탄소중립을 위한 고분자 기체분리막의 기술 동향

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Technological Trends in Polymer Gas Separation Membrane for Carbon Neutrality

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요　약: 대부분의 국가들은 온실가스 배출량을 줄이고 기후변화에 적응하기 위한 행동계획인 NDC (National Determined Contribution)를 법률화 했다. NDC 목표 달성을 위해 다양한 기술이 개발되고 있으며, 특히 가스상의 온실가스나 에너지원의 정화를 위해 분리막 수요가 증가하고 있다. 따라서, 본 논문은 다양한 재료 중 실현 가능한 제조 공정과 쉬운 스케일업의 장점을 가지고 있는 고분자 막의 기술 동향을 제공할 것이다.

Abstract: Many countries have passed laws to achieve Nationally Determined Contribution (NDC) which is a climate action plan to reduce greenhouse gas emissions and adapt to climate impacts. Although there are various technologies to achieve NDC targets, membrane technologies pose dramatical attractions for the purification of gaseous greenhouse gases or energy sources. Therefore, this review will provide the technological trends of polymeric membranes among various materials due to the advantages of the feasible fabrication process and easy scale-up.

Keywords: polymer membrane, hydrogen, methane, carbon dioxide, separation

1. Introduction

The reckless energy consumption on human desire is fueling the flames of climate change, casting a shadow over ecosystems and heightening economic vulnerabilities. For carbon neutrality, we must pour efforts into pioneering technologies for capturing, harnessing, and storing of greenhouse gases. Simultaneously, we must pivot towards embracing clean energy sources such as hydrogen or ammonia to steer us away from the precipice of environmental disaster.

Interestingly, green-tech predominantly relies on gaseous elements like carbon dioxide, ammonia, methane, nitrogen, hydrogen, and fluoride-based gas. These gases require separation from the air or purification to be harnessed as clean energy sources. Each gas necessitates specific purification or separation processes tailored to its intended use. However, these processes inevitably demand additional energy consumption, posing a challenge from a thermodynamic standpoint. Hence, there is a pressing need to innovate energy-efficient purification techniques to advance both carbon neutrality objectives and industrial applications.

Pressure swing adsorption (PSA) stands as a stalwart in industrial technology, adept at selectively purifying gases through the meticulous manipulation of adsorption and desorption via pressure adjustments on adsorbents. However, its efficacy comes at a hefty price, both in

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terms of treatment costs and the sheer scale of equipment required, necessitating expansive installations[1]. While PSA boasts several triumphant applications such as H_2 purification from NH_3 purge gas, nitrogen separation from air, facilitating enhanced oil recovery, and CO_2 removal from natural gas, it is not without its drawbacks. Operating at a minimum pressure of 10 bar and grappling with the thermodynamic intricacies of exothermic or endothermic processes during adsorption and desorption. PSA falls short of being hailed as a low-energy solution.

Membrane processes represent a paradigm shift away from energy-intensive methods. Compared to PSA, membrane technology slashes energy consumption by a staggering 50% or more. Also, membrane processes boast a laundry list of advantages over conventional techniques: reduced capital costs, streamlined operations, heightened selectivity, minimal energy usage, and superior gas removal efficiency. Their mechanical simplicity adds another feather to their cap, while their modular design enables easy scalability, offering operators unparalleled flexibility. In light of these compelling advantages, a thorough review of recent technical trends in membrane technology promises to illuminate its potential as a transformative force in gas purification and separation.

2. History

The genesis of membrane-based separations traces back to the groundbreaking solution-diffusion mechanism of Thomas Graham proposed in 1866[2]. Despite this early understanding of mass transport and gas diffusion through polymer films, it was not until the last four decades that membranes found widespread industrial application in gas separation.

The monumental leap occurred in 1980 with the introduction of Prism membranes manufactured by Permea (Monsanto), revolutionizing H_2 separation from ammonia plant purge gas streams[3]. Shortly thereafter, cellulose triacetate (CTA) membranes emerged for CO_2/H_2 separation by Separex in 1982, followed by for CO_2 separation the first spiral wound membrane based on cellulose acetate plant established in EOR Cynara in 1983.

The innovation continued unabated: polysulfone hollow fiber membranes (HFM) for O_2/N_2 separation were developed by Dow Chemicals in 1984, Furthermore, composite HFM was introduced for O_2/N_2 separation by IMS in 1987, and polyimide (PI) membranes for H_2 separation by Ube in 1989. In 1991, Delair developed membranes for air separation based on Polyphenylene oxide. Later on, in 1994, Medal developed polyimide HFM for CO_2/CH_4 separation. Kvaerner conducted the first field test of membrane contactors in 1998, marking another milestone.

