Multi-processes VOCs Compression & Condensation + Membrane Separation + Flare Combustion Recovery Treatment

Photo of 800Nm³/h Dichloromethane gas recovery equipment on site

Volume III·Edition: 202107

Three key processes in VOCs treatment:

1. Source reduction: The raw and auxiliary materials containing low VOCs content and featuring low reactivity shall be adopted and the the production processes shall be improved as well.

2. Source recovery: VOCs shall be collected at the source where they are generated. By virtue of efficient and environment-friendly recycling processes, VOCs can be collected, buffered and reused, and the amount of collected VOCs can be reduced, which is the most important part throughout the processes of VOCs treatment.

3. End-of-pipe treatment: For most of the fugitive emissions and a small part of the organized emissions of VOCs, the end-of-pipe treatment processes based on "combustion" is usually adopted due to their low concentration and complex composition.

Fig. 1:Photo of 500Nm³/h Propanone waste gas recovery equipment on site

The comprehensive VOCs treatment technology is composed of two categories, namely **category A** of recovery combination technology and **category B** of destructive combination technology. ①

The VOCs treatment with compression and condensation, absorption and adsorption, and **membrane separation & concentration** is defined as **category A technology**, also known as the source recovery combination technology.

The VOCs treatment with **explosion-proof flare**, **Regenerative Thermal Oxidizer (RTO)** and **Regenerative Catalytic Oxidizer (RCO)** is defined as **category B technology**, also known as destructive combination technology for end-of-pipe emission treatment.

It is difficult to achieve the goal of VOCs treatment alone pure with category A or category B treatment processes technology, so the multi-processes VOCs treatment technology with the combination of category A and category B is usually required to realize the safe, stable and efficient operation of the VOCs treatment device. In practice, the combination of category A and category B processes, such as A+A, A+B, A+A+A, A+A+B, A+A+A+B is adopted.

We recommend two typical VOCs source recovery treatment processes, namely A+A+A and A+A+B, of which A+A+A refers to the processes flow of compression & condensation + membrane separation & concentration+ resin adsorption and A+A+B is the processes flow of compression & condensation + membrane separation & concentration + VOCs explosion-proof flare. They can not only realize the source recovery of VOCs, but also meet the waste gas emission standards.

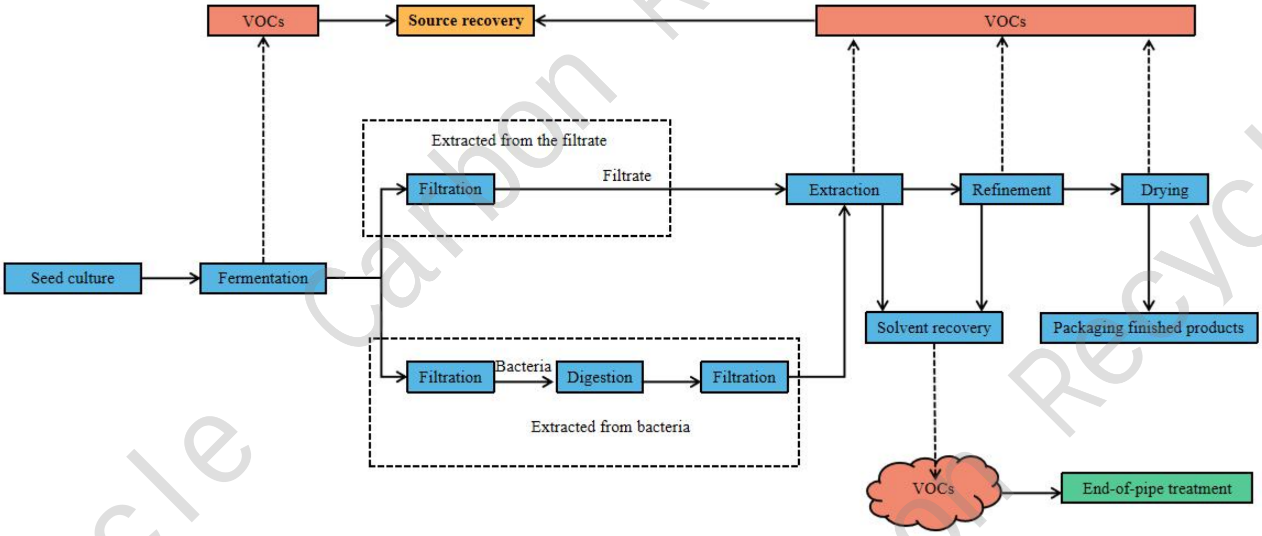

Fig. 2:Fermentation in pharmaceutical production processes, VOCs source recovery and end-of-pipe treatment processes①

