Removal of CO2 from Flue Gas by Membrane Separation Technology

Zihan Zhao[1, *, †], Shiying Chen[2, †], Qichen Peng[3, †]

[1]School of Science, Hainan University, Hainan, China

[2]School of Reading, Nanjing University of Information Science and Technology, Nanjing, China

[3]School of Materials Engineering and Science, Beihua University, Jilin, China

*Corresponding author: 20203106418@hainanu.edu.cn

†These authors contributed equally.

Abstract. As the main gas of the greenhouse effect, carbon dioxide (CO_2) must be effectively captured and recycled, and the high separation efficiency and low cost of membrane separation make it stand out to remove CO_2 among many gas separation methods. Considering the gas contained in the flue, a more efficient CO_2 membrane separation method is proposed, that is, improving the separation coefficient by adopting a separation device coupled with multi-layer separation membrane and absorption membrane. If this method is used, the separation quality can be improved, the purity of CO_2 will be close to 99%, and the cost for the developed separation technology can be greatly reduced. As a result, this research is devoted to describe a novel method of removing CO_2 from the flue gas, which is by combining separation membrane and absorption membrane. The method can reduce the cost and external pollution, combined with various advantages, to improve the separation quality as far as possible.

Keywords: Membrane Separation, Flue Gas, CO_2 Removal, Coupling Technology.

1. Introduction

With the intensification of the greenhouse effect, carbon dioxide (CO_2), as the major role leading to that, has attracted widespread attention. Over the past century or so, the rate of increase of CO_2 concentration in the global atmosphere has been about 0.4% per year [1]. In the 21st century, the global average temperature will also see an increase at a rate of 0.02-0.05 ℃ per year [2]. The rising temperature will seriously affect the ecological balance and pose a potential threat to the normal existence of human beings. Therefore, the greenhouse effect must be controlled. Carbon emission reduction in the energy sector is the key to reducing the total amount of CO_2 emissions [3]. Besides using green energy to replace fossil fuels, carbon sequestration and utilization are important ways to prevent the further aggravation of the greenhouse effect [4]. The greenhouse effect is increasingly aggravated due to the large amount of CO_2 emissions, and the main source of CO_2 in the atmosphere is the combustion of fossil flues. Controlling CO_2 emission contributes to the alleviation of the aggravation of the greenhouse effect.

The main components of gases in the flue are nitrogen, CO_2, oxygen and other gases. The removal of CO_2 from coal-fired power plants flue gases can effectively reduce the CO_2 content that release into the atmosphere. It is of great significance for curbing the trend of global warming. At present, the traditional methods for removing CO_2 from flue gas mainly include low temperature distillation, physical adsorption, chemical absorption, and dissolved coal extraction technology. And to some extent, they have the problems of complex equipment, high energy consumption and high cost. To select an appropriate CO_2 removal method, the electric power production energy source it consumed must be considered first. Low-energy consumption technology can lessen the impact on efficiency of the power plant and further reduce the cost. The difficulty in operating is that the chemical properties of CO_2 are stable. Besides, CO_2 will be diluted by nitrogen in the air during the capture process, and the content is large. But membrane separation method can solve the above problem well, so it is gaining traction.

Since the first gas separation membrane device was developed by a subsidiary of Monsanto Company in 1979, membrane separation technology has developed continuously with its advantages of low energy consumption, simple and flexible device, and no secondary pollution. With the gradual upgrading of technology, the efficiency of CO_2 removal can be greatly improved to more than 80%. At the same time, the high-pressure working environment lays a foundation for subsequent storage and opens up a new way of CO_2 removal technology. This makes the technology have great development potential. However, the current CO_2 membrane separation technology still has two shortcomings. It is difficult to obtain high-purity CO_2, and the combination of laboratory research results and real production is not sufficient.

