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PRELIMINARY DESIGN OF 100,000 TONS/YEAR METHANOL PROJECT

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ABSTRACT

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This paper focuses on the methanol synthesis process. Methanol is a very important organic chemical raw material and fuel, which is applied in many fields.

Firstly, the development of methanol production, methanol synthesis process and methanol development prospect are introduced. The Lurgi process was used to synthesize methanol under low pressure. The crude methanol obtained from the synthesis tower is refined by three-tower distillation process.
Then, the detailed material balance calculation of methanol synthesis and distillation process, as well as the calculation of distillation tower are carried out.

Finally, the discharge of wastewater, waste gas and waste residue are strictly controlled to reduce environmental pollution.

Key words
Distillation, matrial balance calculation, methanol, synthesis process

CONCEPT DEFINITIONS

List of abbreviations

Al_2O_3	Aluminum oxide
CH_4	Methane
CH_3CH_2OH	Ethanol
CH_3OCH_3	Dimethyl ether
CH_3OH	Methanol
C_4H_9OH	N-butanol
$C_4H_{10}O$	Isobutanol
CuO	Copper oxide
CO	Carbon monoxide
CO_2	Carbon dioxide
H_2	Hydrogen
H_2O	Water
N_2	Nitrogen
NaOH	Sodium hydroxide
O_2	Oxygen
P	Pressure
ZnO	Zinc oxide

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1 INTRODUCTION

Methanol is an important organic chemical raw material and high-quality fuel, which is widely used in many fields such as chemical industry, medicine, forestry product processing. Methanol production is one of the important product series in the world's chemical industry, which has a wide range of application space in many fields. By the end of 2016, the total demand of global methanol production has exceeded 16 million tons, and is on the rising trend, with great development potential and economic value. (Wang 2019, 23-28.).

The shortage of oil resources has become a worldwide problem. According to the data from world oil analysis, the world's proven recoverable oil reserves are 270 billion tons, and the annual consumption of 6 billion tons of oil resources shows that the global oil resources can maintain consumption for up to 50 years, and the energy crisis is gradually prominent. Taking China's energy structure as an example, China's coal reserves are very rich. The research on the utilization and development technology of coal resources can fundamentally alleviate the energy crisis caused by China's oil shortage. Production of synthesis gas is the key technology of coal energy conversion, which is of great significance to its development and research. At this stage, the existing production equipment and production line scale of most methanol production enterprises in China cannot meet the growing demand of methanol production. The supply of methanol products was once tight, and the price of methanol products gradually increased. The product sales situation is very good. (Wang 2019, 23-28.).

Take Lianyungang port of China as an example. From October 2016 to October 2017, Lianyungang imported methanol in total 1,065,000 tons, accounting for about 10% of the total imports of the same period in China, and 26% of the total imports of Jiangsu Province. The imported methanol mainly comes from Iran, New Zealand, Qatar, Venezuela and other countries, and all delivered to local chemical production enterprises in Lianyungang. The main reason for such a large amount of imported methanol is that the capacity utilization rate of Chinese methanol production enterprises is relatively low and the output growth rate is small, which cannot meet the demand of the rapidly growing new chemical plants. (Qin, Peng & Zhu 2017, 45.).

Therefore, the design of an efficient and economic methanol project is in line with today's industrial needs in China and even in the world. It can also make a small contribution to the environmental pollution and energy crisis the world is about to face. This project mainly analyzes the nature, use and production and consumption status of methanol all over the world, briefly introduces and compares various existing production processes of methanol, focuses on Lurgi process, designs the production, separation and distillation tower purification stages of methanol in detail, and makes the most ideal design scheme of annual output of 100,000 tons of methanol through material balance calculation. The project is located in Dalian City, Liaoning Province, China. After the completion of the project, it will meet the methanol demand of Liaoning Province, the old industrial base of China. It is also hoped that through this thesis work, the readers will realize that the world's oil is not inexhaustible, and the use of alternative fuel to oil has become the trend of the world.

2 METHANOL OVERVIEW

Methanol is an important organic chemical raw material and high-quality fuel, which is widely used in many fields such as chemical industry, medicine, forestry product processing. Methanol product is one of the important product series in the world chemical industry, which has a wide range of applications in many fields. (Zhou 2018, 30-31.).

2.1 Properties of Methanol

The molecular formula of methanol is CH_3OH. Is a colorless, transparent, flammable, toxic, volatile liquid, slightly alcohol flavor. The molecular mass of methanol is 32.04, relative density is 0.7914, melting point is - 97.8 °C, boiling point is 64.7 °C, flash point (open cup) is 16 °C, self-ignition point is 473 °C, refractive index is 1.3287, surface tension is 45.05 mN/m, vapor pressure is 12. 265 KPa, viscosity is 0.5945 MPa·s. It is miscible with water, ethanol, ether, benzene, ketones and most other organic solvents. The explosive mixture of vapor and air is 6.0% - 36.5%. It is active in chemical properties and can produce chemical reactions such as oxidation, esterification and carbonylation. (Zhou 2018, 30-31.).

2.2 Function of Methanol

Methanol is an important organic chemical raw material and high-quality fuel, widely used in fine chemicals, plastics, medicine, forest products processing and other fields. Methanol is mainly used to produce formaldehyde, which accounts for half of the total output of methanol. Formaldehyde is an indispensable raw material for the production of various synthetic resins. Methyl acrylate, dimethyl terephthalate, methylamine, methylaniline and methane chloride can be produced by using methanol as methylation reagent. Carbonylation of methanol can produce acetic acid, acetic anhydride, methyl formate and other important organic synthesis intermediates. They are raw materials for the manufacture of various dyes, drugs, pesticides, explosives, spices, and paint. At present, the synthesis of glycol, acetaldehyde, and ethanol from methanol has been paid more attention. (Zhou 2018, 31-32.).

Methanol is also an important organic solvent, its solubility is better than ethanol, it can be used to prepare paint. As a good extractant, methanol can be used to separate some substances in analytical chemistry. Methanol is also a promising clean energy. With its advantages of safety, low cost, full combustion, high utilization rate and environmental protection, methanol fuel has become one of the development directions of automotive fuel. In addition, fuel grade methanol can also meet the requirements of environmental protection when it is used for heating and power generation. Methanol can also be fermented to produce methanol protein, which is rich in vitamins and protein. It has the advantages of high nutritional value and low cost. It has a broad application prospect as a feed additive. (Zhou 2018, 30-35.).

2.3 Development of methanol production process

Methanol is the simplest monohydric alcohol. In 1661, R. Bolye, a British chemist, first found methanol in the liquid products after wood carbonization, therefore methanol is commonly known as wood essence and wood alcohol. In nature, only some leaves or fruits contain a small amount of free methanol, most of which exist in the form of esters or ethers. In 1857, M. Berthelot of France hydrolyzed chloromethane in alkaline solution to produce methanol in laboratory. (Olah & Goeppert 2007, 35-47.).

In 1923, BASF company of Germany first realized the industrial production of methanol with syngas under high pressure. Until 1965, this high-pressure process was the only way to synthesize methanol. In 1966, Imperial Chemical Industries developed the low-pressure process and then the medium pressure process. In 1971, Lurgi company of Germany successively developed a low-pressure process suitable for natural gas residue as raw material. Since the low-pressure process has obvious advantages over the high-pressure process in energy consumption, plant construction and production capacity of single series reactors, most of the new methanol production units have adopted the low-pressure process since the mid-1970s. The typical methanol synthesis processes in the world mainly include Imperial Chemical Industries process, Lurgi process and Mitsubishi Gas Chemical Company process. (Olah & Goeppert 2007, 35-47.).

At present, methanol production process presents the following development trends. The raw materials used for methanol production are gradually transformed into tail gas of hydrocarbon and natural gas processing. From the whole methanol production cost, the cost of using natural gas as raw material to produce methanol is about 50% lower than that of using solid materials, and the cost of using acetylene tail gas as raw material will be lower. Around the world, methanol produced with natural gas as raw material accounts for about 90% of the total production, and coal as raw material only accounts for about

2%. FIGURE 1 shows the raw material composition of methanol production in China in 2012. Due to the energy structure of rich coal and poor oil, China's use of coal as raw material to produce methanol is increasing. (Liang 2017, 26-28.).