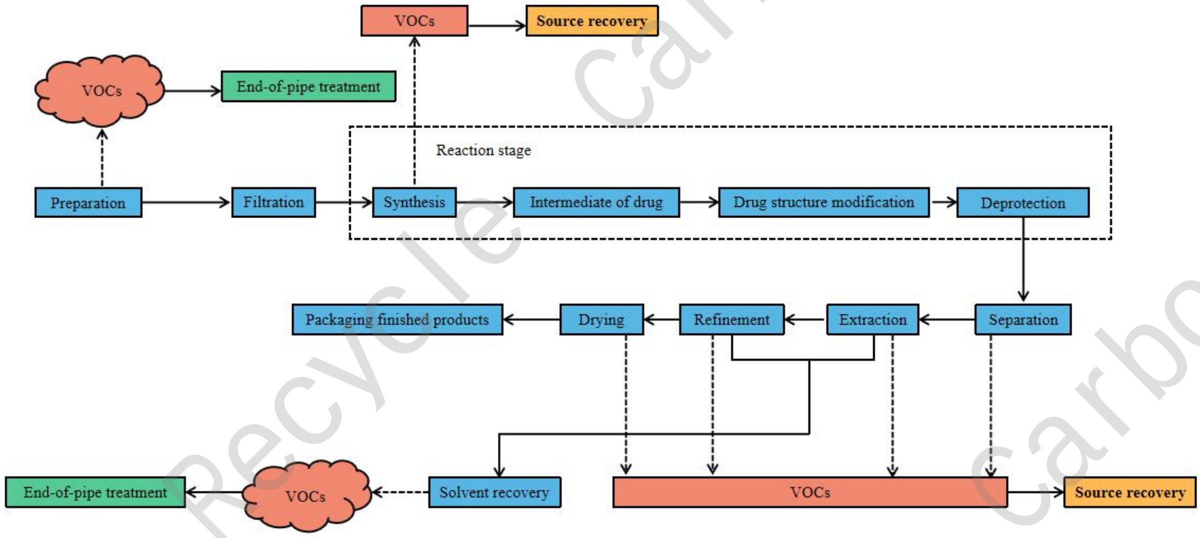

Fig. 3:Chemical synthesis in pharmaceutical production processes, VOCs source recovery and end-of-pipe treatment processes①

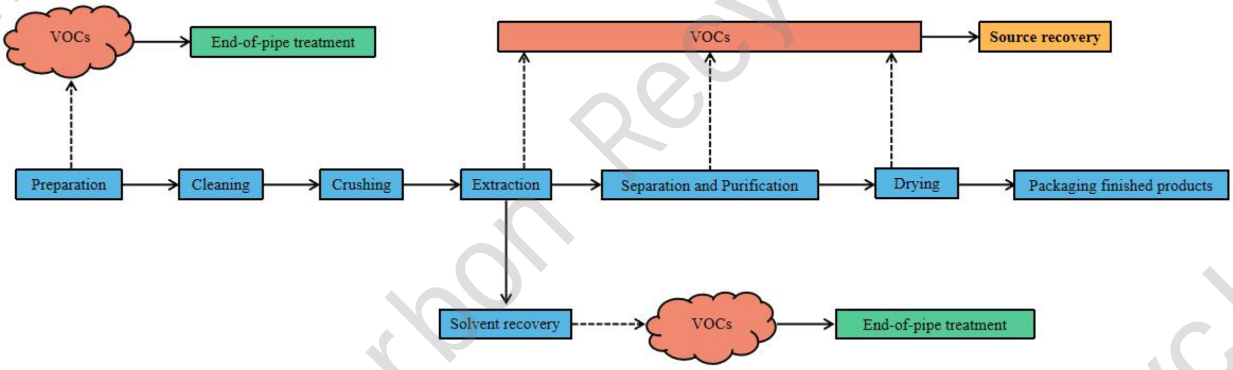

Fig. 4:Extraction in pharmaceutical production processes, VOCs source recovery and end-of-pipe treatment processes①

Note: ①Excerpted *from the Handbook of VOCs Treatment and Use,* compiled by the Department of Atmospheric Environment and the Environmental Planning Institute of the Ministry of Ecology and Environment of the People's Republic of China.

