https://doi.org/10.3311/PPch.42466

Periodica Polytechnica Chemical Engineering

Polymeric Hollow Fiber Membranes for Biogas Enrichment: Influence of Materials Selections Fabrication Parameters and the Potential of Artificial Intelligence

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Received: 11 October 2025, Accepted: 19 January 2026, Published online: 16 February 2026

Abstract

Membrane based gas separation is a next-generation technology for CO_2 capture and biogas upgrading, offering lower energy consumption and reduced chemical use compared to conventional methods. Hollow fiber membranes have emerged as a leading solution due to their energy efficiency, compact design, and high separation performance. However, the trade-off between permeability and selectivity remains a challenge, driving innovations in advanced materials such as polymeric, blended, and mixed-matrix membranes, which enhance efficiency and stability for superior gas separation. To further optimize membrane performance and scale-up production, mathematical modeling plays a crucial role in predicting separation efficiency and guiding material selection. However, traditional models often struggle to accurately capture dynamic behaviors and variations in feed conditions. Recent advancements in artificial intelligence (AI) and machine learning have transformed membrane design by enabling rapid material screening, performance prediction, and process optimization, significantly reducing experimental efforts. The integration of advanced materials, AI-driven modeling, and digital optimization will drive the next generation of high-performance membranes, offering sustainable solutions to global environmental challenges.

Keywords

CO_2 capture, methane enrichment, biogas, hollow fiber membranes, artificial intelligence

1 Introduction

Development in CO_2 capture technologies is imperative to mitigate greenhouse gas emissions from industrial and energy sectors, directly addressing climate change. Advancements focus on sustainable methodologies such as direct air capture powered by renewable energy, electrochemical CO_2 reduction, and bio-based absorbents to improve efficiency and scalability. The advancement of these technologies is crucial for enabling a circular carbon economy and achieving carbon neutrality. In the pursuit of sustainable energy solutions, biogas has emerged as a promising renewable alternative, derived from organic waste. As a significant renewable energy resource, biogas offers substantial environmental benefits throughout its production and utilization. It can be effectively harnessed for electricity generation in co-generation systems or combined heat and power (CHP) applications, injected into household pipeline systems for distribution, and used as a transportation fuel [1]. Many countries now have filling stations offering either 100% methane or blends of biogas and natural gas [2].

Biogas typically consists of approximately 45–70% methane and 30%–55% carbon dioxide [3]. In addition to these primary components, biogas contains trace amounts of other gases, such as hydrogen sulfide and water vapor. The calorific value of biogas is primarily determined by its CH_4 content, making CO_2, though inert, undesirable as it reduces the overall energy value [4]. To utilize biogas

Cite this article as: Murtaza, T., Zia-ul-Haq, M., Sulaiman, M., Ching, O. P., Jamil, A., Maqsood, K., Ramzan, N. "Polymeric Hollow Fiber Membranes for Biogas Enrichment: Influence of Materials Selections Fabrication Parameters and the Potential of Artificial Intelligence", Periodica Polytechnica Chemical Engineering, 2026. https://doi.org/10.3311/PPch.42466

as a vehicle fuel or for injection into the natural gas grid, it must be upgraded to enhance its methane concentration and eliminate harmful impurities that could damage engines or fuel cells or pose toxicity risks. This requirement has driven the development of various technologies designed to treat biogas and achieve a specific composition suitable for these applications.

Numerous technologies have been developed for biogas upgrading, with the most widely used and established methods focusing on the physicochemical removal of CO_2. Common approaches include physical absorption, chemical absorption, adsorption, cryogenic separation, pressure swing adsorption (PSA), chemical hydrogenation, and membrane-based separation techniques [5]. Some of these technologies are commercially available today. Physical absorption, for instance, leverages the differing solubilities of CO_2 and CH_4 in various solvents. By selecting a solvent with high CO_2 solubility but minimal affinity for CH_4, the two gases can be effectively separated. Key factors influencing the selection and performance of these technologies include raw biogas consumption, heat and energy demands, operating costs, CH_4 losses and recovery rates, purification efficiency, and outlet pressure [6]. Among these technologies, membrane technology stands out for its exceptional performance and numerous advantages as depicted in Fig. 1 [7]. Notably, it offers lower energy demand, leading to reduced operational costs, greater cost-effectiveness compared to other methods, and higher purification efficiency, making it a highly attractive option for biogas upgrading [8].

Membrane-based separation processes are highly compelling for biogas upgrading due to their minimal energy requirements, remarkable selectivity, simple module design and construction, and cost-effectiveness [9]. Membrane technology offers high methane recovery efficiency and enables the capture of pure CO_2. However, conventional organic and inorganic membranes used for gas separation in commercial applications are constrained by a trade-off between permeance and selectivity, as demonstrated by the Robeson upper bound graph [10]. Membranes are classified based on material, bulk structure, membrane module configuration, and transport mechanisms [11]. Membranes can be made from polymeric materials, inorganic materials, or a combination of both. Each type of material offers distinct advantages and disadvantages. Polymeric membranes are widely used due to their ease of fabrication and lower cost compared to inorganic membranes [12]. Moreover, the Robeson upper bound illustrates a fundamental trade-off between the two key performance metrics for most polymeric membranes: permeability and selectivity as shown in Fig. 2 [13]. This means that as the permeability of a membrane increases, its selectivity tends to decrease, and vice versa. This limitation poses a challenge in designing membranes that simultaneously achieve high gas flux and precise separation efficiency, driving ongoing research to develop advanced materials and techniques to overcome this barrier [14]. For CO_2 removal from biogas, a wide range of membrane materials has been extensively studied. Most materials developed before 1991 fall within the performance limits defined by the 1991 Robeson upper bound. Over the past two decades, significant advancements have been made to enhance gas permeability and selectivity, leading to the development of novel materials that pushed the upper bound forward, resulting in the updated 2008 Robeson upper bound. Materials such as thermally rearranged (TR) polymers, fixed-site carrier membranes (FSC), mixed-matrix membranes (MMMs), and high free volume polymers have demonstrated exceptional performance, surpassing the Robeson upper bound and offering improved efficiency for gas separation applications [8].

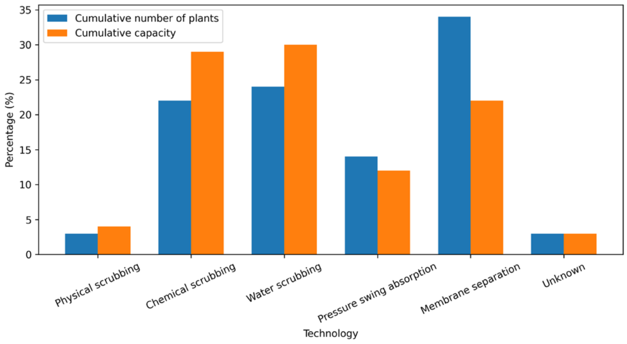


Fig. 1 Market share of biogas upgrading and purification technologies [7]

Furthermore, membrane performance is also heavily influenced by fabrication methods and module design. Hollow fiber membranes (HFMs) are particularly notable

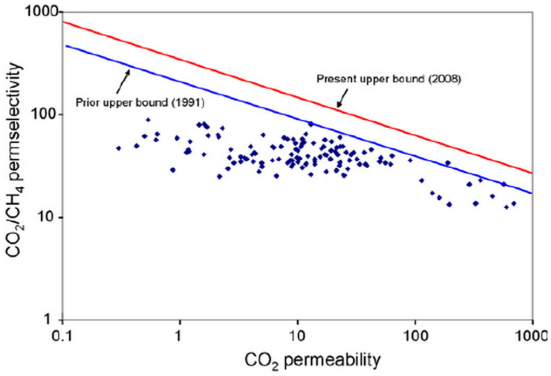


Fig. 2 Robeson's prior and present trade-off curve for CO_2 and CH_4 gas pair [13]

for their self-supporting structures and high packing density [15, 16]. For instance, a spiral-wound module with a 20 cm diameter and 1 m length provides 20–40 m^2 of membrane area, while a hollow fiber module using 100 µm fibers can offer approximately 300 m^2 of membrane area [16].