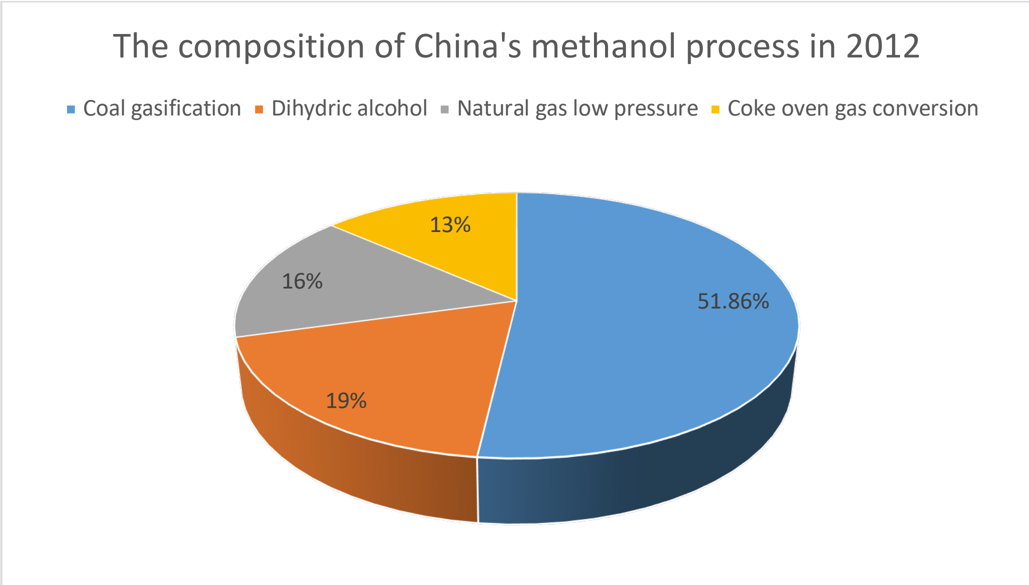

FIGURE 1. The composition of China`s methanol process in 2012 (Adapted from Li 2013, 35)

Methanol production scale is gradually changing to large-scale production. Only by continuously promoting the development of methanol production towards the direction of large-scale, can further reduce the cost of methanol production and improve economic efficiency. Fully recover and utilize the heat in the production system. Using the heat in the system to produce high pressure steam can be used to drive the boiler feed pump, compressor, circulating water pump and other equipment, improve the utilization efficiency of heat energy, and further save resources. A new by-product medium pressure steam methanol synthesis tower is used in the production, which can reduce the energy consumption in the production process and effectively control the production cost. The latest energy-saving technologies such as pre conversion, H_2 recovery and process condensate saturation are used to reduce the consumption of methanol and improve economic benefits. (Liang 2017, 26-28.).

2.3.1 Development of methanol industry in China

After more than ten years' development, the productivity of methanol industry in China has been improved significantly. In 1991, China's methanol production capacity was only 700,000 tons, and China's methanol production capacity increased with each passing year. At present, China has abundant capacity to produce methanol from coke oven gas and other raw materials. The development of methanol as an alternative to petroleum fuel has sufficient production and capacity guarantee. It can be seen that China's methanol production has increased in the past decade (FIGURE 2). In 2018, China's methanol production has reached 47.56 million tons and has great development potential. China's market demand for methanol has great potential. (CIIN 2020, 47).

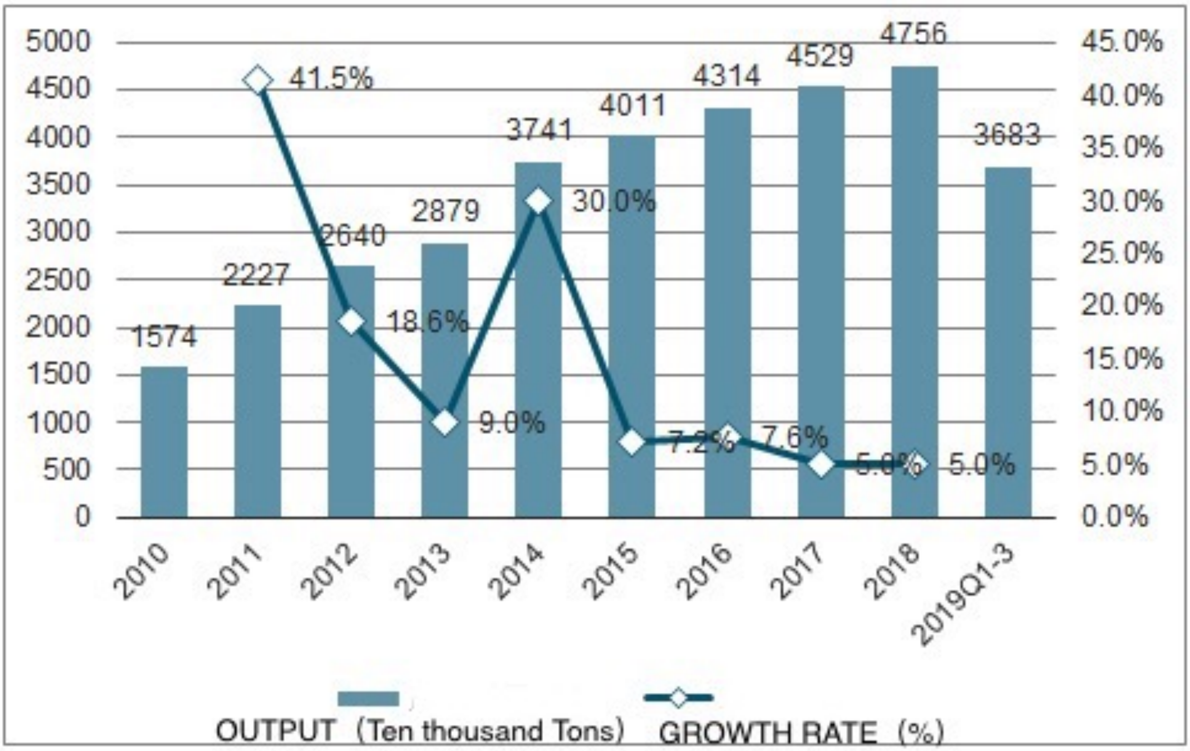

FIGURE 2. Methanol production and growth trend in China in 2010-2019 (Adapted from CIIN 2020, 47)

2.4 Methanol synthesis method

Methanol synthesis is a reversible strong exothermic reaction controlled by thermodynamics and kinetics. In general, the conversion of carbon monoxide (CO) and carbon dioxide (CO_2) in one-way reactor is less than 100%. In the outlet gas of the reactor, the methanol content is only 3 % - 6 %. Unreacted CO, CO_2 and hydrogen (H_2) need to be separated from methanol, and then further compressed and recycled into the reactor. (Deng 2018.).

2.4.1 Common methanol synthesis method

The earlier developed zinc chromium catalyst has low activity, and only when the reaction temperature reaches 300 ℃, it has enough activity. In order to ensure the high methanol content in the gas at the outlet of the reactor, the reaction pressure above 30 MPa is generally used. Copper based catalysts have high catalytic activity, and show good activity when the reaction temperature is 270 ℃, generally using medium or low pressure synthesis pressure. (Deng 2018.).

At present, methanol production technology mainly adopts two processes, i.e. medium pressure process and low-pressure process, and the low-pressure process is the main one. The methanol produced by these two methods accounts for more than 80% of the world's methanol production. High pressure method: (19.6-29.4 MPa) is the initial method of methanol production, using zinc chromium catalyst, reaction temperature 360-400 ℃, pressure 19.6-29.4 MPa. Due to the high consumption of raw materials and power, high reaction temperature, high content of organic impurities in crude methanol, and large investment, the development of high-pressure process has been in a state of standstill for a long time. (Deng 2018.). The low-pressure method: (5.0-8.0 MPa) is a methanol synthesis technology developed in the late 1960s. The low pressure method is based on the copper based catalyst with high activity, whose activity is significantly higher than that of the zinc chromium catalyst, and the reaction temperature is low (240-270 ℃). Under low-pressure, higher methanol yield can be obtained, and the selectivity is good, the side reaction is reduced, the methanol quality is improved, and the raw material consumption is reduced. In addition, due to the low-pressure, the power consumption is reduced a lot, and the process equipment is easy to manufacture. (Deng 2018.).

With the large-scale methanol industry, if the low-pressure method is adopted, the process pipeline and equipment will be larger, so the synthesis pressure will be increased properly on the basis of the low-pressure method, that is, the medium-pressure method (9.8-12.0 MPa) will be developed. The copper-based catalyst with high activity is still used in the medium-pressure method, and the reaction temperature is the same as that of the low-pressure method, but the corresponding power consumption increases slightly due to the increase of the pressure. (Deng 2018.).