I. Multi-processes recovery treatment of compression & condensation + membrane separation & concentration + resin adsorption/VOCs explosion-proof flare

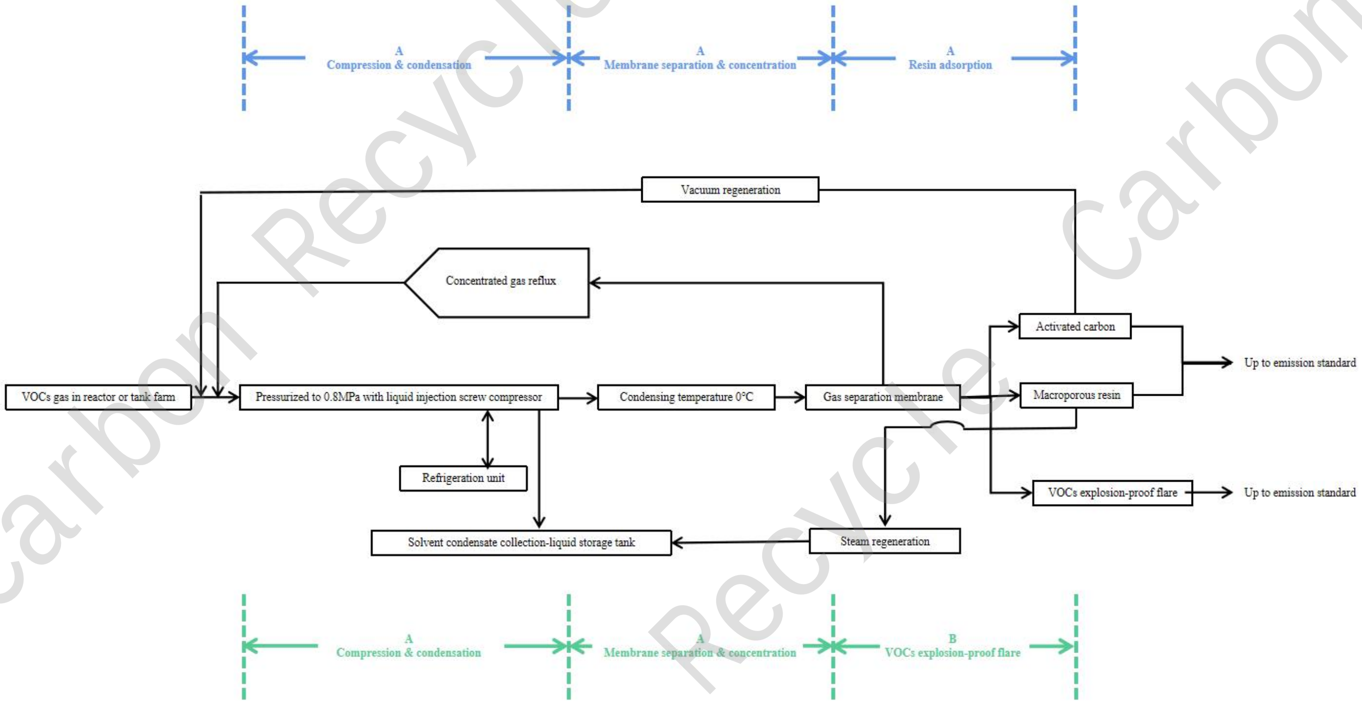

Fig. 5:Flow chart of typical A+A+A and A+A+B VOCs recovery and treatment

The volatile organic compounds (VOCs) from the reactor are compressed to the pressure above 0.8MPa with a liquid injection screw compressor, and the compressed volatile organic compounds (VOCs) is fed into the condenser, which is cooled down to 0°C; in the volatile organic compounds (VOCs) in the condenser, the partial pressure of vapor will greatly exceed that of the corresponding saturated vapor, which will be liquefied. About 50%-80% of the volatile organic compounds (VOCs) can be condensed into liquid for recovery, which flows into the liquid storage tank. The Uncondensed volatile organic compounds (VOCs) will be fed into the gas separation membrane module at a lower concentration.

The volatile organic compounds (VOCs) will be concentrated on the surface of the gas separation membrane, which will permeate the gas separation membrane. On the other side of the membrane (permeate side), the volatile organic compounds (VOCs) with a lower concentration can be concentrated and fed back to the inlet of the liquid injection screw compressor, which will be subjected to compression cascade processing. The concentration of residual volatile organic compounds (VOCs) in the surplus gas (surplus side) after membrane separation is extremely low. If the trace non condensable volatile organic compounds (VOCs) on the surplus side meet the standard, the emission can be directly achieved; otherwise, it can be fed into the resin adsorption (activated carbon) device for further processing. If vacuum regeneration is used, the regenerated gas still contains the enriched VOCs with a certain concentration, which will be sent back to the front end of the liquid injection screw compressor for cascade processing; if the VOCs regeneration is adopted, the regenerated condensate will be recovered.

A small amount of VOCs that is combustible can also be directly burned and destroyed by the VOCs explosion-proof flare, and the waste gas emitted can be up to the standard.