Table 1 offers a comprehensive comparison of various types of available membrane modules, highlighting key parameters such as packing density, cost, and pressure drop. Today, most gas separation membranes are developed as hollow fiber modules, with less than 20% as spiral-wound modules. Despite the advantages of hollow fiber geometry, cost-effectiveness remains a key parameter for commercialization. Hollow fiber modules cost 2–5 USD/unit area,compared to 10–100 USD for spiral-wound modules. Additionally, their cylindrical shape can withstand transmembrane pressures up to 1000 psi, and their compact design reduces space requirements for setup and scaling. This makes HFMs highly efficient for large-scale gas separation processes.

Most reviews focus on hollow fiber membrane synthesis, inorganic fillers, and their applications, with few addressing spinning parameters or their impact on performance. While artificial intelligence (AI) and machine learning (ML) have improved understanding and optimization, their use in membrane technology is limited and mostly focused on flat-sheet membranes. Rodero et al. [8] give a comprehensive overview of advancement of membrane technology for biogas upgradation and discuss the MMMs performance based on CO_2/CH_4 selectivity and the key challange is the defect free MMMs membranes and their study found that polymeric membranes with 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) are the only once to separate the H_2S and CO_2 simultaneously. Similarly Galizia et al. [17] in their review article highlights the less use of membranes for natural gas separation likely about 10% and the reason is low permeation and selectivity, also highlight the plasticization issue of the membrane material due to CO_2 and other hydrocarbons. Beyond experimental investigations, theoretical analyses have been carried out to quantify CO_2 transfer behavior in hollow fiber membrane contactors handling CO_2/N_2 gas mixtures. Rather than relying on a single modelling approach, these studies explore both lumped and spatially distributed descriptions to clarify the roles of fluid dynamics, phase-to-phase mass transfer resistance, and partial membrane wetting on absorption rates. Related modelling efforts addressing CO_2 removal from aqueous media using similar contactor configurations indicate that stripping performance is primarily controlled by coupled diffusion and reaction processes, as well as by the selected flow configuration [18].This review highlights AI and ML applications in CO_2 separation and explores their potential for fabricating defect-free hollow fiber membranes and applicatons in material advancement, with future directions suggested. Process/optimization stages in AI and ML program to optimize the dope fluuid flow rate, effect on pore size and effect on morphology is shown in Table 2 [19–21].

Table 1 Comparison of HFM modules with plate and frame and spiral wound modules

Property	Membrane geometry		
	Plate and frame	Spiral wound	Hollow fiber
Manufacturing cost, USD/m^2	50 to 200	10 to 100	2 to 5
Packing density	Low	Low	High
Pressure drop	Low	Low	Low
Suitability for high pressure	Moderate	Yes	Yes
Surface area (per unit volume)	Low	Low	High
Space required	Large	Large	Low

Table 2 HFMs process/optimization stages

Process/optimization stage	Modelling/optimization approach	Key HFM structural parameters	Effect on CO_2/CH_4 separation performance	Relevance to biogas upgrading	Ref.
Spinning parameter optimization	Predictive and data-driven process modelling	Pore architecture, selective layer thickness, morphology uniformity	Controls gas transport pathways and minimize defects	Enhances membrane efficiency and operational stability	[19]
Phase inversion and solidification control	Kinetic and regression-based modelling	Pore size, pore size distribution, macro void formation	Balances permeability and selectivity	Improves CO_2 removal from biogas	[20]
Structural property optimization	Metaheuristic and swarm-based optimization techniques	Overall microstructure and material properties	Enables optimal permeability–selectivity trade-off	Supports rational HFM design for biogas upgrading	[21]

2 Gas separation mechanism

Gas separation processes play a crucial role in numerous industrial applications, including biogas purification, air separation, and CO_2 capture. These processes leverage the distinct physical properties of gases, such as molecular size, polarity, and diffusivity [22]. The separation can be accomplished using various methods, tailored to the type of membrane and the specific application as shown in Fig. 3 [23]. In porous membrane-based separation, gas molecules pass through pores within the membrane material [24]. This method primarily depends on the size and shape of the pores, which facilitate the easier passage of smaller gas molecules compared to larger ones. As the gas mixture moves through the porous structure, components with smaller kinetic diameters permeate more quickly, while those with larger molecules are hindered as depicted in Fig. 3 (a) to (c). This selective permeation results in the separation of gases based on their molecular sizes. In contrast, dense membranes lack visible pores and instead rely on the principles of solubility and diffusivity to achieve separation as shown in Fig. 3 (d) [25]. Gas separation mechanisms often involve the dissolution and diffusion of gas molecules through membrane materials. In this process, gas molecules first dissolve into the membrane material and then diffuse through it. Separation is achieved based on the differences in solubility of each gas within the membrane. Gases with higher solubility in the membrane permeate more rapidly, while those with lower solubility pass through more slowly. This approach is particularly effective for separating gases with distinct chemical properties, such as CO_2 from N_2 or O_2. Diffusion-based separation relies on the varying rates at which different gas molecules move through the membrane material. In porous membranes, lighter gases with smaller molecular sizes diffuse more quickly than heavier gases. In dense membranes, separation is governed by both solubility and diffusion rates, allowing for selective permeation of specific gases. Solubility-based separation, a key mechanism in dense membrane processes, involves gas molecules dissolving into the membrane material before diffusing through it. This method leverages differences in solubility to achieve efficient gas separation [26]. Gases that exhibit higher solubility in the membrane material diffuse more easily, enabling their separation based on solubility differences. This principle is widely applied in processes such as CO_2 capture, where the higher solubility of CO_2 in specific polymer membranes compared to other gases allows for its selective extraction from gas mixtures.

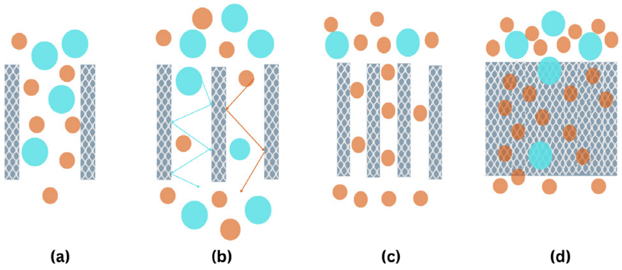


Fig. 3 Schematic illustration of gas separation mechanisms across membranes with varying porosity: (a) convective flow, (b) Knudsen diffusion, (c) molecular sieving, (d) sollution diffusion [23]

These separation mechanisms are essential for designing efficient and effective systems for gas purification, storage, and industrial applications. The selection of membrane material and the specific separation process depends on the properties of the gas mixture and the requirements of the intended application.