In 1995, Pakistan saw the installation of the largest plant featuring cellulose acetate-based membranes for CO_2/CH_4 separation, underscoring the commercialization and potential of membrane technology. ABB/MTR introduced Teflon-based composite membranes for CO_2 removal in 2008, while GKSS/MTR scaled up polyethylene oxide membranes for CO_2 separation between 2008 and 2010[4].

More recent advancements include the extensive exploration of the gas-sweetening properties of 4,4'-(Hexafluoroisopropylidene)diphthalic dianhydride (6FDA) based Polyimide membranes and their copolymers from 2013 to 2016. Moreover, since 2020, there has been a surge in research focusing on green approaches for gas separation, particularly evident in the investigation of on-board inert gas generation systems for biogas purification, as illustrated in Fig. 1[4].
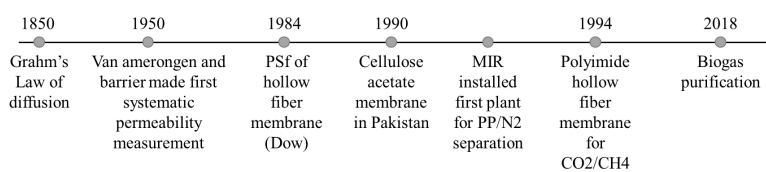

Fig. 1. A Schematic Diagram of Milestones in the progress of membrane gas separation technology.

3. Solution-Diffusion Mechanism

Commercially viable applications for gas separation membranes operate on the well-established solution-diffusion mechanism, widely regarded as the predominant theory of transport[5]. This mechanism elucidates the journey of gas molecules through non-porous polymeric or dense membranes, unfolding in three distinct phases.

Firstly, the desired gas molecules are absorbed onto the upstream surface of the polymer. Subsequently, they actively diffuse through the membrane, navigating its structure. Subsequently, the molecules desorb at the downstream side of the membrane, completing their journey[6]. The driving force behind this intricate process is the pressure difference across the membrane, augmented by various interactions such as absorption and diffusion rates within the membrane material[7].

The gas flux of H_2, CH_4, and CO_2 through the membrane can be shown using the following Eq. 1

$$J_{H_2, CO_2, CH_4} = \frac{P_e \left(P_f^n - P_P^n \right)}{\delta} \tag{1}$$

Where P_f and P_p represent H_2, CO_2, and CH_4 partial pressure on the Permeate and the feed side, respectively, where δ represents the thickness of the coated layer, and P_e is an intrinsic characteristic of the membrane, which varies with temperature. The exponent n is associated with the transport mechanism governing the flux of H_2, CO_2, and CH_4, typically ranging between 0.5 and 1. For membranes thicker than 30 μm, primarily transport is governed by solution-diffusion across the lattice, where n = 0.5. Conversely, in thinner membranes, diffusion takes place from bulk to the chemical adsorption and the membrane surface becomes more prominent, potentially increasing n up to 1. Pe permeability is commonly defined by an Arrhenius equation[8]:
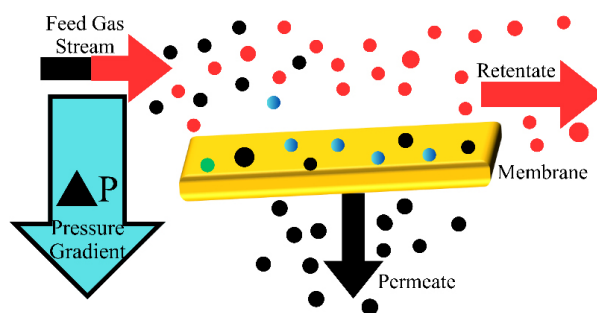

Fig. 2. Schematic diagram of solution-diffusion theory for gas separation membranes[10].

Table 1. Physical Properties of CO_2, CH_4, and H_2[12]

Gas	Kinetic diameter (nm)	Critical temperature (K)
CO_2	0.330	304.1
CH_4	0.380	190.6
H_2	0.289	33.2

$$P_e = Pe° \exp\left(-\frac{E_a}{RT} \right) \tag{2}$$

Where, T, R, E_a, and Pe° represent temperature, gas constant, activation energy, and pre-exponential factor respectively[9].

To evaluate the membrane's performance, it's essential to evaluate the selectivity and permeability of gases[11]. Typically, in polymers, the diffusivity of the penetrant rises as the kinetic diameter decreases and the free volume increases. Likewise, CO_2, CH_4, and H_2 solubility values exhibit that H_2 has high diffusivity as evidenced by the low kinetic diameter of 0.289 nm depicted in Table 1.