This research analyzes the basic principle and instrument structure of membrane separation technology to remove carbon dioxide. These membranes with the use of materials show high permeability coefficient, such as perovskite hollow fiber membrane. According to the principles and characteristics of separation membrane and absorption membrane, combined with the features of various materials, a high-quality CO_2 removal device and a set of technological process are created. The device based on CO_2 membrane separation technology was optimized and upgraded to improve the purity and separation efficiency of the obtained CO_2. Relevant technical evaluation and comparison are carried out to clear the advantages in different technical conditions.

2. Principle of membrane separation

The common membrane separation technology can be classified into two kinds, including gas separation technology and gas absorption technology. The gas separation technology mainly depends on the gas separation membrane of different materials to distinguish the gas with different permeability ability, and the gas absorption technology is the result of the coupling of the traditional chemical absorption technology and membrane separation.

Separating membrane is selective and the separation mechanism is mainly dissolution-diffusion [5]. When mixed gases pass through the separation membrane, their relative penetration rates vary according to the diffusivity and solubility of various gases. As shown in Figure 1, CO_2 is used to represent the gas with a faster penetration rate, and the nitrogen is used to represent the gas with a slower penetration rate. It can be seen that the gas with a faster penetration rate will be enriched on the permeation side of the separation membrane, where under the action of large pressure difference between the two sides of the separation membrane. While the gas with slower penetration rate will be enriched on the retention side of the membrane, so as to basically separate the mixed gas with larger difference of penetration rate.

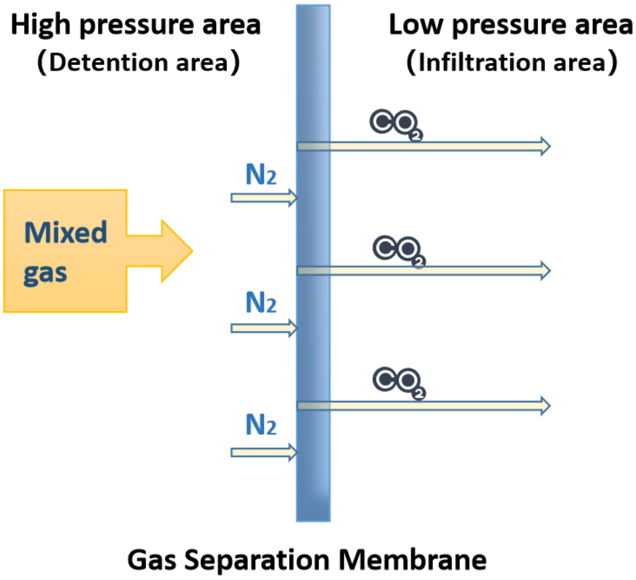

Figure 1. Working principle of gas separation membrane

Membrane absorption technology usually adopts hollow fiber membrane, which is mainly used to separate gas and absorption liquid, and provides enough contact area. It has no selectivity. As shown in Figure 2, taking the process of capturing CO_2 by membrane absorption as an example, the absorption liquid can react with CO_2 at a fast rate. Under the action of concentration difference, CO_2 in the mixed gas reacts with the absorption liquid at the interface between the gas phase and the liquid phase, and diffuses to the liquid phase side through the membrane pore. Nitrogen, methane and other inert gases have no affinity with the absorbent, and can only remain flowing in the gas phase side. Therefore, the membrane absorption technology can also effectively separate the gas mixture.