3 Hollow fiber membranes

HFMs are composed of thin polymeric tubes with diameters ranging from 50 to 200 μm [27]. Fig. 4 [21] shows the schematic and field emission scanning electron microscope (FESEM) image of a hollow fiber. The selective layer, responsible for gas separation, is positioned on the outer surface of the fibers, which is exposed to the high-pressure gas stream [27].

A hollow fiber membrane module typically contains tens of thousands of these parallel fibers, with both ends sealed in epoxy tube sheets to create a structured and efficient separation unit [28]. The permeance was calculated by Eq. (1) [29].

$$\frac{P_i}{l} = \frac{Q}{T}\frac{273.15}{A\Delta p_i}, \tag{1}$$

$$a_{ij} = \frac{p_i}{p_j}. \tag{2}$$

In Eq. (1) P_i/l is the permeance expressed in gas permeation unit (GPU), where P is the permeance, l is the membrane thickness, A is the effective membrane area (cm^2) and Δp_i is the pressure difference between the feed and permeate side (cmHg; 1 cmHg = 1.33 KPa). T is the temperature at which permeation was performed. The ratios of the permeability of pure gas i and pure gas j is defined as an ideal selectivity (α_{ij}) as shown in Eq. (2).

3.1 Phase inversion methods for hollow fiber membranes

The commercialization of membrane technology for separation purposes was initially delayed due to the absence of facilities capable of producing high-performance and

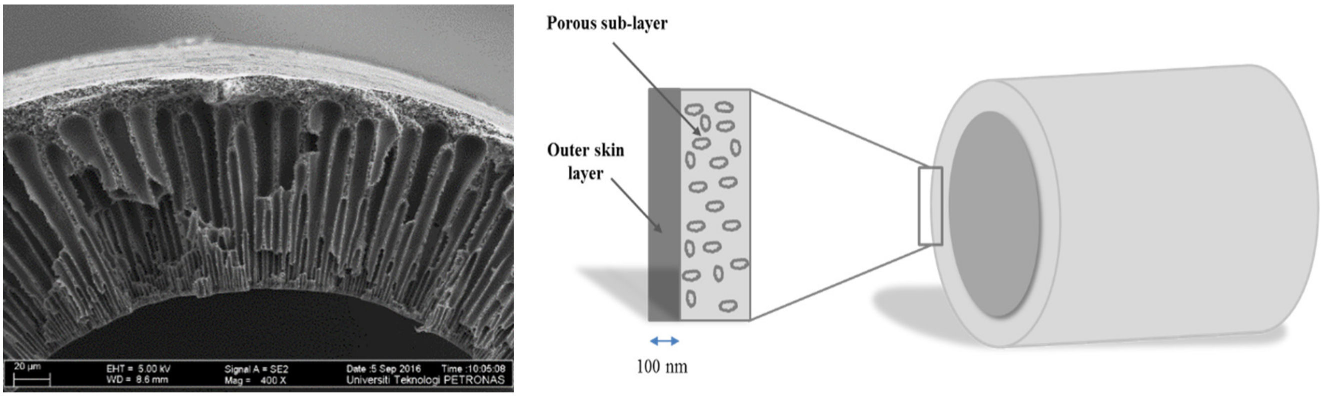


Fig. 4 Structure of asymmetric membrane fibers [21]

cost-effective membrane modules. A significant breakthrough occurred when Loeb and Sourirajan developed a novel phase inversion method, enabling the production of cellulose acetate (CA) membranes with a selective thin layer at the sub-micrometer level. This advancement laid the groundwork for the widespread commercial use of gas separation membranes. Today, most industrial-scale membranes are manufactured as hollow fiber modules using the phase inversion technique. As depicted in Fig. 5 [7], hollow fiber spinning technology can be divided into four primary methods: melt spinning, dry spinning, wet spinning, and dry/wet spinning.

3.1.1 Dry-wet spinning

This process involves extruding a polymer solution through a spinneret into a coagulation bath filled with a nonsolvent.

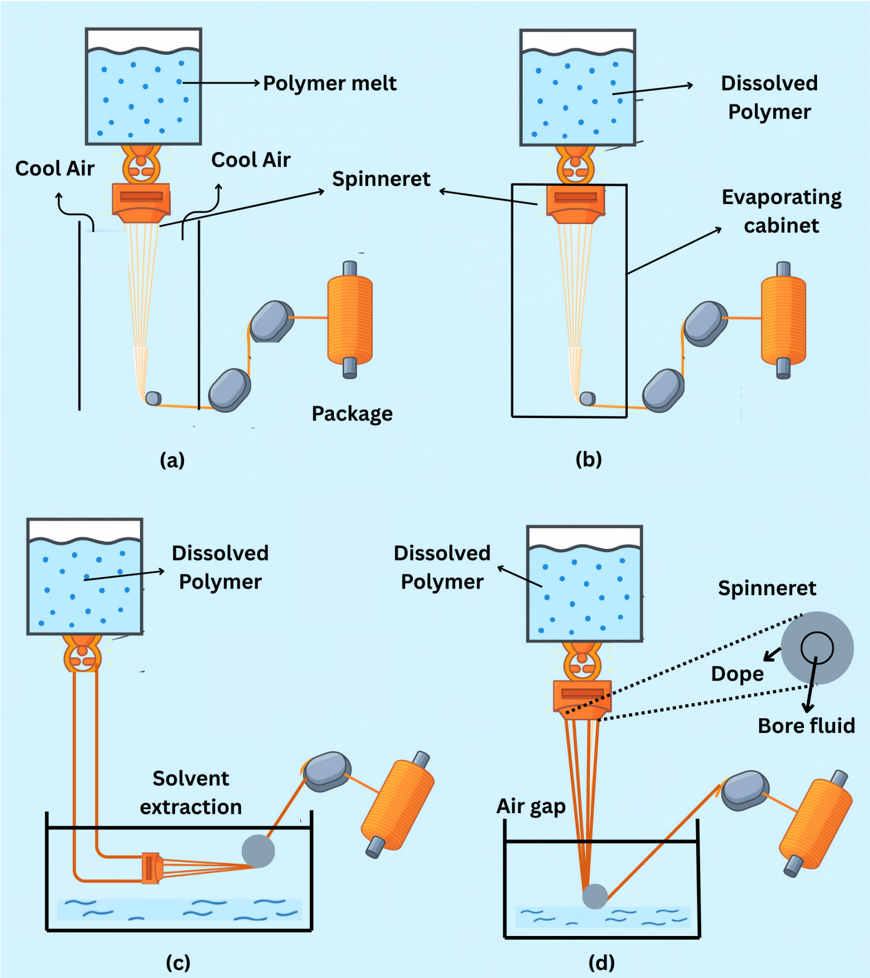


Fig. 5 Schematic representation of: (a) melt spinning; (b) dry spinning; (c) wet spinning; and (d) dry/wet spinning processes [7]

As the solvent diffuses into the coagulation bath, phase separation occurs, leading to the formation of a porous membrane structure. The hollow fiber shape is achieved by using a spinneret designed with an annular orifice, which creates the tubular geometry of the fibers [30, 31].