Copper based catalyst is a kind of catalyst for methanol synthesis at low temperature and low pressure. Its main component is copper oxide (CuO) / zinc oxide (ZnO) / aluminum oxide (Al_2O_3). The operating temperature of low and medium pressure method is 210-300 ℃, and the pressure is 5 MPa-10 MPa, which is much lower than that of traditional synthesis process. It is favorable for methanol balance. The characteristics of copper-based catalysts is that, the copper-based catalysts have good activity, one-way conversion rate of 7% ~ 8%. The copper-based catalysts have good selectivity, more than 99%, the impurities are only trace methane, dimethyl ether (CH_3OCH_3), methyl formate, easy to get high-purity methanol; Poor high-temperature resistance, sulfur sensitive. (Luan & Ge 2006, 7-9.).

At present, there are three main methods of methanol production. Direct oxidation of methane, Methane (CH_4) reacts with oxygen (O_2) to produce methanol (CH_3OH). Methanol is synthesized from CO and H_2. Liquefied petroleum gas oxidation method. Based on the investment cost, production cost and product yield, the low-pressure method is selected as the methanol production process. Under the heating pressure of CO and H_2, methanol is synthesized under the action of catalyst. The main reaction formula is:
$CO + H_2 \rightarrow CH_3OH$

3 PRODUCTION METHOD AND PROCESSING OF METHANOL

Coal is gasified to obtain gas, which is desulfurized and decarbonized to remove the gas unfavorable to the methanol synthesis process, and then compressed and heated to make the raw gas meet the conditions required for methanol synthesis, and then sent to the synthesis tower. Because the one-way conversion rate of the methanol synthesis process is low, the reflected gas needs to be compressed by a circulating compressor, and then entered the synthesis tower again for synthesis Methanol. Finally, the crude methanol obtained by the synthesis is rectified in three-towers to obtain qualified refined methanol products. (Zeng 2005, 1-5.).

3.1 Production process

With the development of science and technology, the technology of methanol production is also developing. Although there are different technologies, the technological process of coal to methanol basically consists of four processes: gasification, i.e. raw coal is gasified to obtain crude syngas (main components are CO, CO_2 and H_2). Transformation, i.e. water gas is transformed to obtain appropriate hydrogen carbon ratio. Purification, i.e. CO_2 and sulfur impurities are removed. Synthesis and rectification, that is, methanol is synthesized under the action of catalyst and refined methanol is obtained through rectification (Wang 2014, 69-74). In the above four processes, coal gasification is the most critical core technology. At the same time, due to more carbon and less H_2 after coal gasification, in order to obtain a proper methanol synthesis gas (hydrogen carbon ratio 2.05 ~ 2.15). It is necessary to recover H_2 from the purge gas after methanol synthesis in order to effectively utilize coal resources and reduce energy consumption. (Zeng 2005, 1-5.).

3.1.1 Production principle of gas making section

In China, the raw materials for methanol production and manufacturing include gas, liquid and solid raw materials. Gas raw materials include natural gas, coke oven gas, acetylene tail gas, refinery gas and blast furnace gas; liquid raw materials include naphtha, heavy oil and residual oil; solid raw materials include coke, anthracite and lignite. It can be seen from the TABLE 1 that the investment and cost of methanol production from coal are the highest. However, with the shortage of oil energy, and the world's coal reserves far exceed natural gas and oil. From a long-term strategic point of view, coal will eventually be the dominant way to produce methanol in the future.

TABLE 1. The economic effect of methanol production from different raw materials (Adapted from Yang, 2012, 56)

	Lignite	Coke-oven gas	Natural gas	Acetylene tail gas
Investment	100%	70% ～ 85%	65%	35%
Production cost	100%	90%	50% ～ 55%	40%

In the synthesis of methanol, the first step is to prepare the oxides of H_2 and carbon. If methanol is synthesized from H_2 and CO, the molecular ratio of the two should be n (H_2): n (CO) = 2:1, and the reaction with CO_2 is n (H_2): n (CO_2) = 3:1. Generally, the feed gas for methanol synthesis contains H_2, CO and CO_2, so it should meet the following requirements: $\frac{n(H_2)-n(CO_2)}{n(CO\ )+(CO_2)}=2$.

In the production of methanol feed gas, the hydrocarbon or carbon containing resources such as natural gas, petroleum gas, naphtha, heavy oil, coal and acetylene tail gas are generally converted by steam conversion or partial oxidation to produce a mixture mainly composed of H_2, CO and CO_2, as well as residual unconverted methane or a small amount of nitrogen. Methane and nitrogen do not participate in methanol synthesis reaction, they are inert gases, the lower the content, the better, but it is related to the method of preparing feed gas. In addition, according to different raw materials, the feed gas may contain a small amount of organic sulfur and inorganic sulfur compounds. (Wang 2001.).

In order to meet the hydrogen carbon ratio, if the hydrogen carbon in the feed gas is unbalanced, when the hydrogen is more and the carbon is less, the carbon shall be supplemented during the manufacturing of the feed gas. Generally, CO_2 shall be used, and the raw material shall enter the conversion equipment at the same time. Otherwise, if there is more carbon, the excess carbon (in the form of CO_2) shall be removed in the later process.

3.1.2 Production principle of methanol synthesis section

The methanol synthesis gas enters into the methanol synthesis tower after preheating. Under the action of copper-based catalyst, CH_3OH from CO and H_2; CH_3OH and water (H_2O) from CO_2 and H_2. The equation is:

$CO+2H_2=CH_3OH$
$CO_2+3H_2=CH_3OH+H_2O$

In the reaction process, there are still the following side reactions. CH_3OCH_3, CH_3CH_2OH and N-butanol (C_4H_9OH) from CO and H_2. The equation is:

$2CO+4H_2=CH_3OCH_3+H_2O$
$2CO+4H_2=CH_3CH_2OH+H_2O$
$4CO+8H_2=C_4H_9OH+3H_2O$

At the same time, there are also methyl formate, methyl acetate and other higher alcohols, higher alkanes, and inversion reactions. The heat from the synthesis reaction is recycled by the medium pressure steam produced outside the reaction tube. (Chai 2010).

3.1.3 Production principle of methanol rectification section

In addition to water, the crude methanol also contains different amounts of impurities. In order to obtain the product methanol meeting the requirements of the standard, the impurities must be removed. In industrial production, methanol is separated from other components by distillation, mainly using the different boiling points of each component. (Wang 2004.).

Methanol distillation is a continuous process in which vaporization and partial condensation are used simultaneously and repeatedly to completely separate the components in the mixture. In order to complete this process, the unit adopts the three-tower distillation process to remove the dissolved gas and low boiling point impurities in the crude methanol in the tower, and remove the water and heavy components in the pressurized tower and atmospheric tower, therefore as to prepare the refined methanol products meeting the quality assessment standards. (Wang 2004.).

3.2 Brief introduction of production process

First, the gas is converted into syngas by Kellogg gasification process. The raw gas is desulfurized by ZnO first, and then converted into syngas by secondary reformer, the second is the synthesis of methanol. The synthesis gas is pressurized to 5.14 MPa, heated to 225 ℃ and then input into the shell and tube reactor. Under the action of copper-based catalyst, methanol is synthesized, and then the rectification of methanol. In this process, the crude methanol is refined to refined methanol by three-tower rectification process. (Zhang & Li 2012.).

At present, most methanol plants in China use Lurgi process to use shell and tube type synthesis tower, which is filled with catalyst in the tube, and the boiling water between the tubes is 2.5-4.0 MPa. The reaction gas goes through the tube, and the reaction heat is transferred to the boiling water between the tubes through the tube wall to generate steam. The temperature in the center of the tube is not much different from that in the boiling water by 10 degrees, and the reaction pressure is 5-10 MPa.

The recovery of crude methanol is completed by condensation, as shown in the FIGURE 3. The methanol synthesis gas is increased to 5.2 MPa by compressor, mixed with the circulating gas in the proportion of 1:5, heated to 220-230 ℃ by heat exchanger, the outgoing gas containing about 7% methanol and temperature of about 250 ℃ is cooled by heat exchange to 85 ℃, then cooled by water, separated into the separation tower, and the obtained crude methanol enters the methanol storage tank, the unreacted gas is recycled to improve the conversion rate. (Benyounes & Haddou 2018, 13-18.).

