RESEARCH ARTICLE

Analysis of the effect of temperature on coal consumption of coal gasification to methanol

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Received: January 26, 2022; **accepted:** May 20, 2022.

In order to further optimize the process of methanol production and improve the one-way conversion rate of total carbon, a new coal-to-methanol catalytic treatment process was designed. The temperature influence on the coal consumption of coal-to-methanol process was studied. The development status of domestic methanol synthesis technology was illustrated followed by the designing of raw materials. The methanol synthesis process scheme was developed based on the experimental procedures, and the chemical reaction equations of methanol synthesis were demonstrated. The conversion rates of CO and CO_2 at the different temperatures were analyzed to verify the effectiveness of this method. The results showed that the methanol mass fraction in the reactor outlet reached the highest level when the coolant temperature reached 187℃. The carbon monoxide-to-methanol reaction and the carbon dioxide-to-methanol reaction demonstrated different sensitivities to the coolant temperatures. The total carbon conversion rate reached the highest level at 193°C with the maximum value of 0.556. The results of the experiments confirmed that this method had certain applicability and was worthy of promotion.

Keywords: methanol production; chemical equipment; one way conversion of total carbon; methanol mass fraction.

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Introduction

China is not only a big producer of methanol but also a big demander for it. According to the statistics of methanol industry, the total output of methanol in China reached 63.57 million tons in 2020 with an annual growth rate of 2.27%, while the annual growth rate of compound methanol import to China was over 15% [1]. Methanol is not only an important basic chemical raw material but also a new alternative energy resource. Methanol occupies a very important position in the national economy in recent years, which is mainly due to the continuous development of methanol industrials and development of downstream products using methanol as raw material, among which the most important is the research and development of methanol fuel and new products, refined as methanol hydrocarbon [2, 3]. In recent years, with the shortage of global energy resources, many countries with the abundance in coal chemical industry field launched a fierce market competition. The capability of equipment manufacturing and the capacity of production in such industries in China are still at a low level. Therefore, the main equipment and materials used in the field of coal chemical industry mainly depend on imports, which is not conducive to the development of China's coal chemical industry.

Based on these facts, more attentions have been paid on the production of methanol resources in China, which include the production process, improve the resource conversion rate, and alleviate the problem of coal shortage.

The main characteristics of methanol process in China are that (1) coal is mostly used as the main raw material and (2) the industrial structure needs to be further improved. The current major problems are that, although there are many production units being built, the scales of these units are all relatively small, and the raw material route and process technology are not unified [4]. Due to the high expectation of a new alternative fuel, alcohol ether fuel, the development of methanol industry in China has entered the peak stage, which means almost “everywhere” in China. Methanol produced with coal as raw material is a resource-consuming product with low added value. It is very uneconomical to rely on massive export to absorb the excess capacity. Therefore, various effective measures should be taken to curb the excessive growth of methanol industry, and some projects should be postponed. Meanwhile, the process to eliminate a number of methanol production units with small scale, heavy pollution, high energy consumption, backward technology production equipment should be accelerated. The advantage of methanol industry scale is very significant, so that it is necessary to promote the upsizing of methanol industrials and the concept of “large methanol” production. Methanol, as the basic product of the coal-led chemical production chain, has been widely used in many fields [5, 6]. The process of coal-to-methanol synthesis has always been studied with perseverance, which includes optimizing the synthesis process, improving the operating rate of production equipment, and achieving the purpose of increasing the methanol production capacity and reducing the ton of methanol consumption [7].

Methanol, also known as wood alcohol, has very little free methanol content in nature. Therefore, it needs to be prepared manually. Methanol is the simplest saturated alcohol and an important chemical basic raw material and clean liquid fuel, which has a wide range of applications in many fields. Methanol is a colorless, transparent, flammable, and explosive liquid at room temperature [8]. Methanol is mutually soluble with water and is a good solvent for many organic compounds [9]. However, methanol is very toxic and direct contact with methanol liquid or vapor should be avoided. Some conventional physical properties of methanol are listed in Table 1. As a basic raw material of the chemical industry, methanol reacts with a series of substances, which makes methanol a very wide range of industrial applications [10]. The downstream products of methanol are rich in variety, mainly including formaldehyde, acetic acid [11], and dimethyl ether [12].