The dry/wet spinning technique helps minimize defects by extending the air gap between the spinneret and the coagulation bath. Polymers like polyimide (PI) and polysulfone (PSF), which are commonly used for CO_2/CH_4 separation, typically have high glass transition temperatures, making melt spinning unsuitable for producing hollow fiber membranes. As a result, solution spinning, particularly the dry/wet method, is the preferred and most widely used process for preparing membranes in biogas separation applications.

3.1.2 Wet spinning

Similar to dry-wet spinning, this method involves extruding the polymer solution directly into the coagulation bath without any prior exposure to air. This approach allows for finer control over the pore structure and morphology of the resulting membranes. An example of this wet spinning technique is the use of 6FDA-durene polyimide, which is employed for CO_2/CH_4 separation due to its effective performance in gas separation applications [21].

3.1.3 Dry spinning

The dry spinning method for HFM synthesis involves extruding a polymer solution through a spinneret into a heated environment, where the solvent evaporates, leaving behind a solid fiber structure [27]. In this process, the polymer is dissolved in a volatile solvent to form a viscous solution, which is then forced through an annular spinneret. As the solution exits the spinneret, it enters a heated chamber or air gap, where the solvent rapidly evaporates, causing the polymer to solidify into a hollow fiber. The hollow core is maintained by introducing a bore fluid (gas or liquid) through the center of the spinneret, which prevents the fiber from collapsing during the drying process.

3.1.4 Melt spinning

In melt spinning, the polymer is first melted and then extruded through a spinneret into a cooling chamber, where it solidifies into fibers. HFMs can be created by using a spinneret with an annular orifice, which allows air or inert gas to flow through the center of the fiber. This prevents the fiber from collapsing and maintains its hollow structure as it solidifies [20].

3.1.5 Thermal-induced phase separation

In the thermally induced phase separation (TIPS) process, a polymer solution is heated to fully dissolve the polymer and then rapidly cooled to trigger phase separation. During this process, the polymer-rich phase solidifies to form the membrane structure, while the solvent-rich phase creates the porous network. HFMs can be produced by extruding the polymer solution through a spinneret and directly into a cold quenching bath, which solidifies the structure and establishes the desired hollow fiber geometry [32].

4 The selection of appropriate materials

The Robeson upper bound graph illustrates the inherent trade-off between permeability and selectivity in gas separation membranes, particularly when comparing glassy and rubbery polymers. Glassy polymers, commonly used in HFMs, offer high selectivity due to their rigid molecular structure, which enhances separation efficiency. However, this rigidity limits gas transport, resulting in lower permeability and reduced throughput. On the other hand, rubbery polymers exhibit higher permeability, allowing for greater gas flow through the membrane. Yet, their more flexible molecular structure leads to lower selectivity, as they provide less control over the selective passage of gases. This trade-off is a crucial consideration in gas separation applications, where achieving an optimal balance between high permeability (for efficient gas throughput) and selectivity (for effective separation) is essential to meet performance requirements. The Robeson upper bound serves as a benchmark, emphasizing that no material can surpass this limit, highlighting the fundamental challenge in membrane design [30].

Nevertheless, polymer membranes are widely utilized for gas separation, their surface properties often present limitations. Developing new polymeric materials can enhance membrane separation performance, but this approach is often time-consuming and expensive. To achieve rapid and cost-effective improvements in membrane performance, it is crucial to assess the material's physical and chemical properties, such as permeability and selectivity. This evaluation helps identify optimal modifications or enhancements that can be implemented efficiently, ensuring better membrane performance without significant delays or costs. Table 3 illustrates the polymers used for CO_2 separation from CH_4 gas in the literature [33–39].

5 Improving the polymeric membrane performance

To improve the performance of polymeric membranes often blending of glassy and rubbery polymers is considered.

Table 3 Glassy and rubbery polymer performance

Polymeric HFMs	Gas pair	Permeation [GPU] CO_2	Selectivity	Testing conditions	Ref.
Glassy polymer					
PES	CO_2/CH_4	85.1	35.5	25 °C, 1 bar	[33]
CTA	CO_2/CH_4	110	22–28	35 °C, 31.3 bar	[34]
PEI	CO_2/CH_4	7.53	17.9	30 °C and 2 atm	[35]
Matrimid	CO_2/CH_4	17.7	24.3	30 °C and 2 atm	[35]
PVC	CO_2/CH_4	24	0.937	25 °C, 5 bar	[36]
Rubbery polymer					
PVDF	CO_2/CH_4	250	3	25 °C, 1 bar	[37]
Uio-66 / Pebax	CO_2/CH_4	225	17	25 °C, 2 bar	[38]
P-MIL-53, PDMS	CO_2/CH_4	40.24	32.03	35 °C, 5 bar	[39]

Notes: polyethersulfone (PES), cellulose triacetate (CTA), polyetherimide (PEI), Matrimid® polyimide, poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVDF), and polydimethylsiloxane (PDMS), along with MOF-based composite systems such as UiO-66/Pebax and P-MIL-53.

Another method is incorporation of inorganic nanoparticles to improve the performance. Grafting, crosslinking are also the other methods to improve the trade off limit [40].

5.1 Blending

Polymer blending is a highly effective and efficient technique for modifying membranes using existing materials, offering notable advantages in terms of cost and time savings. By combining the properties of different polymers, this method allows for the creation of new materials with tailored characteristics to meet specific requirements. Polymer blends are particularly favored in membrane development due to their simplicity, cost-effectiveness, and ability to consistently deliver reliable results. However, a key challenge in polymer blending lies in achieving molecular-level miscibility between the components. The thermodynamics of polymer blends play a critical role in determining factors such as the dispersion state, morphology of the two-phase mixtures, and interphase adhesion, all of which significantly influence the properties and performance of the final membrane product [41, 42].

Polymer blends can be categorized into three types: miscible, immiscible, and partially miscible. In a miscible blend, the two polymers form a homogeneous, single-phase system, where they dissolve into each other at the molecular level due to hydrogen bonding and physical interactions. In contrast, an immiscible blend results in a heterogeneous phase, where the polymers do not dissolve into each other, creating distinct interfaces between the components. A partially miscible blend occurs when one polymer partially dissolves into the other, resulting in a partially homogeneous, heterogeneous phase [43]. Table 3 provides a brief comparison of glassy-glassy, glassy-rubbery, and rubbery-rubbery polymers, highlighting their distinct properties and behaviors in polymer blends.

This approach offers a cost-effective and time-efficient solution, enabling the integration of the beneficial properties of different materials to develop new compounds with tailored characteristics. By combining the strengths of various polymers, it becomes possible to achieve enhanced performance without significant financial or time commitments, making it an attractive strategy for membrane modification and material development [44]. Membranes created through blending demonstrate excellent mechanical strength, processability, and permeability, along with unique properties that differ from those of individual polymers [45]. Lamlong and Taweepreda [46] developed blended polyvinyl chloride-polyethylene glycol (PVC-PEG) membranes that exhibited high gas permeability but low gas selectivity. Salleh et al. [47] produced carbon fiber HFMs using blends of polyetherimide and 6 wt% polyvinylpyrrolidone (PVP), achieving selectivity values of 55.33 for CO_2/CH_4 and 41.50 for CO_2/N_2. Polyetherimide and polysulfone are glassy polymers and showed superior separation performance for CO_2 separation [48, 49]. Kapantaidakis and Koops [50] demonstrated that adding Matrimid to PES HFMs could markedly enhance membrane permeability compared to unmodified PES. Table 4 summarizes polymer blends employed for CO_2/CH_4 separation that have exhibited superior separation performance..