II. Compression & condensation + membrane separation & concentration recovery treatment and nitrogen reuse processes

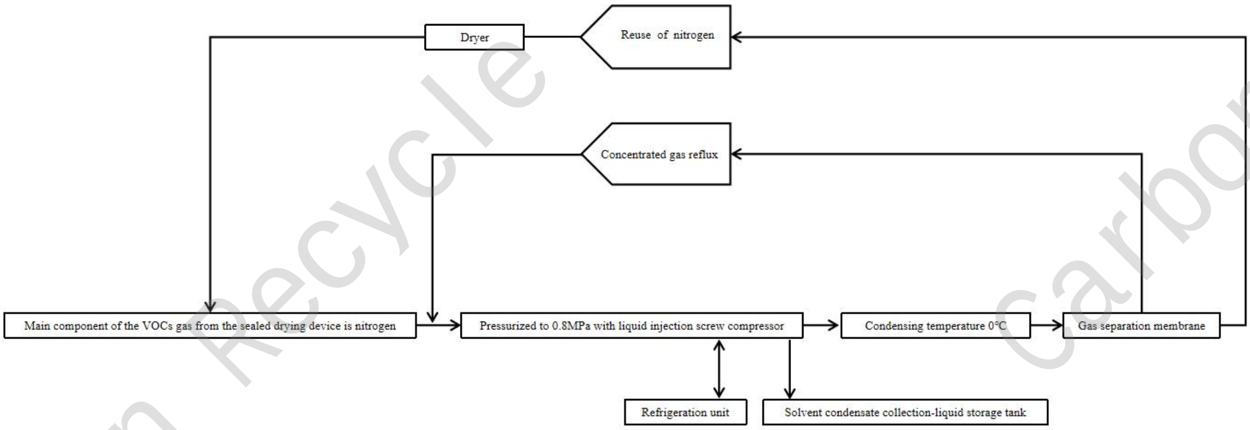

Fig. 6:VOCs solvent recovery and zero emission processes in dryer and three-in-one section

The volatile organic compounds (VOCs) from the reactor are compressed to the pressure above 0.8MPa with a liquid injection screw compressor, and the compressed volatile organic compounds (VOCs) is fed into the condenser, which is cooled down to 0°C; in the volatile organic compounds (VOCs) in the condenser, the partial pressure of vapor will greatly exceed that of the corresponding saturated vapor, which will be liquefied. About 50%-80% of the volatile organic compounds (VOCs) can be condensed into liquid for recovery, which flows into the liquid storage tank. The Uncondensed volatile organic compounds (VOCs) will be fed into the gas separation membrane module at a lower concentration.

The volatile organic compounds (VOCs) will be concentrated on the surface of the gas separation membrane, which will permeate the gas separation membrane. On the other side of the membrane (permeate side), the volatile organic compounds (VOCs) with a lower concentration can be concentrated and fed back to the inlet of the liquid injection screw compressor, which will be subjected to compression cascade processing. The concentration of residual volatile organic compounds (VOCs) in the surplus gas (surplus side) after membrane separation is mainly composed of the nitrogen; after being dried, it will be further fed into the closed dryer (closed container) as a "nitrogen blanket" for recycling.

In this processes realizes, VOCs organic solvent recovery (1), reuse of nitrogen (2) and zero emission of waste gas (3) are realized.

Fig. 7:Photo of 600Nm³/h propylene oxide solvent recovery equipment on site

Fig. 8:Photo of 300Nm³/h methyl tert-butyl ether (MTBE) recovery equipment on site

III. Why can the efficiency of solvent recovery be improved by compression and condensation?

In the chemical production processes, a vacuum pump is usually used to collect VOCs generated in a reactor or other form of reaction device in vacuuming method. According to Dalton's law, the partial vapor pressure of various gases in the mixed gas is equal to the percentage of the gas by volume. Taking the mixture of Dichloromethane and air as an example, the saturated vapor pressure of Dichloromethane at 20°C is 47.39KPa, and the proportion of Dichloromethane in the mixed gas is about 46.8%. Considering the insignificant change in gas pressure before and after the condenser, the temperature of the mixed gas is lowered to 0°C. The saturated vapor pressure of Dichloromethane at 0°C is 19.2KPa, and the proportion of Dichloromethane in the mixed gas is about 18.9%.

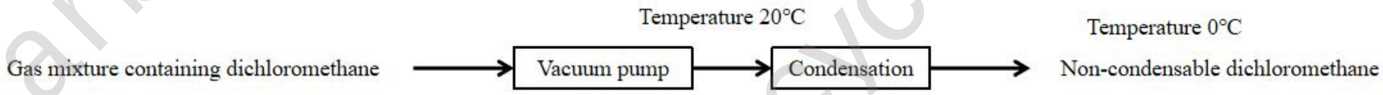

Fig. 9：Pure condensation processes

According to the figure above, with the processes shown in Fig. (7), the temperature of the mixed gas of Dichloromethane and air is reduced from 20°C to 0°C by pure condensation (without compression) processes, and only about 74% of the Dichloromethane is condensed and precipitated, which becomes a liquid solvent.

