

The Overview of Membrane System on CO₂ Removal from High Pressure Natural Gas

Yixin Fu^{1*}

¹Guangdong Technion Israel Institution of Technology, Shantou, Guangdong Province, China, 515000

*Corresponding author. Email: Yixin.fu@gtiit.edu.cn

ABSTRACT

Being a kind of important energy and chemical raw material, natural gas can replace fossil fuel for instance coal to cut down the net CO₂ discharge. For natural gas purification, separation using membrane technology are considered to be an attractive alternative method. It is necessary to remove acid gases and other impurities for instance, carbon dioxide, hydrogen sulfide. In order to satisfy the transportation regulations and terms of usage, noble gases such as N₂ should be added. From the point of view of financial benefits, for industrial production and applications asymmetric membranes are considered to be a considerable solution. This article overviews the latest developments in various natural gas asymmetric membrane purification technologies, the removal of CO₂ from CH₄ are mainly focused, the separation of N₂ and H₂S from CH₄ are also mentioned. By comparing different material types, polymer membranes, inorganic membranes, mixed-matrix membranes (MMM) and carbon molecular sieve membranes (CMS) are introduced. The related preparation methods and transmission characteristics of various asymmetric membranes are discussed. In practical applications, the asymmetric structure of the hollow fiber of polymer, mixed-matrix membranes (MMM) and carbon molecular sieve membrane (CMS) is mainly studied.

Keywords: CO₂ Removal, membrane, natural gas.

1. INTRODUCTION

Remove CO₂ from natural gas is necessary since CO₂ has some negative influence on the natural gas grid such as reducing the natural gas heat value, corrosion the nature gas pipeline, and can form hydrates which may damage the pumps or other equipment easily. Look back to the history of society development, every major advancement in civilization is accompanied by further improvements and updates in the usage of energy by mankind. In the past 100 years, industrialization have been completed in developed countries and abundant of the earth's natural resources have been consumed, especially energy resources. Therefore, the demand of natural gas has been increased a lot in the past decades. The traditional chemical absorption is still considered to be the state-of-the-art technology. Because of the extensive usage of natural gas, purification of acid gases has become the largest gas separation process.

Although the traditional absorption process by using amine currently take up a great proportion an absolute large proportion in removing acid gas impurities, disadvantages like high energy consumption, complex

operation, relatively large investment cost and corrosion of facilities are still exists and need to be improved.

Analogously, cryogenic distillation and pressure swing adsorption (PSA) processes for nitrogen separation also face energy consumption problems. Membrane systems possess huge potential in natural gas sweetening because of its advantage such as low capital and operation cost, more environmentally friendly and more flexible. Until now, several different types of membranes are already commercially available. However, a limitation can be found in the permeability-selectivity tradeoff relation.

This article mainly focuses on the effect of membrane separation process, for instance, the permeance (productivity) and selectivity (efficiency). In order to fulfill the requirement of high permeance and selectivity, researched on different kinds of membrane materials, such as inorganic membranes, mixed-matrix membranes (MMM), polymeric membranes, and carbon molecular sieve membranes (CMS).

2. THE CLASSIFICATION OF THE MEMBRANES

2.1 Polymeric Membranes

2.1.1 Manufacture approach

As the first asymmetric membrane to be successfully applied in practice, the anisotropic Loeb-Sourirajan membrane was prepared by the precipitation method to reduce the transport resistance of the membrane, because the polymer is needed in two parts, the raw material cost will be increased to 50g per m². [1]. On the contrary, because a porous carrier and a thin selective layer inside a composite film are able to be derived into two different layers, it can be optimized in different methods. This is a possible method to overcome the limitations of the Loeb-Sourirajan film[2]. Flat sheet membranes and hollow fiber membranes (HOF) are known as the two different types of the composite film.

The spiral winding module contains a number of flat plates to expand the contact surface area with the gas inlet. In order to acquire relatively low resistance and separation layers with no flaw, a few of manufacturing methods have been developed, for example, interface polymerization, solution casting, dip coating, and spin coating. Dip coating and spin coating are usually been applied for basic research in the lab-scale experiment.

Comparing to the spiral wound membrane, hollow fiber membrane is being wider used because its lower production cost. [3].

2.1.2 Conventional polymeric membranes

Solution-diffusion process is the principle of polymeric membranes that primarily focus on gas separation. Currently, polymer membrane dominates the membrane market because of it has the advantages such as low raw material cost and convenience for quantity manufacturing. , Malaysia-Thailand Joint Development Zone utilized a membrane desulfurization system which is able to reduce the natural gas CO₂ concentration from 36% to 16% to fulfill relevant regulations [4]. In carbon dioxide separation platforms, Cellulose acetate (CA)membranes are being used the most widely. The original design of CA is for water desalination by fabricating reverse osmosis membranes. Under the industry conditions, if the CA thickness is less than 0.1 μm, CO₂ gas permeation unit is 100–200 GPU and a CO₂/CH₄ selectivity is 10–15, [5]. On the basis of varies of versatile membrane materials which are applied in CO₂/CH₄ separation, the cellulose acetate membrane separation property “upper-bound” is proposed by Robeson (always lower).