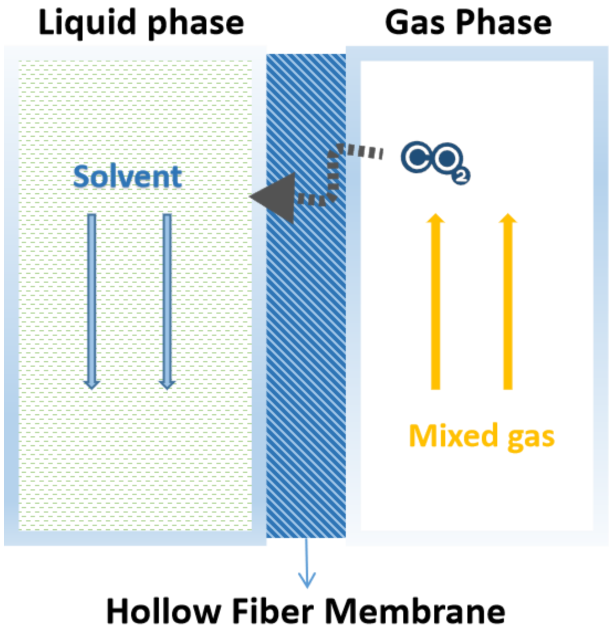

Figure 2. Schematic illustration of membrane absorption technology

3. Types of materials used in membrane separation

In the process of removing CO_2 by membrane separation technology, the material of the membrane directly determines the solubility coefficient and diffusion coefficient of the gas, and also determines the removal effect. It often uses an asymmetric membrane containing a selection layer and a support layer. The selection layer needs to be thin and highly selective, while the support layer needs to be a porous support material with high permeability. For the separation of CO_2 and N_2 as the main component, CO_2 has better coagulability and smaller kinetic diameter, which is more advantageous than N_2 in terms of both thermodynamics and kinetics. This also puts forward corresponding requirements for the membrane material. At present, two kinds of membrane are widely used, organic polymer membrane and inorganic membrane.

Most of the membranes used for CO_2 removal are organic polymer membranes, such as polysulfone (PSF), polycarbonate (PC), cellulose acetate (CA) and polyimide (PI). This kind of membrane is relatively cheap and widely used in the industrial field. However, the heat resistance of some membrane itself or membrane components is poor [6] so the operating temperature should not be too high. The erosion resistance of the membrane is also poor.

At the same time, the selectivity and permeability of most organic polymer membrane are inversely proportional [7]. For example, polyimide (PI) has good strength, chemical stability and selectivity, but poor permeability to CO_2. In this case, the PI can be used to synthesize PI materials containing some substituents by the chemical modification method. This can not only retain its original good selectivity, but also greatly improve the gas permeability capacity. Hou et al. analyzed the effects of UiO-66(Zr) membrane and chemically modified UiO-66(Zr)-$(COOH)_2$ membrane on CO_2/N_2 (15:85) permeation selectivity and permeation flux of CO_2 capture in the mixed system [8], as shown in

Figure 3, it was found that the double carboxyl group-modified parent material could theoretically break away from the Robeson upper limit, and the selectivity and permeability of the membrane were greatly improved.

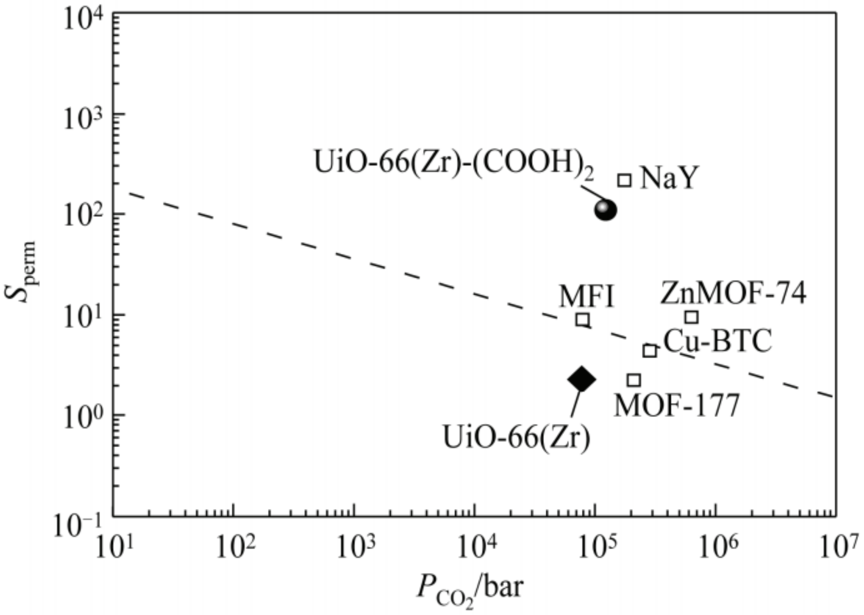

Figure 3. Comparison of permeability of UiO-66(Zr) membranes before and after chemical modification [8]

