ISSN: 2664-9640

Membrane gas separation technology application

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Abstract

Due to its benefits, such as high efficiency and energy savings, membrane gas separation technology is increasingly being utilized in numerous parts of industrial production. Gas separation technology is becoming more and more common in today's world. Advanced membrane material research has already made significant strides, and our use of membrane materials has steadily moved from lab tests to practical manufacturing. At the moment, membrane separation performs well in processes like air separation, helium extraction, carbon capture, etc., and as a result, some novel procedures and solutions have progressively been developed in conjunction with the performance of membranes.

Keywords

Gas separation, membranes, helium extraction, carbon capture.

1. Preface

Gas membrane separation technology is a more mature separation technology developed in the 20th century, it has the advantages of energy saving, high efficiency, simple operation, easy use, no secondary pollution, and recovery of organic solvents compared with the traditional adsorption, freezing and condensation separation, but due to the lack of high-efficiency membrane separation material varieties, the current gas membrane separation technology is only applicable to certain fields, such as air separation oxygen enrichment technology, natural gas extraction in Helium, carbon dioxide capture and other applications, can also be extended to more areas, so the continuous research and development of gas membrane separation technology, including membrane materials, membrane components, and optimization, membrane technology, etc.

2. Membrane separation principle

The membrane section is divided into symmetric membrane, asymmetric membrane, composite membrane, flat membrane, tubular membrane, hollow fibre membrane, etc.

For non-porous membrane materials, the transfer of gases through the membrane

is generally explained by the dissolution-diffusion mechanism, and the process of gas transmission through the membrane can be divided into three steps.

In the first step, the gas is dissolved by adsorption on the surface of the upstream side of the membrane.

In the second step, the gas on the upstream surface of the membrane diffuses through the membrane, driven by the concentration difference.

The third step, the desorption of gas from the downstream surface of the membrane, is the rate control step for gas permeation through the membrane because of the slow permeation and diffusion process of the gas within the membrane.

For porous membrane materials, the transfer of gases through the membrane is generally explained by Knudsen diffusion, surface diffusion, capillary condensation and molecular sieve

ISSN: 2664-9640

fractionation diffusion. Due to the differences in pore size and pore surface properties of porous membrane materials, the degree of interaction between gas molecules and the membrane can vary, so in practice the gas transfer mechanism in the membrane is often a combination of these mechanisms.

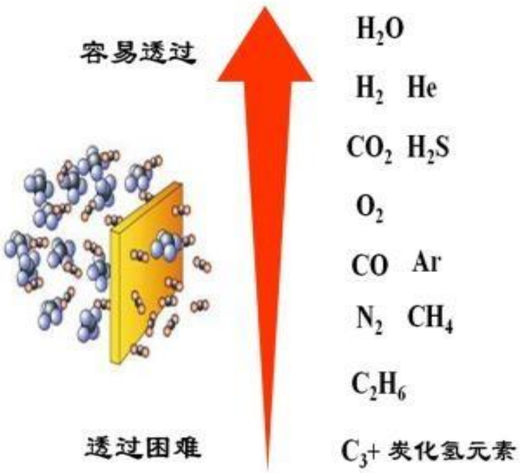

Figure 1 Schematic diagram of common gas membrane permeation rates

3. Common applications

3.1. Oxygen-enriched membranes

Oxygen-rich air is usually referred to as "oxygen-rich air" when the volume fraction of oxygen exceeds 20.93%. In addition to the important role of ordinary air, such as combustion and breathing, oxygen-rich air also has obvious energy-saving and environmental effects, medical and health functions. The main methods of producing oxygen-rich air in industry are deep-cooling separation, variable pressure adsorption and oxygen-rich membrane methods. The deep cooling separation method can obtain high purity oxygen with a purity of 99% or more, butthemethodhas high requirements for ancillary devices such as compressors and heat exchangers, and is suitable for large-scale production of high purity oxygen. The variable pressure adsorption method is generally used in small to medium scale production of medium oxygen (60% to 90% volume fraction), while the oxygen enriched membrane method is mainly used in small scale production where the oxygen volume fraction requirement is not high (<40%). Compared with other methods, the oxygen-enriched membrane method is characterised by simple equipment, easy operation,safety,fast start-up,no environmentalpollution,lowinvestment, significant energy saving, green and environmental protection.