5.2 Incorporation of fillers

A recent innovation combining inorganic and polymeric membrane approaches is mixed matrix membranes. These membranes feature a heterogeneous gas separation

Table 4 Polymeric blend hollow fiber membranes and their CO_2/CH_4 separation performance

Polymer A	Polymer B	Gas permeation CO_2	Selectivity CO_2/CH_4	Testing conditions	Ref.
PEI	PVP	1.66	63.6	25 °C, 7 bar	[49]
PES	Matrimid	31–60	40–35	25 °C	[50]
PBI	Matrimid	4.81	41.81	35 °C, 10 atm	[51]
PIM-1	Matrimid	243.2	34.3	25 °C, 1 atm	[52]
Poly (ether-b-amide)	Polysulfone	260	32	25 °C, 100 psi	[53]

Note: Polybenzimidazole (PBI), polymer of intrinsic microporosity-1 (PIM-1)

layer, consisting of discrete inorganic particles dispersed within a continuous polymeric phase. This hybrid design enhances performance by leveraging the strengths of both materials [54]. The incorporation of dispersed particles in membranes can influence gas permeability in three ways:

1. the particles may act as molecular sieves, selectively altering permeability based on molecular size;
2. they can disrupt the polymeric matrix, creating additional microcavities and increasing permeability;
3. they may act as barriers to gas transport, reducing permeability.

These effects depend on the nature of the particles and their interaction with the polymer matrix [54]. MMMs offer a promising solution to overcome the limitations of both molecular sieves and polymers, enabling CO_2 separation performance that can surpass Robeson's upper bound. By combining the selective properties of inorganic fillers with the processability of polymers, MMMs achieve enhanced gas separation efficiency, making them a significant advancement in membrane technology [55]. Table 5 [19, 27, 48, 53, 56–59] presents the incorporation of various fillers into polymer matrices to fabricate MMMs, along with a comparison of their performance.

Recent work highlights next-generation CO_2-separation membranes – especially advanced polyimides and mixed-matrix systems – designed to handle humid, H_2S-rich biogas (Table 6 [60–62]). Modeling studies of hollow-fiber membrane contactors describe CO_2 absorption from N_2 using detailed mass-transfer equations across gas, membrane, and liquid zones. Similar mathematical frameworks are applied to CO_2 stripping from water, emphasizing equilibrium behavior and the influence of membrane wetting. Pilot-scale tests with commercial polyimide modules under real biogas conditions show solid performance but also reveal durability challenges under moisture and H_2S exposure [60].

Table 5 Mixed matrix membranes and their separation performance

Polymer	Filler	CO_2 permeation [GPU]	Gas pair	Selectivity	Testing conditions	Ref.
Ultem®1000	MIL-53	27.9	CO_2/N_2	29.7	35 °C, 0.50 MPa	[53]
PSf	Graphene oxide (GO)	74.47	CO_2/CH_4	29.9	25 °C, 1–5 bar	[56]
CA	NH2-MIL-53(Al) filler	2.85	CO_2/CH_4	11.8	30 °C, 3 bar	[57]
PEI	Montmorillonite	130	CO_2/CH_4	18.35	25 °C, 4 bar	[27]
PSf	Fumed silica	90.04	CO_2/CH_4	32.74	25 °C, 5 bar	[58]
CA, PDMS	NH2-MIL-53(Al)	8.23	CO_2/CH_4	26.6	3 bar, 25 °C	[19]
Ultem®1000	ZIF-8	26	CO_2/N_2	36	7 bar, 35 °C	[59]
PSf	TNTs	120	CO_2/CH_4	25.93	25 °C, 3 bar	[48]

Notes: Ultem® 1000 (polyetherimide, PEI), polysulfone (PSf), cellulose acetate (CA)

Table 6 Quantitative comparison of commercial hollow fiber membranes for biogas

Material/module	Feed conditions	CO_2 permeance (GPU)	CO_2/CH_4 selectivity	Impurities impact	Ref.
PSF/PDMS HF module (airrane, commercial)	Synthetic/biogas	158 GPU (CO_2 pure)	26.5	Baseline industrial membrane data (mixed gas, 7–10 bar).	[60]
Cellulose acetate-based carbon HF	Real biogas, 20 bar, ~1 ppm H_2S, humid	–	CH_4 purity ~96% (implies reasonable selectivity)	CO_2 permeance drops under humidity; H_2S reduces permeability by ~70%.	[61]
Cellulose triacetate CA 200 nm HF	~31 bar with C_2–C_3 and acid gases	~115 GPU (CO_2)	~22	Maintains performance in presence of complex contaminants.	[62]

6 Parameters effecting the hollow fiber membranes performance

The fabrication of HFMs is governed by numerous conditions that significantly influence the phase inversion kinetics, thereby determining the membrane's morphology and permeation properties. This section examines the impact of critical production parameters, including dope viscosity, dope flow rate, air gap and take-up speed, on the final membrane characteristics.

6.1 Dope viscosity

Dope viscosity is a critical parameter governing the solvent-coagulant exchange rate during the phase inversion process, which directly influences the spinning of membrane fibers. This exchange leads to the formation of polymer-rich and polymer-lean phases, creating an initially unstable membrane structure that stabilizes during solidification. The solvent-coagulant interaction also triggers the formation of macrovoids, typically exhibiting finger-like or sponge-like structures. Macrovoid formation can be minimized by optimizing spinning parameters such as dope viscosity, air gap, polymer concentration, delayed demixing, addition of high-viscosity components, surfactants, high shear rates, elevated coagulation bath temperatures, or high elongational draw [63]. Among these, increasing dope viscosity – either by adding viscous components or raising polymer concentration is the most straightforward approach. Jamil et al. [64] investigated the impact of dope viscosity on polyetherimide (PEI) HFMs, identifying 25 wt.% PEI as the critical concentration for optimal morphology. Peng et al. [65] explored the interplay between dope viscosity, air gap, and take-up speed on the morphology of PSF, P84, and CA membranes, emphasizing their interdependence. Spinning fibers at critical parameter values effectively eliminated macrovoids, demonstrating the importance of precise control over these variables in membrane fabrication.