Din, *et al*. reported a new way of methanol production [4]. In their study, ZnO was used to promote the catalytic hydrogenation of nano-carbon fiber-based Cu-ZrO_2 to methanol, and the CO_2 in the process was reheated for completely recovery and utilization. However, the cost of this method was high, and the carbon conversion rate was still low. Therefore, it was not suitable for promotion and application. For the purpose to improve the production capacity utilization by optimizing the alcohol production process and improving the total carbon one-way conversion rate, this study explored methanol production process in coal catalytic treatment and related chemical equipment.

Materials and methods

Design of methanol production by catalytic treatment of coal

According to the annual 280 days of continuous treatment of 100,000,000 m^3 coalbed methane (CBM) process design [13], the component content and flow rate of coalbed methane were listed in Table 2, which were used to determine the process flow, material balance, and chemical equipment specifications of CBM non-catalytic conversion to methanol (CH_3OH). Accordingly, the methanol synthesis process in this study was

Table 1. Conventional physical properties of methanol.

Nature	Numerical value
Melting point (°C)	-97.68
Standard boiling point (°C)	64.7
Sui boundary temperature (°C)	239.35
Critical pressure (Bar)	80.84
Critical volume (m^3/kmol)	0.117
Critical compressibility factor	0.222
Melting heat (J/g)	103
Lower limit volume of spontaneous combustion in air (%)	6
Upper limit volume of spontaneous combustion in air (%)	36
Flash point (°C)	12
Vapor pressure at 20°C (mmHg)	96.6
Liquid viscosity at 25°C (MPa·S)	0.541
Heat generation at 25°C (KJ/mol)	-239.03
Dielectric constant at 25°C	32.7
Thermal conductivity at 25°C (W/m·K)	0.202
Density at 25°C (g/cm^3)	0.787

Table 2. Composition and flow of coalbed methane.

	CH_4	CO_2	O_2	N_2
CBM composition (volume fraction)/%	50.00	0.10	6.27	43.63
Component flow/m^3/h	7500.0	15.0	940.5	6544.5