4. Polymeric Membranes for H_2, CO_2, CH_4

Polymeric membranes, derived from polyamides, polycarbonates, polyacrylates, polyaniline, and polypyrrole, exhibit optimal permeability and selectivity for carbon dioxide (CO_2) separation, with some reaching performance levels close to Robeson's upper bound. Variations among these patents within each polymeric system
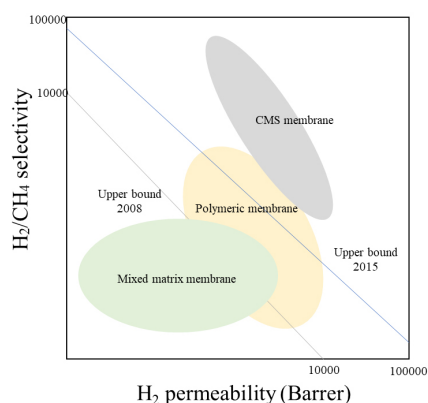
Fig. 3. H_2/CH_4 separation in the polymeric membrane, CMS membrane, and MMMs.

Fig. 4. Separation efficiency of polymeric membranes for H_2/CH_4 gas pair.

arise from the inclusion of bulky substituents and functional groups into the polymer, along with differences in casting mechanisms. Notably, polysulfone is considered a remarkable material for CO_2 separation due to its outstanding thermal and chemical durability as a thermoplastic polymer. However, recent advancements have seen polyimide-based membranes surpassing polysulfone, showcasing superior permeability and selectivity properties alongside reliable mechanical strength, resilience against plasticization, and thermal stability[13].

Nabilah Fazil and colleagues conducted experiments involving fillers employed in polymeric membranes to enhance gas separation performance. They synthesized mixed matrix membranes (MMMs) by blending using the dry phase inversion method, glassy Polyethersulfone (PES) polymer and multi-walled carbon nanotubes (MWCNTs) have been used to produce rubbery block copolymers of polyether block amide (Pebax-1657). Subsequently, the polyether block amide/Polyethersulfone polymer blend mixed matrix membrane containing 10wt% MWCNTs exhibited the utmost performance in CO_2/CH_4 selectivity CH_4 permeability, and CO_2 permeability comparatively pure Pebax-1657, with differences of 66.3% and 11.6%, respectively[14]. In a separate study, Abid Hussain and collaborators synthesized polymeric and mixed matrix membranes using a blend of cellulose acetate (CA) and polyethylene glycol (PEG)
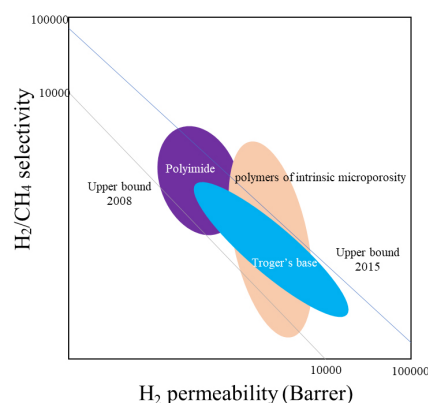
at a 10 wt% concentration, along with varying concentrations of MWCNTs (5, 10, and 15 wt%). The permeation findings show that CO_2/CH_4 selectivity significantly improved. Aside from this, in mixed gas experiments, the CO_2/CH_4 selectivity remarkably enhanced by 13 times, when incorporation of 10% PEG and 18 times for mixed matrix membrane with 10% incorporation of MWCNTs. However, the tensile strength of the mixed matrix membrane was 13 MPa[15].

Li Huang and collaborators examined the selectivity and permeability of polymeric membranes, (MMMs), and carbon molecular sieve (CMS) for H_2/CH_4 gas separation, as illustrated in Fig. 3[17]. Thus, findings indicate that CMS membranes and polymeric membranes demonstrate exceptional H_2/CH_4 separation properties, whereas MMMs, despite being extensively researched, exhibit comparatively lower performance[16].

Additionally, in Fig. 4, the H_2/CH_4 separation outcomes of polymeric membranes are either near or slightly surpass the 2015 upper bound, indicating the promising results by microporous polymers. These polymers, predominantly exemplified by polymers of Troger's base (TB) polymers, polyimides (PI), and polymer of intrinsic microporosity (PIM) emerge as reliable candidates for membrane preparation for the separation of H_2/CH_4. Intriguingly, some polymer of intrinsic microporosity exhibit higher selectivity in aged membranes compared to fresh samples[16].

Thermally rearranged polymers (TR-polymers) belong to the category of heterocyclic rings are examples of aromatic polymers such as polybenzimidazoles (PBI), polybenzothiazoles (PBZ), polybenzoxazoles (PBO), and renowned for their exceptional thermal and chemical properties, even under harsh conditions, ortho-functional polyimide precursors are thermally converted into TR-polymers. This transformation yields micro cavities characterized by an hourglass shape, and a narrow size distribution leading to heightened selectivity and permeability. TR-polymer membranes demonstrate remarkable results for CO_2/N_2 and CO_2/CH_4 in term of separation impacted by factors like functional groups within the preparation method of precursor polymers, copolymerization, and the polymer backbone[17,18].