In the membrane absorption technology, it will also produce different effects when different material membrane collocates absorption liquid. Khaisri et al. adopted MEA to absorb simulated flue gas (air with a large amount of CO_2), combined with PP, PVDF, PTFE respectively, and compared the results [9]. The physical parameters of some membrane materials are shown in Table 1, and the results show that PTFE is the most stable among the three materials. Therefore, the absorption membrane and the use of the absorption fluid with the tacit coordination is also important.

Table 1. Physical parameters of different absorption membranes

Membrane materials	Inner diameter/μm	Outside Diameter/μm	Pore size/μm	Porosity	Solution system
PP	244	300	-	0.35	MEA, AMP
PP	1000	2000	-	0.35	MEA, AMP
PP	250	550	0.25	0.7	H_2O, NaOH
PP	600	1000	0.27	0.79	CORAL20
PP	270	300	0.02	0.3	DEA, NaOH
PP	344	442	0.02-0.2	>0.45	PG, MEA, MDEA
PP	340	426	-	0.139	NaOH
PP	400	500	-	0.6	NaOH
PP	600	1000	0.20	0.4	PZ, MDEA, AMP
PTFE	1000	1913	1.0	0.7	H_2O, NaOH
PTFE	1000	1700	-	0.4	MEA
PVDF	830	1070	0.03	0.5	H_2O, NaOH
PVDF	830	1070	0.03	-	MEA, TEA
PVDF	607	907	0.04	-	Na_2CO_3
PVDF	300	514	-	0.698	H_2O
PVDF	1400	2200	0.20	0.5	PZ, MDEA, AMP

Common inorganic membrane materials include metals, metal oxides and ceramics. Compared with organic membrane, inorganic membrane has better chemical stability, and has obvious advantages in the separation process with high temperature and corrosion. For example, the zeolite membrane has small pore size, inorganic crystal structure, high temperature resistance and chemical degradation resistance. But the selectivity and permeability of most inorganic membrane materials cannot meet standard, and they are still in the stage of laboratory research and cannot be used in large-scale industrial applications.

4. Improved membrane separation technology

4.1. Separating apparatus

In addition to N_2 and CO_2 which are more abundant in the flue gas, there are a variety of other gases there, such as sulfur dioxide, so it is difficult to obtain higher purity of carbon dioxide. In order to fully capture and recycle CO_2, the advantages of high separation quality and low cost of membrane separation and membrane absorption technology can be used in combination. Meanwhile, the structure of the device is shown in Figure 4, and a three-layer membrane structure can be set to separate CO_2 from impurity gas for many times. What's more, setting the separation device in the form of multiple cylindrical sleeves can increase the contact area between the gas and the membrane, and improve the separation efficiency. Among them, separation membrane 1 can be inorganic membrane. This membrane has strong chemical stability and high temperature resistance but the separation effect is weak and just can initially separate CO_2. Separation membrane 2 is organic polymer membrane. Because of its high selectivity and permeability ability, CO_2 can be further removed. Outside the absorption membrane, alcohol amine solution and other solutions that can fully absorb CO_2 are used as absorption liquid, so that CO_2 can diffuses into the absorption solution and flows out.