6.2 Dope flow rate

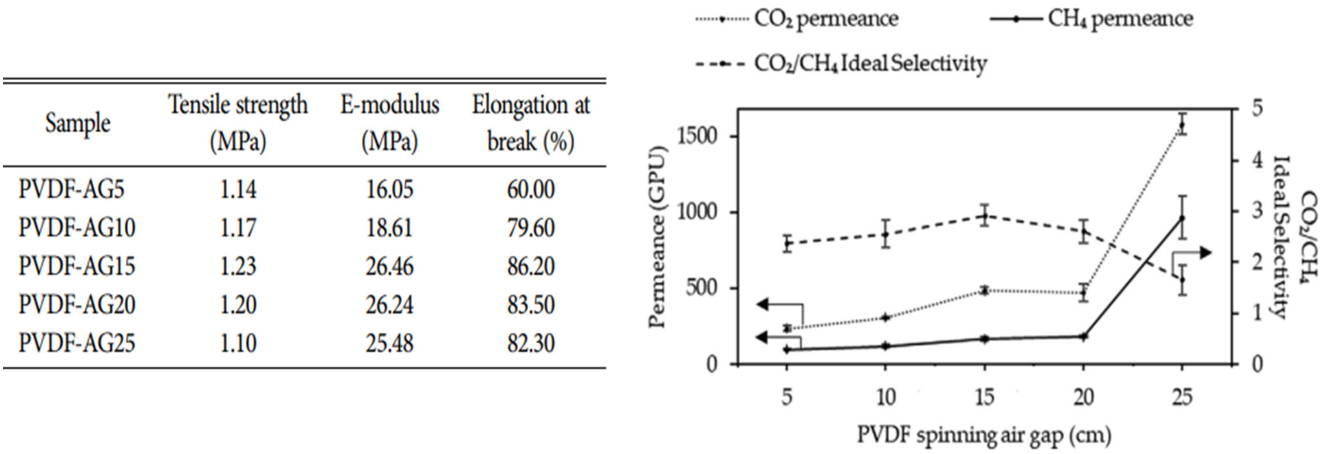
The dope flow rate, defined as the rate at which the polymer solution is extruded during fiber spinning, plays a critical role in determining the fiber's morphology, pore structure, and permeability. Excessive flow rates can lead to a defective or thicker selective outer layer, while insufficient flow rates may result in a defective dense outer layer [66]. Woo et al. [67] examined the effects of varying dope flow rates (1.05, 1.50, 2.25, and 3.00 mL/min) at a constant bore flow rate of 2.0 mL/min. Their findings showed that increasing the dope flow rate caused the outer and inner fiber diameters to expand and the walls to thicken. However, higher flow rates also led to reduced CO_2 permeance and CO_2/N_2 selectivity, attributed to unfavorable cavity radii and increased mass transfer resistance. This outcome is likely due to inadequate liquid-liquid de-mixing during phase inversion, causing skin layer defects and a denser support layer with higher resistance. Consequently, the optimal dope flow rate was determined to be 1.05 mL/min, combined with a bore flow rate of 2.0 mL/min.

6.3 Air gap

The air gap (AG) in HFM modules is crucial for minimizing gas flow resistance and optimizing separation performance. It allows for better pressure drop control and enhances mass transfer efficiency. While extending the AG promotes adequate skin layer formation by exposing fibers to ambient conditions for longer periods, excessive AGs can introduce defects due to gravitational effects and elongation stresses. Poor management of the AG interval during spinning can lead to structural defects, such as inner lumen distortions and macrovoid formation [68].

Ding et al. studied the impact of varying AG distances (5–25 cm) on the CO_2 permeation performance, mechanical strength, and morphology of polyvinylidene (PVDF) HFMs [37]. It is reported that increasing the AG reduced inner lumen defects but, beyond a certain threshold, led to larger macrovoids and increased membrane porosity. The optimal membrane, exhibited maximum CO_2 permeability and CO_2/CH_4 selectivity at a 15 cm air gap as shown in Fig. 6 [33]. Mechanically, PVDF with AG distance of 15 cm (PVDF-AG15) showed a 64% improvement in strength compared to membrane at 5 cm AG. Additionally, PVDF-AG15 demonstrated the highest elongation at break, indicating superior resistance to deformation. Thus, PVDF-AG15 was identified as the optimal configuration, balancing performance and mechanical integrity.

Jamil et al. [69] investigated the impact of AG on the morphology of the PEI HFMs (Table 7) [70]. They observed that at larger air gaps, dry processes dominated, leading to finger-like pores extending to the outer skin layer and the formation of larger macrovoids beneath it, which could compromise separation efficiency. Conversely, when the air gap was reduced to zero, wet processes took precedence, causing immediate solidification and the creation of macrovoids below the outer skin layer. The study found that air gaps of 15 and 20 cm yielded optimal results, producing minimal macrovoids and uniform finger-like pores beneath



Sample	Tensile strength (MPa)	E-modulus (MPa)	Elongation at break (%)
PVDF-AG5	1.14	16.05	60.00
PVDF-AG10	1.17	18.61	79.60
PVDF-AG15	1.23	26.46	86.20
PVDF-AG20	1.20	26.24	83.50
PVDF-AG25	1.10	25.48	82.30

Fig. 6 Mechanical and CO_2/CH_4 separation performce of PVDF HFMs [33]

Table 7 Air gap effect on hollow fober membranes [69]

Air gap effect	Positive impact	Negative impact	Underlying mechanisms
Increase in air-gap distance	Improved skin-layer formation	Delayed demixing → weak/porous skin	Slower solvent–non-solvent exchange
	Enhanced selectivity	Excessive thinning → mechanical fragility	Partial solvent evaporation
	Thinner fiber wall from stretching	Macrovoid formation at long air gaps	Polymer chain relaxation
	Suppressed macrovoids (moderate range)	Over-dense skin → lower permeance	Gravitational stretching
Moderate air-gap range	Balanced permeability–selectivity	Sensitive to humidity and temperature fluctuations	Controlled phase-separation kinetics
	More stable asymmetric structure		Balanced evaporation *vs.* coagulation
Excessively long air-gap	–	Structural collapse/defects	Excessive solvent loss
		Non-uniform outer skin	Overstretching of nascent fiber
		Reduced gas permeance	Delayed demixing instability

a thin skin layer. Mubashir et al. [70] studied the effect of arir gap distance on the morphology and gas permeation (CO_2, N_2, and CH_4) behavior of the CA HFMs. Gas pair selectivities (CO_2/CH_4, CO_2/N_2) of CA-HFMs were also increased on the increment of air gap distance from 0.0 cm to 5.0 cm, However, beyond this airgap opposite trend prevailed. These outcomes were primarily attributed to the increased polymer orientation, which effectively reduced the formation of macrovoids in the HFMs, thereby enhancing the selectivity of gas pairs.

6.4 Take up speed

Take-up speed, the rate at which membranes are collected post-extrusion, significantly influences fiber structure, porosity, and separation efficiency. It induces elongational stress on nascent fibers, combining gravitational force, stretching from the take-up unit, and viscous drag in the coagulation bath [65]. Mubashir et al. [70] observed that higher take-up speeds reduced gas permeances while improving ideal selectivities owing to its morphological structure as shown in Fig. 7 [70]. For instance, CO_2,

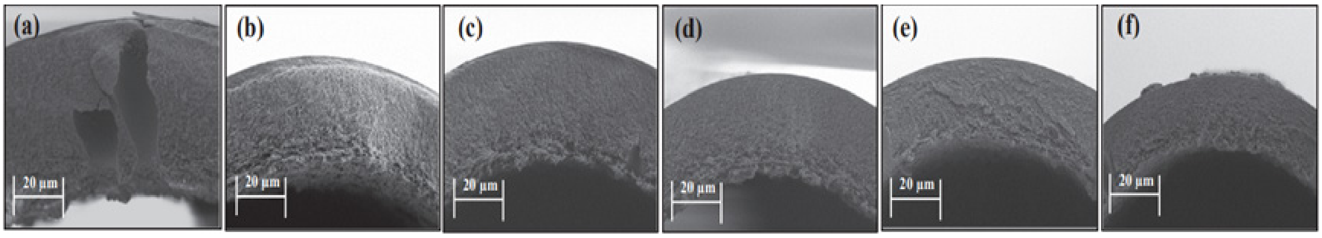


Fig. 7 FESEM images of HFMMMs spun with an air gap distance of 2.5 cm and take-up speeds of: (a) free fall; (b) 4.2 m/min; (c) 6.2 m/min; (d) 8.2 m/min; (e) 10.2 m/min; (f) 12.2 m/min [70]

N_2, and CH_4 permeances in Hollow Fiber Mixed Matrix Membranes (HFMMMs) decreased from 20.2 to 7.5 GPU, 9.8 to 1.1 GPU, and 4.6 to 0.9 GPU, respectively, while CO_2/N_2 and CO_2/CH_4 selectivities rose from 4.4 to 7.5 and 2.1 to 6.6. These changes stem from increased polymer orientation and packing at higher speeds, minimizing non-selective voids and Knudsen pores. The denser layer formed under higher speeds further enhanced selectivity, optimizing membrane performance.

