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# Polymeric and Hybrid Membranes for Achieving Ultra-Low Sulfur Fuel Requirements

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## ABSTRACT

This review aims to explore membrane-based alternative methods for removing harmful sulfur compounds in fuels to replace the inefficient conventional techniques. Membrane-based methods provide an efficient route to achieve very low sulfur content in fuels (< 10 ppm), as required by international environmental policies. A systematic review of 42 experimental studies reported over the period from 2005 to 2025, being the timeframe that would most likely encompass an actual paradigm change in membrane-based technologies. The data were retrieved from scientific databases, including Scopus, Web of Science, ScienceDirect, and ACS, to evaluate the performance of polymer and composite membranes for desulfurization. Innovative membrane systems like polydimethylsiloxane (PDMS), polyethylene glycol (PEG), polyimide, and mixed-layer membranes (MMMs) were found to be highly effective in both evaporation- and permeability-based desulfurization processes. PEG-PI MMMs reinforced with metal organic frameworks (MOFs) demonstrated removal efficiencies as high as 80% and a permeability of > 200 g/m²·h, which were significantly higher compared to that for neat polymeric membranes. The key separation principles include diffusion-dissolution, facilitated transport with π complexes ($Ag^+$, $Cu^{2+}$, MOFs), and molecular sieving. Finally, in spite of challenges such as polymer swelling and stability remaining, polyethylene glycol (PEG) and polyimide (PI)- MMMs, especially those enhanced with metal-organic frameworks (MOFs), stand out as strategic industrial candidates due to the best balance of flow, selectivity, and stability. The future direction must urgently focus on long-term stability testing using real fuel streams rather than model fuels to confirm the practical viability of these integrated membranes.

## 1. INTRODUCTION

The gasoline quality is one of the key environmental issues for all oil refineries worldwide, and sulfur content is a very important parameter in tight fuel specifications [1]. High sulfur content of fossil fuels, in particular gasoline and diesel fuel, pollutes the environment and causes serious human health problems when burned [2, 3]. Sulfur dioxide (SOx) is a primary emitter, boosting nitrogen oxide (NOx) levels in vehicle exhausts, forming acid rain, and fueling global warming. It may also have adverse effects on ecosystems and the built environment, contribute to respiratory illnesses, and induce heart diseases and asthma [3, 4]. Moreover, sulfur compounds present in feedstocks corrode the equipment, deactivate catalysts, and diminish the quality of products in petrochemical process plants [5]. Hence, the regulatory limitations on sulfur content are tightening; most developed countries and China have intended to lower it to less than 10 ppm [6, 7]. For these environmental problems and the needs of industrial applications, various desulfurization methods have been developed, such as hydrogenation desulfurization (HDS), extractive desulfurization, oxidative desulfurization, biological desulfurization, adsorption desulfurization, and membrane technology [8]. Although HDS is the most common and effective industrial method for reducing sulfur content to less than 1 ppm, it requires significant equipment investments, high hydrogen consumption, and harsh operating conditions of high temperatures and pressures. It can lower the octane number of gasoline by saturating olefins and aromatics [8, 9]. In contrast, membrane pervaporation desulfurization (PV) has emerged as a promising alternative because the process comes with several advantages, such as low operation and investment costs, high separation efficiency, easy operation, and easy scalability to adapt to changes in the flow of the procedure [10]. PV purifies specific components from a liquid stream via partial evaporation with a non-porous selective membrane. Commercial processes like the S-Brane technology of W.R. Grace & Co. demonstrated its industrial applications at substantially lower temperatures and pressures, giving a much lower requirement for hydrogen in combination with HDS processes. Polymeric Membranes: The majority of membrane applications employ polymeric materials because of their low material cost, permeability, mechanical stability, and ease of processing and fabrication over a range of applications [11].

Polymers such as polydimethylsiloxane (PDMS) [12, 13], PEG [14], and polyurethane (PU) [15] have been widely used in desulfurization. However, many challenges associated with polymeric membranes prevent their performance and long-term stability. One of the most pronounced issues is that high loading of permeable components can cause membrane swelling, making it less selective, and it might lead to chemical degradation, especially when temperature and pressure become higher [16-18]. In addition, polymeric membranes typically experience a “trade-off” phenomenon between permeability and selectivity, where increased selectivity reduces flux and the other way around, limiting overall performance [19-21]. Furthermore, various polymeric membranes show unsatisfactory internal separation capacity, resulting in relatively low enrichment factors for sulfur compounds [22]. In addition, their relatively unreactive nature makes them quite rigid to undergo chemical modifications, and sharpen enrichment factors at higher temperatures. In addition, their relatively unreactive nature makes them quite rigid to undergo chemical modifications and sharpen enrichment factors at higher temperatures. Although hydrogenation (HDS) is the industrial backbone of desulfurization, its demanding operating requirements (high temperatures and pressures), high costs, and negative impact on octane number make it unsuitable for achieving ultra-low sulfur requirements (< 10 ppm) economically. In contrast, membrane pervaporation (PV) technology has emerged as a promising alternative that reduces energy and process requirements. However, conventional polymer membranes continue to struggle with the challenge of polymer swelling and the inherent trade-off between permeability and selectivity. The knowledge gap and the urgent need for this review lie in providing a comprehensive critical evaluation of the latest next-generation membranes, particularly MMMs enhanced with advanced materials (such as MOFs) [23] .These have demonstrated revolutionary results in overcoming the permeability/selectivity trade-off and enhancing chemical stability [21]. Evaluating the current performance of these materials and the separation mechanisms they use (such as facilitated transport via π-complexes) places them in the context of future work aimed at achieving sustainable industrial viability.

The object of this study is to obtain an integrated and comparative investigation of polymer membranes applied in membrane evaporation desulfurization. The project will develop a comparative critical review of polymer materials, the principle of operation of polymer separation, and current performance characteristics, including positive/negative aspects in each case. Furthermore, in this study, an attempt has been made to provide both neglected and emergent areas on membrane evolution as well as recommendations for the design of next-generation membranes with enhanced performance. This includes solving current challenges and placing them into the context of future work toward improving the desulfurization process for fuels.

## 2. METHODOLOGY FOR LITERATURE SELECTION

To establish this review, a systematic search was carried out on the period from 2005 through 2025, which represents the development era of membrane desulfurization. The year 2005 represents a pivotal point when research began following the introduction of ultra-low sulfur fuel regulations worldwide, using polymeric and hybrid membranes. The review reflects current advancements and emerging trends in the field. The search criteria depend on the strategy of using key terms related to pervaporation, membranes, and sulfur compounds (thiophene, benzothiophene, dibenzothiophene) with secondary filters for common polymers (PDMS, PEG, polyimide, polyphosphazene) and fillers (MOFs, zeolites, graphene oxide, Ag$^+$, Cu$^{2+}$, Ni$^+$). Inclusion criteria required that studies:

(a) The investigated polymeric or MMM membranes for liquid-phase desulfurization.

(b) Studies with clear quantitative performance results data like flux, enrichment factor, and undefined experimental conditions.

(c) Only English full-text, peer-reviewed articles are included.

Modeling or simulation works are also considered if directly related to sulfur transport through membranes. Modeling or simulation works also considered if directly related to sulfur transport through membranes.

The exclusion criteria involve studies focusing solely on gas separation, adsorption, or oxidation without membranes; reviews or patents lacking new data; and non-English or inaccessible sources. A reference manager was used to remove duplicate records, and the articles were screened in two stages (title/abstract and full-text). For each included study, data was extracted on membrane type, filler content, thickness, feed composition, operating conditions, and performance parameters.