Plasticization is very important for practical natural gas purification because it can lead to low gas selectivity

of the membrane. High concentration of CO₂ leads to plasticized, the polymeric chain is incompactly accumulated, which accelerates the penetration of CH₄ and reduces the related selectivity. Various methods have been developed in order to solve this problem, among them, crosslinking, which come to a realize by several methods such as thermal, UV and chemical treatments is being considered as one of the most effective methods through restrain swelling and mobility segmentally.

2.2 Inorganic Membranes

2.2.1 Properties and defects

Under corrosive conditions, for instance, high temperature and high pressure, inorganic films are considered to explore higher separation performance than polymer films [8]. There are two types of inorganic membranes which are porous type and nonporous type. However, quantity production of inorganic films for gas separation are a problem to industrial application. Mixed-conducting oxide ceramic and molten carbonate phases are contained in the two-phase composite which are typically being considered as the material of nonporous inorganic membranes. Typically, the CO₂ permeance is relatively low when using nonporous inorganic membranes, but the CO₂/CH₄ selectivity of the membrane is absolute. Therefore, the performance of the membranes have no advantage when competing to other membranes. [9].

2.2.2 Zeolite membranes

Zeolite membranes show higher performance than polymer membranes in natural gas purification due to the remarkable chemical resistance of polymer membranes to CO₂ plasticizing effect. In general, the mechanism of zeolite membranes are preferential adsorption and molecular sieve separation, in order to separate CO₂ from CH₄. It is important to note that permeability and the selectivity of the membranes are functions of pressure for both pure gases and mixtures. As the pressure increases, the CO₂ permeability decreases more significantly than CH₄ permeability, so the CO₂/CH₄ selectivity becomes worse for pure gas stream or mixed gas stream. In addition, the selectivity of mixed gas is slightly higher than ideal gas due to the permeability of CO₂ in the mixture is 17-29% lower than that of pure CO₂ and the permeability of CH₄ in the mixture is 23-40% lower than that of pure CH₄. In addition, even in hot and humid conditions for 4 days, the obtained film still maintained high and stable performance. Besides, by applying size-sieving effect, zeolite membranes have great development prospects to remove nitrogen from methane.

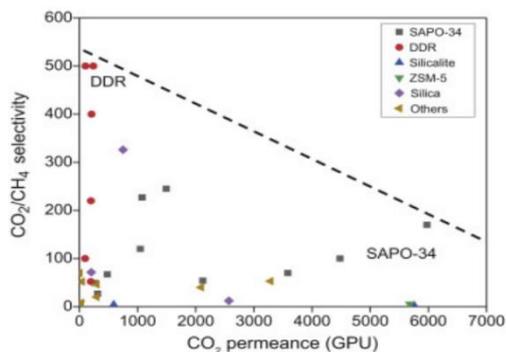


Fig 1. CO₂ permeance of different type of zeolite membranes.

2.2.3 MOFs membranes

However, even different pore sizes and structures are tried and tested, for CO₂/CH₄ separation, unsatisfying results are reported even the most advanced MOF membranes are used because generally, the selectivity of the membrane was below 10, the result is lower than polymeric membranes and zeolite membranes. The flexibility of MOFs should be the reason behind this phenomenon according to the available experimental result. In general, the zeolite membrane with excellent molecular sieve separation performance showed higher natural gas purification performance than the metal organic framework membrane on the account of priority adsorption separation. So far, developing scalable and cost-effective, defect-free crystalline nonporous membranes which are being used for gas separation has remained a major challenge. For instance, at the membrane-support interface undesirable symbiosis and the cracks and bubbles might be formed when remove the solvent and activate the membranes. The stability of MOF membranes operating under extremes conditions for a long time in natural gas purification besides on the manufacture and the gas separation property.

2.3 Mixed-Matrix Membranes

Attribute to the aim of balance the membrane properties like permeability and selectivity, polymer membranes need to be integrated to acquire better performance. In the last few years, mixed-matrix membranes (MMM) have gained widespread attention and become a promising solution to this problem. Polymer matrix which are introduced by nanomaterials that can be well controlled structures, MMM combines the machinability of the polymer with the excellent separation properties of the fillers. Nanomaterials 1D, 2D and 3D have been developed as the filler in MMMs. However, because of the challenges of manufacturing thin and perfect mixed-matrix film layers, the researchers focused on the manufacture of dense films rather than asymmetric films.