The compression and condensation fall into the category A recycling combination technology. The "Isotherm compression" processes is adopted; a liquid injection screw compressor is equipped after the vacuum pump, so the pressure of the Dichloromethane mixture at 0°C is increased from atmospheric pressure to 900KPa (absolute pressure), that is, the gauge pressure is 800KPa. Then, the mixed gas is cooled down to 0°C as shown in Fig. (10) Diagram of the compression and condensation processes.

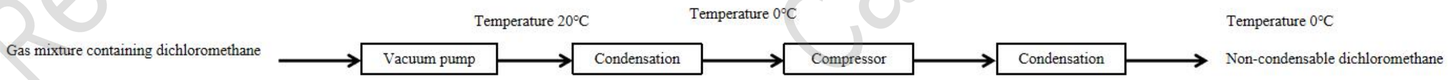

Fig. 10:Compression condensation processes

It can be calculated based on the law of partial pressure with the concentration c=18.9%, and the partial pressure of Dichloromethane is:

$$\mathbf{Pv=c\times P=18.9\times(800+101.325)=170.3KPa}$$

However, according to the law of partial pressure, the saturated vapor pressure at 0°C is only related to temperature. The saturated vapor pressure at 0°C is 19.2KPa, so 170.3KPa is much greater than this value; the excess Dichloromethane will become liquid. The partial pressure of Dichloromethane in the gas state will be maintained at Pv = 19.2KPa. It is shown in the calculation that the Dichloromethane content in the gas is:

$$\mathbf{c=Pv\div P=19.2\div(101.32+800)\times 100\%=2.1\%}$$

Pv－Partial pressure of a certain gas; c-Volume concentration of a certain gas; P-Pressure of the gas as a whole.

Based on the above calculation, after the mixture of dichloromethane and air are compressed at 20°C to 800KPa (gauge pressure), and then cooled down to 0°C. Only 2.1% dichloromethane gas that is not condensed will remain in the mixed gas, and about **97.6%** dichloromethane will be condensed and precipitated, which becomes a solvent.

Comparing the above two processes, the recovery efficiency of compression + condensation is 1.32 times higher than that of the pure condensation processes. That is, the compression and condensation processes recovers more Dichloromethane solvent, which makes it easier to meet the emission standard of the waste gas.

During the compression processes, the temperature is always controlled below t°C, far away from the explosive limit of Dichloromethane gas, so it is a safe "Isothermal compression" processes.

V. Membrane separation

Fig. 11:Photo of 200Nm³/h N-hexane recovery equipment on site

1. What is a membrane②?

The "membrane" is a general term for a thin layered substance for isolation, of which the thickness can range from a few microns to a few millimeters. The "membrane" here refers specifically to materials with selective separation function, also known as separation membrane, through which one or several substances in the fluid can permeate while the other one or several substances cannot, thereby playing the role of separation, purification and concentration. The membrane is also defined as "a three-dimensional structure" internationally. "The size of one dimension in three dimensions is much smaller than the other two, and mass transfer can be realized due to various driving forces."

The membrane has two outstanding features: (1) The membrane is the interface between two phases, which is in contact with the fluids on both sides. (2) The membrane has selective permeability. As for the separation membrane, the external energy or chemical potential difference is the driving force, so that the different substances in the mixture can be separated via the selective permeation of the separation membrane to realize the processes of separating, purifying and concentrating.

Generally, the membrane separation processes is characterized of advantages of operation at room temperature, without phase change, small footprint, high efficiency and energy saving and zero pollution during the production processes.

The membrane separation can be started/stopped quickly, which cannot be achieved by other separation technologies. In theory, the membrane separation can be started/stopped instantaneously. Therefore, compared with traditional gas separation technology (such as cryogenic separation, adsorption separation, etc.), it has unique advantages.

Note: ②Excerpted from *Application Fundamentals of Membrane Separation Materials* published by the Chemical Industry Press in January 2019, authored by Xiao Chang fa, Liu Zhen, etc.

2. Composition of the membrane

The membrane usually consists of three layers, namely a base layer, a support layer and a dense layer. The asymmetric membrane is composed of a dense and thin skin layer and a porous support layer, of which the dense skin layer mainly plays a role of separation; lowering the thickness of the skin layer can increase the permeation rate.