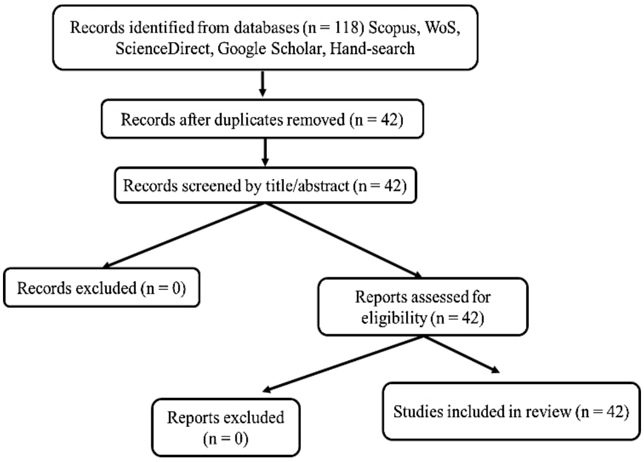

**Figure 1.** PRISMA flow diagram showing 118 records identified, 42 screened after duplicates removed, and 42 studies included in the final review

The 2005 onward was selected because it represents a period during which regulatory and technological shifts in fuel quality controls occurred. Euro IV fuel quality standard in 2005, which limited sulfur levels in diesel to 50 ppm and laid the groundwork for even lower limits under Euro V [24]. These regulatory changes aligned with improvements in experimental methodologies and reporting standards in membrane research, making post-2005 data more comparable and reliable. Experimental data became more standardized, allowing meaningful comparison. Tools like Research Rabbit are also used to visualize citation networks and trace thematic evolution within this research framework. Earlier publications often lacked consistent reporting of essential variables such as filler concentration, feed composition, temperature, and membrane thickness. These inconsistencies make direct statistical or meta-analytical analysis unreliable. After that, the extracted data was analyzed using Python (version 3.13.7) to generate graphical visualizations such as scatter plots, heat maps, and boxplots that highlight relationships among flux, enrichment factor, and operating temperature.

Limitations: The review acknowledges some methodological limitations. It may be missed studies written in languages other than English, industrial patents, or older works published before 2005. No formal statistical meta-analysis was conducted because many studies did not report their data consistently. Even with these limitations, this review provides a focused and dependable evaluation of experimental studies on membrane-based fuel desulfurization. The whole selection process is shown in the PRISMA flow diagram in Figure 1.

## 3. MEMBRANE TRNASPORT MECHANISMS

### 3.1 Solution-diffusion mechanism

The separation of sulfur-containing compounds from fuels using membrane technologies is governed by intrinsic transport characteristics that control the migration of species within the membrane structure. Polymeric membranes are widely applied in this context because they offer cost-effectiveness, operational simplicity, mechanical robustness, and suitability for large-scale industrial applications [9, 25-27]. The degree of efficiency of polymer membranes as a function of the nature and chemical structure of the polymer material, temperature, and pressure during work under the membrane. The concentration of sulfur-containing components in the feed significantly affects their transport through dense membranes, a process that is predominantly governed by the solution–diffusion mechanism. This model is widely known as the transport model of non-porous membranes, which popularized pervaporation separation membranes [28]. This mechanism proceeds through three sequential stages: initial adsorption of sulfur molecules at the membrane surface, followed by diffusion of the dissolved species within the polymer matrix, and finally desorption on the permeate side of the membrane. In this circumstance, increasing the adsorption capacity could be attributed to the higher adsorption force of fuel components on the polymer material. Alternatively, membranes based on PEG polymers have a relatively high adsorption capacity for some sulfur compounds, such as thiophene, due to their polarity [29-31]. The rate of intrinsic diffusion is affected by several factors, most notably the flexibility of the polymer chains and the size of the available free spaces, in addition to the molecular size of the transported compound [32, 33]. Various studies have shown that PDMS membranes exhibit a transition behavior dominated by the diffusion phase, rather than dissolution. It is worth noting that the reverse adsorption phase is often rate-non-limiting when appropriate vacuum conditions are applied on the permeation side [34, 35]. Despite its simplicity, the solution–diffusion model is constrained by the well-known permeability–selectivity trade-off, where increased permeation rates are often accompanied by reduced separation efficiency for sulfur compounds [36]. This behavior is clearly observed in PDMS membranes, where increasing flux leads to decreasing selectivity, and vice versa. Moreover, membrane swelling induced by high concentrations of permeating species can reduce selectivity and accelerate chemical degradation, thereby limiting the long-term industrial applicability of polymeric membranes [37]. On the other hand, the facilitated transport mechanism is a promising option to overcome this challenge, as this mechanism relies on a reversible chemical reaction between sulfur compounds and transporters embedded within the membrane [38]. Transition metal ions have been used as effective carriers in this context, such as silver ($Ag^+$), copper ($Cu^{2+}$), nickel ($Ni^+$), manganese ($Mn^+$), and lead ($Pb^+$), as these ions form π-complex bonds with the aromatic rings of thiophene, enhancing its adsorption and transport across the membrane [39]. There are notable discrepancies that exist in the performance of polymeric membranes such as PEG, PDMS, and PI. These variations originated mainly from chemical structure differences among polymers. PEG membrane systems show higher flux due to their flexible and hydrophilic ether linkages, resulting in enhanced solubility and diffusion of polar sulfur compounds. In contrast, PI-based membranes, characterized by rigid aromatic backbones and low chain mobility, achieve higher selectivity but reduced flux. PDMS-membrane-based membranes are highly permeable to swelling, further demonstrating the inherent permeability–selectivity trade-off. Such distinctions underscore how polymer chain rigidity, polarity, and free-volume distribution govern transport behavior under the solution–diffusion mechanism.

### 3.2 Facilitated transport via PI-complexation

An effective strategy for enhancing membrane performance involves facilitated transport, which relies on specific and reversible interactions between the target sulfur compounds and functional carriers incorporated within the membrane matrix. In fuel desulfurization, the preferred components (such as thiophene compounds) often contain pi-bonds. In this approach, metal ions such as silver ($Ag^+$), copper ($Cu^+$), lead (II) ($Pb^{2+}$), nickel (II) ($Ni^+$), and cerium (IV) ($Ce^{4+}$) act as carriers that selectively enhance the transport of sulfur-containing species across the membrane [40]. The essential process involves the creation of π-complexes by these ions in conjunction with aromatic thiophene molecules [39, 41] For instance, various research results demonstrate how metal ions can play such a role. In the case of in situ synthesized metal cation incorporated membranes, the formation of pi complexes between thiophene species and silver ions has been suggested to explain the enhancement in membrane flux and selectivity. As the silver ions have a vacant d orbital as an acceptor and sulfur in thiophene can provide a free pair of electrons, this assumption is justified [42]. Similarly, the $Cu^{2+}$ copper ion may bind reversibly and specifically with thiophene by π-complex formation, which is more selective. Furthermore, copper and nickel ions can also bind to the delocalized electrons in the aromatic ring of thiophene and create a pi-complexation reaction [43]. Experimental results demonstrate that ions such as $Cu^{2+}$, $Mn^{2+}$, and $Pb^{2+}$ can simultaneously improve thiophene selectivity while increasing membrane flux at elevated operating temperatures. This confirms the facilitated transport mechanism [39]. Although the strength of the interaction between the metal ions and thiophene may vary (with Ni (II), Ce (IV), and Cu (II) interacting with variable strength, where Ni (II) > Ce (IV) > Cu (II)). The most affinity ions, such as $Cu^{2+}$, may exhibit the best overall performance due to their high loading capacity and superior free volume properties of the PDMS-dopamine/copper membranes [44].