(PIMs) offer solubility, a significant advantageous approach for solution-based membrane fabrication, alongside remarkable properties in CO_2/N_2 and CO_2/CH_4 separation and permeability. Recent advancements in PIM modifications have centered on functionalizing them with tetrazole groups (TZPIMs), and CO_2-philic pendants. CO_2 selectivity and permeability over lighter gas molecules are enhanced by the robust interaction among tetrazole groups in TZPIMs and CO_2 molecule. Consequently, TZPIMs have exhibited CO_2 permeability exceeding 3000 barrer with a CO_2/N_2, while the selectivity achieved approximately 30[18].

Furthermore, polyether block amide (Pebax) consists of linear chains comprising flexible polyether segments and rigid polyamide segments, imparting notably, high gas permeability and mechanical strength. The polar segments in both blocks exhibit a strong chemical attraction for CO_2, resulting in excellent CO_2/N_2 and CO_2/H_2 separations in polyether block amide membranes. These membranes have comprised a CO_2 permeability of 132 barrer, with CO_2/H_2 and CO_2/N_2 selectivities of 6.1 at 258°C and 3 atm. In recent times, a polyether block amide/PEG blend has garnered attention due to its elevated CO_2 selectivity and permeability, attributed to high gas solubility[19]. Tingxu Yang and colleagues reported that polybenzimidazoles membranes exhibit a
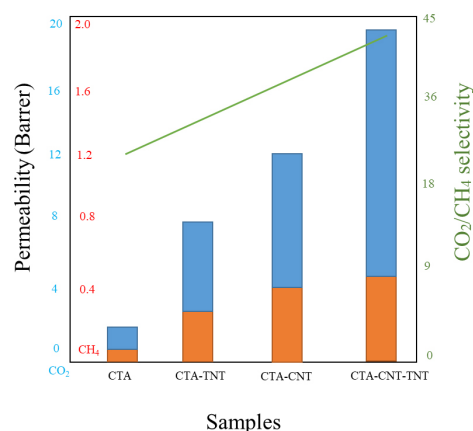

Fig. 5. Bar graph illustrates the single gas permeability and selectivity of the synthesized membranes for CO_2 and CH_4.

high CO_2/H_2 selectivity alongside a comparatively low H_2 permeability. Commercial polybenzimidazoles membranes, manufactured by PBI Products, Inc., showcase an H_2 permeability of 3.7 barrer, with an ideal CO_2/H_2 selectivity of 8.7 at 358°C[20]. In a separate investigation, Chhabilal Regmi and collaborators fabricated a cellulose triacetate (CTA) polymer matrix and incorporated Trinitrotoluene (TNT) functionalized carbon nanotubes (CNT) as nanofillers. The pristine membrane exhibited a CO_2/CH_4 selectivity of 25.08 with a CO_2 permeability of 3.01 barrer upon the incorporation of hybrid fillers (TNT@CNT). Notably, permeability increased nearly six-fold. Furthermore, the CO_2/CH_4 selectivity showed improvement from the incorporation of single fillers (TNT/CNT) were integrated with hybrid fillers (TNT@CNT), achieving a value of 42.98, in the sequence of CTA < CTA-TNT < CTA-CNT < CTA-TNT@CNT, as depicted in Fig. 5[21,22].

Additionally, Murali *et al.* explored the impact of incorporating (MWCNT) affecting the gas permeation properties of H_2, CO_2, and N_2 in polyether block amide membranes. They demonstrated that including MWCNTs increased the membrane's free volume[23]. Tseng *et al.* demonstrated significantly enhanced CO_2 flux and CO_2/N_2 selectivity were evaluated using MWCNT−polyimide nanocomposite[24]. Furthermore, Manoj M. Rajpure investigated cellulose acetate poly-

mer-based MMMs incorporating MgO nanorods as fillers. Notably, a remarkable increase in gas permeation was observed due to the disruption of the polymer chain. The impact of feed pressure and different nanorods loadings (5, 10, and 15 wt%) on the gas permeability and selectivity of CA-based MMMs were investigated at 25°C and 1 to 4 bar gas pressure. The results indicated that the MgO-15/CA MMMs exhibited the highest H_2 permeability reaching 77.80 barrer, a 45% increase over pure CA, with a two-fold increase in CO_2/H_2 selectivity and unchanged CH_4/H_2 selectivity. In contrast, MgO-5/CA MMMs exhibited the highest CO_2 permeability of 62.90 barrer, along with an increase in CH_4/CO_2 selectivity from 22.30 to 24.30[25].