2.3.1 1D-material mixed-matrix membranes

As one of the representation of one-dimensional materials, multiwalled carbon nanotubes (MWCNTs) have continuous smooth internal channels as well as well-defined interlayer spacing of ~3.4 Å that could provide additional pathways to strengthen CO₂ separation [10]. The CO₂ permeance have been increased by adding multiwalled carbon nanotubes to polymer chain packing. On the other hand, the strong molecular interaction between CO₂ and polar groups enhances the membrane selectivity. However, multiwalled carbon nanotubes are easy to agglomerate for the reason that the strong van der Waals interaction led to bad dispersion inside MMM. In order to optimize this problem, -OH and -NH₂ were used to improve multiwalled carbon nanotubes. The MMMs containing 2.0 wt% MWCNT-NH₂ shows the most attractive performance with CO₂ permeance of 130 GPU and selectivity over 100 for CO₂/CH₄ (10/90 vol%) at 28 °C and 2 bar. Besides, -NH₂ groups increase the interaction between the filler and matrix and also act as the CO₂ carriers. Meanwhile, 1D MMMs faces challenges in constructing directional channels and avoiding internal channels being blocked by polymer chains.

2.3.2 2D-material mixed-matrix membranes

The 2D packing has an extended lateral size and ultra-thin thickness to provide a continuous transport channel for gas molecules under precise control. The function groups that contain oxygen strengthen the interaction between the polymer matrix during the mixed-matrix membrane manufacture and the interaction with CO₂ during the separation processes as well. Furthermore, 2D MOF is an attractive filler in MMM for CO₂ purification. The results indicate that selectivity enhanced due to the size selective effect on CO₂/CH₄, which are performed by ordered pores in MOFs. Effective methods should be made to find out industriously to prevent random orientation of the channels for 2D-material MMMs.

2.3.3 3D-material mixed-matrix membranes

Compared with 1D and 2D materials, three dimensions nanofillers, for instance, zeolite, MOF and COF (covalent organic frameworks) in MMM do not involve orientation problems. Nevertheless, problems as following still exist in MMMs fabrication:

- a. choosing the filler and matrix properly;
- b. creating perfect membrane surface;
- c. enhancing compatibilities between phases;
- d. discovering transport channels which are reasonable;
- e. using hollow fiber structure to replace dense MMMs

The results shows that polymer dominates the minimum performance of MMMs and the fillers which interact with the matrix also play an important role[12,13]. In the coming research, the selection of filler and matrix, the removal of two-phase imperfections, the development of the hollow fiber structure of MMMs will be the main topics.

Since high permeability is more important in industrial processes, certain thickness of polymer matrix is needed so that the fillers are able to be fully contained inside. However, MMMs should be noticed that the thickness should be as thick as possible.

2.4 Carbon Molecular Sieve Membranes

Attribute to the molecular effect, carbon molecular sieve (CMS) membranes are being regarded as a possible alternative. it's worth noting that, two kinds of pores are existed in CMS membranes, which are micropores (7–20 Å) and ultra-micropores (< 7 Å), they can be introducing by bimodal distribution as following.

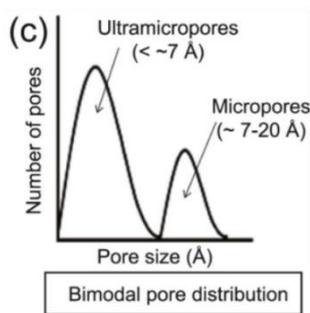


Fig 2. Number of poles in CMS hollow fiber membranes

From the commercial point of view, CMS hollow fiber membranes are highly recommended due to their superior separation performance. A pilot-scale plant based on recycled CA carbon hollow fiber membranes has been reported built to transform biogas into vehicle fuel in Norway.

After the removal of H₂S and H₂O in the pretreatment, within 8 days CMS hollow fiber showed 97 mol% CH₄ and recovery of methane is 98% in single stage gas separation process under stable operation condition, which indicated the CMS hollow fiber feasibility under industrial operation condition.

For industrial applications, high structural strength is required in order to obtain CMS asymmetric membranes which are able to keep high performance under harsh operating conditions. Furthermore, manufacture costs need to be decreased in order to make CMS membranes be able to be used in large scale natural gas purification.