Even silver nanoparticles (AgNPs) can synergistically facilitate thiophene transport, with $Ag^0$ acting as a Lewis acid and thiophene as a Lewis base, leading to an affinity between them, as well as a π-π stacking interaction that accelerates at higher temperatures [40]. These findings demonstrate that careful selection of suitable metal ions can significantly improve membrane performance, enabling separation efficiencies that surpass the conventional permeability–selectivity limitations observed in pervaporation processes.

### 3.3 Pore flow and size exclusion in hybrid membranes

Understanding the mechanisms of mass transfer in such membranes contributes to their development, which is not only based on the traditional adsorption and diffusion model, but extends to include the contribution of fillers in creating new paths for the penetration of molecules, through either pore-flow mechanisms or size exclusion, or both, in addition to interaction with preferential adsorption.

Pore-flow transport has been widely reported as one of the key contributors to enhanced membrane permeability when inorganic fillers are incorporated into polymer matrices [45]. Experimental studies indicate that these fillers introduce additional interconnected pathways within the membrane structure, which facilitate molecular transport and reduce mass transfer resistance. For instance, the incorporation of MIL-101(Cr) into PDMS membranes has been shown to generate supplementary free-volume regions that act as efficient transport channels, leading to improved permeation performance [46]. Similar trends have been observed in zeolite-based hybrid membranes, where the intrinsic porosity of fillers such as CuY promotes the diffusion of small sulfur-containing molecules through the polymer phase [47]. These observations suggest that membrane performance is strongly influenced not only by filler type but also by dispersion quality and polymer–filler interfacial compatibility [48]. Even at the level of modified polymers, the introduction of PEG groups into polyimide-block-polyethylene glycol membranes can lead to a “significant increase in permeation pathways” [14]. The variation in performance among hybrid membranes incorporating different fillers could be explained by differences in filler dispersion and interfacial compatibility with the polymer matrix. Zeolite-filled membranes generally show enhanced selectivity through rigid molecular sieving, whereas MOF- and COF-based fillers often increase permeability by creating additional nanoporous transport channels. Inconsistent dispersion or formation of interfacial voids may cause conflicting flux–selectivity trends under seemingly similar operating conditions. Therefore, the overall separation efficiency depends not only on filler type but also on the degree of polymer–filler interaction and microstructural homogeneity. Table 1 provides an overview of different membrane systems and challenges mentioned in the literature.

Size exclusion: The size exclusion mechanism is a fundamental principle in particle size-based separation, whereby the membrane or filler pores can allow smaller molecules to pass through while preventing larger ones [49]. In some studies, this mechanism provides an explanation for the membrane’s selectivity; for example, PDMS membranes are observed to exhibit higher selectivity toward thiophene than 2-methyl-thiophene, and this difference is attributed mainly to the variation in molecular sizes of these solutes [50]. This suggests that the variation in molecular sizes directly affects the ability of molecules to penetrate membrane pores or available channels.

However, the role of size exclusion is not always dominant and depends on the relationship between pore size and the sizes of the molecules to separate. In certain MOF membranes, e.g., UiO-66-$NH_2$ membranes [51], where the pore diameters are greater than the kinetic diameters of thiophene (0.53 nm) and hydrocarbons like n-octane (0.43 nm), the experiments indicate that molecule exclusion should not significantly influence the enrichment factor. Under such circumstances, size variations might not be drastic enough to cause adamant exclusion; therefore, the relevance of other processes, such as preferential adsorption, is realize [51]. Fillers also help to alter the internal structure of the polymer membrane, for instance, by enhancing fractional free volume (FFV) and intersegmental d spacing [44, 52]. These changes in the internal structure mean more space for molecular motions, enhancing permeability. Synthesis techniques like cross-linking also restrict the movement of polymer chains, thus controlling the effective pore size or fractional free volume, which can affect size-based separation [53, 54]. To maximize the effectiveness of the membrane separation process, pore flow, size exclusion, and preferential adsorption must be combined. Preferential adsorption of sulfur compounds (such as thiophene, which is more polar than hydrocarbons) is an essential part of most desulfurization systems, particularly those MOF or transition metal ion type [10, 23]. Molecules of sulfides, adsorbed, passed on effectively through the membrane by channels and routes formed by fillers. For example, the incorporation of copper ($Cu^{2+}$) or silver (AgNPs) ions into membranes through the formation of S-M bonds or π-complexations could enhance thiophene permeation through the membrane. Through chemical interaction in desulfurization processes, these enhance the performance of the porous structure and allow enhanced overall and integrated separation performance [39, 55]. Thus, a comprehensive comparison of different membrane systems, their applications, and associated challenges reported in the literature is provided in Table 1.

**Table 1.** Membrane-based desulphurization techniques: Materials, applications, and challenges compared

| Method | Typical Materials | Applications | Challenges |
|---|---|---|---|
| Blending | PEG/PU; PDMS/PS; PES/F127 | Desulfurization; dehydration; fuel cells | Phase separation; low flux |
| MMMs / Hybrid | PDMS+AgY; PI+ZIF-8; PEG+CuY | Desulfurization; alcohol/water separation | Voids; filler agglomeration |
| Crosslinking | PI (6FDA); PDMS; PEG; PVA | Desulfurization; SRNF; gas separation | Reduced permeability; solvent swelling |
| Surface modification | PDMS; PU; PVDF | Water/alcohol separation; isomer recovery | Flux decline; interfacial instability |
| Inorganic / MOFs | UiO-66-$NH_2$; Cu-MOF | Sulfur adsorption; desulfurization | Weak adhesion; poor reproducibility |
| Copolymers | Pebax 2533; PUU; PEG/PI | Ethanol recovery; aromatics separation | Water swelling; low permeability |

## 4. MEMBRANE MATERIALS

Membrane material is the key element in removal technologies of fuel sulfur, as its physical and chemical properties directly affect the separation efficiency and membrane performance under different operating conditions [37, 53]. Polymeric membranes have shown great potential in this field due to their low cost, ease of formation and processing, mechanical stability, and compatibility with various inorganic materials and catalysts [1, 56]. There is a variety of polymers used to prepare desulfurization membranes. They can be classified according to their properties as hydrophilic, hydrophobic, or copolymers. Some also feature internal porosity, which contributes to enhanced transport performance.

Polydimethylsiloxane (PDMS) is one of the most common polymers in this context, featuring high chemical stability and good permeability to organic liquids. However, its membranes suffer from the swelling phenomenon when exposed to fuel compounds such as thiophene, which negatively affects the selectivity and accelerates the deterioration of the chemical structure, especially at high temperatures [34, 37, 57]. This polymer also exhibits a clear inverse relationship between permeability and selectivity, whereby improving one property often comes at the expense of the other [34, 57]. Other polymers used include PU and polyurea/polyurethane (PUU) copolymers [58], as well as polyimide (PI), which is knowns for its high thermal and mechanical stability and resistance to organic solvents. Previous studies have shown that PI 6FDA-BDAF membranes are capable of achieving high flow rates with significant enrichment factors, and their performance has been further enhanced through cross-linking techniques [1, 5, 52].