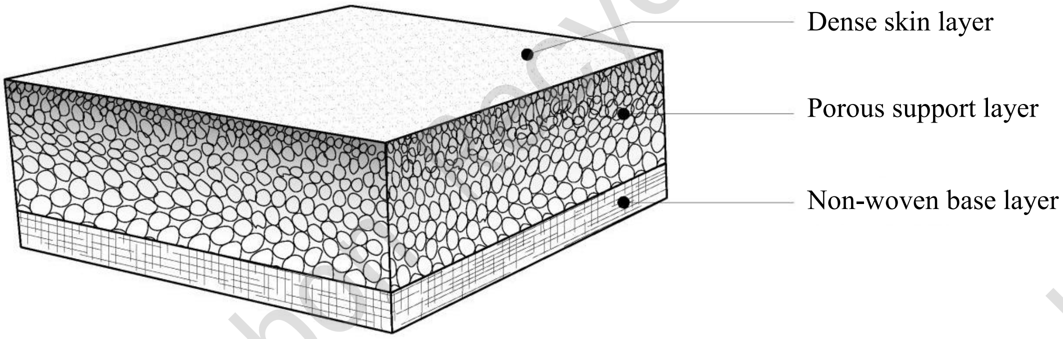

Fig. 12：Three-layer structure of the membrane

3. Fundamental mass transfer mechanism of membrane separation

The fundamental mass transfer mechanism of membrane separations is dissolution and diffusion. The skin layer on the surface of the membrane can be seen as a dense and non-porous neutral interface. The separated substances go into the membrane in a dissolved manner. Their dissolution rate on the membrane surface is different, and the diffusion rate in the membrane body is also different, so the rate of adsorption from the membrane varies. The substance with high dissolution rate and fast diffusion rate will penetrate the dense membrane and be concentrated on the other side of the membrane. Most of the substances with low dissolution rate and slow diffusion rate cannot penetrate the dense membrane. By difference in the dissolution and diffusion rate of the two substances, they are separated. Since most membranes are made of organic polymer materials, according to the principle that like dissolves like, the organic gases are more easily dissolved in the membrane, which means that organic gases are more permeable.

4. Gas permeation in the rubbery polymer membrane

After the following three steps, the VOCs pass through the membrane from the high partial pressure side to the low partial pressure side: ①The gas is adsorbed and dissolved on the high partial pressure side of the membrane; ②Under the action of the concentration difference, the gas dissolved on the membrane surface in the high partial pressure diffuses to the low partial pressure side surface; ③The gas reaching the membrane surface in the low partial pressure side is absorbed from the membrane body; see Fig. (13)for details.