Organic oxygen-rich membrane materials mainly include cellulose acetate, polysulfone (PSF), polyimide (PI), etc. Liu Guangxian et al.[1] prepared a PI oxygen-rich membrane with an oxygen-rich volume fraction of 28%; Ismail et al. [2] produced a highly selective PSF hollow fibre membrane with silicone rubber plugs for separation of oxygen and nitrogen systems with a separation factor of 7.32. Currently PSF membranes are mainly used as support materials for composite separation membranes. Inorganic oxygen-rich membranes are oxygen-rich membranes made of inorganic materials such as metals, metal oxides, ceramics, carbon, porous glass, etc. The advantage is that high separation factors can be obtained, but the permeation flux is low. Tin et al. [3] prepared carbon membranes to increase the selectivity of oxygen and nitrogen from 6.4 to 8.8; Mark［4］ reported that the separation factor of oxygen and nitrogen with porous carbon membranes can reach 30 at 25°C.

At present, the large-scale application of gas separation oxygen-rich membrane is mainly polymer organic membrane, this kind of membrane usually has good flexibility, permeability selectivity but there is a low permeability rate, not high temperature, corrosion resistance and other shortcomings; inorganic membrane in the high temperature, corrosive media and other aspects of the unique physical and chemical properties but its selectivity is poor manufacturing costs thanthe polymer membrane much higher［5］. The composite oxygen-rich membrane can combine the excellent performance of both, both high permeability and high selectivity and can achieve flexibility, strength, aging resistance and other properties of the unity is one of the direction of oxygen-rich membrane materials research and development.

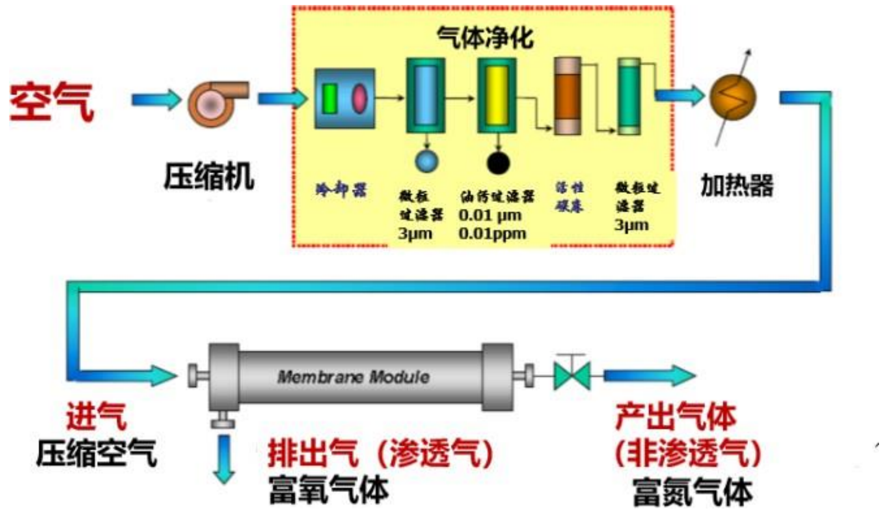

Fig. 2 Schematic diagram of the operation of the oxygen-enriched membrane

At present, the membrane method of oxygen-enriched combustion energy-saving technology has become very mature. Joshi et al. showed that NOx emissions were reduced by 40% to 50% in a natural gas-fired glass kiln after six months of continuous oxygen-enriched experiments. Corning in the United States reported the experimental results on the transformation of manifold glass kilns to oxyfuel［6］, for 165t/d kiln oxyfuel, so that NOx reduced by 81%, natural gas savings of 45%, and that oxygen-rich combustion so that the age of the furnace can beincreased from the original 20 months to 3 years, operating cost savings of 12% ~ 13%, the cost per ton of kiln decreased by 8%. On the domestic side, Jinzhou Petrochemical in late 2019 adopted the membrane method of partial oxygen-enriched combustion, and the fuel gas consumption per unit feed of the equipment was reducedfrom 16.8Nm^3 /t to 14.93Nm^3 /t after commissioning, with an energy saving rate of 11.1% and good economic benefits.