Since hydrophilic polymers can interact with polar compounds such as thiophene and they have high selectivity, the research on hydrophilic polymer is popular. PEG belongs to such a class of materials, which has shown good long-term stability, and cross-linked PEG membranes have also been successful for desulfurization of FCC gasoline [13, 53]. Polyvinylpyrrolidone (PVP) and cellulose triacetate (CTA) have also been used successfully in applications with similar types of applications [13, 59, 60]. ts structure allows for control of the solubility coefficient in accordance with the physical and chemical properties of the components to be separate. Intrinsically micro-porous polymers (PIMs) also arrive as viable contenders in this field, as they consist of tiny nano-voids that facilitate quick transport channels and increase the effective surface area. PIM-1 is one of the more high profile of these polymers, and it has been mixed with other polymers in order to enhance its overall performance [19]. Polyether-block-amide (Pebax) is a good example among the block copolymers, which consist of elastomeric polyether blocks that are accountable for permeability improvement and rigid polyamide blocks that provide mechanical strength to the membrane and limited swelling [60, 61]. With the progress of the enhancing membrane performance concepts, researchers have turned towards including inorganic materials as fillers in so-called MMMs. This is in order to overcome the traditional trade-off between permeability and selectivity and enhance the overall stability of the membrane [48]. Among these materials, the utilization of zeolites has been cultivated. This material possesses a uniform porous structure that may be functionalized by adding silver (AgY), nickel (Ni2+Y), or copper (CuY) ions for the formation of bonds with sulfur compounds that enhance the adsorption process and selectivity [39, 47]. Dramatic performance enhancement was noted upon mixing CuY zeolite with PEG or $Ni^{2+}Y$ zeolite and PDMS [45, 55]. Table 2 summarizes the main polymers used in desulfurization, their fillers, key functions, potential compatibility issues, and references, while Figure 2 provides a visual comparison of different membrane classes in terms of flux, selectivity, stability, swelling resistance, and scalability. The chart is constructed based on data extracted from previous studies [62-71].

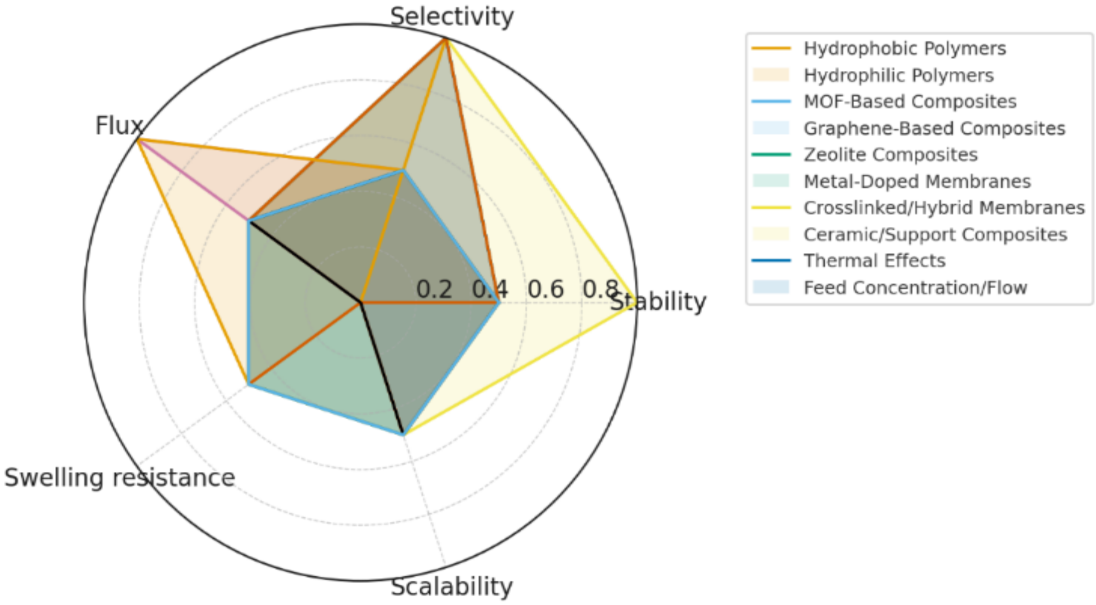

**Figure 2.** Radar chart comparing the overall performance profiles of seven major membrane classes across five key metrics
Note: The evaluated membrane classes include hydrophilic/hydrophobic polymers (blue), MOF-based (red), graphene-based (green), zeolite composites (orange), metal-doped (purple), cross-linked/hybrid (brown), and ceramic-supported (gray). Each axis represents a key performance metric (flow, selectivity, stability, swelling resistance, and scalability) on a printed scale from 0 (poor) to 1 (excellent). Flux is measured in kg/(m²·h), while selectivity is measured by the enrichment factor (EF). The chart constructed based on data extracted from previous studies

**Table 2.** Summary of MMMs based on polymer matrix type, fillers, key properties, and associated challenges

| Ref. | Polymer Matrix | Filler Type | Filler Function | Compatibility Problem |
|---|---|---|---|---|
| [13] | PEG/PVDF | ZIF-8 (layer-by-layer) | Increases enrichment and selectivity; prevents PEG leakage | N/A |
| [23] | Matrimid® 5218 PI | ZIF-8 | Increases $CO_2$ permeability; reduces flexibility | Voids at >20 wt% |
| [37] | PDMS | TEOS | Enhances sulfur selectivity; reduces flow | Dense structure, no defects |
| [39] | PMePP | $Cu^{2+}$, $Mn^{2+}$, $Pb^{2+}$ (ion exchange) | Improves thiophene selectivity | N/A |
| [40] | Pebax 2533 | Ag–PDA/GNS | Improves compatibility, swelling resistance, and thiophene transport | N/A |
| [42] | PDMS | $Ag_2O$ | Improves desulfurization | N/A |
| [44] | PDMS | Dopamine nanoparticles ($Cu^{2+}$, $Ni^{2+}$, $Ce^{4+}$) | Increases free volume; facilitates thiophene transport | Agglomeration above 7 wt% |
| [45] | PDMS | CPO-27-Ni | Increases free void volume and permeability | N/A |
| [47] | PEG | CuY-zeolite | Increases flux and thiophene adsorption | Flow–selectivity trade-off |
| [48] | PP–PE | $Al_2O_3$ nanoparticles | Increases permeability flux; temperature-dependent enrichment | N/A |
| [50] | PDMS | $Ni^{2+}Y$ (Zeolite) | Increases flow and enrichment factor | Possible interfacial voids |
| [54] | PDMS | MIL-101(Cr) | Increases permeability, selectivity, and free volume | Agglomeration above 6 wt% |
| [55] | PEG | CuBTC (MOF) | Improves desulfurization and thiophene selectivity | Typical MOF issues (possible clumping) |
| [57] | PDMS | AgY (Zeolite) | Improves evaporation and octane/thiophene separation | N/A |
| [61] | Pebax® 2533 | ZIF-8 | Improves gas selectivity and permeability | Voids/agglomeration at > 5 wt% |
| [69] | Crosslinked PI | $TiO_2$ nanoparticles | Increases compressive strength | No significant effect on flow or rejection |
| [70] | CA | ZnO–Zeolite | Enhances wettability and performance | N/A |
| [71] | Sodium Alginate | ZIF-L & ZIF-8 | Increases permeability and stability | N/A |

Note: PDMS: Polydimethylsiloxane; PI: Polyimide; PP-PE: Polypropylene-Polyethylene blend; CA: Cellulose Acetate; PMePP: Poly(3-methyl-1-pentene); PEG: Polyethylene Glycol; PVDF: Polyvinylidene Fluoride; MOF: Metal-Organic Framework; TEOS: Tetraethyl orthosilicate; PDA: Polydopamine; "N/A" indicates no significant compatibility issues reported in the referenced study.