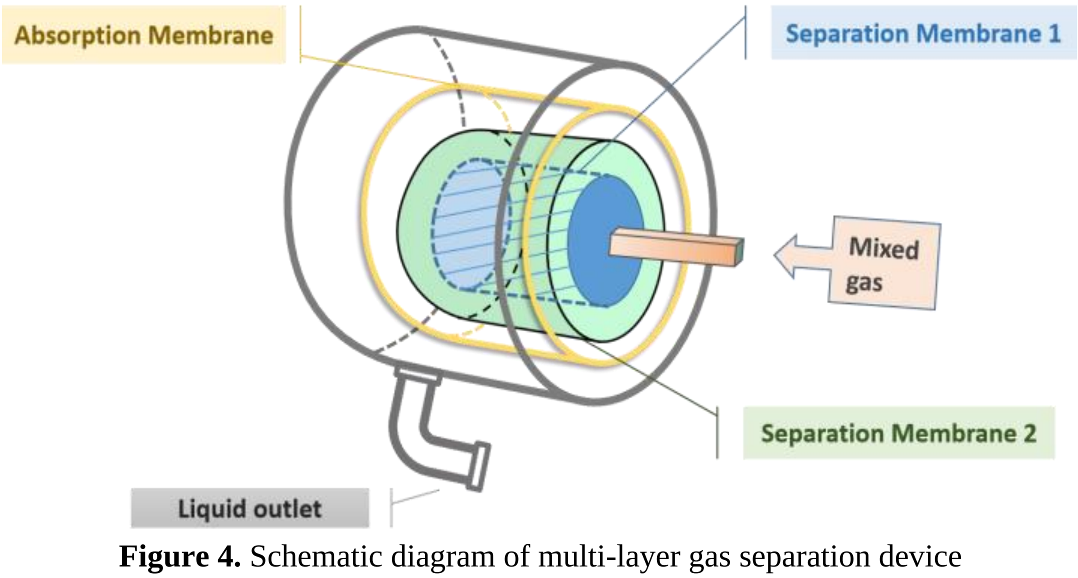

Figure 4. Schematic diagram of multi-layer gas separation device

The use of membrane materials and absorption fluids in the device also targets a purer CO_2. The permeability of the membrane determines the amount of the mixed gas treatment in a certain contact area and time, while the selectivity of the membrane determines the energy consumed to treat the same amount of the gas mixture, which further affects the separation cost. To deal with the large amount of flue gas emitted from the plant, when applied in the actual production, the penetration and selection ability of the membrane is particularly critical. Wang et al. introduced the melt quenching method after polymerizing the ZIF-62 film by in-situ solvothermal method in order to prevent the decrease of permeability caused by the long-term accumulation of the metastable organic film with the minimum volume, and developed a method with a selective ability and MOFs glass membrane with both permeability [10]. The CO_2/N_2 selectivity of the glass membrane reached 34.5, and the CO_2 permeation amount was 36 GPU. As shown in Figure 5, the two indicators of the membrane have obvious advantages.

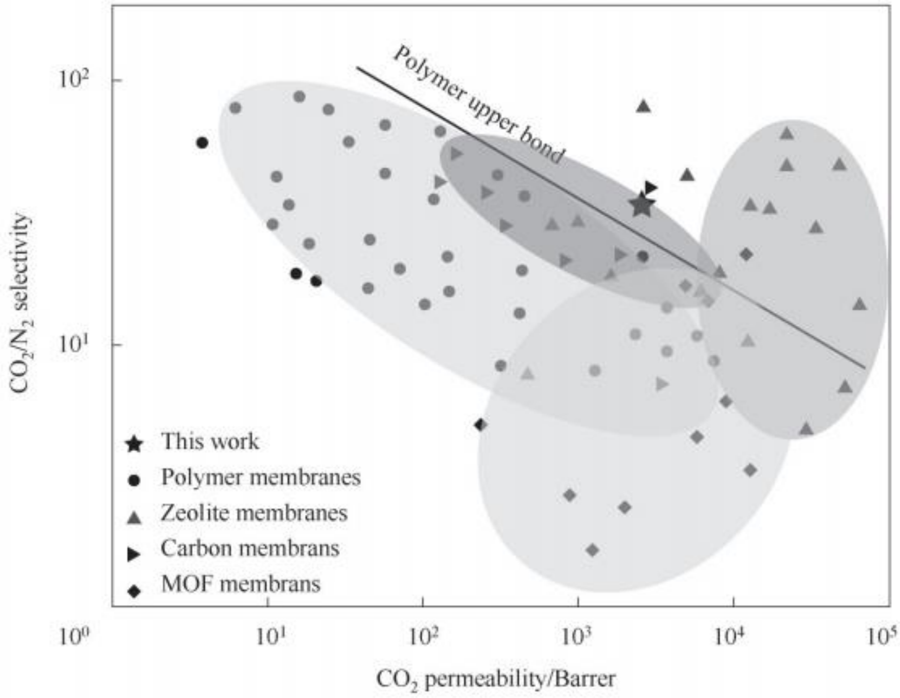

Figure 5. Separation properties of MOF glass membrane [10]