3.2. Hydrogen separation

The separation of hydrogen using the membrane method is often applied in the petrochemical industry, where set membrane groups are used to recover hydrogen from ammonia slack gas, synthetic methanol slack gas and refinery gas. Common ammonia plant slack gas and alcohol slack gas hydrogen recovery processes are as follows.

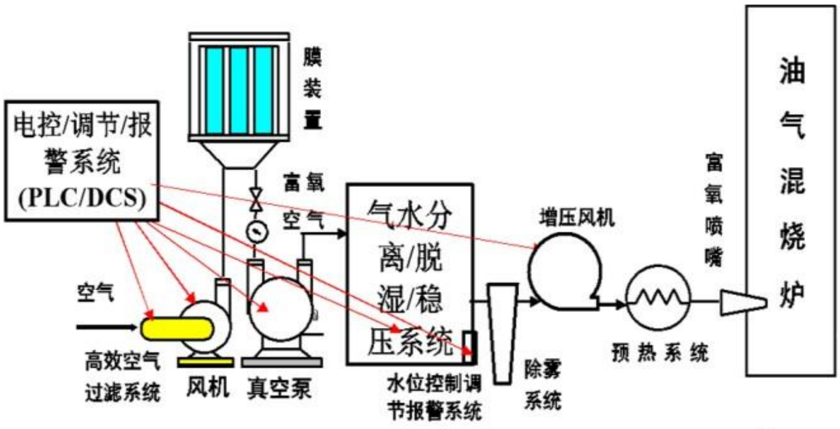

Fig. 3 Oxygen-rich combustion in the heating furnace

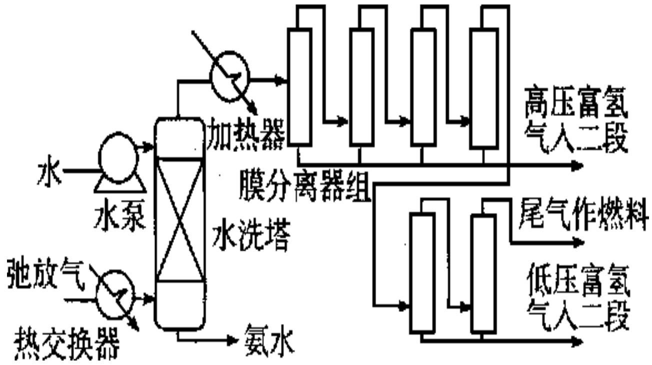

Figure 4 Schematic diagram of the hydrogen recovery process from ammonia plant slack gas

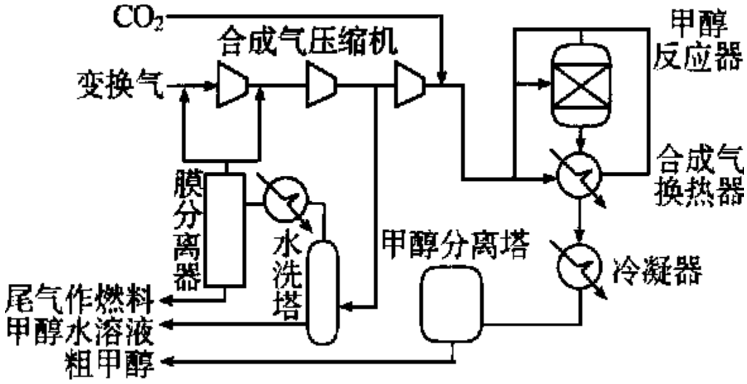

Figure 5 Schematic diagram of the hydrogen recovery process from methanol slack gas

During the refining and petrochemical production process a large amount of hydrogen-containing gas is produced in the past and, as there is no suitable recovery method, it has to be discharged or burned off. According to foreign statistics, the hydrogen burnt worldwide accounts for about 40% of the refinery's hydrogen volume,which is a huge loss. Therefore, in recent years, in addition to the development of hydrogen production plants, foreign countries have also paid special attention to the recovery of H_2 from various hydrogen-containing tail gases. Since the emergence of effective hydrogen separation and recovery technologies such as membrane method, PSA and deep cooling method, all countries have attached great importance to the recovery of hydrogen from hydrogen-containing tail gases. Since the 1980s, the US and Japan have successfully used gas membrane separation technology to recover hydrogen from refinery gas. The Japanese Department of Aerospace has compared three separation methods, such as membrane separation, PSA and deep cooling separation, to recover hydrogen from refinery gas, and the results of the comparison are shown in the following table[7] .