Utilization of metal-organic frameworks (MOFs) was found to be successful, as it was endowed with outstanding features like high surface area and porosity. When MIL-101(Cr) is applied in PDMS membranes, flow is enhanced along with an enrichment factor due to its nature as a "mass transfer highway" [45, 54]. Other MOFs such as CuBTC, CPO-27-Ni, and UiO-66-$NH_2$ have also shown remarkable performance due to their preferential adsorption of thiophene and their interaction with transition metal ions [45, 51, 62-64]. Materials such as graphene oxide (GO) and graphene nanosheets (GNS) have also been incorporated into membrane development, especially after being modified with polydopamine (PDA) layers and loaded with silver nanoparticles (AgNPs), where improved hydrophobicity and facilitated transport were observed [40, 65]. Additionally, materials such as hollow Ag/$SiO_2$ nanoparticles and carbon nanotubes (CNTs) have been incorporated as fillers to achieve advanced separation performance [66, 67]. The incorporation of these fillers achieves several goals: enhancing permeability by opening intra-membrane pathways or increasing free volume, improving selectivity through preferential adsorption or complex interactions, and strengthening mechanical and thermal stability and swelling resistance [23, 40, 68]. In general, in comparing these different types of membrane systems explored above, PEG and PI-based MMMs are the most well rounded in terms of performance. PEG systems have relatively higher selectivity than the others based on the excellent interaction between strong polar–sulfur, and PI-based membranes have good thermal and mechanical stability with moderate flux. PDMS membranes have high permeability but tend to swell and lose selectivity. Hence, the PEG- and PI-based MMMs yield the best flux/selectivity/stability trade-off of all samples, and they came out as promising candidates for practical desulfurization.

## 5. OPERATING CONDITIONS ANDTHEIR EFFECT ON PERFORMANCE

While the membrane material is the prime element that determines performance and separation efficiency, the overall performance of the system is vitally affected by external operating conditions. To improve the efficiency of membrane efficiency in desulfurization, it is essential to understand how these conditions—such as temperature, pressure, and sulfur compound concentration—control the flow and permeability characteristics and their interaction with the membrane structure. These process conditions are critical parameters to determine the efficiency of membrane separation, controlling the characteristics of flow and permeable media as well as interaction at the surface of a membrane. Table 3 shows the performance of polymer based desulfurization membranes according to the previously published scientific literature.

### 5.1 The effect of temperature on membrane separation performance

Temperature has a direct impact on membrane performance [37]; Figure 3A and 3B illustrate the effect of temperature on flux and enrichment factor. Several studies have reported that increasing temperature results in higher permeability flux [37, 72]. This is attributed to the enhanced movement of molecules within the membrane and the high vapor pressure of sulfur compounds, which increases the driving force for transport across the membrane [73]. For example, the permeate flux of the 6FDA-BDAF membrane increased from 7.96 to 37.61 kg/(m²·h) when the operating temperature was raised from 50 to 90°C [5]. However, the effect of temperature on the enrichment factor is not constant, as in some cases an initial increase is observed, followed by a subsequent decrease [53], or a continuous decrease with the rise in temperature [58, 68, 74]. This is due to the trade-off between adsorption selectivity and diffusion selectivity, where increasing temperature reduces the difference in solubility between sulfur compounds and hydrocarbons and thus leads to a decrease in selectivity [55, 75]. The effect of temperature on membrane permeability is commonly described using the Arrhenius relationship [76]. This relationship describes how the permeability of a particular component changes with absolute temperature:

$$J = A\,exp\left(-\frac{Ep}{RT}\right) \tag{1}$$

where, *J* is the permeability flux, *A* (or $J_o$) is the pre-exponential factor, *Ep* is the activation energy of pervaporation and R is the gas constant.

To improve readability and reduce reliance on large tables, the experimental and reported performance data of polymeric and MMMs are summarized in graphical form. Instead of presenting extensive tabulated values of flux and enrichment factor for each membrane–feed system (see e.g., PDMS/PAN, PDMS/PEI, PEG/PES, PI-based composites, and PU blends). The results were converted into comparative graphical figures to enhance readability and reduce reliance on large data tables. Figure 3 illustrates the combined influence of operating temperature and membrane material on sulfur separation performance. Figure 3A presents a heat map of the average conditional enrichment factor (EF) per 10°C interval, organized by membrane type, allowing a comparison between pure polymer membranes and composite mixed-matrix membranes (MMMs). This visualization highlights the synergistic effect of material composition and operating temperature on separation efficiency. Figure 3B shows a scatter plot of permeability flux (J, in kg/(m²·h))versus enrichment factor (EF), where polymeric and MMM systems are distinguished. The point size reflects the operating temperature, while the trend lines illustrate the relationship between temperature and performance for key material groups. Figure 4 further depicts the relationship between permeability flux and enrichment factor for a range of polymeric and MMM membranes used in desulfurization, illustrating the well-known permeability–selectivity trade-off. Different membrane types are identified using distinct symbols, providing a comparative overview of their separation performance. These visualizations provide an immediate and clearer alternative to classical tables, allowing trends to be more easily identified and cross-comparisons among various polymers, fillers, and operating conditions to be performed. The data was processed and analyzed using Python (version 3.13.7).

Permeability pressure is one of the factors determining the driving force between the two sides of the membrane [68]. Results indicate that increasing it leads to a decrease in permeation flux as a result of a decrease in the partial pressure difference [53]. Regarding the enrichment factor, some studies have shown that it may initially increase and then decline [77]. The driving force for mass and heat transfer in a membrane evaporation (PV) process is determined by the chemical potential difference between the permeate and the feed. This difference is created by applying a vacuum or sweep gas flow at the permeate side. It is explained by the solution-diffusion equation, which includes the permeate pressure [78]:

$$J_i = \left(\frac{P_i}{L}\right)\left(c_{i0}\, e^{-\frac{V_i p_0}{R\,T}} - c_{ip}\, e^{-\frac{V_i p_p}{R\,T}}\right) \tag{2}$$

where, $J_i$ is the molar flux of component *i* (mol·m⁻²·s⁻¹), *Pi* is the permeability of component *i*. *L* is the membrane thickness (m), $c_{i0}$and $c_{ip}$ are the concentrations of component *i* at the feed and permeate interfaces within the membrane (mol·m⁻³). $V_i$ Is the partial molar volume of component i (m³·mol⁻¹). $p_0$, $p_p$ are the feed and permeate pressures (Pa). R is the universal gas constant (J·mol⁻¹·K⁻¹). In addition, T is the absolute temperature (K).