Jiang et al. used Pebax (with ether oxygen bond structure) as the polymer matrix and used PEI functionalized ZIF-8 (Zeolitic imidazolate frameworks-8) as the filler to make PEI-ZIF-8@Pebax membrane material [11], using the CO_2 active site provided by the large amine group on PEI and the hole window size of 0.34 nm of ZIF-8 material, the intrinsic permeability and selectivity of the membrane was greatly improved. Therefore, an active group with a reversible reaction with CO_2 can be introduced to promote the rapid passage of CO_2. In addition, a porous membrane material with a moderate sieve aperture can also be used to enhance the selectivity of the membrane by adjusting the aperture size of the material. At the same time, the porous membrane material can reduce the mass transfer resistance and improve the permeability.

Whether the cooperation of the absorption membrane material and the absorption liquid is tacit understanding is the decisive factor for the separation ability of the absorption film in the device, so the compatibility of the absorbent and the film material, mainly depends on the influence of the absorbent on the structure of the membrane material and the mass transfer resistance. Feron et al. used the CORAL solvent as the absorption liquid to study the mass transfer stability of the PP membrane contactor when separating the flue gas, and found that the PP membrane is not easily moistened with by the CORAL solvent [12]. Therefore, the absorbent that we use needs to cooperate with the absorption film with good compatibility in the separation process of the flue gas to ensure the efficient and orderly separation of the gas.

4.2. Separation process

The complete process of CO_2 removal in the flue gas is shown in Figure 6. The discharged flue gas is cooled after compression, dust removal and desulfurization, and the gas already cooled enters the multilayer membrane gas separation device shown in Figure 4. After the diffusion to the CO_2 of the liquid phase flows out with the absorption liquid and flows to the heat exchanger, the heat is absorbed into the regeneration device. After CO_2 regeneration, CO_2 can be dried to successfully remove CO_2 in the flue gas. At the same time, the poor liquid flowing out from the regeneration device enters the poor liquid pump through the heat exchanger and returns to the multi-layer membrane gas separation device again. This formed an automatic circulation system, constantly send the lean liquid back to the gas separation device, in order to capture the remaining lean liquid in the CO_2. Therefore, CO_2 can be removed more efficiently and adequately, and at less cost compared to conventional chemical absorption and physical sorption methods. The energy loss of the whole process is less and will not cause environmental pollution.