Table 1 Comparison of methods for recovering hydrogen from refinery gas

The Process	Hydrogen recovery/%	Producthydrogen concentration φ/%	Flow rate / (N m^3 $\cdot h^{-1}$)	Power consumption/kW	Steam consumption/ (kg$\cdot h^{-1}$)	Cooling water consumption / (t$\cdot h^{-1}$)	Investment costs/US$ million	Equipment area/m^2
Membrane separation (80©°C)	87	97	73,940	220	230	38	1.12	8.0
Membrane separation (120©°C)	91	96	76 619	220	400	38	0.19	4.8
Absorption	73	98	60 010	370	-	64	2.03	60.5

As can be seen from the comparison in Table 1, membrane separation has thelowest energy consumption and its investment costs can be saved by more than 50%.

Table 2 Hydrogen recovery by membrane method in different refinery gases

Refinery gas	**Separate objects**	**In raw material gas** H_2 Concentration φ/%	**In permeable gas** H_2 Concentration φ/%	**Hydrogen recovery rate/%**
Catalytic reforming tail gas	H_2/CH_4	70 to 80	90-97	75 to 95
Catalytic Cracking Dry Gas	H_2/CH_4	15 to 20	80-90	70 to 80
Hydrofinishing tail gas	H_2/CH_4	60 to 80	85 to 95	80-95
PSA desorption	H_2/CH_4	50 to 60	80-90	65 to 85

A diagram of the process for recovering hydrogen from hydrocracking tail gas using membrane separation technology is shown below.

ISSN: 2664-9640

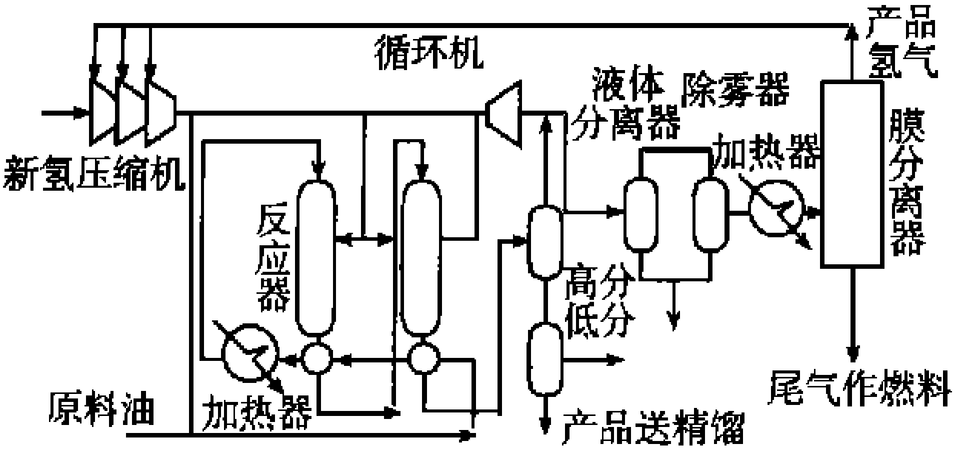

Figure 6 Schematic diagram of the hydrogen recovery process from hydrocracking tail gas

3.3. Membrane VOC Recovery for Petrol Filling Stations

In the process of refuelling and unloading, a large number of hydrocarbon VOCs (volatile organic compounds) are generated in petrol stations. These VOCs are not only hazardous to human health, but also pollute the environment and waste a lot ofoil resources, so it is necessary to carry out unloading and refuelling oil and gas recovery. Usually membrane separation recovery oil and gas process are: membrane +cooling or condensation, membrane + absorption, membrane + adsorption and other combined processes and only use the membrane without involving other treatment processes of a single membrane separation method, a single membrane separation oil and gas recovery has a simple process, small footprint, high degree of automation, more suitable for petrol stations with little space, safety and automation requirements of high occasions, a single membrane separation method principle is to use hydrocarbons VOCs and air through the membrane at different rates to achieve the separation of hydrocarbon VOCs and air, the driving force is the pressure difference between the inlet side of the membrane and the permeate side.