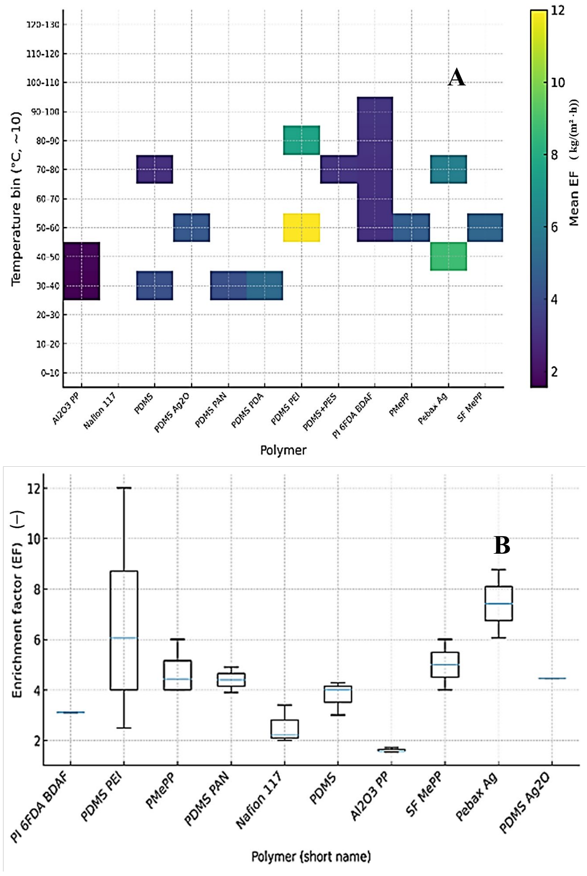

**Figure 3.** Combined effect of operating temperature and membrane material on sulfur separation performance
(A) Heat map showing the average conditional enrichment factor (EF) across 10°C temperature intervals for different membrane types.
(B) Scatter plot of permeability flux (J) versus enrichment factor (EF) for polymeric and mixed-matrix membranes, with data grouped according to membrane class.

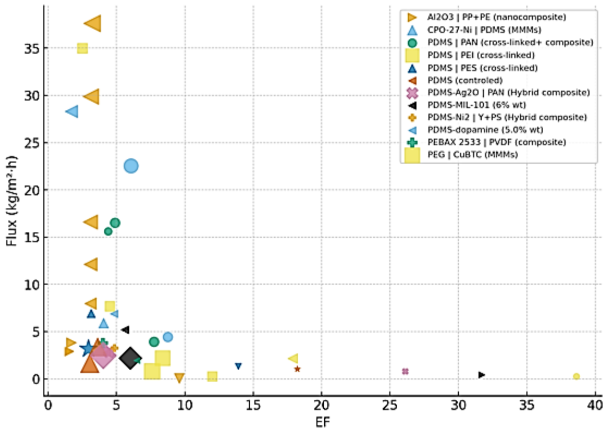

**Figure 4.** Relationship between permeability flux (J) and enrichment factor (EF) for polymeric and mixed-matrix membranes used in desulfurization, illustrating the permeability–selectivity trade-off among different membrane types

### 5.3 Type and concentration of sulfur compounds

The efficiency of sulfur compound separation has been shown to depend strongly on the molecular characteristics of the permeating species and their affinity toward the membrane material [47, 60]. Several studies report that compounds with lower molecular weight generally exhibit higher permeation flux and enrichment factors compared to bulkier sulfur species, following an inverse relationship with molecular size [79]. Increasing sulfur concentration in the feed phase typically enhances permeation flux due to the higher driving force; however, this improvement is often accompanied by a decline in the enrichment factor [53]. This behavior has been attributed to membrane swelling, which reduces selectivity by enlarging transport pathways [42]. Notably, once a critical concentration is reached, further increases in sulfur content tend to have a limited impact, as the membrane approaches a swelling equilibrium state [80, 81]. The sulfur enrichment factor is used as an indicator of the separation selectivity of sulfur compounds. It is defined as the ratio of the sulfur content in permeate to the sulfur content in the feed [82]:

$$\alpha = \frac{C'A}{CA} \tag{3}$$

where, $\alpha$ is the sulfur enrichment factor, C′A is the sulfur content in the permeate, CA is the sulfur content in the feed.

The solubility parameter defined as the square root of the cohesive energy per molar volume [83]:

$$\delta = \left(\frac{E_{coh}}{V}\right)^{\frac{1}{2}} \tag{4}$$

where, $\delta$ is the solubility coefficient $(J/cm^3)^{1/2}$, $E_{coh}$ is the cohesion energy (J/mol) and V is the molar volume ($cm^3/mol$).

### 5.4 Membrane thickness

Membrane thickness is a crucial structural parameter influencing permeation behavior, as numerous studies have demonstrated an inverse relationship between active-layer thickness and permeability flux [84, 85]. Thinner membranes generally allow faster mass transport due to reduced diffusion resistance, which explains why normalized flux values are often used when comparing membranes of different thicknesses [85, 86]. In addition, hydrodynamic conditions play a secondary role; increasing the feed flow rate or Reynolds number has been reported to lower boundary-layer resistance, resulting in modest improvements in both flux and enrichment factor [80, 82]. These effects are commonly interpreted using the solution–diffusion framework, which incorporates membrane thickness as a key variable governing mass transfer [71]:

$$J_i = P_i \frac{c_i F}{\delta} \tag{5}$$

$$Pi = \frac{J_i * l}{(Pio - Pil)} \tag{6}$$

where, $J_i$ is the fractional flux of the component, $Pi$ is the permeability of the component $i$, $c_iF$ is the concentration of the component $i$ in the bulk fluid, δ is the film thickness, $Pi$ is the permeability of component $i$. $J_i$ is the total flux of component i and l is the membrane thickness (m).

## 6. EFFECT OF MEMBRANE MATRIX TYPE AND FILLER CONCENTRATION

After reviewing the mechanisms that govern the transport of sulfur compounds across membranes (Section 3), it is important to understand that the physical and chemical properties of the membrane material are the main element that determines the effectiveness of these mechanisms. Parameters such as polymer polarity, chain rigidity, and free-volume distribution play a decisive role in determining transport behavior within the solution–diffusion framework. Consequently, variations in membrane performance are primarily linked to the nature of the polymer matrix and its interaction with incorporated fillers. This section therefore examines how different membrane materials and filler concentrations influence separation efficiency, stability, and long-term performance. The nature of the polymer used determines the basic properties of the membrane, both in terms of selectivity and stability. Hydrophobic polymers such as PDMS, PU, and PI are commonly used due to their high permeability and chemical stability [40, 57, 87]. However, it may suffer from swelling problems in the presence of high fuel concentrations [40]. On the other hand, hydrophilic polymers such as PEG and PVP are preferred for polar sulfur compounds, and cellulose triacetate (CTA) and PVP have demonstrated excellent swelling stability [13, 88]. Among these, polyimide (particularly 6FDA-BDAF) has demonstrated high fluxes up to 37.61 kg/(m²·h) and enrichment factors reaching 3.136 [5]. The block copolymer PEBAX offers a favorable balance between permeability and mechanical strength due to its bi-block structure, as evidenced by Pebax-Ag-PDA/GNS membranes, which achieved a flux of 4.42 kg/(m²·h) and an enrichment factor of 8.76 at 40°C [60, 61]. Polyphosphazenes such as PMePP and PBPP exhibit notable thermal resistance and performance, with PBPP achieving an enrichment factor of 11.92 at 55°C [18, 22]. Additionally, polyurethane/PEG blends have shown enhanced properties, reaching an enrichment factor of 6.00 and a flux of 2.20 kg/(m²·h) [58]. Various modification strategies further improved membrane performance; for instance, PEG/PU blends achieved a flux of 2.5 $kg/(m^2 \cdot h)$ and an enrichment factor of 4.03 [31], while chemical crosslinking, such as in PEG and PDMS/PEI systems, has improved both selectivity and structural stability [13, 37, 45]. Excellent results were also obtained with organ minerals added. Metal ion-incorporated zeolites (e.g., CuY, NiY) increased the permeability and selectivity simultaneously [39, 47, 89]. Silver oxides ($Ag_2O$) selectively reacted with thiophene [40, 68, 90]. MOF materials have contributed to significantly enhanced separation performance, such as MIL-101(Cr), CuBTC, CPO-27-Ni, ZIF-8, and UiO-66-$NH_2$ [45, 46, 55, 91, 92]. Furthermore, the addition of alumina particles and GNS-PDA-AgNPs enhanced both performance and resistance to swelling [40, 44, 48]. A persistent challenge in membrane design has been the trade-off between permeability and selectivity; however, recent advances—particularly involving MOF-based modifications—have uccessfully mitigated this limitation, enabling simultaneous enhancement of both properties, with UiO-66-$NH_2$-based membranes exemplifying this breakthrough [45, 51, 61]. The inconsistencies among studies employing similar filler–matrix systems often result from differences in filler particle size, loading concentration, and the interfacial bonding between filler and polymer phases. In addition, the variations in experimental conditions like temperature, feed composition, and sulfur compound type can affect the real material behavior. Establishing standard experimental protocols would improve comparability and deepen understanding of structure–property relationships in these hybrid membranes. Table 3 illustrates the various types of membrane materials and highlights how their intrinsic properties influence overall system performance.