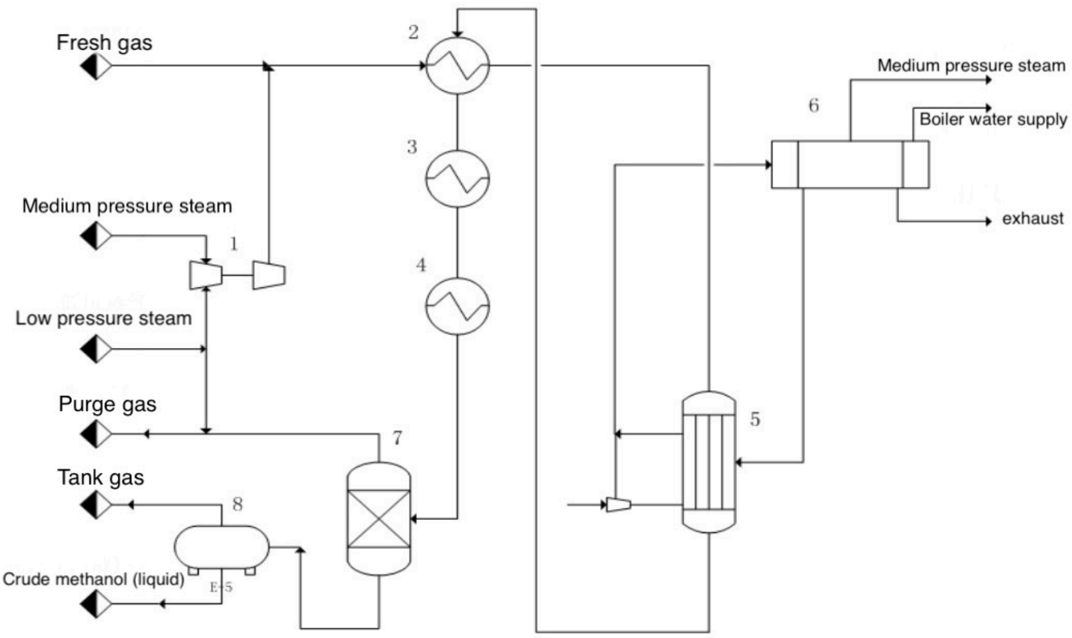

FIGURE 3. Lurgi process flow chart (Adapted from Benyounes & Haddou 2018, 15)
1. Compressor 2. Heat exchanger 3. Boiler water preheater 4. Water cooler
5. Synthesis tower 6. Steam drum 7. Methanol separator 8. Crude methanol storage tank

The main advantages of Lurgi process are as follows: the temperature distribution of catalyst bed in the reactor is uniform, and most of the bed temperature is between 250-255 ℃. Due to the large volume ratio of heat transfer surface and bed, the heat transfer is rapid, and the temperature in the same plane of the bed is small, which is conducive to prolonging the catalyst life and allowing higher CO in the feed gas. The temperature of catalyst bed can be controlled by adjusting the steam pressure of steam drum, with accurate and sensitive effect. It can recover high-level heat energy and make rational use of energy. The methanol content at the outlet of reactor is high, the equipment is compact and it is convenient to start and stop and the side reaction of reaction is less and the impurities in crude methanol are less. The Lurgi process also uses an air-cooled reactor, which reduces the energy consumption per ton of methanol and increases the amount of medium pressure steam by-product. (Yang 2003.).

Copper based catalyst is a kind of catalyst for methanol synthesis at low temperature and low pressure. Its main component is CuO/ ZnO/ Al_2O_3. The operating temperature of low and medium pressure method is 210-300 ℃, and the pressure is 5 MPa-10 MPa, which is much lower than that of traditional synthesis process. It is favorable for methanol balance. The characteristics of copper-based catalyst is that, the copper-based catalyst have good activity, one-way conversion rate of 7% ~ 8%, and it have good selectivity, the impurities are only trace methane, CH_3OCH_3, methyl formate, easy to get high-purity methanol; poor high-temperature resistance, sulfur sensitive. (Benyounes & Haddou 2018, 15.).

3.3 Methanol rectification process

Three-tower distillation process is adopted in methanol distillation process (FIGURE 4). Crude methanol (74 °C, 0.4 MPa) from the methanol synthesis unit enters the predistillation tower through the feed pump of the pre tower. The reboiler of the pre tower is heated with low-pressure steam of 0.4 MPa. Impurities with low boiling point, such as CH_3OCH_3, are discharged from the top of the tower. After the water is cooled and separated, it is used as fuel. The recovered methanol liquid is used as the reflux of the tower through the reflux pump of the pre tower. (Wang 2004, 22-25.).

The crude methanol liquid at the bottom of the pre rectifying tower enters the pressurized rectifying tower through the feeding pump of the pressurized tower. The reboiler of the pressurized tower uses 1.3 MPa low-pressure steam as the heat source. The methanol gas (0.6 MPa, 122 °C) is distilled from the top of the pressurized tower. After the regular pressure tower reboiler, the methanol gas is condensed, and the refined methanol returns to the reflux tank of the pressurized tower. Part of the refined methanol flows through the reflux pump of the pressurized tower, return to the pressurized distillation tower as the reflux, and the other part enters the refined methanol metering tank after being cooled by the methanol cooler of the pressurized tower. (Wang 2004, 22-25.).

The bottom kettle liquid (0.6 MPa, 125 °C) of the pressurized distillation tower enters the atmospheric distillation tower for further distillation. The reboiler of atmospheric tower uses methanol gas from the top of pressurized distillation tower as heat source. The refined methanol gas (0.13 MPa, 67 °C) is discharged from the top of the atmospheric distillation tower. After being condensed and cooled by the condenser of the regular pressure tower, part of it is returned to the atmospheric distillation tower, and the other part is pumped into the refined methanol metering tank for storage. The product refined methanol is delivered from the refined methanol metering tank to the refined methanol storage tank by the refined methanol pump. (Wang 2004, 22-25.).

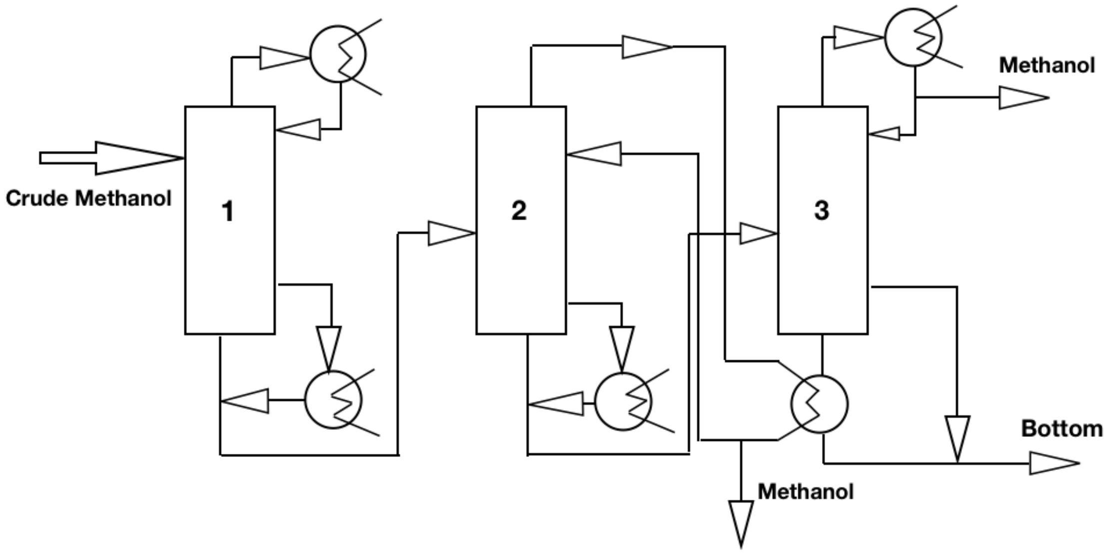

FIGURE 4. Three-tower distillation process (Adapted from Zhu 2018)
1. pre rectifying tower 2. pressurized rectifying tower 3. atmospheric rectifying tower

In order to prevent the corrosion of equipment such as formic acid and CO_2 contained in the crude methanol, a proper amount of caustic soda solution is prepared in the methanol solution after the feed pump of the pre-tower to adjust the PH value of the crude methanol solution. The non-condensable gas discharged from each tower of the methanol rectification system enters the fuel gas system. After the distillation residue discharged from the bottom of atmospheric distillation tower is cooled to 40 ℃ by wastewater cooler, it is sent to biochemical treatment unit by wastewater pump. The refined methanol from methanol distillation is stored in the refined methanol storage tank. The refined methanol storage tank is two 30,000 m^3 fixed storage tanks, and the storage capacity is calculated according to the output of 15 days. (Feng & Li 2009.).