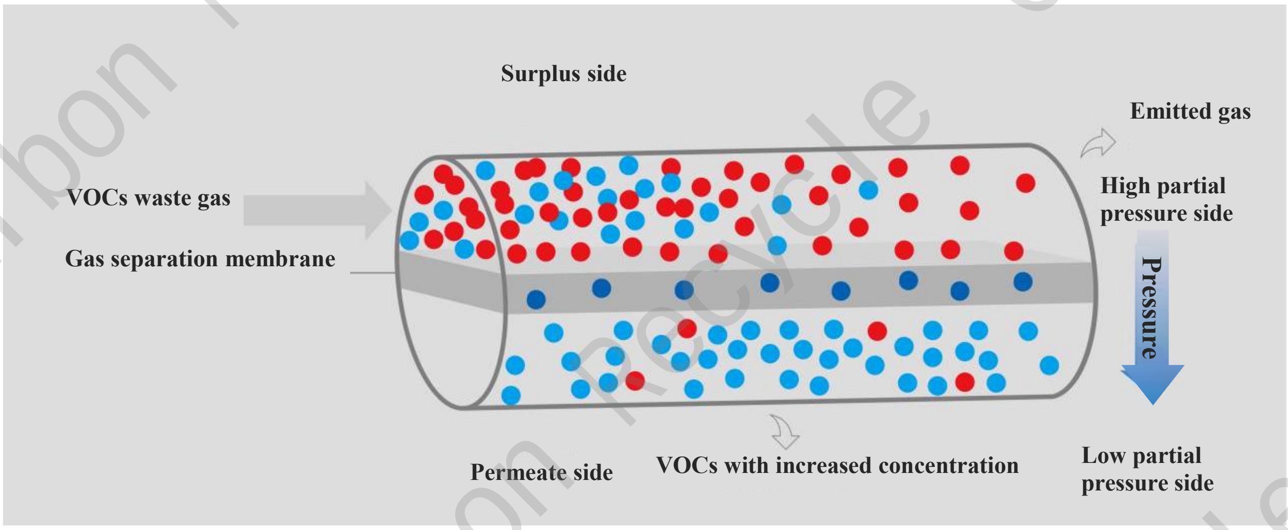

Fig. 13: Separation of gas in the membrane by dissolution and diffusion

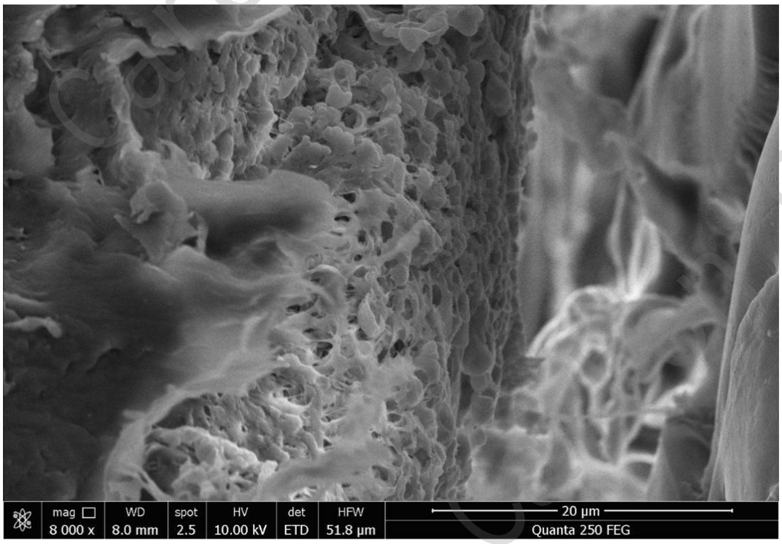

Fig. 14: Microporous structure of the support layer in the membrane under the electron microscope (Nanjing Carbon Recycle Biomass Energy Co.,Ltd.)

5. Why the recovering combination technology of membrane separation (category A) is applied?

The compressed VOCs are fed into the condenser, part of which are condensed. The condensed VOCs are then introduced to the membrane separation module; as driven by the pressure difference, the VOCs permeate the membrane and become permeate gas. The remaining gas that is "blocked" by the membrane and has not passed through the separation membrane is mainly air. The VOCs in the permeate gas is concentrated, which will be circulated to the inlet of the liquid injection screw compressor for cascade compression, and then condensed again. The system will run in such a cascade repeatedly; therefore, most of the VOCs are condensed into liquid, which pave the road for subsequent resource utilization and emission up to standard.

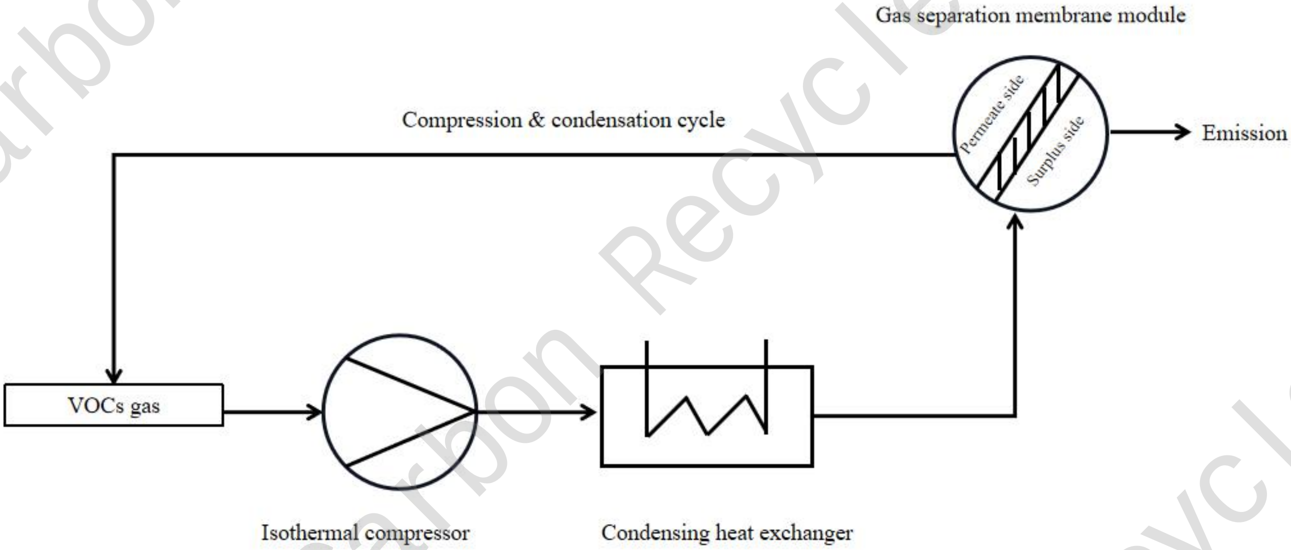

Fig. 15:Flow chart of VOCs recovering combination technology of membrane separation (category A)

V. VOCs explosion-proof flare (AFB series)

Fig. 16: Photo of VOCs flare with premixed combustion

The explosion-proof flare falls into the category the destructive combination of VOCs (Category B). Compared with the Regenerative Thermal Oxidizer (RTO) and Regenerative Catalytic Oxidizer (RCO) of the same category (Category B), it features higher safety in use, which has three most important safety features:

1. Premixed combustion ③

Firstly, the progress of the combustion processes depends on the chemical kinetics of fuel oxidation. Secondly, it also depends on the diffusion processes of the mixture of fuel and oxidant (combustion-supporting gas). The (VOCs) flare with premixed combustion type can be started fast, almost taking no time for pre heating preparation; it also features fast burning rate, short flame without obvious flame profile, high burnout rate with nearly zero chemical incomplete combustion loss, which is dynamic combustion.