**Table 3.** Comparative summary of polymer-based membranes used in desulfurization applications

| Membrane Category | Composition / Additives | Main Mechanism or Effect | Performance Trend / Note |
|---|---|---|---|
| **Hydrophobic Polymers** | PDMS, PU, PI | Swelling at high permeate concentration | ↓ Selectivity; degradation risk at high T/P |
| **Hydrophilic Polymers** | PVP, PEG, CTA | Polar affinity toward sulfur compounds | ↑ Sulfur selectivity over hydrocarbons |
| **MOF-Based Composites** | PDMS–MIL-101(Cr), PDMS–CuBTC, PDMS–UiO-66 | Nanoporous structure ↑ surface area | Optimal loading ↑ flux & EF; excess → agglomeration |
| **Graphene-Based Composites** | PDMS–GO, PEG–GO | $\pi$–$\pi$ interactions; mechanical reinforcement | ↑ Stability & sulfur uptake |
| **Zeolite Composites** | PDMS–ZSM-5, PEG–ZSM-5 | Molecular sieving → selective diffusion | ↑ Enrichment factor for small sulfur molecules |
| **Metal-Doped Membranes** | PMePP–Mn, PDMS–Cu, PDMS–Fe | Metal–thiophene $\pi$-complexation | ↑ Flux & selectivity (esp. at high T) |
| **Cross-linked / Hybrid Membranes** | Cross-linked PI, PEG/TEOS, PDMS/PEI, PDMS/PAN | Reduced swelling; solvent stability | ↑ Durability; tunable permeability |
| **Ceramic / Support Composites** | PDMS/ceramic, PDMS/PAN | Mechanical reinforcement; limits swelling | Suitable for high-pressure use |
| **Thermal Effects** | All polymer types | ↑ T → ↑ flux, ↓ EF | Requires temperature optimization |
| **Feed Concentration / Flow** | All polymer types | ↑ Flow → improved mass transfer | Critical for scale-up & efficiency |

Note*:* The arrows indicate performance trends, where ↑ represents an increase or improvement and ↓ represents a decrease or reduction. EF refers to the enrichment factor, while T and P denote temperature and pressure, respectively.

### 6.1 Critical analysis of trade-offs and industrial prospects for membrane systems

This section provides a comparative and critical evaluation of the performance of polymer and hybrid membranes based on data from over 40 experimental studies (summarized in Tables 1-3). The aim is to correlate laboratory-level performance with real-world industrial challenges and identify promising strategies for large-scale application. This evaluation reveals that performance variations stem primarily from differences in polymer polarity, chain stiffness, and the quality of interfacial bonding between the filler and matrix. While conventional polymers such as polydimethylsiloxane (PDMS) remain attractive due to their low cost and expandability, they suffer significantly from swelling and a clear trade-off between permeability and selectivity [35]. Swelling, caused by a high concentration of permeable components, reduces membrane selectivity and may accelerate its chemical degradation, especially under harsher operating conditions [18]. As a result, MMMs represent a crucial strategy for overcoming the limitations of classical trade-offs and improving chemical stability [35]. These membranes, especially those enhanced with smart fillers such as metal-organic frameworks (MOFs), successfully promote both flow and selectivity simultaneously. However, the most critical challenges facing MMMs and hindering their industrial application are poor reproducibility and intercompatibility, as well as filler agglomeration and void formation problems at high filler concentrations [16, 21]. Despite these obstacles, PEG and polyimide (PI)-based MMMs emerge as strategic industrial candidates because they achieve the best overall balance between flow, selectivity, and stability [36]. To translate this laboratory performance into real-world industrial viability, urgent focus must be placed on three key areas of work: (a) conducting long-term stability tests using real fuel streams (e.g., liquid catalytic cracking fuel FCC) rather than model fuels, (b) using advanced molecular simulations to predict sulfur transport pathways and optimize filler distribution, and (c) developing thin-film asymmetric composite membranes with "smart" fillers.

#### 6.1.1 Classical trade-offs and limitations of pure polymeric membranes

The differences in performance between conventional polymer membranes (such as PDMS, PEG, and PI) originated mainly from differences in polymer polarity, chain stiffness, free volume distribution, and interpolymer-filler bond quality [37]. Pure polymer membranes are low-cost and easy to manufacture, but they face critical limitations that hinder their industrial scalability. The most prominent of these limitations include:

Polymer swelling. Excessive swelling—especially in hydrophobic polymers such as PDMS when exposed to high concentrations of permeable sulfur compounds—is one of the most significant problems affecting their long-term performance and stability. Swelling leads to:

- A sharp decrease in selectivity: High loads of permeable components cause the membrane to become less selective [52].
- Accelerated chemical degradation: Swelling can lead to chemical degradation, especially at high temperatures and pressures, posing a challenge to the application of polymer membranes under industrial conditions [18].
- Disruption of structural stability: Swelling threatens the stability of membranes and reduces their service life [52].

Permeability/Selectivity Trade-off. All pure polymers show an inherent trade-off between high permeability and high selectivity. This variation limits overall performance and differs depending on the polymer's chemical structure [37]:

- PDMS: It exhibits high permeability but poor selectivity and severely damaged by swelling, illustrating the inherent trade-off between permeability and selectivity [18].
- PEG: It achieves good selectivity and relatively higher flux compared to others due to flexible ether bonds and hydrophilic properties that enhance the solubility of polar sulfur compounds and facilitate their diffusion. However, its stability may be lower compared to polyimide (PI) [20].
- PI (Polyimide): It exhibits excellent thermal and mechanical stability and high selectivity. However, due to its rigid aromatic structures and low chain mobility, it offers lower flux. These limitations confirm that single-polymer-based membranes struggle to overcome the classic trade-off between permeability and selectivity, thus limiting their practical industrial applications [35]. To overcome these challenges, research has turned to the use of MMMs [19].

### 6.1.2 Critical challenges of mixed matrix

MMMs are characterized by their chemical and mechanical stability [93, 94]. These systems show the operational advantages of polymers, such as ease of fabrication and low cost [94], with the functional properties of inorganic materials, such as molecular sieving or preferential adsorption. Therefore, they considered a strategy for overcoming the trade-off between permeability and selectivity. However, significant practical challenges continue to prevent their scalability, preventing their efficient transition from laboratory research to industrial deployment. These challenges include:

Filler Agglomeration. Filler agglomeration becomes a major problem at relatively high filler concentrations (typically exceeding 5%–7% by weight), as observed in ZIF-8 and MIL-101(Cr)-based mixed matrix membranes [95]. Agglomeration has adverse effects on membrane performance, including:

- Non-selective void formation: Agglomeration disrupts microstructure homogeneity and forms voids at the filler-polymer interface, which act as nonselective leakage pathways [21].
- Microstructure homogeneity disruption: The homogeneity required for efficient separation is lost [96].
- Reduced selectivity: The creation of random pathways instead of ordered nanostructured transport channels [97].
- Poor reproducibility: Agglomeration results in inconsistent membrane performance across different fabrication lots [97].