In a recent investigation conducted by Prajwal Sherugar et al., significant selectivity and permeability for CO_2/CH_4 gas separation were achieved. Mixed matrix membranes were effectively produced using Palladium/graphitic carbon nitride ($Pd/g-C_3N_4$) as a nano-additive, with the MMM loaded with 300 mg of the nano-additive. The nano-additive exhibited greater permeability compared to the unfilled membrane, at 2 bar pressure, nearly 5 times for CH_4 and 10 times for CO_2, however, the achieved selectivity of 5.25 for CO_2/CH_4. These results underscore the remarkable properties of Palladium/graphitic carbon nitride as nano-additives in mixed matrix membranes, enhancing the separation and permeability of both pure and mixed gas[26].

4.1. Scale-up of polymeric membrane for H_2 separation membrane

In the 1970s, the first polymeric membrane was reported for effective use of membrane gas separation technologies, focusing on removing H_2 from ammonia purge gas streams[27].

At present, the H_2 demand is around 45 million tons per year[28]. To foster this challenge to promote the development of membrane technologies appropriate for H_2. For instance, Hydrogen is recovered from different refineries, chemical streams, and petrochemicals using membrane processes like the PRISM membrane sys-

tems established by Monsanto and the Polysep membrane systems scaled by universal oil products (UOP), however, currently, sold by Air Products and Chemicals Inc. In addition, both membrane systems are based on polymeric asymmetric materials, which are made of layers of at least two distinct polymers or a single polymer. Consequently, the active polymer layer is likely made of polysulfone. While the Polysep system is based on a spiral wound sheet type contactor, the Prism system is based on a hollow fiber construction. H_2 may be recovered from reactor streams using either method, with purities ranging from 70 to 99% by volume and recoveries from 70 to 95%. Moreover, since 2000, more than 430 patents for hydrogen-selective membranes have been granted[29].

4.2. Role of polymeric membrane in CO_2 capture

There are currently more than 20 significant CO_2 membrane removal plants constructed worldwide, including the Separex membranes in Spain and the Cameron facility in Southeast Asia[30]. Applications for CO_2 separation can be divided into three main categories based on the essential elements of the separation: CO_2/N_2 separation, CO_2/CH_4 separation, and CO_2/H_2 separation. The membrane requirements and considerations vary significantly across different applications due to the diverse process conditions found in industrial CO_2 separation processes[31].

4.2.1. CO_2/CH_4 separation

The most significant commercial use of membrane-based CO_2 separation is for natural gas sweetening, which involves the removal of acid gas from natural gas. However, membrane technology only accounts for around 5% of this industry, which has been dominated by amine absorption technology. Currently, Ube Industries (Japan), MTR, Inc. (US), Honeywell UOP, Schlumberger, Air Liquide (France), and Air Products are major participants in the CO_2 separation membrane industry[32]. However, for a long time, the most frequently used materials at the industry level are few such as Cellulose Acetate membrane. Furthermore,

another commercial membrane material for CO_2/CH_4 separation is called matrimid; it has a CO_2/CH_4 selectivity of 30 to 60. Additionally, Polysulfone membranes have been used to separate CO_2/CH_4, exhibiting permeability values of 20~40 barrer and CO_2/CH_4 selectivity of 15~35[33]. In addition, all manufacturers fabricate CO_2 separation membranes by varying in selective thickness layer leading to different permselectivity.

4.2.2. CO_2/N_2 separation

Membrane separation is challenging for post-combustion flue gas due to high water-saturated flow, and low CO_2 partial pressure. Moreover, high CO_2 permeability above 500 GPU and a minimum selectivity of 40 is required to make a remarkable membrane in this area. According to literature, since 2011, the Norwegian University of Science and Technology (NTNU) has been working to scale up the facilitated transport membrane with industrial partners (Air Products-USA), Tiller Plant (Trondheim Norway), coal power station (Sines Portugal), and colacem cement plant (Gubbio, Italy). NTNU first produced flat sheet membrane modules and later shifted its focus to hollow fiber membranes for increased packing density due to the large flue gas volume. During a testing period of up to six months, the manufactured membrane showed good long-term stability. Additionally, the membrane showed outstanding resistance to pollutants (such as SOx and NOx)[34].

Among the first companies to do CO_2 capture pilot testing is MTR. Nonetheless, the second generation of Polaris membranes exhibits a two-fold CO_2 permeance (2000 GPU) with identical CO_2/N_2 selectivity (50), whereas their first-generation membranes display a CO_2 permeance of about 1000 GPU. A flue gas CO_2 capture pilot test using spiral wound modules of the first generation Polaris membrane was conducted in 2011 with a daily capacity of one ton of CO_2, and subsequently in 2015, the capacity was increased to twenty tons. Throughout 1000-hour stability tests, this membrane demonstrated good stability[35].