4 MATERIAL BALANCE CALCULATION OF METHANOL PRODUCTION

As a kind of process calculation, material balance calculation of methanol production is the main basis of chemical process design, equipment selection, production management and process conditions selection. It plays an important role in balancing raw materials, product quality, selecting the best process conditions, determining operation control indexes and reasonably treating production wastewater, waste gas and waste residue. First of all, we determine the parameters of the equipment selected in this design through material balance calculation.

4.1 Material balance calculation of methanol synthesis section

The thesis project annual output of 100,000 tons of refined methanol, calculated by 320 working days per year. The content of methanol in refined methanol is: 99.95%. Composition of crude methanol: [Lurgi low pressure synthesis process] CH_3OH: 93.98%, CH_3OCH_3: 0.2%, Isobutanol ($C_4H_{10}O$): 0.02% and H_2O: 5.8%. Therefore, the output of refined methanol per hour is: $(100000 \times 1000) \div (320 \times 24) = 13020.83\ \mathrm{kg/h}$. The output of crude methanol per hour is: $(13020.83 \times 99.95\%) \div 93.98\% = 13847.97\ \mathrm{kg/h}$ (Chopy 2005.).

The relative molecular mass of CH_3OH is 32, CH_3OCH_3 is 46, $C_4H_{10}O$ is 74 and H_2O is 18, according to the components of crude methanol, the amount of each component is calculated as follows: (Chai 2010, 15-17) The output of methanol per hour is 13014.32 kg/h, the output of CH_3OCH_3 per hour is 27.70 kg/h, the output of $C_4H_{10}O$ per hour is 2.77 kg/h and the output of H_2O per hour is 803.18 kg/h. By dividing the hourly kilogram output of methanol, CH_3OCH_3, $C_4H_{10}O$ and water by their relative molecular mass, we can get the molar output per hour, which are respectively: methanol is 406.70 kmol/h, CH_3OCH_3 is 0.60 kmol/h, $C_4H_{10}O$ is 0.037 kmol/h and H_2O is 44.62 kmol/h.

The chemical reaction of methanol synthesis is as follows:

Main reaction: $CO+2H_2=CH_3OH$ (1)

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

$CO+3H_2=CH_4+H_2O$ (3)

$4CO+8H_2=C_4H_9OH+3H_2O$ (4)

$CO_2+H_2=CO+H_2O$ (5)

In production, it is measured that 7.56m^3 (0.34 kmol) of methane is generated per 1t of crude methanol produced, so the hourly production of CH_4 is: 7.56×13.84797 = 104.69m^3 (4.67 kmol, 74.78 kg).

Ignoring the feed gas, according to (2),(3) & (4), the amount of water generated by reaction (5) is 44.62-0.60-0.037×3-4.67 = 39.239 kmol/h, that is, the water generated in CO inversion is 39.239 kmol/h, equal to 878.95 m^3/h. The solubility of each component in methanol at 5.06 MPa and 40 °C is: H_2 is 0, CO is 1.008 m^3/h, CO_2 is 5.501 m^3/h, nitrogen (N_2) is 0.504 m^3/h, Ar is 0.529 m^3/h and CH_4 is 1.008 m^3/h. (Wang 2001, 114-202.).

$G_{\text{Fresh gas}}$ for fresh gas quantity, Purge gas is 9% of fresh gas. $G_{\text{Fresh gas}}=G_{\text{Purge gas}}+G_{\text{Consume gas}}=G_{\text{Consume gas}}+9\%G_{\text{Fresh gas}}=30483.143+0.09G_{\text{Fresh gas}}$ $G_{\text{Fresh gas}}=33497.96$ m^3/h (Fang 1990, 76-89). Fresh gas consists of H_2, CO, CO_2 and N_2. Respectively:H_2: 63.88%, CO: 33.21%, CO_2: 2.9%, N_2: 0.01%. It is found that the methanol content in the gas from the methanol synthesis tower is 7.12%. Set the gas output of the tower as $G_{\text{out of the tower}}$. It is also known that the gas after alcohol contains 0.61% alcohol. Therefore: $G_{\text{After alcohol}}=G_{\text{Fresh gas}}-G_{\text{Gas consumed}}+G_{CH4}=33497.96-30483.143+105.698=3120.515$ m^3/h, $G_{\text{Out of the tower}}=128217.07$ m^3/h, $G_{\text{Recycle gas}}=G_{\text{out of the tower}}-G_{\text{After alcohol}}\times G_{\text{Produce}}+G_{CH4}-G_{\text{Dissolution}}=128217.07-3120.515-10299.668+105.698-8.021=114916.56$ m^3/h. By summing up the above calculation results, the circulating gas flow and composition of methanol production can be obtained. (TABLE 2)

TABLE 2. Circulating gas flow volume and composition of methanol production

Components	CO	CO_2	H_2	N_2	CH_4	Ar	CH_3OH	H_2O	Total
Flow m^3/h	7231.27	4023.76	91178.39	3667.37	5506.80	2644.18	701.28	11.51	114964.56
Composition %	6.29	3.50	79.31	3.19	4.79	2.30	0.61	0.01	100

$G_{\text{Into the tower}}=G_{\text{Circulating gas}}+G_{\text{Fresh gas}}=114964.56+33497.96=148462.52$ m^3/h, In the same way as calculating the circulating gas flow of methanol production, we can calculate the gas flow into the tower of methanol production.

4.2 Material balance calculation of methanol rectification section

Crude methanol was rectified by three-tower distillation process. Crude methanol contains CH_3OH, CH_3CH_2OH, C_4H_9OH and H_2O. The composition of them is 93.98%, 0.20%, 0.02% and 5.80%. Through their respective proportion in crude methanol, the hourly output can be calculated, which is convenient for the design of distillation column. The methanol content in refined methanol is 99.95%. Under the condition of 320 working days, the annual refined methanol production divided by the production time can get the static methanol production per hour. $(100000 \times 1000) \div (320 \times 24) = 13020.83\ \mathrm{kg/h}$

4.2.1 Material balance calculation of pre tower

First, calculate the material balance of the feed. The feed material includes crude methanol, alkali liquor and soft water. Refer to TABLE 3 for the material composition of them. Crude methanol: $(13020.83 \times 99.95\%) \div 93.98\% = 13847.97\ \mathrm{kg/h}$. Alkali solution: in order to prevent the corrosion of process pipeline and equipment, 8% sodium hydroxide (NaOH) solution reacts with the acid substance in crude methanol to make it weak alkaline. The alkali consumption per ton of crude methanol is calculated as 0.1 g. Then NaOH is consumed: $0.1 \times 13.84797 = 1.385\ \mathrm{kg/h}$, Change to alkali solution: $1.35 \div 8\% = 17.31\ \mathrm{kg/h}$, Soft water: if the soft water is added by 20% of refined methanol, the soft water shall be added:$13020.83 \times 20\% - 17.31 \times 92\% = 2588.24\ \mathrm{kg/h}$.

TABLE 3. Feed composition of pre tower

	CH_3OH	H_2O	NaOH	CH_3CH_2OH	C_4H_9OH	Total
Crude methanol kg/h	13014.32	803.18		27.70	2.77	13847.97
Alkaline liquid kg/h		15.925	1.385			17.31
Soft water kg/h		2588.24				2588.24

Then, calculate the material balance of the discharge. Composition of pre-tower discharge (TABLE 4): Tower bottom: methanol 13014.32 kg/h. And tower bottom water: crude methanol water content 803.18 kg/h, alkali liquor with water: 15.925 kg/h, soft water: 2588.24 kg/h, and total is 3407.345 kg/h. $C_4H_{10}O$ and high boiling matter at the bottom of the tower is 2.77 kg/h, CH_3OCH_3 and low boiling matter at tower top is 27.70 kg/h.

TABLE 4. Composition of pre tower discharge

	CH_3OH	H_2O	NaOH	CH_3CH_2OH	C_4H_9OH	Total
Tower top kg/h				27.70		27.70
Tower bottom kg/h	13014.32	3407.345	1.385		2.77	16425.82
Total kg/h	13014.32	3407.345	1.385	27.70	2.77	16453.52

4.2.2 Material balance calculation of main tower

According to the ratio of 2:3 of the output of the pressurized tower and the atmospheric tower, the liquid in the atmospheric tower contains 1% methanol (Liu 2013). First, calculate the material balance of the feed. Pressure tower: prognosis crude methanol 16453.52 kg/h. Atmospheric tower: $16453.52 - 13014.32 \times 2/5 \times 1/0.9995 = 11245.19$ kg/h

Then, calculate the material balance of the discharge.