The main improvement of this process is that the oil and gas is "breathed" from the storage tank, rather than directly from the oil and gas recovery line, and the process is that the oil and gas from the refuelling oil and gas recovery line is first recovered to the storage tank, and then the oil and gas breathed from the storage tank is treated by membrane separation. The membrane separation process, in which the storage tank acts as a buffer and the inlet pressure of the membrane module can be controlled very precisely, offers the possibility of practical application of the process.

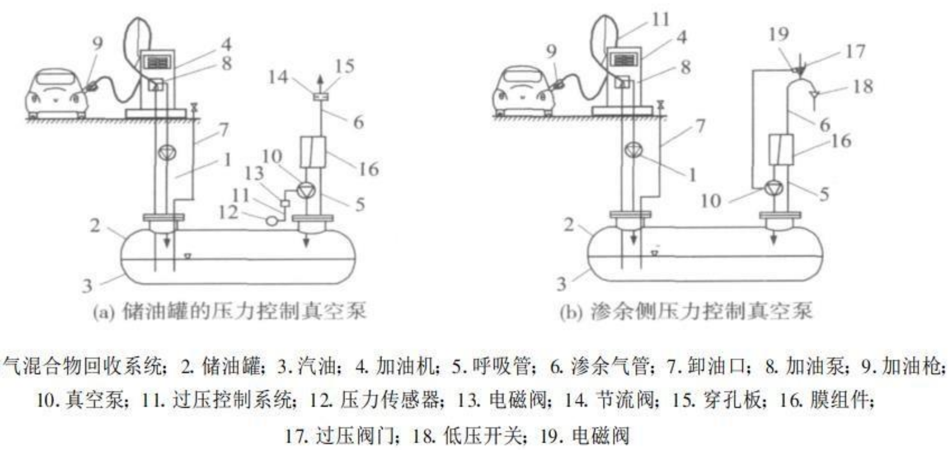

Figure 7 Tank oil and gas recovery system

Membrane VOC recovery is characterised by a small footprint and a high degree of automation. Throughout the membrane gas separation process, there is a need to improve the separation coefficient and permeate gas transmission as well as simplify the process and improve the stability of the control system.

3.4. Helium extraction from natural gas by membrane

Due to its extremely low boiling point (-268.85℃), strong diffusivity, insolubility in water and good thermal conductivity, helium plays an irreplaceable rolein defence, biomedical, nuclear and cryogenic industries and is therefore the subject of much research. The main technologies for helium extraction from natural gas are deep cooling, pressure swing adsorption, absorption and membrane permeation separation. The basic principle is that the boiling points of the different components of natural gas are different, and it is difficult to liquefy He at low temperatures, while CH_4, N_2 and other alkanes can be liquefied and separated from He by low temperature distillation. [8] Although this technology can extract high purity He from

natural gas, it has low operational flexibility, large investment in equipment and high operating costs. Due to the low He content of natural gas in China, the cost of extracting He from natural gas by the deep cooling method is high, which restricts the scale up of natural gas helium extraction plants in China [9]. The adsorption method is based on the difference of the adsorption capacity of each component in natural gas on the surface of the adsorbent to separate out the He in it. In recent years, with the

development of separation membrane technology, membrane separation technology

with the advantages of high separation efficiency, low operational energy consumption and high operational flexibility has been gradually applied to the experimental research process of natural gas helium extraction, showing good application prospects.

He separation membranes can be divided into inorganic membranes and polymermembranes. According to the characteristics of membrane materials can be divided into rubber state membrane and glass state membrane. For inorganic membranes, Fu et al. [10] doped Ni in silica membranes by sol-gel method and the experimental results showed a great improvement in the resistance to densification of silica membranes. The separation coefficient of He/CH_4 was up to 600 at 300 °C. Campo et al. [11] prepared a carbon molecular sieve membrane using cellophane as a precursor and increased the permeation rate of He from 3.33×10^{-12} mol/(m^2 -s-Pa) to 33.67×10^{-9} mol/(m^2 -s-Pa); compared with inorganic separation membranes, polymer separation membranes have the advantages of low production cost, good flexibility and easy Choi et al. [12] prepared polyimide based gas separation membranes based on thermalrearrangement reaction, which have high selectivity and high permeability with a permeation rate of 368.33×10^{-9} mol/(m^2 -s-Pa) for He and a selectivity coefficient of 165 for He/CH4 and 61 for He/N2. Due to the excellent gas separation performanceof polyimide membrane materials have been applied in the field of natural gas helium