Moreover, in a recent study, porous graphene membranes with a two-dimensional selective layer had a remarkable commercialized potential for CO_2 capture. Likewise, this study reported CO_2/N_2 selectivity of approximately 53 and CO_2 permeability of 10,420 with a 20% CO_2 concentration. Notably, incorporating pyridinic nitrogen at the pore edges of graphene through the oxidation of ammonia to a single graphene layer, provided exceptional binding sites for CO_2[36].

4.2.3. CO_2/H_2 separation

In most cases, pre-combustion CO_2 capture from syngas involves CO_2/H_2 separation. Herein, discussed CO_2-selective membrane as at the same time selectivity of both still remains a challenge due to H_2 being a highly diffusive gas, conversely, CO_2 shows high solubility. The CO_2/H_2 selectivity of CO_2-philic membranes without the enhanced transport agent is typically low (< 30), suggesting that the presence of water vapors as a transport agent significantly enhances CO_2/H_2 perm selectivity as syngas easily saturated with water [37]. On the contrary, as reported in the literature, under pre-combustion conditions, all of the studied PDMS, Pebax, and crosslinked PEG membranes had comparatively low CO_2/H_2 separation capabilities[38].

4.3. Implications of polymeric membrane in CH_4 recovery

In a reported study, Polyethersulfone (PES) hollow fiber membrane (HFM) was fabricated through a dry-wet phase inversion procedure, based on the single-gas permeability findings from the lab-scale experiment, mixed gas modeling is used to predict and optimize the pilot plants. The pilot plant's working conditions limit the purity of CH_4 to above 99%, while the Retentate stream contains 5 ppm of H_2S. Over 90% is the acceptable CH_4 recovery ratio achieved during the procedure[39].

In addition, another study was conducted with polyimide fibre membranes (Model CO-C07FH, from UBE, Japan) and polysulfone fibre membranes (with the name PRISM, from Air Products) to evaluate the

membranes ability to produce biomethane, actual biogas was used. whereas, both membrane materials were found to be appropriate based on test findings[40]. It was evident that to get the Retentate CH_4 content to exceed 95% volume percentage using both membranes [41].

5. Challenges and Future Perspectives

Polymeric membranes encounter a well-known trade-off between permeability and selectivity, famously known as the Robeson upper bound. In 1999, Freeman *et al.* proposed a theory for enhancing polymeric membrane performance, emphasizing the need for increased backbone stiffness, inter-chain separation, and improved solubility selectivity to surpass existing upper bounds[12]. However, information on polymer membranes exhibiting high selectivity for the H_2/CO_2 pair remains limited. While selectivity for H_2/CO_2 ranges from 0.5 to 4.0 for most polymers, specially synthesized laboratory polymers often fail to surpass these bounds[30]. Polymer blending, particularly combining glassy and rubbery polymers, remains an underexplored area in gas separation membranes, offering numerous opportunities to enhance membrane performance[31]. Future research could focus on developing methods to control the extent of physical aging in membranes to improve gas separation performance.

Moreover, highly rigid polymer chains contribute to increased microporosity and free volume but often lead to weak mechanical properties. Thus, achieving a balance between mechanical strength and gas separation performance in highly porous membranes is crucial [17]. Additionally, minor gas components such as CO, NH_3, H_2S, SOx, and NOx, present in both natural and flue gases, can degrade polymeric materials, reducing performance and causing premature aging. However, research on the effects of these components on membranes remains scarce in patent literature. Therefore, given the importance of maintaining membrane performance and efforts to prevent membrane degradation,

further investigation in this area is warranted[2].

Acknowledgements

Reference

1. R. S. K. Valappil, N. Ghasem, and M. Al-Marzouqi, "Current and future trends in polymer membrane-based gas separation technology: A comprehensive review", *J. Ind. Eng. Chem.*, **98**, 103-129 (2021).

2. P. Pandey and R. S. Chauhan, "Membranes for gas separation", *Prog. Polym. Sci.*, **26**, 853-893 (2001).

3. P. Bernardo, E. Drioli, and G. Golemme, "Membrane gas separation: A review/state of the art", *Ind. Eng. Chem. Res.*, **48**, 4638-4663 (2009).

4. P. Bernardo and G. Clarizia, "30 years of membrane technology for gas separation", *Chem. Eng. Trans.*, **32**, 1999-2004 (2013).

5. R. W. Baker, "Future directions of membrane gas separation technology", *Ind. Eng. Chem. Res.*, **41**, 1393-1411 (2002).

6. L. M. Gandia, G. Arzamedi, and P. M. Diéguez, "Renewable hydrogen technologies: Production, purification, storage, applications and safety", pp. 245-268, Elsevier, Amsterdam, Netherlands (2013).