Pressure tower: Top $13014.32 \times 2/5 \times 1/0.9995 = 5208.33$ kg/h

Tower kettle $16453.52 - 5208.33 = 11245.19$ kg/h

Atmospheric tower: Top $13014.32 \times 3/5 \times 99\% \times 1/0.9995 = 7734.37$ kg/h

Methanol in tower kettle 99.32 kg/h

Water 3407.345 kg/h

NaOH 1.385 kg/h

High boiling matter 2.77 kg/h

According to the above calculation, TABLE 5 is obtained.

TABLE 5. Summary of material balance of methanol distillation tower (Adapted from Yan 2005)

Components	Materials	Discharge at the top of the pressure tower	Discharge at the top of the atmospheric tower	Discharge at the kettle of the atmospheric tower
Methanol kg/h	13014.32	5208.33	7734.37	99.32

NaOH kg/h	1.385			1.385
Water kg/h	3407.345			3407.345
High boiler kg/h	2.77			2.77
Total kg/h	16425.82	5208.33	7734.37	3510.82

5 CALCULATION AND SELECTION OF MAIN EQUIPMENT

As the main basis of chemical process design, process pipeline, equipment selection, production management and process conditions selection, process calculation plays an important role in balancing raw materials, product quality, selecting the best process conditions, determining the operation control indicators, and reasonably using the production wastes, waste gas and waste heat. The selection of equipment in methanol synthesis directly affects the quality of methanol products. Quality of refined methanol is 99.95% and the alcohol content in residual liquid is 1%. The operating conditions of the project is that, the tower top pressure is 0.01 10^6 Pa, the tower bottom pressure is 130,000 Pa, the tower top temperature is 67 ℃, the tower bottom temperature is 105 ℃, the reflux temperature is 40 ℃, and the feed temperature is 124 ℃.

5.1 Calculation of tower height

The saturated vapor pressure of methanol P_{CH3OH} = 705.38 KPa and the saturated vapor pressure of water P_{H2O} = 229.47 KPa when at 124 °C; The saturated vapor pressure of methanol P_{CH3OH} = 439.08 KPa and the saturated vapor pressure of water P_{H2O} = 123.18 KPa when at 105 °C; The saturated vapor pressure of methanol P_{CH3OH} = 111.61 KPa and the saturated vapor pressure of water P_{H2O} = 27.33 KPa when at 67 °C. (Cao 2005.). At these three different temperatures, methanol also has different volatility.

Because $\alpha=\frac{P^*_{CH_3OH}}{p^*_{H_2O}}$ (α is average volatility of liquid in tower, P is pressure)

$$124°C,\quad \alpha_{124°C}=\frac{705.38}{229.47}=3.074$$

$$105°C,\quad \alpha_{105°C}=\frac{439.08}{123.18}=3.565$$

$$67°C,\quad \alpha_{67°c}=\frac{111.61}{27.33}=4.084$$

Average volatility:

$$\alpha=\sqrt{\alpha_{124}\alpha_{105}}=\sqrt{3.074\times 3.565}=3.310$$

The calculation of the average volatility of the liquid in the tower helps us to know the loss degree of materials in the methanol production process, so that we can get more accurate methanol production quantity.

5.1.1 Find the minimum number of theoretical plates

The mole fraction of methanol in refined methanol X_D is 0.999, the mole fraction of methanol in the residue X_W is 0.006. According to the Fenske equation, the Fenske equation in continuous fractional distillation is an equation used for calculating the minimum number of theoretical plates required for the separation of a binary feed stream by a fractionation column that is being operated at total reflux (Jones & Pugado 2006, 200). In the equation, X_{D1} is (1-X_D) and X_{W1} is (1-X_W). So X_{D1}=0.001, X_{W1}=0.994.

The minimum number of theoretical plates $N_m=\frac{\lg\left(\frac{X_D}{X_{D1}}\frac{X_{W1}}{X_W}\right)}{\lg\alpha}=\frac{\lg\left(\frac{0.999}{0.001}\times\frac{0.994}{0.006}\right)}{\lg 3.310}$=10.04 (Tian 2007)

N_m is the minimum number of theoretical plates required at total reflux.

5.1.2 Find the actual number of theoretical plates

According to the Fenske equation: The actual number of theoretical plates minus the minimum number of theoretical plates divided by the actual number of theoretical plates plus one equals 0.45 (Jones & Pugado 2006, 200). Through the above calculation, we have obtained the minimum number of theoretical plates, so the actual number of theoretical plates can be obtained by substituting the numerical value into the formula.

In the equation, N is the actual number of theoretical plates, N_m is the minimum number of theoretical plates.

$$\frac{N-N_m}{N+1}=0.45 \tag{6}$$

Actual number of theoretical plates N ≈ 19.87

5.1.3 Determination of feed plate position

When the feed position is higher than the optimal feed position, the light component in the liquid phase composition of the feed plate in this state will be higher than the light component in the liquid phase composition of the plate in the optimal position, and the heavy component will be lower than the liquid phase composition in the optimal position. Compared with the optimal position, the number of trays in the distillation section will be reduced, and the number of trays in the extraction section will be increased, so the product quality at the top of the tower will be decreased (light component content), the quality of the heavy component in the tower kettle will be increased (heavy component content). Similarly, when the position of the feed port is lower than the optimal feed port, the light component in the liquid phase composition of the feed plate in this state should be lower than the light component in the liquid phase composition of the plate in the optimal position, and the heavy component is higher than the liquid phase composition in the optimal position. Specifically speaking, rectification is better than the best position with the increase of the number of trays in the section, the number of trays in the retention section decreases, so the product quality at the top of the tower will be improved (the content of light components) and the quality of heavy components at the bottom of the tower will be decreased (the content of heavy components). (Xu 2019, 230-232.).

$$\alpha_1 = \sqrt{4.083 \times 3.074} = 3.543$$

$$N_{\min} = \frac{1}{\ln \alpha_1}[(\frac{x_D}{1-x_D})(\frac{1-x_F}{x_F})] - 1 = 3.731$$

$$\frac{N_1 - 3.731}{N_1 + 2} = 0.45, \quad N_1 = 8.42$$

X_F is the mole fraction of methanol in the feed liquid phase.

5.1.4 Determine the height of packing layer

When bulk metal ring saddle D_N 76 packing, height equivalent of theoretical plates (HETP) is 0.65 ㎜. The packing height of distillation section is 9.452 m. The height of the packing layer in the stripping section is 7.8 m. According to the recommended sectional height of bulk packing, the distillation section is divided into two sections, each section is 5 m high, and the lifting section is divided into two sections, each section is 3.9 m high. (Li & Mai 1983, 32.).

5.2 Determination of tower diameter

In this design, the flooding point gas velocity method is used to calculate the appropriate empty tower gas velocity. Take flooding point rate as $\frac{u}{u_F}=0.7$, Calculation of the pan point gas velocity of the adjustable packing based on Bain Hogan correlation:

$$\lg\left[\frac{u^2{}_F}{g}\left(\frac{a_t}{\varepsilon^3}\right)\left(\frac{\rho_V}{\rho_L}\right)\mu_L^{0.2}\right]=A-K\left(\frac{w_L}{w_V}\right)^{1/4}\left(\frac{\rho_V}{\rho_L}\right)^{1/8} \tag{7}$$

A& K is the correlation constant A=0.06225， K=1.75, Constants A and K are related to the shape and material of packing; g is the acceleration of gravity, which is 9.81 m/s^2 ; u_F is the flooding point gas velocity; ε is the void ratio of packing layer; ρ_V & ρ_L is density of gas phase and liquid phase; μ_L is the viscosity of liquid. If the nominal diameter of bulk metal ring saddle bulk packing is 76 mm, it can be seen a_t =57.6 ε=97% (Li & Mai 1983, 38).

5.2.1 Calculation of column diameter in distillation section

Relevant parameters of the first plate on the top of the tower, Gas flow $q_{n,V}$=1076.87 kmol/h; Liquid flow $q_{n,L}$=326.27 kmol/h. It is calculated that the gas phase composition of the first plate on the top of the tower is 0.999 and the liquid phase composition is 0.995. The average molar mass of gas phase (M_V) is 32.03 kg/kmol, the average molar mass of liquid phase (M_L) is 31.97 kg/kmol.