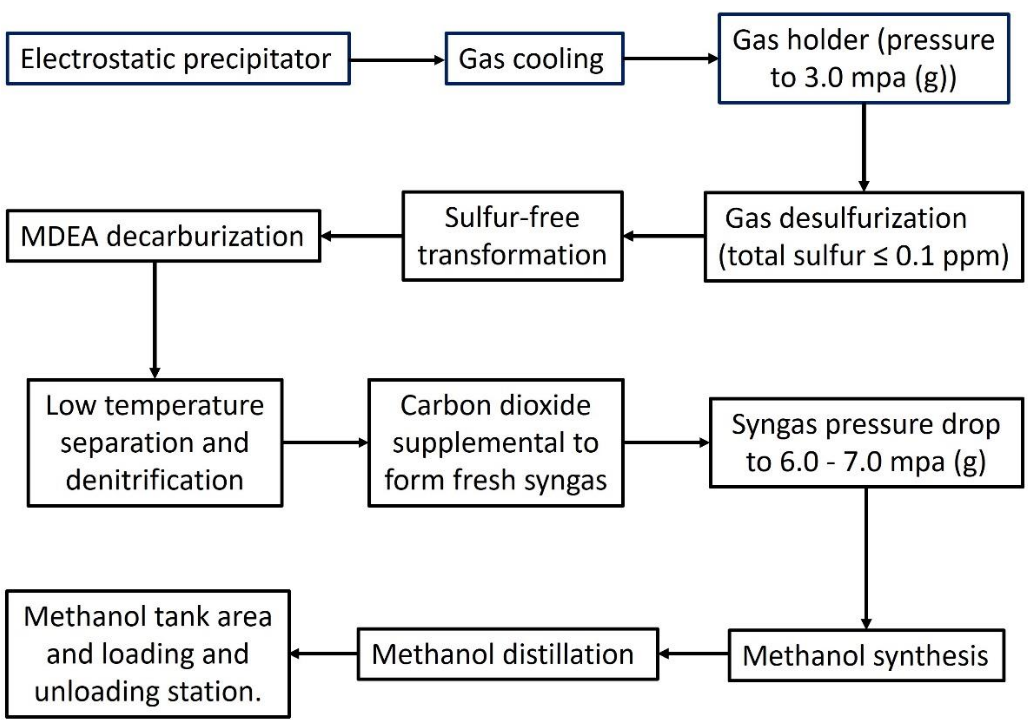

Figure 1. The scheme for methanol synthesis process.

designed as in Figure 1. In this scheme, the conversion unit did not depend on the sulfur content in the gas. Therefore, it did not need to add sulfide to the high purity gas for conversion and, in further, to avoid increasing the burden of the subsequent gas purification unit. However, the incapability of control the reaction temperature accurately was still a problem. To solve this problem, the desulfurization transformation was carried out in three steps (Figure 2). In the beginning of reaction, the temperature of the desulfurized mine hot furnace was increased to about 330°C through

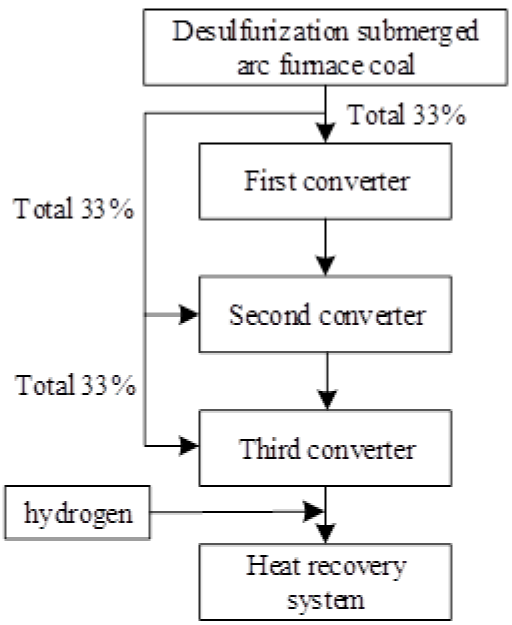

Figure 2. Diagram of piecewise transformation reaction.

the gas heat exchanger by adding superheated steam to the first gas converter that contained about 33% of the total gas for reaction to reduce the concentration of CO to 5% and increase the converter temperature to 500°C. The processed condensate was then added to the converter to reduce the temperature to about 330°C. The second stream was supplied with 33% of the total gas and 45% of CO to the second converter. After the reaction, the CO concentration was reduced to 5% and the temperature was increased to 500°C. The converter temperature was reduced to about 330°C after adding processed condensate. The third stream of 33% of the total gas with 25% of CO was supplied to the third converter with the reactor temperature was about 330°C. After the reaction, the temperature was increased to 500°C, and the CO concentration was reduced to 5%. The hydrogen vs. carbon ratio was adjusted with the purified gas from the bypass. The gas, then, entered the heat recovery system. Second, a circulating compressor was set in the reformer to circulate part of the gas from reformer outlet to the reformer inlet to control the temperature of reformer reaction. After the feeding gas and circulating gas were mixed, the CO concentration was reduced and then entered the converter. Since it was difficult to separate CO and N_2 even at low temperatures, the low temperature separation and denitrification procedures were eliminated from this study, and methanol synthesis was carried out eventually by using highly active catalysts to eliminate the adverse effects of high nitrogen content on methanol synthesis.