Peng et al. [65] investigated three polymer systems – PSF, P84, and CA in NMP solvent – and found that increasing elongational stretch effectively eliminates macrovoids in hollow fibers, provided polymer concentrations exceed their critical values. The authors suggested that high elongational rates promote chain packing and create more mono-disperse interstitial spaces, which hinder external coagulant penetration and suppress macrovoid formation. Table 8 [37, 50, 67, 71] summarizes the impact of spinning parameters on the CO_2 permeation and selectivity of the developed HFMs.

7 Role of artificial intelligence in membranes

Despite significant progress in materials science, the development of high-performance membranes remains inadequate to meet industrial demands. Traditional approaches to membrane design rely heavily on trial-and-error methods, which are inefficient, costly, and impractical given the vast combinatorial space of potential materials. Accurate predictive tools for membrane gas separation performance are essential to accelerate development and reduce expenses. Furthermore, many membranes fail to advance beyond laboratory-scale testing, with their experimental separation performance frequently falling short of theoretical predictions [72].

Mathematical modeling plays a critical role in optimizing membrane design and scaling up production processes. However, conventional models often lack the granularity to accurately describe dynamic behaviors or account for variations in feed conditions. In this context, artificial neural networks (ANNs) and ML have emerged as transformative tools for modeling complex, nonlinear systems [73]. By leveraging computational power and advanced data analytics, ML algorithms can identify intricate patterns and correlations within large datasets, enabling the optimization of membrane materials, structures, and processes These algorithms excel at predicting key performance metrics, such as selectivity, permeability, and stability, with high accuracy. This predictive capability allows researchers to rapidly screen and prioritize promising membrane candidates for specific applications, significantly enhancing the efficiency of membrane discovery and development [74]. The integration of ML into

Table 8 The effect of spinning parameters on the gas separation performance of hollow fiber membranes

Polymer	Parameter	P (CO_2) [GPU]	Selectivity	Condition	Ref.
PES/PI	Air gap		(CO_2/N_2)	25 °C, 4 bar	[50]
	1–10 cm	57–130	14.8–1.8		
	5–20 cm	30–77	14.9–1.8		
	6–31 cm	79–193	2.2–1.3		
Polyaniline			(CO_2/N_2)		[71]
	2.5 cm	2.29	1.12		
	30 cm	1.38	17.9		
	50 cm	0.59	14.75		
PVDF			(CO_2/CH_4)	25 °C, 2 bar	[37]
	5 cm	200	2		
	10 cm	250	2.5		
	15 cm	500	3		
	20 cm	500	2.7		
	25 cm	1500	1.5		
TR-PBO	Dope flow rate (mL/min)		(CO_2/CH_4)	25 °C, 1–6 bar	[67]
	1	2500	16		
	1.5	1900	14		
	2	1400	11.5		
	3	1000	10.4		

Notes: Polyimide (PI) blends, poly(vinylidene fluoride) (PVDF), and thermally rearranged polybenzoxazole (TR-PBO) membrane science thus represents a paradigm shift, offering new opportunities to bridge the gap between theoretical predictions and industrial-scale performance [75].

ML is broadly categorized into two main types: supervised and unsupervised learning, each with distinct characteristics [76]. Unsupervised learning operates solely on input features (denoted as "x") and is commonly used for tasks such as clustering, dimensionality reduction, and pattern recognition. In contrast, supervised learning utilizes both input features ("x") and corresponding labels ("y"), enabling the creation of mapping functions through regression or classification algorithms. These approaches are particularly valuable in the design and optimization of membrane separation processes. A summary of the inputs and outputs for various ML models is provided in Table 9 [77–79], highlighting their applications in this field.

The development of a membrane performance model involves a systematic process: data collection, model design, training, evaluation, and optimization as shown in Fig. 8. High-quality data ensures a robust foundation, while model design aligns with specific predictive goals. Training enables pattern recognition, evaluation assesses accuracy, and optimization enhances predictive reliability. This structured approach ensures the model delivers precise, actionable insights for membrane applications.

The application of ANNs in membrane research holds significant promise for advancing membrane development and optimization. ANN models can accurately predict membrane performance, optimize material selection, and guide experimental processes, thereby enhancing the efficiency and effectiveness of membrane technologies in applications such as water treatment and gas separation. Yampolskii et al. [80] used a database of 122 glassy and 27 rubbery polymers, 80% of the data was used for training *via* group contribution method. The resulting quantitative structure-property relationship (QSPR) demonstrated superior predictive accuracy for high-permeability polymers compared to low-permeability ones, highlighting

Table 9 Models used in ML and their inputs and output parameters

Model	Inputs	Outputs	Ref.
Regression Model	Material properties (e.g. polymer composition, structure) Operational conditions (e.g. pressure, temperature, gas flow rate) Feed gas characteristics (e.g., concentration, gas type)	Predicted membrane performance (e.g., permeability, selectivity) System performance under various conditions	[77]
Random Forest Model	Real-time operational data (e.g., temperature, pressure, flow rate) Historical performance data (e.g., past flux rates, fouling) Membrane material and system design parameters	Dynamic prediction of membrane performance over time (e.g., flux, fouling) Decision-making insights for process optimization	[78]
Surrogate Models	System parameters (e.g., membrane material, operating conditions) Simulation or experimental data (if available)	Approximate performance predictions (e.g., separation efficiency) Reduced computational cost for predicting outcomes	[79]

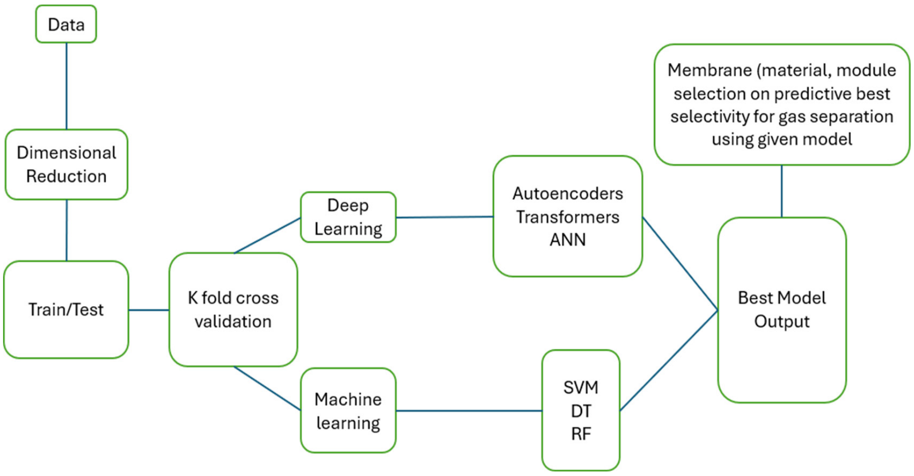


Fig. 8 The strategy of the model in ML

the potential of ANNs in optimizing membrane materials and performance. In another study, Hasnaoui et al. [77] employed an ANN regression model to predict the permeability of O_2, N_2, CO_2, and CH_4 in various polymers.