7. J. D. Perry, K. Nagai, and W. J. Koros, "Polymer membranes for hydrogen separations", *MRS Bulletin*, **31**, 745-749 (2006).

8. S. Uemiya, "State-of-the-art of supported metal membranes for gas separation", *Sep. Purif. Technol.*, **28**, 51-85 (1999).

9. G. Bagnato, A. Iulianelli, A. Vita, C. Italiano, M. Laganà, C. Fabiano, C. Rossi, and A. Basile, "Pure hydrogen production from steam reforming of biosources", *Int. J. Membr. Sci. Technol.*, **2**, 49 (2015).

10. S. Elhenawy, M. Khraisheh, F. AlMomani, and M.

Hassan, "Key applications and potential limitations of ionic liquid membranes in the gas separation process of CO_2, CH_4, N_2, H_2 or mixtures of these gases from various gas streams", *Molecules*, **25**, 4274 (2020).

11. Y. Alqaheem, A. Alomair, M. Vinoba, and A. Pérez, "Polymeric gas-separation membranes for petroleum refining", *Int. J. Polym. Sci.*, **2017**, 4250927 (2017).

12. V. Bondar, B. Freeman, and I. Pinnau, "Gas transport properties of poly(ether-b-amide) segmented block copolymers", *J. Polym. Sci., Part B: Polym. Phys.*, **38**, 2051-2062 (2000).

13. S. E. Kentish, C. A. Scholes, and G. W. Stevens, "Carbon dioxide separation through polymeric membrane systems for flue gas applications", *Recent Pat. Chem. Eng.*, **1**, 52-66 (2008).

14. N. Fazil, H. Mukhtar, D. F. Mohshim, and R. Nasir, "Gas permeation properties of multiwalled carbon nanotubes on polyether block amide (Pebax-1657)/polyethersulfone (PES) blend mixed matrix membrane for CO_2/CH_4 separation", *Solid State Phenom.*, **307**, 258-263 (2020).

15. A. Hussain, S. Farrukh, A. Hussain, and M. Ayoub, "Carbon capture from natural gas using multi-walled CNTs based mixed matrix membranes", *Environ. Technol.*, **40**, 843-854 (2019).

16. L. Huang, Z. Xing, X. Zhuang, J. Wei, Y. Ma, B. Wang, X. Jiang, X. He, L. Deng, and Z. Dai, "Polymeric membranes and their derivatives for H_2/CH_4 separation: State of the art", *Sep. Purif. Technol.*, **297**, 121504 (2022).

17. Z. P. Smith, D. F. Sanders, C. P. Ribeiro, R. Guo, B. D. Freeman, D. R. Paul, J. E. McGrath, and S. Swinnea, "Gas sorption and characterization of thermally rearranged polyimides based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)", *J. Membr, Sci.*, **415**, 558-567 (2012).

18. S. H. Han, N. Misdan, S. Kim, C. M. Doherty, A. J. Hill, and Y. M. Lee, "Thermally rearranged (TR) polybenzoxazole: Effects of diverse imidiza-

tion routes on physical properties and gas transport behaviors", *Macromolecules*, **43**, 7657-7667 (2010).

19. S. Janakiram, M. Ahmadi, Z. Dai, L. Ansaloni, and L. Deng, "Performance of nanocomposite membranes containing 0D to 2D nanofillers for CO_2 separation: A review", *Membranes*, **8**, 24 (2018).

20. T. Yang, G. M. Shi, and T. S. Chung, "Symmetric and asymmetric zeolitic imidazolate frameworks (ZIFs)/polybenzimidazole (PBI) nanocomposite membranes for hydrogen purification at high temperatures", *Adv. Energy Mater.*, **2**, 1358-1367 (2012).

21. C. Regmi, S. Ashtiani, Z. Hrdlička, and K. Friess, "CO_2/CH_4 and H_2/CH_4 gas separation performance of CTA-TNT@CNT hybrid mixed matrix membranes", *Membranes*, **11**, 862 (2021).

22. G. Veréb, P. Kassai, E. Nascimben Santos, G. Arthanareeswaran, C. Hodúr, and Z. László, "Intensification of the ultrafiltration of real oil-contaminated (produced) water with pre-ozonation and/or with TiO_2, TiO_2/CNT nanomaterial-coated membrane surfaces", *Environ. Sci. Pollut. Res.*, **27**, 22195-22205 (2020).

23. G. Murali, S. R. Abid, M. Amran, R. Fediuk, N. Vatin, and M. Karelina, "Combined effect of multi-walled carbon nanotubes, steel fibre and glass fibre mesh on novel two-stage expanded clay aggregate concrete against impact loading", *Crystals*, **11**, 720 (2021).

