 47 ℃, the relative density is 0.7915 (20 ℃ / 4 ℃), the lower limit of explosion limit is 6%, the upper limit is 36.5%, and it is miscible with water, ethanol, ether, benzene,

acetone and most organic solvents.

It is an important organic chemical raw material and high quality fuel. It is mainly used in the manufacture of formaldehyde, acetic acid, methyl chloride, methylamine, dimethyl sulfate and other organic products. It is also one of the important raw materials of pesticide and medicine. Methanol can also be used as fuel instead of gasoline.

Methanol is the main component of fake wine, excessive consumption will lead to blindness, even death!

In recent years, methanol technology has developed rapidly, and the main trends are as follows:

The raw materials of production are turned to natural gas and hydrocarbon processing tail gas. According to the actual situation of methanol production, the investment of using natural gas as raw material can be reduced by 50% compared with using solid as raw material, and the economic effect of using acetylene tail gas is more significant. At present, natural gas is the main raw material for methanol production in the world, accounting for about 90%, while coal only accounts for 2%. In recent years, the proportion of methanol produced from coal is increasing gradually, which is related to China's energy structure[1].

The largest production scale of single series is 2.25 million tons per year, that is, the daily output of single series is 7500 tons. The investment and cost per unit product can be reduced after scale expansion.

## 3. Synthesis of Methanol

### 3.1 Reaction Principle of Methanol Synthesis

For methanol synthesis, the heterogeneous (heterogeneous) catalytic process of either zinc chromium catalyst or copper based catalyst follows the following process: a) diffusion gas diffusion from gas phase to catalyst interface; b) adsorption chemical adsorption of various gases on the active surface of the catalyst, in which CO is adsorbed on Cu2 +, H2 is adsorbed on Zn2 + and heterocracking occurs; c) Surface reaction the reaction of chemically adsorbed reactants on the active surface to produce products; d) desorption of reaction products; E) diffusion diffusion of reaction product gas from the catalyst interface into the gas phase; and the rate of methanol synthesis reaction. It is the sum of the speed of each of the five processes mentioned above, but the speed of the whole process depends on the completion rate of the slowest step. The results show that a, e (diffusion) is the fastest, B (adsorption) and D (analysis) are carried out faster, while the reaction rate of process C (surface reaction) at the active interface of catalyst is the slowest. Therefore, the whole reaction process depends on the rate of surface reaction. The reaction rate of methanol synthesis can be accelerated by increasing the pressure and temperature. However, from the thermodynamic point of view, since the reaction of methanol synthesis by CO, CO2 and H2 is a strong exothermic volume reduction reaction, increasing the pressure and lowering the temperature is conducive to the chemical equilibrium moving towards the direction of methanol formation, and also conducive to inhibiting the side reaction.

Methanol synthesis is a complex and reversible chemical reaction on many copper based catalysts.

Main chemical reactions:

$CO+2H_2 \rightarrow CH_3OH+102.5kJ/mol$

$CO_2+3H_2 \rightarrow CH_3OH+H_2O+59.6kJ/mol$

$CO+H_2O \rightarrow CO_2+H_2+41.19\ kJ/mol$

Side reaction of methanol synthesis:

The side reactions of methanol synthesis may produce alcohols, hydrocarbons, aldehydes, ethers,

esters and elemental carbon.

The reaction formula is as follows:

Hydrocarbons: $CO + 3H_2 \rightarrow CH_4 + H_2O$

$2CO+2H_2 \rightarrow CH_4+CO_2$

$CO_2+4H_2 \rightarrow CH_4+2H_2O$

$2CO+5H_2 \rightarrow C_2H_6+2H_2O$

$3CO+7H_2 \rightarrow C_3H_8+3H_2O$

$nCO+(2n+2)\ H_2 \rightarrow CnH_2n+2nH_2O$

Alcohols: $3CO + 3H_2 \rightarrow C_2H_5OH + CO_2$

$3CO+6H_2 \rightarrow C_3H_7OH+2H_2O$

$4CO+8H_2 \rightarrow C_4H_9OH+3H_2O$

$CH_3OH+nCO+2nH_2 \rightarrow CnH_2n+CH_2OH+nH_2O$

Aldehydes: $CO + H_2 \rightarrow HCHO$

Ethers: $2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O\ 2CH_3OH \rightarrow CH_3OCH_3$

## 3.2 Production Method of Methanol

### 3.2.1 Production Method of Methanol from Natural Gas

Natural gas is the main raw material for methanol production. The main component of natural gas is methane, with a small amount of other alkanes, olefins and nitrogen. There are steam conversion, catalytic partial oxidation and non catalytic partial oxidation for methanol feed gas production from natural gas. Steam conversion is the most widely used method, which is carried out under normal pressure or pressure in tubular furnace. As the reaction endothermic must be supplied from outside to maintain the required conversion temperature, it is usually achieved by burning some fuel gas between the tubes. The steam for conversion is directly produced on the device by the heat of flue gas and conversion gas.