The equipment for methanol production from the coal gas

Equipment used in this study included electric dust removal unit, gas cooling unit, gas holder, gas compression pressurization unit, TSA gas purification unit, conversion cooling unit, desulfurization unit, decarbonization unit, CO_2 liquefaction unit, methanol synthesis tower, hydrogen recovery unit and methanol distillation unit (Figure 3). In addition, a torch discharge system was set up to deal with equipment, pipeline safety valve, pressure relief valve, discharge valve, and other abnormal operation (or accident) discharge of combustible matter. The fuel must be discharged when starting and stopping the system and must be discharged when the system was temporarily out of balance in trial operation. The collected fuel was sent to the torch for burning and discharging in time to ensure the safe operation of the system. The torch discharging system must be conformed to the atmospheric emission standards and reduced the pollution to the environment.

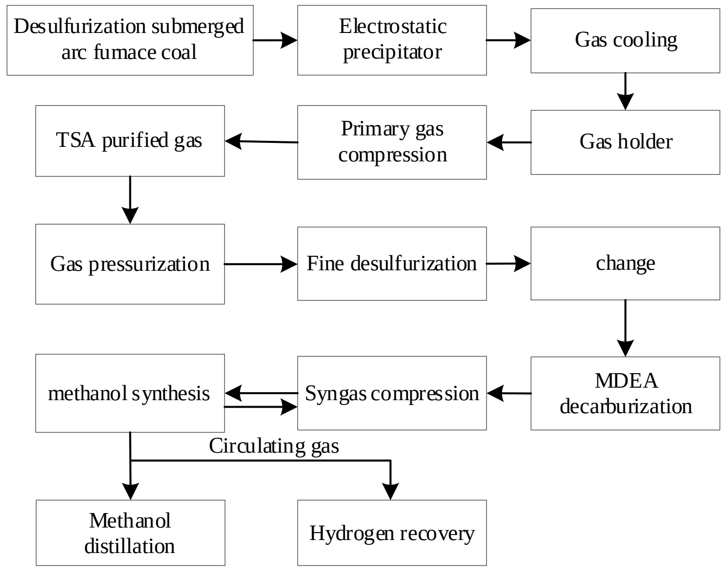

Figure 3. Process flow chart of methanol production from coal catalysis.

Results and discussion

Effect of coolant temperature on reactor performance

The distribution curves of bed temperature and methanol mass fraction along the reactor tube length at different coolant temperatures were shown in Figure 4, while the temperature was the only changing factor. The results showed that temperature distribution curve of the reactor decreased with the decrease of the coolant temperature (Figure 4A), which might be caused by the low-temperature coolant took away a lot of heat in the reactor. It has been known that low temperature is conducive to prolong the catalyst life, which indicates that low coolant temperature is beneficial to the catalyst life. The methanol mass fraction distribution curve in the first half reaction time of the reactor (between 0-4 minutes) increased with the increase of coolant temperature but reversed in the second half of the reaction time (Figure 4B). The methanol mass fraction in the front section of the reactor was the highest one when the coolant temperature was 227°C, but it reversed from 5 minutes and reached the lowest level at the reactor outlet. The results indicated that lower coolant temperature was more conducive to methanol synthesis. The above phenomena confirmed that the effect of temperature on the reaction kinetics was dominant in the initial stage of the reaction, and the effect of temperature on the chemical equilibrium was dominant later. The results also demonstrated that the mass fraction of methanol at the outlet of the reactor was the highest one when the coolant temperature reached 187°C. Because the synthesis of methanol is a strong exothermic reaction, low temperature is conducive to improve the chemical equilibrium constant and promote the synthesis of methanol. On the other hand, too low temperature will limit the reaction kinetics and hinder the synthesis of methanol. Therefore, these two conflicting effects jointly determine the degree of methanol synthesis, and it is important to select the appropriate coolant temperature.

Effect of coolant temperature on one-way conversion

In order to evaluate the impact of coolant temperature on the overall process, the impacts of coolant temperature on the one-way conversion rate of coke oven gas to methanol process including reaction conversion rate, exhaust gas emission, equipment energy consumption, energy cost, investment, and

A.