8 Optimization of hollow fiber membranes *via* AI methods

ML methods are gaining increasing popularity within the membrane research community for predicting the physical properties as well as gas separation performance of polymeric and MMMs. Shahsavand and Chenar [81] conducted a comprehensive study on CO_2 and methane separation using hollow fiber membranes made of poly-phenylene oxide (PPO) and Cardo-type polyimide (CPI). The research employed artificial intelligence, specifically radial basis function (RBF) and multi-layer perceptron (MLP) neural networks, to predict membrane permeances and separation factors, comparing their performance against traditional software (table curve or TC). Experimental CO_2/CH_4 gas separation data were used to train the models. Results demonstrated that both RBF and MLP networks outperformed conventional software in predictive accuracy, with RBF networks excelling due to their superior noise-filtering capabilities. Neural networks provided reliable predictions, even under noisy conditions, and accurately modeled the separation performance of PPO and CPI membranes across various operational scenarios. This study highlights the potential of AI-driven approaches to optimize membrane material selection and enhance gas separation processes. Similarly, in another study, Guan et al. [78] employed ML to design MMMs for CO_2 separation using metal organic frameworks (MOFs). Random forest (RF) models, trained on CO_2/CH_4 separation data, identified optimal MOF properties: pore size >1 nm and surface area ~800 m^2/g. These models guided the synthesis of copper-based metal-organic framework with tetrahydroxyquinone linker (Cu-THQ) and copper-based catecholate MOF (Cu-CAT-1), blended with Pebax-2533 and polymer of intrinsic microporosity-1 (PIM-1) polymers. The resulting MMMs achieved CO_2 separation performance exceeding the 2008 Robeson upper bound, validating ML's potential to optimize membrane materials, reduce experimental effort, and enhance gas separation efficiency.

Daglar and Keskin [82] pioneered a molecular simulation-assisted ML strategy to evaluate the gas separation potential of MOF incorporated polymer MMMs. Using the Maxwell model, they calculated the separation performance of 31,494 MMMs for six gas mixtures, incorporating gas permeability data from molecular simulations for MOFs and polymers data from experiments. The dataset was split into 80% for training and 20% for testing, with results validated against experimental literature. A tree-based pipeline optimization tool (TPOT) selected the best ML algorithm from eight models, optimizing parameters for accuracy. Key descriptors, including pore size and geometry, were identified as critical for prediction accuracy, while minimizing computational burden. The optimized ML model was extended to predict gas permeability and selectivity for 1,000 hypothetical MOF/polymer MMMs, demonstrating ML's potential to streamline material discovery and reduce experimental efforts, despite lacking experimental validation for hypothetical MOFs. This study highlights ML's transformative role in accelerating the development of high-performance membrane materials. Jung et al. [83] developed a neural network-based methodology for modeling CO_2 separation in HFM systems, including single- and multi-stage modules with and without recycle operations. Training data was generated using explicit configuration models, and the multilayer perceptron neural network's performance was evaluated. For single-stage modules, the model achieved high accuracy in recovery predictions (R = 98.86% without recycling, R = 96.07% with recycling), though recycling slightly reduced performance. In contrast, recycling improved prediction accuracy for three-stage modules. The study highlights the MLP model's effectiveness, particularly in complex multi-stage configurations, demonstrating its potential for optimizing membrane-based CO_2 separation processes.

Guan et al. [78] utilized an ANN model to examine the correlation between different input parameters and permeate purity. Three essential factors must be precisely chosen: feed composition, membrane selectivity, and pressure ratio. The model includes an input layer that processes the input data, followed by a hyperbolic tangent sigmoid transformation, and then 1 to 10 hidden layers containing 1 to 10 nodes each. The output is produced *via* a logarithmic sigmoid transformation. The dataset consists of 1000 points for model training and an additional 500 points for testing. The study evaluated one hundred different ANN configurations to assess membrane gas separation performance, ranking their effectiveness based on R^2 values. The authors tested various network structures by adjusting the number of hidden layers and nodes. The best-performing model comprised five hidden layers with four nodes each, delivering high predictive accuracy with a root mean squared error

(RMSE) of 0.0230 and a correlation coefficient of 0.9824. Therefore, the integration of artificial intelligence into scientific fields, particularly in industrial applications such as membrane gas separation, plays a crucial role in enhancing process efficiency and effectiveness. Pan et al. [84] study applied support vector regression (SVR) to relate key structural features of carbon molecular sieve (CMS) membranes, such as fractional free volume, carbon residue, and interlayer spacing, to their gas-separation performance. The approach identified the dominant factors controlling permeability and selectivity, providing a data-driven framework for targeted membrane design and optimization. The main factors affecting CMS membrane are the carbon residue, the FFV of the precursor, and the ratio of gas kinetic diameters [84].

9 Conclusion and future trends

HFMs have proven to be a transformative technology in gas separation applications, offering high efficiency, compact design, and scalability. Their ability to separate gases such as CO_2, CH_4, N_2, and O_2 makes them indispensable in industries like biogas upgrading, carbon capture, and air separation. Advances in material science, particularly the development of MMMs and the integration of nanomaterials, have significantly enhanced membrane performance, pushing the boundaries of permeability and selectivity beyond traditional limits. Furthermore, the incorporation of AI and ML has revolutionized membrane design and optimization, enabling faster and more accurate predictions of membrane performance. These advancements have positioned HFMs as a key player in addressing global challenges related to climate change, energy sustainability, and industrial gas purification.

Future advancements in HFM technology should focus on material innovation by exploring advanced materials such as MOFs, covalent organic frameworks (COFs), and TR polymers to enhance gas separation efficiency. The development of polymeric blends and hybrid materials that balance permeability, selectivity, mechanical stability, and cost-effectiveness is also crucial. Nanotechnology integration, particularly the use of nanoparticles, nanocomposites, and 2D materials like graphene oxide and MXenes, should be further investigated to improve membrane strength, fouling resistance, and separation performance. AI and ML can play a transformative role by enabling predictive modeling, optimizing fabrication parameters, and implementing real-time monitoring and adaptive control systems for enhanced operational efficiency. Sustainability and scalability must also be prioritized by developing eco-friendly membrane materials and fabrication processes while scaling up production to meet industrial demands for biogas upgrading, carbon capture, and hydrogen production. By pursuing these strategies, HFM technology can continue evolving to provide innovative and sustainable solutions for gas separation, aligning with global energy and environmental goals.

Acknowledgements

The work is supported by the National Research Program for Universities (NRPU), Higher Education Commission Pakistan, No. 20-15709/NRPU/R&D/HEC/2021.

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