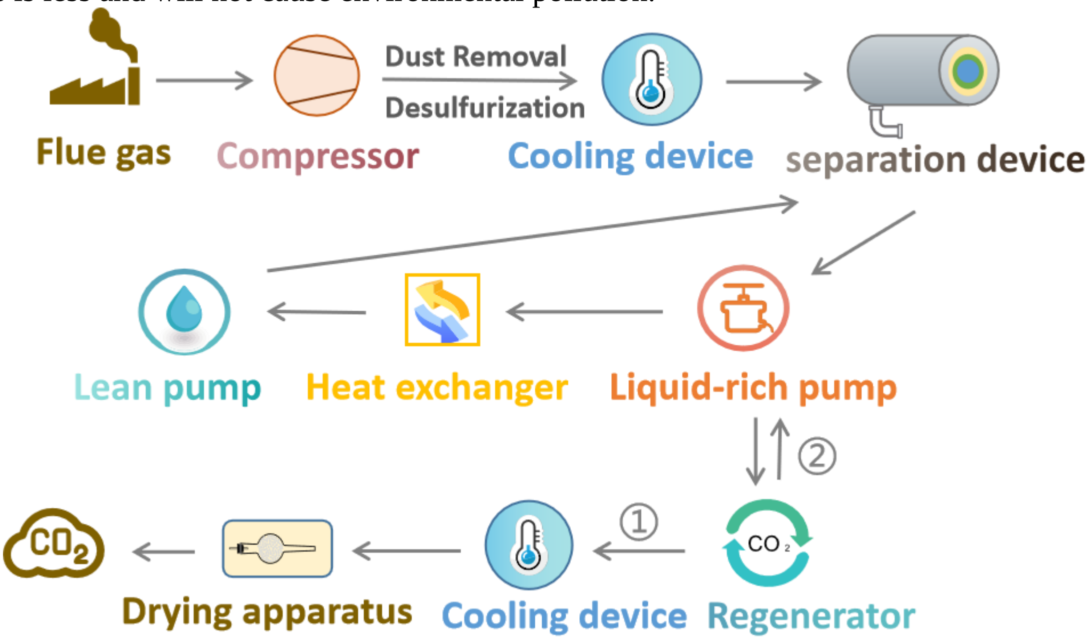

Figure 6. CO_2 removal process in flue gas

5. Technical evaluation and comparison

We combine the membrane separation and membrane absorption technology to adopt a multilayer membrane separation of CO2 in the flue gas, which fundamentally improves the separation quality. At the same time, there are many other advantages: (1) device small size, light weight, saving area, unlimited application; (2) large area, better gas contact, fast separation speed, high mass transfer coefficient; (3) simple operation process, low energy consumption, no environmental pollution, daily maintenance is simple; (4) device reliability, and can be flexibly combined with other equipment; (5) low cost, broad development prospects; (6) can be used under high pressure conditions, small reaction loss. However, there are still some problems. For example, this separation technology requires high requirements for each layer, and different kinds of membrane and absorption liquid coordination will also produce different separation effects, which needs more experimental data to explore.

Compared with this method and the conventional gas separation technology, as shown in Table 2, the advantages of the membrane separation technology are more highlighted. Although the technology of chemical absorption separation of CO_2 is relatively mature, it still faces the problems of poor absorption capacity, high energy consumption and high cost, while physical adsorption avoids the problems of high cost and complex equipment, but with the increase of temperature, the absorbable capacity will gradually decrease, which will affect the separation quality; the low-temperature separation method is not only huge in equipment, but also great in energy consumption, its energy consumption is 55%-95% of coal-fired energy [13].

Through the comparison, we can find that the advantages of the membrane separation technology are relatively obvious in a variety of methods, which can not only avoid the defects of the traditional separation technology, but also further ensure the quality of the gas separation by combining the separation membrane and the absorption membrane. At the same time, the membrane method can be actively coupled with other methods, combined with different advantages, and it is also necessary to develop a more suitable separation technology for other mixed gas characteristics except the flue gas and maximize the advantages of membrane separation.

Table 2. Comparison of each gas separation method

Methods	Advantages	Disadvantages	Purpose	Ref.
Chemical absorption	Large contact area	High operating costs High energy consumption Poor absorption capacity	For low CO_2 concentration	[13-14]
Physical adsorption	Simple process Low energy consumption	Poor adsorption capacity Low recovery rate	For high CO_2 concentration	[15]
Low temperature separation	High separation capability	High energy consumption High cost Huge equipment	For CO_2 Removal in higher depth of the occasion	[16]
Membrane separation	Instrument miniaturization Low energy consumption low cost Green and pollution-free	Imperfect application details	For equipment size and weight constraints	[17-18]

6. Conclusions

The application principle, material classification and application advantages of membrane separation technology are introduced, and a membrane separation device suitable for CO_2 removal in flue gas is also proposed. The device continues the advantages of membrane separation technology, including less energy consumption, simple device and low cost. It combines the bidirectional advantages of separation membrane and absorption membrane, linearly enlarges the membrane contact area, and greatly improves the separation coefficient. At the same time, the process of the rich and poor liquid pump cycle conversion is used, as far as possible to avoid the CO_2 residue is discharged into the atmosphere, exacerbating the greenhouse effect. Through the comparison of multiple gas separation methods, the membrane separation technology has obvious advantages, which can be summarized as the most promising gas separation technology in the future. Although the current technical details are not perfect enough to be large-scale used for the market, but with the development of more related experiments and the expansion of data, the membrane method will gradually become the mainstream direction of gas separation technology.