B.

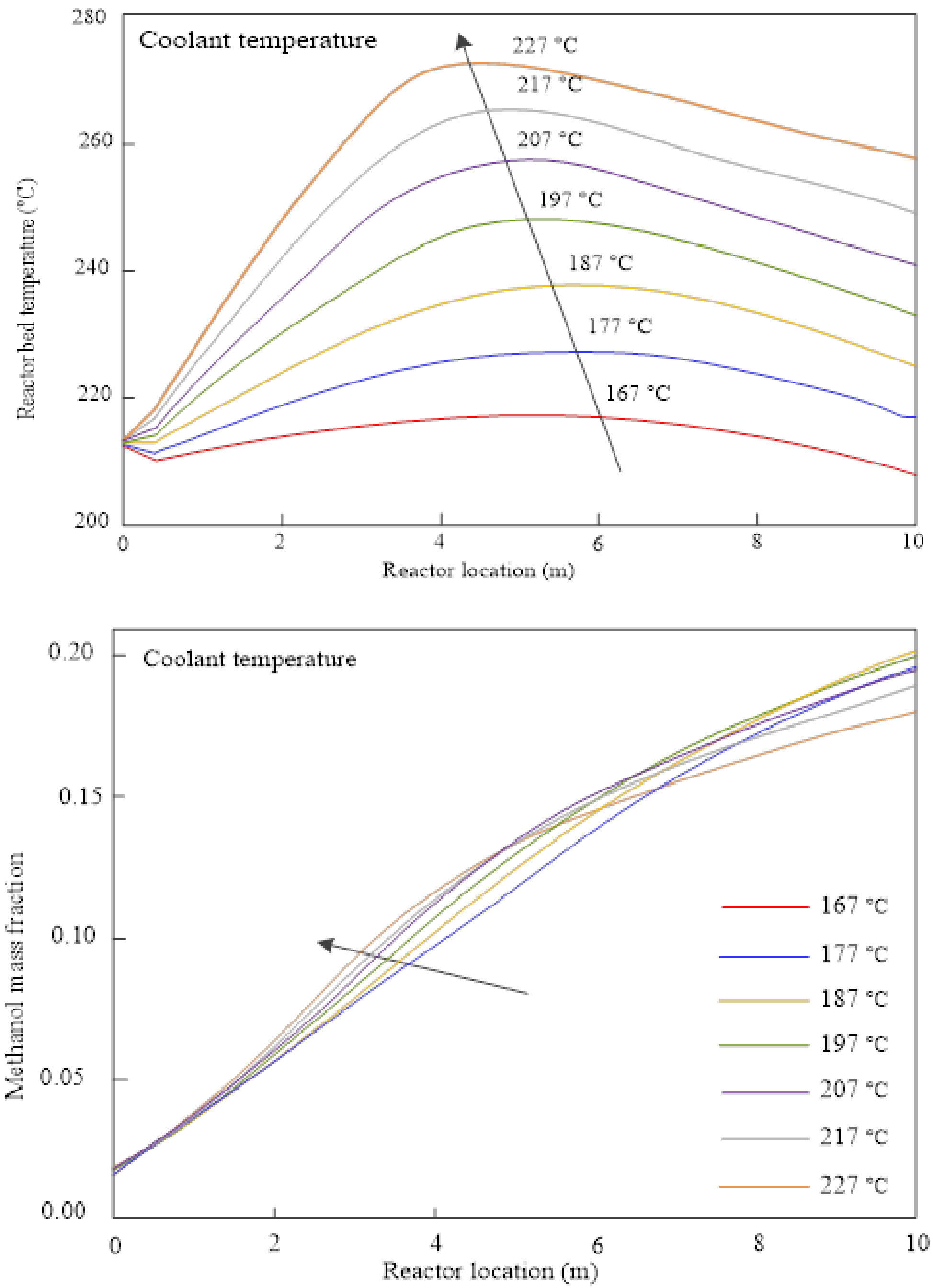

Figure 4. Effects of coolant temperature on temperature distribution curve (A) and methanol mass fraction distribution curve (B) in reactor.