Due to excessive hydrogen and insufficient carbon monoxide and carbon dioxide in the syngas produced by natural gas steam reforming method, the first way to solve this problem in industry is to adopt steam conversion method with carbon dioxide added to achieve appropriate ratio. Carbon dioxide can be supplied externally or recovered from flue gas of reformer. The other method is the two-stage conversion method with natural gas as raw material, that is, steam conversion of natural gas is carried out in the first stage of conversion, and only about 1 / 4 of methane is reacted, and the second stage is partially oxidized[2]. Not only the ratio of syngas is appropriate, but also the temperature of the second stage reaction is raised to above 800 ℃, The amount of residual methane can be reduced and the effective gas component of methanol synthesis can be increased.

### 3.2.2 Production Method of Methanol from Coal and Coke

Coal and coke are the main solid fuels for producing methanol crude feed gas. The process route of methanol production from coal and coke includes gasification of fuel, desulfurization of gas, transformation, decarbonization and methanol synthesis and refining.

Using steam and oxygen (or air, oxygen rich air) to heat process coal and coke is called solid fuel gasification. The combustible gas obtained from gasification is generally called gas, which is the initial feed gas for methanol production. The main equipment of gasification is gas generator. According to the movement mode of coal in the furnace, the gasification methods can be divided into fixed bed (moving bed) gasification method, fluidized bed gasification method and entrained flow bed gasification method. In China, the gasification of methanol from coal and coke is

generally carried out by the fixed bed intermittent gasification method, and the ucj furnace is used for the gasifier. In foreign countries, there are three kinds of coal gasifiers: Koppers totzek, lurge and Winkler. The second and third generation coal gasifiers are mainly Texaco and shell Koppers.

### 3.2.3 Production Method of Combined Alcohol

It is a kind of purification process of syngas, which is developed to replace a new process of removing trace carbon oxides from copper ammonia solution used in many synthetic ammonia production in China.

The process condition of combined methanol production is to add a set of methanol synthesis device between the outlet of compressor section 5 and the inlet of copper washing process, including methanol synthesis tower, circulator, water cooler, separator, crude methanol storage tank and other related equipment. The process flow is that the outlet gas of compressor section 5 enters methanol synthesis tower first, and most of the carbon monoxide and carbon dioxide that should be removed in copper washing process are put into methanol synthesis tower first In the methanol synthesis tower, it reacts with hydrogen to generate methanol. After CO production of methanol, the content of carbon monoxide in the gas entering the copper washing process is significantly reduced, which reduces the copper washing load. At the same time, the carbon monoxide index of the shift process can be appropriately relaxed to reduce the steam consumption of the shift. Moreover, the carbon monoxide delivered by the first few cylinders of the compressor becomes effective gas, and the power consumption of the compressor is reduced.

## 3.3 Comparison of Methanol Production Methods

(1) Before entering the steam reformer, the natural gas needs to be purified to remove harmful impurities, and the sulfur content of the purified gas is required to be less than 0.1ml/m3.

(2) The ratio of hydrogen to carbon in the crude feed gas made from coal and coke is too low, so the shift process must be carried out after gas desulfurization. The excess carbon monoxide is converted into hydrogen and carbon dioxide, and then the excess carbon dioxide is removed by decarbonization process.

(3) After CO production of methanol, the energy consumption is obviously reduced, which can save 50 kW. H of electricity and 0.4 t of steam per ton of ammonia, equivalent to 2 million kJ of energy consumption. In order to ensure the service life of methanol catalyst and the quality of methanol products, attention must be paid to the fine desulfurization and rectification of feed gas.

Although the investment cost of natural gas to methanol is lower than that of coal to methanol, China is rich in coal and less in gas, and the regional cost is quite different. However, the production of methanol from coke oven gas is a way to turn waste into treasure. However, the trend of environmental protection is increasingly severe. The coking industry mainly supports medium-sized capacity, individual or small-scale production capacity, and there are many problems in the early-stage whitening, and the device needs innovation and transformation The production of methanol from alcohol uses the surplus hydrogen of synthetic ammonia for by-product methanol, which makes full use of ammonia gas and achieves the effect of energy saving and emission reduction[3]. It not only produces synthetic ammonia but also produces methanol, which makes rational use of resources and achieves multiple business purposes. It is a process that is often used at present.

## 4. Conclusion

Methanol can be produced only by adding two sets of methanol synthesis and rectification

equipment by making full use of the existing ammonia production unit. Therefore, the investment is saved, the production is put into use quickly, and the combined alcohol production has obvious economic benefits for the whole system. In addition, the CO content of the gas entering the process is reduced, the equipment load is reduced, and the index of the previous process is appropriately relaxed to reduce energy consumption Local regional environment, product requirements, environmental issues and other indicators to select the appropriate production methods, play a real role.

## References


*[1] Sun Kai. (2017). Problems and countermeasures in petroleum equipment management in the new period. Chemical Engineering Management no.13, pp.160-160.*

*[2] Yang Haiquan. (2016). Analysis and management of hidden accident hazards in enterprises and countermeasures. Chemical Industry Management no.24, pp.131-131.*

*[3] Yang Xiaodong. (2018). Hidden safety hazards and countermeasures in the maintenance of chemical equipment. Petrochemical Technologyno.5, pp.286-286.*