24. H.-H. Tseng, I. A. Kumar, T.-H. Weng, C.-Y. Lu, and M.-Y. Wey, "Preparation and characterization of carbon molecular sieve membranes for gas separation—the effect of incorporated multi-wall carbon nanotubes", *Desalination*, **240**, 40-45 (2009).

25. M. M. Rajpure, R. B. Mujmule, U. Kim, and H. Kim, "Fabrication of MgO nanorods blended cellulose acetate-based mixed matrix membranes for selective gas separation of H_2/CH_4, CO_2/CH_4 and H_2/CO_2: Effect of loading and pressure", *Int. J. Hydrogen Energy*, **50**, 615-628 (2024).

26. P. Sherugar, A. M. Antony, N. A. H. M. Nordin, S. A. Patil, and M. Padaki, "Tailoring the $CH_4/CO_2/N_2$ separation performance of ultrapermeable poly-

meric composite membranes by altering the concentration of Pd/g-C$_3$N$_4$", *Fuel*, **361**, 130731 (2024).

27. R. Spillman, "Economics of gas separation membrane processes", *Membrane Separations Technology - Principles and Applications*, pp. 589-667, Elsevier, Amsterdam, Netherlands (1995).

28. P. Hoffmann, "Tomorrow's energy, revised and expanded edition: Hydrogen, fuel cells, and the prospects for a cleaner planet", MIT press, Cambridge, Massachusetts London, England (2012).

29. J. A. Ritter and A. D. Ebner, "State-of-the-art adsorption and membrane separation processes for hydrogen production in the chemical and petrochemical industries", *Sep. Sci. Technol.*, **42**, 1123-1193 (2007).

30. K. Dalane, Z. Dai, G. Mogseth, M. Hillestad, and L. Deng, "Potential applications of membrane separation for subsea natural gas processing: A review", *J. Nat. Gas Sci. Eng.*, **39**, 101-117 (2017).

31. Z. Dai and L. Deng, "Membranes for CO$_2$ capture and separation: Progress in research and development for industrial applications", *Sep. Purif. Technol.*, **335**, 126022 (2023).

32. R. W. Baker and B. T. Low, "Gas separation membrane materials: A perspective", *Macromolecules*, **47**, 6999-7013 (2014).

33. S. Singh, A. M. Varghese, K. S. K. Reddy, G. E. Romanos, and G. N. Karanikolos, "Polysulfone mixed-matrix membranes comprising poly (ethylene glycol)-grafted carbon nanotubes: Mechanical properties and CO$_2$ separation performance", *Ind. Eng. Chem. Res.*, **60**, 11289-11308 (2021).

34. Z. Dai, S. Fabio, N. G. Marino, R. C. Riccardo, and L. Deng, "Field test of a pre-pilot scale hollow fiber facilitated transport membrane for CO$_2$ capture", *Int. J. Greenh. Gas. Con.*, **86**, 191-200 (2019).

35. L. S. White, X. Wei, S. Pande, T. Wu, and T. C. Merkel, "Extended flue gas trials with a membrane-based pilot plant at a one-ton-per-day carbon capture rate", *J. Membr. Sci.*, **496**, 48-57 (2015).

36. K.-J. Hsu, S. Li, M. Micari, H.-Y. Chi, L. F. Villalobos, S. Huang, L. Zhong, S. Song, X. Duan, and A. Züttel, "Graphene membranes with pyridinic nitrogen at pore edges for high-performance CO$_2$ capture", *Nat. Energy*, DOI:10.1038/s41560-024-01556-0.

37. Y. Han and W. W. Ho, "Polymeric membranes for CO$_2$ separation and capture", *J. Membr. Sci.*, **628**, 119244 (2021).

38. C. A. Scholes, J. Bacus, G. Q. Chen, W. X. Tao, G. Li, A. Qader, G. W. Stevens, and S. E. Kentish, "Pilot plant performance of rubbery polymeric membranes for carbon dioxide separation from syngas", *J. Membr. Sci.*, **389**, 470-477 (2012).

39. K. H. Kim, K. J. Baik, I. W. Kim, and H. K. Lee, "Optimization of membrane process for methane recovery from biogas", *Separ. Sci. Technol.*, **47**, 963-971 (2012).

40. M. T. Khalid, T. Anjum, A. L. Khan, F. Rehman, M. Aslam, M. A. Gilani, F. H. Akhtar, M. Lee, I. S. Chang, and M. Yasin, "Task-specific polymeric membranes to achieve high gas-liquid mass transfer", *Chemosphere*, **313**, 137603 (2023).

41. V. Vrbová and K. Ciahotný, "Upgrading biogas to biomethane using membrane separation", *Energy Fuels*, **31**, 9393-9401 (2017).