Poor Interfacial Compatibility. Poor adhesion between the polymer and the filler leads to the formation of interfacial voids, which act as non-selective leakage pathways [4]. The filler efficiency depends on successful interfacial bonding:

- Zeolites: These materials promote molecular sieving; however, their effectiveness requires strong interfacial bonding [50]. For example, PDMS-$Ni^{2+}Y$ membranes may suffer from potential interfacial voids.
- MOFs: These materials introduce additional nanochannels that enhance permeability [23], but their efficiency depends heavily on good dispersion and interfacial cohesion.

Poor interfacial compatibility remains one of the major obstacles to the transformation of hybrid matrix membranes from laboratory research to industrial applications.

## 6.2 Industrial feasibility

The industrial feasibility of polymeric and hybrid membranes cannot be evaluated solely on laboratory permeation data; instead, it requires a holistic assessment that integrates cost, long-term stability, module design, and pilot-scale performance. Recent studies show that while high-performance MMMs—particularly those incorporating MOFs such as UiO-66-$NH_2$, ZIF-8, or MIL-101(Cr)—exhibit excellent permeability–selectivity combinations under model fuel conditions, their translation to industrial environments remains limited by incomplete durability verification and insufficient techno-economic analysis [98-100].

### 6.2.1 Evidence from pilot- and semi-pilot-scale studies

Pilot-scale and semi-pilot-scale studies have tested the performance of polymer membranes and hybrid composites against real fuel matrices (FCC and straight-run gasoline, diesel, and jet fuel). These studies confirm that testing on typical fluids improves understanding of fundamental phenomena but often underestimates the complexity of problems that arise when operating on real feeds. This includes competitive adsorption of aromatics, fibrosis/blockage by heavy fuel compounds, and partial degradation of filler edges under fuel contaminants [101, 102].

Practical experiments have confirmed these differences; for example, a pilot-scale experiment on diesel desulfurization using activated carbon showed a desulfurization rate of over 90% under laboratory conditions, with total sulfur remaining below 2 ppm up to ~20–22 mL of treated fuel per gram load at laboratory scale-up. Upon scaling up the process by approximately 15-fold, the penetration capacity decreased to ~15–17 mL/g, but the removal rates remained high. The repeated operation cycles showed stable efficiency up to cycle 6–7, after which performance began to decline due to pore clogging by diesel derivative residues and loss of specific surface area of the absorbent material. These results illustrate the practical difference between the model fluids and the actual feedstock [101].

When considering the operational aspects, experiments fed with the actual fuel typically ranged from 50 to 300 operating hours when reported. During these periods, both temporary high sulfur reduction levels (≥ 90% in many cases) and gradual stabilization problems (deterioration of permeability, increased resistance due to clogging) were observed. However, some operations extend to much longer periods (> 1000 h), limiting the conclusions regarding industrial readiness [103].

The Stability Issues. Stability issues in membranes used in desulfurization processes become clearly apparent when exposed to actual fuel. Flexible PDMS membranes exhibit good permeability but are susceptible to swelling and plasticization by aromatic compounds present in gasoline/diesel. This leads to a decrease in selectivity in the medium term (especially during continuous operation exceeding ~100 h in some tests) [104]. In addition, the effect of competitive adsorption shows where di- and polyaromatic compounds compete with sulfur compounds for adsorption sites or adsorbent folds, contributing to a decrease in recoverable capacity after regeneration. This behavior has been observed in real-world desulfurization studies [101]. As well as, microporous MOFs exhibit excellent performance in model fluids, but exposure to fuel contaminants can lead to framework degradation or pore blockage. This problem is exacerbated by variations in filler dispersion within the polymer matrix [105]. Heavy deposits and aromatic base compounds are another issue that can clog microchannels within the membranes and/or at the filler-polymer interface, resulting in reduced permeability and increased selectivity losses over repeated operating and regeneration cycles [101]. The key functional differences between polymeric membranes and MMM systems, linking laboratory performance to operational behavior in real fuel matrices, and identifying factors affecting scalability are summarized in Table 4 below.

**Table 4.** Comparison of polymer classes and MMMs in real feeds vs. model fluids

| Membrane Type | Performance in Model Fuels | Performance in Real Fuels | Main Limitations |
|---|---|---|---|
| PDMS | High permeability | Loss of selectivity; swelling | Aromatic plasticization |
| PEG | Good selectivity | Poor structural cohesion | Moisture sensitivity |
| PI | High stability | Physical aging | Lower flux |
| MMMs | High selectivity | Depends on filler dispersion | Agglomeration, voids |

Research Gaps to Transition to Industrial Scale. Despite advances in the development of polymer and hybrid membranes, significant research gaps still hinder the transition of these technologies from the laboratory to full-scale industrial application, which remains limited, as long-term real-world feeding studies are limited to ≤ 300 h; extended operational data (≥ 1000 h) needed to assess real-world service life [103]. There is also a lack of assessments that use typical industrial separation units, limited testing on industrial module types (spiral-wound, hollow-fiber), and gaps in understanding flow pressure, energy loss, and mechanical stress load [106].

A deeper understanding of the mechanisms of structural degradation and chemical aging within membranes remains essential, and these can be revealed through surface analyses such as BET, FTIR, and XRD after extended operating periods. Finally, the variability in the reactivity of sulfur compounds in the real feedstock is a complex and insufficiently documented factor, requiring further studies to determine the impact of these compounds on membrane lifespan and performance under industrial conditions [107].

In terms of industrial readiness, rigid polyimide-based films and hybrid films with good filler dispersion and interface cohesion exhibit the highest industrial maturity indicators due to their resistance to stretching and aging compared to flexible polymers. However, the main challenge remains ensuring long-term stability under harsh operating conditions, developing effective regeneration protocols, and designing processing units capable of meeting actual feed characteristics and industry requirements [108].

## 7. CONCLUSIONS

Polymer and hybrid membranes are among the most promising alternatives for sustainable desulfurization. A critical evaluation of 40 pilot studies shows that the variability in performance of these membranes stems primarily from differences in polymer polarity, chain stiffness, and the quality of the interfacial bond between the filler and the matrix. Polyethylene glycol (PEG) membranes show higher flow rates due to hydrophilic ether bonds, while polyimide (PI) systems achieve superior selectivity thanks to their solid aromatic structure and low free volume. Although conventional membranes such as PDMS and PEG remain cost-effective, they suffer from significant swelling and a trade-off between permeability and selectivity. The incorporation of inorganic fillers such as metal-organic frameworks (MOFs) has proven capable of overcoming this trade-off and simultaneously improving both selectivity and flux. However, challenges such as clumping, poor reproducibility, and inter-compatibility issues remain major obstacles to the industrial scaling up of MMMs. To move from laboratory performance to industrial scale, future work must urgently focus on three areas that stem directly from these constraints:

(a) Conducting long-term stability tests using real fuel streams (e.g., liquid catalytic cracking fuel) rather than model fuels;

(b) Using advanced molecular simulations to predict sulfur transport pathways and optimize filler distribution; and

(c) Developing asymmetric thin-layer composite membranes and “smart” fillers to enhance structural robustness. Considering these challenges and opportunities, polyimide/MOF-based MMMs emerge as a strategic candidate for industrial applications.

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