The mass flow of liquid phase $w_L=q_{n,L}\times M_L$=326.27×31.97=10430.85 kg/h. Gas phase mass flow $w_V=q_{n,V}\times M_V$=1076.87×32.03=34492.15 kg/h (Qi & Du 1982)
Substitute the Bain Hogan correlation to get:

$$\lg\left[\frac{u_F}{9.81}\left(\frac{57.6}{0.97^3}\right)\left(\frac{1.147}{754}\right)0.318^{0.2}\right]=0.06225-1.75\left(\frac{10430.85}{34492.15}\right)^{1/4}\left(\frac{1.147}{754}\right)^{1/8}$$

u_f=6.27 m/s Therefore： u=0.7u_f=4.39 m/s

$$D = \sqrt{\frac{4V}{\pi u}} = \sqrt{\frac{4 \times 1076.87 \times 22.4}{3.14 \times 3600 \times 1.147}} = 1.394\ \mathrm{m}$$

The column diameter in distillation section is 1.394 m.

5.2.2 Calculation of column diameter in stripping section

When the concentration on a plate of a distillation complex tower is similar to or equal to the concentration of raw materials, the feed liquid is introduced from this tower, which is called the feed plate. Stripping section refers to the section of distillation tower below the feeding plate, which is used to extract volatile components from the falling liquid. (Guo & Tian 2000, 78-82.).

The mass flow of liquid phase is:

$w_L = q_L \times M_L = 326.27 \times 22.70 = 7406.329\,kg/h$

Gas phase mass flow is:

$w_V = q_{n,V} \times M_V = 545.24 \times 26.51 = 14454.31\,kg/h$ (Qi & Du 1982)

Substitute the above formula to get:

$$\lg\left[\frac{u^2{}_F}{9.81}\left(\frac{57.6}{0.97^3}\right)\left(\frac{0.814}{830}\right)0.195^{0.2}\right] = 0.06225 - 1.75\left(\frac{7406.329}{14454.31}\right)^{1/4}\left(\frac{0.814}{830}\right)^{1/8}$$

u_f=2.45 m/s Therefore: u=0.7u_f=1.72 m/s

$$D = \sqrt{\frac{4V_s}{\pi u}} = \sqrt{\frac{4 \times 545.24 \times 22.4}{3.14 \times 3600 \times 1.72}} = 1.58m \quad \text{(Palmeira \& Matos 2015)}$$

The column diameter in stripping section is 1.58 m.

5.3 Calculation of pipe diameter

The calculation of the diameter of methanol production equipment includes the diameter of the outlet pipe at the top of the tower, the diameter of the reflux pipe at the top of the tower, the diameter of the feed pipe, the diameter of the outlet pipe at the bottom of the tower and the diameter of the reflux pipe at the bottom of the tower. The calculation of pipe diameter is very important in the calculation of the whole equipment.

It is known that the saturated methanol steam discharge u is 30 m/s, Gas phase density ρ_V=1.147 kg/m^3. First calculate the volume flow q=8.35 m^3/s, then the area of the outlet pipe is obtained by the volume flow rate multiplied by the saturated methanol steam discharge u, and finally the pipe diameter is calculated.

$$q_{V,s} = \frac{W_{V_1}}{\rho_{V_1}} = \frac{34492.15}{1.147 \times 3600} = 8.35\, m^3/s$$

$$\mathrm{d} = \sqrt{\frac{4\mathrm{q}}{\pi \mathrm{u}}} = \sqrt{\frac{4 \times 8.35}{3.14 \times 30}} = 0.595\ \mathrm{m} = 595\ \mathrm{mm}$$

According to GB 8163-87, seamless steel pipe with diameter of 600 mm×16 mm is selected. Its inner diameter d = 600-2×16 = 568 mm, re accounting u = 32.97 m/s. (GB 8163-87 is the Chinese national standard of "seamless steel for fluid transportation")

The steam from the top of the distillation tower is condensed, part of the condensate is returned to the distillation tower as reflux, and the rest of the distillate is the top product. The liquid from the bottom of the tower is partially gasified by the reboiler, and the steam rises along the tower. The remaining liquid is the product at the bottom of the tower. The ratio of the liquid quantity reflux into the tower top to the product quantity on the tower top is called reflux ratio, which will affect the separation effect and energy consumption of distillation operation. (Li 2005, 20-22.).

It is known that u is 2 m / s, Liquid phase density ρ_L=754.0 kg/m^3.

$$q_{V,s} = \frac{W_{L_1}}{\rho_{L_1}} = \frac{10430.85}{754 \times 3600} = 3.84 \times 10^{-3}\, m^3/s$$

$$\mathrm{d} = \sqrt{\frac{4\mathrm{q}}{\pi \mathrm{u}}} = \sqrt{\frac{4 \times 3.84 \times 0.001}{3.14 \times 2}} = 0.0495\ \mathrm{m} = 49.5\ \mathrm{mm}$$

According to GB 8163-87, seamless steel pipe with diameter of 65 mm×4mm is selected. Its inner diameter d = 65-2×4 = 57 mm, re accounting u = 1.5 m/s.

It is known that u is 2 m/s, Liquid phase density ρ_L=830 kg/m^3. The calculation method of the feed pipe diameter is as follows.

$$M_F=32.04\times0.415+18.02\times0.585=23.83\ kg/kmol$$

$$q_{V,s}=\frac{W_L}{\rho_L}=\frac{531.63\times23.83}{830\times3600}=4.24\times10^{-3}\ m^3/s$$

$$d=\sqrt{\frac{4q}{\pi u}}=\sqrt{\frac{4\times4.24\times0.001}{3.14\times2}}=0.0520\ m=52\ mm$$

According to GB 8163-87, seamless steel pipe with diameter of 65 mm×4 mm is selected. Its inner diameter d = 65-2×4 = 57 mm, re accounting u = 1.66 m/s.

It is known that u is 2 m / s. The calculation method of liquid outlet pipe diameter of tower kettle is as follows.

$$M_L=32.04\times0.006+18.02\times0.994=18.10\ kg/kmol$$

$$\rho_L=0.006\times706.5+0.994\times954.95=953.46\ kg/m^3$$

$$q_{V,s}=\frac{W_L}{\rho_L}=\frac{312.66\times18.10}{953.46\times3600}=1.64\times10^{-3}\ m^3/s$$

$$d=\sqrt{\frac{4q}{\pi u}}=\sqrt{\frac{4\times1.64\times0.001}{3.14\times2}}=0.0324\ m=32.4\ mm$$

According to GB 8163-87, seamless steel pipe of 40 mm×3.5 mm is selected. Its inner diameter d = 40-2×3.5 = 43 mm, re accounting u=1.13 m/s.

It is known that u is 30 m/s. The calculation method of reflux steam diameter in tower bottom is as follows.

$$M_V=32.04\times0.021+18.02\times0.978=18.33\ kg/kmol$$

$$\rho_V=\frac{PM}{RT}=\frac{101.325\times18.33}{8.314\times378}=0.591\,kg/m^3$$

$$q_{V,s}=\frac{W_V}{\rho_V}=\frac{545.24\times18.33}{0.591\times3600}=4.70\,m^3/s$$

$$d=\sqrt{\frac{4q}{\pi u}}=\sqrt{\frac{4\times4.7}{3.14\times30}}=0.447\ m=447\ mm$$ (Diao & Wang 2006)

From GB 8163-87 Check and choose= 480mm×16mm Seamless steel pipe. Its inner diameter d=480-2×16=448 mm, recalculation u=29.83 m/s. Elliptical head is adopted, with straight edge height of 40 mm, so thickness of 4 mm and head height of 400 mm.

Tower kettle height is 2620 mm, the tower top height is 920 mm, the jacking pipe height is 240 mm. Open 4 manholes, install the manholes with the distillation section spacing of 600 mm, the distillation section spacing of 540 mm, and the feed port spacing of 1200 mm. Tower height = 25640 mm.

6 WASTEWATER, WASTE GAS AND WASTE RESIDUE TREATMENT

The process of methanol production with coal as raw material takes a long time, which may produce waste water, waste gas and waste residue in each process, and have a certain impact on the environment. The waste gas, waste water and waste residue of the coal to methanol plant are discharged in a large and continuous way, in which the gas contains toxic and harmful gases such as CO, hydrogen sulfide, ammonia, the waste water contains toxic and harmful elements such as sulfur, arsenic, phosphorus and solid coarse and fine slag. Therefore, we can find that there are many kinds of harmful substances in the three wastes, and the degree of harm is different, which can cause a greater degree of corrosion damage to production equipment, but also to human body, natural environment, therefore it is significance to treat the three waste before discharge.