extraction. The industrialized membranes of Prisson Membrane (USA) and UBE(Japan) both use polyimide membranes for natural gas helium extraction. The selectivity coefficients of He/CH4 and He/N_2 of Prisson Membrane can reach about 120 and 50. [13]There is still a lack of corresponding high-performance polyimide membrane materials in China, and there are no commercialized polyimide based He separation membrane modules for the time being.

Compared to deep cooling, membrane natural gas helium extraction technology has the advantages of low investment, low energy consumption, low operating costs and high operational flexibility. In recent years, the research of membrane natural gas helium extraction technology in China has become hot, and some of them are already in the industrial trial stage, but commercial He separation membranes are still mainly imported, and they are mainly

ISSN: 2664-9640

general purpose gas separation membranes, and there are few functional membranes for He separation.

3.5. Carbon capture

Compared with other methods, the membrane separation method has theadvantages of high separation efficiency, low energy consumption, simple operation (easy to scale up and self-control), environmental friendly and small footprint, etc. Moreover, the higher the concentration of CO_2 , the more economical the membrane separation method is, which is one of the most promising methods for CO_2 gas separation.[14]

Table 3 Common carbon capture methods

Catching methods	Principle	Features
Physical absorption method	Under specific conditions of low temperature and high pressure, organic solvents such as water, methanol and polyesters with high solubility, good selectivity and stable properties for carbon dioxide are used as absorbents, with subsequent changes in operating conditions to release carbon and solvent regeneration without chemical reactions during the separation process	Good absorption, low energy consumption, regeneration of the absorber without heating, solvent is not easy to corrode the equipment, but its disadvantage is poor absorption selectivity and low recovery rate. It is suitable for mixed gases with high carbon dioxide content.
Chemical absorption method	Absorbents such as MEA react with CO2 to form a more stable carbamate, and through a regeneration process release CO2 and absorbent regeneration	The chemical absorption method is technically mature and suitable for fixed point, high emission conditions.
Membrane Separation	The separation of components of a gas mixture is achieved by using the difference in the dissolution and diffusion rates of different gases in a membrane. Depending on the material, membranes used for selective separation can be divided into inorganic membranes (e.g. metal and ceramic membranes) and organic membranes (e.g. aromatic polyamide membranes, polyethersulfone membranes, cellulose membranes etc.).	Although the membrane separation method is easy to operate, simple process, long service life and low energy consumption, the membrane material has low heat resistance and low separation efficiency, making it difficult to obtain high purity CO2

ISSN: 2664-9640

Cryogenic distillation	The physical process of separating CO2 by low temperature condensation using the different relative volatilities of the components in the raw gas, generally after several compressions and coolings, causing a phase change to separate the CO in the gas by distillation2	No chemical reagents are used in the process, which meets environmental requirements; however, the high energy consumption of the temperature change process and the large number of moving equipment are its disadvantages.
Variable Pressure Adsorption	Selection of adsorbents for adsorption performance	Meets the requirements for gas partitioning and buffering.

The membranes used for CO_2 membrane separation include inorganic membranes, organic polymer membranes, of which inorganic membranes are mainly porous membranes. The difference in pore size and the nature of the surface inside thepore makes the interaction between CO_2 and the medium different, thus showing different separation effects on CO_2 . The mechanisms of gas transfer include Nusson diffusion, surface diffusion, capillary coalescence and molecular sieving. Compared with polymer membranes, inorganic membranes have the advantages of high stability,good strength, long life and easy control of pore size and pore size distribution; however, due to material and manufacturing process limitations, inorganic membranes have high manufacturing costs, brittle materials and installation and sealing difficulties, so the current research on CO_2 separation inorganic membranes is mostly at the laboratory level.