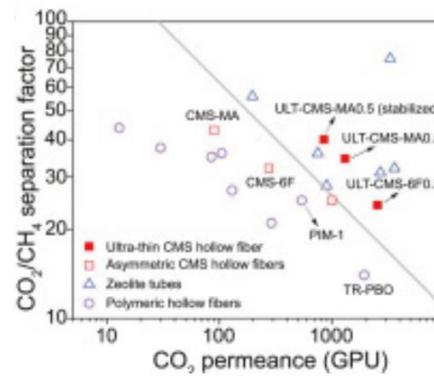


Fig 3. Comparing CO₂/CH₄ separation performance of hollow fiber membranes and tubular membranes. (Gas permeance unit GPU versus. separation factor)[14]

3. COMPARISON OF HOLLOW FIBER AND FLAT MIXED-MATRIX MEMBRANES

By making a comparison between the permeability of flat composite and hollow fiber composite membranes under ideal operating condition the overall properties of flat structure is slightly better to the hollow fiber structure. It might be suggesting that the properties of the hollow fiber configuration is related to the decreasing of the driving force. This effect seems to be caused by Pseudo-bulk concentration gradient. Similarly, on MMMs (mixed-matrix membranes), this effect also exists. According to the work done by Fernández-Barquín A et al [15], no former models can be able to applied to appropriately analytic the dependence of these phase specific diffusivities on the non-uniform pseudo-bulk concentration gradient across the composite.

4. CONCLUSION

Currently, polymeric membranes are still the most mature technology and hold the market no matter in flat configuration or hollow fiber asymmetric membranes. However, there are still many challenges that exist in the development of membranes. Due to the limitation of equipment, this paper cannot carry out field experiment, all the results are oriented from the work before. The conclusion may not be the same as the actual project. The character of membrane technology will become more and more important in the separation process with the development of properties of membranes like plasticizing resistance, gas separation performance and so on. Inorganic membranes, mixed-matrix membranes (MMM) and carbon molecular sieve membranes (CMS) are being regarded as a solution to the problems. However, improving the current manufacture route to reduce the production cost is of great importance. The defects between phases of interfaces are still needed to be solved for MMM and physical aging is also a series issues that needed to be solved for CMS membranes.

REFERENCES

- [1] Baker R W, Low B T. Gas separation membrane materials: a perspective[J]. *Macromolecules*, 2014, 47(20): 6999-7013.
- [2] Baker R W, Lokhandwala K. Natural gas processing with membranes: an overview[J]. *Industrial & Engineering Chemistry Research*, 2008, 47(7): 2109-2121.
- [3] Baker R W. Future directions of membrane gas separation technology[J]. *Industrial & engineering chemistry research*, 2002, 41(6): 1393-1411.
- [4] Bernardo P, Drioli E, Golemme G. Membrane gas separation: a review/state of the art[J]. *Industrial & engineering chemistry research*, 2009, 48(10): 4638-4663.
- [5] Baker, Richard W., and Bee Ting Low. "Gas separation membrane materials: a perspective." *Macromolecules* 47.20 (2014): 6999-7013.
- [6] McKeown N B. Polymers of intrinsic microporosity[J]. *International Scholarly Research Notices*, 2012, 2012.
- [7] Park H B, Jung C H, Lee Y M, et al. Polymers with cavities tuned for fast selective transport of small molecules and ions[J]. *Science*, 2007, 318(5848): 254-258.
- [8] Kosinov N, Gascon J, Kapteijn F, et al. Recent developments in zeolite membranes for gas separation[J]. *Journal of Membrane Science*, 2016, 499: 65-79.
- [9] Chung S J, Park J H, Li D, et al. Dual-phase metal-carbonate membrane for high-temperature carbon dioxide separation[J]. *Industrial & engineering chemistry research*, 2005, 44(21): 7999-8006.
- [10] Mallakpour S, Zadehnazari A. Effect of amino acid-functionalized multi-walled carbon nanotubes on the properties of dopamine-based poly (amide-imide) composites: An experimental study[J]. *Bulletin of Materials Science*, 2014, 37(5): 1065-1077.
- [11] Sun H, Wang T, Xu Y, et al. Fabrication of polyimide and functionalized multi-walled carbon nanotubes mixed matrix membranes by in-situ polymerization for CO₂ separation[J]. *Separation and Purification Technology*, 2017, 177: 327-336.
- [12] Mahajan R, Koros W J. Factors controlling successful formation of mixed-matrix gas separation materials[J]. *Industrial & Engineering Chemistry Research*, 2000, 39(8): 2692-2696.
- [13] Zimmerman C M, Singh A, Koros W J. Tailoring mixed matrix composite membranes for gas separations[J]. *Journal of membrane science*, 1997, 137(1-2): 145-154.
- [14] C. Zhang, R. Kumar, W.J. Koros *AIChE J.*, 65 (2019), pp. 16611-16617
- [15] Fernández-Barquín A, Casado-Coterillo C, Etxeberria-Benavides M, et al. Comparison of flat and hollow - fiber mixed - matrix composite membranes for CO₂ separation with temperature[J]. *Chemical Engineering & Technology*, 2017, 40(5): 997-1007.