income were analyzed in Figure 5. Maximizing economic benefits while reducing environmental pollution was the ultimate goal of optimization. The one-way conversion rates of CO, CO_2, and total carbon change were significantly related to the increase of coolant temperature. When the coolant temperatures reached 189°C and 197°C, the one-way conversion of CO and CO_2 reached the maximum levels of 0.773 and 0.276, respectively. These results indicated that the reactions of CO to methanol and CO_2 to methanol were sensitive to the coolant temperature. At

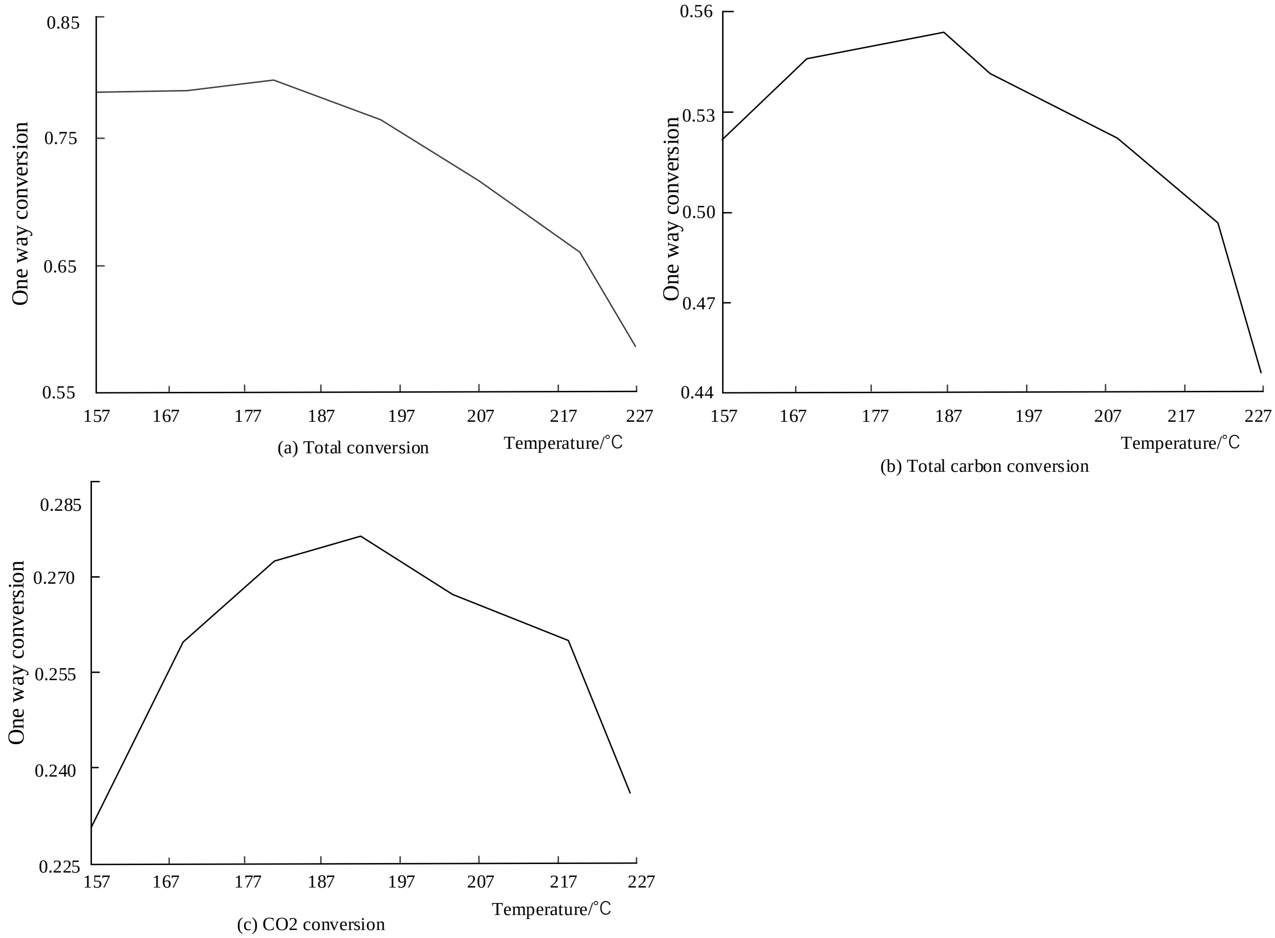

Figure 5. Effects of coolant temperature on one-way conversion.

193°C, the one-way conversion of total carbon reached the maximum value of 0.556. Obviously, higher total carbon conversion indicated the less unreacted gas, so more methanol production, and less unreacted gas circulation and relaxation.

Realization of methanol industrial production

This study mainly focused on the synthesis of methanol from carbon oxide and hydrogen such as the production method of syngas hydrogenation to methanol and the synthesis of methanol from hydrogen and carbon monoxide under the action of catalyst. The yield was low due to the harsh conditions of the synthesis process and the influence of chemical equilibrium on the conversion rate. A large amount of syngas not involved in synthesis could only be recycled resulting in a lot of waste. The industrial synthesis of methanol is mainly based on gas-solid multiphase catalytic process. The catalysts include *Zn-Cr* based catalysts and copper-based catalysts (*Cu-Zn-Al* or *Cu-Zn-Cr*). Chemical reaction equation for synthesis of methanol (CH_3OH) are as follows:

Main reactions:

$$CO + 2H_2 = CH_3OH + 102.5kJ/mol \quad (1)$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \quad (2)$$

Side reactions:

$$2CO + 4H_2 = CH_3OCH_3 + H_2O + 200.2kJ/mol \quad (3)$$

$$CO + 3H_2 = CH_4 + H_2O + 115.6kJ/mol \quad (4)$$

$$4CO + 8H_2 = C_4H_9OH + 3H_2O + 49.62kJ/mol \quad (5)$$