References

[1] Ding Yihui, Sun Ying. New Progress in International Climate Change Research [J]. Advances in Climate Change Research. 2006. 2(4): 161-166.

[2] IPCC. Climate change 1995: The science of climate change. Contribution of Working group I to the Second Assessment Report of the IPCC (Houghton, J. T. eds). Cambridge University Press. 1996.

[3] Yang Kaiyu. Research progress of carbon dioxide capture technology in coal-fired power plants [J]. Energy and Energy Conservation, 2022, (01):49-53.

[4] Wang Jiaming, Ruan Xuehua, He Gaohong. Research progress of membrane materials for different industrial carbon dioxide separation systems [J]. Chinese Journal of Chemical Engineering. 2022: 1-23.

[5] Mulder M, translated by Li Lin. Basic Principles of Membrane Technology (Second Edition). Beijing: Tsinghua University Press, 1999.

[6] BREDESEN R, JORDAL K, BOLLAND O. High-temperature mem branes in power generation with CO2 capture[J]. Chemical Engineering and Processing, 2004, 43: 1 1291158.

[7] Qi Xiwang, Chen Cuixian et al. Membrane Science and Technology. 1996(2): 1.

[8] Hou Dandan, Liu Dahuan, Yang Qingyuan, Zhong Chongli. Research progress of metal-organic framework materials in gas membrane separation[J]. Progress in Chemical Industry, 2015, 34(8): 2907-2915.

[9] KHAISRI S, DEMONTIGNY B. Comparing mem-brane resistance and absorption performance of three different membranes in a gas absorption membrane contactor[J]. Sep. Purif. Technol, 2009, 65(3):290-297 .

[10] Wang Y H, Jin H, Ma Q, et al. A MOF glass membrane for gas separation[J]. Angewandte Chemie International Edition, 2020, 59(11): 4365-4369.

[11] Jiao C L, Li Z D, Li X X, et al. Improved CO2/N2 separation performance of Pebax composite membrane containing polyethyleneimine functionalized ZIF-8[J]. Separation and Purification Technology, 2021, 259: 118190.

[12] Feron P H M, Albert E Jansen. CO2 separation with polyolefin membranecontactors and dedicated absorption liquids: performances and prospects. Separation and Purification Technology, 2002, 27: 231. 242 .

[13] Li Jin, Liu Zhengxiu, Wei Qingchao, Tian Xiujun, Chen Rui. CO2 capture technology in the flue gas of thermal power plant and applied analysis of membrane absorption[J]. Electric power technology. 2010. 19(9): 1-5.

[14] ALCHEIKHHAMDON Y, HOORFAR M. Natural gas purification from acid gases using membranes: A review of the history, features, techno-comercial challenges, and process intensification of commercial membranes[J]. Chemical Engineering and Processing: Process Intensification, 2017, 120: 105-113.

[15] Anand B. Rao, Edward S.Rubin. An assessment of carbon capture technology and research opportunities[J]. Environ. Sci. Technol. 2002, 36(20): 4467 4475.

[16] KUUSKRAA. Reviewand evaluation of the CO2 capture project by the technology advisory board[M]. Carbon dioxide capture for storage in deep geologic formations-result from the CO2 capture project I.ELSEVIER, UK, 2005: 37-46.

[17] Liao Chuanhua. Mechanism and model of inorganic membrane gas separation [N]. Silicate Bulletin, 2004, 2.

[18] Zhang Xuemo, Chu Zheng, Gu Junqi. Progress and evaluation of the de-CO2 technology [J]. Chemical Industry and Engineering Technology. 2001.22(2): 14-23.