6.1 Pollution of methanol production to environment

The oil and water discharged from the methanol separator and the leakage of the packing of each delivery pump; The most serious pollution of water source in methanol production is the residual liquid discharged from the bottom of distillation tower; Coal water separated from gas and liquid in gasification section. (Yu & Jia 2004, 15-23.).

The expansion gas from methanol expansion tank contains more CO and organic poisons. Non-condensable gas discharged from the top of pre tower during distillation. Others, such as a small amount of non-condensable gas containing alcohol on the top of the distillation column. The flue gas discharged from the boiler contains powder. Dust produced in the process of coal transportation, crushing, screening and drying in the coal preparation system. (Ma, Han, Gao, Wang & Jiang 2008, 30-45.). And about the waste residue is the waste slag mainly comes from the bottom of the gasifier and the boiler.

6.2 Processing method

This chapter mainly discusses the treatment methods of waste water and waste gas. As compared with gas and liquid, solid waste such as waste residue directly harm personnel and equipment relatively small. Equipped with garbage truck to clean up the accumulated materials in time to reduce land occupation, and cover the accumulated materials with cloth, which should not be put for a long time, so as to prevent the air environment of the plant from being polluted by dust flying due to weather, according to the different carbon content, different ways of resource utilization are selected for treatment. The spent catalyst containing precious metals produced by each unit of coal to methanol, such as spent catalyst of shift reaction, spent catalyst of methanol synthesis unit and spent catalyst of sulfur recovery unit, will be returned to the manufacturer for comprehensive utilization. The gasifier slag discharged from the coal gasification plant and the boiler slag and fly ash discharged from the coal-fired steam boiler shall also be considered for comprehensive utilization, such as being sent to the local cement plant or building material enterprise for cement, brick plant and other raw materials for building materials. Waste catalysts and adsorbents that cannot be recycled but are hazardous will be entrusted to units with hazardous waste treatment qualifications for disposal. Domestic waste will be handed over to local environmental sanitation department for unified disposal. (Xue 2012, 175.).

6.2.1 Wastewater treatment method

As long as the toxicity of the wastewater with organics as the main pollutant does not reach the serious inhibition effect, it can be generally treated by biological method. Generally, it is considered that biological method is the most economical and effective way to remove the organics in the wastewater, especially for the organic wastewater. (Yu & Jia 2004, 15-23.).

In this design, anaerobic and aerobic combined biological treatment method is selected, which is a biochemical water treatment process developed in recent years for advanced treatment of high concentration organic sewage (FIGURE 5). After the sewage is collected by the drainage system, it will enter the grid well of the sewage treatment station, after the particles and sundries are removed, it will enter the regulating tank for homogenization and equalization. The regulating tank is equipped with a pre aeration system, and then the signal will be transmitted by the level controller, and it will be sent to the primary sedimentation tank by the lift pump for sedimentation. The wastewater flows automatically to A-level biological contact oxidation tank for acidification, hydrolysis, nitrification and denitrification, reducing the concentration of organic matter, removing part of ammonia nitrogen, and then flows into O-level biological contact oxidation tank for aerobic biochemical reaction. In this case, most of the organic pollutants are degraded through biological oxidation and adsorption. The effluent flows automatically to the secondary sedimentation tank for solid-liquid separation, and the supernatant of the sedimentation tank flows into the disinfection tank It is dissolved in contact with chlorinated tablets and discharged after killing harmful bacteria in water.

The sundries left by the grid are regularly loaded into the trolley and dumped to the waste dump. The sludge in the secondary sedimentation tank is partially returned to the A-level biological treatment tank, and the other part of the sludge is regularly pumped and transported to the sludge tank for digestion, and the supernatant on the sludge tank is returned to the regulating tank for further treatment. (Meng 2016, 135-148.). The advantages of A/ O process in treating methanol wastewater are as follows: this process not only exerts the advantages of anaerobic biochemical energy in treating high concentration organic wastewater, but also avoids the disadvantages of weak resistance to load impact of biological contact oxidation process. It can completely digest the main pollutant methanol in wastewater, which basically does not need further treatment measures. (Gude 2020.).

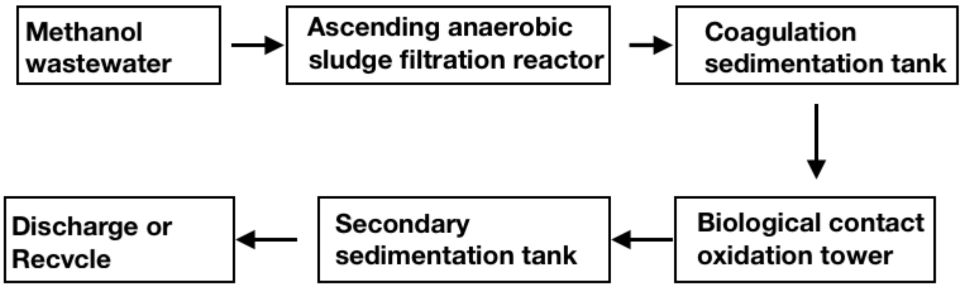

FIGURE 5. A/O Biochemical process for methanol treatment (Adapted from Gude 2020)

6.2.2 Waste gas treatment method

The non-condensable gas discharged from each tower of the methanol rectification system is sent to the fuel gas system for fuel, the expansion gas discharged from the methanol expansion tank is also sent to the fuel gas system. The analytical gas discharged from the stripping tower is sent to the flare of the gasification system for combustion and the acid gas desulfurization recovery system of the desulfurization section.

The flue gas of the boiler is separated by high-efficiency cyclone to remove 85% of the smoke and dust, and then sent to the rotary dryer of the coal preparation system. After the waste heat of the flue gas of the boiler is used to heat the raw material to recover the waste heat, the secondary dedusting of the wet deduster is carried out, and then the induced draft fan is sent to the chimney to discharge into the atmosphere. The dust generated by the crushing and screening of the raw coal is discharged into the atmosphere after the bag dedusting. (Ma 2008, 30-45.).

7 CONCLUSION

After a period of data query, literature search, design sorting, under the guidance and help of teachers, the author successfully completed the design. The design process is advanced and feasible, energy saving and environmental protection, with a certain cost advantage. The mechanical equipment in the design has been rechecked and meets the standards. In the selection of catalysts for methanol synthesis, copper-based catalysts are selected based on the comprehensive comparison of various commonly used catalysts and the principle of advanced technology and investment saving, with good activity and selectivity. In the process of methanol synthesis, the shell and tube methanol synthesis process is selected, the catalyst temperature distribution in the reactor is uniform, the bed plane temperature difference is small, the high heat energy can be recovered, the energy utilization is reasonable, and the methanol content at the outlet of the reactor is high. In the separation of crude methanol, the three-tower distillation process is selected, which can make good use of heat energy and get the effect of energy saving, which is recognized by the industry. In the treatment of wastewater, waste gas and waste residue, according to the actual situation, the waste is recycled to the maximum extent and turned into a treasure. It not only meets the requirements of environmental protection, but also reduces the comprehensive cost of production.

In this design, the atmospheric tower in the methanol separation process is designed. As the recovery ratio of pressure tower and atmospheric tower is 2:1, the output of atmospheric tower is 7066.18 kg / h, the feed temperature is 124 ° C, the top temperature is 67 ° C, and the bottom temperature is 105 ° C. According to the physical parameters, a packed distillation tower with a diameter of 1.6 m is designed. The height of the packing layer is 17.8 m, and the height of the fine sliding section is 10 m, which is divided into two sections, each section is 5 m, and the height of the lifting section is 7.8 m, which is also divided into two sections, each section is 3.9m; the designed tower height is 2564 m.

If the design can be implemented, the plant will be located in the seaport city of Dalian. Dalian is the international shipping center in East China and the international logistics center in East China. It has developed port, highway and railway transportation capacity. Dalian also has two enterprises with an annual refining capacity of over 20 million tons and excellent petrochemical construction facilities. After the project is put into operation, 100,000 tons of methanol products are produced every year, which can be supplied by sea, road and railway to the northern part of China with great demand for energy, with a good sales space. The methanol project should be carried out in strict accordance with the safety regulations from the construction to the production, because most of the raw materials and products are inflammable and explosive substances, which operate under high temperature and pressure, and mainly exist in the state of gas and liquid. Many of them are extremely flammable and toxic, which are easy to leak and evaporate, which brings insecurity and great danger to all kinds of work. Therefore, it is the most important thing for the operation of the plant to strictly control the discharge of waste.

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