$$CO_2 + H_2 = CO + 3H_2 - 42.9kJ/mol \quad (6)$$

$$nCO + 2nH_2 = (CH_2)n + nH_2O + Q \quad (7)$$

Industrial methanol synthesis is dominated by gas-solid heterogeneous catalytic process. According to the non-circulation of heat exchange mode, industrial methanol synthesis units can be divided into two categories: (1) multistage cold shock or multistage heat exchange type, such as ICI four stage cold shock type, radial synthesis tower, *etc*. and (2) continuous heat exchange type, such as Lurgi tubular type, domestic unique casing type, *etc*. In addition, some new reactors (or ideas) are still springing up. The synthesis of methanol from syngas is not a very favorable reaction in thermodynamics, so that effective industrial production can be achieved only under certain temperatures, pressures, and catalysts. The reaction equilibrium of methanol synthesis is greatly affected by pressure. Copper based catalysts can generally operate at a low pressure of 5 MPa due to their low requirements for active temperature and pressure.

Conclusion

This study designed a new methanol production process method for coal catalytic treatment and investigated the influence of temperature on methanol production. The conversion rates of CO and CO_2 were calculated, which verified the effectiveness of the method. The results showed that the temperature profile of the reactor decreased as the coolant temperature decreased because the cryogenic coolant took away a lot of heat. The mass fraction of methanol at the reactor outlet was at the highest level when the coolant temperature reached 187°C. The different temperature effects indicated that the reactions of CO with methanol and CO_2 with methanol were sensitive to coolant temperature. At 193°C, the unidirectional conversion of total carbon reached the maximum level of 0.556. Additional studies are needed in this field such as the influence of environmental factors, which may lead to the proposition of a more reasonable production process.

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