As with inorganic membranes, conventional organic polymer membranes for gas separation are mainly screened according to the size of the gas molecules, i.e. by increasing the diffusion coefficient D to facilitategas separation, while the diffusion rate will increase with pressure, which requires the gas mixture to be separated to be pressurised, which will consume a lot of energy and is not conducive to energy conservation. Gas permeation through dense polymer membranes is usually explained using the dissolution-diffusion mechanism［15.16］ . The permeation of gases through polymer membranes can be explained as consisting of an adsorption process, a diffusion process and a desorption process. In general, the gas permeates and diffuses slowly through the membrane, while both the adsorption and desorptionprocessesonthemembranesurfacereachequilibriumrelatively quickly, so that the diffusion process is the controlling step in gas permeation through the membrane. In recent years, the preparation of energy efficient polymer membranes for gas separation by increasing the solubility factor S has become a more promising research direction.

CO_2 membrane separation method process is relatively simple, no liquidity of the machine, easy to operate, low energy consumption, itsprocess flow is shown below, mainly by the compressed gassourcesystem, filtration and purification processing system, membrane separation system, samplingmeteringsystemfourcomponents.Themembraneseparation system is the core of the whole process and is the main place for gas separation.Thekeyistochoosesuitablemembrane componentsandmembrane materials.

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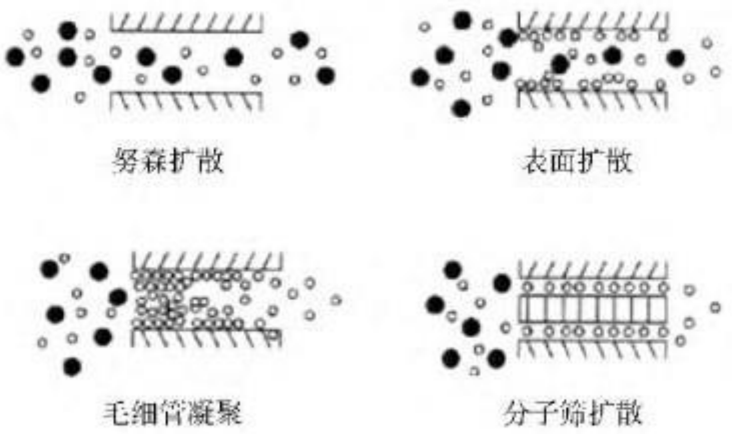

Figure 8 Illustration of the mechanism of CO_2 transfer in porous membranes

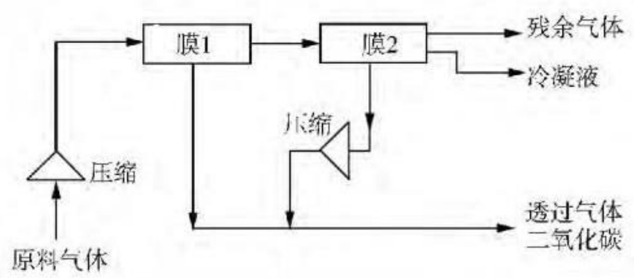

Figure 9 CO_2 Membrane separation process flow

4. Recommendations

Any separation technology has its technical and economic boundaries, and the advantages are most obvious under specific separation objects and working conditions.The integration of membrane treatment technology with other technologies to achieve the optimal process combination and the lowest economic investment is a development direction for membrane treatment technology. In natural gas extraction of helium, there is already a new process of membrane + deep cooling method, and the combination of membrane + PSA method is tried; in the CO2 capture set, the reasonable combination of cryogenic method, PSA and membrane method is explored,and some more economical and efficient process combinations can be come up in the face of a wide range of CO_2 concentration; in the case of deep dehydration of natural gas (water dew point -60°C) the integrated membrane - molecular sieve adsorption dehydration process can be used, which can effectively extend the life of the molecular sieve and increase the gas recovery rate to reduce the size of the plant. In addition, the integrated natural gas purification process of solid desulphurisation - membrane de-CO_2 - membrane dehydration, and the integrated membrane - amine method for the removal of acidic components from natural gas, can make use of the unique advantages of each technology to reduce the investment and operating costs of the plant while meeting the application requirements. The research and development of various integrated technologies The research and development of various integratedtechnologies will certainly open up a wide field for the application of membrane separation technology in the oil and gas industry.

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