Note: ③Excerpted from *Properties and Applications of Gas Combustion,* published by the China Petrochemical Press, editor-in-chief : Song Shao fu and Li Zi hui.

2. Anti-flame burner (AFB)

The metal melt-blown burner is composed of a multi-layer densely woven mixed metal mesh. The evenly mixed combustible gas passes through the multi-layer densely woven composite metal mesh at a certain flow rate to form a thin flame layer on the surface of the metal mesh. The passing speed of the combustible gas is greater than the burning speed of the combustible gas.

Fig. 17:Combustion status of explosion-proof flare under monitoring of CCTV video

3. Safety design

In the design of VOCs flare, not only the fluctuation of the waste gas flow rate of high-concentration VOCs needs to be considered, but also the significant changes in the composition and calorific value of the waste gas in reality needs to be taken into account, so as to meet the emission requirements after combustion. Our company has developed a VOCs explosion-proof flare based on the principle of lean combustion. It is composed of the proportional mixer, homogenization chamber and porous medium burner to achieve full premixed combustion. The premixed combustion has the advantages of full combustion of VOCs components, short combustion flame and smaller footprint of combustion chamber. Moreover, the porous media burners can promote the mass and heat transfer rate of the combustion processes, greatly improving the stability of the combustion flame and ensuring stable combustion under the fluctuation in the intake flow and composition of the VOCs waste gas. Priority is given to preventing backfire and avoiding pre combustion of VOCs explosion-proof flare in the mixing section before the burner.

The safety accidents such as explosion and backfire in the conventional burner mostly occur in the two time periods of ignition and flame out, so processes control in both time periods is the focus in the safety of the combustion flare.

(1) Based on the gas flow rate, air-fuel ratio, and combustion heat designed based on thermal engineering and professional combustion software, the fuel gas flow is controlled on the basis of the combustion state.

(2) Easy ignition: It is powered with an independent branch, which is ignited with high-voltage dual ignition electrodes; the high ignition voltage is 7.5KV, which can result in high success rate in ignition.

(3) Flame and flame temperature monitoring: With the ultraviolet flame (UV) detection probe (working temperature range: -40℃-+120℃). The ultraviolet probe is not sensitive to sunlight and infrared rays, which is designed with anti-interference and short-circuit protection in the flame signal. The measurement range is 190-270nm, and the protection rating is IP65. It features multi-point flame temperature and smoke temperature probe to monitor the burning state of the flare and monitor the temperature of the flue gas.

(4) CCTV video monitoring of flame burning status.

Fig. 18:Waste gas pipe of VOCs flare

(5) The flare for the waste gas of low calorific value is capable of flameless combustion with premixed gas, which features high combustion control to ensure that the combustion temperature is between 760-1300 ℃.

(6) The flare for the waste gas of low calorific value can ensure that the burnout rate of VOCs is greater than 97%. Moreover, the emission of NOx is lower than 15ppm. The waste gas emissions after combustion all meet the environmental protection emission standards.

(7) As made of environment-friendly high-temperature resistant ceramic fiber refractory blocks, the thermal conductivity of ceramic fiber at 1000 ℃ is 0.36 ~ 0.38W/(m*k), so the hazards to nearby operators and equipment is minimized.

VI. Economic analysis of Petroleum ether recovery equipment in raw materials in pharmaceutical cases

The 100Nm³/h Petroleum ether recovery device can recover 77Kg petroleum ether per hour as calculated with the inlet concentration (membrane separation & concentration) of 20% and the recovery rate can reach 99.5%.

At present, the market price of petroleum ether (a mixture of Pentane and Hexane) is about 7,500 yuan/ton, so 57.75 yuan per hour (excluding environmental protection costs) can be saved directly for the enterprise. This device is assumed to run for 8,000 hours per year, so it can save 462,000 yuan per year. This device costs about 1,100,000 yuan, and the payback period of this device is about 2.38 years.

Fig. 19:Photo of 100Nm³/h Petroleum ether solvent recovery equipment on site

Nanjing Carbon Recycle Biomass Energy Co., Ltd.

Official website: http://www.rectec.com.cn

公司地址：南京市江宁区滨江开发区闻莺路 **8** 号

Address: No. 8, Wenying Road, Binjiang Development Zone, Jiangning District, Nanjing 211162 P.R.China

Tel: 0086 2552657661 / 52657665/84414484

E-mail: njcabt@vip.163.com

Careline: Mr. Yang (0)18112083001/Mr. Wang (0)13951616035/Mr. Yang (0)18606197066